

Experimental Study and Modelling of Mechanical Features in an Oxide Layer under Thermal Loadings Zhaojun Tao

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Zhaojun Tao. Experimental Study and Modelling of Mechanical Features in an Oxide Layer under Thermal Loadings. Materials and structures in mechanics [physics.class-ph]. Université de Technologie de Troyes, 2018. English. NNT: 2018TROY0003. tel-02972217

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Thèse de doctorat de l'UTT

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Experimental Study and Modelling of Mechanical Features in an Oxide Layer under Thermal Loadings



Spécialité : Matériaux, Mécanique, Optique et Nanotechnologie

2018TROY0003

Année 2018



THESE

pour l'obtention du grade de

DOCTEUR de l'UNIVERSITE DE TECHNOLOGIE DE TROYES

Spécialité : MATERIAUX, MECANIQUE, OPTIQUE ET NANOTECHNOLOGIE

présentée et soutenue par

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le 12 février 2018

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Experimental Study and Modelling of Mechanical Features in an Oxide Layer under Thermal Loadings

JURY

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Acknowledgements

This PhD work is accomplished with the support of numerous people from UTT and Université de La Rochelle.

First of all, I would like to give my very grateful thanks to Prof. PANICAUD Benoit, my advisor, for all his advices, encouragement and care ever since I started my thesis under his supervision. He is an extraordinary supervisor that is meticulous in science and with plenty of ideas. His patient, amiable, optimistic and humorous characteristics and qualities have provided me a very pleasant environment for research. It is my great honor to work with him to start my research life. In my eyes, he is not only an advisor, but also a friend who shares his experience with me.

I would like to express my deep appreciation to another advisor: Jean-Luc GROSSEAU-POUSSARD, who as well gave me many recommendations and supports throughout my work. I accepted from him lot of good habits during my first contact with scientific research. He is always ready to lend me a hand when I encountered a difficulty.

During these years of my thesis, I was led to carry out experiments using Synchrotron at European Synchrotron Radiation Facility (ESRF) in Grenoble. I extend my sincere thanks to responsibles for the BM02 light line: Nathalie BOUDET and Nils BLANC, as well as responsible for the Sample Environment Support Service: Bernard GORGES and Hugo VITOUX.

Thanks shoud be given to Guillaume GEANDIER, Pierre-Olivier RENAULT and Philippe GOUDEAU, with whose help, we have realized our experiments and data treating. I thank them all for their remarkable talents and skills. I am appreciate that I had the chance and the opportunity to carry out experiments with them.

I would like to thank Guillaume GEANDIER, for his involvement during the various stages of experiments, and especially for his help of data treating and correction of my thesis for the experiment part.

I would like to express my gratitude to all the researchers in the laboratory for the excellence of their hospitality. A great thanks shoud be given to Dr. RAKOTOVAO Felaniaina, for her help with the experimental data. Her thesis is focused on the experimental part, so she gave me many great suggestions when treating the experimental data.

I would like to give many thanks to Régis DETURCHE for training me on the scanning electron microscope and Laurent DANIEL for his help with the software and computer problems.

Thanks should also be given to Regis LENGELLE, who gave me many great suggestions when I encountered problems for finishing the thesis in time. He also gave me advices for the future after the thesis.

Thanks should also be given to Feng, Vincent, Ali, Yangcan, Yuchen, Kai, Jianqiang, Joseph, Yugang, as well as guys from LASMIS whose names hae been mentioned above, for sharing with me a very pleasant and memorable time in this lab. It is wonderful to have them as my colleagues.

Just before going to the financial supports, I would like to thank my family and girlfriend for standing with me during these years.

Last but not least, I would like to give my acknowledgements to China Scholarship Council for funding, which is the prerequisite for my coming to France for this thesis. Thanks should also be given to Campus France, who has given me financial support for the last few months of my thesis.

Introduction

Nowadays, oxidation resistant alloys are widely used in industrial systems working at high temperatures, because it costs less money than the traditional ceramic compounds. These alloys are often exposed to an oxidizing atmosphere and thus an oxide layer grows at the surface of this alloy. Oxidation resistant alloys correspond to those that are able to produce a protective oxide layer, usually consisted of alumina or chromia, showing very low permeability to the oxidation reactants, in order to limit further oxidation. Unfortunately, it is known for many years that there exists a stress accompanying the growth of the oxide layer that can limit the lifetime of the system.

Numerous processes might help to generate stress, and many kinds of mechanisms might take place for the relaxation of this stress. The subsequent effects have been shown to stresses up to several hundred MPa even to a few GPa, or to large deformations of the oxide scale. Both situations are harmful for the oxide scale lifetime and may usually result in mechanical failure to relax the stress. Due to the complex and evolving nature of the materials used, further lifetime optimization only through experiments is uncertain. Thus, there is a growing need for models and simulation tools that will complete the understanding of mechanisms related to materials properties. Further, such advanced models should allow users to predict the stress evolution in the metal/oxide systems.

Some models have been established to predict the growth stresses evolution, but as far as we know, most of them generally consider the isothermal oxidation conditions. However, in real situations, metals or alloys are often oxidized under more or less complex thermal cycling loadings. Moreover, the features of the growth stresses significantly change with the oxidation conditions: temperature, duration, partial pressure of dioxygen, cooling rates, etc. Thus, a model taking into account the most of the oxidation conditions is required.

The primary objective of this work is to develop such a model and a related identification tool, in order to investigate the stress evolution in the metal/oxide systems under thermal cycling loadings, along with the identification of mechanism and materials properties. Then, the model is applied using the experimental data providing from literature for the system NiAl/Al₂O₃. The value of activation energy is compared with that in the publications, in order to valid our method. Finally, it is used to identify the mechanism and materials properties for the system NiCr/Cr₂O₃. In that case, the experimental data provide from experiments performed with our team at European Synchrotron Radiation Facility (ESRF). In this thesis, a list of questions will be answered:

- 1. How to establish a model to describe the mechanical response of material during high temperature oxidation and solve it analytically and numerically?
- 2. How to realize continuous in-situ measurements during the high temperature oxidation using synchrotron radiation and 2D detector and where the uncertainties come from?
- 3. How to choose from different optimization methods in order to have a better optimization result?
- 4. How to identify the mechanisms for the creep behavior in the oxide layer?
- 5. How does some reactive elements change the activation energy of the oxide layer?

This PhD thesis consists in 6 chapters:

The first chapter provides a comprehensive bibliographic review of some phenomena occurring during high temperature oxidation. It corresponds to the thermodynamics of oxidation, kinetics of oxidation and experimental methods for determination of stresses. The phenomena of stress generation, their origins and the different mechanisms of relaxation are also presented.

The second chapter establishes a model, which takes into account several material behaviors and the influence of temperature on material parameters, in order to investigate the stress evolution with time, during the oxidation procedure. The hypotheses and limitations on the model validity are also presented. In order to solve the model, some analytical solutions are considered for both isothermal conditions and non-isothermal conditions, followed by the numerical solutions using Runge-Kutta scheme.

The third chapter presents in details the procedure for the determination of stress in the oxide layer when using synchrotron diffraction with a 2D detector. Every steps for data treatment are also discussed, followed by the analysis of uncertainties coming from different sources.

The fourth chapter presents the identification methodologies for both isothermal conditions and nonisothermal conditions. The verification of the physical consistency of numerical values for some material parameter is also provided, which can confirm our identification procedure. Lastly, two novel methods to identify the parameter of thermal expansion are also proposed.

The fifth chapter presents all the experimental results, from both literature and our own experiments at European Synchrotron Radiation Facility (ESRF), for different thermal solicitations and different materials (NiAl/Al₂O₃, NiCr/Cr₂O₃, with and without reactive elements).

Finally, the sixth chapter presents all the identification results using the identification methodologies from chapter 4 and the experimental data from chapter 5. The identification results are then discussed and compared with the values from literature to identify mechanisms.

Chapter 1 State of art

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1.1 High temperature oxidation

Oxidation resistant alloys are more and more employed in industrial systems working at high temperatures [1], such as thermal power station, gas turbine, nuclear power plant, fuel cell, etc. However, oxidation generally occurs under high temperature conditions. Usually, the metallic alloy is exposed to an oxidizing atmosphere and thus an oxide layer grows at the surface of this alloy, especially at high temperature.

Oxidation resistant alloys correspond to those that are able to produce a protective oxide layer, usually consistuted of alumina or chromia, showing very low permeability to the oxidation reactants, in order to limit further oxidation.

Unfortunately, it has been known for many years that there exists a stress accompanying the growth of the oxide layer and thus influences the structure and the protective properties of the oxide layers [2]–[5]. Regardless of the kind of alloy oxidized or the type of oxide formed, the growing oxide film is usually under compressive stress, and if the stress magnitudes are too high, the oxide layer will break and the metal will be re-oxidized. Therefore, it is very important to determine the strain and stress fields associated to the growth of oxide layers on metallic substrate, during high temperature oxidation and cooling.

Experimental investigations have been conducted for many years to find alloy compositions that will improve the quality of oxide layers (for example the decrease of its permeability that increases the oxidation resistance), to understand their developments and to understand the contributions of alloy components and oxidation conditions [6]–[9]. Exhaustive developments have been performed, but many problems remain to be investigated and the lifetime of metal/oxide systems needs to be enhanced. Stress development and subsequent phenomena, such as crack and delamination, are among the most serious issues limiting the lifetime of oxide/metal systems under high temperatures [10].

In this part, thermodynamics of oxidation at high temperature will firstly be introduced, which allows us to know under which conditions (temperature, O_2 pressure etc...) the oxidation process can occur. Secondly, a presentation of the kinetics of oxidation is done, which gives us information about the rate of the oxidation. Finally, some experimental methods for determination of stresses are given in order to determine the stress in the oxide layer.

1.1.1 Thermodynamics of oxidation at high temperature

1.1.1.1 The basic of thermodynamics

Oxides are the stable states of metals in air (above a critical dioxygen partial pressure or beneath a critical temperature). Thus, metal oxidation is a natural process. When metal is exposed to oxidizing gas, it will be oxidized and form an oxide compound. For 1 mole of dioxygen, the general chemical reaction can be described by:

$$nM+O_2 \Longrightarrow M_nO_2 \tag{1.1}$$

Where n is a stoichiometric coefficient, M represents the metal species, O the oxygen and M_nO_2 the oxide. The forward reaction to form oxide is thermodynamically very favorable, because the corresponding standard free energy, ΔG^0 , is usually very negative (ΔG° is about -550 kJ per mole of O_2 for chromia at 800°C, and around -800 kJ per mole for alumina at 1100°C [11]). Under different temperatures and dioxygen partial pressure, and for an alloy containing many kinds of metallic species, several kinds of oxides can be formed. Thermodynamics predicts that the most stable oxide should form, that is to say, the one that has the lowest free energy of formation (highest in absolute magnitude since they are negative). The molar Gibbs free enthalpy of the oxidation reaction in equation (1.1) is given by:

$$\Delta G_{M_n O_2} = \Delta G^0_{M_n O_2} + RT \ln(P_{o_2})$$
(1.2)

Where $\Delta G^0_{M_n O_2}$ is the standard molar Gibbs free enthalpy of reaction, R is the molar gas constant, T is the temperature and P_{o_2} is the dioxygen partial pressure (to the reference pressure $P^0_{O_2}$ taken equal to 1 bar). The oxidation reaction occurs if $\Delta G_{M_n O_2} < 0$. From the equation (1.2), this gives:

$$\Delta G^{0}_{M_{n}O_{2}} < -RT \ln(P_{o_{2}}) \tag{1.3}$$

Stability maps for oxides under varying environments are used to predict the main oxide phase that will develop, which are called the diagrams of Ellingham-Richardson.

1.1.1.2 Diagram of Ellingham-Richardson

An Ellingham-Richardson diagram provides the standard free energy of formation (ΔG^0) versus temperature for the compounds of a type, e.g. oxides, sulphides, carbides. The data is calculated using the linear approximation of Ellingham-Richardson:

$$\Delta G^0_{M_n O_2} = \Delta H^0_{M_n O_2} + T \Delta S^0_{M_n O_2} \tag{1.4}$$

Where $\Delta H^0_{M_nO_2}$ is the molar enthalpy and $\Delta S^0_{M_nO_2}$ is the molar entropy of reaction, supposed to be temperature independent; both data can be experimentally determined. For example, for a given dioxygen partial pressure, the line $-RT \ln(P_{o_2})$ can be drawn on the Ellingham diagram, and their intersection gives the equilibrium temperature of the oxidation reaction. At lower temperature (than the equilibrium temperature), $\Delta G^0_{M_nO_2} < -RT \ln(P_{o_2})$, the oxide layer is stable. At the opposite, the metal phase is stable at higher temperatures. In a reverse way, we can also use such a diagram to obtain the equilibrium partial dioxygen pressure (usually called oxide dissociation pressure), for a given temperature.

The Ellingham-Richardson diagrams depend on many assumptions such as:

- Thermodynamic equilibrium
- Pure metal phases (no alloy element that could react)

- Activity of 1 mole of dioxygen equal to its chemical potential, directly linked to its partial pressure for a perfect gas
- Linear dependency of the standard Gibbs free enthalpy with temperature (Ellingham-Richardson assumption)

Although some of these assumptions are not strictly always satisfied, the Ellingham-Richardson diagrams is commonly used to predict the oxide phase that can develop under given temperature and oxygen partial pressure. The Ellingham-Richardson diagrams for several oxides are presented in Figure 1.1, with a highlight on the data related to chromia at 1000°C.



Figure 1.1: Ellingham-Richardson diagrams with a highlight on data for chromia formation at 1000°C

1.1.2 Kinetics of oxidation (Rates of oxidation)

Once again we consider the reaction proposed in equation 1.1:

 $nM+O_2 \Rightarrow M_nO_2$

We can see from the Figure 1.2 that the reaction product M_nO_2 (oxide phase) corresponds to the reaction of two reactants (metal and O_2) along an internal and/or external interface.



Figure 1.2: A schematic illustration of an oxide/metal system with internal interface (metal/oxide) and external interface (oxide/gas)

In order for the reaction to proceed further, either metal must be transported through the oxide to the oxide-gas interface and react there, and/or oxygen must be transported to the oxide-metal interface and react there. Therefore, the mechanisms by which the reactants might penetrate the oxide layer are very important to understand the mechanisms by which high-temperature oxidation occurs.

1.1.2.1 Wagner theory of oxidation (parabolic rate law)

For an oxidation process to carry on, it is necessary to assume that the transport processes of ionic and electronic species through the oxide layer are accompanied by ionizing phase-boundary reactions and formation of new oxide at a site whose position depends on whether cations and/or anions are transported through the oxide layer.

With these simple assumptions, in 1933, Wagner was able to develop his well-known theory for the high-temperature oxidation of metals. In fact, this theory describes the oxidation behavior only for the case where diffusion of ions is rate determining and under highly idealized conditions.

If we assume that:

- Cationic transport across the growing oxide layer controls the rate of scaling;
- Thermodynamic equilibrium is satisfied at each interface;

then the process can be analyzed as follows. The outward cation flux, $J_{M^{2+}}$, is equal to the inward flux of cation defects, but its direction is opposite. This model is shown in Figure 1.3:



Figure 1.3: Simple model for diffusion-controlled oxidation

So we can get that the outward cation flux $J_{M^{2+}}$ can be explained as:

$$J_{M^{2+}} = -J_{V_{M}} = D_{V_{M}} \frac{C_{V_{M}}^{"} - C_{V_{M}}^{'}}{h_{ox}}$$
(1.5)

Where h_{ox} is the oxide thickness, D_{V_M} is the diffusion coefficient for cation vacancies, and C_{V_M} and C_{V_M} are the vacancy concentrations at the metal-oxide and oxide-gas interfaces, respectively. And because there is thermodynamic equilibrium at each interface, so $C_{V_M} - C_{V_M}$ is constant, and we get:

$$J_{M^{2+}} = \frac{1}{V_{ox}} \frac{dh_{ox}}{dt} = D_{V_M} \frac{C_{V_M} - C_{V_M}}{h_{ox}}$$
(1.6)

Where V_{ox} is the molar volume of the oxide. From the equation 1.6, we can show that the rate of the oxide thickness is:

$$\frac{dh_{ox}}{dt} = \frac{k}{h_{ox}} \text{ where } k' = D_{V_M} V_{ox} (C_{V_M} - C_{V_M}) * 2$$
(1.7)

When we integrate the equation 1.7 and suppose that h_{ox} =0 at t=0, we can get:

$$h_{\rm or}^2 = k t$$

(1.8)

Which is the common used parabolic rate law.

An improved derivation is given by Wagner theory [12] for thick oxide layer growth. The considered assumptions are listed below [11], [13]:

- The oxide layer is a compact and perfectly adherent layer.
- Migration of ions or electrons across the oxide layer is the rate-controlling process.
- Thermodynamic equilibrium is established at both the metal–oxide and oxide–gas interfaces.
- The oxide layer shows only small deviations from stoichiometry and, hence, the ionic fluxes are independent of position within the oxide layer.
- Thermodynamic equilibrium is established locally throughout the oxide layer.
- Oxygen solubility in the metal may be neglected.
- The layer is thick compared with the distances over which space charge effects occur.

We should pay attention to the fact that the last assumption provides a significant limit for the theory's validity, depending particularly on the charged defect concentrations [13]. Although the reality of the oxide layer growth is generally more complex and provides some other limitations to the theory [14], the Wagner theory describes the growth kinetics with a correct accuracy.

1.1.2.2 Relationships between parabolic rate constants

There are different methods of following the reaction depending on the choice of reaction parameters, and each of them produces its own particular parabolic rate constant, as shown below:

(a) Measurement of the oxide layer thickness (h_{ox}):

$$h_{ox}^{2} = k't \tag{1.9}$$

Where k' is the parabolic kinetics constant and has units of m²s⁻¹

(b) Measurement of the mass increase of the specimen (m)

The parabolic rate mass constant k["] is defined by:

$$\left(\frac{m}{A}\right)^2 = k^{"}t \tag{1.10}$$

Where A is the area over which the reaction occurs; $k^{"}$ is also referred as 'scaling constant' and has units of kg²m⁻⁴s⁻¹

(c) Measurement of metal surface recession (/)

Measuring the thickness of metal consumed leads to the relationship defining k_c

$$l^2 = 2k_c t \tag{1.11}$$

 k_c is called the 'corrosion constant' and has units of m²s⁻¹

(d) Rate of growth of layer of unit thickness

The rational rate constant is defined as the rate of growth over unit area, in equivalents per second, of a layer of unit thickness:

$$k_r = \frac{h_{ox}}{A} \frac{dn}{dt}$$
(1.12)

Where *n* is the number of equivalents in the oxide layer of thickness h_{ox} . k_r is called the theoretical tarnishing constant and has units of equivalents m⁻¹s⁻¹.

It is easy to calculate the value of any rate constant from any others, because they represent the same process; the different relationships are given in Table 1.1:

A	<i>k</i> ′	k"	<i>k</i> _c	<i>k</i> _r
В	$m^2 s^{-1}$	g ² m ⁻⁴ s ⁻¹	$m^2 s^{-1}$	equiv.m ⁻¹ s ⁻¹
k′(m²s⁻¹)	1	$2[\mathbf{M}_X/\overline{\mathbf{V}}Z_X]^2$	$[\overline{\mathbf{V}}_{M}/\overline{\mathbf{V}}]^{2}$	$1/\overline{V}$
k"(g²m⁻⁴s⁻¹)	$0.5[\overline{\mathrm{V}}Z_X / \mathrm{M}_X]^2$	1	$0.5[\overline{\mathrm{V}}_{M} Z_{X}/\mathrm{M}_{X}]^{2}$	\overline{V} / 2[Z _X / M _X] ²
$k_c(m^2s^{-1})$	$[\overline{\mathrm{V}}/\overline{\mathrm{V}}_{_{M}}]^2$	$2[\mathbf{M}_X/\overline{\mathbf{V}}_M\mathbf{Z}_X]^2$	1	\overline{V} / \overline{V}_M^2
k _r (equiv.m ⁻¹ s ⁻¹)	\overline{V}	$2/\overline{V}[\mathbf{M}_X/\mathbf{Z}_X]^2$	\overline{V}_{M}^{2} / \overline{V}	1

Table 1.1 Relationships between the different parabolic rate constants [11]

The relating factor F is given according to A=FB; A is listed horizontally and B vertically. The symbols have the following meaning: \overline{V} is the equivalent volume of the layer ($m^3 equiv$.⁻¹); \overline{V}_M is the equivalent volume of metal ($m^3 equiv$.⁻¹); M_X is the atomic mass of non-metal X (oxygen, sulphur, etc.); Z_X is the valence of X (equiv.).

Because there are so many different ways to express parabolic rate constants, it is necessary to check the definition of a rate constant very carefully when estimating quantitative data.

1.1.2.3 Other kinds of rate law

Under certain conditions, the oxidation follows other kinds of rate law, such as linear rate law, logarithmic rate law, etc.

(a) Linear rate law

When the oxidation of a metal proceeds at a constant rate, it is said to follow the 'linear rate law':

 $h_{ox} = k_1 t$ (1.13) Where h_{ox} is the layer thickness and k_1 is the linear kinetics constant. The units of k_1 is ms⁻¹.

The linear rate law is usually observed when a phase-boundary process is the rate-limiting step for the reaction [11].

(b) Logarithmic rate law

When metals are oxidized under certain condition, usually at low temperatures, the initial oxide formation is characterized by an initial rapid reaction that quickly reduces to a very low rate of reaction. Such behavior follows the rate law described by logarithmic functions:

$$h_{ox} = k_{\log} \log(t + t_0) + A \text{ (direct log law)}$$
(1.14)

$$\frac{1}{h_{ox}} = B - k_{il} \log(t) \text{ (inverse log law)}$$
(1.15)

Where A, B, t_0 , k_{log} , and k_{il} are parameters at a given temperature.

Several interpretations of this type of behavior have been given [4], [15], but due to its complexity, the interpretation of logarithmic rate behavior is still difficult.

1.1.3 Experimental methods for determination of stresses

Although the evidence of stress development can be observed (such as sample elongations or bending, oxide layer buckling and spallation), direct determinations of stresses within oxide layers are not so easy. Thus different techniques have been developed to measure the relaxation strains, such as specimen extension tests and deflection methods [16]. In-situ measurements during oxidation at high temperature present many difficulties, so historically most measurements were taken at room temperature [17]. Then analytical models are used to calculate thermal stresses; finally, the two contributions (determined stresses at room temperature and calculated thermal stresses) are added to find the stresses at high temperature in the oxide layer. But the accuracy of the results from such a method are not always satisfying [17]. For example, it can be highlights that the relaxation stresses are not taken into account during this change of temperature. Recently, many in-situ measurements have been developed and used, such as X-ray diffraction [18]. It is more accurate and can give a better understanding of the process of oxidation because of in-situ conditions.

1.1.3.1 X-Ray diffraction

X-ray diffraction (XRD) are widely used to measure the elastic strain in the crystal lattice and the associated residual stress is determined from the elasticity coefficients of the appropriate crystal lattice plane. Because X-rays impinge over a volume in the sample, several grains and crystals will contribute to the measurement. The exact number of grains and crystals is dependent on the grain size and beam geometry. Even though we usually consider that, the measurement is near the top surface, X-rays penetrate some distance into the material: the penetration depth is dependent on the anode, material and angle of incidence. Thus, the measured strain is fundamentally the average over a few microns depth under the surface of the specimen.

The determination of residual stresses by X-ray Diffraction (XRD) depends on the fundamental interactions between the wave front of the X-ray beam and the crystal lattice. Let us imagine that we have two rays scattered by different atoms as shown in Figure 1.4:



Figure 1.4: Bragg diffraction in a lattice of interreticular distance d

Where λ is the wavelength of the ray, θ is the angle between the ray and the plane of the lattice, d is the interreticular distance between two nearest planes of the lattice. Scattered rays will be in phase only if the path difference is equal to an integer number n of wavelengths, that is:

 $2d\sin(\theta) = n\lambda$

(1.16)

This is now commonly known as Bragg's law and it forms the fundamental basis of (X-ray) diffraction theory.

The elastic strain is then measured as a change in lattice spacing, for a given inclination with respect to the sample surface, from the stress-free situation. The exact strain measurement method using X-ray diffraction (XRD) will be explained in details in experimental part (chapter 3).

1.1.3.2 Other techniques (Raman spectroscopy, deflection methods...)

Nowadays, more and more techniques have been developed and used for stress determination. Laser Raman spectroscopy has been used for chromia layers [19]. Compared to XRD, this method has the advantage that it does not require a too complex experimental environment (a simple laser is used), and that it has better vertical and lateral resolutions (the order of magnitude is around 1 μ m), therefore it can be proficiency used to determine the stress in thinner oxide layers [20].

Another technique, i.e. the photostimulated chromium luminescence spectroscopy, has been proved efficient for stress determination for alumina layers [21], and might allow to determine the stresses developed in the oxide layer below thermal barrier coating [22], [23].

In a different way, if we have a validated model that describes high temperature oxidation of metals, we can use the deflection test in monofacial oxidation (DTMO) to get the stress development in the oxide layer [24]. In this method, a thin metal foil is fixed at one extremity. One side is protected by a

platinum coating and the other one is oxidized. Stresses and strains lead to the curvature of the foil and deflection is measured by a laser, because of the asymmetry of the system.

Although many progresses have been made in stress determination techniques, major limitations remain, so that models and simulations are still essential to have understandings of the likely stress development and resulting mechanical failure mechanisms.

1.2 Stress development and relaxation in oxide films

The existence of stress with the growth of oxide under high temperature oxidation has been known for many years, but the origin of stress generation and relaxation need still to be understood better.

1.2.1 Stress generation

There are two main sources of driven stresses in the oxide layer: the growth stress because of the growth of oxide and the thermal stress because of the temperature change with time and difference of thermal expansion coefficients between oxide and metal substrate.

1.2.1.1 Growth strain

a) Pilling and Bedworth mechanism

There are several possible origins for the growth strain during oxidation [2], the most ancient explanation qualifying this growth strain has been suggested by Pilling and Bedworth [25].

The oxidation reaction product has a molar volume (V_m), which is different from the metal one. Thus, this difference of volume leads to an isotropic growth strain ϵ^{growth} given by:

$$PBR = \frac{V_M(oxide)}{V_M(metal)}$$
(1.17)

$$\varepsilon^{growth} = \sqrt[3]{PBR} - 1 = \varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} \quad \text{(isotropic strain)} \tag{1.18}$$

 V_{M} (*oxide*) and V_{M} (metal) refers to the specific volume of the oxide and the metal phases.

Table 1.2 gives some oxide-metal volume ratios (PBR) of some common metals:

Oxide	Oxide-metal-volume ratio
K ₂ O	0.45
MgO	0.81
Na ₂ O	0.97
AI_2O_3	1.28
ThO ₂	1.30
ZrO ₂	1.56
Cu ₂ O	1.64
NiO	1.65
FeO(on α−Fe)	1.68
Fe₂O₃(on α −Fe)	2.14
Fe₃O₄(on α −Fe)	2.10
TiO ₂	1.70-1.78
CoO	1.86
Cr ₂ O ₃	2.07
Ta ₂ O ₅	2.5
Nb ₂ O ₅	2.68
V ₂ O ₅	3.19
WO ₃	3.30

Table 1.2 Oxide–metal-volume ratios of some common metals [11]

This simple analysis provides relative good results. In particular, the sign of the Pilling-Bedworth ratio indicates if stresses in oxide layer are tensile or more usually compressive. Nevertheless, there are many drawbacks listed as follow [26]:

- The magnitude of the associated stresses is often over assessed, typically several tens of GPa compared with more or less 1GPa from experiments.
- This model supposes that the strain only occurs at the metal/oxide interface, thus, according to this model, only an anionic inward oxidation is able to develop stresses in the layer. Nevertheless, it has been proved that oxides growing by a cationic outward diffusion can also induce a high stress level [2].
- This model does not take into account the influence of oxidation time; thus the associated strain rate is always zero that is not the reality.
- b) Epitaxy mechanism

Another possible origin for the growth strain is the epitaxy (lack of the crystalline lattices) [2]. Epitaxial stress can be developed from lattice incompatibility between the oxide layer and the metallic substrate. A schematic illustration is presented as follow [27]:



Figure 1.5: Lattices epitaxial arrangement through a dislocations structure for a NiO layer on a Ni substrate [27].

The difference in lattice parameters at the interface leads to a mismatch strain. This phenomenon induces stresses at the microscopic level all around the interface, and are often significant through the layer only for thin films [2]. The stresses can be either compressive or tensile according to the epitaxy relationship. However, the oxides formed by high temperature oxidation on oxidation-resistant alloys are often polycrystalline; it is unlikely that coherency stresses are important, so it will be considered in this work that the stresses induced by epitaxy mechanisms do not constitute the main source of the macroscopic stress observed in the growing oxide layer.

c) Oxide growing along the vertical grain boundaries

Over the last decade, a last mechanism has gained considerable interest. Initially suggested and described by Rhines and Wolf [28], it is based on the idea that new oxide formed along grain boundaries lying perpendicular to the interface would generate an in-plane expansion strain. An illustration of this mechanism is provided in Figure 1.6 [3]:



Figure 1.6: New oxide formation resulting from inward diffusion of oxygen and outward diffusion of metal. Oxide growth along grain boundaries lying perpendicular to the interface would induce the inplane compression of the oxide layer [3].

This phenomenon requires concurrent inward diffusion of oxygen and outward diffusion of metal ions, a situation which has been directly evidenced for doped or coated chromia layers [29] and as well as for alumina layers [30].

There exist other models with a microstructural origin. Estrin et al. proposed that the growth strain is related to the grain size evolution [31]. Kamminga et al. proposed a model for the growth strain, based on the presence of spherical defects in a layer considered as an infinite matrix [32]. Some other explanations on the origin of the growth strain were also proposed [14], [33]. Based on the Rhines and Wolf analysis, as well as on the works of Slorovitz and Evans, Stott et al. [34] proposed that the sources of stresses are located at the intersections between the perpendicular grain boundaries and the metal/oxide interface. This model is in agreement with the propositions of Pilling and Bedworth [25], as well as the Rhines and Wolf objections [28]. Stott et al. [34] found the possibility that oxidation takes place via the short-circuits of diffusion in the grain boundaries. The sources of stresses are then periodically distributed at the metal/oxide interface. This system can lead to a calculation by using a technique of geometrical dislocations distributions at the interface. This model can be used to find the microscopic spatial stress field and its time evolution. However, despite of this global character, it is restricted by the spatial localisation of the source term, that is to say, as in the model of Pilling and Bedworth, that an oxide growing by outward diffusion does not develop any stress. What's more, this model cannot be compared easily to experimental results in which only macroscopic stresses are measured.

Tolpygo et al. [35] propose a new approach in a different analysis. They take into account the evolution of the grain size and the width of the grain boundaries on which takes place the growth strain. This model defines the growth strain as the ratio of the oxide volume growing along a grain boundary on the oxide grain volume. That is to say, by hypothesis, that both an inward and an outward flux exist in grain boundaries, in order to form the oxide. The grain diameter is submitted to an evolution caused by its growth [36]. However, we can underline that this model does not take explicitly into account the thickness evolution of the oxide layer.

The model proposed lately by Clarke is also based on a microstructural approach. From the experimental observations in which the growth strain is found to be proportional to the oxide layer thickness, Clarke proposed a mechanism based on geometric microstructural considerations. Here the lateral growth strain would result from the climb of edge dislocations having a Burgers vector parallel to the oxide/alloy interface, in response to trapping of counter-diffusing cations and anions at the core of the dislocations [3]. It is again supposed a mixed flux (inward and outward diffusion) in the short

circuits of diffusion that are the grain boundaries. This hypothesis allows an oxidation reaction in the layer along the grain boundaries. A schematic of the mechanism considered is provided in Figure 1.7



Figure 1.7: Schematic diagram of Clarke's mechanism. Edge dislocation climb results from the local trapping of counter-diffusing metal and oxygen ions. An in-plane growth strain is produced when the dislocations present a Burgers vector parallel to the interface [3].

The demonstration proposed by Clarke leads to the relation:

$$\frac{d\varepsilon^{\text{growth}}}{dt} = \frac{Ar\theta}{ab2(\Delta x)} \frac{dh_{ox}}{dt}$$
(1.19)

Where $\varepsilon^{\text{growth}}$ is the lateral growth strain, *A* is the cross-section for a diffusing cation to attach to the dislocation core, *r* is the ratio of the outward cationic flux to the inward oxygen flux, θ is the disorientation angle between grain boundary and surface, *a* is the average distance between traps, *b*

is the Burgers vector of the dislocation, $2(\Delta x)$ is the average thickness of grain boundaries, and h_{ox} is the thickness of the oxide layer. The theoretical determination of the different coefficients above is not easy, so it is expected to extract them experimentally.

All the previous models are based on stresses located along the grain boundaries perpendicular to the interfaces, which is in agreement with the analyses and observations of Rhines and Wolf. Tolpygo et al. have proposed a microstructural approach based on a volume ratio, like the Pilling and Bedworth analysis, but this new ratio depends on parameters evolving with oxidation time. Stott et al. have proposed that the oxidation takes place via the short-circuits of diffusion in the grain boundaries, and the model of Clarke is an extension of the Stott approach in a more general case: it takes into account the anionic growth. These different models are schematically represented in the Figure 1.8, with their respective assumptions and limitations.



Figure 1.8: Features of some different growth strain models [26]

Recently, Panicaud et al. [37] successively developed a model based on a general thermodynamical explanation, and the model (Equation 1.20) demonstrates that the lateral growth strain rate increased linearly with the oxide thickening rate during isothermal oxidation, which is similar to Clarke model. This approach can also be derived from a micromechanical approach based on a coupling between diffusion of species and mechanical stress at microscopic scale in boundaries and grain boundaries. This model is confirmed by some experiments [35], and is acknowledged and used nowadays by many investigators [38]–[42].

$$\frac{d\varepsilon^{growth}}{dt} = D_{ox}\frac{dh_{ox}}{dt}$$
(1.20)

Where h_{ox} is the thickness of the oxide layer and D_{ox} is a parameter related to some microstructural parameters (which is not a diffusion coefficient), and which may depend on temperature. An anisotropic version of this model has been also proposed.

Parise et al. [43] also considered an anisotropic growth strain model and take into account the anisotropy of the growth strain in the different directions x, y and z (see Figure 1.9). The growth strains are assumed to be equal in the plane parallel to the interface, but it differs in the third direction i.e.

 $\mathcal{E}_{xx,ox}^{g} = \mathcal{E}_{yy,ox}^{g} \neq \mathcal{E}_{zz,ox}^{g}$ (Figure 1.9). The growth strain tensor is given by:

$$\begin{bmatrix} \varepsilon^g \end{bmatrix} = \begin{pmatrix} \varepsilon^g_{xx,ox} & 0 & 0 \\ 0 & \varepsilon^g_{xx,ox} & 0 \\ 0 & 0 & \varepsilon^g_{zz,ox} \end{pmatrix} \text{ and } R_{PB} = (1 + \varepsilon^g_{xx,ox})(1 + \varepsilon^g_{xx,ox})(1 + \varepsilon^g_{zz,ox})$$
(1.21)

For the Zircaloy-4/ZrO₂ system, Parise et al. [43] modeled the DTMO experiment at 450°C using elastic, creep and anisotropic growth strains (as given in Equation 1.21). They identified $\mathcal{E}_{xx,ox}^{g}$ and $\mathcal{E}_{zz,ox}^{g}$ strains from the experimental deflection and found $\mathcal{E}_{xx,ox}^{g} = 0.5\%$, $\mathcal{E}_{zz,ox}^{g} = 54\%$. Indeed, in Parise et al. [43] model, the growth strain is assumed to be mainly along the normal direction of the metal/oxide interface.



Figure 1.9: Description of the anisotropic model by Parise et al. [24]

Recently, Ruan et al. [40] proposed a model to calculate stress in both oxide and metal layer from deflection test in monofacial oxidation (DTMO) experiments. Their model is shown in Figure 1.10:



Figure 1.10 Schematic diagram of the oxide layer/metal substrate system.

They have developed a theoretical model for the more precise and efficient description of residual stress evolutions in the oxide scale/metal substrate system during an isothermal oxidation process, by considering both the elastic strain rate and creep strain rate in both oxide and metal phases and adopting the forward Euler method. The oxidation growth strain generated in the oxide scale is also taken into account and is based on the Clarke model.

They also assumed that stress depends not only on time, but also on z direction, and after using elastic analysis and creep analysis of stress evolution, they found that the oxide stress does not change too much along the z direction as shown in Figure 1.11:



Figure 1.11: The oxide stress distributions along the thickness at different oxidation times: (a) elastic results and (b) creep results. [40]

Their models are similar to ours, except that they use the deflection test in monofacial oxidation (DTMO) experimental results and the models to determine the stress in the oxide and metal layers, and they have considered the curvature of the samples.

We can summarize all the above models in Figure 1.12. In our model, we will mainly consider the growth strain described by Clarke model and generalized by Panicaud et al. and we will assume that the growth strain does not change in the z direction.



Figure 1.12: Summary of growth strain models

1.2.1.2 Thermal stresses

Thermal expansion mismatch is largely known as the main origin for the residual stress in the oxide layers observed at room temperature especially after cooling, and it is thus often considered as the main driving force for mechanical failure.

The free volumetric thermal strain corresponding to a variation of temperature from T1 to T2 is obtained through:

$$\varepsilon_{vol}^{th} = \int_{T_1}^{T_2} \alpha dT \tag{1.22}$$

Where α is the isotropic thermal expansion coefficient, which may depend on temperature. It is in most cases much higher for metals than for oxides, and the larger difference between metal and oxide results in the compression of the oxide layer.

If two planes, perfectly bonded, elastic layers in equal biaxial stress states are considered, and if it is furthermore assumed that the two materials present similar Poisson ratios and that the oxide layer thickness is small in front of the metal one, the in-plane stress in the oxide layer can be expressed as [11]:

$$\sigma_{ox} = -\frac{E_{ox}(\alpha_{ox} - \alpha_m)\Delta T}{1 - \nu}$$
(1.23)

Where the subscripts ox and m respectively refer to the oxide and metal layers, E is the Young modulus of elasticity and v the Poisson ratio. This formulation allows predicting compressive in-plane stresses upon cooling from thermal coefficients data. The stresses can reach several gigapascals. Stresses up to 6 GPa have been reported for alumina layers [9] experimentally. Consequently, alloys are selected and

designed in the first place to match as closely as possible the thermal expansion behavior of the oxides they develop and to be mechanically resistant enough to sustain the inevitable thermal stress. The development of thermal stress is presented in Figure 1.13:



Figure 1.13: Schematic diagram presenting the thermal strain mismatch induced upon cooling between the developed oxide layer and the metallic substrate ; it results an in-plane compression from the adherence of the oxide layer on the metal substrate. [44]

1.2.2 Relaxation of oxide stress

The growth and thermal stresses generated during oxidation may be accommodated by different mechanisms. The most important are the following [11]:

Non-destructive relaxation phenomena:

- Plastic and/or viscoplastic deformation of the substrate.
- Plastic and/or viscoplastic deformation of the oxide.

Destructive relaxation phenomena:

- Cracking of the oxide.
- Spallation of the oxide from the alloy substrate.
- Buckling of the oxide.
- Rumpling of the oxide.

1.2.2.1 Non-destructive relaxation phenomena

The plastic or viscoplastic deformation (creep) of the substrate and the oxide contribute to the relaxation of the stress [5].

For metals, the effects of creep deformation generally become noticeable at approximately 35% of the melting point, and under high temperature, other kinds of plastic deformation is not very realistic [5], so that the creep is the main deformation process.

Generally, under a given stress, the creep phenomenon can be decomposed into three stages:



Fig 1.14: Strain as a function of time due to constant stress over an extended period of time.

In the first state, the strain rate is very high, but it slows with increasing time. This is due to work hardening. The strain rate finally reaches a minimum and this is because of the balance between work hardening and annealing. The second stage is known as steady-state creep and the characterized "creep strain rate" usually refers to the rate in this stage. In the third stage, the strain rate exponentially increases with stress because of necking phenomena by coupling with some damage mechanisms.

The mechanism of creep depends on temperatures and stress; the main kinds of mechanism are:

- dislocation creep

That is to say, plastic deformation occurs in the form of dislocation glide combined with dislocation climb.

Dislocation creep occurs when the layers are under high stresses. The connection between Dislocation creep rate and stress can be expressed in the steady state creep region by the following model [47]:

$$\frac{d\varepsilon_{vplastic}}{dt} = C\sigma^n e^{\frac{-Q_0}{k_B T}}$$
(1.24)

Where in most of cases the exponent of stress is in the range $3 \le n \le 10$.

Therefore, dislocation creep has a strong dependence on the applied stress and no grain size dependence.

- diffusion controlled creep

It contains Bulk diffusion (known as Nabarro-Herring creep, where the creep rate is controlled by lattice diffusion) and Grain Boundary diffusion (known as Coble creep, where the creep rate is controlled by grain boundary diffusion).

In Nabarro-Herring creep, atoms diffuse through the lattice causing grains to elongate along the stress axis. Nabarro-Herring creep has a weak stress dependence (compared to dislocation creep) and a moderate grain size dependence, with the creep strain rate decreasing as the grain size is increased. The connection between Nabarro-Herring creep strain rate and stress can be expressed in the steady state creep region by the following model [45]:

$$\frac{d\varepsilon_{vplastic}}{dt} = \frac{C\sigma}{d^2} e^{\frac{-Q_1}{k_B T}}$$
(1.25)

Where $\varepsilon_{vplastic}$ is the creep strain, *C* is a constant depending on the material and the particular creep mechanism, σ is the applied stress, *d* is the average grain size of the polycrystalline material, Q_1 is the activation energy of self-diffusion, k_B is Boltzmann's constant, and T is the absolute temperature.

Coble creep is a second form of diffusion controlled creep. In Coble creep, the atoms diffuse along grain boundaries to elongate the grains along the stress axis. This causes Coble creep to have a stronger grain size dependence than Nabarro-Herring creep. The connection between Coble creep strain rate and stress can be expressed in the steady state creep region by the following model [46]:

$$\frac{d\varepsilon_{vplastic}}{dt} = \frac{C\sigma}{d^3} e^{\frac{-Q_2}{k_B T}}$$
(1.26)

Where Q_2 is the activation energy of *grain boundary diffusion*. The other symbols have the same meaning as in Equation 1.25. *C* has an adapted value different in both equations 1.24 and 1.25.

Because the activation energy of grain boundary diffusion is smaller than the activation energy of selfdiffusion [46], that is to say, $Q_2 < Q_1$. Therefore, Coble creep occurs at lower temperatures than Nabarro-Herring creep. It also exhibits the same linear dependence on stress as Nabarro-Herring creep.

Many experiments have been made and so-called deformation maps for the various oxides can be derived. Such maps for Cr_2O_3 and Al_2O_3 are shown below in Figure 1.15 and 1.16 for the oxides forming the layers on high temperature materials. Fields are designated in these maps showing the corresponding dominant deformation mechanism at the relevant temperature and shear stress. The calculated value of the constant shear rate $\dot{\gamma}$ resulting from the respective temperature and stress conditions is indicated. These maps known as Ashby maps are plotted for a given oxide grain size.



Figure 1.15: Deformation mechanism map for Cr₂O₃ [48]



Figure 1.16: Deformation mechanism map for Al₂O₃ [48]

The grain size in these maps is $10\mu m$. Grain sizes in oxide films grown on metals are generally smaller. That is to say, in the region of diffusion-controlled creep, the strain rate curves are shifted to lower temperatures and stresses. In other words, a lower stress would be necessary at the same temperature to attain the same constant strain rate.

Although there are different kinds of creep, we can combine them together at macroscopic scale, by using a Norton-Hoff power law to simulate the visco-plastic strain in the metal and in the oxide. For an in-plane stress, without hardening and without plastic threshold [49], we can write:

$$\frac{d\varepsilon_{vplastic}}{dt} = sign(\sigma) \times J \times |\sigma|^{N} = sign(\sigma) \times \frac{1}{2} \left(\frac{|\sigma|}{K}\right)^{N} and \ N \in \mathbb{R}$$
(1.27)

Where J and K are creep coefficients and N is the Norton exponent, which can depend on temperature. It is already a derivative form.

If we compare Norton-Hoff power law with dislocation creep, we can see that:

$$J = f(\operatorname{Ce}^{\frac{-Q_0}{k_B T}})$$
(1.28)

In the same way, we can also compare Norton-Hoff power law with Coble creep, so we can see that:

$$J = f(\frac{C}{d^{3}}e^{-\frac{Q_{2}}{k_{B}T}})$$
(1.29)

And finally, we can compare Norton-Hoff power law with Nabarro-Herring creep, so that we can get:

$$J = f(\frac{C}{d^2} e^{-\frac{Q_1}{k_B T}})$$
(1.30)

In all the above three cases, *J* is a creep coefficient which depends on temperature. Therefore, in our model, we will assume that *J* is a parameter which depends on temperature according to an Arrhenius dependence.

We can find the value of creep parameter *J* for the oxide film from deformation mechanism map, but it concern bulk materials [2], which is not the present case. So in our model, we will use the value of

creep parameter *J* found in publications as an initial data, and we will try to identify the correct value of creep parameter *J* using identification method especially for the oxide films (see chapter 6).

1.2.2.2 Destructive relaxation phenomena

The destructive relaxation phenomena tend to produce the most severe consequences because they can expose fresh metal to the oxidizing environment. There are several phenomena, for example, cracking of the oxide, spallation of the oxide from the alloy substrate, buckling of the oxide and rumpling of the oxide.



Figure 1.17: Schematic diagram of responses of an oxide, which is loaded in compression. (a) Buckling of the oxide, (b) shear cracking of the oxide, and (c) plastic deformation of the oxide and alloy.

We can illustrate it with different examples. For the oxidation of Nb which results from the growth mechanism of Nb_2O_5 , oxide cracking occurs and the oxide is put into tension [11]. Oxides forming on the alkali metals also form under tension because the PBR is less than unity for these systems (Table 1.2). But usually, the oxides are in compression because the growth stresses tend to be compressive [11] and the thermal stresses are usually compressive resulting from the sign of the thermal expansion mismatch between the alloy and oxide [11].



Figure 1.18: Buckling of the alumina scale [11].

Buckling, as illustrated on Figure 1.17(a) and observed with a scanning electron microscope in Figure 1.18, combines local delamination and rumpling of the oxide layer. It is likely to occur when the metal/oxide interface is weaker than the oxide layer (from a resistance to failure point of view). It results from 2D instability of a thin film on a substrate. It is a typical response for oxide layers growing on non-coated and non-doped alloys. The deformation then induces local in-plane tensile stresses likely to prompt through-layer crack nucleation and propagation, eventually leading to the inside oxide layer failure as shown in Figure 1.17(a).

The spalling of a compressively stressed protective oxide layer will occur when the elastic strain energy stored in the oxide layer exceeds the fracture resistance, G_c , of the interface. It can be part of a more

complex process such as in buckling. The elastic strain energy stored in the layer per unit area is $(1-v)\sigma^2 h_{ox} / E$ [11], so that the criterion for failure can be expressed as:

$$(1-\nu)\sigma^2 h_{ox} / E > G_c \tag{1.31}$$

Where *E* is the Young modulus of elasticity of the layer, v is the Poisson's ratio of the layer, h_{ox} is the layer thickness, and σ is the equal biaxial residual stress in the layer.

According to this criterion, oxide layer spallation is favored by a high compressive stress, a high layer thickness and a low interface strength. This simple criterion thus offers a logical understanding of the failure of a flat interface.

Decohesion of films under compression, such as most oxide layers, require either a buckling instability or development of a wedge crack in order to spall [16].

According to elastic mechanics, buckling of a thin film under biaxial compression to form an axisymmetric buckle of radius *a* will occur at a critical stress given by:

$$\sigma_c = 1.22 \frac{E}{1 - v^2} (\frac{h_{ox}}{a})^2$$
(1.32)

However, such a buckle is stable and will not propagate to cause decohesion failure by delamination unless the strain-energy release rate also satisfies Equation 1.31. The buckling stress increases as the square of the layer thickness such that, for thick layers, buckling may not be possible. In this case, shear cracks can form within the oxide and, if Equation 1.31 is satisfied, lead to the layer spallation by a 'wedging mechanism' as illustrated in Figure 1.17(b) (shear cracks form within the oxide layer and propagate toward the surface as well as to and along the interface until total delamination occurs).



Figure 1.19: Surface picture showing local spallations on a flat alumina scale [44].

An example of local spallation of a flat layer is provided in Figure 1.19. Buckling and shear cracking are the main failure mechanisms for chromia layers around 800°C, at which limited viscoplastic relaxation occurs within the oxide layer [44].

As described by Panicaud et al [50], when buckling or shear cracking occurs, it would be necessary to take into account the evolution of the parameters of the model, e.g. the oxidation kinetics constant. But, in our current model, we will assume that no destructive relaxation phenomena occur.

References of chapter 1

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Chapter 2 Modelling part

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As explained in Chapter 1, the presence of residual stresses in thermal oxide layers has been recognized for a long time [1], and for applications it is vital to determine the strain and stress fields associated to the growth of oxide layers on metallic substrate [1].

From an experimental point of view, many experiments have been performed [2][3][4], but some of these experiments determine the residual stresses of oxidized materials after cooling, thus needing the subsequent determination of both thermal and growth stresses by calculation [1]. The direct experimental determination of isothermal stresses evolution is less common.

From a modelling point of view, several models have been established recently to predict the growth stresses [3][5][6][7][8], but they are often valid under isothermal oxidation conditions, such that they cannot be used when the temperature changes. However, in real situations, metals or alloys are often oxidized under thermal cycling loadings, so it is also essential to investigate the stress evolution under thermal cycling loadings.

In this chapter, we will establish a model, which upgrades the isothermal model to take into account different thermomechanical couplings. Firstly, all the basic theories of our model will be explained, followed by some analytical solutions, which allow understanding more deeply the proposed model. Lastly, numerical solutions using Runge–Kutta method [9] are performed.

2.1 Theory

In this part, a methodology to establish our model is given. We start from the hypotheses and the limitations of our model, and then, the differences between strong and weak coupling are explained, as well as a presentation of the different material behavior models such as elasticity, visco-plasticity, growth strain and thermal expansion. Finally, the influence of temperature on the material behavior is discussed. We first start with the general assumptions, which are valid in isothermal or non-isothermal cases, then we will simplify the model for different cases (isothermal, non-isothermal strong coupling).

2.1.1 Hypotheses and limitations on the model

In the proposed model, the following assumptions are made:

- The average stress may be theoretically calculated taking into account the existence of a possible stress gradient. However, only a uniform stress field is considered.
- The force balance equation is considered in a quasi-static domain, which leads to:

$$\int_{H_0}^{H_1} \sigma_m dz = -\int_{H_1}^{H_2} \sigma_{ox} dz$$
(2.1)

- Because we do not consider the curvature of the oxide layer and we have considered that the system is symmetric, the moments balance equation is not needed, whereas in some other models which takes the curvature into account [7], [8], [10], the moments balance equation has to be used.
- The " H_i " positions of the interfaces are defined in Figure 2.1, by reference to a median line H_0 which represents the thickness origin of the symmetrical system, H_1 the metal/oxide interface position, and H_2 is the oxide/air interface position. The subscripts "ox" and "m" refer to oxide and metal respectively.
- The system has an isotropic and biaxial behavior (i.e. the material is isotropic and the stress in the oxide layer is biaxial, that is to say, there is no stress along the z direction in Figure 2.1)
 [1].
- The two-dimensional effects such as rumpling are not considered [11].
- The non-linear mechanical phenomena (buckling, cracking, spalling) are not considered, which corresponds to the system that we have studied.
- Therefore, there is displacement continuity at the oxide/metal interface.
- Only one single phased oxide layer is considered on the metal and this phase is time independent (no other chemical transformation are considered within the bulk of the oxide, except the oxidation itself). This "average oxide" has properties obtained by averaging oxides features [1].
- Chemical deformation due to dissolution of oxygen within the substrate alloy is not considered [1], [6], [12], [13].
- The oxidation kinetics are assumed to be parabolic for the studied systems [1], [5], [13].



Figure 2.1: Geometry and coordinates for the oxide growth on a metal

It is a priori necessary to distinguish two possible cases: symmetrical oxidation (when the two metallic sides are oxidized) and asymmetric oxidation (when the oxide forms on a single side). As previously said, thereafter, the oxidation will always be considered as symmetrical. The strain tensor in the oxide layer or in the metal is then uniform and depends only on time. Furthermore, the strain continuity equation can be decomposed in the following way:

$$(\varepsilon^{elastic} + \varepsilon^{viscoplastc} + \varepsilon^{thermal} + \varepsilon^{growth})_{ox} = (\varepsilon^{elastic} + \varepsilon^{viscoplastc} + \varepsilon^{thermal})_m \quad (2.2)$$

Where ε^{growth} represents the lateral growth strain in the oxide layer, $\varepsilon^{viscoplastic}$ represents the viscoplastic strain in the layer or in the metal, $\varepsilon^{thermal}$ represents the thermal strain in the layer or in the metal and $\varepsilon^{elastic}$ represents the elastic strain in the layer or in the metal.

To obtain the time evolution of the stress within the oxide and the metal, it is necessary to consider a derivative form of the continuity Equation 2.2, which leads to:

 $\left(\frac{d\varepsilon^{elastic}}{dt} + \frac{d\varepsilon^{viscoplastic}}{dt} + \frac{d\varepsilon^{thermal}}{dt} + \frac{d\varepsilon^{growth}}{dt}\right)_{ox} = \left(\frac{d\varepsilon^{elastic}}{dt} + \frac{d\varepsilon^{viscoplastic}}{dt} + \frac{d\varepsilon^{thermal}}{dt}\right)_{m}$ (2.3)

In order to solve this equation, we have to take into account the behavior models for both materials, but before this, we have to distinguish two kinds of couplings of temperature.

2.1.2 Strong and weak couplings

We can divide the influence of temperature into two kinds:

- Strong coupling

A strong coupling means here for a coupling between two variables that is obtained from a modeling process as a consequence. Here, we based our approach on the thermodynamic framework to obtain some strong couplings between different state variables through a relation state.

If we take into account the strong coupling for the influence of temperature on mechanics, that is to say, we take into account the thermal strain ($\varepsilon^{thermal}$) in the Equation 2.2. This strong coupling links mainly the temperature rate to the thermal strain rate (thermal expansion) [14]. Such a strong coupling comes physically from the difference of thermal expansion properties for oxide and metal layers when temperature changes. In general, the expansion parameter for metal is bigger than that of oxide, i.e.

 $\frac{\alpha_m}{\alpha_{ox}} > 1$ [15]. This strong coupling cannot be neglected because it is the main influence when

temperature changes [16]. This term vanishes strictly and only for isothermal transformations.

- Weak coupling

Weak coupling means that we take into account the influence of temperature on material parameters from a methodology that does not derive from a thermodynamic approach. There are a priori two kinds of influence:

Firstly, the material parameters, such as Young's modulus for oxide and metal (E_{ox} and E_m), visco-plastic parameters for oxide and metal (J_{ox} and J_m), and growth strain parameter for oxide D_{ox} , are all changing with temperature. Therefore, we can assume that they are a function of temperature [17].

Secondly, because of the dependence of some parameters on temperature, when we use the differential form in Equation 2.3, some new terms appear.

For example, if we assume that the material behavior model is such that:

$$\varepsilon = f(\mathbf{C})g(\sigma) \tag{2.4}$$

Where ε is the strain and σ is the stress. C is a material parameter, which depends on temperature. Therefore, when we differentiate Equation 2.4 with time t, we can get:

$$\frac{d\varepsilon}{dt} = \frac{d(f(C)g(\sigma))}{dt} = \frac{df(C)}{dT}\frac{dT}{dt}g(\sigma) + \frac{dg(\sigma)}{dt}f(C)$$
(2.5)

Where T is the temperature. The first term in the second member in Equation 2.5 is some new added term that depends on the temperature rate.

To obtain analytical solutions, it will be sometimes easier to neglect the weak couplings.

2.1.3 Behavior models

In order to calculate Equation 2.3, some material behavior models has to be taken into account, namely, elastic model for metal and oxide, visco-plastic model for metal and oxide, growth strain model for oxide and thermal expansion model for metal and oxide.

2.1.3.1 Elasticity (for metal or oxide)

Some hypotheses have been made:

- The material is isotropic and homogeneous, that is to say, the material has the same properties in all the direction and for all the positions [18].
- Only a linear behavior for both materials has been considered.
- The material is under in-plane stress condition ($\sigma_z = 0$) [19].

With these hypotheses, and if the stress direction is as in Figure 2.2, we can simplify the stress tensor:





$$\overline{\overline{\sigma}} \xrightarrow{in-plane} \begin{pmatrix} \sigma_x & \tau & 0 \\ \tau & \sigma_y & 0 \\ 0 & 0 & 0 \end{pmatrix} \xrightarrow{isotropy} \begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
(2.6)

And then, the Hooke model is applied for the elastic strain, for an in-plain stress:

$$\varepsilon^{elastic} = \left(\frac{1-\nu}{E}\right) \times \sigma \tag{2.7}$$

Where *E* is the young modulus; ν is the Poisson ratio. In our case, we assume that the Young's modulus *E* depends on temperature and the Poisson ratio is a constant when temperature changes [17].

Derivative of Equation 2.7 has to be done carefully, because both Young's modulus E and stress σ are changing with time. According to the methodology proposed with Equation 2.5, we have:

$$\frac{d\varepsilon}{dt}^{elastic} = \frac{d}{dT} \left(\frac{1-\nu}{E}\right) \frac{dT}{dt} \times \sigma + \left(\frac{1-\nu}{E}\right) \frac{d\sigma}{dt}$$
(2.8)

The first term in Equation 2.8 appears because of the weak coupling.

We can find the values of *E* at different temperatures in literatures directly or we can calculate them through single-crystal elastic moduli at different temperatures using scale transition methods.
2.1.3.2 Visco-plasticity (for metal or oxide)

Some hypotheses have been made:

- The material is isotropic and homogeneous, that is to say, the material has the same properties in all the direction and for all the positions.
- The material has neither elastic limit nor hardening behavior.
- The material is under in-plane stress condition.

A Norton-Hoff power law is used to simulate the visco-plastic strain in the metal and in the oxide for an in-plane stress, without hardening and without plastic threshold because we are in the zone of temperature, for which the material does not present significant cold plasticity:

$$\frac{d\varepsilon}{dt}^{viscoplastc} = sign(\sigma) \times J \times |\sigma|^{N} = sign(\sigma) \times \frac{1}{2} \left(\frac{|\sigma|}{K}\right)^{N} and N \in \mathbb{R}$$
(2.9)

Where J and K are the creep coefficients ($J = \frac{1}{2} \left(\frac{1}{K}\right)^N$) and N is the Norton exponent, which can

depend on temperature. It is already a derivative form and thus can be used directly in Equation 2.3.

2.1.3.3 Growth strain (for oxide)

Some hypotheses have been made:

- The material is isotropic and homogeneous, that is to say, the material has the same properties in all the direction and for all the positions.
- The kinetics of oxidation follows a parabolic rate law [1].

In chapter 1, we have discussed about different models and origins for growth strain. In our modelling, the Clarke model is used, which is originally proposed by Clarke [20], and has been verified and generalized by Panicaud and al. [5]. Nowadays, it is used by many authors [7][8][11][21] and indicates that the growth strain rate is proportional to the oxide layer kinetics.

$$\frac{d\varepsilon}{dt}^{growth} = D_{ox}\frac{dh_{ox}}{dt}$$
(2.10)

Where $h_{_{ox}}$ is the thickness of the oxide layer and $D_{_{ox}}$ is a parameter related to some microstructural

parameters, which is not a diffusion coefficient and which may depend on temperature. D_{ox} is a parameter related to the growth the oxide layer, which we will be identified in the identification part described in Chapter 4.

It is worth noting that Equation 2.10 depends indirectly on temperature through a kinetic constant. For parabolic evolution of the oxide thickness, we have:

$$h_{ox} = A_{P}\sqrt{t} \Longrightarrow \frac{d\varepsilon}{dt}^{growth} = D_{ox}\frac{dh_{ox}}{dt} = D_{ox}\left\langle\frac{A_{P}}{2\sqrt{t}} + \frac{dA_{P}}{dT}\frac{dT}{dt}\sqrt{t}\right\rangle$$
(2.11)

Where A_p is the parabolic kinetic constant that varies with temperature. The second term in the last member appears because of the weak coupling.

Because of the irreversibility of the processes, the oxide thickness cannot decrease excepted because of thermal expansion effect. Consequently, the Macaulay notation < . > is used to keep only the positive part for the rate of h_{ax} due to the chemical effect.

2.1.3.4 Thermal expansion (for metal or oxide)

A hypothesis has been made:

- The material is isotropic and homogeneous, that is to say, the material has the same properties in all the direction and for all the positions.

For the thermal strain $\varepsilon^{^{thermal}}$, we consider the following equation:

$$\varepsilon^{\text{thermal}} = \int_{T_{\text{ref}}}^{T_{\text{fin}}} \alpha(T) dT + \varepsilon_{\text{ref}}$$
(2.12)

Where T_{fin} is the final temperature, and T_{ref} is a reference temperature (for example: 25°C), and $\mathcal{E}_{ref}^{thermal}$ is the thermal strain at these reference temperature T_{ref} .

The derivative form of Equation 2.12 is:

$$\frac{d\varepsilon}{dt}^{thermal} = \alpha(T)\frac{dT}{dt}$$
(2.13)

2.1.4 Influence of temperature on material parameters

In our model, some material parameters, namely, elastic modulus *E*, kinetic constant A_p visco-plastic coefficient *J*, growth coefficient D_{ox} and thermal expansion parameter α , are changing with temperature. This is one direct improvement to the isothermal model, which has been presently taken into account.

2.1.4.1 Elastic modulus

For elastic modulus, it is classical to consider the evolution of elastic modulus with temperature as a power expansion [22]:

$$E(T) = aT^2 + bT + c \tag{2.14}$$

Where a, b and c are material constants.

Then, it is easy to get the derivative form:

$$\frac{dE(T)}{dT} = 2aT + b \tag{2.15}$$

2.1.4.2 Kinetic constant

For kinetic constant, we assume that the kinetics constant A_p follows an Arrhenius dependence [23]:

$$A_p = A_{p0} \exp(\frac{-Q_a}{RT})$$
(2.16)

Where R=8.314J/ (K*mol), $A_{_{p0}}$ and Q_a are constants.

The derivative form for Equation 2.16 is:

$$\frac{dA_{P}}{dT} = A_{P0}e^{\frac{-Q_{a}}{RT}} \frac{Q_{a}}{RT^{2}} = \frac{A_{P}Q_{a}}{RT^{2}}$$
(2.17)

2.1.4.3 Visco-plastic coefficients

The visco-plasticity recovers several phenomena. For creep with diffusion of punctual defects, different mechanisms can occur either in grains (Nabarro-Herring) or in grain boundaries (Coble) [4]. Following such an explication, the Norton coefficient is given by:

$$J(T) = \frac{\Omega C_{HN} D_{Fick}^{G}(T)}{RTd^{2}(T)} \left(1 + \frac{C_{C} D_{Fick}^{GB}(T) \delta}{C_{HN} D_{Fick}^{G}(T) d(T)} \right)$$
(2.18)

Where Ω is the molar volume, C_{HN} and C_{C} are some numerical constants linked to the geometry, D_{Fick} are the diffusion coefficients in grain (G) and in grain boundaries (GB), R is the gas constant, d is the grain size and δ is the grain boundary average thickness. This expression can be found in [4] and its validity has been verified in [12] in the range of temperature [700°C-900°C] for chromia. By considering either one of the mechanism or the other (but not the mixed case) and if grain size and diffusion coefficient follow an Arrhenius model, we suggest the following expression (where the effect of the microstructure is present in the exponential function):

$$J(T) = \frac{Cste_{J1}}{T} \exp(\frac{-Q_{J1}}{RT})$$
(2.19)

Where $Cste_{J1}$ is a constant, T is the temperature, R=8.314J/(K*mol) and Q_{J1} is the activation energy. When identifying the material parameters in the considered range of temperature, it is also possible to use a simpler equation with the same quality of fitting:

$$J(T) \approx Cste_{J_2} \exp(-Q_{J_2} / RT)$$
(2.20)

Where $Cste_{J2}$ is a constant and Q_{J2} is the activation energy.

For creep effects, other kinds of mechanisms can be found (creep with dislocations... [20]). As a consequence, it is difficult to predict a general model with a universal dependence of the parameters with temperature. It is then always possible to consider the experimental results and try to fit with the best mathematical function [14].

2.1.4.4 Growth coefficient

For the growth coefficient D_{ox} , it is more difficult, because the corresponding mechanisms are not

yet completely established. The D_{ox} parameter depends on microstructural features and may also depend on temperature. According to Clarke [20], the temperature dependence could be:

$$D_{ox}(T) = Cste_{D1} \exp(-Q_1 / RT) + Cste_{D2} \exp(-Q_2 / RT)$$
(2.21)

Other dependence on temperature *T* for this model has been explored in [14] and can vary as:

 $D_{ox}^{\pm 1}(T) = D_0^{\pm 1} \exp(-Q_D / RT)$ (2.22) Where Q_D is the activation energy. *R* is the gas constant. Sign of the exponent depends on the considered system.

2.1.4.5 Expansion parameter

For the expansion parameter α , we assume that it changes with temperature like this [24]: $\alpha = \alpha_0 + \text{DaTO} \times (T - T_0)$ (2.23)

Where α_0 , T_0 and DaT0 are all constants.

2.2 Analytical solutions

With all the assumptions presented in the theory part (Part 2.1), considering the most general couplings (weak and strong), we can obtain:

$$\dot{\mathcal{E}}_{ox} = \dot{\mathcal{E}}_m \tag{2.24}$$

$$\dot{\varepsilon}_{m} = \frac{d}{dT} \left(\frac{1 - v_{m}}{E_{m}(T)} \right) \dot{T} \sigma_{m} + \frac{1 - v_{m}}{E_{m}(T)} \dot{\sigma}_{m} + J_{m}(T) \left| \sigma_{m} \right|^{N_{m}} signe(\sigma_{m}) + \alpha_{m}(T) \dot{T}$$
(2.25)

$$\dot{\varepsilon}_{ox} = \frac{d}{dT} \left(\frac{1 - v_{ox}}{E_{ox}(T)} \right) \dot{T} \sigma_{ox} + \frac{1 - v_{ox}}{E_{ox}(T)} \dot{\sigma}_{ox} + J_{ox}(T) \left| \sigma_{ox} \right|^{N_{ox}} signe(\sigma_{ox}) + D_{ox}(T) \dot{h}_{ox}(t) + \alpha_{ox}(T) \dot{T}$$
(2.26)

$$\sigma_m [H_1(t) - H_0] + \sigma_{ox} [H_2(t) - H_1(t)] = 0$$
(2.27)

With $h_{ox}(t) = H_2(t) - H_1(t)$: oxide layer thickness.

Solving Equation 2.24 to 2.27, finally we can get:

$$\dot{\sigma}_{ox} = \frac{\left((\alpha_m - \alpha_{ox})\dot{T}\theta + \frac{\sigma_{ox}}{\theta} \frac{1 - v_m}{E_m} \dot{\theta} + \sigma_{ox} \frac{2a_m + b_m}{E_m^2} (1 - v_m)\dot{T} - sign(\sigma_{ox}) \frac{1}{2} \left(\frac{|\sigma_{ox}|}{K_{ox}} \right)^{N_{ox}} \theta \right)}{\left(+ \sigma_{ox} \frac{2a_{ox} + b_{ox}}{E_{ox}^2} (1 - v_{ox})\dot{T}\theta - sign(\sigma_{ox}) \frac{1}{2} \left(\frac{|\sigma_{ox}|}{K_m} \right)^{N_m} \theta^{1 - N_m} - D_{ox}\dot{h}_{ox}\theta} \right)} \left(\frac{1 - v_m}{E_m} + \frac{1 - v_{ox}}{E_{ox}} \theta \right)$$
(2.28)

NT.

Where a_m , b_m , c_m and a_{ox} , b_{ox} , c_{ox} are material constants for Young's modulus defined in Equation 2.14, for metal and oxide layer respectively.

A differential equation for $\sigma(t)$ has finally been obtained. We can use Runge–Kutta method to obtain the numerical result, because it is difficult to obtain an analytical solution due to the complexity of the differential equation. Therefore, some special conditions have to be considered in order to get the analytical solution.

2.2.1 Isothermal conditions

Firstly, isothermal conditions are assumed to be satisfied, so that all the material parameters are constant with different temperatures and the differential of temperature over time ($\frac{dT}{dt}$) is 0. Because of this, the final differential equation can be simplified as the following equation system:

$$\dot{\varepsilon}_{ox} = \dot{\varepsilon}_m \tag{2.29}$$

$$\dot{\varepsilon}_m = \frac{1 - v_m}{E_m} \dot{\sigma}_m + J_m \left| \sigma_m \right|^{N_m} signe(\sigma_m)$$
(2.30)

$$\dot{\varepsilon}_{ox} = \frac{1 - v_{ox}}{E_{ox}} \dot{\sigma}_{ox} + J_{ox} \left| \sigma_{ox} \right|^{N_{ox}} signe(\sigma_{ox}) + D_{ox} \dot{h}_{ox}(t)$$
(2.31)

$$\sigma_m [H_1(t) - H_0] + \sigma_{ox} [H_2(t) - H_1(t)] = 0$$
(2.32)

With $h_{ox}(t) = H_2(t) - H_1(t)$: oxide layer thickness.

Oxidation of metals is assumed to be parabolic (diffusion origin). It is true for many metals, when the influence of the chemical kinetics is only considered at short times [25]. Then, the oxide thickness evolution can be mainly written as:

$$h_{ox}(t) = \sqrt{k_{CP}t} = A_p \sqrt{t}$$
(2.33)

Where k_{CP} is the parabolic kinetic constant.

Two different opposite cases have been studied corresponding respectively to internal anionic and external cationic growth [26]. Table 2. summarizes the expressions obtained for the different parameters:

External interface growth	Internal interface growth
$h_{ox}(\mathbf{t}) = H_2(\mathbf{t}) - H_1 = A_p \sqrt{t}$	$h_{ox}(\mathbf{t}) = H_2 - H_1(\mathbf{t}) = A_p \sqrt{t}$
$\dot{h}_{ox}(t) = \frac{A_p}{2\sqrt{t}} = \frac{A_p^2 \theta(t)}{2H_1}$	$\dot{h}_{ox}(t) = \frac{A_p}{2\sqrt{t}} = \frac{A_p^2(1+\theta(t))}{2H_2}$
$\theta(t) = \frac{H_1}{H_2(t) - H_1} = \frac{H_1}{A_p \sqrt{t}}$	$\theta(t) = \frac{H_1(t)}{H_2 - H_1(t)} = \frac{H_2}{A_p \sqrt{t}} - 1$
$\dot{\theta}(t) = -\frac{H_1}{2Ap\sqrt{t^3}} = -\frac{\theta(t)}{2t}$	$\dot{\theta}(t) = -\frac{H_2}{2Ap\sqrt{t^3}} = -\frac{1+\theta(t)}{2t}$

Table 2.1 : Analytical expressions for the parabolic kinetic parameters (H₀=0) [6].

Here external interface growth and internal interface growth will draw almost the same results.

Incorporating Equation 2.32 into Equations 2.31 and 2.30, differential equations for the stress evolution in metal and oxide are obtained. So, we get in the case of external oxidation (H_1 = constant; H_0 = 0):

$$\dot{\sigma}_{m}\left[\frac{1-v_{m}}{E_{m}}+\frac{1-v_{ox}}{E_{ox}}\theta(t)\right]+\sigma_{m}\left[\frac{1-v_{ox}}{E_{ox}}\dot{\theta}(t)\right]-\xi J_{m}\left|\sigma_{m}\right|^{N_{m}}-\xi J_{ox}\left|\sigma_{m}\right|^{N_{ox}}\theta^{N_{ox}}(t)=D_{ox}\dot{h}_{ox}(t)$$
(2.34)

$$\dot{\sigma}_{ox}\left[\frac{1-v_m}{E_m}+\frac{1-v_{ox}}{E_{ox}}\theta(t)\right] - \sigma_{ox}\left[\frac{1-v_m}{E_m}\frac{\dot{\theta}(t)}{\theta(t)}\right] + \xi\theta^{1-N_m}(t)J_m \left|\sigma_{ox}\right|^{N_m} + \xi J_{ox} \left|\sigma_{ox}\right|^{N_{ox}}\theta(t) = -D_{ox}\dot{h}_{ox}(t)\theta(t)$$

$$\xi = \operatorname{signa}(\sigma_{ox}) = -\operatorname{signa}(\sigma_{ox})$$
(2.35)

$$\zeta = signe(O_{ox}) = -signe(O_m)$$
 if $\theta > 0$

These evolution equations are differential equations of the first order with non-constant coefficients (non-linear terms). General solutionning methods for such equations exist, but it is not easy to express the exact solution using simple algebraic functions. Nevertheless, in order to obtain an estimation of some features of the stress evolution problem (characteristic time or possible extremum stress), asymptotic analytic solutions of this system can be found for short and long times [13].

2.2.1.1 Short times solutions

At very short times, the oxide thickness is less than the metal thickness and $\theta >> 1$, so that at short times ($t \rightarrow 0$), for $\sigma_{\alpha x}(t=0) = 0$, Equation 2.35 leads to:

$$\dot{\sigma}_{ox} + \frac{\sigma_{ox}}{2tr_{E}\theta(t)} \approx -\frac{D_{ox}A_{p}^{2}}{2H_{1}}\frac{E_{ox}}{1 - v_{ox}}\theta(t) = -D_{ox}\frac{E_{ox}}{1 - v_{ox}}\frac{A_{p}}{2\sqrt{t}}$$
(2.36)

with the dimensionless parameters:

$$r_E = \frac{E_m}{E_{ox}} \frac{1 - v_{ox}}{1 - v_m}; \theta(t) = \frac{H_1}{A_p \sqrt{t}}$$

The solution of this equation is:

$$\sigma_{ox} = -\frac{D_{ox}H_{1}E_{m}}{1 - v_{m}}(1 - e^{-\frac{A_{p}}{H_{1}r_{E}}\sqrt{t}}) \approx -\frac{D_{ox}A_{p}E_{ox}}{1 - v_{ox}}\sqrt{t} \quad \text{(order 1)}$$
(2.37)

Reporting this solution (at the order 1) in Equation 2.32, the stress in metal can be deduced. This solution set (for metal and oxide) is a couple of results at the same order of approximation. The stress in the oxide depends, at the order 1, only on the elastic mechanical coefficients (E and v) of the oxide layer. The sign of the stress (tensile or compressive) is finally given by the sign of the Dox parameter, all others coefficients being positive. In the oxide layer, the stress growth (in absolute value) can be written as the oxidation time square root.

We have plotted the solution for short times, for the first order of approximation of this solution and compared with the numerical solution, which will be detailed in Section 2.3.



Figure 2.3: Comparison of different solutions. Model parameters: $E_m = 160GPa$; $E_{ox} = 300GPa$; $v_m = 0.3$; $v_{ox} = 0.27$; $K_{ox} = 1 \times 10^{15} Pa^{-1}s^{-1}$ $K_m = 1 \times 10^{15} Pa^{-3.3}s^{-1}$; $A_p = 1.23 \times 10^{-8} m s^{-0.5}$; $\Delta t = 0.5s$; $D_{ox} = 5000m^{-1}$; $\sigma_{ox}(t=0) = \sigma_m(t=0) = 0$; $H_1 = H_2(t=0) = 1 \text{ mm}$.

As shown in Figure 2.3, at the beginning part, the short times solution corresponds well with the numerical solution, and the difference between the first order approximation and the short times solution is very small. Thus, we can use this first order approximation analytical solution to predict the stress evolution at the beginning part.

Using the same method, we can also get the solution for stress in the metal by solving Equation 2.34 [5]:

$$\sigma_{m} = \frac{D_{ox}A_{p}^{2}E_{ox}}{H_{1}(1-v_{ox})}t + \sigma_{m}(t=0) \approx -\frac{D_{ox}A_{p}E_{ox}}{1-v_{ox}}\sqrt{t}$$
(2.38)

2.2.1.2 Long times solution

For infinite long times, the approximation $\theta \ll 1$ appears mathematically justified. However, it means that the thickness of the oxide layer became larger than the metal one. This case corresponds to the global thermodynamic limit, when the whole metal has nearly been consumed in the chemical reaction. But, it does not correspond with experimental situations when the experimentation time is long but remains limited (typically, $\theta \approx H_1 / h_{ox} = 10^{-3} / 10^{-6} = 10^3$). So, the asymptotic calculation at long time needs, to remain realistic, to keep the approximation $\theta \gg 1$.

For long times ($t \rightarrow \infty$, but $\theta >> 1$), Equation 2.35 is then:

$$\dot{\sigma}_{ox} + \left(\frac{1 - v_{ox}}{E_{ox}}\right)^{N_{ox} - 1} \frac{signe(\sigma_{ox}) |\sigma_{ox}|^{N_{ox}}}{\tau_{ox}} \approx 0$$

with the characteristic time:

$$\tau_{ox} = \left(\frac{1 - v_{ox}}{E_{ox}}\right)^{N_{ox}} \times \frac{1}{J_{ox}}$$

Whose solution is:

$$\sigma_{ox}(t) = Cste_1 \times \exp\left(\frac{-(t-t_0)}{\tau_{ox}}\right) \quad \text{when } N_{ox} = 1$$
(2.39)

$$\left|\sigma_{ox}(t)\right| = \frac{E_{ox}}{1 - v_{ox}} \left[(N_{ox} - 1)\frac{t}{\tau_{ox}} + Cste_2 \right]^{\frac{1}{1 - N_{ox}}} \quad \text{when } N_{ox} \neq 1$$
(2.40)

And $\sigma_{ax} = signe(\sigma_{ax}) |\sigma_{ax}(t)|$, Cste₁ and Cste₂ are two integration constants linked to initial conditions.

Using the same method, we can also get the solutions for stress in the metal. Table 2.2 summarizes the results for different visco-plasticity behaviors (for different N_{ox}), both in oxide and metal.

Short time($t ightarrow 0$), $\sigma_{\rm ox}(t=0)=0$ and	Long time($t \rightarrow \infty$), $\theta >> 1$
$\sigma_{_{m}}(t=0)\neq0,\ \theta>>1$	
$\sigma_{ox} = -\frac{D_{ox}H_1E_m}{1-v_m}(1-e^{\frac{A_p}{H_1r_E}\sqrt{t}})$	$\sigma_{ox}(t) = Cste_1 \times \exp\left(\frac{-(t-t_0)}{\tau_{ox}}\right)$
$\sigma_{ox}(\text{order 1}) \approx -\frac{D_{ox}A_pE_{ox}}{1-v_{ox}}\sqrt{t}$	
$\sigma_m = \frac{D_{ox}A_p^2 E_{ox}}{H_1(1 - v_{ox})}t + \sigma_m(t = 0)$	$\sigma_m(\mathbf{t}) = Cste_3 \times \exp\left(\frac{-(t-t_0)}{\tau_{ox}}\right) + \frac{D_{ox}A_p^2}{2H_1}\frac{E_{ox}}{1-v_{ox}}\tau_{ox}$
$\sigma_{ox} = -\frac{D_{ox}H_1E_m}{1-v_m}(1-e^{-\frac{A_p}{H_1r_E}\sqrt{t}})$	$\left \sigma_{ox}(t) \right = \frac{E_{ox}}{1 - v_{ox}} \left[(N_{ox} - 1)\frac{t}{\tau_{ox}} + Cste_2 \right]^{\frac{1}{1 - N_{ox}}}$
$\sigma_{ox}(\text{order 1}) \approx -\frac{D_{ox}A_pE_{ox}}{1-v_{ox}}\sqrt{t}$	$\sigma_{ox} = signe(\sigma_{ox}) \left \sigma_{ox}(t) \right $
$\sigma_m = \frac{D_{ox}A_p^2 E_{ox}}{H_1(1 - v_{ox})}t + \sigma_m(t = 0)$	No simple analytical solution for $\sigma_{\rm m}({\rm t})$
$\sigma_{ox} = -\frac{D_{ox}H_2E_m}{1-v_m}(1-e^{-\frac{A_p}{H_2r_E}\sqrt{t}})$	$\sigma_{ox}(t) = Cste_1 \times \exp\left(\frac{-(t-t_0)}{\tau_{ox}}\right)$
$\sigma_{ox}(\text{order 1}) \approx -\frac{D_{ox}A_pE_{ox}}{1-v_{ox}}\sqrt{t}$	
$\sigma_m = \frac{D_{ox} A_p^2 E_{ox}}{H_2 (1 - v_{ox})} t + \sigma_m (t = 0)$	$\sigma_m(\mathbf{t}) = Cste_3 \times \exp\left(\frac{-(t-t_0)}{\tau_{ox}}\right) + \frac{D_{ox}A_p^2}{2H_2}\frac{E_{ox}}{1-v_{ox}}\tau_{ox}$
$\sigma_{ox} = -\frac{D_{ox}H_2E_m}{1-v_m}(1-e^{\frac{A_p}{H_2r_E}\sqrt{t}})$	$\left \sigma_{ox}(t)\right = \frac{E_{ox}}{1 - v_{ox}} \left[(N_{ox} - 1)\frac{t}{\tau_{ox}} + Cste_2 \right]^{\frac{1}{1 - N_{ox}}}$
$\sigma_{ox}(\text{order 1}) \approx -\frac{D_{ox}A_pE_{ox}}{1-v_{ox}}\sqrt{t}$	$\sigma_{ox} = signe(\sigma_{ox}) \left \sigma_{ox}(t) \right $
$\sigma_m = \frac{D_{ox} A_p^2 E_{ox}}{H_2 (1 - v_{ox})} t + \sigma_m (t = 0)$	No simple analytical solution for $\sigma_{_{m}}({ m t})$

Table 2.2: Synthesis of the different asymptotic solutions for external and internal interface growth

$$(N=1 \text{ and } N \neq 1)$$

From Table 2.2, we can see that the equations at short times remain analogous whatever the creep exponent is, because the beginning of the oxidation is governed by the growth strain [13]. The results for both internal interface growth and external interface growth are similar, we only need to replace H_1 in external interface growth with H_2 for the internal interface growth.

The model developed above gives different stress variations at short and long times. The distinction between the two evolutions, increase (in absolute value) of the oxide stress at the beginning of the oxidation and relaxation at the longest times, implies that an extremum (maximum in absolute value) stress occurs in the stress evolution, for a characteristic oxidation time. That time can be estimated by comparing the different solutions of Table 2.2 (especially σ_m at short and long time when N=1) and

gives $t_{\text{inflexion}} \approx \frac{\tau_{ox}}{2}$. From this characteristic time, the minimal stress value reached in the oxide can be extracted. For example, for N = 1 and at first order ($\theta >> 1$), the expression of this stress is:

$$\sigma_{\min} \approx -\frac{D_{ox}A_p}{J_{ox}\sqrt{2\tau_{ox}}}$$
(2.41)

I propose another way to find the extremum stress. We have combined Equation 2.34 and 2.35 with $\dot{\sigma}_{ox} = 0$. In order to simplify the calculation, we have assumed: $N_{ox} = N_m = 1$. Finally, we can get:

$$\sigma_{\min} \approx -\frac{D_{ox}H_1}{2t(J + \frac{JH_1}{A_p\sqrt{t}} + \frac{1 - v_m}{2tE_m})}$$
(2.42)

This is a function depending on time, so that we cannot use it directly to find the σ_{\min} value. Moreover, if we assume that $t_{\max} \approx \frac{\tau_{ox}}{\tau_{ox}}$, we can finally get:

$$\sigma_{\min} \approx -\frac{D_{ox}H_1}{J_{ox}(2\sqrt{\tau_{ox}} + \frac{\sqrt{2\tau_{ox}}H_1}{A_n})}$$
(2.43)

Comparing Equation 2.41 with 2.43, we can see that the difference for calculating σ_{\min} is very small (see Figure 2.4).



Figure 2.4: Comparing different methods to calculate σ_{\min} . Model parameters: $E_m = 160GPa$; $E_{ox} = 300GPa$; $v_m = 0.3$; $v_{ox} = 0.27$; $K_{ox} = 1 \times 10^{15} Pa^{-1} s^{-1}$ $K_m = 1 \times 10^{15} Pa^{-3.3} s^{-1}$; $A_p = 1.23 \times 10^{-8} m s^{-0.5}$; $\Delta t = 0.5s$; $D_{ox} = 5000 m^{-1}$; $\sigma_{ox} (t = 0) = \sigma_m (t = 0) = 0$; $H_1 = H_2 (t = 0) = 1 \text{ mm}$.

We can also see from Figure 2.4 that there exists a difference for the value of σ_{\min} (about 700MPa) between numerical result (using Runge–Kutta method) and analytical result.

This additional way to the existing approach for extremum determination shows that analytical results only give a qualitative trend under the considered approximation. Only a full simulation is able to predict quantitatively and accurately the stress magnitude and its evolution for all the time.

2.2.2 Non-isothermal conditions

In usual situation, it is more realistic to consider non-isothermal conditions when the materials are oxidized. We divide the solutions into two kinds depending on the different thermal loadings. If the thermal loading is a step like this:



Figure 2.5: Step thermal loading

We can use the Laplace transform to solve the differential equation with some assumptions.

If the thermal loading is periodic like this:





We can use frequency analysis methods to obtain the function for stress vs time.

All these approaches are new contributions for non isothermal conditions.

2.2.2.1 Laplace transform method

In order to get analytical solutions, some supplementary assumptions (beside all the assumptions in Part 2.1.1) have to be made:

- Only strong coupling is considered (there is no temperature-dependence of the material parameters).
- The Norton exponents $N_{ox} = N_m = 1$, that is to say, we assume a diffusion controlled by

creep mechanism for both oxide and metal layer.

- The thermal loading is as shown in Figure 2.5.
- We assume a two-layer system: oxide + metal.
- We consider calculations at macroscopic scale.

With these assumptions, a differential equation for oxide layer can be obtained:

$$\dot{\sigma}_{ox}\left[\frac{1-v_m}{E_m} + \frac{1-v_{ox}}{E_{ox}}\theta(t)\right] - \sigma_{ox}\left[\frac{1-v_m}{E_m}\frac{\dot{\theta}(t)}{\theta(t)}\right] + J_m\sigma_{ox} + J_{ox}\sigma_{ox}\theta(t) = -D_{ox}\dot{h}_{ox}(t)\theta(t) + (\alpha_m - \alpha_{ox})\dot{T}(H_{step}(t-t_1) - H_{step}(t-t_2))\theta(t)$$
(2.44)

*H*_{step} is the Heaviside step function.

When the change of temperature occurs at long time, that is to say, t_1 (start time of changing temperature) >> T_{ox} (characteristic time), we can simplify Equation 2.44 as:

$$\dot{\sigma}_{ox}(1+\frac{1}{r_E\theta(t)}) + \frac{\sigma_{ox}}{2tr_E\theta(t)} + \frac{\sigma_{ox}}{\tau_{ox}}(1+\frac{J_m}{J_{ox}\theta(t)}) = (\alpha_m - \alpha_{ox})\dot{T}\frac{E_{ox}}{1-v_{ox}}(H_{step}(t-t_1) - H_{step}(t-t_2))$$
(2.45)

Because $t >> \tau_{_{ox}}$ and $\theta >> 1$, we can ignore the term $\frac{\sigma_{_{ox}}}{2tr_{_E}\theta(t)}$ and we finally get:

$$\dot{\sigma}_{ox}(1+\frac{1}{r_{E}\theta(t)}) + \frac{\sigma_{ox}}{\tau_{ox}}(1+\frac{J_{m}}{J_{ox}\theta(t)}) = (\alpha_{m} - \alpha_{ox})\dot{T}\frac{E_{ox}}{1 - v_{ox}}(H_{step}(t-t_{1}) - H_{step}(t-t_{2}))$$
(2.46)

If we introduce the variables that will be treated as constants because we may neglect $\theta(t)^{-1}$:

$$A_{1} = (1 + \frac{1}{r_{E}\theta(t)})$$
(2.47)

$$A_2 = (1 + \frac{J_m}{J_{\alpha \nu} \theta(\mathbf{t})}) \tag{2.48}$$

$$A_3 = (\alpha_m - \alpha_{ox}) \frac{E_{ox}}{1 - v_{ox}}$$
(2.49)

Equation 2.46 becomes:

$$A_{1}\dot{\sigma}_{ox} + A_{2}\frac{\sigma_{ox}}{\tau_{ox}} = A_{3}\dot{T}(H_{step}(t-t_{1}) - H_{step}(t-t_{2}))$$
(2.50)

If we assume $\sigma_{ax}(t=0)=0$, we can now use the Laplace transform [27] to solve Equation 2.50:

$$A_{1}p\Sigma_{ox} + A_{2}\frac{\Sigma_{ox}}{\tau_{ox}} = \frac{A_{3}}{p}\dot{T}(e^{-t_{1}p} - e^{-t_{2}p})$$
(2.51)

So now we can solve $\Sigma_{ox}(p)$:

$$\Sigma_{ox}(\mathbf{p}) = \left(\frac{A_3}{p} \dot{\mathbf{T}}(e^{-t_1 p} - e^{-t_2 p})\right) \frac{1}{pA_1 + A_2 / \tau_{ox}}$$

$$= A_3 \dot{\mathbf{T}} e^{-t_1 p} \left(\frac{\tau_{ox} / A_2}{p} - \frac{\tau_{ox} A_1 / A_2}{pA_1 + A_2 / \tau_{ox}}\right) - A_3 \dot{\mathbf{T}} e^{-t_2 p} \left(\frac{\tau_{ox} / A_2}{p} - \frac{\tau_{ox} A_1 / A_2}{pA_1 + A_2 / \tau_{ox}}\right)$$
(2.52)

Finally, we can get $\sigma_{ox}(t)$:

$$\sigma_{ox}(t) = \frac{A_3 \dot{T} \tau_{ox}}{A_2} H_{step}(t-t_1) (1 - e^{-\frac{A_2 t-t_1}{A_1 \tau_{ox}}}) - \frac{A_3 \dot{T} \tau_{ox}}{A_2} H_{step}(t-t_2) (1 - e^{-\frac{A_2 t-t_2}{A_1 \tau_{ox}}})$$
(2.53)

If we calculate the first order approximation, we can get:

$$\sigma_{ox}(t) \approx \frac{A_3 \dot{T}(t-t_1)}{A_1} H_{step}(t-t_1) - \frac{A_3 \dot{T}(t-t_2)}{A_1} H_{step}(t-t_2)$$
(2.54)

From this result, we can calculate the $\Delta\sigma_{ox}$ when temperature changes:

$$\Delta \sigma_{ox} = \sigma_{ox}(t_2) - \sigma_{ox}(t_1) \approx \frac{A_3 T(t_2 - t_1)}{A_1} \approx (\alpha_m - \alpha_{ox}) \frac{E_{ox}}{1 - v_{ox}} \Delta T$$
(2.55)

If we know $\Delta \sigma_{ox}$ and ΔT from the experimental results, and because the Young's modulus and Poison's ratio are supposed to be known, so we can use Equation 2.55 to identify the thermal expansion parameter mismatch $(\alpha_m - \alpha_{ox})$. An example of the $\Delta \sigma_{ox}$ corresponding to a given ΔT with $\sigma_{ox}(t=0)=0$ is shown in Figure 2.7:



Figure 2.7: An example of the $\Delta \sigma_{ox}$ corresponding to the ΔT when using the Laplace method. From Figure 2.7, we can see that if $\sigma_{ox}(t=0)=0$, σ_{ox} keeps 0 until the time t_1 when the temperature changes, and during t_1 and t_2 (temperature is changing), σ_{ox} increases; and after t_2 (temperature stops changing), then σ_{ox} decreases. It offers a new method to identify the thermal expansion parameter mismatch $(\alpha_m - \alpha_{ox})$.

2.2.2.2 Frequency analysis methods

(a) General equations

Frequency analysis methods can be used when the thermal loading is periodic. In order to get an analytical solution, some supplementary assumptions (beside all the assumptions in Part 2.1.1) have to be made:

- Only strong coupling is considered (there is no temperature-dependence of the material parameters).
- The thermal loading is as shown in Figure 2.6.
- We assume a two-layer system: oxide+metal.
- We consider calculations at macroscopic scale.

With these assumptions, a coupled ordinary differential equation can be deduced:

$$\dot{\sigma}_{ox} = \frac{\begin{pmatrix} (\alpha_m - \alpha_{ox})\dot{T}\theta - D_{ox}\dot{h}_{ox}\theta + \frac{\sigma_{ox}}{\theta}\frac{1 - \nu_m}{E_m}\dot{\theta} \\ -sign(\sigma_{ox})\frac{1}{2}\left(\frac{|\sigma_{ox}|}{K_{ox}}\right)^{N_{ox}}\theta - sign(\sigma_{ox})\frac{1}{2}\left(\frac{|\sigma_{ox}|}{K_m}\right)^{N_m}\theta^{1 - N_m} \\ \left(\frac{1 - \nu_m}{E_m} + \frac{1 - \nu_{ox}}{E_{ox}}\theta\right)$$
(2.56)

In order to calculate \dot{h}_{ox} , we should update Table 2. (correct for isothermal conditions) for nonisothermal conditions:

External interface growthInternal interface growth
$$h_{\alpha x}(t) = H_2(t) - H_1 = A_p \sqrt{t}$$
 $h_{\alpha x}(t) = H_2 - H_1(t) = A_p \sqrt{t}$ $\dot{h}_{\alpha x}(t) = \frac{A_p}{2\sqrt{t}} + \frac{A_p Q_a}{RT^2} \frac{dT}{dt} \sqrt{t} = \frac{A_p^2 \theta(t)}{2H_1} + \frac{H_1 Q_a}{RT^2 \theta(t)} \frac{dT}{dt}$ $\dot{h}_{\alpha x}(t) = \frac{A_p}{2\sqrt{t}} + \frac{A_p Q_a}{RT^2} \frac{dT}{dt} \sqrt{t} = \frac{A_p^2 (1+\theta(t))}{2H_2} + \frac{H_2 Q_a}{RT^2 (1+\theta(t))} \frac{dT}{dt}$ $\theta(t) = \frac{H_1}{H_2(t) - H_1} = \frac{H_1}{A_p \sqrt{t}}$ $\theta(t) = \frac{H_1(t)}{H_2 - H_1(t)} = \frac{H_2}{A_p \sqrt{t}} - 1$ $\dot{\theta}(t) = -H_1 \frac{\dot{h}_{\alpha x}}{h_{\alpha x}^2} = -\frac{\theta(t)}{2t} - \frac{\theta(t)Q_a}{RT^2} \frac{dT}{dt}$ $\dot{\theta}(t) = -H_2 \frac{\dot{h}_{\alpha x}}{h_{\alpha x}^2} = -\frac{(\theta(t)+1)}{2t} - \frac{(\theta(t)+1)Q_a}{RT^2} \frac{dT}{dt}$

Table 2.3: Analytical expressions for the parabolic kinetic parameters (H₀=0) under non-isothermal conditions

(b) Fourier expansion for T and σ_{ox}

From a theoretical point of view, if the temperature loading is strictly periodic, then the temperature can be developed in Fourier expansion, such as:

$$T = \overline{T} + \sum_{n=1}^{\infty} T_{an} \cos(\omega_n t + \varphi_{T_n})$$
(2.57)

This temperature loading is supposed to be known. For each mode, the temperature span T_{an} and the temperature phase shift φ_{Tn} are identified as well as the average temperature \overline{T} through the given thermal solicitation, as those shown in Figure 2.8.



Figure 2.8: Explanation of parameters in periodic thermal loading

It is now assumed that the oxide stress may also be expanded in Fourier series, with a mean value that depends on the time and corresponds to the isothermal evolution. This assumption is equivalent to a linearization of the behavior of the system around a working point, meaning that harmonic terms have spans smaller than the average value. We can then write:

$$\sigma_{ox}(t) \approx \overline{\sigma_{ox}}(t) + \sum_{n=1}^{\infty} \sigma_{an} \cos(\omega_n t + \phi_{\sigma n})$$
(2.58)

Time derivative of Equation 2.57 and 2.58 leads to:

$$\dot{T} = -\sum_{n=1}^{\infty} \omega_n T_{an} \sin(\omega_n t + \phi_{Tn})$$
(2.59)

And

$$\dot{\sigma}_{ox} = \frac{d\overline{\sigma}_{ox}}{dt} - \sum_{n=1}^{\infty} \omega_n \sigma_{an} \sin(\omega_n t + \phi_{\sigma n})$$
(2.60)

Applying Equation 2.57 to 2.60 in Equation 2.56, we obtain:

$$\left(\frac{1-\nu_{m}}{E_{m}}+\frac{1-\nu_{ox}}{E_{ox}}\overline{\theta}\right)\frac{d\overline{\sigma_{ox}}}{dt} - \left(\frac{1-\nu_{m}}{E_{m}}+\frac{1-\nu_{ox}}{E_{ox}}\overline{\theta}\right)\sum_{n=1}^{\infty} \omega_{n}\sigma_{an}\sin(\omega_{n}t+\varphi_{\sigma n}) \\
= -(\alpha_{m}-\alpha_{ox})\overline{\theta}\sum_{n=1}^{\infty}\omega_{n}T_{an}\sin(\omega_{n}t+\varphi_{Tn}) - D_{ox}\frac{d\overline{h_{ox}}}{dt}\overline{\theta} + \frac{\overline{\sigma_{ox}}(t)}{\overline{\theta}}\frac{1-\nu_{m}}{E_{m}}\frac{d\overline{\theta}}{dt} \\
+ \frac{\sum_{n=1}^{\infty}\sigma_{an}\cos(\omega_{n}t+\varphi_{\sigma n})}{\overline{\theta}}\frac{1-\nu_{m}}{E_{m}}\frac{d\overline{\theta}}{dt} - sign(\sigma_{ox})\frac{1}{2}\left(\frac{\left|\overline{\sigma_{ox}}(t)+\sum_{n=1}^{\infty}\sigma_{an}\cos(\omega_{n}t+\varphi_{\sigma n})\right|}{K_{ox}}\right)^{N_{m}}\overline{\theta} \quad (2.61) \\
- sign(\sigma_{ox})\frac{1}{2}\left(\frac{\left|\overline{\sigma_{ox}}(t)+\sum_{n=1}^{\infty}\sigma_{an}\cos(\omega_{n}t+\varphi_{\sigma n})\right|}{K_{m}}\right)^{N_{m}}\overline{\theta}^{1-N_{m}}$$

In order to simplify Equation 2.61, some additional assumptions should be added:

- We assume that the stress in the oxide layer is compressive, i.e. $\forall t, \sigma_{ox}(t) < 0$.
- The Norton exponents for the oxide layer $N_{ox} = 1$, that is to say, we assume a diffusion controlled by creep mechanisms for the oxide layer. While in the metal, we have in general $N_m > 1$.
- As for the isothermal conditions, we assume that $\theta >> 1$ for all the studied time.
- Perturbation of the oxide stress is mainly due to perturbation of the temperature evolution. It means that a decoupling is operated between the oxide average stress and its variation. As a consequence, a separate resolution of the problem is possible. One for the mean value that corresponds to the isothermal conditions and another for the variations that corresponds to the temperature variations;
- No perturbation of the oxide thickness evolution is considered, and thus also for $\theta(t)$. In other words, $\theta(t) = \overline{\theta}(t)$ and $h_{ox}(t) = \overline{h_{ox}}(t)$. Strictly, it is more a consequence of the fact that we neglect the weak coupling. Thus the kinetics constant is assumed to be no more coupled with temperature for the analytical results.

Applying those assumptions to Equation 2.61 and after algebraic calculations, we obtain:

$$-\left(\frac{1-\nu_{m}}{E_{m}}+\frac{1-\nu_{ox}}{E_{ox}}\overline{\theta}\right)\sum_{n=1}^{\infty}\omega_{n}\sigma_{an}\sin(\omega_{n}t+\varphi_{on})$$

$$\approx -(\alpha_{m}-\alpha_{ox})\overline{\theta}\sum_{n=1}^{\infty}\omega_{n}T_{an}\sin(\omega_{n}t+\varphi_{Tn})+\frac{\sum_{n=1}^{\infty}\sigma_{an}\cos(\omega_{n}t+\varphi_{on})}{\overline{\theta}}\frac{1-\nu_{m}}{E_{m}}\frac{d\overline{\theta}}{dt}$$

$$-\frac{1}{2}\left(\frac{\sum_{n=1}^{\infty}\sigma_{an}\cos(\omega_{n}t+\varphi_{on})}{K_{ox}}\right)\overline{\theta}+\frac{N_{m}}{2}\frac{\left|\overline{\sigma_{ox}}(t)\right|^{N_{m}}}{\overline{\sigma_{ox}}(t)}\left(\frac{\sum_{n=1}^{\infty}\sigma_{an}\cos(\omega_{n}t+\varphi_{on})}{K_{m}^{N_{m}}}\right)\overline{\theta}^{1-N_{m}}$$
(2.62)

Where the only unknowns are the stress span $\sigma_{an} = f_{an}(T_{an}, \varphi_{Tn}, \omega_n; \text{material parameters})$ and the stress phase shift $\varphi_{\sigma n} = f_{\varphi n}(T_{an}, \varphi_{Tn}, \omega_n; \text{material parameters})$.

(c) Simplified equations

Because of the previous assumptions and especially the assumed linearization, each mode *n* of angular frequency ω_n can be solved separately. Equation 2.62 can then be simplified (and removing the subscript *n* for simplicity) into:

$$-\left(\frac{1-\nu_{m}}{E_{m}}+\frac{1-\nu_{ox}}{E_{ox}}\overline{\theta}\right)\omega\sigma_{a}\sin(\omega t+\varphi_{\sigma})$$

$$\approx -(\alpha_{m}-\alpha_{ox})\overline{\theta}\omega T_{a}\sin(\omega t+\varphi_{T})+\frac{\sigma_{a}\cos(\omega t+\varphi_{\sigma})}{\overline{\theta}}\frac{1-\nu_{m}}{E_{m}}\frac{d\overline{\theta}}{dt}$$

$$-\frac{1}{2}\left(\frac{\sigma_{a}\cos(\omega t+\varphi_{\sigma})}{K_{ox}}\right)\overline{\theta}+\frac{N_{m}}{2}\frac{\left|\overline{\sigma_{ox}}(t)\right|^{N_{m}}}{\overline{\sigma_{ox}}(t)}\left(\frac{\sigma_{a}\cos(\omega t+\varphi_{\sigma})}{K_{m}^{N_{m}}}\right)\overline{\theta}^{1-N_{m}}$$
(2.63)

Because this equation has to be verified for all time, we can resolve separately the factor terms of $sin(\omega t)$ and the factor terms of $cos(\omega t)$. We obtain first:

$$-\left(\frac{1-\nu_{m}}{E_{m}\overline{\theta}}+\frac{1-\nu_{ox}}{E_{ox}}\right)\omega\cos\varphi_{\sigma}=-(\alpha_{m}-\alpha_{ox})\omega\frac{T_{a}}{\sigma_{a}}\cos\varphi_{T}$$

$$+\sin\varphi_{\sigma}\left(-\frac{1}{\overline{\theta}^{2}}\frac{1-\nu_{m}}{E_{m}}\frac{d\overline{\theta}}{dt}+\frac{1}{2K_{ox}}-\frac{N_{m}}{2}\frac{\left|\overline{\sigma_{ox}}(t)\right|^{N_{m}}}{\overline{\sigma_{ox}}(t)}\frac{\overline{\theta}^{-N_{m}}}{K_{m}^{N_{m}}}\right)$$
(2.64)

Second, we have:

$$-\left(\frac{1-\nu_{m}}{E_{m}\overline{\theta}}+\frac{1-\nu_{ox}}{E_{ox}}\right)\omega\sin\varphi_{\sigma} = -(\alpha_{m}-\alpha_{ox})\omega\frac{T_{a}}{\sigma_{a}}\sin\varphi_{T}$$

$$+\cos\varphi_{\sigma}\left(+\frac{1}{\overline{\theta}^{2}}\frac{1-\nu_{m}}{E_{m}}\frac{d\overline{\theta}}{dt}-\frac{1}{2K_{ox}}+\frac{N_{m}}{2}\frac{\left|\overline{\sigma_{ox}}(t)\right|^{N_{m}}}{\overline{\sigma_{ox}}(t)}\frac{\overline{\theta}^{-N_{m}}}{K_{m}^{N_{m}}}\right)$$
(2.65)

And because $\forall t, \overline{\theta} = \theta >> 1$, we obtain:

$$\left(\frac{1-\nu_{ox}}{E_{ox}}\right)\omega\cos\varphi_{\sigma} \approx (\alpha_{m}-\alpha_{ox})\omega\frac{T_{a}}{\sigma_{a}}\cos\varphi_{T} - \sin\varphi_{\sigma}\left(\frac{1}{2K_{ox}}\right)$$
(2.66)

And similarly:

$$\left(\frac{1-\nu_{ox}}{E_{ox}}\right)\omega\sin\varphi_{\sigma} \approx (\alpha_{m}-\alpha_{ox})\omega\frac{T_{a}}{\sigma_{a}}\sin\varphi_{T} + \cos\varphi_{\sigma}\left(\frac{1}{2K_{ox}}\right)$$
(2.67)

Solving Equation 2.66 and 2.67 leads to:

$$\sigma_{a} = \left(\frac{E_{ox}}{1 - v_{ox}}\right) (\alpha_{m} - \alpha_{ox}) T_{a} \cos \varphi_{T} \frac{\cos^{-1} \left(\arctan\left(\frac{1 + \tau \omega \tan \varphi_{T}}{\tau \omega - \tan \varphi_{T}}\right)\right)}{1 + \left(\frac{1 + \tau \omega \tan \varphi_{T}}{\tau \omega - \tan \varphi_{T}}\right) \frac{1}{\tau \omega}}$$
(2.68)

And

$$\varphi_{\sigma} = \arctan\left(\frac{1 + \tau\omega\tan\varphi_{T}}{\tau\omega - \tan\varphi_{T}}\right)$$
(2.69)

Eventually, the two unknown functions are such that: $\sigma_a / \left(\left(\frac{E_{ox}}{1 - v_{ox}} \right) (\alpha_m - \alpha_{ox}) \right) = f_a(T_a, \varphi_T, \tau \omega)$

and $\varphi_{\sigma} = f_{\varphi}(\varphi_T, \tau \omega)$. The latter does not depend explicitly on the temperature span. The material parameters occur only through a characteristic time $\tau = 2K_{ox}\left(\frac{1-v_{ox}}{E_{ox}}\right)$ linked to the relaxation phenomena in the oxide [28] and through the thermal expansion mismatch times the in-plane stiffness for the stress span. Because of the considered assumptions, the growth parameter D_{ox} is not involved in the oxide stress response to the thermal perturbations.

(d) Asymptotic solutions for low and high angular frequencies

It is now interesting to consider the behavior of those formulae for low and high angular frequencies. For low frequency, let us consider $\omega \rightarrow 0$ in Equations 2.68 and 2.69. At first order of the Taylor series expansion, it leads to:

$$\sigma_{a} \approx \left(\frac{E_{ox}}{1-v_{ox}}\right) (\alpha_{m} - \alpha_{ox}) T_{a} \cos \varphi_{T} \frac{\cos^{-1} \left(\arctan\left(\frac{1}{\tan \varphi_{T}}\right)\right)}{-\left(\frac{1}{\tan \varphi_{T}}\right)} \tau \omega$$

$$= \begin{cases} \mp \left(\frac{E_{ox}}{1-v_{ox}}\right) (\alpha_{m} - \alpha_{ox}) T_{a} \tau \omega, \text{ for } \varphi_{T} \neq 0 \\ \left(\frac{E_{ox}}{1-v_{ox}}\right) (\alpha_{m} - \alpha_{ox}) T_{a} \tau \omega = 2K_{ox} (\alpha_{m} - \alpha_{ox}) T_{a} \omega, \text{ for } \varphi_{T} = 0 \end{cases}$$
(2.70)
And

$$\varphi_{\sigma} \approx -\arctan\left(\frac{1}{\tan\varphi_{T}}\right)$$

$$= \begin{cases} \mp \frac{\pi}{2} + \varphi_{T}, \text{ for } \varphi_{T} \neq 0 \\ \frac{\pi}{2}, \text{ for } \varphi_{T} = 0 \end{cases}$$
(2.71)

For high frequency, let us consider $\omega \rightarrow \infty$ in Equations 2.68 and 2.69. At first order of the Taylor series expansion, it leads to:

$$\sigma_a = \left(\frac{E_{ox}}{1 - v_{ox}}\right) (\alpha_m - \alpha_{ox}) T_a, \text{ for } \varphi_T \neq \frac{\pi}{2}$$
(2.72)

And

$$\varphi_{\sigma} = \varphi_T, \text{ for } \varphi_T \neq \frac{\pi}{2}$$
 (2.73)

Equations for $\varphi_T = \frac{\pi}{2}$ are eventually not of interest. Both asymptotic solutions (Equations 2.70 and 2.71, and Equations 2.72 and 2.73) correspond respectively to long and short times. For $\varphi_T = 0$, whatever the mode *n*, the system corresponds to a high-pass filter. Relaxation phenomena only occur significantly at low frequency, i.e. at long times. Low frequency means for any angular frequency inferior to the inverse of the characteristic time.

(e) Theoretical solution for the applied thermal loading

It is now possible to apply the previous methodology to the considered thermal loading presented in Figure 2.6. Strictly, this loading is not periodic/cyclic. However, we will suppose that a specific infinite cyclic thermal loading can lead to an infinite cyclic stress response of the system, obtained by copying the finite response with some adapted periodical boundary conditions. Moreover, to avoid specific value of $\pi/2$ for the temperature phase shift according to Equation 2.73, we choose to translate the time origin to obtain an even function. This is really important only for the phase shift.

The considered specific infinite thermal loading, illustrated in Figure 2.9, is developed in Fourier

expansion following Equation 2.57. It leads to, with $m = \frac{n-1}{2} \in N$ corresponding to odd *n*:



Figure 2.9: Ideal thermal loading based on the Fourier expansion given by Equation 2.74, with $T_{\text{max}} = 1000^{\circ}C; T_{\text{min}} = 800^{\circ}C; \omega_1 = 2\pi/(69.60*60) = 0.001505 rad/s$ (first thermal loading). 31 harmonics have been arbitrarily considered to plot the curve.

$$T = \overline{T} + \sum_{n=1}^{\infty} T_{an} \left(\cos(n\omega_{1}t) \cos(\varphi_{T_{n}}) - \sin(n\omega_{1}t) \sin(\varphi_{T_{n}}) \right)$$

$$= \frac{T_{\max} + T_{\min}}{2} + \sum_{n=1}^{\infty} \frac{T_{\max} - T_{\min}}{\pi n} \left(\sin(n\pi/2) - \sin(3n\pi/2) \right) \cos(n\omega_{1}t)$$
(2.74)
$$= \frac{T_{\max} + T_{\min}}{2} + \sum_{m=0}^{\infty} \frac{T_{\max} - T_{\min}}{\pi (2m+1)} 2(-1)^{m} \cos\left((2m+1)\omega_{1}t\right)$$

We obtain thus $\varphi_{Tn} = 0, \forall n \text{ and } T_{an} = \frac{T_{max} - T_{min}}{\pi(2m+1)} 2(-1)^m$ with $m = \frac{n-1}{2} \in N$. ω_1 is the

fundamental angular frequency corresponding to $n=1 \Leftrightarrow m=0$. Applying Equation 2.68 and 2.69 for each mode *n*, it is possible to write:

$$\sigma_{an} = \left(\frac{E_{ox}}{1 - V_{ox}}\right) (\alpha_m - \alpha_{ox}) T_{an} \cos\left(\frac{\pi}{2} - \arctan(\pi \omega_1)\right)$$

$$= \left(\frac{E_{ox}}{1 - V_{ox}}\right) (\alpha_m - \alpha_{ox}) \frac{T_{\max} - T_{\min}}{\pi (2m + 1)} 2(-1)^m \sin\left(\arctan(\tau (2m + 1)\omega_1)\right)$$
(2.75)
And

$$\varphi_{\sigma n} = \arctan\left(\frac{1}{\pi \omega_{1}}\right) = \frac{\pi}{2} - \arctan\left(\tau(2m+1)\omega_{1}\right)$$
(2.76)

The Bode diagram of Equations 2.75 and 2.76 is plotted for different modes m in Figure 2.11, whereas the spectrogram of the oxide stress under this thermal loading is plotted in Fourier space in Figure 2.12. As expected, it corresponds to a high-pass filter. This theoretical methodology may be applied a priori to any cyclic thermal loading. Providing that a mean behavior can be removed and assuming assumptions of all above, it is possible to investigate some relaxation features of the system as well as its thermal expansion coefficients.



Figure 2.10: Theoretical amplitude Bode diagram of different modes/harmonics corresponding to 20 Log (Equation 2.75). We use: $T_{max} = 1000 \text{ °}C; T_{min} = 800 \text{ °}C;$

$$\begin{aligned} \alpha_{ox} = 5.67 \times 10^{-6} \, K^{-1}; \alpha_m = & 12.93 \times 10^{-6} \, K^{-1} \text{ and } E_{ox} = & 300.4 GPa; v_{ox} = & 0.27; \\ J_{ox} = & 4.05 Pa^{-1}.s^{-1}; \tau \approx & 60000 \ s. \end{aligned}$$

The Young's modulus is expressed in GPa in the gain calculation. Angular frequency corresponds to the fundamental angular frequency ω_1 . For negative values of the amplitude, an absolute value has been applied.



Figure 2.11: Theoretical phase shift Bode diagram of different modes/harmonics corresponding to Equation 2.76. We use: $\tau \approx 60000s$. Angular frequency corresponds to the fundamental angular frequency ω_1 .



Figure 2.12: Frequency diagram of the theoretical amplitude linked to Equation 2.75. We use: $T_{\text{max}} = 1000 \ ^{\circ}C$; $T_{\text{min}} = 800 \ ^{\circ}C$; $\alpha_{ox} = 5.67 \times 10^{-6} K^{-1}$; $\alpha_m = 12.93 \times 10^{-6} K^{-1}$ and $E_{ox} = 300.4 GPa$; $v_{ox} = 0.27$; $J_{ox} = 4.05Pa^{-1}.s^{-1}$; $\tau \approx 60000s$.

We have also valided this method by experiment, the details of experiment can be found in [31].

2.3 Numerical solutions

If we consider both the weak coupling and the strong coupling, it is not easy to get an analytical solution, so we have used Matlab[©] to get numerical solutions.

2.3.1 Runge-Kutta scheme

Runge-Kutta scheme is a well-known and widely used routine for the approximate solutions of ordinary differential equations (ODEs)[29]. The most widely known member of the Runge-Kutta family is generally referred to as "classical Runge-Kutta method", which has been used by us to solve the differential Equation 2.28.

2.3.1.1 Classical Runge–Kutta method

If we have an initial value problem as follows:

$$\dot{\sigma}_{ox} = f(t,\sigma), \sigma_{ox}(t_0) = \sigma_0 \tag{2.77}$$

Where σ_{ox} is an unknown function of time t, and the differential expression σ_{ox} is a function of t and σ_{ox} itself. At the initial time t_0 , σ_{ox} has the value σ_0 . The function f, t_0 and σ_0 are all known.

Now a time step h > 0 is chosen and we define that:

$$\sigma_{ox}^{n+1} = \sigma_{ox}^{n} + \frac{n}{6}(k_1 + 2k_2 + 2k_3 + k_4); t_{n+1} = t_n + h$$
(2.78)

For n=0, 1, 2, 3, ..., and we also define that:

$$k_{1} = f(t_{n}, \sigma_{ox}^{n})$$

$$k_{2} = f(t_{n} + \frac{h}{2}, \sigma_{ox}^{n} + \frac{h}{2}k_{1})$$

$$k_{3} = f(t_{n} + \frac{h}{2}, \sigma_{ox}^{n} + \frac{h}{2}k_{2})$$

$$k_{4} = f(t_{n} + h, \sigma_{ox}^{n} + hk_{3})$$
(2.79)

The classical Runge-Kutta method is a fourth-order method, meaning that the local truncation error is on the order of $O(h^5)$, while the total accumulated error is on the order of $O(h^4)$ [30].

2.3.1.2 Stress variation with the time step

The errors introduced by the numerical solution have to be verified. Firstly, the influence of time step *h* should be discussed.

It is known that smaller time step produces a more precise numerical calculation; of course this is detrimental to the total time of calculation. The results carried in Figure 2.13 agree with this. Indeed, the Runge-Kutta scheme used results from a limited development. Consequently, its precision will be much better when the stress variation rates are small. The results indicate that the difference is only meaningful at the level of the inflexion. On the other hand, the precision increases with the reduction of the time step, its choice has a very small influence, which allows a good compromise with the total calculation time. Henceforth, it will be supposed therefore that the influence of the time step is negligible so long as it is chosen relatively small (we have chosen time step to be 0.5 seconds for the calculation for a total oxidation time of several hours).



Figure 2.13: Time step influence on an external growth in the oxide for isothermal conditions. Model parameters: $E_m = 160GPa$; $E_{ox} = 300GPa$; $v_m = 0.3$; $v_{ox} = 0.27$; $J_{ox} = 1 \times 10^{15} Pa^{-1}s^{-1}$ $J_m = 1 \times 10^{15} Pa^{-3.3}s^{-1}$; $A_p = 1.23 \times 10^{-8} ms^{-0.5}$; $\Delta t = \text{variable}$; $D_{ox} = 5000m^{-1}$; $\sigma_{ox}(t=0) = \sigma_m(t=0) = 0$; $H_1 = H_2(t=0) = 1 \text{ mm}$.

2.3.2 Summary

As a summary of the modelling part shown in Figure 2.14, we have started with some hypothesis. With some assumptions, a force balance equation and a displacement continuity equation are deduced. When thinking about material behaviors for displacement continuity equation, for metallic substrate, elastic behavior, visco-plastic behavior and thermal expansion behavior are considered. For oxide layer, the growth strain is also considered besides all the material behaviors for metal. Finally, an ordinary differential equation (ODE) is deduced.

In order to get an analytical solution, three special thermal loadings are assumed: isothermal, step thermal loading and periodic thermal loading.

For isothermal condition, the results for short times approximation and long times approximation are deduced by other authors [1], combining them together, a characteristic time and a minimum stress value has been obtained [5]. I have tried another way to find the minimum stress value and comparison has been made.

For step thermal loading, the Laplace transform method has been used to solve the ordinary differential equation. We have assumed that there is only strong coupling, and the change of temperature occurs at "long time". With some supplementary assumptions, an equation is deduced to identify $\Delta\sigma$ when temperature changes. This offers a new way to identify the thermal expansion parameter mismatch $(\alpha_m - \alpha_{ox})$.

For periodic thermal loading, a new innovative method is proposed, i.e. the frequency analysis method,. Only strong coupling is considered, and with some other supplementary assumptions, finally we get:

$$\sigma_a \left(\left(\frac{E_{ox}}{1 - v_{ox}} \right) (\alpha_m - \alpha_{ox}) \right) = f_a(T_a, \varphi_T, \tau \omega) \text{ and } \varphi_\sigma = f_\varphi(\varphi_T, \tau \omega). \text{ We can see from the result that}$$

the shift of stress does not depend explicitly on the temperature span, and the material parameters

occur only through a characteristic time $\tau = 2K_{ox}\left(\frac{1-v_{ox}}{E_{ox}}\right)$ linked to the relaxation phenomena in

the oxide and through the thermal expansion mismatch times the in-plane stiffness for the stress span which can also be used to identify some material parameters.

Finally, the numerical solution using Runge-Kutta method is discussed, and the influence of different time step is also discussed. We have drawn the conclusion that the influence of the time step is negligible so long as it is chosen relatively small.



Figure 2.14: Summary of the modelling part

References of chapter 2

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Chapter 3 Experimental part

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3.1 Background of the experiments

As described in Chapter 1, many attempts have been made to determine the stress in the oxide layers [1]–[4]. With the development of more accurate experimental equipments, it is possible to get the stress using synchrotron radiation, which presents many advantages compared to laboratory diffractometers.

In this work, the experiments were specifically carried out in-situ at high temperatures on beamline BM02 at ESRF (European Synchrotron Radiation Facility) in Grenoble (see Figure 3.1), collaborating with several partners:

- Dr. Guillaume GEANDIER (CNRS researcher at the Jean Lamour Institute of Université de Lorraine).
- Dr. Felaniaina Nirisoa RAKOTOVAO (Doctor of University of La Rochelle)
- Pr. Pierre Olivier RENAULT (Professor at the Institut P' of the University of Poitiers).
- Dr. Philippe GOUDEAU (CNRS research director at the Institut P' of the University of Poitiers).
- Dr. Nathalie BOUDET (Scientist at BM02 line of ESRF Grenoble).
- Dr. Nils BLANC (Scientist at the BM02 line of ESRF Grenoble).
- Hugo VITOUX (Technician of the Sample Environment Support Service of ESRF Grenoble).
- Bernard GORGES (Engineer at the Sample Environment Support Service of ESRF Grenoble).



Figure 3.1: BM02 beamline at ESRF Grenoble

The beamline is equipped with a goniometer, a sample carrier, a two-dimensional detector and two photodiodes. [5]

The first photodiode is placed in front of the sample and makes it possible to know the flux of incoming photons.

The second photodiode is placed behind the sample and along the beam axis to allow alignment of the sample surface with the beam, which is important for height adjustment.

The beam of X-rays arriving on the sample is monochromatic, of wavelength 0.062 nm (energy of 20 keV).

The sample carrier has a diameter of 7mm and a depth of 4mm.

An induction furnace was used to simultaneously carry out oxidations with in-situ measurements and especially strain measurements during this oxidation. The induction furnace was provided by the Sample Environment Support Service (see Figure 3.2).



Figure 3.2: Induction furnace of the line BM02 at ESRF Grenoble.

The system consists of a high-power generator (maximum 3kW). The sample carrier is a cylindrical support, surrounded by the induction coil with 7mm diameter and 4mm depth.

A thermocouple is placed at the bottom of this support to control and regulate the temperature (the temperature can reach a maximum value of 1600 °C). The temperature on the surface of the sample was measured by a pyrometer. The speed of heating and cooling can vary between 1 °C/min and 500 °C/min with a temperature of accuracy ± 1 °C.

The main advantage of this furnace is its ability to heat or cool very quickly (thermal characteristic time of the furnace with our metallic specimen is around 13s [6]), with a good control of the heating and cooling speeds, which is an advantage to develop particular experiments (thermal cycling or temperature jumps...).

However, even if the use of one thermocouple and one pyrometer allows a correct knowledge of the oxidation temperature, it cannot be ignored that there may be a temperature gradient between the top and bottom faces of the sample (in contact with the bottom thermocouple). This may generate non-homogeneous expansion of the samples and disturb especially the height adjustment.

The induction furnace is used for the oxidation of samples in air. The X-Ray beam size is $1 \text{ mm} \times 0.1 \text{ mm}$ and the angle of incidence is 5°. The detector is located at a distance of 22 cm from the center of the goniometer. This detector makes an angle of 18° with the incident beam.

The calibration of the detector was carried out using a silicon powder as reference (NIST SRM640), in order to adjust the correspondence between pixel and angular degrees. The calibration is a very important step because a poor positioning of the camera can induce an offset at the pixels and, subsequently, an offset on the positions 2θ of the Debye-Scherrer rings.

In order to make the sample surface parallel to the beam, adjustment steps are required before each experiment to have a better accuracy.

The procedure of adjusting the flatness of the sample is as followed:

- Note the detected intensity I_0 of the uncut incident beam
- Adjust the sample to partially cut off the incident beam, detected intensity is then less than $I_{
 m 0}$
- Rotate the sample around the Ω axis to find the ideal position (position Ω_0) for which the detected intensity is maximum (see Figure 3.3). After this adjustment, the surface of the sample is then parallel to the incident beam
- Adjust precisely the height of the sample so that the detected intensity is equal to $\frac{I_0}{2}$



Figure 3.3: Adjusting the flatness of the sample [7]

By means of these adjustments, the surface of the sample is located at the center of the goniometer, through which the incident beam passes. To give an angle of incidence ω , it is then sufficient to put the motor Ω in the position $\omega = \Omega - \Omega_0$

For the determination of stress, the classical $\sin^2 \psi$ method was used, which is introduced in the Part 3.1.1.

3.1.1 Introduction to the determination of stress by X-Ray Diffraction: the $\sin^2\psi$ method

X-Ray Diffraction is a structural analysis technique dedicated to the study of crystalline solid compounds. This technique, developed at the beginning of the 19th century, makes it possible to determine the crystallographic structure, the phases, the size of the crystallites, the texture and the deformation in materials [8]. The method is non-destructive and is applicable to crystalline materials. The material may be metallic or ceramic, provided that a diffraction peak of suitable intensity to the noise, and free of interferences from neighboring peaks, can be produced [9].

In our case, the analysis by X-Ray Diffraction involves irradiating the surface of a sample with a beam of incident X-ray having a certain wavelength λ (diffraction could be done in multiple wavelength mode in other case). The X-ray diffracted by the sample results from the constructive interferences between the X-ray collectively scattered by the irradiated atoms. These atoms are arranged in crystallographic planes with Miller indices (hkl). Each family of planes is characterized by an interplanar distance $d_{(hkl)}$.

When using X-Ray Diffraction, the strain in the crystal lattice can be measured and the associated stress can be determined from the elastic stiffnesses, using the linear elastic behaviour of the appropriate crystal lattice plane [9]. Because X-ray impinges over an area on the sample, many crystals and grains may contribute to the measurement. The exact number is dependent on the grain size and beam geometry. Although, the measurement is considered to be near surface, X-rays penetrate some distance into the material: the penetration depth is dependent on the anode material and angle of incidence. Hence, the measured strain is essentially the average over a few microns depth under the surface of the specimen.

The fundamental basis of this technique is defined by the Bragg's law [10]:

 $2d_{(hkl)}\sin(\theta) = n\lambda$

(3.1)

Where λ is the wavelength of the ray, θ is the angle between the ray and the plane of the lattice (known as Bragg's angle), $d_{\rm (hkl)}$ is the interplanar distance between two nearest planes of the lattice with the Miller indices {hkl}. Scattered rays will be in phase only if the path difference is equal to an integer number n of wavelengths. Bragg's law relates the interplanar distance $d_{\rm (hkl)}$ to the position θ of the diffraction.

The determination of the residual stresses by X-Ray Diffraction is based on the displacement of the diffraction peaks, i.e. on the variation of the interplanar distance of the family of plans under the influence of stress.

(a) Determination of strain by X-Ray Diffraction (XRD)

When performing strain measurement, the specimen is placed under the X-ray diffractometer, and it is exposed to an X-ray beam that interacts with the crystal lattice to obtain diffraction patterns. By scanning the sample for different angles 2θ , the diffraction peaks can be located.

It has been proved that there is a relationship between the diffraction pattern that is observed when X-rays are diffracted through crystal lattices and the distance between atomic planes (the interplanar spacing) within the material [9]. By changing the interplanar spacing, different diffraction patterns are obtained. Changing the wavelength of the X-ray beam will also result in a different diffraction pattern. The interplanar spacing of a material free of strain will produce a characteristic diffraction pattern for that material. When a material is strained, elongations or contractions are produced within the crystal lattice leading to a change of the interplanar spacing of the {hkl} lattice planes. This induced change in $d_{\rm (hkl)}$ will cause a shift in the diffraction pattern. By precise measurements of this angular shift, the changes in the interplanar spacing can be evaluated and thus the strain within the material can be



Unstrained crystallite

deduced (see Figure 3.4).

Compressed crystallite

Figure 3.4: Illustration for determination of strain by X-Ray Diffraction

Firstly, we need to establish mathematical relationships between the interplanar spacing and the strain. The orthogonal coordinate systems used in the following explanations are defined in Figure 3.5.



Figure 3.5: Coordinate system used for calculating surface strain. Note that σ_1 , σ_2 and σ_3 are the eigen stresses, \mathcal{E}_1 , \mathcal{E}_2 and \mathcal{E}_3 are the corresponding eigen strains (assuming isotropy). σ_3 and \mathcal{E}_3 are normal to the specimen surface

Let us assume that, because the measurement is made mainly on the surface sample, $\sigma_3 = 0$. However, the strain \mathcal{E}_3 will not be equal to zero. The strain \mathcal{E}_3 can be evaluated experimentally by measuring the peak position 2θ , and solving equation 3.2 for a value of d_n (the index n means the normal direction, see Figure 3.6). If we know the unstrained interplanar spacing d_0 , then:

$$\varepsilon_3 = ln \left(\frac{d_n}{d_0}\right) = ln \left(\frac{\sin \theta_0}{\sin \theta_n}\right)$$
(3.2)

It is preferable to use rational deformation, because it considers that the deformation of a material is necessarily finite, in contrast to the conventional deformation which supposes that the deformation is infinitesimal [8].



Figure 3.6: Schematic illustration of diffraction planes parallel to the surface for an angle $\phi \psi$. Note that σ_1 and σ_2 both belong to the plane of the specimen surface

Thus, the strain within the surface of the material can be measured by comparing the unstressed lattice interplanar spacing with the strained interplanar spacing. This, however, requires precise

measurement of both unstrained and strained samples of the material, because the magnitude of this angular shift is typically around 0.02°, corresponding to a strain magnitude around 3×10^{-3} . Equation 3.2 gives the formula for measurements taken normal to the surface. By altering the tilt of the specimen, within the diffractometer, measurements of planes can also be made for different angle ψ (see Figure 3.6) and thus the strains along that direction can be calculated using:

$$\varepsilon_{\phi\psi} = ln \left(\frac{d_{(hkl)}}{d_0}\right) = ln \left(\frac{\sin\theta_0}{\sin\theta_{(hkl)}}\right)$$
(3.3)

Figure 3.6 shows planes parallel to the surface of the material and planes at an angle (ϕ, ψ) to the surface. This illustrates how planes with an angle to the surface are measured by tilting the specimen so that the planes are brought into a position where they will satisfy Bragg's Law.

(b) Determination of stress by X-Ray Diffraction: the $\sin^2 \psi$ method

Whilst it is very useful to know the strains within the material, it is also useful to know the stresses that are linked to these strains. It is important to note that the measured strain corresponds to the elastic part.

Let us imagine that we have a coordinate system $R = (O, \vec{e}_x, \vec{e}_y, \vec{e}_z)$ that is related to the sample, with \vec{e}_z the normal to the surface of the sample (see figure 3.7).



Figure 3.7: Directions and axes of measurement

So that the elongation along the direction $\vec{e}_{\phi\psi}$ (characterized by the angles ϕ and ψ) can be defined as:

$$\mathcal{E}_{\phi\psi} = \vec{e}_{\phi\psi} \cdot \overline{\vec{\mathcal{E}}} \cdot \vec{e}_{\phi\psi}$$
(3.4)
Where

$$\vec{e}_{\phi\psi} = \sin\psi\cos\phi\vec{e}_x + \sin\psi\sin\phi\vec{e}_y + \cos\psi\vec{e}_z$$
(3.5)
In addition, $\overline{\overline{\varepsilon}}$ is the strain tensor (order 2):

$$\overline{\overline{\varepsilon}} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{pmatrix}$$
(3.6)

So that we have the relation:

$$\varepsilon_{\phi\psi} = (\varepsilon_{11}\cos^2\phi + \varepsilon_{22}\sin^2\phi + \varepsilon_{12}\sin 2\phi - \varepsilon_{33})\sin^2\psi + (\varepsilon_{13}\cos\phi + \varepsilon_{23}\sin\phi)\sin 2\psi + \varepsilon_{33}$$
(3.7)

Comparing equation 3.7 with equation 3.3, we can finally get:

$$ln\left(\frac{\sin\theta_{0}}{\sin\theta_{hkl}}\right) = (\varepsilon_{11}\cos^{2}\phi + \varepsilon_{22}\sin^{2}\phi + \varepsilon_{12}\sin2\phi - \varepsilon_{33})\sin^{2}\psi + (\varepsilon_{13}\cos\phi + \varepsilon_{23}\sin\phi)\sin2\psi + \varepsilon_{33}$$
(3.8)

Equation 3.8 is the basic for the $\sin^2 \psi$ method expressed in terms of the elastic strain components. In order to calculate the stress, we need to relate the stress with elastic strain using Hooke's law.

Measurements performed with X-Ray Diffraction allow obtaining directly the elastic strain.

If we assume that elasticity of the material is linear, homogeneous and isotropic, the conversion of elastic strain into stress can be done using Hooke's law according to:

$$\varepsilon_{ij} = \frac{1+\nu}{E}\sigma_{ij} - \frac{\nu}{E}\sigma_{kk}\delta_{ij}$$
(3.9)

Where δ_{ii} is the symbol of Krönecker, *E* is the Young's modulus and *v* is the Poisson's ratio.

If we take equation 3.9 into equation 3.8, we can get:

$$ln\left(\frac{\sin\theta_{0}}{\sin\theta_{hkl}}\right) = \frac{1+v}{E}(\sigma_{11}\cos^{2}\phi + \sigma_{22}\sin^{2}\phi + \sigma_{12}\sin2\phi - \sigma_{33})\sin^{2}\psi + \frac{1+v}{E}(\sigma_{13}\cos\phi + \sigma_{23}\sin\phi)\sin2\psi + \frac{1}{E}(\sigma_{33} - v(\sigma_{11} + \sigma_{22}))$$
(3.10)

Equation 3.10 involves the macroscopic elastic moduli E and v, which can be obtained either experimentally or by scale transition methods. In addition, only a part of the irradiated grains fulfills the Bragg's conditions and thus participates to the deformation response obtained from the shift of diffraction peaks [7]. To take into account of these various aspects related to the anisotropy of the crystallites depending on the planes (hkl), we introduce the radio-crystallographic elasticity coefficients S_{ii} (hkl) that depend on (hkl). Now we can do the following substitution:

$$\frac{1+\nu(hkl)}{E(hkl)} = \frac{1}{2}S_2(hkl) \text{ and } -\frac{\nu(hkl)}{E(hkl)} = S_1(hkl)$$
(3.11)

Equation 3.10 becomes:

$$ln\left(\frac{\sin\theta_{0}}{\sin\theta_{hkl}}\right) = \frac{1}{2}S_{2}(hkl)(\sigma_{11}\cos^{2}\phi + \sigma_{22}\sin^{2}\phi + \sigma_{12}\sin2\phi - \sigma_{33})\sin^{2}\psi + \frac{1}{2}S_{2}(hkl)(\sigma_{13}\cos\phi + \sigma_{23}\sin\phi)\sin2\psi + \left(\frac{1}{2}S_{2}(hkl) + S_{1}(hkl)\right)\sigma_{33} + S_{1}(hkl)(\sigma_{11} + \sigma_{22})$$
(3.12)

Since the surface of the sample is not subjected to any normal stress, we assume that $\sigma_{33} = 0$, for all the points on that surface. In addition, the diffraction measurement is superficial since the penetration depth of the beam is low (around 45 µm for NiCr when the radiation length is 20 keV [11]; it is therefore possible to assume that $\sigma_{33} = 0$ at any point of the volume probed by X-rays. So that Equation 3.12 now becomes:

$$ln\left(\frac{\sin\theta_{0}}{\sin\theta_{hkl}}\right) = \frac{1}{2}S_{2}(hkl)(\sigma_{11}\cos^{2}\phi + \sigma_{22}\sin^{2}\phi + \sigma_{12}\sin2\phi)\sin^{2}\psi + \frac{1}{2}S_{2}(hkl)(\sigma_{13}\cos\phi + \sigma_{23}\sin\phi)\sin2\psi + S_{1}(hkl)(\sigma_{11} + \sigma_{22})$$
(3.13)

Now the stress tensor has the form:

$$\bar{\bar{\sigma}} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & 0 \end{pmatrix}$$
(3.14)

It is therefore possible to determine experimentally all the components of this stress tensor. To achieve such a goal, it is necessary to carry out at least three different measurements corresponding to three values of the angle ϕ judiciously chosen ($\phi = 0^{\circ}, 45^{\circ}, 90^{\circ}$). One possible method to treat the data is the one proposed by Dölle [12], [13], which consists in transforming Equation 3.13 taking into account the values of ϕ considered. Dölle has proposed a method to determine the different components of the stress tensor by separating the terms in $\sin^2 \psi$ (even) from the terms in $\sin 2\psi$ (odd). To do this, it is necessary to determine the Bragg's angle Θ for several values of $\psi > 0$ (ψ^+) as well as for the corresponding $\psi < 0$ (ψ^-). This operation should be repeated at least three times by giving three values of ϕ judiciously chosen. Dölle has proposed to calculate the half-sum (A^+), then the half-difference (A^-) of Equation 3.13 using $\psi = \psi^+$ and $\psi = \psi^-$, we can get:

$$A^{+} = \frac{1}{2} \left[\ln \left(\frac{1}{\theta(\psi^{+})} \right) + \ln \left(\frac{1}{\theta(\psi^{-})} \right) \right]$$

= $\frac{1}{2} S_{2} (\text{hkl}) (\sigma_{11} \cos^{2} \phi + \sigma_{22} \sin^{2} \phi + \sigma_{12} \sin 2 \phi - \sigma_{33}) \sin^{2} \psi$
+ $S_{1} (\text{hkl}) (\sigma_{11} + \sigma_{22}) - \ln(\sin \theta_{0})$ (3.15)

Moreover:

$$A^{-} = \frac{1}{2} \left[\ln \left(\frac{1}{\theta(\psi^{+})} \right) - \ln \left(\frac{1}{\theta(\psi^{-})} \right) \right]$$

$$= \frac{1}{2} S_{2}(hkl) (\sigma_{13} \cos \phi + \sigma_{23} \sin \phi) \sin 2 |\psi|$$
(3.16)

Where $\theta(\psi^+)$ and $\theta(\psi^-)$ denote the sine of Bragg's angle θ obtained respectively for ψ^+ and ψ^- . Let us set successively $\phi = 0^\circ, 45^\circ$ and 90° in Equation 3.15, we have:

$$A_{\phi=0^{\circ}}^{+} = \frac{1}{2} S_{2}(hkl)\sigma_{11}\sin^{2}\psi + S_{1}(hkl)(\sigma_{11} + \sigma_{22}) - \ln(\sin\theta_{0})$$

$$A_{\phi=45^{\circ}}^{+} = \frac{1}{2} S_{2}(hkl)(\sigma_{11} + \sigma_{22} + 2\sigma_{12})\sin^{2}\psi + S_{1}(hkl)(\sigma_{11} + \sigma_{22}) - \ln(\sin\theta_{0})$$

$$A_{\phi=90^{\circ}}^{+} = \frac{1}{2} S_{2}(hkl)\sigma_{22}\sin^{2}\psi + S_{1}(hkl)(\sigma_{11} + \sigma_{22}) - \ln(\sin\theta_{0})$$
(3.17)

If we plot all the three A^{+} as a function of $\sin^{2} \psi$, we should obtain three straight lines, each of one with a slope that depends on at least one component of the stress tensor σ_{ij} . If the value of these three slopes is known from experimental data, we have then a system of three equations with three unknowns (σ_{11}, σ_{22} and σ_{12}), which is possible to solve. We should also pay attention that the three intercepts for the three straight lines should be the same and it can be used to estimate the value of θ_{0} and d_{0} (Bragg's angle and free of stress interplanar distance for the considered plans).

If we set successively $\phi = 0^{\circ}, 45^{\circ}$ and 90° in Equation 3.16, we have:

$$A_{\phi=0^{\circ}}^{-} = \frac{1}{2} S_{2}(hkl) \sigma_{13} \sin 2 |\psi|$$

$$A_{\phi=45^{\circ}}^{-} = \frac{1}{2} S_{2}(hkl) \frac{\sqrt{2}}{2} (\sigma_{13} + \sigma_{23}) \sin 2 |\psi|$$

$$A_{\phi=90^{\circ}}^{-} = \frac{1}{2} S_{2}(hkl) \sigma_{23} \sin 2 |\psi|$$
(3.18)

If we plot all the three A^- as a function of $\sin^2 \psi$, we should also obtain three straight lines, each of one with a slope that depends on at least one component of stress tensor σ_{ij} . If the value of these three slopes is known from experimental data, we have then a system of three equations with two unknowns (σ_{13} and σ_{23}), because two equations are sufficient to solve the two unknowns, we can use the last equation to verify the result.

Using Dölle's method, all the components of the stress tensor σ_{ij} can be calculated. But in reality, we can also make some additional hypotheses to simplify Equation 3.13.

If we assume that:

- Plane stress conditions hold leading to $\sigma_{13} = \sigma_{23} = 0$. This assumption can be justified because the surface of the sample is free of stress and the depth of penetration of X-Ray is low.
- There is no shear stress, so that $\sigma_{12} = \sigma_{21} = 0$. For this hypothesis, we can calculate σ_{12} and σ_{21} using Dölle's method to verify. It can be also verified with classical treatment by checking the linearity of points. With shear component, the graph would lead to an ellipse.
- The stress is isotropic, so that $\sigma_{11} = \sigma_{22} = \sigma$. We can also verify it using Dölle's method or with classical treatment for two perpendicular ϕ .

With these previous assumptions, the stress tensor now becomes:

$$\overline{\overline{\sigma}} = \begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
(3.19)

It corresponds to an in-plane isotropic biaxial stress state. Equation 3.13 now becomes:

$$ln\left(\frac{\sin\theta_0}{\sin\theta_{hkl}}\right) = \left\{\frac{1}{2}S_2(hkl)\sigma\right\}\sin^2\psi + 2S_1(hkl)\sigma$$
(3.20)

Equation 3.20 makes it possible to determine the stress from the measurements of Bragg's angle $\, heta_{hkl}$

for different angles
$$\Psi$$
 by drawing directly the curve $ln\left(\frac{1}{\sin\theta_{hkl}}\right) = f(\sin^2\psi)$.

As a summary, in order to use Equation 3.20 to determine the stress, but we have assumed that the elasticity of the material is linear, homogeneous and isotropic; the stress corresponds to in-plane stress conditions; there is no shear stress, and the stress is isotropic.

3.1.2 Use of synchrotron and 2D detector to get the stress in the oxide layers

Synchrotron radiation is produced from storage rings (particle accelerator), within which charged particles of high velocity are stored. By deceleration and change of trajectory by passing through magnetic coils, these particles will emit electromagnetic waves, known as synchrotron radiations whose wavelengths are directly proportional to the energy of the particles, according to Equation 3.21 [12]:

$$E = hv = \frac{hc}{\lambda} \to \lambda = \frac{hc}{E}$$
(3.21)

According to Equation 3.21, the higher is the energy, the smaller is the wavelength, so that the depth of penetration of the beam is larger. At the ESRF in Grenoble, it is possible to have range of energy varying between 0.001 keV and 750 keV.

Compared to the X-ray beam produced by the laboratory tubes, the synchrotron radiation presents various advantages in our study:

- The wavelength is tunable on a synchrotron beamline, it can be smaller than the X-ray beam (meaning high energy). Thus, the depth of penetration of the beam is larger, which is important in order to study the low growth rate of the chromia layer (thickness is around 3.76 µm after 20 hours of oxidation at 1000 °C for system NiCr₃₀/Cr₂O₃).
- It has a smaller divergence (the order of divergence is 1 μm), which leads to a better peak resolution.
- The evolution of the stresses during the oxidation is fast, especially during the jumps of temperature [4]. A higher intensity beam coupled with a two-dimensional detector with fast electronics offers a greater range of detection of the plans in the Bragg position and especially for short acquisition time (a few tens of seconds).
- The chromia layers that we want to study have smaller thickness compared to the metallic substrate (1000 times less), meaning that the substrate also diffracts. The choice of the wavelength makes it possible to avoid convolution problems that could occur between the peaks of the chromia and those of the substrate.

The detector therefore makes it possible to carry out high quality diffraction measurements with a high dynamic range, corresponding to relatively short acquisition times.

Instead of using 1D detector to get the 1D diffractogrammes, in this work a 2D detector was indeed used. Because the sample is composed with randomly oriented crystallites, only those in Bragg condition diffract. We can then get the Debye-Scherrer rings on the 2D detector (see Figure 3.8).
The reason why we have chosen the beamline at the ESRF in Grenoble is summarized: high flux; tunable energy; goniometer available; 2D detector available.



Figure 3.8: The Debye-Scherrer rings obtained from diffraction of a random polycristal.



Figure 3.9: Schematic geometry used for the experiments and analysis performed in this work.

Figure 3.9 shows the schematic geometry used for the experiments and analysis performed in this work. $k = k_d - k_i$ is the diffraction vector. \mathcal{O} is the angle of incidence. ϕ is the angle of rotation around the normal to the surface (azimuth). \mathcal{V} is the angle between the normal to the surface and the normal to the diffracting plans. 2θ is the angle between the incident beam and the diffracted beam. γ is the angle between the vertical passing through the position of the direct beam and a given position on the diffraction ring.

In order to use the 2D detector for stress determination by diffraction methods, we need to introduce the goniometer conventions that will relate to the orientation of the scattering vector in laboratory (= diffractometer) coordinates to those in sample coordinates (see Figure 3.9). We will consider first a 2D X-ray area detector oriented so that it is normal to the incoming beam and thus records backscattered

beams diffracted from the sample. Diffracted X-rays will form cones that will intersect the detector forming circles known as Debye-Scherrer rings for a certain family of lattice planes. The semi-angles of these cones will be defined as $2\eta = \pi - 2\theta$. Thus, for each point in the detector with coordinates (x, y), the equivalent cone coordinates can be determined using [14]:

$$\tan(2\eta) = \frac{\sqrt{(x - x_0)^2 + (y - y_0)^2}}{z_0}, \ \tan \alpha = \frac{x - x_0}{y - y_0}$$
(3.22)

Where (X_0, Y_0) describes the location of the incident X-ray beam in detector coordinates, and Z_0 is the sample to detector distance. The diffraction vector corresponding to each point of the Debye-Scherrer ring also resides in a cone, in this case, of semi-angle 2η . Because each point in the ring corresponds to a different orientation of the scattering vector, there should exist a transformation that relates its coordinates \vec{q}_L in the lab system to those \vec{q}_S in the sample system.

$$\vec{q}_{L} = \begin{bmatrix} -\cos\eta \\ -\sin\eta\sin\alpha \\ -\sin\eta\cos\alpha \end{bmatrix} = \begin{bmatrix} -\sin\theta \\ -\cos\theta\sin\alpha \\ -\cos\theta\cos\alpha \end{bmatrix}$$
(3.23)

Let (ψ, ϕ) be the polar angles that determine the scattering vector \vec{q}_s in sample coordinates (see Figure 3.9). Then we have:

$$\vec{q}_{s} = \begin{bmatrix} \sin\psi\cos\phi\\ \sin\psi\sin\phi\\ \cos\psi \end{bmatrix} = \begin{bmatrix} q_{1}\\ q_{2}\\ q_{3} \end{bmatrix}$$
(3.24)

We will now consider a sample rotation $(\omega_0, \psi_0, \phi_0)$ defined according to Figure 3.9. The transformation matrix between the two reference systems is then:

$$A = \begin{bmatrix} \cos\psi_{0}\cos\omega_{0}\cos\phi_{0} + \sin\psi_{0}\sin\phi_{0} & -\sin\psi_{0}\cos\omega_{0}\cos\phi_{0} + \cos\psi_{0}\sin\phi_{0} & -\sin\omega_{0}\cos\phi_{0} \\ \cos\psi_{0}\cos\omega_{0}\sin\phi_{0} - \sin\psi_{0}\cos\phi_{0} & -\sin\psi_{0}\cos\omega_{0}\sin\phi_{0} - \cos\psi_{0}\cos\phi_{0} & -\sin\omega_{0}\sin\phi_{0} \\ -\cos\psi_{0}\sin\omega_{0} & \sin\psi_{0}\sin\omega_{0} & -\cos\omega_{0} \end{bmatrix}$$
(3.25)
$$\vec{q}_{S} = A\vec{q}_{L} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} -\cos\eta \\ -\sin\eta\sin\alpha \\ -\sin\eta\cos\alpha \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} -\cos\eta \\ -\sin\theta \\ -\cos\theta\sin\alpha \\ -\cos\theta\cos\alpha \end{bmatrix}$$
(3.26)
$$= \begin{bmatrix} \sin\psi\cos\phi \\ \sin\psi\sin\phi \\ \cos\psi \end{bmatrix} = \begin{bmatrix} q_{1} \\ q_{2} \\ q_{3} \end{bmatrix}$$

For simplicity, let us continue assuming that $\psi_0 = 0$, so that the scattering vector can still be written as in Equation 3.27:

$$\vec{q}_{s} = \begin{bmatrix} -\sin\theta\cos\omega_{0}\cos\phi_{0} + \cos\theta\sin\omega_{0}\cos\phi_{0}\cos\alpha - \cos\theta\sin\phi_{0}\sin\alpha \\ -\sin\theta\cos\omega_{0}\sin\phi_{0} + \cos\theta\sin\omega_{0}\sin\phi_{0}\cos\alpha + \cos\theta\cos\phi_{0}\sin\alpha \\ \sin\theta\sin\omega_{0} + \cos\omega_{0}\cos\theta\cos\alpha \end{bmatrix} = \begin{bmatrix} \sin\psi\cos\phi \\ \sin\psi\sin\phi \\ \cos\psi \end{bmatrix}$$
(3.27)

Therefore we can finally get:

$$\cos\psi = \sin\theta \sin\omega_0 + \cos\omega_0 \cos\theta \cos\alpha \tag{3.28}$$

The two-dimensional detector that we have used is a camera of the type MAR CCD (Charge Coupled Device), having a circular shape with the diameter 133 mm. It is composed of 2048×2048 pixels. Each pixel is equal to $64.576 \mu m \times 64.576 \mu m$. This detector makes it possible to record the different diffraction rings, or Debye-Scherrer rings, coming from all the diffracting planes of the sample. For this kind of detector, the variation of the angle Ψ is obtained as a function of the variation of the angle γ using Equation 3.28. Thus, with such a detector, the values Ψ are obtained by scanning the rings between - 90° and + 90°. In other words, a Debye-Scherrer ring can be divided into sectors, each sector being defined by an angle γ in order to find the corresponding values of Ψ . The origin of this angle γ corresponds to the position of the direct beam on the camera and the intensity of the rings should be maximum along this direction.

For every picture with Debye-Scherrer rings, we divide it into several sectors; each sector is defined by an angle γ . For each sector, the tool PyFAI is used to get the classical Intensity vs 2θ curves, and then, we may fit the peak to get the 2θ values. After that, Equation 3.28 is used to calculate the corresponding ψ . Finally, we can use the $\sin^2 \psi$ method described in Part 3.1.1 to find the value of stress. One picture corresponds to a specific time at a specific temperature. If we repeat this procedure for every time, we can finally get stress vs time. This procedure links the experimental data obtained using 2D detector with the $\sin^2 \psi$ method. We will describe the procedure in details in part 3.2.

3.2 Procedure for data treatment

The data retrieved after each experiment is stored as pictures in pixels. The objective of this step is to determine the stress levels in the oxide layer from these pictures.

The stress induces a shift of the interplanar distances and hence a displacement of the Debye-Scherrer rings. Different conditions determine the geometry of the rings in the detector plane. For samples aligned with the beam and the detector, the rings are perfectly circular if the specimen is free of stress or with stress with revolution symmetry. For samples aligned with the beam but with an angle of the detector, the rings are elliptic if the specimen is free of stress or with stress with revolution symmetry. Other kind of configurations, i.e. without specific symmetry, leads strictly to more complex geometry (Moritz conchoïde...). Because the stress leads to small angular shifts, the distorsion of Debye-Sherrer rings may be approximated at first order by an elliptic distorsion.



Figure 3.10: Illustration of a Debye-Scherrer ring under stress [15]

We will introduce in details the procedure and every steps for determination of the stress from the Debye-Scherrer ring pictures.

3.2.1 From 2D experimental pictures to 1D diffractogrammes

Figure 3.11 shows a picture of the experiment for the system Ni30Cr/Cr₂O₃:



Figure 3.11: Picture with Debye-Scherrer rings recorded for the Ni30Cr / Cr₂O₃ system

It corresponds to a given time t (and a given temperature T). From this 2D picture, firstly, we should transform it into a 1D diffractogram. For doing this, a data processing protocol has been established. There are several steps to perform:

- Step 1: Calibration is made before the considered experiment by using the picture of the reference powder of silicon. With calibration parameters, we correct the detector position referred to beam to make the pixel to 2θ conversion. For a special position (x, y) in the picture in mm, we can transform it into $(2\theta, \gamma)$, using the relation: $r = \sqrt{(x - x_0)^2 + (y - y_0)^2}$, $2\theta = \arctan\left(\frac{r}{d}\right)$, $\gamma = \arctan\left(\frac{x - x_0}{y - y_0}\right)$, where (x_0, y_0)

describes the location of the incident X-ray beam in detector coordinates, and d is the sample to detector distance (see Figure 3.12).



Figure 3.12: Illustration of the sample to detector distance

- Step 2: In order to obtain the maximum number of points on a ring of given index (hkl), it must be subdivided into sectors corresponding to different angles γ' (see Figure 3.13). In this work, the rings were subdivided into 128 sectors γ' whose values are between - 61.5° and + 65.5° with an angular step of $\Delta \gamma \approx 1^{\circ}$.



Figure 3.13: Subdivision of the Debye-Scherrer rings into sectors

- Step 3: For a given radius θ , we can average the intensity of all the pixels in $[\gamma; \gamma + \Delta \gamma]$ (see Figure 3.14). For doing this, we can firstly get the coordinates of all pixels in the considered range, and then sum the associated intensities and average them. We can repeat this procedure for all the different radii θ , for each sector γ .



Figure 3.14: Illustration of averaging the intensity of all the pixels

Step 4: As explained in steps before, with steps 1, we can transform the coordinates of pictures from (x, y) in pixels to (2θ, γ). With steps 2 and 3, we can calculate the average intensity for a given position (2θ, γ). If we repeat this procedure for all the positions (2θ, γ), we can finally get results as shown in Figure 3.15. If we fix γ at the different values, the results can be converted into data columns: 2θ, I(γ₁), I(γ₂),...,I(γ_i), where I(γ_i) corresponds to the intensity of the ring for the sector γ_i (see Figure 3.16.)



Figure 3.15 : Illustration of the intensity map for the coordinates $(2\theta, \gamma)$

All the procedure above can be performed automatically using PyFAI (for transformation of the pixels into degrees) and Fit2D (for subdivision and integration), thanks to the collaboration with Dr. Guillaume GEANDIER.



Figure 3.16: Diffractogram $I(\gamma_i) = f(2\theta)$ corresponding to the system Ni30Cr / Cr₂O₃ for a given picture and some values of γ .

Now we can transform the picture into a diffractogram $I(\gamma_i) = f(2\theta)$ using the procedure described above, and then, we will describe how we can get the sin² ψ curves from this diffractogram.

3.2.2 From 1D diffractograms to $\sin^2\psi$ curves

In this study, three characteristic peaks of chromia were selected to perform the stress analysis, whose index and theoretical positions 2θ are summarized in Table 3.1.

Plans (hkl) Cr₂O₃	Theoretical positions 2θ(°)	
(104)	13.25	
(110)	14.30	
(116)	21.20	

Table 3.1: The theoretical positions used for the diffraction peaks (104), (110) and (116) of chromia[16].

A zoom on the evolution of these diffraction peaks as a function of γ is presented in Figures 3.17 and 3.18.



Figure 3.17: Zoom on the evolution of the peaks (104) and (110) of Cr_2O_3 as a function of γ .



Figure 3.18: Zoom on the evolution of the peak (116) of Cr_2O_3 as a function of γ .

In order to determine the positions of these diffraction peaks, the continuous background is subtracted and peak fit procedures were automatically performed using the Matlab computation program, with the code developed by Pr. Benoît PANICAUD.

For each diffractogram, the program isolates the three peaks in each of the 128 sectors. The continuous background of these peaks is then subtracted with a polynomial function of order 3 and each peak is fitted by means of a pseudo-Voigt function. In order to improve the quality of the simulation, the following criteria were applied:

- Threshold of intensity: an intensity value below which the fit of the peak is not good.
- Threshold of width: a value of width above which the fit of the peak is considered as bad.
- The difference between the experimental position and the theoretical position of the diffraction peaks that should not be too important, otherwise, the fit is removed.

The program considers the peaks that do not meet every one of these criteria as aberrant.

In general, when the oxide layer is under compressive stress, the evolution of the 2 θ position of each of the three peaks as a function of the 128 γ is symmetric with the origin (corresponding to $\gamma = 0$ see Figure 3.20).

Examples of simulations (with or without subtraction of the continuous background + fit) of the peaks, and the curve of $2\theta = f(\gamma)$ are presented in Figures 3.19 and Figure 3.20:



Figure 3.19: Fitting the peaks with pseudo-Voigt functions



Figure 3.20: Evolution of 2θ as a function of γ .

For all the analyzed peaks, the range of variation of the 2 θ position as a function of γ' varies between 2.10⁻² (°) and 15.10⁻² (°) when the temperature varies between 1000 °C and ambient temperature. Knowing this range of variation of 2 θ is essential, because it will determine the level of stresses generated in the oxide layer.

Once the simulation of peaks is carried out successfully, we obtain the positions of the three peaks for all the 128 sectors (128 values of γ), as well as their maximum intensities (I_{max}) and their integral widths β (area under the diffraction peak / I_{max}).

For each of these peaks, the values of Ψ corresponding to the 128 sectors are deduced from the Equation 3.28 ($\cos \psi = \sin \theta \sin \omega_0 + \cos \omega_0 \cos \theta \cos \gamma$), where ω_0 equals 5° in our experiments. With this equation, we can calculate 128 different values of (θ, ψ) . We can then draw the curve

$$Ln\left(\frac{1}{\sin\theta}\right) = f(\sin^2\psi)$$
 using the 128 points. Finally, we will use the $\sin^2\psi$ curves to calculate the

stress using the $\sin^2 \psi$ method.

3.2.3 From sin² ψ curves to stress-time curves

Finally, the $\sin^2 \psi$ method is used to determine the associated stress. In order to plot and fit for the $\sin^2 \psi$ lines, different criteria have also been defined such as the minimum interval of $\sin^2 \psi$ (see Figure 3.21), the admitted regression coefficients and the admitted difference between the points and the fitted curves. Firstly, we use a criteria (n°3) to remove the abnormal points. Secondly, we use a criteria (n°2) (the regression coefficient of the fit) and a criteria (n°1) (the difference between the first point and the last point in the $\sin^2 \psi$ direction) to judge the quality of the fit. If all these criteria are satisfied, we can consider the fitted curves are correct. We can then calculate the stress using Equation 3.20, from the slope of the straight. An example of the lines of the $\sin^2 \psi$ is shown in Figure 3.22.







Figure 3.22: Example of the $\sin^2 \psi$ curve for the system Ni30Cr / Cr₂O₃ after applying all the criteria

After all the procedure above, we can finally get the stress value for a given time and a given temperature. It corresponds only to a point in the stress-time curves, so we should repeat this procedure for thousands of the experimental pictures to get the stress-time curves. The summary of all the procedure to get stress-time curves are shown in Figure 2.14.



Figure 3.23: Summary of all the procedures to get stress-time curves.

3.3 Analysis of uncertainties

During the experiments, we should pay attention that the variations in 2θ that we want to observe are very small. Consequently, the range of variation of the associated deformation is also very small. Thus, the instrumental settings play a very important role. These include:

- Improper calibration of the detector: if the calibration performed with the silicon powder is not perfect, a significant shift of the experimental positions of the diffraction peaks can be observed. This may come from the incorrect positions of the camera and consequently, the pixels recorded have offset. Thus, the evolution of 2θ as a function of the 128 γ remains symmetrical, but the values of 2θ are shifted by a certain quantity.
- A change in the position of the samples due to thermal expansion: In spite of the thermal expansion tests carried out before the experiments, the samples are liable to move during the oxidation under high temperature, which may induce a change in the position of the samples with respect to the incident beam, causing a shift of the Debye-Scherrer rings.
- The decrease of the intensity of the beam during the experiment and refill: Due to a loss of
 electrons in the storage ring, an intensity decrease occur causing a decrease of the intensity of
 the peaks. A refill is an increase of the beam current and the thermal loading may change on
 optics (monochromatic, slits, mirrors, etc...) that may change the peak position on the detector.

There are eventually three main sources of uncertainties during the experiments: 1. Uncertainty coming from the position of the samples. 2. Uncertainty coming from the calibration. 3. Uncertainty coming from fitting for the peaks.

3.3.1 Uncertainty coming from the position of the samples.

There are three main sources for the uncertainty. The first one comes from the position of the samples.

We can use the Equation 3.29 to calculate the uncertainty coming from the position of the samples [17]:

$$\Delta(2\theta)_{\text{position of sample}} = -\frac{180}{\pi} \frac{\delta(\Delta z)}{d} \frac{\sin 2\theta}{\sin \omega}$$
(3.29)

Where *d* is the sample to detector distance, Δz is the change for vertical position of the sample, 2θ is the Bragg's angle, and ω is the angle of inclination (see Figure 3.24).



Figure 3.24: Illustration of some experimental parameters

For example, if we calculate the uncertainty coming from the position of the sample for the peak (104) of Cr_2O_3 , all the parameters are listed below:

$2 heta$ for peak 104 of Cr_2O_3	13.191°	
$\delta(\Delta z)$	0.1µm	
d	150mm	
ω	5°	

Table 3.2: Values for the experimental parameters

With these parameters, we can finally calculate the uncertainty:

$\Delta(2 heta)$ calculated	-0.0001°
$\Delta(2 heta)$ absolute in degrees	0.0001°
$\Delta(2 heta)$ absolute in radians	$1.74 \times 10^{-6} rad$

Table 3.3: Results of 2θ for calculating the uncertainty coming from the position of the sample.

3.3.2 Uncertainty coming from the calibration.

The second source for the uncertainty is the uncertainty coming from the calibration.

If we assume that $\mathcal{E} \approx \frac{\Delta d}{d_0}$, and from Bragg's law, we can get $d = \frac{\lambda}{2\sin\theta}$. With these equations, we can get

can get:

$$\Delta(2\theta)_{calibration} = \frac{2}{\cot\theta} \left[\Delta\varepsilon + \frac{1}{\sin\theta} \left(\frac{\Delta\lambda}{2d_0} + \frac{\lambda}{2} \Delta d_0 \right) \right]$$
(3.30)

Where 2θ is the Bragg's angle. $\Delta\varepsilon$ is the uncertainty for the strain coming from the calibration (in our experiments, we have estimated it as 2×10^{-4} , which comes from applying $\sin^2 \psi$ method to calibrated powder, that is to say, a 2θ dispersion on stress free sample. It is related to the resolution of the detector, beam divergence, quality of optics and beam, machine fluctuations, etc.... λ is the wavelength for the beam. $\Delta\lambda$ is the uncertainty for the wavelength (we can estimate it using Equation 3.21). d_0 is the interplanar distance without stress. Δd_0 is the uncertainty for the interplanar distance without stress.

For example, if we calculate the uncertainty coming from the calibration for the peak (104) of Cr_2O_3 , all the parameters are listed below:

$\Delta \varepsilon$	2×10^{-4}
λ	0.62Å
$\Delta\lambda$	$6.2 \times 10^{-9} \mu m$
<i>d</i> ₀	1.671 Å
Δd_{0}	$4.15 \times 10^{-8} \mu m$
2 heta for peak 104 of Cr ₂ O ₃	13.191°

Table 3.4 : Values for estimating the uncertainty coming from the calibration

With these parameters, we can finally calculate the uncertainty:

$\Delta(2 heta)$ absolute in degrees	0.00479°
$\Delta(2 heta)$ absolute in radians	$8.36 \times 10^{-5} rad$

Table 3.5: Results of 2θ for calculating the uncertainty coming from the calibration

3.3.3 Uncertainty coming from fitting for the peaks.

The third source for the uncertainty is the uncertainty coming from the fitting for the peaks.

When fitting for the peaks, we have used the function Pseudo-Voigt, which is defined as the sum of a Gaussian peak $G(\mathbf{x})$ and a Lorentzian peak $L(\mathbf{x})$, weighted by a fourth parameter η (the "Gaussiannity" with values between 0 and 1), which shifts the profile more towards pure Gaussian or pure Lorentzian when approaching 1 or 0 respectively:

$$PV(x) = \eta G(x) + (1 - \eta) L(x)$$
(3.31)

It is often used as a peak profile in powder diffraction for cases where neither a pure Gaussian or Lorentzian function appropriately describes a peak [18]. From Equation 3.31, we can see that the uncertainty coming from fitting for the peaks using Pseudo-Voigt method is combined of the uncertainty for Gaussian method and the uncertainty for Lorentzian method.

We can use Equation 3.32 to calculate the uncertainty coming from fitting for the peaks:

$$\Delta(2\theta)_{\text{fiting for peaks}} = \frac{|2\theta^{\text{Gauss}} - 2\theta^{\text{Lorentz}}|}{2}$$

For example, if we calculate the uncertainty coming from fitting for the peaks for the peak (104) of Cr_2O_3 , all the parameters are listed below:

(3.32)

$2\theta^{Gauss}$	13.1904°
$2\theta^{Lorentz}$	13.1916°

Table 3.6: Values for estimating the uncertainty coming from fitting for the peaks

With these parameters, we can finally calculate the uncertainty:

$\Delta(2 heta)$ absolute in degrees	0.000625°
$\Delta(2 heta)$ absolute in radians	$1.09 \times 10^{-5} rad$

Table 3.7: Results of 2θ for calculating the uncertainty coming from fitting for the peaks

3.3.4 Total uncertainty

When calculating the total uncertainty, we should consider all the three main sources of uncertainty at the same time. If we suppose that all the three sources influence the total uncertainty influence (assuming that they are not related with each other), we can just sum them up to calculate the total uncertainty [19].

For calculating the corresponding change of stress, we can used two methods: method 1 consider all the changes of parameters that will have an influence on $\Delta\sigma$, and method 2 is a simplification of method 1 which consider only a main parameter that will have an influence. The equation for method 1 is:

$$\Delta \sigma = E \left(\frac{1}{2d_0 \sin \theta} \Delta \lambda + \frac{\lambda}{2d_0 \sin \theta} \cot \theta \Delta \theta + \frac{\Delta d_0}{d_0} \right)$$

= $E \left(\frac{\Delta \lambda}{\lambda} + \cot \theta \Delta \theta + \frac{\Delta d_0}{d_0} \right)$ (3.33)

The equation for method 2 is simply:

$$\Delta \sigma = E \cot \theta \Delta \theta \tag{3.34}$$
 Where *E* is the Young's modulus (we have used *E* = 330.14*GPa* for calculation [20]).

Because we have done the experiments under different temperatures, there is three times where we have introduced the uncertainty coming from the position of the samples:

- 1. When we do the calibration of the height for the calibration sample at room temperature.
- 2. When we do the calibration of the height for the calibration sample at high temperature (different to room temperature).
- 3. When we do the experiments with our samples.

Thus, when we calculate the total uncertainty, there exists a factor 3 before the uncertainty coming from the position of the samples.

Considering all the three sources of uncertainty at the same time, we have used Equation 3.35 to calculate the total uncertainty (method 1):

$$\Delta\sigma(\text{total}) = E\left(\frac{1}{2d_0 \sin \theta} \Delta\lambda + \frac{\lambda}{2d_0 \sin \theta} \cot \theta (3\Delta\theta_{\text{position of sample}} + \Delta\theta_{\text{calibration}} + \Delta\theta_{\text{fiting for peaks}}) + \frac{\Delta d_0}{d_0}\right)$$
$$= \left(\frac{\Delta\lambda}{\lambda} + \cot \theta (3\Delta\theta_{\text{position of sample}} + \Delta\theta_{\text{calibration}} + \Delta\theta_{\text{fiting for peaks}}) + \frac{\Delta d_0}{d_0}\right)$$
(3.35)

The equation for method 2 is simply:

$$\Delta \sigma = E \cot \theta (3\Delta \theta_{\text{position of sample}} + \Delta \theta_{\text{calibration}} + \Delta \theta_{\text{fiting for peaks}})$$
(3.36)
Finally, we can get the results:

$\Delta \sigma$ (method 1)	257MPa
$\Delta \sigma$ (method 2)	142MPa

Table 3.8: Results of total uncertainty

From the results of the uncertainty, we can see that some experimental parameters ($\Delta \varepsilon$, $\Delta \lambda$ etc.) have influence on the final result. Thus, we should pay attention to these parameters when doing experiments, in order to minimize the uncertainty.

We can also see from the result that if we consider all the changes of parameters that will have an influence on $\Delta\sigma$ (method 1), we will have a bigger value of the total uncertainty compared with method 2 which consider only the main parameter that will have an influence. Thus, if we want to calculate the total uncertainty accurately, we should consider every details of the experiments and all the parameters that will have an influence. This aspect should be addressed in a future thesis.

We should pay attention that the total uncertainty will transport the uncertainty to identification result and influence the identification result when using the identification method described in Chapter 4. Thus, we should take into account the total uncertainty in the identification part. But, because we are tring different identification methods and find a best one, we will not consider the total uncertainty in the identification part to simplify the comparation of different identification methods.

As a summary of Chapter 3, we have started by talking about the background of the experiments that we have done on line BM02 at ESRF (European Synchrotron Radiation Facility) of Grenoble. All the experimental parameters are explained. Then, the $\sin^2 \psi$ method used for determination of stress by X-Ray Diffraction is explained, followed by how to use 2D detector and the method to treat the experimental data from 2D to 1D. In the second part, the procedure of treating the experimental data has been shown systematically and some details have been discussed. In the last part, the three main sources for the uncertainty have been explained and calculated to quantify the limits of our approach.

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Chapter 4 Identification methodologies

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4.1 Isothermal conditions

In this chapter, we will consider that we start from the experimental results obtained by the method described in Chapter 3, so that we can use the models described in Chapter 2 to identify some material parameters (such as viscoplastic parameter J, growth parameter D_{ox} , thermal expansion coefficient α , etc..).

Firstly, we will explain the method of identification under isothermal conditions. Even though it has been studied by Panicaud et al. [1], it is important for us to learn about the identification method under isothermal conditions, because it is the basic for the identification method and we will improve and generalize this method to fit parameters for non-isothermal conditions.

In the model under isothermal conditions described in Chapter 2, there are at least a set of 10 parameters which are unknowns: the two elastic coefficients E, $_{\nu}$ for both oxide and metal; the two viscoplastic parameters J, N for both oxide and metal; the oxide growth parameter D_{ox} only for the oxide; and the kinetics coefficient of the global chemical oxidation reaction named A_p (subscript P

stands for a parabolic reaction as observed in the system $Ni_{30}Cr / Cr_2O_3$ for the considered oxidation times). Some values for these parameters can be found in literature. However, it generally corresponds to bulk materials, so that it is not always reliable for oxide layers. Even for metals, it is difficult to use them because it strongly depends on temperature. Consequently, a methodology has to be proposed to determine some of these materials features. Generally, Young modulus and Poisson ratio can be used directly from literature with a quite good confidence. Kinetics coefficient is determined from experiments such as thermogravimetric analysis or can be directly found in literature. For metals, the dominant relaxation mechanism is usually the intragranular creep with a Norton exponent in the range 3–5 [2]. Moreover, it seems reasonable to consider $N_{ox} < N_m$ [1], [3]. Thus, the creep exponent values for metals are fixed and can be temperature dependent. However, at this step, unknowns remain a priori D_{ox} , J_m , J_{ox} , N_m and N_{ox} . To determine those features, we will process with

different methods. Thus, we look for the set of parameters (D_{ox} , J_m , J_{ox} , N_m , N_{ox}). For the system $Ni_{30}Cr / Cr_2O_3$, the following methodology is proposed:

- Step 1: determination of D_{ox} with an approximation through asymptotical analysis at short oxidation times.
- Step 2: determination of viscoplastic parameters with approximations through asymptotical analysis at long oxidation times.
- Step 3: extraction of experimental coordinates of the possible minimum; inflexion point whose coordinates are $(t_{\min}, |\sigma_{ox}|_{\min})$.
- Step 4: for a given value of N_{ox} and from $|\sigma_{ox}|_{\min}$ or t_{\min} , calculation of J_{ox} and of the characteristic time τ_{ox} , using two different methods, to validate the model at zero-order approximation.
- Step 5: optimization of the whole data to extract simultaneously all the unknown parameters.

It is worth noting that the success of the previous steps depends on the experimental curves (shape and number of points). Now, the different steps are briefly detailed.

<u>Step 1:</u> we consider the asymptotical behavior at short oxidation times. According to experiments performed by thermogravimetric analysis or to literature data, the chemical kinetics of the considered system is parabolic, for the considered oxidation times in the range of considered temperatures. Therefore, it has been demonstrated [3] that the oxide stresses evolution with oxidation time is given by the following relation, whatever is the creep exponent:

$$\sigma_{ox}(t) \approx -\frac{D_{ox}A_pE_{ox}}{1 - v_{ox}}\sqrt{t - t_0}$$
(4.1)

From this equation, we can get:

$$\sigma_{ox}^{2}(t) \approx \left(\frac{D_{ox}A_{p}E_{ox}}{1-v_{ox}}\right)^{2} t + Cste \ when \ t \to 0$$
(4.2)

Where $A_p = \frac{M_{ox}}{bM_o \rho_{ox}} \sqrt{k_{MP}}$ is the kinetics coefficient of the global chemical oxidation reaction (M_{ox} ,

 M_o , ρ_{ox} are respectively the molar mass of oxide, the molar mass of oxygen, the volumic mass of oxide; b is a stoichiometric coefficient); *Cste* is an integration constant linked to the initial stress state.

<u>Step 2</u>: mechanical features at long times can also be obtained from different analytical forms. The same asymptotic method is applied for long times as for short times. On one hand, if $N_{ox} \neq 1$ and $N_{ox} = N_m$, it has been demonstrated in Chapter 2 that the oxide stresses evolution with time is given by the following relation:

$$\left|\sigma_{ox}(t)\right| \approx \frac{E_{ox}}{1 - v_{ox}} \left[(N_{ox} - 1)\frac{t - t_0}{\tau_{ox}} + Cste \right]^{\frac{1}{1 - N_{ox}}} \text{ when } t \to \infty$$
(4.3)

And $\sigma_{ox} = |\sigma_{ox}| \times sign(\sigma_{ox})$ where $\tau_{ox} = \left(\frac{1 - v_{ox}}{E_{ox}}\right)^{N_{ox}} \times \frac{1}{J_{ox}}$ is a characteristic time for relaxation

mechanism.

On the other hand, if $N_{ox} = N_m = 1$ and $J_{ox} = J_m = J$, it has also been established in Chapter 2 that the oxide stresses evolution with time is given by the following relation:

$$\sigma_{ox}(t) \approx Cste' \times \exp\left(\frac{-(t-t_0)}{\tau_{ox}}\right) \text{ when } t \to \infty$$
(4.4)

Where $\tau_{ox} = \left(\frac{1 - v_{ox}}{E_{ox}}\right) \times \frac{1}{J_{ox}}$ is a characteristic time for relaxation; *Cste'* is an integration constant.

Following the above analytical forms, a power regression and an exponential regression can be performed to determine the Norton exponent signature. This method allows to determine a numerical value for N_{ax} . In the our case, different power regressions with $N_{ax} \neq 1$ have been tested for the system $Ni_{30}Cr/Cr_2O_3$. It appears that, whatever the specimen, the analysis gives always a Norton exponent close to one or two or around these values. For unity, this seems to correspond with the well-known mechanisms identified for creep relaxation of ceramics at high temperature: these are the Nabarro-Herring and Coble creeps [2], related to the oxide grain boundary sliding mechanism.

Step 3: the asymptotic form of Equation 4.1 (short times) and Equation 4.3 (long times) can also be used in a different way to extract the relaxation features at long times (especially J). It leads to two other methods (these two methods will be explained in step 4 and step 5). In particular, the minimum $(t_{\min}, -|\sigma_{\alpha x}|_{\min})$ of this curve can be experimentally extracted, that is necessary for steps 4 and 5.

<u>Step 4:</u> Especially, if $N_{ox} = N_m = 1$ and $J_{ox} = J_m = J$ (which are strong assumptions at this step of the methodology), we can use the minimum stress value by replacing it in the analytical solutions. Indeed, the minimum value $-|\sigma_{ax}|_{min}$ has been calculated in Chapter 2 and is directly related to J:

$$\sigma_{\min} \approx -\frac{D_{ox}A_p}{J_{ox}\sqrt{2\tau_{ox}}}$$
(4.5)

The associated time t_{\min} corresponding to this minimum stress value can also be used to calculate J :

$$t_{\min} \approx \frac{\tau_{ox}}{2} \text{ with } \tau_{ox} = \frac{1 - v_{ox}}{E_{ox}J}$$
(4.6)

Step 5: We use the first few hours of the experimental stress data to fit for the growth part, but used the "steady-state" period (longer time) to fit for the relaxation part. Even if separating the two phenomena is mathematically correct (as proved by previous fitting with asymptotical approaches), oxidation is a dynamic process. As long as the oxide is growing for isothermal conditions, the growth stress component is active. Likewise, relaxation (without threshold) can also start as early as the oxidation starts. The experimental data reflect the summation of all these strains. One cannot take strictly one part of the data to evaluate one strain, and another part to evaluate another strain. Indeed, it can lead to possible misidentification on the parameters, as sometimes viewed in literature. [4]–[6]

The different known and unknown parameters can be summarized. Unknown parameters are a priori D_{ox} , J_m , J_{ox} , N_m and N_{ox} . To determine those features, we can process with a global inverse method by optimizing an error function. Thus, we look for a set of five parameters (D_{ox} , J_m , J_{ox} , N_m , N_{ox}). It consists in scanning a priori a range of values of a 5-dimensional vector and to find the set of 5 parameters which minimizes the following sum:

$$(D_{ox}, J_m, J_{ox}, N_m, N_{ox}) = Inf_k \left(\sum_j \left\{ \sigma_{exp}(\mathbf{t}_j) - \sigma_{th}(\mathbf{t}_j; (D_{ox}, J_m, J_{ox}, N_m, N_{ox})_k) \right\}^2 \right)$$
(4.7)

In order to reduce the number of a priori unknown parameters, a discussion is done below:

Firstly, the exponent parameter N_{ox} has been extracted from asymptotical method at long times and seems to lead to a unity exponent. Some ceramics exhibit such a Norton stress exponent close to 1. This category of behavior is usually interpreted in terms of boundary creep mechanisms [2]. For example, the Nabarro-Herring and Coble creeps lead to a Norton exponent close to 1. Thus, this value for Nox can be chosen with a good confidence [1]. Moreover, it is possible to check once more that Nox is close to unity from the optimization error function. This has been successfully done, as presented in Panicaud et al. [7]. Nevertheless, tests on this parameter will be done by trying either N_{ox} =1 or N_{ox} =2.

Secondly, the exponent parameter N_m can be chosen directly from the literature with a good confidence, assuming that the mechanisms in bulk metals were well established in the range of the considered temperatures.

Thirdly, concerning J_{ox} , the value for the system $Ni_{30}Cr/Cr_2O_3$ have been obtained from asymptotic identification at long oxidation times. Its determination is correct provided some conditions are respected, especially if τ_{ox} , $t_{\min} - |\sigma_{ox}|_{\min}$ and N_{ox} have no significant errors. Moreover, some tests on the optimization process have shown that the determination methods for J_{ox} have sometimes difficulties to converge [7], [8]. Because it is not completely reliable, the value of J_{ox} should a priori be identified from the optimization process, as it requires less assumptions on the methodology. Its initial value in the optimization process is taken from the asymptotic method.

Fourthly, we could get also some information on J_m directly from literature data. Nevertheless, temperature dependence of this parameter is often too important, because of its sensibility. Even qualitatively good, quantitative values remain yet to be given for each considered alloy. Consequently, we will use the value in the literature carefully; that is to say, we fix the value of J_m using the value in the literature, but if the optimization result is not good, we can change a little bit the value of J_m to improve the optimization result.

Fifthly, for short oxidation times, the D_{ox} coefficients have been deduced with a good accuracy. However, in literature, we can only find information on this parameter for very few systems [9]–[16]. Moreover, its value can have a direct influence on the whole optimization process, depending on the particular shape of the experimental curves at the short oxidation times that is different from a sample to another. Therefore, we can also consider this parameter as unknown. Its initial value in the optimization process is taken from the asymptotic method.

Eventually, a maximum of two parameters are expected from the optimization process so that Equation 4.7 reduces to the following relation with the set of only two unknown parameters:

$$(D_{ox}, J_{ox}) = Inf_k \left(\sum_j \left\{ \sigma_{exp}(\mathbf{t}_j) - \sigma_{th}(\mathbf{t}_j; (D_{ox}, J_{ox})_k) \right\}^2 \right)$$
(4.8)

4.1.1 Illustration of the method

Here we give an example from our experiments:

The material which has been oxidized is $Ni_{30}Cr$. The chemical composition is shown below:

	Ni	Cr	Si	Mn	C(ppm)	P(ppm)	S(ppm)
Ni ₃₀ Cr	69.65	30.22	<0.01	<0.01	230	30	40

Table 4.1: Chemical composition for $Ni_{30}Cr$

The sample has a diameter of 6mm and a depth of 4mm. The size of the grain varies between 20 μm and 50 $\mu m.$

After being oxidized for 7.4 hours at 900 °C (the thermal solicitation is shown in Figure 4.1, we have named this sample as $Ni_{30}Cr_R10$) using the experimental equipment described in Chapter 3, we can obtain the stress-time curve as shown in Figure 4.2. We have chosen peak 110 and psi negative as an example to illustrate the methodology:



Figure 4.1: Thermal solicitation for the sample Ni₃₀Cr-R10



Figure 4.2: Stress-time curve for the sample $Ni_{30}Cr_R10$ with peak 110 and psi negative

As we can see from Figure 4.2, there are many zero values for the stress. This is because the experimental 2D picture is not good enough for some specific times/pictures, corresponding to the fit for the 2θ position or the fit for the straight line $ln\left(\frac{1}{\sin\theta_{hkl}}\right)vs\sin^2\psi$ that does not satisfy the criteria we have set (see Chapter 3). In the identification process, we just need to remove all the zero values from the experimental data.

After removing all the zero values, we have generally used adjacent-averaging method in the software Origin to smooth the data:



Figure 4.3 : Using adjacent-averaging method to smooth the experimental data

We should pay attention that the adjacent-averaging method makes the curve smoother in the relaxation part, so it is easier to fit for the viscoplastic parameter J_{ox} . But as we can see from Figure

4.3, this may also cause an underestimation of some points at the beginning part, and thus make it not so accurate to fit the growth parameter D_{ox} . In our cases, we will save the identification results for both situation and compare them.

There are 2029 non-zero values in the stress-time curve, but there are only less than 100 points at the beginning part. In order to make it easier to fit for the beginning part and thus obtain an accurate D_{ox} value, we have also tried to add arbitrarily some other points at the beginning part (see Figure 4.4). The method to add the points is as followed:

The following example is presented because it shows all the difficulties that have been met during the identification process. The growth part is not correctly observed. Other samples or experiments on the same alloy have proved that the growth follows an evolution as predicted by the model presented in Equation 4.1. Firstly, we can extract the value for the minimum point (t_{\min} , $-|\sigma_{ox}|_{\min}$) from the experimental data. Secondly, From Equation 4.1, we can consider that, at short times, stress and time follow the equation: $\sigma_{ox}(t) \approx -Cste\sqrt{t}$; such that if we replace t and $\sigma_{ox}(t)$ with the point (t_{\min} , $-|\sigma_{ox}|_{\min}$), we can calculate the Cste value.

Finally, we divide the time interval (0, t_{\min}) uniformly by 100, and use the equation $\sigma_{ox}(t) \approx -Cste\sqrt{t}$ to calculate the corresponding stress $\sigma_{ox}(t)$.



Figure 4.4 : Experimental data after adding 100 points at the beginning part

In this case for the sample R10, it is easy and clear to find the minimum point (t_{\min} , $-|\sigma_{ox}|_{\min}$); but in some cases, it is not so clear to find this minimum point, whereas in some others the beginning part present an inflexion part, more or less described from the experimental results. What's more, in some cases, the minimum point perhaps comes from an error of the experiment (the fitting for the peak is not correct etc...). Besides, there may exist a time shift in the experimental data because we have done the experiment in air, that is to say, it is difficult to find the "real" time=0s. All these situations lead to

an uncertainty when fitting for the growth parameter D_{ox} that is different from a sample to another, and that can have an influence for the global fitting of the whole curve.

We have drawn Figure 4.5 to explain the problems for determination of t_{\min} . t_{0T} is the time when we start to increase the temperature. t_{iso} is the time when temperature becomes isothermal. These two values can be determined from our experiments (with an uncertainty assume to be around 10s). t_m is the time when the absolute value of stress reach a maximum, which can be obtained from the stress-time curve. $t_{0\sigma}$ is the time when the stress start to increase significantly and can be measured from the method, which is between t_{0T} and t_{iso} . We know that $t_{\min} = t_m - t_{0\sigma}$, and because $t_{0\sigma}$ is unknown to us, there can exist significant error for determination of t_{\min} .



Figure 4.5: Illustration of problems for determination of t_{\min}

We have previously explained all the process for treating the experimental data, and then, we just use the model to identify the set of parameters (D_{ox}, J_{ox}) . For D_{ox} and J_{ox} , we have used the data from the literature as initial data (= for the first iteration of the optimization), and for the other input parameters, we have directly used the data from the literature:

Parameters	E_{ox} (GPa)	E_m (GPa)	V _{ox}	v _m	$J_{ox}(\operatorname{Pa}^{-N_{ox}}\operatorname{s}^{-1})$
Values	165 [1]	300.4 [17]	0.3 [1]	0.271 [17]	3×10^{-17} [8]
Parameters	$J_m(\mathrm{Pa}^{-N_m}\mathrm{s}^{-1})$	N _{ox}	N_m	$A_p(\mathrm{ms}^{-0.5})$	$D_{ox}(s^{-1})$
Values	1.21×10 ⁻³⁸ [8]	1 (imposed)	4.1 [8]	1.76×10^{-7} [8]	545.76[1]

Table 4.2: Input parameters for the sample R10 (oxidized at 900 °C)

After using Matlab to find the best solution for Equation 4.8, we obtain:

Parameters	$D_{ox}(s^{-1})$	$J_{\alpha x}(\mathrm{Pa}^{-N_{\alpha x}}\mathrm{s}^{-1})$
Values	5.4×10^{4}	4.29×10^{-15}

Table 4.3: Identification results for R10 for the smoothed data.

Finally, we can draw the experimental data and the simulation result together, to see if the simulation result is good or not (see Figure 4.19). The arbitrary initial 100 points are removed from the plot of the curve.



Figure 4.6: Experimental data after being smoothed and simulation results for R10

As we have explained above, we have also used the same method for the data without smoothing, and we have obtained:

Parameters	$D_{ox}(s^{-1})$	$J_{\alpha x}(\mathrm{Pa}^{-N_{\alpha x}}\mathrm{s}^{-1})$
Values	5.66×10^{4}	4.5×10^{-15}

Table 4.4: Identification results for R10 for the data without smoothing.



Figure 4.7: Experimental data without smoothing and simulation results for R10

When comparing the results for simulation with or without smoothing the data, we can see that it is very close (they almost cover each other if we draw them together). This may illustrate from one side that our method is quite robust.

4.2 Non-isothermal conditions

When the sample is oxidized under non-isothermal conditions, it is more difficult to identify the material parameters, because almost all the material parameters depends on temperature [18]. Besides, the model is more complicated, because when under isothermal condition, some parameters are constant, but when under non-isothermal conditions, they become variable. In Chapter 2, we have established a model under non-isothermal conditions. In this part, we will use this model to propose identification methods for some material parameters.

4.2.1 Global optimization

Let us consider that we have already the experimental data for stress vs time (see Chapter 3), and that we have already the model for non-isothermal conditions (see Chapter 2). Now, the first proposed idea is to simulate the experimental data globally to identify some material parameters. In this case, the basic model is similar with isothermal conditions, but the number of variables has now drastically increased. Unicity of the identification is no more guarranted.

4.2.1.1 Analytical method: considering only strong coupling

In chapter 2, we have explained the model under non-isothermal conditions using the Laplace method. If the thermal loading is as in Figure 4.8:





In the proposed model, the following assumptions are made:

- Only strong coupling is considered (there is no explicit temperature-dependence of the material parameters taken into account in the resolution).
- The Norton exponents $N_{ox} = N_m = 1$, that is to say, we assume a diffusion controlled creep mechanism for both oxide and metal layer.
- The thermal loading is as shown in Figure 4.8.
- We assume a two-layers system: oxide + metal.
- We consider calculations at macroscopic scale.

With all those assumptions, an analytical result can be obtained:

$$\sigma_{ox}(t) = \frac{A_3 \dot{T} \tau_{ox}}{A_2} H_{step}(t-t_1) (1 - e^{-\frac{A_2 t-t_1}{A_1 \tau_{ox}}}) - \frac{A_3 \dot{T} \tau_{ox}}{A_2} H_{step}(t-t_2) (1 - e^{-\frac{A_2 t-t_2}{A_1 \tau_{ox}}})$$
(4.9)

With

$$A_{1} = (1 + \frac{1}{r_{E}\theta(t)})$$
(4.10)

$$A_2 = (1 + \frac{J_m}{J_{ox}\theta(t)})$$
(4.11)

$$A_3 = (\alpha_m - \alpha_{ox}) \frac{E_{ox}}{1 - v_{ox}}$$
(4.12)

$$\theta(t) = \frac{H_1}{A_p \sqrt{t}}$$
(4.13)

$$r_{E} = \frac{E_{m}}{E_{ox}} \frac{1 - v_{ox}}{1 - v_{m}}$$
(4.14)

$$\tau_{ox} = \left(\frac{1 - v_{ox}}{E_{ox}}\right) \times \frac{1}{J_{ox}}$$
(4.15)

If there are many steps in the thermal loading, it is easy to change the model to fit for many steps (thus there will be more terms in Equation 4.9).

Even if the model consider only strong coupling, the material parameters could depend a posteriori on temperature and thus can be taken into account a posteriori from the input data.

In Equation 4.9, if we assume that the function for Young's modulus vs temperature E(T) is known, and that the Poisson ratio is constant (independent to a temperature change) and is known. H_1 is the initial thickness of the metal, which is always known. Moreover, we assume that the function for kinetics constant $A_p(T)$ vs temperature is also known, and that the function for visco-plastic coefficient in the metal vs temperature $J_m(T)$ is known. Besides, we can also assume that the function for expansion parameter vs temperature $\alpha(T)$ is known. However, this may lead to a big uncertainty, because in the literature, it is difficult to find an accurate expansion parameter for the material alloy and for the oxide layer. With all these assumptions, Equation 4.9 has only one unknown: the visco-plastic coefficient in the oxide vs temperature $J_{\alpha x}(T)$. Now if we consider the thermal loading shown in Figure 4.8 and the corresponding experimental data obtained using the method explained in Chapter 3, we can use Equation 4.9 to identify this visco-plastic coefficient in the oxide vs temperature steps (Figure 4.8) with different final temperature.

However, when we tried to use this method, a big difference occurs between the simulation result and the experimental data. This may come from the uncertainty of some of the different material parameters, which we have considered as known. Alternatively, it may also come from the assumption that we have considered only strong coupling to obtain Equation 4.9, whereas some material parameters, such as Young's modulus for oxide and metal (E_{ox} and E_m), visco-plastic parameters for oxide and metal (J_{ox} and J_m), and growth strain parameter for oxide D_{ox} , are all a priori changing with temperature. Indeed, we have not considered these weak couplings in the resolution, but only a posteriori. In order to make fewer assumptions and fit globally the experimental data, we have tried a numerical solution: the optimization method.

4.2.1.2 Numerical inverse method

In the model under non-isothermal conditions described in Chapter 2, there are a set of 22 parameters, which are unknown:

Firstly, for the function of Young's modulus vs temperature, there are six parameters: (a, b, c) for both oxide and metal (See Chapter 2).

Secondly, two Poisson's ratio for both oxide and metal, because we consider it as temperature independent.

Thirdly, for the function of viscoplastic parameters J vs temperature, there are four parameters ($Cste_{J2}, Q_{J2}$) for both oxide and metal (See Chapter 2).

Fourthly, two viscoplastic parameters N for both oxide and metal, because we consider it as temperature independent, because only one mechanism in each material is assumed in the range of studied temperature.

Fifthly, for the function of the oxide growth parameter $D_{_{ox}}$ vs temperature, there are two parameters

(Q_D , D_0). We should pay attention that if we choose another model to simulate the D_{ax} vs temperature, there may exist more parameters, but at least two parameters (See Chapter 2).

Sixthly, for the function of kinetics coefficient A_p vs temperature, there are two parameters (A_{p_0} , Q_a) (See Chapter 2).

Finally, for the function of thermal expansion coefficient α vs temperature, there are four parameters (α_0 , DaT0) for both oxide and metal (See Chapter 2).

It is impossible to fit directly a model with 22 unknown variables, so we should fix some of these parameters. What's more, some values can be directly found in literature. Generally, Young modulus and Poisson's ratio can be used directly from literature for different temperatures with a good confidence, for both the metal and the oxide. Kinetics coefficients for different temperatures are determined from experiments such as thermogravimetric analysis or can be directly found in literature. For metals, Norton exponent for different temperatures can be found in literature for $Ni_{30}Cr$, which is exactly the metal that we have investigated [8]. Moreover, it seems reasonable to consider $N_{ox} < N_m$. In our simulations, we have fixed N_{ox} at 1 or 2, to simplify the model. We have tried to fix N_{ox} at 1, 2, 3, and 4, because we consider that $N_{ox} < N_m$ and N_m is around 4, and we find that $N_{ox} = 1 \text{ or } 2$ leads eventually to the best results. However, at this step, unknowns remain a priori 10 parameters for \mathcal{A}_{ox} and two parameters for \mathcal{A}_m . To determine those parameters, there should exist different temperatures for the experimental data to establish equations in order to solve those 10 parameters, but in our case, we only have at most 4 different temperatures per sample, so we still need to decrease the number of the a priori unknown parameters.

For J_m , we could find the value for two different temperatures in literature for $Ni_{30}Cr$, which is exactly the metal that we have used [8]. Therefore, we just use the data in the literature for the two temperatures and extrapolate to find the values for other temperatures. However, we should pay attention that temperature dependence of this parameter is often too important (it changes greatly with temperature) [1]. Even qualitatively good, quantitative and accurate values remain yet to be given for each considered alloy. Consequently, we still think it as a variable, that is to say, if the simulation is not good, we can change its value manually.

For α_{ox} and α_m , we can use manual optimization method to identify them.

We can find directly the values for different temperatures in the literature. For the values of metal, it is more reliable because we have used the same metal, but when it comes to α_{ox} , there may exist differences because it is usually bulk materials in the literature, which is not our case for the oxide. From our model, we can see that the value of $\alpha_{ox} - \alpha_m$ is important, and it has influence only in the range when temperature changes. Thus, we just use the data for α_m and change the α_{ox} manually to obtain good simulations.

At this step, we have only four variables: two parameters for J_{ox} and two parameters for D_{ox} . If the experimental data is for different temperatures, we can use Matlab to find the solution for Equation 4.16:

$$(Q_D, D_0, Cste_{J_2}, Q_{J_2}) = Inf_k \left(\sum_j \left\{ \sigma_{\exp}(t_j) - \sigma_{th}(t_j; (Q_D, D_0, Cste_{J_2}, Q_{J_2})_k) \right\}^2 \right)$$
(4.16)

We should pay attention that it is still difficult to find the global optimization, because we still have many parameters to identify at the same time.

Here we give an example from our experiments.

The material, which we have used to be oxidized, is still $Ni_{30}Cr$. The thermal loading, which we have used, is as shown in Figure 4.9 (we have named this sample $Ni_{30}Cr_R4$).



Figure 4.9: Thermal loading for R4

After using the experimental equipment described in Chapter 3, we can obtain the stress-time curve presented in Figure 4.10 (we have chosen peak 110 and psi negative as an example):



Figure 4.10: Stress-time curve for the sample $Ni_{30}Cr_R4$ with peak 110 and psi negative Finally, we just use our model to identify a set of 4 parameters $(Q_D, D_0, Cste_{J2}, Q_{J2})$. For some of the input parameters, we have used the data from the literature directly:

Parameters	a_{α} (GPa/ K^2)	b _{ax} (GPa/K)	c_{α} (GPa)	$a_m(\text{GPa}/K^2)$	$b_m(\text{GPa}/K^2)$
Values	0[1]	-0.007[1]	308.61[1]	0[17]	-0.05[17]
Parameters	c_m (GPa)	Vax	v_m	$A_{p0}({\rm ms}^{-0.5})$	$Q_a(ev)$
Values	223.65[17]	0.3[1]	0.271[17]	1.547×10 ⁻⁴ [8]	1.036 [8]
Parameters	N _{ox}	N_m	$\alpha_{0m}(10^{-6}\mathrm{K}^{-1})$	$DaT0_m(10^{-6} \mathrm{K}^{-2})$	
Values	1(imposed)	4.1[8](fixed)	12.93[19]	5.7×10 ⁻³ [19]	

Table 4.5: Input parameters for the sample R4 (The data are extrapolated from the data in the referenced publications)

For some other parameters, we have used the data from the publications, but we have changed it manually:

Parameters	$\alpha_{00x}(10^{-6}\mathrm{K}^{-1})$	$DaT0_{ax}(10^{-6} \mathrm{K}^{-2})$	$Cste_{J2m}(\operatorname{Pa}^{-N_m} s^{-1})$	$Q_{J2m}(ev)$
Values	5.67[19]	1.23×10 ⁻³ [19]	6.44×10^{-5} [1]	7.87[1]

Table 4.6: Input parameters, which can be changed manually for the sample R4 (The data is extrapolated from the data obtained in the referenced publications)

After using Matlab to find the best solution for Equation 4.16 and change parameters in Table 4.6 manually, we can find:

Parameters	$Q_{D}(ev)$	D_0	$Cste_{J2ax}(\operatorname{Pa}^{-N_{ax}}\mathrm{s}^{-1})$	$Q_{J2ox}(ev)$	$\alpha_{0ax}(10^{-6}\mathrm{K}^{-1})$
Values	0.53	5.27×10^{5}	1.54×10^{-12}	0.89	9.67

Table 4.7: identification results for R4.

Finally, we can draw the experimental data and the simulation result together, to see if the simulation result is visually good or not (see Figure 4.11).



Figure 4.11: Experimental data and simulation results for R4 using global optimization method

Nevertheless, we should pay attention that the result is obtained from a numerical optimization: we should check if the result has a physical meaning (see Part 4.3). After some tests, we have found that

even though we can use Matlab to find the numerical solution for Equation 4.16, it does not lead to parameters with a satisfying physical meaning (i.e. the activation energy for metal or oxide is often too big or too small). This may come from that there are too many parameters if we optimize the experimental data globally. Thus, another method, which optimizes the parameters step by step (temperature by temperature), has also been developed.

We have also tried to add points at the beginning part as shown in Figure 4.4 for the first palier at 1000°C, but Matlab cannot find a solution in this case.

4.2.2 Optimization step by step

We have explained the procedure of global optimization for non-isothermal conditions. From the procedure, we can see that there are too many parameters to fit at the same time, which may lead to difficulties to obtain a convergent result with correct physical meaning of the parameters. Thus, the method of optimization step by step has been established. The main idea of this method is to fit the material parameters at a given temperature, so that for such a temperature, it is under isothermal conditions and we can use the method from the Part 4.1 to obtain an optimized result with an easier method.

There are roughly two main steps: the first step is to use numeric optimization method to obtain $J_{
m ax}$

for every temperature plateau and D_{ox} for the first temperature plateau. The second step is to use a manual optimization method for all the data to identify $\Delta \alpha$.

4.2.2.1 Numerical optimization method to get J and Dox for each temperature plateau

In this step, we just use the same method described in Part 4.1 for the first temperature step. We have considered that the temperature is fixed, so it is similar to isothermal conditions. From the second temperature plateau, we have assumed that there is only relaxation, which can be verified from the fact that there is no evolution of the integrated intensities and widths for these plateau [20]. The growth of the oxide layer is finished (i.e. for temperature beneath the first plateau $\dot{h}_{ox} = 0$), because it has been done at the maximum temperature (during the first plateau). For the other plateau, the growth strain is then negligible. What's more, from a thermal point of view, the corresponding mechanisms are not activated. Thus, whatever the reason, this numerically equivalent to assume $D_{ox} = 0$ for the second and the following temperature plateau and only one parameter J_{ox} to fit for the second temperature plateau and the followings.

We have fixed $D_{ox} = 0$ for the second and the following temperature plateau because from the picture of intensity vs time, we can see that the oxide layer only grows during the first temperature plateau.

Here we still consider the example for $Ni_{30}Cr_R4$.

We have started by treating the second temperature plateau, which corresponds to 900 °C. Because

 J_{ox} only change the shape of the stress vs time curve, translation of the stress vs time curve does not change the value of J_{ox} ; so technically, we can translate arbitrarily the initial time for the second temperature step at 0. Because we want to fit for the relaxation behavior of the material, we have set the initial stress as the value of the first point to consider on the stress vs time curve.

Then, we can use Matlab to obtain the parameter \sim	J_{ox} at 900 °C for Nox = 1
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Parameter	$J_{ox}(\mathrm{Pa}^{-1}\mathrm{s}^{-1})$	
Value	1.5×10^{-16}	

Table 4.8: Identification results for $Ni_{30}Cr_R4$ at 900 °C.

Finally, we can draw the experimental data and the simulation result together, to see if the simulation result is good or not visually (Figure 4.12) :



Figure 4.12: Fitting the parameter J_{ox} for $Ni_{30}Cr_R4$ at 900 °C

Then, we just repeat the procedure for the temperature 800 °C, and 700 °C.

For 800 °C, we have obtained (Figure 4.13):

Parameter $J_{ox}(\mathrm{Pa}^{-1}\mathrm{s}^{-1})$	
Value	4.98×10^{-17}

Table 4.9: Identification results for $Ni_{30}Cr_R4$ at 800 °C.



Figure 4.13: Fitting the parameter J_{ox} for $Ni_{30}Cr_R4$ at 800 °C

For 700 °C, we have obtained (Figure 4.14)

Parameter	$J_{ox}(\mathrm{Pa}^{-1}\mathrm{s}^{-1})$	
Value	1.27×10^{-17}	

Table 4.10: identification results for $Ni_{30}Cr_R4$ at 700 °C.



Figure 4.14: Fitting the parameter $\,J_{_{ox}}$ for $\,N\!i_{_{30}}Cr_R4$ at 700 °C

When comparing the simulation results with the experimental data for 900 °C, 800 °C and 700 °C, we can see that the simulation results are straighter than the experimental data. This may come from the fact that we have chosen $N_{ox} = 1$ in this case.

Although the fit seems worse here than when using the global optimization, the physical meaning is clearer (see Part 4.3), in relation with the methodology used.

Now we have obtained the values of J_{ox} for three different temperatures. For the first temperature plateau, we have now to identify two parameters: $D_{_{ox}}$ and $J_{_{ox}}$. Here we have tried two different methods:

a) Method 1 to simulate the first temperature plateau

The easiest idea is to use numeric optimization method directly to identify $D_{_{ox}}$ and $J_{_{ox}}$ together, using Matlab. For doing this, we have repeated the same procedure described in Part 4.1, that is to say, firstly, we use adjacent-averaging method in the software origin to smooth the experimental data. Secondly, we add arbitrarily 100 points at the beginning part of the stress vs time curve to help the fit to converge and to obtain a correct range value for the parameter $D_{_{ox}}$ modeling the growth phenomenon. Thirdly, we use Matlab to solve Equation 4.8. Finally, we can obtain the result:

Parameters	$J_{ox}(\mathrm{Pa}^{-1}\mathrm{s}^{-1})$	$D_{\alpha x}(s^{-1})$
Values	1.43×10^{-14}	4.66×10^{4}

Table 4.11: Identification results for $Ni_{30}Cr_R4$ at 1000 °C (Method 1).

If we draw the experimental data and the simulation result together, we will obtain (Figure 4.15):



Figure 4.15: Fitting the parameter J_{ax} and D_{ax} for $Ni_{30}Cr_R4$ at 1000 °C (Method 1).

If we draw the difference between experimental data and simulation result for many pairs of ($D_{\scriptscriptstyle ox}$, $K_{ox} = \frac{1}{2.I}$), we can see from Figure 4.16 that the minimum locates in a "valley". This phenomenon

tell us that there may exist other pairs of (D_{ox} , $K_{ox} = \frac{1}{2J_{ox}}$), that could be minimum point (but
somewhere else in the valley). One difficulty for the optimization of parameters of such a system is to be sure to obtain a global minimum, not only a local one.



Figure 4.16: Difference between experimental data and simulation result for many pairs of (D_{ox} ,

$$K_{ox} = \frac{1}{2J_{ox}}$$
) for $Ni_{30}Cr_R4$ using method 1

If we draw Ln(J(T)) vs $\frac{1}{T}$ using the data that we have obtained for 700, 800, 900 and 1000°C (method 1), we can have:



Figure 4.17: Linear fit of Ln(J(T)) vs $\frac{1}{T}$ for $Ni_{30}Cr_R4$ using method 1

We can see from Figure 4.17 that the data for 700, 800 and 900 °C seems to give a straight line, but there is a jump for 1000°C using method 1. Although the fitting for 1000 °C using method 1 is not bad, the physical significance of this difference is not really clear, so we have tried to use another method, which is based on the temperature continuity of the considered physical parameter.

b) Method 2 to simulate the first temperature plateau

The other method, which has been proposed, is based on the fact that $J_{ox}(T)$ should have a physical significance. In Chapter 2, we have explained that the parameter $J_{ox}(T)$ can be described as:

$$J(T) \approx Cste_{J_2} \exp(-Q_{J_2} / RT) \tag{4.17}$$

Where $Cste_{J2}$ is a constant and Q_{J2} is the activation energy.

So after some mathematical operations, we can get:

$$Ln(J(T)) \approx Ln(Cste_{J2}) - \frac{Q_{J2}}{R} \frac{1}{T}$$
(4.18)

If we draw the line of Ln(J(T)) vs $\frac{1}{T}$ for different temperatures, we should get a straight line if only one mechanism occurs, and we can calculate the activation energy Q_{J2} from the slope of this line. Now we can explain the procedure for method 2:

Firstly, we use the values obtained for J_{ox} at 700, 800 and 900°C to get a straight line and extrapolate the value of J_{ox} expected for 1000 °C.

Secondly, when fitting for the first temperature plateau at 1000 °C, we fix the parameter J_{ox} at the value that has been extrapolated, and we choose to fit only the parameter D_{ox} .

Thirdly, we fit once again the first temperature plateau fixing D_{ax} at the value we have found and fit for a last step only the parameter J_{ax} .

That is to say, we have fitted D_{ox} and J_{ox} one by one, but we have started by using a value for J_{ox} that has been extrapolated. The aim is to obtain a set of values that converges toward more accurate values with physical meaning.

Compared with method 1, method 2 is easier to find the parameters J_{ox} and D_{ox} with physical meaning; whereas when using method 1, we may find a solution, which is mathematically consistent and fit very well the experimental data, but J_{ox} may not have a correct physical significance.

Here we still give the example of $Ni_{30}Cr_R4$ at 1000 °C.

With the values of J_{ox} at 700, 800 and 900°C, we can use a linear fit to obtain the theoretical Ln(J(T)) vs $\frac{1}{T}$ (see Figure 4.18) and then we can extrapolate the value at other temperatures:



Figure 4.18: Using linear fit of Ln(J(T)) vs $\frac{1}{T}$ for 700, 800 and 900°C , to extrapolate the value of J_{ox} at 1000 °C for $Ni_{30}Cr_R4$

We can see from Figure 4.18 that if we draw Ln(J(T)) vs $\frac{1}{T}$ using the data of 700, 800 and 900 °C, it is almost a straight line, which is physically correct when considering a single mechanism for relaxation in the oxide. Whereas from Figure 4.12 to Figure 4.14, we can see that the fit of the experimental data seem not to be very good (maybe also due to the choice of Nox). This aspect will be

The linear fit function for Ln(J(T)) vs $\frac{1}{T}$ is:

$$Ln(J(T)) = -14127\frac{1}{T} - 24.384$$

discussed further.

(4.19)

Then, we just set T = 1273K to obtain the value of J_{ox} at 1000 °C (see Table 4.12).

Parameter	$J_{ox}(\mathrm{Pa}^{-1}\mathrm{s}^{-1})$	
Value	3.89×10^{-16}	

Table 4.12 : Extrapolated value of J_{ox} at 1000 °C for $Ni_{30}Cr_R4$

After fixing $J_{ox} = 3.89 \times 10^{-16} \text{ Pa}^{-1} \text{s}^{-1}$ to obtain D_{ox} , and then fixing D_{ox} at the value we have obtained, it is possible to fit for J_{ox} ; we can finally obtain a pair of D_{ox} and J_{ox} (see Table 4.13):

Parameters	$J_{ox}(\mathrm{Pa}^{-1}\mathrm{s}^{-1})$	$D_{ox}(s^{-1})$
Values	3.88×10^{-16}	2007.2

Table 4.13: Identification results for $Ni_{30}Cr_R4$ at 1000 °C (Method 2).

If we draw the experimental data, the simulation results for method 1 and method 2 together, we can see that there is difference (see Figure 4.19). Usually, method 1 fits better for the beginning part of the stress vs time curve (the growth stress part). Whereas, method 2 fits better the relaxation part. In our cases, we have systematically calculated with both methods 1 and 2 for every sample and finally compare them.



Figure 4.19: Comparison of methods 1 and 2 with the experimental data for $Ni_{30}Cr_R4$ at 1000 °C.

Moreover, if we draw Ln(J(T)) vs $\frac{1}{T}$, we can see that method 2 has a better physical meaning, according to literature (becaure of the R-square coefficient and of the value of the slope):



Figure 4.20: Comparison of Ln(J(T)) vs $\frac{1}{T}$ using method 1 and 2 for $Ni_{30}Cr_R4$

Thus, in our cases, we have tried both method 1 and method 2 for the first temperature plateau. And then, we compare them and choose the best one. In the case of $Ni_{30}Cr_R4$, we have chosen method 2 because it has an easier physical significance and the fit of the stress vs. time curve is not so bad and quite acceptable.

4.2.2.2 Fitting for all the temperature plateaus

In the part 4.2.2.1, we have fitted the experimental data for each temperature plateau. In this part, we will try to use the parameters obtain in part 4.2.2.1 and fit the data for all the temperature plateaus at the same time.

We have fitted some material parameters for different temperatures. In order to use them when temperature changes, we should try to fit for the parameter vs temperature function.

For J_{ox} , we have four values because of the four different temperatures (sometimes three for some samples), so we can use Equation 4.18 to find the equation for J_{ox} .

For D_{ox} , when fitting for each temperature plateau, we have assumed that it only has value for the first temperature plateau; for the other, it is supposed to be zero. This assumption may be wrong, so we have also tried another variant method: we assume that the parameters J_{ox} and D_{ox} have the same activation energy ($Q_J = Q_D$), which is a strong hypothesis. Thus, we assume that the limitant mechanism for creep is the same as for growth strain, in the oxide layer. This is consistent with the proposition found in [3]. Because, we need the slope for line $Ln(D_{ox})$ vs $\frac{1}{T}$, and we only have the value for D_{ox} at 1000 °C, so we can finally obtain the function for D_{ox} .

After some tries, we have found that D_{ox} has a significant influence on the first temperature step, but little influence for the other steps. It does not change too much the shape of the stress vs time curve for the other temperature steps.

Because we have the functions for D_{ox} and J_{ox} , we can now use these functions to obtain a simulation result, and compare it with the experimental data.

In this step, we have also to change the value of α manually (we have called this manually optimization method in Part 4.4.2) to fit for the stress jump between two different temperature plateaus, which is also a method to identify the parameter α (see Part 4.4).

After all the steps above, we can finally draw the simulation result together with the experimental data (Figure 4.21) for this approach:



Figure 4.21: Experimental data and simulation results for R4

Compared with global optimization (see Figure 4.11), visually, the simulation result obtained by step by step method followed by manual method seems worse than the one obtained by global optimization, but in reality, the global optimization may lead to results which are mathematically correct, but does not have a clear physical meaning. We will explain the verification of the physical significance for J_{ox} in the next part.

4.3 Verification of the physical consistency of numerical values for J(T)

We have obtained the values for J_{ox} at different temperatures, it is then important to verify if it has physical meaning.

For J_{ox} , from Equation 4.18, if we draw the line of Ln(J(T)) vs $\frac{1}{T}$ for different temperatures, we should get a straight line.

We also use the example of $Ni_{30}Cr_R4$. If we draw this curve Ln(J(T)) vs $\frac{1}{T}$ for different temperatures for step by step method and global optimization method, we can find:



Figure 4.22: Comparison of the Ln(J(T)) vs $\frac{1}{T}$ curve for $Ni_{30}Cr_R4$ using step by step method and global optimization method.

From Figure 4.22, we can see that the line of step by step method is straighter than the one for the global optimization method. After searching the value of activation energy in literature, in this example, we found that step by step method gives an activation energy (1.2eV) as consistent as the global optimization method (0.88eV), which is not necessarily the case for all the samples.

In some cases, this is the way in which we confirm the material parameters that we have found are good or not. If the activation energy we have found does not have physical meanings (it does not match the values in the range from literature, typically inferior to 0.1 eV or superior to 5 eV), we are sure that it is not a good value. Else, if the activation energy has physical consistency with literature and the fit for experimental data seems quite good, it is likely that we have found a correct material parameter, because all the parameters we have found have a clear physical meaning and they are based on a physical model.

4.3.1 Calculation of activation energy

From Equation 4.18, we can now calculate the activation energy \mathcal{Q}_{J2} from the slope of the straight

line
$$Ln(J(T))$$
 vs $\frac{1}{T}$ (see Figure 4.22).

For example, for the sample $Ni_{30}Cr_R4$ using step by step method, we can obtain the activation energy:

Parameter	$Q_J(ev)$	
Value	1.2	

Table 4.14 : Activation energy value for the sample $Ni_{30}Cr_R4$ using step by step method

4.4 Identification of $\Delta \alpha$

Another advantage of our model is that it can be used to identify the thermal expansion coefficient $\Delta \alpha$. We have tried two methods, the analytical method with some assumptions and find a mathematical expression for $\Delta \alpha$, and the manual optimization method which identify $\Delta \alpha$ by comparing the experimental data and the simulation results.

4.4.1 Analytical method

In Chapter 2, we have used the Laplace method to find the expression for $\Delta\sigma_{ox}$ between two temperatures:

$$\Delta \sigma_{ox} = \sigma_{ox}(\mathbf{t}_2) - \sigma_{ox}(\mathbf{t}_1) \approx \frac{A_3 \dot{T}(\mathbf{t}_2 - \mathbf{t}_1)}{A_1} \approx (\alpha_m - \alpha_{ox}) \frac{E_{ox}}{1 - v_{ox}} \Delta T$$
(4.20)

We can also obtain:

$$\Delta \alpha = (\alpha_m - \alpha_{ox}) = \Delta \sigma_{ox} \frac{1 - v_{ox}}{E_{ox} \Delta T}$$
(4.21)

If we know $\Delta \sigma_{ox}$ and ΔT from the experimental result, and because the Young's modulus and poison's ratio are known, so we can use Equation 4.21 to identify the thermal expansion coefficient $\Delta \alpha$.

4.4.2 Manual optimization method

Although we can use an analytical method to obtain the value of $\Delta \alpha$, it is easier to do it by using the manual optimization method.

It is the same process described in Part 4.2.2.2. Firstly, we have obtained the equation for parameters J_{ox} and D_{ox} vs temperature from fitting the result for each temperature plateau.

Secondly, we use the $\Delta \alpha$ value in the literature as initial value, and all the functions for parameters as input, to fit all the temperature plateaus at the same time.

If the fit is visually different from the experimental data, we change the value of $\Delta \alpha$ manually. The main idea is the same as the one with analytical method (using $\Delta \sigma_{ox}$ when temperature change to identify $\Delta \alpha$), but it is easier to perform (see Figure 4.23).



Figure 4.23: Illustration of using manual optimization method to identify $\Delta \alpha$

In the case of identification of $\Delta \alpha$ for the sample R4, we can find the expansion parameters for metal and oxide as shown in Table 4.15:

Parameters	$\alpha_{0ax}(10^{-6}\mathrm{K}^{-1})$	$DaT0_{ax}(10^{-6} \mathrm{K}^{-2})$	$\alpha_{0m}(10^{-6}\mathrm{K}^{-1})$	$DaT0_m(10^{-6} \mathrm{K}^{-2})$
Values	5.67[19]	1.23×10 ⁻³ [19]	12.93[19]	5.7×10^{-3} [19]

Table 4.15: Expansion parameters for the sample R4

After using the manual optimization method, we have identified α_{0ox} to be 9.67 10^{-6} K⁻¹ with all the other expansion parameters staying the same. That is to say, α_{0ox} is the key parameter that influences mainly the jump of stress when temperature changes.

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Chapter 5 Experimental results

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5.1 Experimental results from publications

In this chapter, we will present all the experimental results that we have obtained using the method described in Chapter 3 and those obtained from different publications.

For the use of our models described in Chapter 2 and the proposed identification methods described in Chapter 4, we need experimental data. To begin with, we have found some experimental results from publications.

In these publications, data are often represented with images, which makes it difficult to extract the raw numbers, so we have used Graph digitizer to digitize the data. There are mainly four steps:

1. Obtain the graph in the publications

The image can be obtained through the html version of the paper, or by taking a screenshot of the pdf file.

2. Set the scale

We have to define the axis and set the scale. This is how we can define the coordinates of each point. The more precise, the better the results will be.

3. Digitize the data points

In this step, we have to indicate where the points are located.

4. Export the data

Finally, we can export the data into Matlab to be used.

An example of graph digitizer is shown in Figure 5.1:



Figure 5.1: illustration of Graph digitizer using the data from [1], [2]

5.1.1 Different thermal solicitations

The first criterion to obtain the experimental results from publications is the thermal solicitation. We have three main kinds of thermal solicitations: cyclic loadings, step loadings and isothermal conditions.

5.1.1.1 Cyclic loadings and step loadings

In chapter 2, we have defined cyclic loadings and step loadings. In publications, it is not frequent to find examples of experimental data for these kinds of solicitations. Fortunately, we have found some. For example, we can find the data for measured strain relaxation in α -Al₂ O_3 grown on Ni–50Al in [1], [2]. After using Graph digitizer, we can get the experimental data for both cyclic loadings and step loadings:



Figure 5.2: Measured stress vs time in α -Al $_2O_3$ TGO at 1100 and 950 °C [1], [2]

Figure 5.2 shows measurements of creep relaxation in α -Al₂O₃ growing on a single crystal samples of β -Ni-50Al(NA1). After 400 min of oxidation at 1100°C, after the completion of the $\theta \rightarrow \alpha$ phase transformation, the temperature of this sample was suddenly decreased to 950°C. This temperature's change applies a compressive stress to the oxide, because the coefficient of thermal expansion of the

bulk metal substrate is larger than that the one of the thin oxide. The temperature was subsequently returned to 1100 °C, for which a small and rapidly decaying tensile stress was eventually observed.



Figure 5.3: Measured stress vs time in α -Al2O3 TGO at 1100, 1050, 1000, and 950 °C

Figure 5.3 shows measurements of creep relaxation in α -Al₂ O_3 growing on another single crystal samples of β -Ni-50Al(NA2). Sample NA2 was also initially oxidized at 1100°C followed by temperature changes to 1050, 1000, and 950°C where creep relaxation was monitored.

It is then possible to use Figure 5.2 and Figure 5.3 as experimental data to identify the material parameters that will be presented in Chapter 6.

5.1.1.2 Isothermal conditions

Although relatively few published studies have dealt with the experimental determination of stress generated during the oxidation of material when temperature changes, it is easier to find the experimental data in publications under isothermal conditions. For example, we can find growth stress evolution in α -Cr2O3/NiCr30 determined by Raman spectroscopy under isothermal conditions in [3].



Figure 5.4: Growth stress evolution in α -Cr2O3/NiCr30 determined by Raman spectroscopy [3] Another example is shown in Figure 5.5, we can find strain in α -Al₂O₃ growing on different Fe-based alloys during oxidation at 1000°C [4].



Figure 5.5: strains in α -Al₂ O_3 growing on different Fe-based alloys during oxidation at 1000 °C [4]

5.1.2 Different materials

Another criterion to obtain the experimental results from publications is the different kinds of materials. We have focused on two main kinds of material systems: the system $NiAl/Al_2O_3$ and the system $NiCr/Cr_2O_3$. Moreover, in the case of reactive element addition, the later will influence the growth stresses [4], so we can also consider the materials with reactive element addition as a specific kind of material.

In Table 5.1, we have listed all the experimental data that we have found in the publications.

Materials	Thermal loadings(°C)	Sources
Peak 100 single crystals of	1100-1050-1000-950	[2]
stoichiometric β-NiAl	1100-950-1100	
Fe-20Cr-10Al-0.0035Y	1100	[5]
Ni-50Al-10Pt		
Ni-37Al-10Pt	1100	
Ni-25Al-20Pt	*	[1]
Ni-25Al-20Pt-0.2Hf	1100	
	1100-1050-1100	
β-NiAl	1100-950-1100-room	
	temperature	
Fe28Al	1000	-
Fe40Al		[4]
Fe40AlHf	During cooling	
FeCrAl	•	
Ni-55Al	1000	
	1100	-
Ni-40Al	1100-950-1100	[6]
	950	
Fe20Cr10Al0.04Y		
Ni50Al0.06Zr	1100	
Ni-40Al		
Fe28Al5Cr0.05Zr		
Fe40Al0.04Hf	+	
Fe20Cr10Al (FeCrAl)	1000	[7]
Fe28Al5Cr (Fe3Al)		
FeCrAl	1000	1

	1100	
FeCrAlY	1000	
	1100	
Fe-20Cr-10Al		
Fe-28Al-5Cr	1000	[8]
H2- annealed Fe-28Al-5Cr	*	
NiAl 100 single crystals		
NiAl 110 single crystals	1100	[9]
NiAl 111 single crystals	*	
H2-annealed Fe–28Al–5Cr	1100	
alloy	During cooling	
untreated Fe–28Al–5Cr	1100	[10]
alloy	During cooling	
	950	
	1000	
	1050	
bulk NiCrAlY	1100	[11]
	During cooling	
	1100-1000-1100-room	
	temperature	
	900	
	850	
NiCr30	800	[3]
	750	
	700	

Table 5.1: Experimental data for different thermal loadings and different materials found in literature

5.2 Experimental results from ESRF

In order to verify and apply the identification method described in Chapter 4, we need many experimental data. Even though we can find some in the publications, we do not sometimes know with correct accuracy the materials that have been used in these works. Besides, in order to verify the identification method by calculating the activation energy and to propose mechanistic explanations of the coupling of stress with oxidation, it is better to have a series of experimental data with the same material, but different thermal solicitations. Thus, we have also performed experiments at European Synchrotron Radiation Facility (ESRF).

5.2.1 Different thermal solicitations

To begin with, we have fixed the material using Ni-30Cr. The chemical composition of Ni-30Cr is given in table 5.2:

	Ni	Cr	Si	Mn	С	Р	S
Ni-30Cr	<mark>69.65%</mark>	30.22%	<0.01%	<0.01%	230ppm	30ppm	40ppm

Table 5.2: The chem	nical compositio	n of Ni-30Cr
Table Siel The cheft	near compositio	

The sample has a diameter of 6mm and a depth of 4mm. The size of the grain varies between 20 μm and 50 $\mu m.$

For the thermal solicitations, we have considered 9 different kinds of thermal solicitations, listed in table 5.3:

Code name			Temperature	for plateau(°C)		
R4	1000(3h)	900(3h)		800(3h)		700(3h)
R13	1000(3h)		850(3h)			
R2		900(3h)		800(3h)		700(3h)
R11		900(3h)	850(3h)	800(3h)	750(3h)	
R15			850(3h)	800(3h)	750(3h)	700(3h)
R3				800(3h)		700(3h)
R14	1000(7.4h)					
R10		900(7.4h)				
R16				800(7.4h)		

Table 5.3: Different kinds of thermal solicitations for the experiments done at ESRF

It has to be notice that these 9 different thermal soliciations correspond to only 4 chromia microstructures initially built at respectively 1000, 900, 850 and 800 $^\circ C$

Now we will present the experimental result for the nine different kinds of thermal solicitations one by one. For R4 and R13, we will give the raw experimental data for different diffraction peaks and different psis values and show how we have chosen from them. For the other samples, we will only consider the result of a specific peak and psi we have chosen.

1. R4

The thermal solicitation for the sample Ni30Cr-R4 is shown in Figure 5.6:



Oxidation time

Figure 5.6: Thermal solicitation for the sample Ni30Cr-R4

After using the method described in Chapter 3, we can find the stress-time curve for peak 104, peak 110 and peak 116 for both psi positive(ψ^+) and psi negative(ψ^-).

In the case of Ni30Cr-R4, the result for the peak 116 is not good, so we can only get the result for peak 104 and peak 110 as shown in Figure 5.7:



Figure 5.7: The stress-time curve for the sample Ni30Cr-R4 for different peaks and different psis

We can see from Figure 5.7 that for the plateaus at 700 °C, 800 °C and 900 °C, the shape of the stresstime curve is similar for peak 104 (ψ^+ and ψ^-) and peak 110 (ψ^+ and ψ^-). The main difference exists for the plateau at 1000 °C. For peak 104, we can see that there are no points at the very beginning part (the first 100 seconds), which is very important for the identification of the parameter D_{ox} , so we will not consider peak 104 in our identification part. For peak 110, after comparing the shape of stresstime curve at 1000 °C for ψ^+ and ψ^- , we have finally chosen ψ^- because the stress-time curve is smoother, which is better for the identification of the parameter J_{ox} (we have not considered the mean value for ψ^+ and ψ^- , because they are similar). Thus, the final stress-time curve for the sample Ni30Cr-R4 that will be used in the identification part, is shown in Figure 5.8:



Figure 5.8: The final stress-time curve for the sample Ni30Cr-R4

We can see from Figure 5.8 that the relaxation for the plateaus at 700 °C, 800 °C and 900 °C is very clear, with an evolution of this relaxation for these 3 plateaus, whereas the growth part for the first plateau at 1000 °C is not so clear.

2. R13

The thermal solicitation for the sample Ni30Cr-R13 is shown in Figure 5.9:





In the case of Ni30Cr-R13, only the stress-time curves for peak 104 and peak 110 with psi negative (ψ^-) are good, as shown in Figure 5.10:



Figure 5.10: The stress-time curves for the sample Ni30Cr-R13 for different peaks with psi negative

We can see from Figure 5.10 that the stress-time curve almost overlaps each other for the plateau at 1000°C and 850 °C. For the first plateau, even though the data for peak 104 is smoother, it does not have enough points at the very beginning part, which is important to identify the parameter D_{ox} . Thus,

we have chosen only the peak 110 psi negative (ψ^-) as the final stress-time curve for the identification part as shown in Figure 5.11.



Figure 5.11: The final stress-time curve for the sample Ni30Cr-R13

We can see from Figure 5.11 that the relaxation part for the plateau at 850 °C is clear. The growth part for the plateau at 1000 °C is difficult to see.

3. R2

The thermal solicitation for the sample Ni30Cr-R2 is shown in Figure 5.12:



Figure 5.12: Thermal solicitation for the sample Ni30Cr-R2

In the case of Ni30Cr-R2, only the stress-time curves for peak 104 and peak 110 with psi negative (ψ^-) are good. We have chosen peak 110 psi negative (ψ^-) as the final stress-time curve for the identification part to have a better identification as shown in Figure 5.13.



Figure 5.13: The final stress-time curve for the sample Ni30Cr-R2

We can see from Figure 5.13 that the relaxation part for the plateaus at 800 $^{\circ}$ C and 700 $^{\circ}$ C is clear, and the growth part for the plateau at 900 $^{\circ}$ C is clear.

4. R11

The thermal solicitation for the sample Ni30Cr-R11 is shown in Figure 5.14:



Figure 5.14: Thermal solicitation for the sample Ni30Cr-R11

In the case of Ni30Cr-R11, only the stress-time curves for peak 104 and peak 110 with psi positive (ψ^+) are good, we have chosen peak 110 psi positive (ψ^+) as the final stress-time curve for the identification part.



Figure 5.15: The final stress-time curve for the sample Ni30Cr-R11

We can see from Figure 5.15 that the relaxation part for the plateaus at 850 °C and 800 °C is clear, whereas for the plateau at 750 °C, it is flat, so the relaxation behavior is not so clear. For the first plateau at 900 °C, we can see the growth part, but because there are not enough experimental data at the beginning part, the growth part is not so clear.

5. R15

The thermal solicitation for the sample Ni30Cr-R15 is shown in Figure 5.16:



Figure 5.16: Thermal solicitation for the sample Ni30Cr-R15

In the case of Ni30Cr-R15, only the stress-time curves for peak 104 and peak 110 with psi negative (ψ^-) are good, we have chosen peak 110 psi negative (ψ^-) as the final stress-time curve for the identification part to identify parameters as shown in Figure 5.17.





We can see from Figure 5.17 that the relaxation part for the plateaus at 800 °C and 750 °C is clear, whereas for the plateau at 700 °C, there are not enough experimental data at the end of the plateau, so the relaxation part is not clear. The growth part for the first plateau at 850 °C is clear.

6. R3

The thermal solicitation for the sample Ni30Cr-R3 is shown in Figure 5.18:



Figure 5.18: Thermal solicitation for the sample Ni30Cr-R3

In the case of Ni30Cr-R3, only the stress-time curves for peak 104 and peak 110 with psi negative (ψ^-) and psi positive (ψ^+) are good ; we have finally chosen peak 104 psi-, as shown in Figure 5.19:



Figure 5.19: The final stress-time curve for the sample Ni30Cr-R3

We can see from Figure 5.19 that the relaxation part for the plateau at 700 °C is clear, whereas the quality of the first plateau at 800 °C is not very good, because there are some blank areas. This may come from the fact that we have defined strong criteria to remove the experimental data.

7. R14

The thermal solicitation for the sample Ni30Cr-R14 is shown in Figure 5.20:



Figure 5.20: Thermal solicitation for the sample Ni30Cr-R14

In the case of Ni30Cr-R14, only the stress-time curves for peak 104 and peak 110 with psi negative (ψ^{-}) are good, we have chosen peak 110 psi- as shown in Figure 5.21:



Figure 5.21: The final stress-time curve for the sample Ni30Cr-R14

We can see from Figure 5.21 that the relaxation part is not so clear because of the small jumps at the end of the plateau. There also exist a blank area at the end of the plateau, which may come from the fact that criteria to remove the experimental data are too strong. The growth part is not clear because there are not enough experimental data at the beginning part.

8. R10

The thermal solicitation for the sample Ni30Cr-R10 is shown in Figure 5.22:



Figure 5.22: Thermal solicitation for the sample Ni30Cr-R10

In the case of Ni30Cr-R10, only the stress-time curve for peak 110 with psi negative (ψ^{-}) is good, so we do not need to choose among peak and psi. The final stress-time curve is shown in Figure 5.23:



Figure 5.23: The final stress-time curve for the sample Ni30Cr-R10

We can see from Figure 5.23 that the relaxation part is clearer compared with Ni30Cr-R14. We can also see the growth part, but because of the lack of experimental data at the beginning part of the plateau, it is not very clear.

9. R16

The thermal solicitation for the sample Ni30Cr-R16 is shown in Figure 5.24:



Figure 5.24: Thermal solicitation for the sample Ni30Cr-R16

In the case of Ni30Cr-R16, only the stress-time curves for peak 104 and peak 110 with psi negative (ψ^{-}) are good ; we have chosen peak 104 psi- as shown in Figure 5.25:



Figure 5.25: The final stress-time curve for the sample Ni30Cr-R16

We can see from Figure 5.25 that the relaxation part is not so clear, because there are some small jumps. Besides, the plateau is almost flat, which make it difficult to see the relaxation part. The growth part is not clear neither, because there are not enough experimental data at the beginning part.

5.2.2 Different materials with the same thermal solicitations

As we have explained before, reactive element addition may be added to the alloy, and they will influence the growth stresses [4], so we can also consider these material with reactive element addition as a specific kind of material. The reactive element additions are introduced into the alloys in order to improve the protective properties of thin oxide films. It has been shown that these elements generally segregate at the grain boundaries of the oxide and at the metal/oxide interface [12]. It has also been demonstrated that this segregation may cause an inversion of the growth mechanism of the layer, inducing a reduction of the oxidation kinetics and, above all, the disappearance of the phenomena of local decohesion at the metal/oxide interface [12]. In addition, it has been observed that the residual stress levels in the chromium oxide layers can be significantly lowered [13][12]. Some authors have suggested that, because of this segregation at grain boundaries, non-destructive relaxation modes, such as viscoplastic deformation of thin chromia films, would be more easily

activated [14]. However, to our knowledge, no measure has been carried out in order to demonstrate quantitatively the influence of the reactive elements on the mechanical properties of the chromia layers. Thus, we have added the reactive elements, in order to find out the influence on the mechanical properties.

The metal substrates are Ni-28Cr. The chemical composition of Ni-28Cr is given in Table 5.4:

	Ni	Cr	Si	Mn	С	Р	S
Ni-28Cr	71.2%	28.28%	<0.01%	<0.01%	230ppm	30ppm	40ppm
Table 5.4: The chemical composition of Ni-28Cr							

We should pay attention that we have changed the substrates from Ni-30Cr to Ni-28Cr, but the experimental data for stress vs time curve is still the same without reactive element [12].

The reactive element we have used is yttrium in the form of an oxide (Y_2O_3). Yttrium oxide (also known as yttria) was deposited on the surface of the substrates by the technique of physical vapor deposition(PVD) [12], with three quantities corresponding to deposition times of 10 s, 50 s and 100 s.

The thermal solicitation for the sample Ni28Cr with different exposition times is always the same, as shown in Figure 5.26:



Figure 5.26: Thermal solicitation for the sample Ni28Cr with different exposition times

In order to call the sample more easily, we have given code names for the sample Ni28Cr with different exposition times corresponding to different quantity of Y2O3 in the alloy, as shown in Table 5.5:

code name	Reactive elements
R34	Y_2O_3 $t = 10s$
R38	$Y_2O_3 t = 50s$
R32	$Y_2 O_3 t = 100s$

Table 5.5: Code name for the sample Ni28Cr with different exposition times

1. R34

Following the method described in Chapter 3, we can find the stress-time curve for peak 104, peak 110 and peak 116 for both psi positive(ψ^+) and psi negative(ψ^-). After comparing them, we have finally chosen peak 116 psi+ as shown in Figure 5.27:



Figure 5.27: The final stress-time curve for the sample Ni28Cr-R34

We can see from Figure 5.27 that the relaxation part for the plateaus at 900 °C and 800 °C is clear. The growth part for the first plateau at 1000 °C is not so clear because of the lack of experimental data at the beginning part.

2. R38

After using the method described in Chapter 3, we can find the stress-time curves for peak 104, peak 110 and peak 116 for both psi positive(ψ^+) and psi negative(ψ^-). After comparing them, we have finally chosen peak 116 psi+ as shown in Figure 5.28:



Figure 5.28: The final stress-time curve for the sample Ni28Cr-R38

We can see from Figure 5.28 that the relaxation part for the plateaus at 900 °C and 800 °C is clear, whereas the relaxation part for the plateau at 1000 °C is not clear because of the small jumps at the end of this plateau. The growth part is only slightly visible for the plateau at 1000 °C, because there are not too many experimental data at the beginning part (even though we can see a small part of the

growth part, it seems difficult to use directly these experimental data to fit for the growth parameter D_{ax}).

3. R32

After using the method described in Chapter 3, we can find the stress-time curve for peak 104, peak 110 and peak 116 for both psi positive(ψ^+) and psi negative(ψ^-). After comparing them, we have finally chosen peak 104 psi+ as shown in Figure 5.29:



Figure 5.29: The final stress-time curve for the sample Ni28Cr-R32

We can see from Figure 5.29 that the relaxation part is clear for the plateau at 900 °C, whereas it is not clear for the plateau at 800 °C, because the plateau seems roughly plat. Compared with R34 and R38, there are more experimental data at the beginning part. We can see the growth part at the beginning of the plateau at 1000 °C.

As a summary of this chapter, we have collected experimental data for the identification part, so we firstly try to find as much data as possible in the publications. In order to obtain the numerical data from these publications, we have used a digitalization process. There are many kinds of thermal solicitations and materials, so we have tried to separate them by thermal solicitations and materials types. On the same time, we have done our own experiments to complete those data, but also to have better understanding of the material, and to choose the thermal solicitations. In order to understand better the oxidation process, we have considered a same material with different thermal solicitations. Thus, we can learn about the influence of the thermal solicitations. Then, we have also considered reactive elements with different exposition times, under the same thermal solicitations. Thus, we can learn about the influence of the reactive elements with different quantity in the alloy.

Now, with these experimental data, the next step is to perform the identification procedure described in Chapter 4 and to analyze the results from a physical point of view, which will be done in the next chapter.

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Chapter 6 Identification results

Tables

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In this chapter, we will present all the results that we have obtained using the identification method described in Chapter 4. As discussed in Chapter 4, the step-by-step optimization method has a better physical meaning than the global optimization method. Thus, we will focus on this step-by-step method in the present chapter.

6.1 The system NiAl/Al₂O₃

To begin with, we have chosen the system $NiAl/Al_2O_3$. In chapter 5, we have presented many samples with different base materials and thermal loadings. In order to use the step-by-step optimization method, we will focus only on the samples with step loadings.

We can find the data for measured strain relaxation in α -Al₂ O_3 grown on Ni–50Al in [1,2]. After using Graph digitizer, we can obtain the experimental data for step loadings:



Figure 6.1: Measured stress vs time in α -Al₂ O_3 TGO at 1100, 1050, 1000, and 950 °C

Figure 6.1 shows measurements of creep relaxation in α -Al₂ O_3 growing on a single crystal samples of β -Ni-50Al. the later was also initially oxidized at 1100°C followed by temperature changes to 1050, 1000, and 950°C where creep relaxation was monitored.

6.1.1 The input parameters

For the Young's modulus in the metal NiAl, we can find the data in the publication [3]:

 $E_{\rm m} = -0.04 \times T + 199.8$ Where $E_{\rm m}$ is in GPa and T is in K.

For the Young's modulus in the oxide layer, we have used the data in the publication [4]:

$$E_{ox} = -0.06944 \times T + 420.3$$
(6.2)
Where E_{ox} is in GPa and T is in K.

(6.1)

And in the publication [4], we can also find that:

$$v_{ox} = 0.24$$
 , $v_{m} = 0.3$ (6.3)
Where v_{ox} is the Poisson's ratio in the oxide layer and v_{m} is the Poisson's ratio in the metal.

From the publication [5], we can find the kinetics of Al_2O_3 -scale growth by oxidation at 1100 °C:

$$A_n = 3.46 \times 10^{-9} m \cdot s^{-0.5} \tag{6.4}$$

Because we have assumed that $D_{ax} = 0$ for the other temperature plateau except the first one in the step-by-step optimization method, we do not need the value of A_p for the other temperature plateau.

From the publication [6], we can obtain the creep exponent in the metal:

$N_{\rm m} = 4.4$	(6.5)
With all these functions, we can obtain the parameters for each temperature plateau:	

Temperat ure(K)	$E_{ox}(\text{GPa})$	E_m (GPa)	U _{ox}	\mathcal{U}_m	$A_p(m \cdot s^{-0.5})$	N_m
1373	324.96	144.88	0.24	0.3	3.46×10 ⁻⁹	4.4
1323	328.43	146.88	0.24	0.3	3.46×10 ⁻⁹	4.4
1273	331.90	148.88	0.24	0.3	3.46×10 ⁻⁹	4.4
1223	335 37	150.88	0.24	03	3.46×10^{-9}	44

Table 6.1: The input material parameters for each temperature plateau

For the visco-plastic parameters J_{ox} and J_m , because there are not enough data in the publications for different temperature plateau, we will treat these two parameters as unknowns, and use the present optimization method to identify them.

For the creep exponent in the oxide N_{ox} , many publications [7–12] have suggested it to be unity. In order to verify the mechanisms for the creep in the oxide layer, we have chosen and tested N_{ox} to be 1 or 2 respectively. It is because when fitting the experimental data using our identification method, sometimes Nox=1 fits better, sometimes Nox=2 does better.

Concerning the growth parameter D_{ox} , as described in the step-by-step method, we will set it as 0 for the temperature plateau at 1050, 1000, and 950 °C. For the first temperature plateau at 1100 °C where the growth of the oxide film occurs, we will use the optimization method to identify it. We should pay attention that, because the experimental data is not so clear at the beginning part of the first temperature plateau, the identification for the growth parameter D_{ox} may not be as accurate as expected.

6.1.2 The optimization result using step by step method

As described in the Chapter 4, we should firstly treat the data for the second temperature plateau, which is the plateau at 1050 $^{\circ}$ C.

After using the identification method, we can obtain the simulation results as shown in Figure 6.2:



Figure 6.2: Fitting of the parameter ${J}_{ox}$ and ${J}_{m}$ for lpha-Al $_2O_3$ at 1050 °C using different N_{ox}

The identification results are shown in Table 6.2:

Parameters	J_{ox}	$J_m({\rm Pa}^{-4.4}{\rm s}^{-1})$
$N_{ox} = 1$	$6.24 \times 10^{-15} Pa^{-1}s^{-1}$	4.65×10^{-42}
$N_{ox} = 2$	$3.8 \times 10^{-23} \text{ Pa}^{-2} \text{s}^{-1}$	3.62×10^{-42}

Table 6.2: Identification results for α -Al₂O₃ at 1050 °C.

Then, we have just to repeat the procedure for the temperature 1000 °C, and 950 °C.

For the temperature plateau at 1000 °C, we can obtain the simulation results as shown in Figure 6.3:



Figure 6.3: Fitting of the parameter $\, J_{_{ox}}$ and $\, J_{_m}$ for $\, lpha$ -Al $_2O_3$ at 1000 °C using different $\, N_{_{ox}}$

The identification results are shown in Table 6.3:

Parameters	J_{ox}	$J_m({\rm Pa}^{-4.4}{\rm s}^{-1})$
$N_{ox} = 1$	$1.22 \times 10^{-15} Pa^{-1}s^{-1}$	3.24×10^{-42}
$N_{ox} = 2$	$5.19 \times 10^{-24} \text{ Pa}^{-2} \text{s}^{-1}$	3.61×10^{-42}
Table C.2. Ideati		0.00

Table 6.3: Identification results for α -Al₂ O_3 at 1000 °C.

For the temperature plateau at 950 °C, we can obtain the simulation results as shown in Figure 6.4:



Figure 6.4: Fitting of the parameter $\,J_{_{ox}}$ and $\,J_{_m}$ for $\,lpha$ -Al $_2O_3$ at 950 °C using different $\,N_{_{ox}}$

The identification results are shown in Table 6.4:

Parameters	$J_{ox}(\mathrm{Pa}^{-\mathrm{N}_{\mathrm{ox}}}\mathrm{s}^{-1})$	$J_m({\rm Pa}^{-4.4}{\rm s}^{-1})$
$N_{ox} = 1$	$8 \times 10^{-16} Pa^{-1}s^{-1}$	3.84×10^{-42}

$N_{ox} = 2$	$2.64 \times 10^{-24} \ Pa^{-2}s^{-1}$	3.55×10^{-42}
Table 6.4: Identification results for α -Al ₂ O ₃ at 950 °C.		

From Table 6.4, we can see that the value of J_m is very small compared with the value of J_{ox} . This may be linked to the fact that if we assume an average stress of 250MPa in the oxide layer with a thickness of 1 μm , and a thickness of 1.4 mm for the substrate, we can calculate the maximum stress in the substrate is 0.35 MPa, which is practically 1000 times lower than that generated in the oxide layer. Thus, the deformation of the substrate during the oxidation is very small.

At last, for the first temperature plateau at 1100 °C, we have two methods to fit it.

6.1.2.1 Method 1 to simulate the first temperature plateau

The first approach is to use numeric optimization method directly to identify D_{ox} , J_{ox} and J_m all together using Matlab. As described in Chap 4, we have added arbitrarily some points at the beginning part of the stress vs time curve to make the fit easier for the parameter D_{ox} . After using Matlab, we have obtained:





Parameters	J _{ox}	$J_m({\rm Pa}^{-4.4}{\rm s}^{-1})$	$D_{ox}(m^{-1})$
$N_{ox} = 1$	$1.93 \times 10^{-14} \text{ Pa}^{-1} \text{s}^{-1}$	5.51×10^{-53}	-2.24×10^{4}
$N_{ox} = 2$	$2.84 \times 10^{-23} Pa^{-2}s^{-1}$	1.99×10^{-48}	-1.85×10^{4}
Table (Fuldentification results for an ALC) at 1100 °C with method 1			

The identification results are shown in Table 6.5:

Table 6.5: Identification results for α -Al₂ O_3 at 1100 °C with method 1.

From Figure 6.5, we can see that the fit does not follow the experimental data well. Firstly, this may come from the fact that we do not have experimental data for the first 100 minutes (we have added points at the beginning part). Secondly, we have tried to identify three parameters at the same time,
which is difficult to find a single solution from an optimization point of view. Thirdly, we have only around fifty points for this temperature plateau, which may be insufficient for us to find a good result. All the reasons above may cause a big uncertainty for the value of J_{ox} , J_m and D_{ox} found for this temperature plateau.

If we draw $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ using the data that we have obtained for 950, 1000, 1050 and 1100°C (method 1) with Nox=1, we can obtain:



Figure 6.6: Linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for α -Al₂ O_3 using method 1 and Nox=1

We can see from Figure 6.6 that the data for 950, 1050 and 1100 °C seems to give a straight line, but there is a small gap for 1000°C using method 1. From the slope of Figure 6.6, we can now calculate the activation energy Q_J from the slope of the straight-line $Ln(J_{ox}(T))$ vs $\frac{1}{T}$:

Parameter	$Q_J(ev)$
Value	3 22

Table 6.6 : Activation energy value for the sample α -Al₂O₃ using method 1 to fit for the firsttemperature plateau with Nox=1

This value of activation energy is comparable to the value found by extrapolating the data of A.P. Paulikas et al in the publication [2] (where they found 3.16 eV), for fine grained α -Al₂O₃ bulk ceramics normalized to $1.5 \mu m$ grain size and 100 MPa of stress. This value of activation energy is consistent with a grain-boundary diffusion controlled creep mechanism [2].

If we draw $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ using the data that we have obtained for 950, 1000, 1050 and 1100°C (method 1) with Nox=2, we can now have:



Figure 6.7: Linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for α -Al₂ O_3 using method 1 and Nox=2

We can see from Figure 6.7 that the data for 950, 1000 and 1100 °C seems to give a straight line, but there is a big gap for 1050°C using method 1. Compared with Figure 6.6, we can see that when Nox=2, the linearity of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ is worse than with Nox=1 (according to the R-square value shown in both figures).

From the slope of Figure 6.7, we can now calculate the activation energy Q_J from the slope of the straight-line $Ln(J_{ox}(T))$ vs $\frac{1}{T}$:

Parameter	$Q_J(ev)$
Value	2.66

Table 6.7 : Activation energy value for the sample α -Al₂O₃ using method 1 to fit for the first temperature plateau with Nox=2

We should pay attention that, the activation energy value deduced from the linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ is comparable with the value found by A.P. Paulikas et al in the publication [2],. Whereas the value for J_m is not so good. In fact, the value for J_m almost remains the same for the different temperature plateau at 1050, 1000, and 950 °C and it is smaller for the temperature plateau at 1100 °C. Thus, it would induce a very small value for the activation energy of J_m . Firstly, this may be due to the fact that the value of J_m is very small (magnitude with the order of $10^{-42} Pa^{-N_m}s^{-1}$), thus it is difficult to identify with accuracy J_m and J_{ox} at the same time. Secondly, as the maximum stress in the substrate is practically 1000 times lower than that generated in the oxide layer, the deformation of the substrate during the oxidation is very small comparing with that in the oxide layer. Thirdly, because the fitting at 1100 °C is not so good, it leads to a bigger uncertainty for the value of J_m at this temperature plateau.

6.1.2.2 Method 2 to simulate the first temperature plateau

Method 2 for fitting the first temperature plateau is based on the fact that $J_{ox}(T)$ should have a physical significance.

With the values of J_{ox} at 950, 1000 and 1050°C (which are the same values used for method 1), we can still use a linear fit to obtain the theoretical $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ (see Figure 6.8 and Figure 6.9) and then we can extrapolate the value at higher temperatures, such as 1100°C:



Figure 6.8: Using linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for 950, 1000 and 1050°C, to extrapolate the value of J_{ox} at 1100 °C for α -Al₂ O_3 with Nox=1



Figure 6.9: Using linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for 950, 1000 and 1050°C, to extrapolate the value of J_{ox} at 1100 °C for α -Al₂ O_3 with Nox=2

For the value of J_m , because it does not change too much when temperature changes, we have also fixed the value ($J_m = 4 \times 10^{-42} \text{ Pa}^{-4.4} \text{s}^{-1}$ for Nox=1 and $J_m = 3.6 \times 10^{-42} \text{ Pa}^{-4.4} \text{s}^{-1}$ for Nox=2) After setting $J_{ox} = 1.23 \times 10^{-14} \text{ Pa}^{-1} \text{s}^{-1}$ for Nox=1 and $J_{ox} = 9.67 \times 10^{-23} \text{ Pa}^{-2} \text{s}^{-1}$ for Nox=2 to obtain D_{ox} , we can finally obtain:



Figure 6.10: Fitting of the parameter D_{ox} for α -Al₂ O_3 at 1100 °C using different N_{ox} (Method 2 for fitting the first temperature plateau)

By comparing Figure 6.5 and Figure 6.10, we can see that the fitting for the first temperature plateau is not better when using method 2.

The identification results are shown in Table 6.8:

Parameters	J_{ox}	$D_{ox}(m^{-1})$
$N_{ox} = 1$	$1.39 \times 10^{-14} \text{ Pa}^{-1} \text{s}^{-1}$	-1.62×10^{4}
$N_{ox} = 2$	$1.18 \times 10^{-22} \text{ Pa}^{-2} \text{s}^{-1}$	-1.50×10^{4}

Table 6.8: Identification results for α -Al₂ O_3 at 1100 °C with method 2.

Now if we draw the line of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for Nox=1 and 2, we can obtain:



Figure 6.11: Linear fit of $Ln(J_{ax}(T))$ vs $\frac{1}{T}$ for α -Al₂ O_3 using method 2

for Nox=1 (left) and Nox=2 (right)

We obtain the activation energy as shown in Table 6.9:

Parameter	$Q_J(ev)$
$N_{ox} = 1$	2.94
$N_{ox} = 2$	3.86

Table 6.9 : Activation energy value for the sample α -Al₂O₃ using method 2 to fit the values for the first temperature plateau, with Nox=1 and 2

Compared with method 1, for Nox=1, method 1 and method 2 give a comparable result (3.22eV and 2.94eV respectively), whereas for Nox=2, a bigger difference occurs (2.66eV and 3.86eV respectively). If we draw all the activation energies together, we can get:



Figure 6.12: Comparison of activation energies using different Nox and methods, with values from publication

We can see the relative deviation from the publication as shown in Figure 6.12. From this figure, we may consider that Nox=1 seems to be better in this case, as it has smaller relative deviation to the data found in the publication [2].

The characteristic time defined as $\tau_{ox} = \left(\frac{1 - v_{ox}}{E_{ox}}\right)^{N_{ox}} \times \frac{1}{J_{ox}}$ can also be calculated for the first

temperature plateau, as shown in Table 6.10:

	N _{ox} =1	N _{ox} =1	N _{ox} =2	N _{ox} =2
	method 1	method 2	method 1	method 2
Characteristic time	121.18s	168.26s	0.19s	0.05s

Table 6.10: Calculation of characteristic time for different Nox and methods

By comparing between method 1 and method 2, we can see that method 2 has a longer characteristic time, which can also be seen from Figure 6.5 and Figure 6.10. We should pay attention that the characteristic time we have obtained (with the order around 150s maximum) is very small comparing with that in the Figure 6.5 and Figure 6.10. This may be because the fit does not follow the experimental data well and a big uncertainty exists for the value of $J_{\alpha x}$.

By comparing Figure 6.11 with Figure 4.17 and Figure 6.7, the linearity of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for method 2 is better than for method 1 (we can see it by comparing the R-square of linear fit), but the activation energy value found by method 1 is closer to that in the publications. We can also see that the fitting for the first temperature plateau is similar using method 1 and 2. Thus, we could not draw a conclusion which method is better for this case.

For the value of D_{ox} , we have found a value around $-2 \times 10^4 m^{-1}$ using method 1 and $-1.55 \times 10^4 m^{-1}$ using method 2. Whereas in the publication [10], we could find the value of D_{ox} is $-1.41 \times 10^3 m^{-1}$ for

the system FeCrAlY/Al₂O₃ at 1100 °C. The difference may come from the fact that the base material is not the same, and it may be because the fitting for the first temperature plateau is not good.

As a summary for the system β -NiAl/Al₂O₃, we have used the model to identify the experimental data in the publication [1,2]. By fitting the line of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for different temperature plateau, we

have obtained the activation energy for different Nox and different methods. Compared with the activation energy found in the publication [2], we could say that Nox=1 has a smaller relative deviation. When comparing method 1 and method 2, we can see that method 1 has a smaller relative deviation,

but the linearity of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ of method 2 is better. It is difficult to say which method is better

in this case.

6.2 The system NiCr/Cr₂O₃

We consider now the method of identification using our own experimental data. Indeed, experiments have been done at European Synchrotron Radiation Facility (ESRF) for the system NiCr/Cr₂O₃ containing or not Y2O3 as a reactive element.

6.2.1 The input parameters

Firstly, we should have the values of some input parameters. These input parameters can be found directly or extrapolated from the publications. We assume that these values are correct without uncertainties.

For the Young's modulus in the metal NiCr, we can find the data in the publication [10]. After fitting for these data, we can obtain:

 $E_{\rm m} = -0.05 \times T + 223.65 \tag{6.6}$ Where $E_{\rm m}$ is in GPa and T is in K.

For the Young's modulus in the oxide layer, we have used the data in the publication [13] for fitting:

$$E_{ox} = -0.007 \times T + 308.61$$
Where E_{ox} is in GPa and T is in K.
$$(6.7)$$

And in the publication [10], we can also find that:

$$v_{ox} = 0.27$$
, $v_{m} = 0.3$ (6.8)
Where v_{ox} is the Poisson's ratio in the oxide layer and v_{m} is the Poisson's ratio in the metal.

From the publication [14], we can find the kinetics of Cr_2O_3 -scale growth by oxidation:

$$A_p = \exp(\frac{-12018.6}{T} - 8.774341) \tag{6.9}$$

Where A_p is in $m \cdot s^{-0.5}$ and T is in K.

From the data in the publication [10], we can extrapolate the creep parameter $J_{\rm m}$ in the metal:

$$J_{\rm m} = \exp(\frac{-91403}{T} - 9.6502)$$
(6.10)
Where $J_{\rm m}$ is in $Pa^{-N_{\rm m}} \cdot s^{-1}$ and T is in K.

And from the publication [15], we can obtain the thermal parameter α for both metal and oxide layers:

$$\alpha_m = 12.93 \times 10^{-6} + 5.7 \times 10^{-9} T \tag{6.11}$$

$$\alpha_{ox} = 5.67 \times 10^{-6} + 1.23 \times 10^{-9} T \tag{6.12}$$

Where α_m and α_{ox} are in $\frac{10^{-6}}{K}$, and T is in K.

Temperature (K)	$E_{ox}(\text{GPa})$	E_m (GPa)	U _{ox}	v_m	$A_p(m \cdot s^{-0.5})$	N_m	$J_m(\operatorname{Pa}^{-N_m} \mathrm{s}^{-1})$
1273	299.7[13]	160 (extrapolat ed)	0.27	0.3	1.4×10 ⁻⁸ [14]	3.3 (extrapolat ed)	4.23×10 ⁻³⁶ (extrapolated)
1173	300.4[13]	165[10]	0.27	0.3	4.31×10 ⁻⁹ [14]	4.1[10]	1.21×10 ⁻³⁸ [11]
1073	301.1[13]	170[10]	0.27	0.3	2.36×10 ⁻⁹ [14]	4.9[10]	8.3×10 ⁻⁴² [11]
973	301.8[13]	175 (extrapolat ed)	0.27	0.3	6.7×10^{-10} (extrapolated)	5.7 (extrapolat ed)	1.03×10^{-45} (extrapolated)

With all these functions for input parameters, we can calculate the parameters for fixed temperatures:

Table 6.11: The input material parameters for fixed temperatures

For the visco-plastic parameter J_{ox} in the oxide layer, because there are not enough data in the publications for the different considered temperatures, we will treat this parameter as unknowns, and use the optimization method to identify it.

For the creep exponent in the oxide N_{ox} , many publications [7–12] have suggested it to be unity. In order to verify the mechanism for the creep in the oxide layer, we have chosen and tested N_{ox} to be 1 or 2 respectively.

Concerning the growth parameter D_{ox} , as described in the step by step method, we will set it as 0 for the temperature plateaus except the first temperature plateau. For the first temperature plateau, we will use the optimization method to identify it.

6.2.2 Different thermal solicitations

As described in Chapter 5, firstly, we have fixed the material using Ni-30Cr.

For the thermal solicitations, we have considered 9 different kinds of thermal solicitations, listed in table 6.12:

Code name	Temperature for plateau(°C)						
R4	1000(3h)	900(3h)		800(3h)		700(3h)	
R13	1000(3h)		850(3h)				
R2		900(3h)		800(3h)		700(3h)	
R11		900(3h)	850(3h)	800(3h)	750(3h)		
R15			850(3h)	800(3h)	750(3h)	700(3h)	
R3				800(3h)		700(3h)	
R14	1000(7.4h)						
R10		900(7.4h)					
R16				800(7.4h)			

Table 6.12: Different kinds of thermal solicitations for the experiments done at ESRF

We should pay attention that 9 different kinds of thermal solicitations shown in table 6.12 corresponds to 4 microstructures constructed at 1000 °C(R4, R13 and R14), 900 °C(R2, R11 and R10), 850 °C(R15) and 800 °C(R3 and R16).

6.2.2.1 9 different kinds of thermal solicitations **10. R4**

The thermal solicitation for the sample Ni30Cr-R4 is shown in Figure 6.13:



Oxidation time

Figure 6.13: Thermal solicitation for the sample Ni30Cr-R4

After using the step-by-step identification method, firstly, we can obtain the simulation results for the temperature plateaus at 700, 800 and 900 °C, except for the first temperature plateau as shown in Figure 6.14:



Fitting for the parameter J_{ox} for $Ni_{30}Cr_R4$ at 700 °C using different Nox

Figure 6.14: Fitting of the parameter J_{ox} for $Ni_{30}Cr_R4$ at 700,800 and 900 °C with different Nox

We can see from Figure 6.14 that the fitting is not as good as expected. This may be because we have fixed $D_{ox} = 0$ for all these temperature plateaus. We can fit better if D_{ox} remains as a variable and fit for J_{ox} and D_{ox} at the same time. But as shown in the thesis of F. Rakotovao [16], the microstructure hass been built during the first temperature plateau, the thickness and microstructure do not change for the other temperature plateau, so it is reasonable to assume $D_{ox} = 0$ for these temperature plateau.

For the first temperature plateau at 1000 °C, we have firstly and arbitrarily added some points at the beginning part of the stress vs time curve to make the fit easier for the parameter D_{ox} , and then we have used method 1 and 2 with Nox=1 and 2 to fit the data ; the results are shown in Figure 6.15(a):



Figure 6.15(a): Fitting for the first temperature plateau at 1000 °C for $Ni_{30}Cr_R4$ using different methods and Nox.

In order to see easily what happened at the beginning part, we can zoom in as shown in Figure 6.15(b):



Figure 6.15(b): Zoom in for the beginning part.

We can see from 6.15(b) that method 1 fit better the beginning part of the experimental data, both for Nox=1 and 2. The result for Nox=1 or Nox=2 does not change too much for method 2, but we can see a bigger difference for method 1.

After using all these steps, we can summarize the simulation results:

$\begin{array}{ c c c c c }\hline \mbox{Temperat}\\ ure(K) & Method \\ ure(K) & 1 & 1 & 1.43 \times 10^{-14} & 4.66 \times 10^4 \\ \hline 1273 & 1 & 1.43 \times 10^{-14} & 4.66 \times 10^4 \\ \hline 2 & 3.79 \times 10^{-23} & 5.19 \times 10^4 \\ \hline 2 & 3.88 \times 10^{-16} & 2.007 \times 10^3 \\ \hline 2 & 1.88 \times 10^{-24} & 2.709 \times 10^3 \\ \hline 1173 & 1 & 1.5 \times 10^{-16} \\ \hline 1173 & 1 & 1.5 \times 10^{-16} \\ \hline 2 & 4.47 \times 10^{-25} & 1 \\ \hline 1073 & 1 & 4.98 \times 10^{-17} & 1 \\ \hline 2 & 1.11 \times 10^{-25} & 1 \\ \hline 973 & 1 & 1.27 \times 10^{-17} & 1 \\ \hline 2 & 1.76 \times 10^{-26} & 1 \\ \hline \end{array}$					
$\begin{array}{ c c c c c c c } & 1 & 1 & 1.43 \times 10^{-14} & 4.66 \times 10^4 \\ \hline 1273 & 2 & 3.79 \times 10^{-23} & 5.19 \times 10^4 \\ \hline 2 & 3.88 \times 10^{-24} & 2.007 \times 10^3 \\ \hline 2 & 1.88 \times 10^{-24} & 2.709 \times 10^3 \\ \hline 1173 & 1 & 1.5 \times 10^{-16} \\ \hline 2 & 4.47 \times 10^{-25} \\ \hline 1073 & 2 & 1 & 4.98 \times 10^{-17} \\ \hline 2 & 1.11 \times 10^{-25} \\ \hline 973 & 1 & 1.27 \times 10^{-17} \\ \hline 2 & 1.76 \times 10^{-26} \\ \hline \end{array}$	Temperat ure(K)	Method	Nox	$J_{\mathrm{ax}}(\mathrm{Pa}^{-N_{\mathrm{ax}}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1	1	1.43×10 ⁻¹⁴	4.66×10 ⁴
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	1273		2	3.79×10 ⁻²³	5.19×10 ⁴
$\begin{tabular}{ c c c c c c } \hline & & & & & & & & & & & & & & & & & & $		2	1	3.88×10 ⁻¹⁶	2.007×103
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			2	1.88×10 ⁻²⁴	2.709×10 ³
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	1173		1	1.5×10 ⁻¹⁶	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			2	4.47×10 ⁻²⁵	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1073		1	4.98×10 ⁻¹⁷	
973 1 1.27×10 ⁻¹⁷ 2 1.76×10 ⁻²⁶			2	1.11×10 ⁻²⁵	
2 1.76×10 ⁻²⁶	973		1	1.27×10 ⁻¹⁷	
			2	1.76×10 ⁻²⁶	

Table 6.13: Simulation results for $Ni_{30}Cr_R4$ using different methods and Nox.

We can draw the linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R4$ for Nox=1(left) and Nox=2(right) as shown in Figure 6.16:



Figure 6.16: Linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R4$ for Nox=1(left) and Nox=2(right)

We should pay attention that the only difference between method 1 and method 2 is the fitting for the first temperature plateau. Thus, the J_{ox} value is the same for method 1 and 2 except for this first temperature plateau.

We can see from Figure 6.16 clearly that method 2 has a better linearity for the fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$. The activation energy of method 1 is almost double compared to method 2.

For the value of D_{ox} , we can see that the value obtained from method 1 (with the order 10^4) is almost 10 times that of method 2 (with the order 10^3). The values obtained from Nox=1 and Nox=2 are quite similar.

11. R13

The thermal solicitation for the sample Ni30Cr-R13 is shown in Figure 6.17:



Oxidation time

This sample has only two temperature plateau, so it is not possible to use method 2 to fit for the first temperature plateau.

Fitting for the temperature plateau at 850 °C is shown in Figure 6.18:



Figure 6.18: Fitting the parameter $\,J_{_{ox}}$ for $\,Ni_{_{30}}Cr_R13$ at 850 °C with different Nox

When fitting for the first temperature plateau at 1000 °C, we can only use method 1 and different Nox to fit it, as shown in Figure 6.19:



Figure 6.19: Fitting for the first temperature plateau at 1000 °C for $Ni_{30}Cr_R13$ using different Nox

We can see from Figure 6.19 that the fit for Nox=1 and Nox=2 is similar at the beginning part of the experimental data, but Nox=2 fit better at the end part of the experimental data.

Temperature (K)	Nox	$J_{\alpha x}(\operatorname{Pa}^{-N_{\alpha x}}\operatorname{s}^{-1})$	$D_{ox}(m^{-1})$
1273	1	4.71×10^{-14}	5.15×10^4
	2	1.25×10 ⁻²²	6.31×10 ⁴
1123	1	6.94×10 ⁻¹⁷	
	2	1.69×10 ⁻²⁵	

After using all these steps, we can obtain the simulation results:

Table 6.14: Simulation results for $Ni_{30}Cr_R13$ using different Nox

We can draw the linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R13$ for Nox=1 and Nox=2 as shown in Figure 6.20:



Figure 6.20: Linear fit of $Ln(J_{ax}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R13$ for Nox=1 and Nox=2

We can see from Figure 6.20 that the linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for Nox=1 and Nox=2 is parallel, that is to say, the activation energy for Nox=1 and Nox=2 is almost the same. Moreover, we have found a relative high activation energy value compared to $Ni_{30}Cr_R4$. We should be careful about the value

of activation energy we have found for $Ni_{30}Cr_R13$, because there are only two temperature plateau for this sample and we can only use method 1 to identify the parameters.

For the value of D_{ax} , we have found a similar value for Nox=1 and Nox=2 with the order 10^4 , and it is also comparable with the value found for $Ni_{30}Cr_R4$ using method 1.

12. R2

The thermal solicitation for the sample Ni30Cr-R2 is shown in Figure 6.21:



Figure 6.21: Thermal solicitation for the sample Ni30Cr-R2

There are three temperature plateau, so we can use method 2 to fit for the first temperature plateau. After using the step-by-step identification method, we can obtain the simulation results for the other temperature plateau except for the first temperature plateau (800 and 700 °C), as shown in Figure 6.22:



Figure 6.22: Fitting of the parameter J_{ox} for $Ni_{30}Cr_R^2$ at 800 and 700 °C with different Nox

For the first temperature plateau at 900 °C, we have used method 1 and 2 with Nox=1 and 2 to fit the data; the results are shown in Figure 6.23:



Figure 6.23: Fitting for the first temperature plateau at 900 °C for $Ni_{30}Cr_R2$ using different methods and Nox.

We can see from Figure 6.23 that method 1 and Nox=1 fit the best the experimental data. Method 2 and Nox=1 seems to ignore the experimental data at the beginning part. The results of method 1 and 2 for Nox=2 are similar, both of which managed to fit the beginning part of the experimental data.

After using all these steps, we can obtain the simulation results:

Temperature (K)	Method	Nox	$J_{\alpha}(\mathrm{Pa}^{-N_{\mathrm{cr}}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
	1	1	2.73×10 ⁻¹⁵	6.9×10 ⁴
1173		2	3.06×10 ⁻²³	7.16×10 ⁷
	2	1	1.92×10 ⁻¹⁶	8.26×10 ³
		2	3.85×10 ⁻²⁵	7.95×10 ⁶
1073		1	4.72×10 ⁻¹⁷	
		2	1.03×10 ⁻²⁵	
973		1	1.9×10 ⁻¹⁷	
		2	2.77×10 ⁻²⁶	

Table 6.15: Simulation results for $Ni_{30}Cr_R2$ using different methods and Nox.

We can draw the linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R^2$ for Nox=1(left) and Nox=2(right) as shown in Figure 6.24:



Figure 6.24: Linear fit of $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R^2$ for Nox=1(left) and Nox=2(right)

We can see from Figure 6.24 that the value of activation energy for method 1 is always 2 to 3 times bigger than that of method 2. Even though the R-square of Nox=2 is always better than that of Nox=1, we can see from Figure 6.23 that Nox=1 fits better for the beginning part of the stress-time curve. Thus, it is difficult to say which value of Nox is better.

For the value of D_{ox} , we can see a big difference between Nox=1 and Nox=2 both, for method 1 and method 2, whereas for $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R13$, the value is always similar for Nox=1 and Nox=2. The value for Nox=1 is similar and comparable to that of $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R13$, whereas the value for Nox=2 is 10^3 bigger than the value of $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R13$. This is because Nox=1 fits better for the beginning part of the stress-time curve. Finally, when fixing Nox=1, we can obtain a robust value for Dox.

13. R11

The thermal solicitation for the sample Ni30Cr-R11 is shown in Figure 6.25:





After using the step-by-step identification method, we can obtain the simulation results for the other temperature plateau except for the first temperature plateau (850, 800 and 750 °C), as shown in Figure 6.26:



Fitting for the parameter J_{ox} for $Ni_{30}Cr_R11$ at 850 °C using different Nox

Figure 6.26: Fitting of the parameter J_{ox} for $Ni_{30}Cr_R11_{at\,750,800}$ and 850 °C with different Nox

For the first temperature plateau at 900 °C, we have used method 1 and 2 with Nox=1 and 2 to fit the data; the results are shown in Figure 6.27:



Figure 6.27: Fitting for the first temperature plateau at 900 °C for $Ni_{30}Cr_R11$ using different methods and Nox.

We can see from Figure 6.27 that the fitting for method 1 and 2 is similar both for Nox=1 and Nox=2. The results using Nox=2 seem to fit better at the beginning part of the experimental data.

After using all these steps, we can obtain the simulation results:

Temperature (K)	Method	Nox	$J_{ax}(\mathrm{Pa}^{-N_{ax}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
	1	1	2.39×10 ⁻¹⁵	2.98×10 ⁴
1173		2	8.06×10 ⁻²⁴	5×10 ⁴
	2	1	2.06×10 ⁻¹⁵	2.65×10 ⁴
		2	1.28×10 ⁻²³	7.96×10 ⁴
1123		1	1.48×10 ⁻¹⁶	
		2	7.09×10 ⁻²⁵	
1073		1	6.2×10 ⁻¹⁷	
		2	2.54×10 ⁻²⁵	
1023		1	1.2×10 ⁻¹⁸	
		2	3.28×10 ⁻²⁷	

Table 6.16: Simulation results for $Ni_{30}Cr_R11$ using different methods and Nox.

We can draw the linear fit of $L_{T}(J_{ox}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R11$ for Nox=1(left) and Nox=2(right) as shown in Figure 6.28:



Figure 6.28: Linear fit of $L_{T}(J_{cx}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R11$ for Nox=1(left) and Nox=2(right)

We can see from Figure 6.28 that the fit for method 1 and method 2 is similar, and the R-square is always good for all the four different situations. We have obtained a value of activation energy around 5ev for all the situations.

For the value of D_{ox} , the result for method 1 and method 2 is similar. The value for Nox=2 is 2 to 3 times bigger than that of Nox=1, and all the values of D_{ox} have an order of 10^4 .

14. R15

The thermal solicitation for the sample Ni30Cr-R15 is shown in Figure 6.29:





There are 4 temperature plateaus in total, but after fitting, we have found that the fitting for the temperature plateau at 700 °C is too bad (the experimental data is almost flat for this temperature plateau). Thus, we have decided not to use the data for this temperature plateau at 700 °C. After using the step-by-step identification method, we can obtain the simulation results for the other temperature plateau except for the first temperature plateau (800 and 750 °C), as shown in Figure 6.30:



Figure 6.30: Fitting of the parameter J_{ox} for $Ni_{30}Cr_R15$ at 750 and 800 °C with different Nox

For the first temperature plateau at 850 °C, we have used method 1 and 2 with Nox=1 and 2 to fit the data; the results are shown in Figure 6.31:



Figure 6.31: Fitting for the first temperature plateau at 850 °C for $Ni_{30}Cr_R15$ using different methods and Nox.

We can see from Figure 6.31 that method 1 and Nox=1 fit the best the experimental data. In general, method 1 fit better at the beginning part of the experimental data, whereas method 2 seems to ignore the beginning part of the experimental data. The tendency of the fitting for Nox=1 and Nox=2 is roughly similar, whereas a small difference exists.

After using all these steps, we can obtain the simulation results:

Temperature (K)	Method	Nox	$J_{\alpha}(\mathrm{Pa}^{-N_{\alpha}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
	1	1	1.8×10 ⁻¹⁵	4.39×10 ⁴
1123		2	3.93×10 ⁻²⁴	5.07×104
	2	1	1.72×10 ⁻¹⁶	6.88×10 ³
		2	8.24×10 ⁻²⁵	1.15×10 ⁴
1073		1	3.75×10 ⁻¹⁷	
		2	1.43×10 ⁻²⁵	
1023		1	1.72×10 ⁻¹⁶	
		2	8.24×10 ⁻²⁵	

Table 6.17: Simulation results for $Ni_{30}Cr_R15$ using different methods and Nox. We can draw the linear fit of $_{Lre(J_{ox}(T))}$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R15$ for Nox=1(left) and Nox=2(right)

as shown in Figure 6.32:



Figure 6.32: Linear fit of $L_{T}(J_{ox}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R15$ for Nox=1(left) and Nox=2(right)

We can see from Figure 6.32 that the R-square for Nox=2 is better than that of Nox=1. Method 2 always has a better linearity for the fit both for Nox=1 and Nox=2. The activation energy value for method 1 is 1.5 to 2 times bigger than that for method 2.

For the value of D_{ox} , the values for Nox=1 and Nox=2 are similar. The value of D_{ox} for method 1 is 5 to 10 times bigger than that of method 2. For all the fours situations, they all have an order around 10^4 .

15. R3

The thermal solicitation for the sample Ni30Cr-R3 is shown in Figure 6.33:





This sample has only two temperature plateau, so it is not possible to use method 2 to fit for the first temperature plateau.

Fitting for the temperature plateau at 700 °C is shown in Figure 6.34:



Figure 6.34: Fitting of the parameter J_{ox} for $Ni_{30}Cr_R3$ at 700 °C with different Nox

When fitting the first temperature plateau at 800 °C, we can only use method 1 and different Nox to fit it, as shown in Figure 6.35:



Figure 6.35: Fitting for the first temperature plateau at 800 °C for $Ni_{30}Cr_R3$ using different Nox We can see from Figure 6.35 that Nox=2 fits better the experimental data compared with Nox=1. After using all these steps, we can summarize the simulation results:

Temperature (K)	Nox	$J_{\alpha}(\operatorname{Pa}^{-N_{\alpha}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
1073	1	1.89×10 ⁻¹⁵	5.14×10 ⁴
	2	6.34×10 ⁻²⁴	7.4×10^4
973	1	1.05×10^{-17}	
	2	1.69×10 ⁻²⁶	

Table 6.18: Simulation results for $Ni_{30}Cr_R3$ using different Nox

We can draw the linear fit of $L_{n(J_{ox}(T))}$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R3$ for Nox=1 and Nox=2 as shown in Figure 6.36:



Figure 6.36: Linear fit of $L_{T}(J_{cx}(T))$ vs $\frac{1}{T}$ for $Ni_{30}Cr_R3$ for Nox=1 and Nox=2

We can see from Figure 6.36 that the fit seems parallel for Nox=1 and Nox=2, with an average activation energy around 5 ev. However, we should pay attention that there are only 2 points for calculating the activation energy, there may exists a big uncertainty for the value of activation energy obtained.

For the value of D_{ox} , it is similar for both Nox=1 and Nox=2, with an order of $10^4 m^{-1}$.

16. R14

The thermal solicitation for the sample Ni30Cr-R14 is shown in Figure 6.37:



Figure 6.37: Thermal solicitation for the sample Ni30Cr-R14

For this sample, we have only one temperature plateau, so we can only use method 1 to fit it, as shown in Figure 6.38:



Figure 6.38: Fitting for the temperature plateau at 1000 °C for $Ni_{30}Cr_R14$ using different Nox

We can see from Figure 6.38 that both Nox=1 and Nox=2 managed to fit for the beginning part of the experimental data. The fit for Nox=1 is able to simulate accurately more experimental data at the beginning part of the experimental data, whereas the fit for Nox=2 seems to fit better at the end part of the experimental data.

After using all these steps, we can obtain the simulation results:

Temperature (K)	Nox	$J_{\alpha}(\operatorname{Pa}^{-N_{\alpha}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
1273	1	1.23×10 ⁻¹⁴	3.49×10 ⁴
	2	3.37×10 ⁻²³	3.16×10 ⁴

Table 6.19: Simulation results for $Ni_{30}Cr_R14$ using different Nox

After comparing with $Ni_{30}Cr_R4$ (see Table 6.13) and $Ni_{30}Cr_R13$ (see Table 6.14) which starts also at 1000 °C, we can see that the value for J_{ox} and D_{ox} is close for $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R14$. However, the value of J_{ox} for $Ni_{30}Cr_R13$ is about 3 times bigger than that of $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R14$.

17. R10

The thermal solicitation for the sample Ni30Cr-R10 is shown in Figure 6.39:



Figure 6.39: Thermal solicitation for the sample Ni30Cr-R10

For this sample, we have only one temperature plateau, so we can only use method 1 to fit it, as shown in Figure 6.40:



Figure 6.40: Fitting for the temperature plateau at 900 °C for $Ni_{30}Cr_R10$ using different Nox

We can see from Figure 6.40 that Nox=1 seems to fit a little better at the beginning part of the experimental data, whereas Nox=2 seems to fit better at the end part of the experimental data.

After using all these steps, we can obtain the simulation results:

Temperature (K)	Nox	$J_{\alpha}(\operatorname{Pa}^{-N_{\alpha}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
1173	1	4.5×10 ⁻¹⁵	5.66×10 ⁴
	2	3.6×10 ⁻²³	1.29×10 ⁵

Table 6.20: Simulation results for $Ni_{30}Cr_R10$ using different Nox

After comparing with $Ni_{30}Cr_R^2$ (see Table 6.15) and $Ni_{30}Cr_R^{11}$ (see Table 6.16) which starts at 900 °C, we can see it is comparable when Nox=1 for J_{ox} and D_{ox} . It is also comparable for J_{ox} with $Ni_{30}Cr_R^2$ when Nox=2, but the value of D_{ox} changes a lot (with an order of 10^7 for $Ni_{30}Cr_R^2$).

18. R16

The thermal solicitation for the sample Ni30Cr-R16 is shown in Figure 6.41:



Figure 6.41: Thermal solicitation for the sample Ni30Cr-R16

For this sample, we have only one temperature plateau, so we can only use method 1 to fit it, as shown in Figure 6.42:



Figure 6.42: Fitting for the temperature plateau at 800 °C for $Ni_{30}Cr_R16$ using different Nox

We can see from Figure 6.42 that Nox=2 seems to fit better at the beginning part of the experimental data, whereas the fit for Nox=1 seems to ignore the beginning part of the experimental data. The simulation result seems not fit very well the experimental data. This may be because the experimental data is not good (we can see a small jump in the middle of the experimental data). If we divide the experimental data into two parts, we can see that Nox=2 managed to fit the beginning part and Nox=1

tries to fit for the end part. It is difficult to fit these two parts at the same time, so we have obtained a big difference between the simulation result and experimental data.

Temperature (K)	Nox	$J_{\alpha}(\operatorname{Pa}^{-N_{\alpha}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
1073	1	1.37×10^{-16}	6.44×10 ³
	2	2.56×10 ⁻²⁴	2.7×10^{4}

After using all these steps, we can obtain the simulation results:

Table 6.21: Simulation results for $Ni_{30}Cr_R16$ using different Nox

After comparing with $Ni_{30}Cr_R3$ (see Table 6.18) which starts at 800 °C, we can see it is comparable for Nox=2, whereas the identification values for both J_{ox} and D_{ox} for Nox=1 are 10 times smaller than that of $Ni_{30}Cr_R3$.

6.2.2.2 Calculating for activation energies

As a summary of all the samples above, we have drawn all the Ln(Jox) vs 1/T for Nox=1(left) and Nox=2(right), as shown in Figure 6.43:



Figure 6.43: Ln(Jox) vs 1/T for all the above samples with Nox=1(left) and Nox=2(right)

We can see from Figure 6.43 that for a given temperature, there are many different values of Ln(Jox); this is because the microstructure is different growing during the first temperature plateau with different initial temperatures [16]. That is to say, when the temperatures for the first temperature plateaus are different, the microstructures of the oxide layers are different. Thus, in order to obtain the activation energy for one special microstructure, we should fix the temperatures for the first temperatures temperature plateaus.

Microstructure constructed at 1000 °C

If we draw only for $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R13$ which start at 1000 °C, they should have the same microstructure:



Figure 6.44: Ln(Jox) vs 1/T for $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R13$ with Nox=1(left) and Nox=2(right)

We have calculated the activation energy value separately for $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R13$ and found a big difference (1.22 ev and 5.35 ev respectively). We can see from Figure 6.44 clearly that this may be because we have a bad identification of J_{ox} at 1000 °C, which also explains the reason why the value of J_{ox} for $Ni_{30}Cr_R13$ is about 3 times bigger than that of $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R14$.

If we remove the value of J_{ox} at 1000 °C for $Ni_{30}Cr_R13$ and for $Ni_{30}Cr_R4$, for method 1, we have left 5 points for both Nox=1 and Nox=2. With these 5 points, we can calculate the activation energy for this kind of microstructure starting at 1000 °C:



Figure 6.45: Linear fit for $Ni_{30}Cr_R4$ and $Ni_{30}Cr_R13$ with Nox=1(left) and Nox=2(right) after removing some points

By comparing with the value obtained from publication of Tsai et Huntz [17] and from the thesis of F. Rakotovao [16], we can see that the values of activation energy for both Nox=1 (1.2eV) and Nox=2 (1.6eV) are well comparable. For example, in the thesis of F. Rakotovao[16], she found 1.347eV. In this thesis, by comparing with the values in the publication of Tsai et Huntz [17], F. Rakotovao has identified

the mechanism which may govern diffusion-creep as intergranular diffusion of the oxygen anions (interstitials or vacancies).

Microstructures constructed at other temperatures (900 °C, 850 °C and 800 °C)

After trying to repeat the same procedure for the microstructures constructed at other temperatures, we could not get a linear fit for the Ln(Jox) vs 1/T. Thus, we could not obtain a valid activation energy value for the microstructures constructed at other temperatures.

Because we can get a valid activation energy for the microstructure constructed at 1000 °C, we will focus on this first temperature plateau and use it in the Part 6.2.3 where a reactive element is added to the alloy.

Comparison between Nox=1 and Nox=2

By comparing the fitting procedure for Nox=1 and Nox=2, we can see that sometimes Nox=1 fits better the experimental data, but sometimes Nox=2 does better. If we compare the linear fit for Ln(Jox) vs 1/T and also the activation energy, we could see that the activation energy is always comparable. To obtain a simulation of the results, it shows that we can choose either Nox=1 or Nox=2 depending on the fitting of experimental data, and finally we can obtain an activation energy which is robust regardless to the choice of Nox.

6.2.2.3 Discussion about Dox and $\Delta \alpha$

We have suggested in Chapter 2 that the value of Dox should be a function of 1/T. Thus, we can draw Dox vs 1/T for Nox=1 and 2 as shown in Figure 6.46:



Figure 6.46: Dox vs 1/T for Nox=1(left) and 2(right)

In Figure 6.46(right), the Dox value for R2 when Nox=2 is very high (with order of 10^7) and very far away from the Dox value found for other samples with the same first temperature plateau (R10 and R11), so we have removed it.

We cannot see any linearity from Figure 6.46. This may be because the lack of Dox values, as we only have Dox values for the first temperature plateau. For a given temperature, with different methods and different thermal loadings, we have different Dox values.

We can see from Figure 6.46 that for the samples with the first temperature plateau at 1000 °C, that is to say R4, R13 and R14, the Dox value is close for method 1 with Nox=1. Whereas we have only one value for method 2, so we cannot compare with other points. For the samples with the first temperature plateau at 900 °C, that is to say R2, R10 and R11, we can see that the Dox values for

method 1 are bigger than that for method 2, which is the same tendency for R15 with first temperature plateau at 850 °C. For the samples with the first temperature plateau at 800 °C, that is to say R3 and R16, we can see a big difference for R3 and R16 using the same method (method 1).

We can conclude that for a given first temperature plateau (the same microstructure), a given method and a given Nox, the Dox value almost has the same order. Secondly, when the first temperature plateau decreases, the value of Dox stays at the same order of 10^4 ; it is difficult to see a tendency for the value of Dox.

Discussion about $\Delta \alpha$

As shown in Chapter 4, an advantage of our model is that it can be used to identify the thermal expansion coefficient $\Delta \alpha$. We have used the manual optimization method described in Chapter 4 to fit for the samples with temperature changes, that is to say, the samples: R4, R11, R15, R2, R3 and R13.

For all the samples above, we have found similar expansion parameters for metal and oxide as shown in Table 4.15:

Parameters	$\alpha_{0ox}(10^{-6} \mathrm{K}^{-1})$	$DaT0_{ox}(10^{-6} \mathrm{K}^{-2})$	$\alpha_{0m}(10^{-6}\mathrm{K}^{-1})$	$DaT0_m(10^{-6} \mathrm{K}^{-2})$
Values	9.67	1.23×10^{-3}	12.93	5.7×10^{-3}

Table 6.22: Fitting results using manual optimization method for expansion parameters

We have changed the value α_{0ox} from $5.67 \times 10^{-6} \text{ K}^{-1}$ in the publication [15] to $9.67 \times 10^{-6} \text{ K}^{-1}$, with the other parameters stay the same value in the publication and found a best fit. This means that α_{0ox} is the key parameter that influences mainly the jump of stress when temperature changes. Because our model has taken into account all the material behavior when temperature changes and obtained a new value for α_{0ox} , it is interesting to use this new value of α_{0ox} .

6.2.3 Different materials with the same thermal solicitations

In order to find out the influence of reactive elements on the mechanical properties of the chromia layers, we have done a series of experiments using the reactive element Y_2O_3 . The later has been introduced by using different exposition times in a PVD chamber in order to vary the quantity of Y_2O_3 in the alloy. The metallic substrates are always Ni-28Cr, for which the chemical composition can be seen in Chapter 5.

The thermal solicitation for the sample Ni28Cr with different exposition times is always the same, shown in Figure 6.47:



Oxidation time

Figure 6.47: Thermal solicitation for the sample Ni28Cr with different exposition times

In order to call the sample more easily, we have given code names for the sample Ni28Cr with different quantity of Y2O3, as shown in Chapter 5. When the exposition time increases the quantity of reactive element in the NiCr alloy increases also.

After using the same procedure described above (step by step method), we can finally draw the Ln(Jox) vs 1/T for Nox=1 and 2 as shown in Figure 6.48 and Figure 6.49:



Figure 6.48: Ln(Jox) vs 1/T for R32, R34 and R38 with Nox=1



Figure 6.49: Ln(Jox) vs 1/T for R32, R34 and R38 with Nox=2

The identification results for R32 are shown in Table 6.23:

Temperature (K)	Method	Nox	$J_{\alpha}(\mathrm{Pa}^{-N_{\alpha}}\mathrm{s}^{-1})$	$D_{ox}(m^{-1})$
	1	1	2.7×10 ⁻¹⁶	2.72×10 ³
1273		2	6.02×10 ⁻²⁵	2.99×10 ³
	2	1	2.63×10 ⁻¹⁶	2.67×10 ³
		2	5.43×10 ⁻²⁵	2.75×10 ³
1173		1	2.8×10 ⁻¹⁷	
		2	4.53×10 ⁻²⁶	
1073		1	1.97×10 ⁻¹⁸	
		2	2.48×10 ⁻²⁷	

Table 6.23: Simulation results for $Ni_{28}Cr_R32$ using different methods and Nox. The identification results for R34 are shown in Table 6.24:

Temperature (K)	Method	Nox	$J_{\alpha}(\mathrm{Pa}^{-N_{\alpha}}\mathrm{s}^{-1})$	$D_{ax}(m^{-1})$
	1	1	6.9×10 ⁻¹⁶	4.24×10 ³
1273		2	5.29×10 ⁻²⁴	1.21×10 ⁴
	2	1	1.75×10 ⁻¹⁶	1.37×10 ³
		2	6.58×10 ⁻²⁵	1.65×10 ³
1173		1	5.59×10 ⁻¹⁷	
		2	1.38×10 ⁻²⁵	
1073		1	1.78×10 ⁻¹⁷	
		2	3.11×10 ⁻²⁶	

Table 6.24: Simulation results for $Ni_{28}Cr_R34$ using different methods and Nox.

The identification results for R38 are shown in Table 6.25:

Temperature (K)	Method	Nox	$J_{\alpha}(\operatorname{Pa}^{-N_{\alpha}}\operatorname{s}^{-1})$	$D_{\alpha}(m^{-1})$
	1	1	3.32×10 ⁻¹⁶	3.17×10^3
		2	9.57×10^{-25}	4.37×10^{3}
1273	2	1	2.34×10^{-16}	2.4×10^3
		2	5.44×10 ⁻²⁵	2.68×10^{3}
1173		1	4.76×10^{-17}	
		2	8.66×10^{-26}	
1073		1	7.65×10^{-18}	
		2	1.1×10^{-26}	

Table 6.25: Simulation results for $Ni_{28}Cr_R38$ using different methods and Nox.

We can see clearly that the slope of the line Ln(Jox) vs 1/T for R32, R34 and R38 changes both for Nox=1 and Nox=2. Thus, we can consider that the presence of reactive element seems to have an influence on the diffusion-creep mechanism in the oxide layer.
6.2.3.1 Calculating for activation energies

The value of activation energy varies with different optimization methods and different Nox as shown in Figure 6.50:



Figure 6.50: Results for the value of activation energy using different methods and different Nox

In order to obtain the evolution of the activation energy vs the Y_2O_3 content and compare with the results in the thesis of F. Rakotovao [16], we have calculate the mean value of the activation energies for the different methods and different Nox.

If we draw the average activation energy calculated from the line Ln(Jox) vs 1/T vs exposition times, we can obtain



Figure 6.51: Illustration of activation energy vs Y2O3 content

We have used $Ni_{30}Cr_R4$ as a reference sample without reactive element. From Figure 6.51, we can see clearly that the quantity of reactive element Y₂O₃ changes the activation energy associated to the diffusion-creep mechanism in the chromia layers.

If we draw a linear fit for the activation energy vs exposition time of the reactive element Y_2O_3 , we can obtain a linear fit the R-square equals 0.9, which may indicate that the exposition time changes the activation energy quite linearly. There are many publications [18–20] which have claimed that the reactive element can change the growth mechanism in the oxide layer, but to our knowledge, such a linear change has never been observed. However, there may exist uncertainty when calculating the activation energy using the different optimization methods and the different Nox values, and we have calculated a mean value and finally obtain a quasi-linear fit for the activation energy vs Y_2O_3 content.

When comparing with the results in the thesis of F. Rakotovao [16], the author has found that the activation energy does not change for the lower Y2O3 contents in the alloy (when the exposition time is 10s and 50s), and it is about the same activation energy (about 1.35 eV) than without reactive element. It is only when the Y2O3 content is maximum (when the exposition time changes to 100s), that the activation energy changes suddenly to 2.073 eV, which indicates the change of the mechanism dominating the transport of species during the creep procedure. Whereas in the present case, a continuous variation of the activation energy is obtained. Thus, qualitatively the activation energy increases with the Y_2O_3 content. While, quantitatively, the same activation energy is obtained for the raw material, but the final activation energy value is a little bit different. However, both analysis seem to demonstrate the change of mechanism that governs the diffusion-creep mechanism.

6.2.3.2 Discussion about Dox

We can also draw the value of Dox vs Y2O3 content, as shown in Figure 6.52:



Figure 6.52: Illustration of Dox value vs Y₂O₃ content for Nox=1(left) and Nox=2(right)

In Figure 6.52, because Dox value for R4 using method 1 is too high (with the order $5x10^4$), we could not see it.

From Figure 6.52, we can see that when using method 1, the Dox value decreases when the exposition time increases both for Nox=1 and Nox=2. Whereas for method 2, the Dox value seems to keep the same value. As it is known that the Dox value is related to the growth of oxide layer, for which the mechanism is modified with the supply of reactive elements, it is more likely to assume that the Dox value may change with Y_2O_3 content. Thus, the result of method 1 may be better than that of method 2 for Dox. We can also see from Figure 6.52 that the value of Dox for the material without reactive element is about 10 times bigger than that with reactive element. This may be because the presence

of reactive element slows down the kinetics of oxidation. The reactive element addition modifies the rate at which reactants are transported across the oxide layer to slow down the dominant diffusing species and hence reduce the oxidation rate [21].

In conclusion, firstly, we have used our model to identify the experimental data from the publications [1,2] for the system NiAl/Al₂O₃. For the input parameters, we have found in the publications and we assumed that the values are quite correct. After using the step-by-step method to identify $J_{\alpha x}$ for different temperature plateau, we can calculate the activation energy from the fitting of Ln(Jox) vs 1/T. The activation energy that we have found is quite comparable with that founded by the authors of [1,2].

Secondly, we have used our methods to identify the experimental data done at European Synchrotron Radiation Facility (ESRF) for the system NiCr/Cr2O3. We have fixed the base metal and tested it for different solicitations of thermal loadings. We have identified J_{ox} and D_{ox} for the different temperature plateau. By comparing with the activation energy values in the thesis of F. Rakotovao [16] and the publication of Tsai et Huntz [17], we can also try to identify the mechanism responsible for the stress release by creep.

Lastly, we have used our methods to identify a series of NiCr alloys with different quantity of the reactive element Y_2O_3 , under the same thermal loadings. After calculating the activation energy for different quantity of reactive element, and compared with the raw material, we have found a quasi-linear change of the activation energy which indicates a modification of the mechanism which governs the diffusion-creep.

Beside J_{ox} , we have also obtain the value of D_{ox} using the optimization method. As the experimental data may be sometimes not sufficient, we have tried to smooth the experimental data, but it is still difficult to fit, and thus we have a big uncertainty on the parameters deduced from the fit. In order to improve the optimisation method, a detailed calculation of the uncertainty for every steps from treating the experimental data to the identification procedure is needed, which may be performed in the future.

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Conclusion

In the present research work, oxide scale growth and associated stress during high temperature oxidation are investigated. The main objective is to establish a model to identify the mechanical parameters under thermal solicitations when temperature changes, in order to improve the understanding of the mechanisms leading to the development and relaxation of stress in the oxide layer developed in high temperature oxidation. Two different oxides, alumina and chromia, under different thermal solicitations (isothermal and non-isothermal solicitations) are studied and used as experimental data. The later are used to identify the mechanical parameters of material, which are compared with those obtained from publications. This work establishes a model considering different material behaviors (elasticity, visco-plasticity, growth strain in the oxide layer and thermal expansion) to describe the response of material during high temperature oxidation. It leads us to focus on the influence of material parameters on the development and relaxation of stress in the growing oxide layers at high temperature.

A model is developed to describe the response of material during high temperature oxidation. To establish this model, firstly, some hypotheses are made in order to deduce a force balance equation and a displacement continuity equation. Secondly, different material behaviors (elasticity, visco-plasticity, growth strain in the oxide layer and thermal expansion) are considered. Finally, an ordinary differential equation (ODE) is deduced. In order to get an analytical solution, three specific thermal loadings are assumed: isothermal, step thermal loading and periodic thermal loading. For isothermal condition, a characteristic time and a minimum stress value have been obtained using a new procedure. Comparison has also been made with the values in literature. For step thermal loading, the Laplace transform method has been proposed to solve the ordinary differential equation. With some supplementary assumptions, an equation is deduced to identify $\Delta \alpha$ when temperature changes. This offers a new way to identify the thermal expansion parameter mismatch ($\alpha_m - \alpha_{ox}$). For periodic thermal loading, a new innovative method is proposed, i.e. the frequency analysis method. In order to get a numerical solution, the Runge-Kutta method is used and discussed. The Influence of different time step is discussed and an expected conclusion is drawn that the influence of the time step is negligible so long as it is chosen relatively small.

Experiments have been performed on beamline BM02 at ESRF (European Synchrotron Radiation Facility) of Grenoble, because of its high flux, tunable energy, goniometer available and 2D detector available. The diffraction with synchrotron radiation coupled with an induction furnace has been implemented to realize continuous measurements during the high temperature oxidation in the chromia layers. The use of synchrotron radiation and 2D detector makes it possible to carry out high quality diffraction measurements with a high dynamic range, corresponding to relatively short acquisition times. The oxidation conditions explored are generally those applied in the previous works carried out by Kemdehoundja and Guérain. In general, these oxide layers have been developed between 700 °C and 1000 °C for oxidation times ranging from 3 hours to 40 hours. The cooling rate was set at 150 °C/min to minimize the activation of the stress relaxation mechanisms during the cooling steps. The procedure for treating the experimental data from pictures captured by 2D detector to stress-time curve for the oxide layer has been detailed and explained gradually. Lastly, the three main sources (position of the sample, calibration and fitting for the peaks) of uncertainties have been explained and calculated to quantify the limits of our experimental approach.

The identification methodologies have been presented in details for both isothermal conditions and non-isothermal conditions. For isothermal conditions, an example has been made to explain the method firstly established by Panicaud et al. For non-isothermal conditions, two methods (global

optimization and optimization step by step) have been proposed, discussed and compared. Global optimization tries to identify all the material parameters at the same time using all the experimental data from different temperature plateau. Whereas, optimization step by step method firstly tries to identify only Jox and Dox for a fixed temperature using the experimental data of one single temperature plateau, and then use manual optimization method for all the experimental data to identify $\Delta \alpha$. Even though the global optimization method fits better the experimental data of stress vs time curve, the step by step method leads to parameters , which are more physically relevant, because they correspond to an Arrhenius behavior with values of the activation energy that agree well with the ones of bibliography. Thus, we have chosen the step by step method to identify experimental data.

Some experimental data, which can be used to identify material parameters, have been presented. It mainly consists of the experimental data for the system NiAl/Al₂O₃ that has been found in publications, and that for the system NiCr/Cr₂O₃ providing from experiments done on beamline BMO2 at ESRF. For the system NiAl/Al₂O₃, a specific example of thermal solicitation has been chosen. After using the step by step method, the activation energy has been found, which is comparable with that found in publications. For the system NiCr/Cr₂O₃, nine different thermal solicitations, corresponding to four initially built microstructures, have been used. From the value of activation energy, the mechanism for the creep behavior has been identified. Moreover, in order to find out the influence of reactive elements on the mechanical properties of the chromia layers, a series of experiments using the identification method, we have found that the presence of reactive element in the NiCr alloy seems to change the activation energy linearly. As far as we know, this is the first time that a linear influence is found.

Perspectives / Prospects

At the end of this work, a number of perspectives can be mentioned.

Firstly, a detailed calculation of the uncertainties for each step from the 2D detector picture to the identification result should be performed, in order to find out which parameters have the greater influence. The uncertainties comes from the experimental equipment, the procedure for treating the experimental data and the identification method. It would be interesting to be able to find out which step should be careful dealt.

Secondly, more experimental investigations can be done for the system NiAl/Al₂O₃. In this work, we have only used the experimental data from the publications, but details about the base material are unknown for us, which may influence the input parameters and finally influences the identification results. Besides, the beginning part of the first temperature plateau is often missing, which leads to the difficulty to identify Dox. It would be advantageous to carry out complementary in situ measurements using our own base material for the system NiAl/Al₂O₃.

Thirdly, more kinds of thermal solicitations can be done, especially for the cyclic loadings. We can change the first temperature plateau, the temperature span and the temperature phase shift, and to fit using the frequency analysis methods, in order to validate this method, especially the Bode diagram of the system.

Fourthly, in order to use the step by step method with more accuracy, it would be wise to increase the number of temperature plateaus. This would allow Arrhenius plots to be made from more Jox values for the same microstructure. Temperature jumps of only 50 °C downwards should make it possible to achieve this objective and therefore to gain access to more reliable values of the activation energies.

Finally, because there is a relationship between the stress in the oxide layer and that in the metal, we can also calculate the stress in the metal from the 2D detector picture, focusing on the peak of the metal. As the peak of metal exists at the very beginning part of the experiment, it would also be interesting to be able to obtain the stress at the very beginning in the metal. As regards to this aspect, a thesis work is currently under way at the University of Technology of Troyes and University of La Rochelle.

French Summary

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Introduction

De nos jours, les alliages résistants à l'oxydation sont largement utilisés dans les systèmes industriels fonctionnant à haute température, car ils coûtent moins cher que les composés céramiques traditionnels. Ces alliages sont souvent exposés à une atmosphère oxydante et donc une couche d'oxyde se développe à la surface de cet alliage. Les alliages résistants à l'oxydation correspondent à ceux qui sont capables de produire une couche d'oxyde protectrice, habituellement constituée d'alumine ou de chrome, présentant une très faible perméabilité aux réactifs d'oxydation, afin de limiter l'oxydation ultérieure. Malheureusement, il est connu depuis de nombreuses années qu'il existe une contrainte accompagnant la croissance de la couche d'oxyde qui peut limiter la durée de vie du système.

De nombreux processus pourraient aider à générer des contraintes, et de nombreux types de mécanismes pourraient avoir lieu pour la relaxation de ces contraintes. Les observations ont montré des contraintes allant jusqu'à plusieurs centaines de MPa, voire quelques GPa, ou de grandes déformations de l'oxyde. Les deux situations sont néfastes pour la durée de vie de l'oxyde et peuvent généralement entraîner une défaillance mécanique pour détendre les contraintes. En raison de la nature complexe et évolutive des matériaux utilisés, l'optimisation de la durée de vie par des expériences est difficile. Ainsi, il existe un besoin croissant de modèles et d'outils de simulation qui complèteront la compréhension des mécanismes liés aux propriétés des matériaux. En outre, de tels modèles avancés devraient permettre aux utilisateurs de prévoir l'évolution des contraintes dans les systèmes métal / oxyde.

Certains modèles ont été établis pour prédire l'évolution des contraintes de croissance, mais pour autant que nous le sachions, la plupart d'entre eux considèrent généralement les conditions d'oxydation isotherme. Cependant, dans des situations réelles, les métaux ou les alliages sont souvent oxydés sous des chargements thermiques plus ou moins complexes. De plus, les caractéristiques des contraintes de croissance changent significativement avec les conditions d'oxydation: température, durée, pression partielle de dioxygène, vitesses de refroidissement, etc. Ainsi, un modèle prenant en compte la plupart des conditions d'oxydation est nécessaire.

L'objectif principal de ce travail est de développer un tel modèle et un outil d'identification associé, afin d'étudier l'évolution des contraintes dans les systèmes métal / oxyde sous charges thermiques, ainsi que l'identification des propriétés du mécanisme et des matériaux. Ensuite, le modèle est appliqué en utilisant les données expérimentales fournies par la littérature pour le système NiAl / Al₂O₃. La valeur de l'énergie d'activation est comparée à celle des publications, afin de valider notre méthode. Enfin, il est utilisé pour identifier les propriétés du mécanisme et des matériaux pour le système NiCr / Cr_2O_3 . Dans ce cas, les données expérimentales proviennent d'expériences réalisées par notre équipe à l'European Synchrotron Radiation Facility (ESRF). Dans cette thèse, une liste de questions sera posée et nous chercherons à y apporter des réponses :

1. Comment établir un modèle pour décrire la réponse mécanique du matériau pendant l'oxydation à haute température et le résoudre analytiquement et numériquement?

2. Comment réaliser des mesures in situ continues pendant l'oxydation à haute température en utilisant le rayonnement synchrotron et d'où proviennent les incertitudes?

3. Comment choisir parmi différentes méthodes d'optimisation afin d'avoir un meilleur résultat d'optimisation?

- 4. Comment identifier les mécanismes du comportement au fluage dans la couche d'oxyde?
- 5. Comment certains éléments réactifs modifient-ils l'énergie d'activation de la couche d'oxyde?

Cette thèse de doctorat consiste en 4 parties:

La première partie établit un modèle qui prend en compte plusieurs comportements matériels et l'influence de la température sur les paramètres du matériau, afin d'étudier l'évolution des contraintes avec le temps, au cours de la procédure d'oxydation. Les hypothèses et les limites sur la validité du modèle sont également présentées. Afin de résoudre le modèle, certaines solutions analytiques sont considérées à la fois pour les conditions isothermes et les conditions non isothermes, suivies des solutions numériques utilisant le schéma de Runge-Kutta.

La seconde partie présente en détail la procédure de détermination de la contrainte dans la couche d'oxyde lors de l'utilisation de la diffraction synchrotron avec un détecteur 2D. Chaque étape du traitement des données est également présentée et discutée, suivie de l'analyse des incertitudes provenant des différentes sources.

La troisième partie présente les méthodologies d'identification pour les conditions isothermes et les conditions non isothermes. La vérification de la cohérence physique des valeurs numériques pour certains paramètres matériels est également fournie, ce qui peut confirmer notre procédure d'identification. Enfin, deux nouvelles méthodes d'identification du paramètre de dilatation thermique sont également proposées.

La quatrième partie présente tous les résultats expérimentaux, issus de la littérature et de nos propres expériences à l'European Synchrotron Radiation Facility (ESRF), pour différentes sollicitations thermiques et différents matériaux (NiAl / Al_2O_3 , NiCr / Cr_2O_3 , avec et sans éléments réactifs) et aussi les résultats d'identification en utilisant les méthodologies d'identification et les données expérimentales. Les résultats d'identification sont ensuite discutés et comparés aux valeurs de la littérature pour identifier les mécanismes.

1. Modélisation

1.1 théorie

Dans cette partie, une méthodologie pour établir notre modèle est donnée. Nous partons des hypothèses et des limites de notre modèle, puis nous expliquons les différences entre couplage fort et faible, ainsi qu'une présentation des différents modèles de comportement matériel tels que l'élasticité, la visco-plasticité, la déformation de croissance et la dilatation thermique. Enfin, l'influence de la température sur le comportement du matériau est discutée. Nous partons d'abord des hypothèses générales, valables dans les cas isothermes ou non isothermes, puis nous simplifierons le modèle pour différents cas (couplage fort isotherme, non isotherme).

1.1.1 Hypothèses et limites sur le modèle

Dans le modèle proposé, les hypothèses suivantes sont faites:

- La contrainte moyenne peut être théoriquement calculée en tenant compte de l'existence d'un gradient de contrainte possible. Finalement, seul un champ de contrainte uniforme est considéré.

- L'équation de l'équilibre des forces est considérée dans un domaine quasi-statique, ce qui conduit à:

$$\int_{H_0}^{H_1} \sigma_m dz = -\int_{H_1}^{H_2} \sigma_{ox} dz$$

(1.1)

- Puisque nous ne considérons pas la courbure de la couche d'oxyde et que nous avons considéré que le système est symétrique, l'équation d'équilibre des moments n'est pas nécessaire, alors que dans d'autres modèles qui prend en compte la courbure [1–3], l'équation d'équilibre des moments doit être utilisée.

- Les positions "Hi" des interfaces sont définies dans la Figure 1.1, en référence à une ligne médiane H0 qui représente l'origine de l'épaisseur du système symétrique, H1 à la position d'interface métal / oxyde et H2 à la position d'interface oxyde / air. Les indices "ox" et "m" désignent respectivement l'oxyde et le métal.

- Le système a un comportement isotrope et biaxial (c'est-à-dire que le matériau est isotrope et que la contrainte dans la couche d'oxyde est biaxiale, c'est-à-dire qu'il n'y a pas de contrainte dans la direction z) [4].

- Les effets bidimensionnels tels que le « rumpling » (ondulation de la couche) ne sont pas pris en compte [5]

- Les phénomènes mécaniques non linéaires (flambage, fissuration, écaillage) ne sont pas pris en compte, ce qui correspond au système que nous avons étudié.

- Par conséquent, il existe une continuité de déplacement à l'interface oxyde / métal.

- Une seule couche d'oxyde monophasée est considérée sur le métal et cette phase est indépendante du temps (aucune autre transformation chimique n'est considérée dans la masse de l'oxyde, à l'exception de l'oxydation elle-même). Cet " oxyde moyen " possède des propriétés obtenues en faisant la moyenne des caractéristiques des oxydes.

- La déformation chimique due à la dissolution de l'oxygène dans l'alliage du substrat n'est pas considérée [4,6-8].

- Les cinétiques d'oxydation sont supposées paraboliques pour les systèmes étudiés [4,8,9].



Figure 1.1: Géométrie et coordonnées de la croissance d'oxyde sur un métal

Il est a priori nécessaire de distinguer deux cas possibles: l'oxydation symétrique (lorsque les deux côtés métalliques sont oxydés) et l'oxydation asymétrique (lorsque l'oxyde se forme d'un seul côté). Comme cela a été dit précédemment, l'oxydation sera toujours considérée comme symétrique. Le tenseur de déformation dans la couche d'oxyde ou dans le métal est alors uniforme et ne dépend que du temps. De plus, l'équation de continuité de contrainte peut être décomposée de la manière suivante:

 $(\varepsilon^{elastic} + \varepsilon^{viscoplastc} + \varepsilon^{thermal} + \varepsilon^{growth})_{ox} = (\varepsilon^{elastic} + \varepsilon^{viscoplastc} + \varepsilon^{thermal})_m$ (1.2) Où ε^{growth} représente la contrainte de croissance latérale dans la couche d'oxyde, $\varepsilon^{viscoplastic}$ représente la déformation visco-plastique dans la couche ou dans le métal, $\varepsilon^{thermal}$ représente la déformation thermique dans la couche ou dans le métal et $\varepsilon^{elastic}$ représente la déformation élastique dans la couche ou dans le métal et $\varepsilon^{elastic}$ représente la déformation élastique dans la couche ou dans le métal.

1.1.2 couplage forts et faibles

Nous pouvons diviser l'influence de la température en deux sortes:

- Couplage forts

Un couplage fort signifie ici un couplage entre deux variables issues d'un processus de modélisation. Ici, nous avons basé notre approche sur le formalisme thermodynamique pour obtenir des couplages forts entre différentes variables d'état.

Si on prend en compte le couplage fort pour l'influence de la température sur la mécanique, c'est-àdire qu'on prend en compte la déformation thermique $\varepsilon^{thermal}$ dans l'équation 1.2. Ce couplage fort lie principalement le taux de température à la vitesse de déformation thermique (dilatation thermique) [10]. Un tel couplage fort vient physiquement de la différence des propriétés de dilatation thermique pour les couches d'oxyde et de métal lorsque la température change. En général, le coefficient de

dilatation pour le métal est plus grand que celui de l'oxyde, c'est-à-dire $\frac{\alpha_m}{\alpha_{ox}} > 1$ [11]. Ce couplage fort

ne peut pas être négligé car c'est l'influence principale lorsque la température change [12]. Ce terme disparaît strictement et uniquement pour les transformations isothermes.

- Couplage faibles

Un couplage faible signifie que nous prenons en compte l'influence de la température sur les paramètres matériaux à partir d'une méthodologie qui ne dérive pas d'une approche thermodynamique. Il y a a priori deux types d'influence:

Tout d'abord, il y a plusieurs paramètres matériaux, tels que le module de Young pour l'oxyde et le métal (Eox et Em), les paramètres visco-plastiques pour l'oxyde et le métal (Jox et Jm) et le paramètre

de déformation de croissance pour l'oxyde Dox. Par conséquent, nous pouvons supposer qu'ils sont fonction de la température [13].

Deuxièmement, en raison de la dépendance de certains paramètres sur la température, lorsque nous utilisons la forme différentielle dans l'équation 1.2, de nouveaux termes apparaissent.

Par exemple, si nous supposons que le modèle de comportement matériel est tel que :

$$\varepsilon = f(\mathbf{C})g(\sigma) \tag{1.3}$$

Où ε est la contrainte et σ est la contrainte. C'est un paramètre matériau qui dépend de la température. Par conséquent, lorsque nous différencions l'équation 1.2 avec le temps t, nous pouvons obtenir:

$$\frac{d\varepsilon}{dt} = \frac{d(f(C)g(\sigma))}{dt} = \frac{df(C)}{dT}\frac{dT}{dt}g(\sigma) + \frac{dg(\sigma)}{dt}f(C)$$
(1.4)

Où T est la température. Le premier terme du second membre de l'équation 1.4 est un nouveau terme ajouté qui dépend du taux de température (vitesse de chauffage ou de refroidissement).

Pour obtenir des solutions analytiques, il sera parfois plus facile de négliger les couplages faibles.

1.2 Solutions analytiques

Avec toutes les hypothèses présentées dans la partie théorique (Partie 1.1), en considérant le couplage le plus général (faible et fort), on peut obtenir:

$$\dot{\mathcal{E}}_{ox} = \dot{\mathcal{E}}_m \tag{1.5}$$

$$\dot{\varepsilon}_{m} = \frac{d}{dT} \left(\frac{1 - v_{m}}{E_{m}(\mathbf{T})} \right) \dot{T} \sigma_{m} + \frac{1 - v_{m}}{E_{m}(\mathbf{T})} \dot{\sigma}_{m} + J_{m}(\mathbf{T}) \left| \sigma_{m} \right|^{N_{m}} signe(\sigma_{m}) + \alpha_{m}(\mathbf{T}) \dot{T}$$
(1.6)

$$\dot{\varepsilon}_{ox} = \frac{d}{dT} \left(\frac{1 - v_{ox}}{E_{ox}(T)} \right) \dot{T} \sigma_{ox} + \frac{1 - v_{ox}}{E_{ox}(T)} \dot{\sigma}_{ox} + J_{ox}(T) \left| \sigma_{ox} \right|^{N_{ox}} signe(\sigma_{ox}) + D_{ox}(T) \dot{h}_{ox}(t) + \alpha_{ox}(T) \dot{T}$$
(1.7)
$$\sigma \left[H_{ox}(t) - H_{ox}(T) \right] + \sigma \left[H_{ox}(t) - H_{ox}(T) \right] = 0$$
(1.8)

 $\sigma_{m}[H_{1}(t) - H_{0}] + \sigma_{ox}[H_{2}(t) - H_{1}(t)] = 0$ (1.8)

Avec $h_{ox}(\mathbf{t}) = H_2(\mathbf{t}) - H_1(\mathbf{t})$: épaisseur de couche d'oxyde.

En résolvant l'équation 1.5 à 1.7, enfin nous pouvons obtenir:

$$\dot{\sigma}_{ox} = \frac{\left((\alpha_m - \alpha_{ox})\dot{T}\theta + \frac{\sigma_{ox}}{\theta} \frac{1 - v_m}{E_m} \dot{\theta} + \sigma_{ox} \frac{2a_m + b_m}{E_m^2} (1 - v_m)\dot{T} - sign(\sigma_{ox}) \frac{1}{2} \left(\frac{|\sigma_{ox}|}{K_{ox}} \right)^{N_{ox}} \theta \right)}{\left(+ \sigma_{ox} \frac{2a_{ox} + b_{ox}}{E_{ox}^2} (1 - v_{ox})\dot{T}\theta - sign(\sigma_{ox}) \frac{1}{2} \left(\frac{|\sigma_{ox}|}{K_m} \right)^{N_m} \theta^{1 - N_m} - D_{ox}\dot{h}_{ox}\theta} \right)}$$

$$\left(\frac{1 - v_m}{E_m} + \frac{1 - v_{ox}}{E_{ox}} \theta \right)$$
(1.9)

Où am, bm, cm et aox, box, cox sont des constantes matériaux pour le module de Young pour la couche de métal et d'oxyde respectivement.

1.3 Solutions numériques

Si l'on considère à la fois le couplage faible et le couplage fort, il n'est pas facile d'obtenir une solution analytique, nous avons donc utilisé Matlab pour obtenir les solutions numériques.

Le schéma de Runge-Kutta est une méthode bien connue et largement utilisée pour les solutions approximatives des équations différentielles ordinaires (ODE). Le membre le plus connu de la famille Runge-Kutta est généralement appelé "méthode classique de Runge-Kutta", qui a été utilisée pour résoudre l'équation différentielle 1.9.

2. Partie expérimentale

2.1 Contexte des expériences

Dans ce travail, les expériences ont été spécifiquement réalisées in situ à haute température sur la ligne BM02 de l'ESRF (European Synchrotron Radiation Facility) à Grenoble (voir Figure 2.1), en collaboration avec plusieurs partenaires:



Figure 2.1: BM02 beamline à l'ESRF Grenoble

- Dr. Guillaume GEANDIER (chercheur CNRS à l'Institut Jean Lamour de l'Université de Lorraine).
- Dr. Felaniina Nirisoa RAKOTOVAO (Docteur de l'Université de La Rochelle)
- Pr. Pierre Olivier RENAULT (Professeur à l'Institut P' de l'Université de Poitiers).

- Dr. Philippe GOUDEAU (Directeur de Recherche CNRS à l'Institut P' de l'Université de Poitiers). - Dr. Nathalie BOUDET (Scientifique à la ligne BM02 de l'ESRF Grenoble).

- Dr. Nils BLANC (Scientifique de la ligne BM02 de l'ESRF Grenoble).
- Hugo VITOUX (Technicien du Service de Support Environnemental Echantillon de l'ESRF Grenoble).
- Bernard GORGES (Ingénieur au Service de Support Environnemental Echantillon de l'ESRF Grenoble).

La ligne de lumière est équipée d'un goniomètre, d'un porte-échantillon, d'un détecteur bidimensionnel et de deux photodiodes [14].

La première photodiode est placée devant l'échantillon et permet de connaître le flux des photons entrants.

La seconde photodiode est placée derrière l'échantillon et le long de l'axe du faisceau pour permettre l'alignement de la surface de l'échantillon avec le faisceau, ce qui est important pour le réglage de la hauteur.

Le faisceau de rayons X arrivant sur l'échantillon est monochromatique, de longueur d'onde de 0,062 nm (énergie de 20 keV).

Un four à induction a été utilisé pour effectuer simultanément des oxydations avec des mesures insitu et notamment des mesures de déformation au cours de cette oxydation. Le four à induction a été fourni par le Sample Environment Support Service de l'ESRF (voir la figure 2.2).



Figure 2.2: Four à induction de la ligne BM02 à l'ESRF Grenoble.

Le système se compose d'un générateur de haute puissance (maximum 3kW). Le porte-échantillon est un support cylindrique, entouré par la bobine d'induction avec un diamètre de 7 mm et une profondeur de 4 mm.

Un thermocouple est placé au bas de ce support pour contrôler et réguler la température (la température peut atteindre une valeur maximale de 1600°C). La température à la surface de l'échantillon a été mesurée à l'aide d'un pyromètre. La vitesse de chauffage et de refroidissement peut varier entre 1 ° C / min et 500 ° C / min avec une température de précision ± 1 ° C.

Le principal avantage de ce four est sa capacité à chauffer ou refroidir très rapidement (temps caractéristique thermique du four avec notre échantillon métallique est d'environ 13s), avec un bon contrôle des vitesses de chauffage et de refroidissement, ce qui est un avantage pour développer des expériences particulières (cycle thermique ou sauts de température ...).

Cependant, même si l'utilisation d'un thermocouple et d'un pyromètre permet une connaissance correcte de la température d'oxydation, on ne peut ignorer qu'il peut y avoir un gradient de température entre les faces supérieure et inférieure de l'échantillon (en contact avec le thermocouple inférieur). Ceci peut générer une expansion non homogène des échantillons et perturber notamment le réglage en hauteur.

Le four à induction est utilisé pour l'oxydation des échantillons dans l'air. La taille du faisceau de rayons X est de 1 mm x 0,1 mm et l'angle d'incidence est de 5 °. Le détecteur est situé à une distance de 22 cm du centre du goniomètre. Ce détecteur fait un angle de 18 ° avec le faisceau incident.

L'étalonnage du détecteur a été réalisé à l'aide d'une poudre de silicium comme référence (NIST SRM640), afin d'ajuster la correspondance entre les degrés pixels et angulaires. L'étalonnage est une étape très importante car un mauvais positionnement de la caméra peut induire un décalage sur les pixels et, par la suite, un décalage sur les positions des anneaux de Debye-Scherrer.

Afin de rendre la surface de l'échantillon parallèle au faisceau, des étapes de réglage sont nécessaires avant chaque expérience pour avoir une meilleure précision.

Pour la détermination des contraintes, la classique méthode $\sin^2 \psi$ a été utilisée

2.2 Procédure de traitement des données

Les données récupérées après chaque expérience sont stockées sous forme d'images en pixels. L'objectif de cette étape est de déterminer les niveaux de contrainte dans la couche d'oxyde à partir de ces images.

La contrainte induit un déplacement des distances interréticulaires et donc un déplacement des anneaux de Debye-Scherrer. Différentes conditions déterminent la géométrie des anneaux dans le plan du détecteur. Pour les échantillons alignés avec le faisceau et le détecteur, les anneaux sont parfaitement circulaires si l'éprouvette est exempte de contrainte ou avec des contraintes ayant une symétrie de révolution. Pour les échantillons alignés avec le faisceau mais avec un angle du détecteur, les anneaux sont elliptiques si l'échantillon est exempt de contrainte ou avec des contraintes ayant une symétrie de révolution. D'autres types de configurations, c'est-à-dire sans symétrie spécifique, conduisent strictement à une géométrie plus complexe (conchoïde de Moritz...). Parce que la contrainte conduit à de petits déplacements angulaires, la distorsion des anneaux de Debye-Sherrer peut être approchée au premier ordre par une distorsion elliptique.

2.2.1 Des images expérimentales 2D aux diffractogrammes 1D

La figure 2.3 montre une image de l'expérience pour le système Ni30Cr / Cr2O3.





Il correspond à un temps t donné (et à une température T donnée). A partir de cette image 2D, d'abord, nous devons la transformer en un diffractogramme 1D. Pour ce faire, un protocole de traitement de données a été établi. Il y a plusieurs étapes à effectuer:

- Etape 1: L'étalonnage est effectué avant l'expérience considérée, en utilisant l'image de la poudre de référence de silicium. Avec les paramètres d'étalonnage, nous corrigeons la position du détecteur par rapport au faisceau pour que le pixel soit converti en 2θ . Pour une position donnée (x, y) dans l'image

en mm, nous pouvons la transformer en $(2\theta, \gamma)$, en utilisant la relation: $r = \sqrt{(\mathbf{x} - \mathbf{x}_0)^2 + (\mathbf{y} - \mathbf{y}_0)^2}, \ 2\theta = \arctan\left(\frac{r}{d}\right), \ \gamma = \arctan\left(\frac{x - x_0}{y - y_0}\right)$, où $(\mathbf{X}_0, \mathbf{y}_0)$ décrit

l'emplacement du faisceau de rayons X incident dans les coordonnées du détecteur, et est d la distance entre l'échantillon et le détecteur (voir Figure 2.4).



Figure 2.4: Illustration de l'échantillon à la distance du détecteur

- Etape 2: Pour obtenir le nombre maximum de points sur un anneau d'indice donné (hkl), il faut le subdiviser en secteurs correspondant à différents angles γ (voir Figure 2.5). Dans ce travail, les anneaux ont été subdivisés en 128 secteurs dont les valeurs sont comprises entre - 61,5 ° et + 65,5 ° avec un pas angulaire de $\Delta \gamma \approx 1^{\circ}$.



Figure 2.5: Subdivision des anneaux de Debye-Scherrer en secteurs

- Etape 3: Pour un rayon θ donné, on peut faire la moyenne de l'intensité de tous les pixels entre $[\gamma; \gamma + \Delta \gamma]$ (voir Figure 2.6). Pour ce faire, nous pouvons d'abord obtenir les coordonnées de tous les pixels de la plage considérée, puis additionner les intensités associées et les calculer en moyenne. Nous

pouvons répéter cette procédure pour tous les rayons θ différents, pour chaque secteur γ . Pratiquement, une extension angulaire $d\theta$ autour de chaque rayon est considérée pour la somme.



Figure 2.6: Illustration de la moyenne de l'intensité de tous les pixels

- Étape 4: Comme expliqué dans les étapes précédentes, avec les étapes 1, nous pouvons transformer les coordonnées des images de (x, y) on $(2\theta, \gamma)$. Avec les étapes 2 et 3, nous pouvons calculer l'intensité moyenne pour une position $(2\theta, \gamma)$ donnée. Si nous répétons cette procédure pour toutes les positions $(2\theta, \gamma)$, nous pouvons finalement obtenir des résultats comme le montre la figure 2.7. Si nous fixons γ aux différentes valeurs, les résultats peuvent être convertis en colonnes de données $2\theta, I(\gamma_1), I(\gamma_2), ..., I(\gamma_i)$:, où $I(\gamma_i)$ correspond à l'intensité de l'anneau pour le secteur (voir la figure 2.8)



Figure 2.7 : Illustration de la carte d'intensité pour les coordonnées $(2\theta, \gamma)$

Toute la procédure ci-dessus peut être effectuée automatiquement en utilisant PYFAI (pour la transformation des pixels en degrés) et Fit2D (pour la subdivision et l'intégration), grâce à la collaboration avec le Dr Guillaume GEANDIER.



Figure 2.8: Diffractogramme $I(\gamma_i) = f(2\theta)$ correspondant au système Ni30Cr / Cr₂O₃ pour une image donnée et quelques valeurs de γ .

2.2.2 Des diffractogrammes 1D aux courbes $\sin^2\psi$

Dans cette étude, trois pics caractéristiques de chromine ont été sélectionnés pour effectuer l'analyse des contraintes, dont l'indice et les positions théoriques 2θ sont résumés dans le tableau 2.1:

Plans (hkl) Cr ₂ O ₃	Theoretical positions 2θ(°) [15]
(104)	13.25
(110)	14.30
(116)	21.20

Tableau 2.1: Les positions théoriques des pics de diffraction (104), (110) et (116) de chromine.

Afin de déterminer les positions de ces pics de diffraction, le bruit de fond continu est soustrait et des procédures d'ajustement de pic ont été automatiquement effectuées en utilisant le programme de calcul Matlab avec le code développé par Pr. Benoît PANICAUD.

Pour chaque diffractogramme, le programme isole les trois pics dans chacun des 128 secteurs. Le bruit de fond continu de ces pics est ensuite soustrait avec une fonction polynomiale d'ordre 3 et chaque pic est ajusté au moyen d'une fonction pseudo-Voigt. Afin d'améliorer la qualité de la simulation, les critères suivants ont été appliqués:

- Seuil d'intensité: une valeur d'intensité en dessous de laquelle l'ajustement du pic n'est pas bon.

- Seuil de largeur: une valeur de largeur au-dessus de laquelle l'ajustement du pic est considéré comme mauvais.

- La différence entre la position expérimentale et la position théorique des pics de diffraction ne devrait pas être trop importante, sinon, l'ajustement est supprimé. Le programme considère comme aberrants les pics qui ne répondent pas à chacun de ces critères. En général, lorsque la couche d'oxyde est sous contrainte de compression, l'évolution de la position 2θ de chacun des trois pics en fonction du 128 est symétrique par rapport à l'origine.

Pour tous les pics analysés, la plage de variation de la position 20 en fonction de γ varie entre 2.10⁻² (°) et 15.10⁻² (°) lorsque la température varie entre 1000°C et la température ambiante. Connaître cette plage de variation de 20 est essentiel, car il déterminera le niveau de contraintes générées dans la couche d'oxyde.

Pour chacun de ces pics, les valeurs ψ correspondant aux 128 secteurs sont déduites de l'équation $\cos \psi = \sin \theta \sin \omega_0 + \cos \omega_0 \cos \theta \cos \gamma$, ω_0 est égale à 5 ° dans nos expériences. Avec cette équation, nous pouvons calculer 128 valeurs différentes de (θ, ψ) . Nous pouvons ensuite dessiner la

courbe $Ln\left(\frac{1}{\sin\theta}\right) = f(\sin^2\psi)$ en utilisant les 128 points. Enfin, nous utiliserons les courbes $\sin^2\psi$

pour calculer la contrainte en utilisant la méthode des $\sin^2 \psi$.

2.2.3 Des courbes sin² ψ aux courbes de contrainte-temps

Enfin, la méthode des sin² ψ est utilisée pour déterminer la contrainte associée. Afin de tracer et d'ajuster les lignes, différents critères ont également été définis tels que l'intervalle minimum de $\sin^2 \psi$, les coefficients de régression admissible et la différence admissible entre les points et les courbes ajustées (voir la figure 2.9).





Tout d'abord, nous utilisons le critère 3 pour supprimer les points anormaux. Deuxièmement, nous utilisons le critère 2 (le coefficient de régression de l'ajustement) et le critère 1 (la différence entre le

premier point et le dernier point dans la direction du $\sin^2 \psi$) pour juger de la qualité de l'ajustement. Si tous ces critères sont satisfaits, on peut considérer que les courbes ajustées sont correctes. Nous pouvons ensuite calculer la contrainte, à partir de la pente de la droite.

Après tout le processus ci-dessus, nous pouvons enfin obtenir la valeur de la contrainte pour un temps donné et une température donnée. Il correspond seulement à un point dans les courbes de contrainte-

temps, donc nous devons répéter cette procédure pour des milliers d'images expérimentales pour obtenir les courbes contrainte en fonction du temps.

2.3 Analyse des incertitudes

Au cours des expériences, nous devons faire attention que les variations de 2θ ce que nous voulons observer sont très faibles. Par conséquent, la plage de variation de la déformation associée est également très faible. Ainsi, les paramètres instrumentaux jouent un rôle très important. Ceux-ci inclus:

- Mauvais étalonnage du détecteur: si l'étalonnage réalisé avec la poudre de silicium n'est pas parfait, on observe un décalage significatif des positions expérimentales des pics de diffraction. Cela peut provenir des positions incorrectes de la caméra et par conséquent, les pixels enregistrés ont un décalage. Ainsi, l'évolution de 2θ en fonction de la 128 γ reste symétrique, mais les valeurs de 2θ sont décalées d'une certaine quantité.

- Une modification de la position des échantillons due à la dilatation thermique: Malgré les essais de dilatation thermique effectués avant les expériences, les échantillons sont susceptibles de bouger lors de l'oxydation à haute température, ce qui peut induire un changement de position de l'échantillon par rapport au faisceau incident, entraînant un décalage des anneaux de Debye-Scherrer.

- La diminution de l'intensité du faisceau pendant l'expérience et le remplissage: En raison d'une perte d'électrons dans l'anneau de stockage, une diminution d'intensité se produit provoquant une diminution de l'intensité des pics. Une recharge est une augmentation du courant de faisceau et la charge thermique peut changer sur les optiques (monochromateurs, fentes, miroirs, etc ...) qui peuvent changer la position de pointe sur le détecteur.

Il existe trois principales sources d'incertitudes au cours des expériences:

- 1. Incertitude provenant de la position des échantillons.
- 2. Incertitude provenant de l'étalonnage.
- 3. Incertitude provenant de l'ajustement pour les pics.

3. Méthodologies d'identification

3.1 Conditions isothermes

Dans ce chapitre, nous considérerons que nous partons des résultats expérimentaux obtenus par la méthode décrite en partie 2, afin de pouvoir utiliser les modèles décrits en partie 1 pour identifier certains paramètres matériaux (tels que paramètres viscoplastiques, paramètres de croissance, coefficient de dilatation thermique, etc.).

Dans un premier temps, nous expliquerons la méthode d'identification dans des conditions isothermes. Même si cela a déjà été étudié par Panicaud et al., il est important pour nous de connaître la méthode d'identification en conditions isothermes, car c'est la base de la méthode d'identification. Nous allons améliorer et généraliser cette méthode pour tenir compte des conditions non isothermes.

Dans le modèle sous conditions isothermes décrit en partie 2, il existe un ensemble de 10 paramètres inconnus: les deux coefficients élastiques E et v, à la fois pour l'oxyde et le métal; les deux paramètres viscoplastiques J et N, à la fois pour l'oxyde et le métal; le paramètre de croissance d'oxyde D_{ox} seulement pour l'oxyde; et le coefficient cinétique de la réaction d'oxydation chimique globale nommée A_p (l'indice p signifie une réaction parabolique telle qu'observée dans le système

 $Ni_{30}Cr / Cr_2O_3$ pour les temps d'oxydation considérés). Certaines valeurs de ces paramètres peuvent être trouvées dans la littérature. Cependant, il correspond généralement à des matériaux en volume, de sorte qu'il n'est pas toujours fiable pour les couches d'oxyde. Même pour les métaux, il est difficile de les utiliser car cela dépend fortement de la température. Par conséquent, une méthodologie doit être proposée pour déterminer certaines de ces caractéristiques des matériaux. Généralement, le module d'Young et le coefficient de Poisson peuvent être utilisés directement à partir de la littérature avec une assez bonne confiance. Le coefficient cinétique est déterminé à partir d'expériences telles que l'analyse thermogravimétrique ou peut être directement trouvé dans la littérature. Pour les métaux, le mécanisme de relaxation dominant est généralement le fluage intragranulaire avec un exposant Norton dans la gamme 3-5. De plus, il semble raisonnable de considérer $N_{ox} < N_m$. Ainsi, les valeurs d'exposant au fluage pour les métaux sont fixés. Cependant, à cette étape, les inconnues restent a priori D_{ox} , J_m , J_{ox} , N_m et N_{ox} . Pour déterminer ces fonctionnalités, nous allons traiter avec différentes méthodes. Ainsi, nous recherchons l'ensemble (D_{ox} , J_m , J_{ox} , N_m , N_{ox}).

Pour le système $Ni_{30}Cr/Cr_2O_3$, la méthodologie suivante est proposée:

- Etape 1: détermination D_{ox} d'une approximation par analyse asymptotique à des temps d'oxydation courts.

-Etape 2: détermination des paramètres viscoplastiques avec des approximations par analyse asymptotique à des temps d'oxydation longs.

- Etape 3: extraction des coordonnées expérimentales du minimum possible (point d'inflexion dont les coordonnées sont ($t_{\min}^{}, |\sigma_{ox}|_{\min}$).

- Etape 4: pour une valeur donnée de N_{ox} et de $|\sigma_{ox}|_{\min}$ ou t_{\min} , calcul de J_{ox} et du temps caractéristique τ_{ox} , en utilisant deux méthodes différentes, pour valider le modèle à une approximation d'ordre zéro.

- Etape 5: optimisation de l'ensemble des données pour extraire simultanément tous les paramètres inconnus.

Il est à noter que le succès des étapes précédentes dépend des courbes expérimentales (forme et nombre de points).

3.2 Conditions non-isothermes

Lorsque l'échantillon est oxydé dans des conditions non isothermes, il est plus difficile d'identifier les paramètres du matériau, car presque tous les paramètres du matériau dépendent de la température. En outre, le modèle est plus compliqué, car en condition isotherme, certains paramètres sont constants, mais dans des conditions non isothermes, ils deviennent variables. Au partie 1, nous avons établi un modèle dans des conditions non isothermes. Dans cette partie, nous utiliserons le modèle pour proposer des méthodes d'identification pour certains paramètres matériaux.

3.2.1 Optimisation globale

Considérons que nous avons déjà les données expérimentales pour la contrainte en fonction du temps, et que nous avons déjà le modèle pour les conditions non isothermes. Maintenant, la première idée proposée est de simuler les données expérimentales globalement pour identifier certains paramètres matériaux. Dans ce cas, le modèle de base est relativement similaire avec les conditions isothermes, mais le nombre de variables a maintenant augmenté.

Dans le modèle sous conditions non isothermes décrit au partie 1, il existe un ensemble de 22 paramètres, inconnus:

Premièrement, pour la fonction du module de Young en fonction de la température, il existe six paramètres (a, b, c) pour l'oxyde et le métal.

Deuxièmement, deux coefficient de Poisson pour l'oxyde et le métal, parce que nous le considérons comme indépendant de la température.

Troisièmement, pour la fonction des paramètres viscoplastiques J en fonction de la température, il existe quatre paramètres ($Cste_{I2}, Q_{I2}$) pour l'oxyde et le métal.

Quatrièmement, deux paramètres viscoplastiques N pour l'oxyde et le métal, parce que nous considérons comme indépendant de la température.

Cinquièmement, pour la fonction du paramètre de croissance de l'oxyde D_{ox} en fonction de la température, il y a deux paramètres (Q_D , D_0). Nous devrions faire attention que si nous choisissons un autre modèle pour simuler D_{ox} vs la température, il peut exister plus de paramètres, mais au moins deux paramètres.

Sixièmement, pour la fonction du coefficient de cinétique A_p en fonction de la température, il y a deux paramètres (A_{a0} , Q_a).

Enfin, pour la fonction du coefficient de dilatation thermique α en fonction de la température, il existe quatre paramètres (α_0 , DaTO) pour l'oxyde et le métal.

Il est impossible d'ajuster directement un modèle avec 22 variables inconnues, nous devrions donc corriger certains de ces paramètres. De plus, certaines valeurs peuvent être directement trouvées dans la littérature. Généralement, le module d'Young et le coefficient de Poisson peuvent être utilisés directement à partir de la littérature pour différentes températures avec une bonne confiance, à la fois pour le métal et l'oxyde. Les coefficients cinétiques pour différentes températures sont déterminés à partir d'expériences telles que l'analyse thermogravimétrique ou peuvent être directement trouvés dans la littérature. Pour les métaux, l'exposant de Norton pour différentes températures peut être trouvé dans la littérature pour $Ni_{30}Cr$, qui est exactement le métal que nous avons étudié. De plus, il semble raisonnable de considérer $N_{ox} < N_m$. Dans nos simulations, nous avons fixé N_{ox} à 1 ou 2, pour simplifier le modèle. Nous avons essayé de fixer $N_{_{ox}}$ à 1, 2, 3 et 4, parce que nous considérons $N_{ox} < N_m$ et N_m est autour de 4, et nous trouvons que $N_{ox} = 1 \ or \ 2$ mène finalement aux meilleurs résultats. Cependant, à cette étape, les inconnues restent a priori 10 paramètres. Pour déterminer ces paramètres, il devrait exister différentes températures pour que les données expérimentales établissent des équations afin de résoudre ces 10 paramètres, mais dans notre cas, nous avons seulement 4 températures différentes par échantillon, nous devons donc diminuer le nombre des paramètres inconnus a priori.

Pour J_m , nous pourrions trouver la valeur pour deux températures différentes dans la littérature pour $Ni_{30}Cr$, qui est exactement le métal que nous avons utilisé. Par conséquent, nous utilisons simplement les données dans la littérature pour les deux températures et extrapolons pour trouver les valeurs pour d'autres températures. Cependant, nous devons faire attention que la dépendance de la température de ce paramètre est souvent trop importante (elle change beaucoup avec la température). Même qualitativement bonnes, des valeurs quantitatives restent encore à donner pour chaque alliage considéré. Par conséquent, nous le considérons toujours comme une variable, c'est-à-dire que si la simulation n'est pas bonne, nous pouvons changer sa valeur manuellement.

Pour α_{ox} et α_m , nous pouvons utiliser la méthode d'optimisation manuelle pour les identifier.

Nous pouvons trouver directement les valeurs pour différentes températures dans la littérature. Pour les valeurs de métal, c'est plus fiable parce que nous avons utilisé le même métal, mais quand il s'agit de α_{ox} , il peut y avoir des différences parce qu'il s'agit généralement de matériaux en volume dans la littérature, ce qui n'est pas le cas. À partir de notre modèle, nous pouvons voir que la valeur de $\alpha_{ox} - \alpha_m$ est importante, et qu'elle n'a d'influence que dans la plage lorsque la température change. Ainsi, nous utilisons simplement les données et les modifions manuellement pour obtenir de bonnes simulations.

À cette étape, nous avons seulement quatre variables: deux paramètres pour J_{ox} et deux paramètres pour D_{ox} . Si les données expérimentales sont pour différentes températures, nous pouvons utiliser Matlab pour trouver la solution pour l'équation 3.1:

$$(Q_D, D_0, Cste_{J_2}, Q_{J_2}) = Inf_k \left(\sum_j \left\{ \sigma_{exp}(t_j) - \sigma_{th}(t_j; (Q_D, D_0, Cste_{J_2}, Q_{J_2})_k) \right\}^2 \right)$$
(3.1)

Nous devons faire attention qu'il est encore difficile de trouver l'optimisation globale car nous avons modifié certains paramètres manuellement, mais nous pouvons obtenir une bonne simulation.

3.2.2 Optimisation palier par palier

Nous avons expliqué la procédure d'optimisation globale pour les conditions non isothermes. De la procédure, nous pouvons voir qu'il y a beaucoup de paramètres pour les optimiser en même temps, ce qui peut conduire à des difficultés pour obtenir un résultat convergent, avec une signification physique correcte de ces paramètres. Ainsi, une méthode d'optimisation étape par étape a été établie. L'idée principale de cette méthode est d'adapter les paramètres du matériau à une température donnée, de sorte que pour une telle température, il se trouve dans des conditions isothermes et on peut utiliser la méthode de la partie 3.1 pour obtenir un résultat optimisé.

Il y a environ deux étapes principales: la première étape consiste à utiliser la méthode d'optimisation

numérique pour obtenir J_{ox} pour chaque palier de température et D_{ox} pour le premier palier de température. La deuxième étape consiste à utiliser une méthode d'optimisation manuelle pour toutes les données afin d'identifier $\Delta \alpha$.

Dans la première étape, nous utilisons simplement la même méthode décrite dans la partie 3.1 pour le premier palier de température. Nous avons considéré que la température est fixe, c'est donc similaire aux conditions isothermes. A partir du deuxième palier de température, nous avons supposé qu'il n'y a que relaxation, ce qui peut être vérifié par le fait qu'il n'y a pas d'évolution des intensités intégrées et des largeurs pour ces paliers. La croissance de la couche d'oxyde est terminée (pour la température sous le premier plateau $\dot{h}_{ox} = 0$), car elle a été faite à la température maximale (pendant le premier plateau). Pour les autres plateaux, la contrainte de croissance est donc négligeable. De plus, d'un point de vue thermique, les mécanismes correspondants ne sont pas activés. Ainsi, quelle que soit la raison, cela équivaut numériquement à supposer $D_{ox} = 0$ pour le deuxième plateau de température et les suivants. C'est-à-dire, il y a deux paramètres (D_{ox} et J_{ox}) à optimiser au premier palier de température et un seul paramètre à optimiser au second palier de température et aux suivants.

Il y a deux méthode pour identifier le premier palier. L'idée la plus simple consiste à utiliser directement la méthode d'optimisation numérique pour identifier D_{ox} et J_{ox} , simultanément, avec Matlab. Pour ce faire, nous avons répété la même procédure décrite dans la partie 3.1, c'est-à-dire d'abord, nous utilisons la méthode de moyenne adjacente dans le logiciel Origin pour lisser les données expérimentales. Deuxièmement, nous ajoutons 100 points au début de la courbe contrainte / temps pour faciliter l'ajustement du paramètre D_{ox} modélisant le phénomène de croissance. Troisièmement, nous utilisons Matlab pour résoudre l'équation 3.1. Enfin, nous pouvons obtenir le résultat.

L'autre méthode, qui a été proposée, est basée sur le fait que cela devrait avoir une signification physique.

Dans un premier temps, nous utilisons les valeurs J_{ox} obtenues à 700, 800 et 900 ° C pour obtenir une droite et extrapoler la valeur J_{ox} attendue pour 1000 ° C.

Deuxièmement, en ajustant pour le premier palier de température à 1000 ° C, nous fixons le paramètre J_{ox} à la valeur qui a été extrapolée, et nous choisissons d'adapter uniquement le paramètre D_{ox} .

Troisièmement, nous ajustons à nouveau le premier palier de température fixant D_{ox} à la valeur que nous avons trouvé et n'adaptons que le paramètre J_{ox} . C'est-à-dire que nous avons ajusté D_{ox} et J_{ox} un par un, mais nous avons commencé en utilisant la valeur J_{ox} extrapolée. Le but est d'obtenir un ensemble de valeurs qui convergent vers des valeurs plus précises par itérations successives.

Par rapport à la méthode 1, la méthode 2 est plus facile pour trouver les paramètres J_{ox} et D_{ox} avec unesignification physique; alors que lorsque nous utilisons la méthode 1, nous pouvons trouver une solution mathématiquement cohérente qui correspond très bien aux données expérimentales, mais J_{ox} peut ne pas avoir une signification physique correcte.

3.3 Vérification de la cohérence physique des valeurs numériques pour J (T)

Nous avons obtenu les valeurs J_{ox} pour différentes températures, il est alors important de vérifier si elle a une signification physique.

Pour J_{ox} , si nous dessinons la ligne Ln(J(T)) vs $\frac{1}{T}$ pour différentes températures, nous devrions obtenir une ligne droite.

Nous utilisons l'exemple de $Ni_{30}Cr_R4$. Si nous tirons Ln(J(T)) vs $\frac{1}{T}$ pour différentes températures pour la méthode palier par palier et la méthode d'optimisation globale, nous pouvons trouver:



Figure 3.1: Comparaison de la courbe Ln(J(T)) vs $\frac{1}{T}$ pour $Ni_{30}Cr_R4$ en utilisant la méthode

palier par palier et la méthode d'optimisation globale.

À partir de la figure 3.1, nous pouvons voir que la ligne de la méthode palier par palier est fitte mieux les points que celle de la méthode d'optimisation globale. Après avoir recherché la valeur de l'énergie d'activation dans la littérature, nous avons trouvé dans cet exemple que la méthode palier par palier

donne une énergie d'activation (1.2eV) aussi cohérente que la méthode d'optimisation globale (0.88eV), ce qui n'est pas forcément le cas pour tous les échantillons.

Dans certains cas, c'est ainsi que nous confirmons que les paramètres matériaux que nous avons trouvés sont bons ou non. Si l'énergie d'activation que nous avons trouvée n'a pas de signification physique (elle ne correspond pas aux valeurs de la littérature, typiquement inférieure à 0,1 eV ou supérieure à 5 eV), nous sommes sûrs que ce n'est pas une bonne valeur. Sinon, si l'énergie d'activation a une cohérence physique avec la littérature et que l'adéquation aux données expérimentales semble bonne, il est probable que nous ayons trouvé un paramètre matériau correct.

Bien que l'optimisation globale corresponde mieux aux données expérimentales de la courbe contrainte / temps, la méthode palier par palier conduit à des paramètres de signification physique plus cohérente, car elle semble correspondre à un mécanisme d'Arrhenius avec une valeur d'énergie d'activation qui cadre bien avec celles de la bibliographie. Ainsi, nous nous concentrerons principalement sur la méthode palier par palier.

3.4 Identification de $\Delta \alpha$

Un autre avantage de notre modèle est qu'il peut être utilisé pour identifier le coefficient de dilatation thermique $\Delta \alpha$.

Premièrement, nous avons obtenu l'équation pour les paramètres J_{ox} et D_{ox} en fonction de la température de l'ajustement du résultat pour chaque palier de température.

Deuxièmement, nous utilisons la valeur $\Delta \alpha$ dans la littérature comme valeur initiale, et toutes les fonctions pour les paramètres en entrée, pour s'adapter à tous les plateaux de température en même temps.

Si l'ajustement est visuellement différent des données expérimentales, nous changeons la valeur de manuellement (voir Figure 3.2).





4. Résultats d'identification

Dans cette partie, nous présenterons tous les résultats que nous avons obtenus en utilisant la méthode d'identification décrite à la partie 1. Comme discuté à la partie 3, la méthode d'optimisation palier par palier a une meilleure signification physique que la méthode d'optimisation globale. Ainsi, nous allons nous concentrer sur cette méthode palier par palier dans la présente partie.

4.1 Le système NiAl / Al₂O₃

Pour commencer, nous avons choisi le système NiAl / Al₂O₃. On peut trouver de nombreux échantillons avec différents matériaux de base sous divers chargements thermiques dans la littérature. Afin d'utiliser la méthode d'optimisation palier par palier, nous allons nous concentrer sur les échantillons avec des charges non-isothermes.

Nous pouvons trouver les données pour la relaxation de la déformation mesurée sur Ni-50Al dans littérature [16,17]. Après avoir utilisé le numériseur graphique, nous pouvons obtenir les données expérimentales pour les différents paliers:



Figure 4.1: Contrainte mesurée en fonction du temps dans α -Al₂O₃TGO à 1100, 1050, 1000 et 950 °C

Comme décrit dans la partie 3, nous devons d'abord traiter les données pour le deuxième palier de température, qui est le plateau à 1050 ° C.

Après avoir utilisé la méthode d'identification, nous pouvons obtenir les résultats de la simulation comme indiqué dans la Figure 4.2:



Figure 4.2: Ajustement du paramètre J_{ox} et J_m pour α -Al₂ O_3 à 1050 ° C en utilisant différents N_{ox}

Ensuite, il suffit de répéter la procédure pour la température de 1000 ° C et 950 ° C.

Pour le plateau de température à 1000 ° C, nous pouvons obtenir les résultats de la simulation comme indiqué dans la figure 4.3:



Figure 4.3: Ajustement du paramètre J_{ox} et J_m pour α -Al $_2O_3$ à 1000 ° C en utilisant différents N_{ox}

Pour le plateau de température à 950 ° C, nous pouvons obtenir les résultats de la simulation comme indiqué dans la figure 4.4:



Figure 4.4: Ajustement du paramètre J_{ox} et J_m pour α -Al₂ O_3 à 950 ° C en utilisant différents N_{ox}

Enfin, pour le premier palier de température à 1100 ° C, nous disposons de deux méthodes pour l'ajuster.

La première approche consiste à utiliser directement la méthode d'optimisation numérique pour identifier D_{ox} , J_{ox} et J_m simultanément, en utilisant Matlab. Comme décrit à la partie 3, nous avons ajouté arbitrairement quelques points au début de la courbe contrainte / temps pour faciliter l'ajustement du paramètre.

La méthode 2 pour ajuster le premier palier de température est basée sur le fait que $J_{ox}(T)$ devrait avoir une signification physique.

Avec les valeurs J_{ox} de 950, 1000 et 1050 ° C (qui sont les mêmes valeurs utilisées pour la méthode

1), nous pouvons toujours utiliser un ajustement linéaire pour obtenir le $Ln(J_{ox}(T))$ vs $\frac{1}{T}$, puis nous pouvons extrapoler le valeur à des températures plus élevées, telles que 1100 ° C.

Par rapport à la méthode 1, pour Nox = 1, la méthode 1 et la méthode 2 donnent un résultat comparable (3.22eV et 2.94eV respectivement), tandis que pour Nox = 2, une plus grande différence se produit (2.66eV et 3.86eV respectivement). Si nous rassemblons toutes les énergies d'activation ensemble, nous pouvons obtenir:



Figure 4.5: Comparaison des énergies d'activation en utilisant différents Nox et méthodes, avec des valeurs d'une publication [17]

Par rapport à l'énergie d'activation trouvée dans la publication, on pourrait dire que Nox = 1 a une déviation relative plus faible. En comparant la méthode 1 et la méthode 2, nous pouvons voir que la

méthode 1 a un écart relatif plus petit, mais la linéarité de $Ln(J_{ox}(T))$ vs $\frac{1}{T}$ de la méthode 2 est

meilleure. Il est difficile de dire quelle méthode est la meilleure dans ce cas.

4.2 Le système NiCr/Cr₂O₃

Nous considérons maintenant la méthode d'identification en utilisant nos propres données expérimentales. En effet, des expériences ont été menées à l'installation européenne de rayonnement synchrotron (ESRF) pour le système NiCr / Cr_2O_3 contenant ou non Y_2O_3 en tant qu'élément réactif.

4.2.1 Différentes sollicitations thermiques

Pour les sollicitations thermiques, nous avons considéré 9 différents types de sollicitations thermiques, listés dans le tableau 4.1:

Code	Temperature (°C)					
R4	1000(3h)	900(3h)		800(3h)		700(3h)
R13	1000(3h)		850(3h)			
R2		900(3h)		800(3h)		700(3h)
R11		900(3h)	850(3h)	800(3h)	750(3h)	
R15			850(3h)	800(3h)	750(3h)	700(3h)
R3				800(3h)		700(3h)
R14	1000(7.4h)					

R10	900(7.4h)		
R16		800(7.4h)	

Tableau 4.1: Différents types de sollicitations thermiques pour les expériences effectuées à l'ESRF

Après avoir utilisé la méthode d'identification, on peut obtenir:



Figure 4.6: Ln(Jox) vs 1/T pour tous les échantillons ci-dessus avec Nox = 1 (à gauche) et Nox = 2 (à droite)

Nous pouvons voir sur la figure 4.6 que pour une température donnée, il existe de nombreuses valeurs différentes de Ln (Jox); ceci est dû au fait que la microstructure est différente au cours du premier palier de température avec des températures initiales différentes. C'est-à-dire que lorsque les températures pour les premiers plateaux de température sont différentes, les microstructures des couches d'oxyde sont différentes. Ainsi, afin d'obtenir l'énergie d'activation pour une microstructure spéciale, nous devrions fixer les températures pour les premiers plateauxes pour les premiers plateauxes pour les premiers plateauxes de températures d'activation pour une microstructure spéciale, nous devrions fixer les températures pour les premiers plateauxes.

Pour microstructure construite à 1000 ° C, on peut obtenir :



Figure 4.7: Ajustement linéaire pour $Ni_{30}Cr_R4$ et $Ni_{30}Cr_R13$ avec Nox = 1 (à gauche) et Nox = 2 (à droite) après avoir supprimé certains points

En comparant avec la valeur obtenue de la publication de Tsai et Huntz et de la thèse de F. Rakotovao, on peut voir que les valeurs d'énergie d'activation pour Nox = 1 (1.2eV) et Nox = 2 (1.6eV) sont bien comparables. Par exemple, dans la thèse de F. Rakotovao, elle a trouvé 1,347eV. Dans cette thèse, en comparant avec les valeurs de la publication de Tsai et Huntz, F. Rakotovao a identifié le mécanisme qui peut régir le fluage par diffusion comme diffusion intergranulaire des anions d'oxygène (interstitiels ou lacunes).

Après avoir essayé de répéter la même procédure pour les microstructures construites à d'autres températures, nous n'avons pas pu obtenir un ajustement linéaire pour le Ln (Jox) vs 1 / T. Ainsi, nous n'avons pas pu obtenir une valeur d'énergie d'activation valide pour les microstructures construites à d'autres températures.

Puisque nous pouvons obtenir une énergie d'activation valide pour la microstructure construite à 1000 °C, nous allons nous concentrer sur ce premier palier de température et l'utiliser dans le cas où un élément réactif est ajouté à l'alliage.

Comparaison entre Nox = 1 et Nox = 2

En comparant la procédure d'ajustement pour Nox = 1 et Nox = 2, nous pouvons voir que parfois Nox = 1 correspond mieux aux données expérimentales, mais parfois Nox = 2 fait mieux. Si nous comparons l'ajustement linéaire pour Ln (Jox) vs 1 / T et aussi l'énergie d'activation, nous pouvons voir que l'énergie d'activation est toujours comparable. Pour obtenir une simulation des résultats, on montre que l'on peut choisir Nox = 1 ou Nox = 2 en fonction de l'ajustement des données expérimentales, et enfin on peut obtenir une énergie d'activation robuste quel que soit le choix de Nox.

Discussion sur Dox

Nous avons suggéré à la partie 1 que la valeur de Dox devrait être fonction de 1 / T. Ainsi, nous pouvons dessiner Dox vs 1 / T pour Nox = 1 et 2, comme le montre la Figure 4.8:



Figure 4.8: Dox vs 1/T pour Nox=1(à gauche) and 2(à droite)

Dans la figure 4.8 (droite), la valeur Dox pour R2 lorsque Nox = 2 est très élevée (avec un ordre de 10⁷) et très éloignée de la valeur Dox trouvée pour les autres échantillons ayant le même premier plateau de température (R10 et R11) ; nous l'avons enlevé.

Nous ne pouvons pas voir de linéarité à partir de la figure 4.8. Cela peut être dû au manque de valeurs Dox, car nous n'avons que des valeurs Dox pour le premier palier de température. Pour une température donnée, avec différentes méthodes et différentes charges thermiques, nous avons différentes valeurs de Dox.

On peut voir sur la figure 4.8 que pour les échantillons ayant le premier palier de température à 1000 ° C, c'està-dire R4, R13 et R14, la valeur de Dox est proche pour la méthode 1 avec Nox = 1. Alors que nous avons seulement une valeur pour la méthode 2, nous ne pouvons donc pas comparer avec d'autres points. Pour les échantillons ayant le premier palier de température à 900 ° C, soit R2, R10 et R11, on peut voir que les valeurs Dox pour la méthode 1 sont plus grandes que pour la méthode 2, ce qui est la même tendance pour R15 avec plateau de température à 850 ° C. Pour les échantillons ayant le premier palier de température à 800 ° C, c'està-dire R3 et R16, on peut voir une grande différence pour R3 et R16 en utilisant la même méthode (méthode 1). Nous pouvons conclure que pour un premier palier de température donné (la même microstructure), une méthode donnée et un Nox donné, la valeur de Dox a presque le même ordre. Deuxièmement, lorsque le premier palier de température diminue, la valeur de Dox reste au même ordre de 10⁴; il est difficile de voir une tendance pour la valeur de Dox.

4.2 Différents matériaux avec les mêmes sollicitations thermiques

Afin de connaître l'influence des éléments réactifs sur les propriétés mécaniques des couches de chromine, nous avons réalisé une série d'expériences en utilisant un élément réactif. Ce dernier a été introduit en utilisant différents temps d'exposition dans une chambre de PVD afin de faire varier la quantité de Y₂O₃ dans l'alliage. Les substrats métalliques sont toujours Ni-28Cr.

La sollicitation thermique pour l'échantillon Ni28Cr avec des temps d'exposition différents est toujours la même, comme indiqué à la figure 4.9:



Figure 4.9: Sollicitation thermique pour l'échantillon Ni28Cr avec différents temps d'exposition

Afin d'appeler l'échantillon plus facilement, nous avons donné des noms de code pour l'échantillon Ni28Cr avec une quantité différente de Y2O3:

code	Eléments réactifs
R34	Y_2O_3 $t=10s$
R38	Y_2O_3 $t = 50s$
R32	Y_2O_3 t = 100s

Tableau 4.1: Nom de code de l'échantillon Ni28Cr avec différents temps d'exposition

Après avoir utilisé la même procédure décrite ci-dessus (méthode palier par palier), nous pouvons enfin dessiner le Ln (Jox) vs 1 / T pour Nox = 1 et 2 comme montré dans la Figure 4.10 et la Figure 4.11:



Figure 4.10: Ln(Jox) vs 1/T pour R32, R34 et R38 avec Nox=1



Figure 4.11: Ln(Jox) vs 1/T pour R32, R34 et R38 avec Nox=2

Nous pouvons voir clairement que la pente de la ligne Ln (Jox) vs 1 / T pour R32, R34 et R38 change à la fois pour Nox = 1 et Nox = 2. Ainsi, on peut considérer que la présence d'élément réactif semble avoir une influence sur le mécanisme de diffusion-fluage dans la couche d'oxyde.

La valeur de l'énergie d'activation varie en fonction des différentes méthodes d'optimisation et des différents Nox, comme indiqué à la figure 4.12:


Figure 4.12: Résultats de la valeur de l'énergie d'activation en utilisant différentes méthodes et différents Nox

Afin d'obtenir l'évolution de l'énergie d'activation par rapport au contenu de Y_2O_3 et de comparer avec les résultats de la thèse de F. Rakotovao, nous avons calculé la valeur moyenne des énergies d'activation pour les différentes méthodes et différents Nox.

Si nous tirons l'énergie d'activation moyenne calculée à partir de la ligne Ln (Jox) vs 1 / T vs temps d'exposition, nous pouvons obtenir :



Figure 4.13: Illustration de l'énergie d'activation par rapport au contenu de Y2O3

Nous avons utilisé comme échantillon de référence sans élément réactif. A partir de la figure 4.13, on voit clairement que la quantité d'élément réactif Y_2O_3 modifie l'énergie d'activation associée au mécanisme de diffusion-fluage dans les couches de chromine.

Si nous établissons un ajustement linéaire pour l'énergie d'activation en fonction du temps d'exposition de l'élément réactif Y_2O_3 , nous pouvons obtenir un ajustement linéaire du R^2 égal à 0,9, ce qui peut indiquer que le temps d'exposition change l'énergie d'activation assez linéairement. Il y a

beaucoup de publications qui ont prétendu que l'élément réactif peut changer le mécanisme de croissance dans la couche d'oxyde, mais à notre connaissance, un tel changement linéaire n'a jamais été observé. Cependant, il peut exister une incertitude lors du calcul de l'énergie d'activation en utilisant les différentes méthodes d'optimisation et les différentes valeurs Nox, et nous avons calculé une valeur moyenne et obtenu finalement un ajustement quasi linéaire pour l'énergie d'activation vs Y_2O_3 .

En comparant avec les résultats de la thèse de F. Rakotovao, l'auteur a découvert que l'énergie d'activation ne change pas pour les teneurs inférieures en Y_2O_3 de l'alliage (quand le temps d'exposition est de 10s et 50s), en ayant la même énergie d'activation (environ 1,35 eV) que sans élément réactif. Ce n'est que lorsque la teneur en Y_2O_3 est maximale (lorsque le temps d'exposition passe à 100s) que l'énergie d'activation change brusquement à 2,073 eV, ce qui indique le changement du mécanisme dominant le transport des espèces pendant la procédure de fluage. Alors que dans le cas présent, une variation continue de l'énergie d'activation est obtenue. Ainsi, qualitativement, l'énergie d'activation est obtenue pour la matière première, mais la valeur finale de l'énergie d'activation est un peu différente. Cependant, les deux analyses semblent démontrer le changement de mécanisme qui régit le mécanisme de diffusion-fluage. Il faut rappeler que l'analyse des données expérimentales n'a pas été faite de la même façon dans les deux travaux.

Discussion sur Dox

Nous pouvons également tracer la valeur du contenu Dox vs Y2O3, comme indiqué dans la Figure 4.14:



Figure 4.14: Illustration de la valeur de Dox par rapport au contenu de Y2O3 pour Nox = 1 (à gauche) et Nox = 2 (à droite)

Dans la figure 4.14, parce que la valeur Dox pour R4 en utilisant la méthode 1 est trop élevée (avec l'ordre 5x10⁴), nous ne pouvions pas le voir.

À partir de la figure 4.14, nous pouvons voir que lors de l'utilisation de la méthode 1, la valeur de Dox diminue lorsque le temps d'exposition augmente à la fois pour Nox = 1 et Nox = 2. Alors que pour la méthode 2, la valeur Dox semble garder la même valeur. Comme il est supposé que la valeur de Dox est liée à la croissance de la couche d'oxyde, pour laquelle le mécanisme est modifié avec l'apport d'éléments réactifs, il est assez probable que la valeur de Dox change avec la teneur en Y₂O₃. Ainsi, le résultat de la méthode 1 peut être meilleur que celui de la méthode 2 pour Dox. On peut également voir sur la figure 4.14 que la valeur de Dox pour le matériau sans élément réactif est environ 10 fois plus grande que celle avec l'élément réactif. Cela peut être dû au fait que la présence d'un élément réactif ralentit la cinétique d'oxydation. L'addition d'éléments réactifs modifie la vitesse à laquelle les

réactifs sont transportés à travers la couche d'oxyde pour ralentir les espèces diffusantes dominantes et ainsi réduire la vitesse d'oxydation.

Conclusion

Dans le présent travail de recherche, la croissance de l'oxyde et les contraintes associées à l'oxydation à haute température sont étudiés. L'objectif principal est d'établir un modèle pour identifier les paramètres mécaniques sous sollicitations thermiques lorsque la température change, afin d'améliorer la compréhension des mécanismes conduisant au développement et à la relaxation des contraintes dans la couche d'oxyde développée lors de l'oxydation à haute température. Deux oxydes différents, l'alumine et la chromine, soumis à différentes sollicitations thermiques (sollicitations isothermes et non isothermes) sont étudiés et utilisés comme données expérimentales. Les derniers sont utilisés pour identifier les paramètres mécaniques du matériau, qui sont comparés à ceux obtenus à partir des publications. Ce travail établit un modèle prenant en compte différents comportements de matériaux (élasticité, visco-plasticité, déformation de croissance dans la couche d'oxyde et dilatation thermique) pour décrire la réponse du matériau lors de l'oxydation à haute température. Il nous conduit à nous concentrer sur l'influence des paramètres matériaux sur le développement et la relaxation des contraintes dans les couches d'oxyde lors de leur croissance à haute température.

Un modèle est développé pour décrire la réponse du matériau lors de l'oxydation à haute température. Pour établir ce modèle, d'une part, des hypothèses sont faites pour en déduire une équation d'équilibre des forces et une équation de continuité des déplacements. Deuxièmement, différents comportements de matériaux (élasticité, visco-plasticité, déformation de croissance dans la couche d'oxyde et dilatation thermique) sont considérés. Enfin, une équation différentielle ordinaire (ODE) est déduite. Afin d'obtenir une solution analytique, trois chargements thermiques spécifiques sont supposés: isotherme, chargement thermique par paliers et chargement thermique périodique. Pour l'état isotherme, un temps caractéristique et une valeur de contrainte minimale ont été obtenus en utilisant une nouvelle procédure. Une comparaison a également été faite avec les valeurs de la littérature. Pour le chargement thermique par paliers, la méthode de transformation de Laplace a été proposée pour résoudre l'équation différentielle ordinaire. Avec quelques hypothèses supplémentaires, une équation est déduite pour identifier quand la température change. Cela offre une nouvelle façon d'identifier la non-concordance des paramètres de dilatation thermique entre métal et oxyde. Pour le chargement thermique périodique, une nouvelle méthode innovante est proposée, à savoir la méthode d'analyse de fréquence. Afin d'obtenir une solution numérique, la méthode Runge-Kutta est utilisée et discutée. L'influence de différents pas de temps est discutée et une conclusion attendue est tirée que l'influence du pas de temps est négligeable tant qu'elle est choisie relativement petite.

Des expériences ont été réalisées sur la ligne BM02 de l'ESRF (European Synchrotron Radiation Facility) de Grenoble, en raison de son flux élevé, de son énergie accordable, de son goniomètre disponible et de son détecteur 2D disponible. La diffraction par rayonnement synchrotron couplée à un four à induction a été mise en œuvre pour réaliser des mesures continues lors de l'oxydation à haute température dans les couches de chromine. L'utilisation du rayonnement synchrotron et du détecteur 2D permet de réaliser des mesures de diffraction de haute qualité avec une dynamique élevée, correspondant à des temps d'acquisition relativement courts. Les conditions d'oxydation explorées sont généralement celles appliquées dans les travaux antérieurs réalisés par Kemdehoundja et Guérain. En général, ces couches d'oxyde ont été développées entre 700 °C et 1000 °C pour des temps d'oxydation allant de 3 heures à 40 heures. La vitesse de refroidissement a été fixée à 150 °C/ min pour minimiser l'activation des mécanismes de relaxation des contraintes pendant les étapes de refroidissement. La procédure de traitement des données expérimentales à partir d'images capturées par un détecteur 2D menant à une courbe contrainte-temps pour la couche d'oxyde a été détaillée et expliquée progressivement. Enfin, les trois sources principales (position de l'échantillon, calibration et

ajustement des pics) des incertitudes ont été expliquées et calculées pour quantifier les limites de notre approche expérimentale.

Les méthodologies d'identification ont été présentées en détail pour les conditions isothermes et les conditions non isothermes. Pour les conditions isothermes, un exemple a été fait pour expliquer la méthode mise en place par Panicaud et al. Pour les conditions non isothermes, deux méthodes (optimisation globale et optimisation étape par étape) ont été proposées, discutées et comparées. L'optimisation globale tente d'identifier tous les paramètres du matériau en même temps en utilisant toutes les données expérimentales de différents paliers de température. Tandis que la méthode d'optimisation étape par étape essaye d'abord d'identifier uniquement Jox et Dox pour une température fixe en utilisant les données expérimentales d'un seul palier de température, puis d'utiliser la méthode d'optimisation manuelle avec toutes les données expérimentales pour identifier $\Delta \alpha$. Bien que la méthode d'optimisation globale corresponde mieux aux données expérimentales de la courbe contrainte-temps, la méthode pas à pas conduit à des paramètres plus pertinents physiquement, car ils correspondent à un comportement d'Arrhenius avec des valeurs d'énergie d'activation qui concordent bien avec ceux de la bibliographie. Ainsi, nous avons choisi la méthode étape par étape pour identifier les données expérimentales.

Certaines données expérimentales, qui peuvent être utilisées pour identifier les paramètres matériels, ont été présentées. Il s'agit principalement des données expérimentales pour le système NiAl / Al₂O₃ qui ont été trouvées dans les publications, et pour le système NiCr / Cr₂O₃ provenant des expériences réalisées sur la ligne de faisceau BMO2 à l'ESRF. Pour le système NiAl / Al₂O₃, un exemple spécifique de sollicitation thermique a été choisi. Après avoir utilisé la méthode étape par étape, l'énergie d'activation a été trouvée, ce qui est comparable à celle trouvée dans les publications. Pour le système NiCr / Cr₂O₃, neuf sollicitations thermiques différentes, correspondant à quatre microstructures différentes initialement construites, ont été utilisées. A partir de la valeur de l'énergie d'activation, le mécanisme du comportement au fluage a été identifié. De plus, afin de connaître l'influence des éléments réactifs sur les propriétés mécaniques des couches de chromine, une série d'expériences utilisant l'élément réactif Y₂O₃ avec des quantités différentes dans l'alliage a également été présentée. Après avoir utilisé la méthode d'identification, nous avons constaté que la présence de cet élément réactif dans l'alliage NiCr semble modifier linéairement l'énergie d'activation. Pour autant que nous sachions, c'est la première fois qu'une telle influence linéaire est trouvée.

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Zhaojun TAO Doctorat : Matériaux, Mécanique, Optique et Nanotechnologie Année 2018

Etude expérimentale et modélisation des caractéristiques mécaniques d'une d'oxvde couche SOUS charges thermiques

La qualité des couches protectrices d'oxyde thermiques se développant à haute température à la surface des matériaux métalliques dépend des niveaux de contraintes générées et de leurs mécanismes de relaxation. Dans ce travail, un modèle et un outil d'identification ont été développés afin d'étudier l'évolution des contraintes dans les systèmes métal / oxyde sous charge thermique, ainsi que l'identification du mécanisme et des propriétés des matériaux. Le modèle est appliqué en utilisant les données expérimentales fournies par la littéra-ture pour le système NiAl/Al203. La valeur de l'énergie d'activation est comparée à celle des publications, afin de valider notre méthode. L'évolution des contraintes des couches de chromine formées sur Ni30Cr et Ni28Cr ont pu être mesuré par diffraction in situ à haute température sur rayonnement Synchrotron, en découplant les effets liés à l'activation thermique de ceux liés à la taille de grain. La valeur de l'énergie d'activation associée (environ 1,4 ev) a montré, par comparaison avec les données de la littérature, que ce mode non destructeur de relaxation est gouverné par le transport des anions d'oxygène aux joints de grains de l'oxyde. Lorsque l'élément réactif Y2O3 a été ajouté au substrat métallique Ni28Cr, un changement linéaire de l'énergie d'activation a été noté lors de l'augmentation de la quantité d'élément introduit. Pour autant que nous le sachions, c'est la première fois qu'une influence linéaire est trouvée.

Mots clés : oxydation - simulation par ordinateur rayons X, diffraction - nickel, alliages - matériaux, propriétés mécaniques.

Experimental Study and Modelling of Mechanical Features in an Oxide Layer under Thermal Loadings

The quality of protective oxide scales developing at the metallic alloys surface at high temperature depends on the stress generation and relaxation mechanisms. In this work, a model and a related identification tool have been developed in order to investigate the stress evolution in the metal/oxide systems under thermal cycling loadings, along with the identification of mechanism and materials properties. The model is applied using the experimental data providing from literature for the system NiAl/Al2O3. The value of activation energy is compared with that in the publications, in order to valid our method. In situ high temperature oxidation coupled with Synchrotron X-rays diffraction was used to measure the stress evolution of chromia scales grown on Ni30Cr and Ni28Cr, with dissociating the effects related to thermal activation and grain size. Confrontation of the obtained activation energy (around 1.4ev) with literature results has shown that the creep was likely governed by grain boundary transport of oxygen species. When the reactive element Y2O3 was added to the metallic substrate Ni28Cr, a linear change of the activation energy was noted when increasing the amount of introduced element. As far as we know, this is the first time that a linear influence is found.

Keywords: oxidation - computer simulation - X-ray, diffraction - nickel, alloys - materials, mechanical properties.

Thèse réalisée en partenariat entre :







Ecole Doctorale "Sciences pour l'Ingénieur"