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Solute clustering in multicomponent aluminium alloys

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Preface and contribution of authors

As the first author of the four manuscripts included within this thesis, I prepared all of the samples, ran the majority of experiments and performed a significant portion of the analysis and writing of the manuscripts.

This work would not have been possible without the endless technical and scientific advice from both my supervisors, Dr. Frédéric De Geuser and Dr. Alexis Deschamps. The countless hours of dedication and support given Dr. Frédéric De Geuser result in the concept of solute clusters as fluctuations in solute concentration which is a theme throughout the thesis. He is the author behind the model used for interpretation of the small angle scattering data. Significant contribution to the discussion and global view of clustering and its kinetics comes from Dr. Alexis Deschamps. In particular, he suggested investigating the effect of reversion on the clustering kinetics.

Atom probe tomography experiments were performed at the University of Rouen with the help of Dr. Williams Lefebvre and Dr. Ivan Blum under the framework of 2 calls for projects with the French METSA network.

Dr. Christophe Sigli from Constellium C-TEC Voreppe, France, provided the materials studied and contributed to the discussion of the results.

1 Introduction

A. Wilm's discovery of age hardening in aluminium 1904 [1,2] inspired research on how aluminium alloys gain strength – a concept instrumental for developing the Aluminium industry. A breakthrough came in 1938 when a structure contributing to age hardening of aluminium was reported by A. Guinier and G.D. Preston in an Al-Cu alloy using X-ray diffraction [3,4]. The precipitation of a new phase from a super saturated solid solution is the base for this hardening. Alloys whose strength is in part attributed to formation of precipitates from the added solutes (alloying elements) have been termed age hardening alloys. Naturally, the extensive theoretical research into the field of aluminium and its alloys led to a better understanding of how to obtain and optimize desired products. Today, Aluminium alloys can be designed to meet specific requirements for being light weight, corrosion resistant, malleable, have useful mechanical properties while remaining affordable. The possibility to fully recycle sets of alloys increases the value of Aluminium with respect to the environment. The age hardened alloys have been the backbone material for the transportation industries with wide applications from automotive body panels to space vehicles. Of course, other common uses of Aluminium alloys exist such as packaging.

The formation of second phase particles during age hardening can be essentially summarised as follows:

- A super saturated solid solution is obtained by solution heat treatments. In this state, the majority of alloying elements (e.g. Cu, Si, Mg, Li, Ag) are distributed near randomly. In addition, an above equilibrium concentration of vacancies exists. After quenching to room temperature, this solid solution becomes thermodynamically metastable.
- 2) This metastable random supersaturated solid solution decomposes into a more organised structure. Secondary phases composed of solutes are formed through vacancy aided diffusion. The reactions are driven by the material's aim to reduce its internal energy and organise in a more stable configuration.

The sequence of events that occur during age hardening is strongly dependent on the alloying elements and their ability to diffuse in the solid solution. The ever-growing demand for specific property sets has increased the chemical and processing complexity of alloys resulting in more diverse precipitates.

The characterisation of precipitates, their formation mechanisms and contributions to properties remains an active topic for research. Global bulk indirect techniques such as electrical resistivity and differential scanning calorimetry (DSC) complimented with mechanical measurements such as hardness tests provide evidence for the precipitation reactions taking place. Diffraction methods, such as X-ray diffraction, help characterize the crystalline structure of precipitates. More specific diffraction or scattering method such as small-angle scattering (SAS), are capable of characterizing the shape and quantity of precipitates from a bulk average perspective. The increasing power of local direct techniques makes it possible to explore at smaller and finer

scales. Electron microscopy with near atomic resolution, has served as a loyal tool for characterizing the structures, shapes and sizes of isolated observable precipitates. In recent years, atom probe tomography (APT) has provided a deeper look at the chemical arrangement at the atomic scale. These techniques provide snap shots of the microstructure along the ageing path of a material; however, questions concerning the mechanisms and kinetic nature of age hardening arise.

One such challenge is posed by the evolution of hardness of a super saturated solid solution at room temperature. The process is termed 'natural ageing' and occurs in most alloys. The striking difference between 'natural' and 'artificial' ageing is the temperature at which secondary phases are formed. Proposed theoretical explanations involve sub-nanometer solute rich regions forming over time through vacancy aided solute diffusion. These objects are very small and remain coherent with the aluminium crystal, yet their presence obstructs the motion of dislocations and affects mechanical properties. The term 'solute clusters' has become a staple for describing the solute distributions after natural ageing. From an experimental point of view, observation of such objects is not readily achieved by electron microscopy. Solute rich objects can be detected and identified using APT; however, the presence of vacancies within clusters or their association with them is not accessible. Positron annihilation, which is sensitive to the local environment around vacancies, provides further insight to the solute vacancy interactions. Numerical calculations and modelling maybe another approach towards validating the solutevacancy interactions albeit robust and accurate interaction potentials are necessary. Synergetic combinations of experimental methods, theoretical hypotheses and numerical simulations are required to quantitatively analyse and provide a deeper understanding of natural age hardening in aluminium.

1.1 **Definition of 'solute clusters'**

The term 'solute' describes any element added to a host 'solvent/matrix'. The solvent/matrix is aluminium in our case. The most common solutes added to Al are Cu, Si, Mg, Zn and Li. The term 'cluster' suggests a group of solutes situated closely together. These definitions, however, can not separate groups of solute atoms that are fortuitous and solely due to the discrete nature of the distribution of solutes in the matrix to those that are forming due to the solid solution decomposition. It seems then reasonable to adopt a more statistical approach to the notion of clustering. Hence, for the purpose of this document we will define the term as follows:

'Solute clusters are chemical fluctuations of a non-random solid solution.'

The nature of this term makes it very encompassing and covers several types of chemical fluctuations. For example, precipitates, which are the primary strengthening phase sought after in many aluminium alloys, would fit this description. However, they have additional important criteria such as significantly tighter stoichiometry and often having a different crystal structure from the host. It is therefore important to make a distinction, that despite solute clusters and precipitates both fitting the above description, this document focus on clusters. Clusters are of great importance as they may exist before any precipitation has taken place and involve solutes necessary for precipitation.

1.2 Thesis approach

The objective of this research project is to address the formation of solute clusters in multicomponent Aluminium alloys. In order to address the complexity of solute interactions in an alloy with a high number of solutes, we have chosen to study in parallel the combination of lower order alloys. In the specific case of the alloy of interest Al-Cu-Li-Mg, we therefore have studied in addition the Al-Cu-Mg and Al-Cu-Li systems, in the aim to better understand the individual solute interactions between Cu, Mg and Li within Al. This study has been undertaken by characterising clusters with respect to their quantity, chemical content and thermal stability. The kinetics of clustering are investigated using in-situ experiments and connections between solutes and excess vacancies available for diffusion are established. The crucial effects of specific alloying elements on clustering and its kinetics are made evident by the post reversion ageing behaviour of alloys. The results are summarised under the following structure with each chapter designed to become a stand-alone publication:

• A combined characterisation of clusters in naturally aged Al-Cu-(Li, Mg) alloys using small-angle neutron and X-ray scattering and atom probe tomography

We develop an interpretation model for the contrast in small-angle scattering (SAS) arising from solute concentration fluctuations - clusters. The model effectively captures the scattering from clusters in the Al-Cu-Mg, Al-Cu-Li and Al-Cu-Li-Mg systems using two complementary radiations – neutrons and X-rays. We take advantage of the differences in scattering factor for specific alloying elements with respect to the radiation used to provide information on the specific solute species in clusters. The results are complimented and compared with atom probe tomography (APT) and show promising agreement in terms of the Mg/Cu ratio of solute clusters in the alloys.

• Clustering kinetics during natural ageing in Al-Cu-(Li, Mg) alloys

The kinetics of solute clustering are characterised through the evolution of intensity during insitu SAS using both neutrons and X-rays, differential scanning calorimetry (DSC) and microhardness experiments. Applying the previously proposed interpretation model reveals the complex interplay between solutes during clustering. The critical role of Mg for the abundant formation of Cu rich clusters is made evident. DSC results suggest that several solute cluster families are likely to co-exist in the more complex alloys.

• Thermal stability and post-reversion formation of solute clusters in Al-Cu-(Li, Mg) alloys

The hypothesis of plural cluster families is tested through ramp heating in-situ SAS and DSC experiments. Excellent correlation between temperature and changes to intensity and heat flux

confirm the multitude of cluster types present in the natural ageing condition. Using the chemical information accessible through in-situ SAS experiments, dissolution of cluster families is identified with Cu rich clusters dissolving at lower temperature followed by those containing both Cu and Mg. Dissolution of selected cluster families is achieved by short isothermal reversion treatments and the post-reversion formation of clusters is analysed. Dissolution of Cu-Mg rich clusters at 250 °C creates a super saturated solid solution that decomposes with comparable kinetics as that obtained after quench from 500 °C. A link between Mg and excess vacancies available for diffusion is proposed.

• The effect of Mg concentration on clustering in Al-Cu-Li-Mg alloys

In this section, we revisit the natural ageing kinetics of the Al-Cu-Li and Al-Cu-Li-Mg alloys with a focus on the Mg concentration. A Mg diffusion couple between a Mg rich and a Mg free alloy is analysed by time and space resolved in-situ SAS with X-rays, and complimented by DSC and micro-hardness. An excellent correlation between the solute clustering kinetics and the Mg concentration is shown. In the fully clustered state, the quantity of clusters and the micro-hardness match the Mg concentration gradient. As soon as any Mg is present in the solution it accelerates the clustering of Cu. The link between Mg and vacancies available for diffusion is evidenced.

Links are established between the principal chapters described above. Each chapter holds its own conclusion and discussion. A global summary taking into consideration the findings of all chapters is given at the end of this manuscript.

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2 Literature review

Age hardened aluminium alloy systems are members of the 2xxx, 6xxx and 7xxx series designated by the Aluminium Association. Alloys primarily alloyed with Copper (Cu) are classified as the 2xxx series. Other minor alloying elements such as Magnesium (Mg) are common additions to these alloys as they affect precipitation positively. Lithium (Li) additions made to Al-Cu series result in a rare and much desired simultaneous density reduction and strength increase [1,2]. No other elements (aside from Beryllium-Be which is highly toxic) yield such results. Formation of a high number density of T_1 (Al₂CuLi) secondary precipitate phase lies at the origin of the increase in strength [3]. Precipitation strengthened Al-Cu-Li alloys are often used for structural applications in the aerospace industry [4].

The 6xxx series are alloyed with both Magnesium (Mg) and Silicon (Si). These alloys present a balance between medium strength, good formability and high toughness allowing them to be formed effectively into products which can be strengthened through precipitation post shaping (bake hardening effect) [9,10]. These alloys find extensive use in the automotive industry as in the recent 'full Aluminum' body Ford F150 [7]. The 7xxx series on the other hand, are among the strongest Aluminium alloys when precipitation hardened. These alloys are primarily alloyed with Zn and Mg. The primary strengthening come from the formation of Zn and Mg rich precipitates during artificial ageing ($\eta' - MgZn_2$). Copper (Cu) is a common further addition resulting in higher strength and density of the η' phase [8]. Rolled plates, extruded or forged structure from alloys such as the 7075 and 7050 are commonly used in the aeronautical industry.

2.1 A solid solution and the basics of precipitation

The precipitation from a solid solution and related changes to mechanical properties have been widely investigated from both experimental and theoretical viewpoints. Continuous precipitation sequences through a cascade of metastable phases are often proposed as a kinetic path followed by the material [9–19]. The starting point is always a solid solution. To obtain such a solid solution an alloy of chemical composition X_0 is heated to temperature T_α in the α region as shown in the equilibrium phase diagram (Figure 1). Holding the system long enough for diffusion effects to equilibrate the solute will dissolve and form a homogeneous phase α . The distribution of solute in this state at thermodynamic equilibrium is random and the vacancy concentration is high due to the elevated temperature. Quenching involves the rapid cooling of a sample from this single-phase region to the two-phase region $\alpha + \beta$ with the aim of freezing the system. A frozen system is referred to be a super saturated solid solution (SSSS) as the concentration of B is above the equilibrium. Such a solution will likely decompose over time towards the more stable equilibrium $\alpha + \beta$ phases.



Figure 1 Schematic illustration of a binary equilibrium phase diagram

The driving force for decomposition of a SSSS comes from the high Gibbs free energy of the system in its frozen state. This energy is progressively reduced by changing the organisation of solutes from near random state to more structured through the nucleation of precipitates which classically have a volume V and a surface area A. Nucleation can be a self-induced process in the matrix, homogeneous, or initiated at defects in the matrix such as dislocations, heterogeneous. Independent of the mode of nucleation the reduction in free energy imposes a critical size for nucleation and a corresponding energy barrier. In the simplest case of homogeneous nucleation of a spherical object with volume $V = \frac{4}{3}\pi r^3$ and area $A = 4\pi r^2$ make it such that a critical radius and energy can be schematically represented as in Figure 2.



Figure 2 Change in energy (ΔG) versus size (r) indicating the critical size (r*) and activation energy (ΔG^*) for classical nucleation. Adapted from [20]

The path a real system takes to reduce its high energy SSSS is in reality strongly dependent on many factors such as the types of solutes, interactions between solutes and interactions with other microstructural features such as vacancies and dislocations. To visualise this path in a multi-component system, one can imagine a landscape with valleys and peak as a representation of the energy field. Peaks would indicate high and unstable positions whereas valleys are more stable. The precipitation sequence is the route a system takes from a peak down to a lower position. During the initial stages of decomposition, a solid solution can stagnate at local minima termed metastable states. Theoretically, if sufficient time is present the system will overcome such local minima and reach its most stable position, the equilibrium. In practice, local minima are overcome by additional energy from external sources like deformation (dislocation movements) and heating during artificial ageing.

Designs of thermo-mechanical processing routes aim to tune local minima and the barriers they pose for precipitation. For example, deformation before artificial ageing has been shown to positively affect the precipitation of the desired T_1 (Al₂CuLi) phase in Al-Cu-Li-X alloys [21–23]. Dislocations help nucleate the precipitates through solute segregation and speed up kinetics [24,25]. An example where thermo-mechanical processing can be used to mitigate a negative effect of metastable state on precipitation comes from the Al-Mg-Si alloys [26,27]. These systems reach a metastable state during room temperature exposure where Si rich solute cluster dominate the microstructure. These clusters limit the number of solutes available for precipitation. To counter such effects, pre-ageing heat treatments are applied where more favourable Si-Mg rich clusters are made dominant [19,28,29].

Alloy design, with respect to the chemical composition, remains as the most basic strategy to fine tune the energy landscape of a system. Two recent examples are highlighted. Additions of Mg to Al-Cu-Li systems profoundly affect the behaviour of Cu leading to segregation of solute on dislocations during heating to precipitation temperatures. These segregates accelerate T_1 (Al₂CuLi) precipitation [25]. Addition of Sn to Al-Si-Mg alloys plays a critical effect on the clustering of Si. The high binding energy and suitable solubility of Sn, reduce excess vacancies in the SSSS and significantly retards Si cluster formation while allowing for precipitation of desired phases at higher temperature [30,31].

2.2 Solute clusters

Mechanical properties of age hardening alloys evolve if a SSSS is left to age at room temperature. An increase of hardness after quench from solution temperature was first reported by A. Wilm more than a century ago [32]. The evolution of hardness stabilizes after a period of time at room temperature to a value referred to as naturally aged, which is below the peak hardness achieved by precipitation. The behaviour gets even more intriguing when alloys are heated to precipitation temperature from their naturally aged state. In some cases, hardness decreases during heating before any precipitation phases have formed. Electrical resistivity behaves in the same manner. The magnitude and rates of these effects vary from alloy to alloy emphasising the importance of chemistry. These observations strongly suggest the presence of metastable solute rich domains which form during or directly after quench from solution treatment temperature. These objects are dissolving or evolve during heating to precipitation temperatures [33,34].

The nomenclature used for solute rich domains can lead to some confusion with authors using the general term 'solute clusters', while others use a more specific term 'Guinier-Preston (GP) zones' based on work of the researchers who first discovered them [35,36]. These terms and their interpretations are described below to justify selecting 'solute clusters' to describe solute rich domains within the remainder of this work.

The zones reported by Guinier and Preston in their original work give rise to specific X-ray diffraction streaks for an Al-Cu alloy [35,36]. The corresponding real space objects are twodimensional patches of copper atoms along the 100 planes of aluminium. Direct observation of such objects has been made and indeed GP zones are single layers of copper coherent with the aluminium matrix (Figure 3) [37]. Other more complex variants are also shown in Figure 3 and described as steps along the continuous precipitation sequence of an Al-Cu alloy towards its equilibrium θ (Al₂Cu) phase [37,38]:

SSSS \rightarrow GP zones \rightarrow GP2/ $\theta'' \rightarrow \theta' \rightarrow \theta$ (Al₂Cu)



Figure 3 A group of GP zones having different morphologies along the evolution from GP zones to more stable precipitates. The insert shows corresponding simulations results. Adapted from [37]

Early work on nucleation of precipitates developed a theory based on periodic fluctuation of composition around the average of an alloy [33,39–42]. This description of the solid solution is broad and encompasses early stages of formation for most objects and in particular precipitates. Small scale chemical fluctuations which retain the host crystal structure are also a suitable candidate for explaining the two stage hardening and resistivity behaviour observed for some alloys [43–45]. Ringer and Polmear were among the first to provide direct experimental evidence of solute clusters through atom probe field ion microscopy on an Al-Cu-Mg system [9,10,46,47]. The theoretically proposed small scale solute rich aggregates were confirmed. Solute clusters form a sub-class describing the early stages of decomposition of a super saturated solid solution. The maintained coherency with the host matrix makes solute clusters similar to GP zones. However, the absence of the specific mono-layer structure exhibited by GP zones in Al-Cu-Mg alloys [48–50] makes solute clusters a more general term. Clusters have been documented in many other systems [51–57].

2.2.1 Solute clusters in the Al-Cu-Mg system

Solute clusters in the Al-Cu-Mg system were reported alongside the intense research of phase transformations taking place during precipitation hardening. Early work was focused on the sequence from observable GPB zones towards subsequent precipitation phases through means of X-ray diffraction, hardness and resistivity measurements [48,49]. Complementary information on the evolution, structure and strengthening has come from a wide range of techniques including but not limited to microscopy and differential scanning calorimetry [58–62]. Numerical simulations aided towards understanding the crystallography and chemistry of

experimentally encountered zones and precipitates [50,63,64]. Finally atom probe tomography has made valuable contributions to the field and added the direct observation of solute clusters [10,54,65–67].

The rapid hardening behaviour exhibited by Al-Cu-Mg alloy at elevated temperatures followed by a hardness plateau before precipitation (Figure 4 A) has been attributed to the formation of Cu-Mg co-clusters, which have been observed by APT [9,67]. Such clusters have been linked to the presence of quenched-in vacancies that bind to Mg atoms, migrate towards sinks and establish vacancy-Mg-Cu complexes at elevated temperatures [68]. Further APT reports showed good correlation between the presence of Cu-Mg clusters independent of dislocations and the rapid hardening event [65]. In addition, these results suggest that Cu-Cu and Mg-Mg clusters do not express correlations with hardness. On the other hand, a significant increase in isotropic scattering during in-situ Small-Angle X-ray Scattering (SAXS) at 200 °C suggest that Cu is also clustering during rapid hardening as the scattering contribution of Mg is very low when X-rays are used [69]. Diffusion couple studies analysed through hardness and atom probe evidence that above a critical amount of Cu rapid hardening diminishes [70]. Nevertheless, the strengthening due to clusters is largely determined by the number density of Cu-Mg clusters, which have varying Mg ratio and strengthening potential as shown in Figure 5 [70].



Figure 4 A) Rapid hardening phenomenon for an Al-1.1Cu-1.7Mg (at.) alloy aged at 150 °C. Section I represents the rapid hardening, followed by a plateau in hardness II and the precipitation hardening region in III. Adapted from [9]. B) Age hardening of two Al-Cu-Mg alloys at 25 °C. Adapted from [71].



Figure 5 Hardness increment observed with increase in a) Mg and b) Cu concentration along diffusion couples between Al-Cu and Al-Cu-Mg alloys. Adapted from [70]

An increase in hardness similar to that of rapid hardening occurs for Al-Cu-Mg alloys during the first 24 hours at room temperature after quench - natural ageing (Figure 4 B) [71,72]. The change in hardness has been explained through modulus hardening due to the formation of solute clusters similar to those observed during rapid hardening [72]. APT results reveal the formation of Cu rich clusters immediately after quench and the presence of Cu-Mg co-clusters for prolonged ageing times. Cu-Mg clusters are responsible for the major contribution to the natural age hardening of these alloys in a similar manner as those during rapid hardening. The Mg/Cu ratio of co-clusters has also been shown to evolve over time at room temperature and approach unity. Ramp heating DSC studies identify an exothermic peak that has been attributed to the formation of Cu-Mg clusters with the aid of atom probe as show in Figure 6 [71,72]. Prolonged exposure at room temperature was shown to diminish the magnitude of this heat effect and strongly suggest that the objects formed during a heating ramp are the same as those forming during natural ageing. The following endothermic event, peak II in Figure 6, is attributed to the dissolution of Cu-Mg clusters previously formed. There are no clearly defined endothermic effects due to dissolution of Cu-Cu or Mg-Mg clusters which have previously been identified in these alloys. The next pair of peaks, III and IV, correspond to the formation and dissolution of precipitates which may be a mix of several phases like the GPB, S1 and S2 (variants of the S phase) [12,14,73].



Figure 6 DSC curves of an Al - 1.2 Cu - 1.2 Mg alloy after ageing intervals at 25 °C. Adapted from [71]

2.2.2 Solute clusters in Al-Cu-Li-X system

Li has been introduced as an alloying element due to its potential to increase Young's modulus and decrease density. The addition of Li to basic Al-Cu alloys and to more complex Al-Cu-Mg alloys leads to changes in the precipitation sequence. The formation of the T_1 precipitate, Al₂CuLi phase one unit cell thin plate on the $\{111\}$ planes, has been of particular interest due to its potent strengthening [4,74,75]. The formation of the T_1 phase has been shown to strongly depend on deformation and in recent work on the early stages of ageing [22–25,76–79]. GP zones and variants have been observed and reported for Al-Cu-Li alloys and suggest that solute clustering occurs in these alloys [25,79-82]. Decreus et al. showed using anomalous SAXS that Cu-rich solute clusters existed after natural ageing in an Al-Cu-Li-Mg alloy [23,81]. Araullo-Peters et al. evidenced segregation of solute on dislocations by APT as shown in Figure 7 and such segregation has been shown to accelerate precipitation kinetics [24,25]. The distribution of solute in the material before precipitation during artificial ageing plays an important role on the balance of precipitates forming and as such is of critical importance [83–85]. In particular, Malard et al. evidenced the dissolution of solute clusters present in the naturally aged material prior to precipitation of the T₁ phase through short isothermal treatment and SAXS an DSC experiments as highlighted in Figure 8 [85]. Coincidence Doppler broadening and 3DAP show clustering of solutes and vacancies during quench [86]. The comparison of Al-Cu-Mg-Ag and Al-Li-Cu-Mg-Ag alloys suggest an alteration of the Mg-vacancy trapping mechanism which lowers its effect when Li is present [13,86]. It is interesting to note that the low amount (<1 wt. %) of Li added to current generation of Al-Cu-Li alloys does not result in spinodal structure which has been observed for high Li content binary Al-Li alloys [87–89]. Despite some reports

identifying homogeneous δ' (Al₃Li) phase or heterogeneously wetting GP zones [78,79,90], Li clustering is not observed in most recent alloys of low Li content when analysed by 3DAP [91].



Figure 7 2D solute concentration profiles along a dislocation after heating to precipitation hardening temperature. Adapted from [24].



Figure 8 A) Comparison between experimental SAXS and fits for cases where scattering originates from clusters, platelets or a combination. B) DSC thermograms evidencing dissolution of clusters. Adapted from [85].

2.2.3 Some specific cases of solute clusters

Despite the Al-Si-Mg system being out of the focus of this work it provides valuable contributions and ideas towards solute clusters. The relationship between different solutes, and solutes and excess vacancies has been studied in the Al-Mg-Si system [56,92–95]. Solute clustering occurs at room temperature in a similar manner as the 2xxx series but has a negative influence on formability and subsequent precipitation kinetics [6,29,52,92,96]. The formation of Si rich solute clusters is deemed responsible for locking the necessary solute in clusters which cannot continuously evolve to the desired precipitates as may be the case in Al-Cu systems [34]. Complex ageing sequences and pre-ageing treatments have been proposed and industrially

adopted to mitigate the negative effects of Si rich clusters [29,57,96–98]. The intimate relationship between solutes and vacancies towards control of precipitation have also been evidenced as alternative routes [99]. The delayed formation of Si rich clusters has been reported in recent work focused on the effect of minor alloying elements such as Sn [30].

2.3 Characterisation of solute clusters

Evidence for the presence of solute clusters in many aluminium alloys has been presented in the previous sections. Wide range of techniques have been employed with the most obvious measuring the changes to mechanical properties such as hardness and strength. Techniques such as differential scanning calorimetry and resistivity are often complementary to mechanical measurements and give indirect global evidence of clusters in terms of the evolution of heat associated with formation or dissolution and the changes to electrical conductivity. The extremely small scale, diffuse interfaces, high number densities and low chemical contrast make direct local observation of clusters challenging using electron microscopy with only rare reports in the literature [100].

Atom probe tomography, giving access to atom-by-atom analysis and imaging, stands as an indispensable tool for studying the structure of solid solutions and solute clusters [101,102]. APT generates large data sets of several millions of atoms with spatial and chemical identities at near atomic in depth resolution and slightly larger in plane resolution [103]. The progressive deconstruction and time-of-flight nature of APT make it equally sensitive to all elements. This unique feature provides otherwise inaccessible information on clustering of similar elements, like Mg and Si in Al, and composition of the host matrix [6,104]. The large data available from APT has promoted many statistical approaches towards identifying and finding clusters [105,106,106–112]. The most commonly employed technique uses the maximum separation method which identifies solutes as belonging to a cluster if they are within a specified distance. In many cases the process is iterated for several separation distances and extremely small clusters of less than e.g. 10 atoms are ignored. An alternative procedure considers solute nearest neighbour distance and compares them to the same data set when randomly labelled [65,108,109,113].

Using the data sets it is possible to calculate radial distribution functions, which are defined by the average concentration distribution of component i, $\langle C_i^X(r) \rangle$, around a given solute, X, normalized to the overall concentration of i atoms, C_i^0 [114,115]:

$$RDF = \frac{\langle C_i^X(r) \rangle}{C_i^0} \tag{1}$$

It is important to note here that no assumptions based on crystallography, size or number are made when calculating the above expression. The quality of an RDF(r) from atom probe depends directly on the spatial resolution which is not perfect in all dimensions. Nevertheless, these functions are oscillations around unity describing the correlation of solute around a specific central atom i as shown in Figure 9 [114]. If no correlation exists between i and the solute at r the function is 1. The amplitude of oscillations in an RDF:

$$\gamma_{RDF}(r) = [RDF(r) - 1] \tag{2}$$

is a measure of the positive or negative auto-correlation of the solute. Experimentally calculated RDFs can be used to characterise the nucleation of phases, structures due to spinodal decomposition and clustering [114,116,117].



Figure 9 Experimental RDF(r) for aged Ni-5.2 Al - 14.2 Cr at. % alloy. The start of phase separation is indicated by a shift in Al-Al RDF. Adapted from [114].

Small angle scattering (SAS) experiments are measurements of the fluctuations of scattering factor density (Patterson function) and provide excellent global statistical information due to the large analysed volumes. These fluctuations originate from features in the sample such as precipitates or clusters. In an isotropic system of average scattering factor density $\bar{\rho}$, the intensity arising from a fluctuation in scattering factor density $\eta = \rho - \bar{\rho}$ (arising, in our case from a fluctuation in solute concentration) can be written [118]:

$$I(q) = \int_0^\infty 4\pi r^2 \gamma(r) \frac{\sin(qr)}{qr} dr$$
(3)

where $q = 4\pi/\lambda \sin(\theta)$ is the scattering vector for a radiation with wavelength λ , scattering at an angle θ , and $\gamma(r)$ is the so-called correlation function by introduced by Debye and Bueche [119]:

$$\gamma(r) = \langle \eta(\vec{r_1})\eta(\vec{r_2}) \rangle \text{ with } r = |\vec{r_1} - \vec{r_2}| = constant$$
(4)

 $\gamma(r)$ is the auto-correlation of scattering factor density fluctuation and is related to the SAS intensity through a Fourier transform. It can be re-written as:

$$\gamma(r) = \overline{\eta^2} \gamma_0(r) \text{ with } \gamma_0(0) = 1 \tag{5}$$

with $\gamma_0(r)$ the normalized correlation function. In the absence of long range order (other than that of the underlying crystal giving rise to Bragg peaks), both $\gamma(r)$ and $\gamma_0(r)$ go to zero for large r. By definition, $\gamma(0) = \overline{\eta^2}$, i.e. the mean square fluctuation of scattering factor density.

Provided that the intensity in known over a wide enough range, the correlation function can be obtained by inverse Fourier transform:

$$\gamma_{SAS}(r) = \frac{1}{2\pi^2} \int_0^\infty I(q) q^2 \frac{\sin(qr)}{qr} dq \tag{6}$$

In particular, for r = 0:

$$\overline{\eta^2} = \frac{1}{2\pi^2} \int_0^\infty I(q) q^2 \, dq \tag{7}$$

Because this integral is always equal to the mean square fluctuation of the scattering factor density, irrespective of the shape of the features, it is often called the *invariant*.

Despite being calculated through very different means, the amplitude of oscillations in an RDF, $(\gamma_{RDF}(r))$ from atom probe and the auto-correlation of the chemical fluctuations in the real space $(\gamma_{SAS}(r))$ calculated from the intensity in the reciprocal space (I(q)) are measurements of the chemical fluctuations and are both proportional to $\gamma_0(r)$. The radial distribution function (RDF) which is a standard tool to describe the solute fluctuations in atom probe tomography [114,120] and the auto-correlation of scattering factor density fluctuation from SAS have been linked in [117] to reveal the unmixing of an Fe-Cr system. We will closely follow this methodology and add specific solute auto-correlation from SAS using contrast variation arising from X-rays and neutrons [121].

2.4 Conclusions

The root of all precipitation sequences for Aluminium alloys is the decomposition of a solid solution. Early theories propose the formation of solute rich regions as an explanation to the changes in mechanical properties observed. The kinetic nature of decomposition has been tackled through introduction of an invisible player – the vacancy – which governs diffusion in Aluminium. An intimate relationship between solutes and vacancies allows for global and easily accessible trends to be explained in simple systems. The theories have been revisited on periods corresponding to the development of new characterisation techniques which in turn provide novel data. With the latest development of atom probe tomography, solute clusters have been directly imaged and confirmed; however, questions concerning the kinetic nature of the clustering reactions remain. Furthermore, the growing demand for specific property sets has escalated the complexity of alloys making the direct application of previously proposed theories difficult. The principal goals of the following texts are oriented towards a characterisation technique able to monitor the kinetic evolution of cluster chemistry during formation and attempt to establish relationships between the solutes and vacancies.

2.5 References

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3 Materials and experimental methodology

The materials selected to investigate solute clustering will be described in this chapter. The procedures for obtaining the desired states of clustering through appropriate heat treatment, ageing and reversion will be detailed. The characterization of solute clusters has been carried out using the following techniques:

- Differential scanning calorimetry (DSC)
- Small Angle Scattering (SAS) using X-rays (SAXS) and neutrons (SANS)
- Atom probe tomography (APT)

providing complimentary information on the spatial dimensions, quantity, chemical composition and thermal properties of clusters. The effect of solute clusters on the hardness have also been studied through common metallurgy procedures. The diverse data collected throughout the course of this PhD work reflect changes in the distribution of solute and have motivated a comparison using procedures which will be described in the following chapters.

3.1 Materials employed

The Al-Cu-Mg alloy system has been at the origin of age hardening since the phenomenon was discovered by Wilm in 1906 [1,2]. A substantial and very rapid increase in hardness at elevated temperatures, and similar magnitude but slower hardening at room temperature, have been attributed to cluster hardening via solute clustering in a high purity Al-Cu-Mg alloy [3–6]. DSC experiments on Al-Cu-Mg alloys reveal strong heat effects due to the formation and dissolution of clusters [4,7]. As such the Al-Cu-Mg system stands as a good reference material for solute clusters and is employed throughout this work.

The third-generation Al-Cu-Li alloys have been widely used in the aerospace industry due to their high specific strength and good damage tolerance. Over the years, research has predominantly focused on the complex precipitation path followed by these alloys during artificial ageing. Clustering and segregation of solute have been briefly explored at elevated temperatures as their dissolution provides the solute for desired precipitation reactions. The necessity of adding Mg (as a minor-alloying element) for promoting precipitation of the desired T_1 phase has been evaluated and linked to the presence of Mg containing precursors [8]. We thus choose to focus on the room temperature solute clustering and explore two Al-Cu-Li alloys modelling the commercial AA2050. The first is a base Al-Cu-Li, while the second has a minor addition of Mg (Al-Cu-Li-Mg).

The materials were provided by Constellium Technology Center (CTEC) Voreppe, France as 27 mm thick slabs. The composition of these alloy is presented in Table 2.1. The formation of solute clusters at room temperature, their thermal stability and chemical composition have been investigated. The combination of all 3 alloys helps investigate the importance of specific solutes to clustering and further elucidate the importance of solute-vacancy interactions.
Alloy	Cu	Li	Mg	Al
Al-Cu-Mg	1.08 (2.5)	0	1.69 (1.5)	bal.
Al-Cu-Li	1.48 (3.5)	3.48 (0.9)	0	bal.
Al-Cu-Li-Mg	1.48 (3.5)	3.48 (0.9)	0.44 (0.4)	bal.

Table 1 Composition of the aluminium alloys studied in at. % (wt. %)

Diffusion couples between the Al-Cu-Li-Mg and the Al-Cu-Li alloys were fabricated to study the effect of Mg concentration on solute clustering at room temperature. The individual alloy slabs were annealed at 500 °C before being joined using linear friction welding by Thompson Friction Welding (UK). Friction welding, being a solid state joining process, was chosen to ensure no solute loss which could be an issue via conventional fusion welding techniques [9]. After joining, the samples were heat treated at 515 °C for 336 hours to establish a smooth Mg gradient across the welds spanning approximately 2 mm. The gradient was further increased through hot rolling to approximately 10 mm [10].

3.2 Thermal processing for clustered states

The material was received in the as fabricated condition which had no special control for cooling post casting or record of the time spent at room temperature. In order to standardize the starting point, all samples were homogenized at 500 °C in a Carbolite LHT6/30 air furnace for 24 h and scalped to remove oxidized surfaces. The slabs were hot rolled, while keeping the material above 350 °C, to a thickness of approximately 3.5 mm. The same hot rolling procedure was also performed on the diffusion couple samples. The 3.5 mm plates were used as *starting material* throughout the course of this project.

To begin the natural ageing studies, starting material was solution heat treated at 505 °C in a Carbolite 4 CTF12/65 air tube furnace for 30 minutes and quenched directly into a large volume of water at 20 °C. Material in this condition was labelled to be 'As Quenched' (AQ) indicating a state where all solid is expected to be in solution. This is the super saturated solid solution which has the highest potential for solute clustering. To prevent natural ageing, which can take place at room temperature, as quenched material was immediately tested or stored in a freezer at -52 °C before experiments. As quenched samples stored for longer than 6 months were resolution treated and quenched before testing to ensure they are in the 'As Quenched' condition.

Room temperature natural ageing simply implies leaving the as quenched material on a desk for a desired duration. In order to test the kinetics of the natural ageing process, samples were tested by differential scanning calorimetry (DSC) and micro-hardness serving as ex-situ points for specific ageing times. The kinetics were also continuously followed via in-situ small angle scattering. Ageing for 72 hours has been chosen as sufficient time for the main part of the clustering process to be completed in all 3 alloys. This holds particular importance as samples in this state are stable and show no evolution if aged longer. This was verified by ageing up to

6-months post quench. Samples aged for 72 hours are labelled as the 'Naturally Aged' (NA) condition.

'Isothermal reversions' were carried out on naturally aged samples with the aim of dissolving clusters that were present in the sample. Samples were manually plunged in a Lauda P18 oil bath maintained at the designated temperature with an accuracy of ± 0.5 °C and the time was recorded by a stop watch. The various temperatures and holding times are summarized in Table 2.2. The temperatures were chosen to be above reaction peak temperatures from ramp heating DSC experiments such that the reaction can be near completion. The time was altered to fine tune the extent of the dissolution reaction and attempt to avoid possible precipitation reactions. After reversion, samples were labelled to be in the 'As Reverted' condition and were tested directly or stored in a freezer at -52 °C. Table 2.3 contains the nomenclature and description used for samples throughout this project.

Alloy	Temperature (°C)	Times (seconds)
Al-Cu-Mg	250	10, 60
	240	5, 10, 30
	235	30, 60
	230	10, 60
	200	5, 10, 15, 20, 30, 60, 120, 300
Al-Cu-Li	200	5, 10, 15, 20, 30, 60, 120
	120	30, 60
Al-Cu-Li-Mg	250	10, 15, 20, 30, 60, 90, 120, 180
	200	5, 10, 15, 20, 30, 60, 120, 300
	120	30, 60, 120

Table 2 Isothermal reversion temperatures and times explored to achieve dissolution of clusters

Table 3 Nomenclature used to identify samples which have undergone thermal processing.

Name	Description
AQ	The sample was solution treated and water quenched. (As Quenched)
xh	The sample has been at room temperature for x hours. (Aged)
NA	The sample has been at room temperature for 72 hours. (Naturally Aged)
AR temp. time	The sample has been at room temperature for 72 hours and isothermally reverted at 'temp' °C for 'time' seconds. (As Reverted)
R temp. age time	The sample has been reverted at the indicated 'temp' °C and aged at room temperature for 'age time' hours. (Reverted and aged)

3.3 Standard metallurgy procedures

Preparing samples for the experiments described below required the use of standard metallurgy procedures to obtain the desired shapes and surface qualities. The bulk blocks were cut into manageable sizes using a hand saw. Samples were obtained by a slow speed cutting saw to ensure minimal deformation. The grinding and polishing required to prepare samples suitable for DSC and SAS was performed using progressively high grit SiC paper while final surface polish for micro-hardness was achieved by 1 µm SiO2 solution. For samples to be tested in the AQ condition, which is the least stable, all preparation was carried out before the solution treatment to reduce the time spent at room temperature. Vickers Micro-hardness measurements were performed on a fully automatic Buehler Tukon 1102 instrument. The polished samples, presenting a parallel surface, were indented using a 200-gram force load for a 10 second duration. At least 10 indents were made in order to present a good estimate of the average material hardness. The chemical composition of the alloys and the Mg solute gradient across diffusion couples were measured using electron probe micro analysis (EPMA). A CAMECA SX 50 microprobe was used at 20 keV and 300 nA while being calibrated for measuring Cu and Mg. The Li concentration was not accessible via the EPMA measurements and was assumed to be constant at the value provided by Constellium.

3.4 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a global bulk characterization technique which gives access to information about the 'total heat' of reactions taking place during an experiment. Standard procedures involve subjecting a sample and a reference to a common thermal route. The reference can be an empty crucible or a piece of pure aluminium with similar mass to the sample being tested. Thermocouples in close proximity to the sample and reference allow for recording the respective temperatures (Figure 10 [11]). When constant heating ramp is applied, heat capacity differences between the sample and the reference will cause a shift between the change in temperature; however, the two will remain parallel as long as no reactions are taking place. When a reaction occurs, for example the sample melts (Figure 11), energy is consumed to overcome the latent heat of fusion causing a deviation from linear heating. The reference, on the other hand, has no such delay and continues to follow linear heating. The DSC signal is the difference between the two temperatures. This signal is converted to a heat flow rate through internal procedures specific to the equipment with a good description presented in [11]. The differential signal can be calculated by subtracting the sample from the reference. In the present work we will consider thermal events costing energy to the system, i.e. endothermic, as negative heat flow and those resulting in an excess energy (exothermic) as positive.



Figure 10 Differential scanning calorimeter cell design. Adapted from [11]



Figure 11 Schematic representation of the origin of DSC heat flow signal

3.4.1 DSC equipment used

The primary instrument used for this project was a heat flux TA Instruments Q200 DSC equipped with a refrigeration cooling system (RSC 90). Experiments were carried out in the temperature range between -50 and 350 °C to study the formation and dissolution of clusters. The cooling system allows for experiments to start at -50 °C, which ensures steady state measurement at temperatures above 0 °C where clustering can occur. In parallel, a Mettler Toledo DSC 3+ Star System equipped with a Huber TC45 refrigeration cooling system was used to observe the signal over a wider temperature range up to 550 °C.

3.4.2 DSC procedures and data interpretation

The DSC instruments were calibrated for temperature using the melting peaks of pure In and Zn. The heat capacity of the DSC cell was calibrated using standard sapphire discs provided by the manufacturer. Samples used for DSC experiments were prepared by slow speed cutting of

3.5x3.5x20 mm bars from the starting material which were then sliced into samples of approximately 2 mm. These samples were subjected to thermal processing to obtain the desired clustered state as described above. The sample weight was recorded using a Mettler Toledo precision scale right before introduction into the DSC. High purity aluminium pans with a cover were used to place the sample on the sample platform in the DSC. The reference platform was occupied by a high purity aluminium pan with a cover from the same lot and was used for a set of experiments. Particular attention was paid to ensure that the time required to weigh and introduce the AQ samples into the DSC was kept to a minimum. If crucibles or covers were damaged when placing the sample in they were discarded due to possible parasitic effects [12].

The experimental procedure used on the TA Instruments DSC consists of three primary sections as depicted in Figure 12.. Heating ramps, 1 and 3, were both performed at the same rate (a choice of 2, 5, 10, 20, 30, 40, 50 or 100 °/min). The raw normalized heat flow obtained by the DSC for 10 °/min ramps 1 and 3 are shown in Figure 13. Three data sets are presented by offsets of 0.05 W/g showing the three alloys. Additionally, the heat flow for a pure aluminium sample subjected to the same procedures (but as a separate experiment) is shown in accordance with each alloy. Pure aluminium does not undergo any thermal events for the temperature range scanned here and it can serve as a reference or baseline. Subtracting the pure aluminium curve from heating ramp 1 should result in a smooth curve near zero as shown by the red curves in Figure 14. Deviations below zero, endothermic, are due to dissolution reactions and positive deviations, exothermic, indicate formation of clusters or precipitates. Global shifts above or below zero correspond to heat capacity and mass differences between the sample, aluminium alloy, and the reference, pure aluminium. Furthermore, rotation of the curves can appear depending on the physical positions of the sample and reference with respect to one another. It is experimentally very difficult to consistently reproduce this positioning.



Figure 12 Heating ramps used to execute DSC two-heat procedure for baseline correction



Figure 13 Raw signals for two heating ramps carried out on the 3 alloys studied and compared with pure aluminium which can be used as a reference.

To correct for the artefacts described above, it is a common DSC practice to adjust the data by fitting a polynomial along sections of the curve containing no heat due to reactions. Subtracting this polynomial, as a baseline, should result in a flat curve with zero heat flow when there are no ongoing reactions. This approach involves a fit whose parameters' physical meaning is hard to justify; hence we propose an alternative to alleviate artefacts in the DSC signal. Our method is based on the observation that during the second ramp, there is no apparent reaction occurring up to a suitable temperature ($\sim 250^{\circ}$ C). This provides an ideal baseline for the first heating ramp. Between ramp 1 and ramp 3 the material's weight is the same, as well as its position, so that all artefacts from heat capacity differences and sample positioning will be removed, leaving only the net signal for clustering reactions.

Comparing heating ramp 3 curves and those for pure Al, it is actually observed that no reactions are occurring up to about 250 °C (Figure 14). The curve begins to deviate above 250 °C due to a reaction. Heating ramp 3 is thus truly a sample specific baseline up to this temperature. Obtaining a baseline up to a higher temperature (350°C) is still possible but requires an extrapolation of the signal obtained in ramp 3 up to 250°C and has not been used. Subtracting the baseline signal from ramp 1 results in a flat curve at zero with deviations indicating the heat of reactions during ramp 1 as shown in Figure 14. For temperature is not affected. All of the differential scanning calorimetry results will be presented after this correction procedure has been applied unless otherwise stated.

The Mettler Toledo DSC 3+ Star system was used to perform scans in a wider temperature range between 30 and 550 °C. This range permits observation of the precipitation reactions until the material reaches a full solid solution. The procedure for these experiments involved a single ramp heating. Samples were placed in high purity aluminium crucibles and covered by lids

without pressing. High purity aluminium crucible with a lid was used as the reference. Reactions occurring during the experiment give rise to the majority of the DSC signal gathered (Figure 15); however, artefacts from the crucibles, the instrument and the evolution of heat capacity with temperature are also present. A baseline is necessary to correct for these artefacts. As a second heating ramp without any reaction in the whole temperature range is not possible, the procedure described previously for the low temperature range (up to 350°C) cannot be applied, so that we used a more traditional baseline correction procedure.



Figure 14 DSC thermograms corrected using the two-heat procedure compared with a standard Al baseline correction

The raw DSC data for a naturally aged Al-Cu-Mg sample heated at 10 °C/min is shown in Figure 15a to describe the baseline correction method used with the Mettler Toledo data. The raw data (blue curve) contains regions where no reactions are expected to take place and these sections can be used as data for baseline fit calculation. Two such regions are highlighted, with a 30 to 100 °C range and above 500 °C where a solid solution is present. There is a very sharp perturbation at 515 °C, which has been ignored. Fitting a 2nd degree polynomial to these regions and subtracting it from the raw data results in a flat curve whose deviations correspond to heat flow due to reactions as shown in Figure 15b. Good agreement is obtained with the data obtained on the same material following the three ramps procedure in the TA Instrument DSC. Formation and subsequent dissolution of solute clusters takes place at temperatures between 0 and 250 °C; hence the majority of DSC results presented will be centred in this range.



Figure 15 a) Full range DSC data obtained using Mettler Toledo instrument and corrected using a baseline approximation from TA instuments two-heat method. b) Comparison of the results obtained by both instruments

3.5 Small angle scattering

In a scattering experiment a monochromatic beam is dispersed (scattered) due to inhomogeneity of a sample. In small angle X-ray scattering (SAXS) the sample is illuminated by a monochromatic X-ray beam and scattering occurs due to fluctuations of the electron density within the material. It is possible to use other sources of light, as in small angle neutron scattering (SANS), where monochromatic neutrons are scattered by the nuclei of atoms. The spread of scattered beams occurs in all directions around a central transmitted beam while maintaining reciprocity – inverse relationship between the length scale of scattering domains and the distance from the direct beam. In this sense, scattering is a global technique which provides cumulative information about the quantity, size and spatial distribution of all scattering domains in a sample.

In this chapter, we will describe the methodology used to gather data from SAS experiments. Scattering data can serve as rich qualitative visual guide to the processes of clustering and precipitation. To access quantitative information interpretation models based on assumptions concerning the product of scattering factors differences between scattering centres and matrix and quantity, or the shape of the inhomogeneity are necessary [13]. We will propose a methodology for adapting an interpretive model to quantify the scattering due to clusters. The model is applied to combined data from two sources of radiation, X-rays and neutrons, to deduce chemical information about scattering domains.

3.5.1 Instrumentation

3.5.1.1 Small angle X-ray scattering instruments

Small angle X-ray scattering (SAXS) experiments were primarily carried out using an in-lab Rigaku MicroMax-007 HF rotating anode with Cu K α X-ray source (λ =1.52Å). Additional experiments were performed at the BM02-D2AM beamline at the European Synchrotron Radiation Facility (ESRF) Grenoble France. The detector used in lab was a DECTRIS Pilatus

300K detector and an XPAD3 was used at BM02-D2AM beamline. Both detectors are photon counting detectors providing excellent statistics due to their very low noise levels. A custom furnace and cooling system (Figure 16) was employed to maintain the sample in the beam under a desired temperature. This allowed for isothermal experiments during which natural ageing can take place and kinetics can be monitored. Furthermore, it facilitated experiments with heating ramps at the same rates as those performed by DSC during which scattering information can be correlated to reactions taking place. The low noise of the detectors and high flux synchrotron light made it possible to record low intensity signals with good statistics.



Figure 16 In house designed furnace for in situ SAXS experiments

3.5.1.2 Small angle neutron scattering instrument

Small angle neutron scattering (SANS) experiments were performed at the Institute Laue-Langevin (ILL) on the D11 line in Grenoble, France. The D11 Nexus detector, mounted on a travelling tray with in vacuum tube was used allowing for data collection over a wide scattering angle. The instrumental set up did not permit for the use of a dedicated furnace and cooling system hence all experiments were all performed at room temperature. A neutron wavelength of 5Å was used, which is above the Bragg cut-off, removing any Bragg diffraction effects including double diffraction.

3.5.2 Experimental procedure

This section outlines the experiments used to gather data for the formation of clusters at room temperature, the dissolution of clusters and to analyse the evolution of cluster composition.

3.5.2.1 Natural ageing

In situ, natural ageing SAXS experiments involved gathering data from a sample continuously over a period of time. This type of data makes it possible to follow the developing solute clusters and capture the kinetics of the reactions taking place. High temporal resolution experiments were carried out at ESRF during the first 16 hours of ageing and longer experimental times were performed in lab. In both cases, natural ageing experiments were carried out at 30 °C. In addition, elevated temperature experiments were performed for the Al-Cu-Li and Al-Cu-Li-Mg alloys at 70 °C and 110 °C at ESRF.

For naturally ageing SANS experiments in situ data was collected at selected points along the process. As quenched samples were introduced and measurements were taken every 10 minutes during the first hour followed by every 40 minutes for an additional 9 hours of natural ageing. This 10-minute period was found to be the minimum for obtaining data with reasonable statistics. The naturally aged condition, representing 72 hours of ageing, was tested as ex situ samples. Matching the ageing time for experiments carried out at ESRF, ILL and in lab made it possible to characterize the chemical evolution of clusters during natural ageing. These results will be discussed in 'Clustering kinetics during natural ageing of Al-Cu-(Li, Mg) alloys'.

The influence of Mg concentration on clustering in Al-Cu-Li-Mg was explored using diffusion couples between Al-Cu-Li and Al-Cu-Li-Mg alloys. SAXS experiments were performed using both instruments on samples whose Mg content was previously measured by electro probe microanalysis (EPMA) and correlated to the position on the sample. The natural ageing progression was monitored in situ for up to 72 hours giving access to the kinetics. An ex situ naturally aged sample was also analysed as a comparison. The combination of a diffusion couple, providing a chemical gradient, and in situ SAXS, providing kinetics has provided results evidencing the importance of Mg on clustering of Cu. These results are presented in 'The effect of Mg concentration on clustering in Al-Cu-Li-Mg alloys'.

3.5.2.2 Reversion

Ramp heating in situ SAXS experiments were performed on the in lab and ESRF instruments. These experiments, referred to as 'reversions', are aimed to follow the scattering signal evolution and compare it to the heat flow detected by DSC using the same heating ramp. These experiments provide additional information to support the identification of the DSC peaks. Applying a heating ramp during a scattering experiment invokes a trade-off between counting time and temperature resolution. The high X-ray flux of ESRF allowed for testing heating rates up to 100 °C/min with counting times of 1 second. In lab experiments, with lower X-ray flux, were used to test the medium to slow heating rates between 20 °C/h and 10 °C/min. The analysis presented in 'Clustering kinetics during natural ageing of Al-Cu-(Li, Mg) alloys' and Thermal stability and post-reversion formation of solute clusters in Al-Cu-(Li, Mg) alloys' are focused on experiments using heating rate at 10 °C/min as they were used by both ESRF and in lab instruments. Unfortunately, no neutron scattering experiments using heating ramps could be carried out.

Experiments referred to as 'isothermal reversions', were carried out on samples heat treated as described in Section 2.2 before being analysed by SAS. The goal was to evaluate the

contribution of clusters to the total scattering intensity. Comparing the naturally aged sample (assumed total scattering due to all clusters) and isothermally reverted samples (assumed only fractional intensity) made it may be possible to correlate certain clusters contribution to intensity. Furthermore, the possibility of some clusters to re-form after being isothermally reverted was explored. Post reversion ageing kinetics were evaluated using both SAS methods employing in situ samples. Due to the slow ageing expected for reverted samples long times were tested on ex situ samples.

3.5.3 Data processing

All data collected using X-rays was background corrected and normalized to absolute units using a glassy carbon sample and in house scripts. The scattering vectors were calibrated using diffraction peaks of silver behenate [14]. Neutron data was background corrected and normalized with respect to sample thickness into absolute units using the Graphical Reduction and Analysis SANS Program package (GRASP). For better comparison between SAXS and SANS, we chose to use cm⁻¹ for the intensity, rather than the Å⁻³ units more conventionally used in SAXS which uses a further normalization by the scattering cross section of an electron. Further details concerning the data interpretation are presented in Chapter 4.

3.6 Atom probe tomography

Three-dimensional atom probe tomography (3D APT) has become a common 'go to' tool for observing nanostructured material [15,16]. A needle-shaped specimen is progressively deconstructed atom by atom in an ultrahigh vacuum providing position and chemical information. The energy of atoms in the tip is increased by application of a high DC voltage between the sample and a counter electrode. Excitations above this energy result in atoms leaving the tip. Applying a high voltage or laser pulsing allows for evaporation to be achieved in a controlled manner [15,16]. Evaporated atoms are accelerated towards a position sensitive detector while chemical information is obtained through time-of-flight calculations as a mass spectrum. The technique achieves excellent resolution perpendicular to the tip curvature; however lower in-plane resolution and detector efficiency are common drawbacks. Nevertheless, the data can be used to reconstruct a 3D image of the atoms in the sample and serve as an excellent source of direct quantitative information [17,18]. Cluster finding algorithms, nearest neighbour distributions (xNND) and radial distribution functions (RDF) can be used to analyse APT data sets in search for clusters. Cluster finding algorithms are based on atoms being separated by minimum distance to be considered as a cluster [19] and therefore may impose some limitations [20,21]. Calculation of nearest neighbour distribution functions (xNND) provide the likelihood of an atom as a specific (x) nearest neighbour to be around another atom. Performing such calculations on a data set and comparing to randomly labelled data set can evidence clustering. Radial distribution functions (RDF) calculate the distribution of solutes around a chosen one. An attempt to correlate RDFs from APT data with a function describing solute fluctuation as observed by SAS experiments is presented in 'A combined characterization of clusters in naturally aged Al-Cu-(Li, Mg) alloys using small-angle neutron and X-ray scattering and atom probe tomography'.

3.6.1 Instrument

Experiments were carried out using a Cameca local electrode atom probe (LEAP) 4000 with help of Dr. Williams Lefebvre. The Groupe de Physique des Matériaux at the university of Rouen is gratefully acknowledged for help with the experiments and the METSA network to provide instrument access time.

3.6.2 Experimental procedure

Samples were prepared by cutting small rods (~0.3 x 0.3 x 15 mm) from the naturally aged material. Final tip specimens for APT were obtained using a standard two-stage electropolishing technique [16] in 2% perchloric acid in 2-butoxyethanol at 15V. Evaporation was achieved in electric mode using a pulse with amplitude of 20% the DC voltage applied at 200 kHz repetition. The temperature of the sample was maintained at 40 K under ultrahigh vacuum on the order of 8 x 10^{-11} Torr during the experiments. The collected data was processed with the aid of Imago Visualization and Analysis Software (IVAS Cameca) package. Volume reconstructions were done following advanced techniques described and reviewed elsewhere [17,18,22]. Solute enriched poles were observed and removed from the volumes used. Radial distribution functions (RDF) for each solute were calculated.

3.7 References

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A combined characterization of clusters in naturally aged Al-Cu-(Li, Mg) alloys using small-angle neutron and X-ray scattering and atom probe tomography

The central subject of this PhD thesis is solute clustering and this chapter will present a methodology developed to characterise these features of the solid solution. The methodology is used throughout the remainder of the thesis and is therefore crucial. We consider all clusters to be chemical fluctuations of the matrix composition. To characterise such fluctuations, we use an interpretation model previously shown by Couturier et al., which grants possibility for direct comparison between small angle scattering and atom probe tomography. In addition, we introduce contrast variation by combining the data obtained from scattering by X-rays and neutrons to gather specific chemical information from the small angle scattering technique. The combination of these techniques and interpretation allows for clusters to be characterised with respected to the mean square concentration fluctuation, the mean square number of excess solute, the correlation length, the interaction length and an estimation of the cluster Mg/Cu ratio.

4 A combined characterization of clusters in naturally aged Al-Cu-(Li, Mg) alloys using small-angle neutron and X-ray scattering and atom probe tomography

4.1 Introduction

Most Aluminium alloys undergo natural ageing after they have been quenched from solution treatment temperature. Natural ageing results in an increase of hardness at room temperature, and has been at the core of the development of age hardening since its discovery by Wilm in 1906 [1,2]. Since Guinier and Preston [3,4] it is known that natural ageing is related to solute clustering at the atomic scale. Although the name "GP zones" is widely used in many Al alloys, it is clear that natural ageing encompasses many different microstructural features. More generally, solute clustering describes the first stages of solute aggregation, in the form of soluterich regions without a specific crystallographic structure. Clustering occurs in many different alloys, and has been particularly studied in Al-Cu-Mg [5-15] and in Al-Mg-Si [16-26]. In Al-Cu-Mg, Mg-Cu rich clusters have been shown to result in a rapid increase of hardness [14,15,27], which has been attributed to the strongly attractive interaction of Mg and Cu atoms. In Al-Mg-Si, clustering that occurs at room temperature [21,24,26] generally has a prominent negative influence on the subsequent precipitation kinetics [16,17] and therefore has been studied to find ways to circumvent this negative effect [28]. In multi-constituent alloys, clustering is known to be intimately related to the complex interactions between the different solutes, and between the solutes and the excess vacancies inherited from the solution heat treatment. For instance, the high binding energy between Sn atoms and vacancies has been used to devise Al alloys where the solute clustering kinetics are delayed by several orders of magnitude [28,29].

Al-Cu-Li based alloys have been the subject of intensive research in the last 10 years, in relation with the development of so-called third generation Al-Li alloys for aerospace applications [30–38]. The precipitate microstructure sought for controlling their strength is formed through a complex sequence of phases, which has been shown recently to depend strongly on the low-temperature microstructure formed during the early stages of ageing [35,36,38]. These Al-Cu-Li alloys usually contain minor additions of Mg, which considerably modifies the subsequent precipitation sequence. Decreus et al. [39] showed using anomalous small-angle X-ray scattering (SAXS) that Cu-rich clusters existed after natural ageing in an Al-Cu-Li-Mg alloy. Since Mg is known to associate strongly with Cu to form stable clusters in Al-Cu-Mg alloys [12,15,23], it is of interest to understand more in detail the respective interactions between Cu, Mg and Li in forming solute clusters during natural ageing. In the present paper, we will therefore evaluate the cluster characteristics in three different alloys illustrating subsets of this system, namely an Al-Cu-Li alloy, an Al-Cu-Mg alloy and an Al-Cu-Li-Mg alloy.

Solute clusters are difficult to characterize directly, being of the same crystal structure as the host Al matrix, showing no sharp interface, and only a mild composition contrast. Therefore, they have been mostly evaluated by indirect techniques, using differential scanning calorimetry

(DSC) [40-42], resistivity [43-45], hardness, or positron annihilation [46-48]. Atom probe tomography (APT), giving access to the solute distribution at the atomic scale, has been used extensively more recently and provided information on the type of solute correlations within the clusters and on their size distribution [7,8,12,15,32,49]. Small-angle scattering techniques (SAXS with X-rays and SANS with neutrons) are well suited to evaluate the solute inhomogeneity at the near-atomic scale [39,50], giving access to information on the size of precipitates or clusters and on their quantity, which is classically the volume fraction for precipitates, although this term is more difficult to define in the case of clusters. Recently, Couturier et al. [51] have devised a methodology to characterize the composition fluctuations arising from Fe-Cr unmixing in a stainless steel from SAXS measurements. This methodology was successfully applied to characterize the amplitude and spatial extension of the composition fluctuations. In a multiconstituent system, however, a single SAXS measurement is insufficient to provide information on the clustering of several solutes, and contrast variation analysis is necessary to separate the contributions of the different solutes. Anomalous SAXS is classically used to evaluate the contribution a specific solute [52], where the X-ray beam energy is varied close to the K-edge of this species. Cu and Zn clustering can be straightforwardly characterized using this technique in Al alloys [52,53], because their K-edges are easily accessible. However, Mg (and even worse, Li) K-edges are not accessible by conventional SAXS beamlines.

An alternative for contrast variation, which has been used for the characterization of oxidedispersion steels before [54], is to perform SAXS and SANS measurements correlatively. SAXS is sensitive to the electron density (which is related to the atomic number) while SANS nuclear scattering cross section is not directly correlated to the position in the periodic table. In the case of dilute alloys, a measure of the sensitivity to a given element can be defined by $(f_i - f_{Al})/f_{Al}$, with f_i and f_{Al} , the scattering factors of element *i* and Al, respectively. The values for the Cu, Li and Mg are given in Table 4. It is clear from this table that because Mg and Al have a similar atomic number, SAXS is essentially blind to Mg clustering. It is much less the case for SANS. In favourable cases, their combination can be therefore expected to provide information on cluster chemistry. In combination with the analysis of the SAXS/SANS intensity using the model of Couturier et al. [50], this contrast variation method will be used in the present case on all three alloys to provide a full quantification of the state of clustering. In addition, the information obtained from this correlative methodology will be further complemented by APT experiments, which give access to a direct spatial view of the solute fluctuations.

Table 4. SAS elemental sensitivity in aluminium alloys as defined by $(f_i - f_{Al})/f_{Al}$, with f_i and f_{Al} the scattering factors of element *i* and Al, respectively

* · · ·	Cu	Mg	Li
SAXS	1.23	-0.08	-0.77
SANS	1.23	0.55	-1.55

4.2 Materials and experiments

Alloys with nominal compositions shown in Table 5 were provided as 27 mm thick plates by Constellium C-TEC, Voreppe, France. The material was homogenized at 500 °C for 24 h,

quenched and subsequently hot rolled to 3 mm thickness at 350 °C. For neutron scattering (SANS) no further thickness reductions was necessary and samples were solution treated at 500 °C for 30 minutes, water quenched, naturally aged when necessary and stored in liquid nitrogen before exposure to the beam. Samples for X-ray scattering (SAXS) were prepared by grinding and polishing down to ~300 μ m, solution treated at 500 °C and water quenched. The further thickness reduction down to 80 μ m was achieved by polishing immediately after quench before exposure to the X-ray beam. Samples referred to be in the 'as quenched' (AQ) condition have been exposed to room temperature for no longer than 5 min for neutrons and 15 min for X-rays. Some of the samples were kept at room temperature for 72 h after quench to allow for natural ageing to take place. These samples are referred to as 'naturally aged' (NA).

Small-angle X-ray scattering (SAXS) experiments were carried out on a laboratory set up using a Rigaku MicroMax-007 HF rotating anode with Cu K_{α} X-ray source (λ =1.52Å). Scattering data was collected using a DECTRIS Pilatus 300K detector which is a noise-less photon counting detector, allowing for excellent statistics even at low counting rates (which is important for the present study). The collected data was background corrected and normalized to absolute units a glassy carbon sample as a secondary calibration standard [55] using in house scripts. For better comparison with neutron scattering, we chose to use cm⁻¹, rather than the units more conventionally used in SAXS which uses a further normalization by the scattering cross section of an electron. The sample-to-detector distance was about 0.6 m, allowing the measurement of scattering vectors ranging between 0.02 and 0.5 Å⁻¹.

Alloy	Cu at. % (wt. %)	Li at. % (wt. %)	Mg at. % (wt. %)	Al	Mg/Cu (at %)
Al-Cu-Mg	1.1 (2.5)	N/A	1.7 (1.5)	Bal.	1.55
Al-Cu-Li	1.5 (3.5)	3.5 (0.9)	N/A	Bal.	0
Al-Cu-Li-Mg	1.5 (3.5)	3.5 (0.9)	0.45 (0.4)	Bal.	0.3

Table 5. Alloy compositions

Small-angle neutron scattering (SANS) measurements were performed at the D11 instrument at the Institute Laue-Langevin (ILL) in Grenoble, France. A neutron wavelength of 5Å was used, which is above the Bragg cut-off, removing any Bragg diffraction effects including double diffraction. Two distinct sample to detector distances were used to capture a wide range of scattering angles from 0.01 < q < 0.6Å⁻¹. The use of two positions required a displacement of the detector which lasted about 1 minute. Thus, in order to increase the time resolution of the SANS measurements on the as quenched samples, only the shortest distance was used. All experimental data have been background corrected, normalized to absolute units and azimuthally averaged using the Graphical Reduction and Analysis SANS Program package (GRASP).

Atom probe tomography (APT) samples were prepared by cutting small rods ($\sim 0.3 \times 0.3 \times 15$ mm) from the naturally aged material. Final tip specimens for APT analysis were obtained using a standard two-stage electropolishing technique [56] in 2% perchloric acid in 2-butoxyethanol at 15V. As quenched samples were not tested due to the long dwell time between

electropolishing and APT data acquisition. APT experiments were carried out using a Cameca LEAP 4000 instrument at Rouen University. The temperature of the sample was maintained at 40 K under ultrahigh vacuum on the order of 8×10^{-11} Torr during the experiments. Evaporation was achieved in electric mode using a pulse with amplitude of 20% the DC voltage applied at 200 kHz repetition. The collected data was processed with the aid of Imago Visualization and Analysis Software (IVAS Cameca) package. Volume reconstructions were done following advanced techniques described and reviewed elsewhere [57–59]. Solute enriched poles were observed and removed from the volumes used for radial distribution functions (RDF) calculations.

4.3 Data interpretation

4.3.1 General framework

Small angle scattering (SAS) experiments are measurements of the fluctuations of scattering factor density and provide excellent statistical information due to the large analyzed volumes. These fluctuations originate from features in the sample such as precipitates or clusters. The use of different sources of radiation permits changes of the nature of scattering factors and in turn provides complimentary information from fluctuations in the same system. When using X-rays, the scattering signal is sensitive to variations in electron density and therefore provides information on the chemical fluctuations via the atomic number. Elements of close atomic number to the host solution, e.g. Si, Mg as solutes in Al, give low scattering whereas elements with large differences such as Cu result in stronger scattering. The nuclear scattering of neutrons is not related to atomic number, allowing for a scattering experiment in which elements with similar atomic number can still generate contrast, e.g. Mg in Al. A combination of scattering experiments with different sources provides a method for characterizing the fluctuations based on their chemical nature.

In an isotropic system of average scattering factor density $\bar{\rho}$, the intensity arising from a fluctuation in scattering factor density $\eta = \rho - \bar{\rho}$ can be written [60]:

$$I(q) = \int_0^\infty 4\pi r^2 \gamma(r) \frac{\sin(qr)}{qr} dr \tag{8}$$

where q is the scattering vector and $\gamma(r)$ is the so-called correlation function by introduced by Debye and Bueche [61]:

$$\gamma(r) = \langle \eta(\vec{r_1})\eta(\vec{r_2}) \rangle \text{ with } r = |\vec{r_1} - \vec{r_2}| = constant$$
(9)

 $\gamma(r)$ is the autocorrelation of scattering density fluctuation and is related to the SAS intensity through a Fourier transform. It can be re-written:

$$\gamma(r) = \overline{\eta^2} \gamma_0(r) \text{ with } \gamma_0(0) = 1 \tag{10}$$

with $\gamma_0(r)$ the normalized correlation function. In the absence of long range order (other than that of the underlying crystal giving rise to Bragg peaks), both γ and γ_0 go to zero for large r. By definition, $\gamma(0) = \overline{\eta^2}$, i.e. the mean square fluctuation of scattering factor density.

When considering concentration fluctuations (with constant atomic volume), the normalized correlation function $\gamma_0(r)$ is technique independent and is essentially geometric (i.e. it is characteristic of the shape of the objects and their interaction, if any). The mean square fluctuation, however, depends on what the technique is actually probing (electrons for X-rays, nuclear scattering length for neutrons, atoms for APT). Its expression will be discussed further in the paper.

Provided that the intensity in known over a wide enough range, the correlation function can be obtained by inverse Fourier transform:

$$\gamma(r) = \frac{1}{2\pi^2} \int_0^\infty I(q) q^2 \frac{\sin(qr)}{qr} dq \tag{11}$$

In particular, for r = 0:

$$\overline{\eta^2} = \frac{1}{2\pi^2} \int_0^\infty I(q) q^2 \, dq \tag{12}$$

Because this integral is always equal to the mean square fluctuation of the scattering factor density, irrespective of the shape of the features, it is often called the *invariant*.

This framework gives the relationship between a description of the chemical fluctuations in the real space $(\gamma(r))$ and the intensity it gives rise to in the reciprocal space (I(q)). The correlation function contains the information on the correlations between the positions of solute atoms. As shown in [51], it is closely related to the radial distribution function (RDF) which is a standard tool to describe the solute fluctuations in atom probe tomography [62,63].

4.3.2 The model for correlation function $\gamma(r)$

The concept of correlation function is very general and holds as well for a 2-phase model where one can distinguish between a matrix and precipitates (including non-particulate systems) or a system where concentration fluctuations are diffuse and can only be described by concentration wave functions.

In the study of precipitation of metals, the interpretation models are usually built up from the calculated correlation function (or SAS intensity) of a single object (precipitate) embedded in a matrix and generalized for an assembly of objects, with or without interactions. The correlation function (and associated SAS signal) of simple precipitate shapes (sphere, flat cylinder, long cylinder...) can be found in the literature [64]. It can be adapted for the particular system: is the concentration uniform in the object? Is the interface abrupt or diffuse? Are all the objects the same size? Are they interfering?

The answers to this questions lead to modification of the form factor, integration of a size dispersion function, use of an inter particles structure factor, all of which are interdependent and the complete modelling can be complex. Although this approach has been proven successful in numerous studies concerning fully formed precipitates in metallic system [37,50], clustering combines all these difficulties: (i) ill-defined shape, (ii) diffuse concentration with no clear interface, (iii) wide size dispersion and (iv) large quantity and number density implying

interference between objects. The combination of these aspects calls for a more statistical description of the concentration fluctuations. As in [51], we use a similar approach to that of Teubner & Strey [65] who built their description of the scattering of microemulsions upon a statistical description of the correlation function. The use of an exponentially decaying correlation (with a correlation length ξ) represents the direct correlation between the domains (clusters) and is general enough to capture the effect of a wide size dispersion and diffuse interfaces. This should be modulated by an oscillating function capturing the interaction between the domains. Oppositely to Teubner & Strey, we used a cos function to that purpose, which, in our experience, better reproduces the experimental data in metallic systems [65]. This model has already been successfully applied to early stages of solid solution unmixing in an Fe-Cr based alloy [51] and can be written:

$$\gamma(r) = \overline{\eta^2} \gamma_0(r) = \overline{\eta^2} \exp\left(-\frac{r}{\xi}\right) \cos\left(\frac{2\pi}{\lambda}r\right)$$
(13)

where the correlation length ξ is a measure of the clusters size and the modulation periodicity λ can be related to the distance between the domains. If λ is much larger than ξ , the objects are non-interacting. Smaller λ indicate much more numerous objects, i.e. higher quantity. The constant $\overline{\eta^2}$ is the mean square fluctuation or scattering invariant.

4.3.3 Corresponding intensity I(q)

The model used for $\gamma(r)$ can be re-injected in Eq. (1) which integral can be analytically calculated. The expression of the intensity gives:

$$I(q) = \overline{\eta^2} \frac{8\pi\xi^3}{(1+\xi^2 q^2)^2} S(q,\lambda,\xi)$$
(14)

The structure factor $S(q, \lambda, \xi)$ is such that its value is 1 when λ is large (small fraction). For decreasing λ , $S(q, \lambda, \xi)$ creates an interference peak at intermediate q before reaching 1 for larger q. $S(q, \lambda, \xi)$ writes:

$$S(q,\lambda,\xi) = \frac{\lambda^4 (1+\xi^2 q^2)^2 (\lambda^4 \xi^4 q^4 + (8\pi^2 \lambda^2 \xi^2 + 2\lambda^4)\xi^2 q^2 - 48\pi^4 \xi^4 - 8\pi^2 \lambda^2 \xi^2 + \lambda^4)}{(\lambda^2 \xi^2 q^2 - 4\pi\lambda \xi^2 q + 4\pi^2 \xi^2 + \lambda^2)^2 (\lambda^2 \xi^2 q^2 + 4\pi\lambda \xi^2 q + 4\pi^2 \xi^2 + \lambda^2)^2}$$
(15)

The positivity of the intensity imposes that $\lambda > \sqrt{12}\pi\xi$. The correlation length ξ is linked to the distance between solutes within a cluster and is hence a measure of the fluctuation size in real space. Figure 17 shows an example of the resulting intensity function fitted to a SAXS pattern obtained on a naturally aged Al-Cu-Li-Mg alloy. In addition to the described contribution of the clusters, we also added a Porod type contribution of large objects (e.g. dispersoids) proportional to $\frac{1}{q^4}$, as well as a constant contribution accounting for the solid solution Laue scattering and other incoherent source of signal (incoherent nuclear scattering for neutrons, fluorescence for X-rays).



Figure 17 Scattering profile for naturally aged Al-Cu-Li-Mg alloy and a corresponding model fit incorporating the scattering intensity due to clusters, large objects and a background constant.

4.3.4 Expression of the mean square fluctuation $\overline{\eta^2}$

While $\gamma_0(r)$ describes the geometric distribution of the fluctuations/clusters, independently of their chemical nature, $\overline{\eta^2}$ is a function of their chemical content. In such, it is technique dependent, since each technique has its own sensitivity to each element (see Table 4). The contribution of each element should be explicated. Let us start with a binary Al-Cu system, for which we assume the atomic volume Ω to be constant. Since $\eta = \rho - \overline{\rho}$, we can write $\overline{\eta^2}$ as:

$$\overline{\eta^2} = \langle (\rho - \overline{\rho})^2 \rangle = \frac{(f_{Al} - f_{Cu})^2}{\Omega^2} \langle (c_{Cu} - \overline{c_{Cu}})^2 \rangle = \frac{(f_{Al} - f_{Cu})^2}{\Omega^2} \overline{\Delta c_{Cu}^2}$$
(16)

where f_i is the (technique dependent) scattering factor. $\overline{\Delta c_{Cu}^2}$ is the mean square concentration fluctuation (independent of the technique). It has no units (it is a square concentration). Although its definition is more general, $\overline{\Delta c_{Cu}^2}$ is such that *in a 2-phase model* with well-defined volume fraction f_v :

$$\overline{\Delta c_{Cu}^2} = \langle (c_{Cu} - \overline{c_{Cu}})^2 \rangle = f_v (1 - f_v) \left(c_{Cu}^p - c_{Cu}^m \right)^2 \tag{17}$$

with c_i^p and c_i^m , the concentration in element *i* of the precipitates and the matrix, respectively. The mean square fluctuation, because it is related to the scattering invariant (i.e. to the integrated intensity) is traditionally used in SAS studies as a measure of the quantity of objects. Indeed, eq. (17) shows that it is related to the volume fraction through a contrast term $(c_{Cu}^p - c_{Cu}^m)^2$. If we can assume that this contrast term is constant, then the integrated intensity is indeed a measure of the quantity of scattering objects. In the early stages of solid solution decomposition, and when we only consider solute clusters, it is reasonable to release the assumption of fixed chemistry of the phases. In this case, the mean square concentration fluctuation $\overline{\Delta c_{Cu}^2}$ is not directly a measurement of the advancement of the reaction, since it may have a non-monotonic behaviour as more and more solutes are involved in the clusters. This can be understood by

looking at the 2-phase model case (eq. (17)) and imagining a fixed number of objects. If the number of solute atoms increase slower than the volume of the objects (i.e. the clusters concentration decreases), then the integrated intensity decreases. However, the reaction has arguably advanced since more solute atoms are involved.

A perhaps better measurement of the advancement of the reaction would be the total number of atoms involved in the clusters. While this is not measured by a scattering experiment, one may consider the mean square number of excess solute atoms. It is similar to what has been described in [60] as the square number of excess electrons by considering the intensity at q = 0 of a single object. At q = 0 all secondary waves being in phase, the intensity is simply the sum of excess electrons square. We can drop the $(f_{Al} - f_{Cu})^2$ term to define the mean square number of excess solute atoms $\overline{\Delta n_{Cu}^2}$. It is related to the mean square concentration fluctuation through:

$$\overline{\Delta n_{Cu}^2} = \frac{\overline{\Delta c_{Cu}^2}}{\Omega^2} \nu_c \tag{18}$$

where v_c is a correlation volume which is equal to $8\pi\xi^3$ in the model of eq. (1) and (14). Finally:

$$\overline{\Delta n_{Cu}^2} = \frac{8\pi\xi^3}{\Omega^2} \overline{\Delta c_{Cu}^2}$$
(19)

This solves the possible ambiguity of the mean square concentration fluctuation: whenever the mean square number of excess solute $\overline{\Delta n_{Cu}^2}$ increases, it means that more solutes are involved in the clusters. It is the sum of the square of the number of solutes in excess, per unit volume.

We should now consider the case of a ternary system, e.g. Al-Cu-Mg. The mean square fluctuation now consists in 3 terms, the Al-Cu interaction term, the Al-Mg interaction term, as well as the Cu-Mg cross term.

$$\overline{\eta^{2}} = \frac{(f_{Al} - f_{Cu})^{2}}{\Omega^{2}} \overline{\Delta c_{Cu}^{2}} + \frac{(f_{Al} - f_{Cu})^{2}}{\Omega^{2}} \overline{\Delta c_{Mg}^{2}} + 2\frac{(f_{Al} - f_{Cu})(f_{Al} - f_{Mg})}{\Omega^{2}} \overline{\Delta c_{CuMg}^{2}}$$
(20)

The cross term explains how there can be negligible signal even for significant clustering if $(f_{Al} - f_{Cu})$ and $(f_{Al} - f_{Mg})$ are of opposite sign. Their presence in the same clusters have compensating effects on the SAS intensity. Since we assumed a single type of fluctuations or clusters, the mass balance imposes:

$$\overline{\Delta c_{CuMg}^2} = \sqrt{\overline{\Delta c_{Cu}^2} \cdot \overline{\Delta c_{Mg}^2}}$$
(21)

Finally, in a ternary Al-Cu-Mg alloys, our model leaves 4 parameters to be determined: $\overline{\Delta c_{Cu}^2}$, $\overline{\Delta c_{Mg}^2}$, ξ and λ . In a single SAS experiment (SAXS or SANS), $\overline{\Delta c_{Mg}^2}$ and $\overline{\Delta c_{Mg}^2}$ are combined in a single $\overline{\eta^2}$ depending on the scattering factors. We thus used combined SAXS and SANS which

were simultaneously fitted to the model using the same 4 parameters $(\overline{\Delta c_{Cu}^2}, \overline{\Delta c_{Mg}^2}, \xi \text{ and } \lambda)$ for both experiments.

4.3.5 The radial distribution function from atom probe tomography and the correlation function

The chemical and spatial information obtained from APT experiments can be statistically analysed to calculate the partial pair correlation function from the radial distribution function (RDF) for solutes present in the dataset [19,63]. The pair correlation function is a measurement of the probability to find a specific pair of atoms at a distance r and is hence a good way of describing solute clustering. Analysis on sufficiently large APT data sets provide good statistics on the correlation of solutes and have been used to estimate solute ratios in clusters [19]. As derived from the RDF, the partial pair correlation function $g_{i-j}(r)$ between element *i* and element *j* can be defined as the average local concentration in element *j* around atoms of *i* at a given distance *r* normalized by the mean concentration of *j*:

$$g_{i-j}(r) = \frac{c_{i-j}(r)}{\overline{c_l}}$$
(22)

The method may be influenced by some of the artefacts associated with the experimental procedure of APT, such as the (anisotropic) spatial resolution; however, their qualitative properties should not be affected. As shown by Couturier et al. [51], the correlation functions for both APT data and SAS data are both measurements of the same fluctuation of solute within the sample. The relationship between the correlation function introduced in the previous sections and the APT RDF can be written:

$$g_{Cu-Cu}(r) - 1 = \gamma_{APT}(r) = \frac{\overline{\Delta c_{Cu}^2}}{c_{Cu}^2} \cdot \gamma_0(r)$$
(23)

where $\gamma_{APT}(r)$ is simply the APT Cu-Cu pair correlation extracted from the RDF minus 1 to allow for a zero value for large r. The value at r = 0 gives the mean square concentration fluctuation.

4.4 Results

4.4.1 Solute correlations obtained from APT

The volumes of the Al-Cu-Mg and Al-Cu-Li-Mg alloy in the naturally aged (NA) condition analysed by atom probe tomography are shown in Figure 18. Microstructural features are not contained in the volumes and hence they are good representations of the NA solid solution. A closer look into the solute distribution is highlighted by the 2D sections. The distributions of solutes appear to be non-random with some correlation between solute existing. Nevertheless, areas of high solute density are not easy to identify with certainty. We calculate the RDFs of all solutes in order to characterise the non-random distribution of solute in the volumes.



Figure 18 Atom probe volumes of naturally aged Al-Cu-Mg and Al-Cu-Li-Mg alloys with corresponding 2D sections

The auto-correlation functions $\gamma_{APT}(r)$ calculated from APT are presented in Figure 19. For the Al-Cu-Mg alloy in the NA condition clustering of solutes is statistically significant as shown by increased correlation of both Cu and Mg atoms and their cross-correlation in Figure 2a. The correlation data indicates an exponential decay with respect to distance. The correlation becomes negligible for distances larger than 2 nm suggesting the presence of very small domains.



Figure 19 Amplitude of the radial distribution functions for solute pairs in (a) Al-Cu-Mg and (b) Al-Cu-Li-Mg alloys in the naturally aged condition. Deviations from zero are indicative of solute correlation

For the Al-Cu-Li-Mg alloy, the correlation functions calculated for all possible solute pairs in the in the NA condition are shown in Figure 19b. The Mg-Mg correlation is shown to be the strongest with $\gamma_{APT}(0)$ values estimated above unity, suggesting that Mg atoms are strongly correlated at distances below 2 nm. The Cu-Cu and Cu-Mg correlations are weaker when compared to that observed for Mg. Li related correlations seem compatible with a random distribution ($\gamma_{APT}(r) \equiv 0$) in all cases. The lack of Li correlation (clustering) allows for the interpretation of the small-angle scattering without Li-related signal.

4.4.2 Experimental results from SANS and SAXS

The raw SAXS 2D patterns are shown on Figure 20. The intensity of these images is essentially isotropic. Their corresponding radially averaged SAXS and SANS 1D scattering profiles are shown on Figure 21 for all alloys in the AQ and NA state. In all cases SANS data appears with an order of magnitude lower intensity as compared to SAXS data because of to the lower scattering cross section of neutrons.



Figure 20 Raw 2Dscatterubg data as captured during SAXS experiments for naturally aged (a) Al-Cu-Li, (b) Al-Cu-Mg and (c) Al-Cu-Li-Mg alloys. The isotropy of the signal permits for radial averaging

The Al-Cu-Li alloy shows only small differences between the AQ and NA conditions (Figure 21a) evidencing the small change to clusters during natural ageing. The SANS curve for this alloy is mainly composed of a combination of typical scattering intensity from large objects and a flat constant intensity as described in Figure 17. It shows a somewhat larger intensity in SAXS, suggesting some degree of clustering of Cu.



Figure 21 Radially averaged profiles of the scattering intensity collected during SAXS (•) and SANS (x) experiments for (a) Al-Cu-Li, (b) Al-Cu-Mg and (c) Al-Cu-Li-Mg alloys. Data for the as quenched (blue) and naturally aged (red) conditions is shown.

Alloys containing Mg show very different curves in the AQ and NA conditions, whether observed by SAXS or SANS, evidencing the occurrence of clustering during natural ageing. In the AQ condition SANS profiles are flat (Figure 21), whereas a small but significant SAXS intensity is recorded. The higher sensitivity of X-rays to Cu suggests that the initial clustering in the AQ state is dominated by Cu. After natural ageing, large scattering signal appears in both alloys with both experimental techniques. The relative increase for SANS intensity is larger than that of SAXS intensity, suggesting clusters have higher concentration of Mg in the naturally

aged condition. The shape of the profiles is similar in SAXS and SANS and will be more precisely evaluated when modelling the SAS signal. Nevertheless, this similarity is compatible with our model using a single type of concentration fluctuations.

The comparison between the Al-Cu-Li and the Al-Cu-Li-Mg alloys, whose composition difference is only 0.4 at% Mg, is particularly interesting. The Al-Cu-Li alloy presents only a very small amount of clustering in the AQ condition which does not evolve much during 3 days of natural ageing. When adding a small amount of Mg (which does not give contrast with X-rays), a dramatic change of scattering is observed. This means that the addition of a small amount of Mg to Al-Cu-Li provokes a major change in the clustering behaviour of Cu atoms.

4.4.3 Application of the model to the SAXS and SANS data

In addition to the experimental data for SANS and SAXS, Figure 21 also shows the model fitted to the data. The agreement is generally excellent, except for the large q range of some SANS patterns where the clustering signal is very low and the SANS signal seems to increase slightly, possibly due to the tail of a Bragg peak situated outside the q range of the experiment. Table 6 shows the values of the mean square concentration fluctuation ($\overline{\Delta c_{Cu}^2}$ and $\overline{\Delta c_{Mg}^2}$), the mean square number of excess solute ($\overline{\Delta n_{Cu}^2}$ and $\overline{\Delta n_{Mg}^2}$), the correlation length ξ and the interaction length λ . We also show on Table 6 an estimation of the cluster Mg/Cu ratio, estimated by:

$$\frac{Mg}{Cu} = \sqrt{\frac{\overline{\Delta c_{Mg}^2 + c_{Mg}^2}}{\overline{\Delta c_{Cu}^2 + c_{Cu}^2}}}$$
(24)

In addition to the parameter values, Table 6 also shows an estimation of the uncertainties on the obtained parameter. This estimation has been obtained by repeating the fit with 100 different random sets of initial guesses of parameters, in order to make sure we explore the complete parameter space. If this procedure results in very different values for a parameter, it means the amount of information is too low to determine this parameter.

Alloy	$\frac{\overline{\Delta c_{Cu}^2}}{(x10000)}$	$\overline{\Delta c_{Mg}^2}$ (x10000)	$\frac{\overline{\Delta n_{Cu}^2}}{(\text{nm}^{-3})}$	$\frac{\overline{\Delta n_{Mg}^2}}{(\text{nm}^{-3})}$	Mg/Cu	ξ (Å)	λ (Å)
Al-Cu-Li AQ	52±36	-	5.3±2.0	-	-	2.5±1.0	38±11
Al-Cu-Li NA	35±25	-	4.8±1.0	-	-	$2.7{\pm}0.7$	43±11
Al-Cu-Mg AQ	54±17	25±46	4.6±0.6	1.9±3.5	0.70	2.2±0.2	36±2.0
Al-Cu-Mg NA	41±9.0	137±31	9.9±1.0	34±11	1.82	$3.0{\pm}0.3$	42 ± 1.0
Al-Cu-Li-Mg AQ	63±44	1 ± 5.0	10.2 ± 1.4	0.1±0.5	0.13	2.9±1.0	44±4.5
Al-Cu-Li-Mg NA	30 ± 0.4	5 ± 0.25	38.9 ± 0.6	7.1±0.14	0.42	5.2 ± 0.05	72±0.5

Table 6. Concentration fluctuations measured by fitting combined data from small angle scattering using both X-rays and neutrons.

4.5 Discussion

Choosing to analyse the solute distribution in the naturally aged condition as observed by APT using RDF gives information on its non-random nature which can be argued to appear visually

in Figure 18. A benefit for using RDFs calculated based on equation 15 is that they do not require assumptions such as: minimum cluster size, minimum distance between solute atoms or an iso-concentration interface to signify a cluster. RDFs are calculated on large volumes and are considered as averages of the ensembles with errors arising only from the method used to collect the data. As such, RDFs are a purely statistical approach and hold true for domains with diffuse interfaces, variable composition and size which is likely the case of clusters. Furthermore, the average nature of RDFs grants the ability to directly compare them to auto-correlations calculated from an interpretation model for the intensity of SAS. The fact that Li shows very low correlation to itself and other solutes (Figure 19) in the APT data suggests that its distribution is near random. Such a distribution of Li will not give rise to scattering factor fluctuations when observed by SAS and hence allows for Li to be dropped from the interpretation of SAS intensity.

Characterisation of the distribution of solute using SAS provides global average data which is visually rich and its azimuthal averaging intuitively shows changes between the AQ and NA condition (Figure 21). Further information can be accessed by making some assumptions necessary to adopt an interpretation framework. The most global assumption is that of a constant atomic volume, Ω , which when taken greatly simplifies the calculations of scattering factor density difference. The signal isotropy, the coherency of solute domains studied mean that lattice strains they impose are low and make constant volume a good approximation. Having this in mind, the model proposed by Couturier et al. [51] is dependent on only 3 parameters which hold physical meaning. The relationship between these parameters and physical properties of solute clusters are discussed below.

The correlation length, ξ , being a measure of the mean distance at which solutes are encountered in a domain is strongly correlated to the mean size of objects. In the initial stages of solute clustering all alloys have very small correlation lengths indicating that clusters are small. The change of scattering intensity between AQ and NA states for Al-Cu-Mg and Al-Cu-Li-Mg alloys results in larger correlation lengths which in turn mean larger clusters. The modulation periodicity, λ , allows the model to capture possible interaction between domains. It can be visualised as the concept of excluded volume when considering precipitation in a two phase model where two precipitates cannot be found on the same point of the lattice. As such the periodicity, λ , is related to the average distance between domains. The relationship between λ and ξ is linked through the correlation volume v_c and the number density of domains. However, due to the global nature of SAS this relationship cannot be separated without assumptions.

The third and final parameter of the interpretation model is the mean square fluctuation, η^2 , which is a constant dependent only on the measurement technique. When normalised by the respective differences of scattering factors it returns the mean square fluctuation in composition, $\overline{\Delta c_t^2}$. Furthermore, $\overline{\Delta c_t^2}$ grants access to the mean squared number of excess solutes, $\overline{\Delta n_t^2}$, which is a measure of the progression of a reaction.

The use of the interpretation model (equation 6) with the calculated parameters presented in Table 6 effectively captures the intensity of SAS experiments (Figure 21) in all cases. In the Mg free alloy, no significant evolution is observed during natural ageing. However, in the two Mg containing alloys, natural ageing results in a strong increase of the number squared of excess

solute (both Cu and Mg), correlation length and periodicity. The Mg/Cu ratio calculated through combined SAS experiments is in excellent agreement with previously reported solute ratios from APT experiments on the same alloy [13]. The lower Mg/Cu ratio in the Al-Cu-Li-Mg alloy can be related to the lower concentration of Mg. Nevertheless, the addition of only 0.45 at. % Mg to the Al-Cu-Li system results in profound changes to the clustering behaviour, in particular of Cu, which is worth further investigation. Forthcoming publication will be devoted to the kinetics of cluster formation in the aim to elucidate this effect.

4.6 Conclusion

We have successfully developed a methodology for characterising the state of solute clustering in aluminium. The complimentary interpretation of SAXS, SANS and APT results has been facilitated by the use of an interpretation model which provides crucial information on the clusters in the system. The main points can be summarised as:

- The non-random solid solutions of aluminium containing solute clusters can be effectively characterized by statistical methods.
- Considering clusters as fluctuations in solute concentration has been shown to yield agreement between APT and SAS techniques.
- In the AQ condition, some Cu rich clusters are already present in the alloys.
- A significant change in the cluster state occurs between the AQ and NA condition.
- In the NA state, Mg is shown to be significantly involved in clusters.
- The drastic increases in quantity of Cu rich clusters by addition of Mg to Al-Cu-Li is strong evidence that Mg positively affects Cu clustering.

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Clustering kinetics during natural ageing of Al-Cu-(Li, Mg) alloys

The previous chapter developed a method for characterizing solute clusters using SAS and reveal a large difference in clusters quantity and type in naturally aged Al-Cu-(Li, Mg) alloys. Here, we take advantage of the possibility to carry out in-situ SAS experiments in order to follow the kinetic nature of clustering from as quenched to naturally aged condition. We compliment the results of SAS with snap shots during natural ageing analysed by DSC and micro-hardness. Mg is identified as a critical component for the clustering of Cu in the alloys studied. Combining these techniques reveals the evolving chemical composition of clusters during natural ageing. The possible presence of more than one family of cluster in these alloys is discussed with regards to different Mg concentrations within clusters.
5 Clustering kinetics during natural ageing of Al-Cu-(Li, Mg) alloys

5.1 Introduction

Natural ageing describes the undergoing changes to the micro-structure, or rather nanostructure, of many Aluminium alloys after they have been quenched from solution treatment temperature. First observed by Wilm in 1906 and later characterised by Guinier and Preston [1–4], the increase of hardness at room temperature experienced during natural ageing is related to the solute distribution at the atomic scale. Solute clustering describes the initial stage of decomposition of a super saturated solid solution into one with solute-rich domains retaining the host crystal structure. Clustering has been particularly studied for the Al-Mg-Si system where precipitation hardening kinetics are decreased subsequently to cluster formation at room temperature; hence revealing complex interactions between solutes and excess vacancies [5–8]. On the other hand, Cu-Mg rich clusters in the Al-Cu-Mg system result in considerable hardness gains for short ageing times at elevated temperature and once again point towards strong interactions between the constituents of the super saturated solid solution [9–11]. The interplay between solutes and solute-vacancies governing solute clustering becomes more complex in multi-constituent alloys and renders necessary to combine several analytical techniques to quantify clustering and its kinetics (Chapter 4).

The multi-constituent, Al-Cu-Li-X alloys, have been of particular interest in recent years due to the development of alloys with attractive combinations of properties for light structure application in the aerospace industry [12]. The desired precipitate microstructure has been the focus of research showing strong dependency on dislocations (deformation) and minor alloying elements [13,14]. Decreus et al. reported the presence of Cu-rich clusters after natural ageing in an Al-Cu-Li-Mg [15] and Araullo-Peters revealed solute segregation on dislocations during early stages of ageing [16]. It becomes clear that solute clusters are an integral part of the structure of these alloys and play a crucial role both directly and indirectly on achieving the desired properties. The present work presents an evaluation of cluster evolution during natural ageing in two Al-Cu-Li and Al-Cu-Li-Mg alloys and compare it to an alloy of the Al-Cu-Mg system.

Solute clusters, being of the same crystal structure as the host Al matrix, showing no interface and only mild compositional contrast have posed great difficulties to be unambiguously characterized. Experimental techniques have been mostly based on global sample methods such as differential scanning calorimetry (DSC) [17], electrical resistivity [18] and of course hardness and tensile tests provide evidence for the formation and evolution of clusters. On the other hand, K. D. Ralston et al. report direct imaging of Cu-Mg clusters by high resolution aberrationcorrected TEM [19]; however this method has proven very difficult due small quantity and low Z-contrast of the solute species associated in individual clusters of a family with large number density. Techniques such as positron annihilation spectroscopy [20] and nuclear magnetic resonance [21] provide more information about the local environment of solutes. Atom Probe Tomography (APT), giving access to the 3D position and chemical identity of atoms, has been extensively used in conjunction with cluster-finding algorithms [9,11,22] to provide information on the correlation of solutes and size distributions of clustered domains. In situ small angle scattering (SAS) techniques, capable of pursuing the evolution of near atomic scale scattering factor inhomogeneity, provide bulk averaged information on the size and quantity of scattering domains [23]. A recently proposed methodology combining contrast variation [24] from correlative scattering by X-rays and neutrons, and a model describing scattering due to compositional fluctuations [25] has successfully provided quantitative measurement of cluster chemistry (Chapter 4). In the following we apply this methodology in conjunction with DSC and hardness to study the evolution of cluster chemistry during natural ageing.

5.2 Materials and experimental methodology

Three subsets of the Al-Cu system were chosen to study the clustering behaviour during natural ageing. The alloys tested have nominal compositions shown in Table 1. The starting material was provided as 27 mm thick plates by Constellium-Voreppe C-TEC, France. The plates were homogenized at 500 °C for 24 h, quenched and subsequently hot rolled to 3 mm at 350 °C. Flat samples from the 3 mm plates were ground and polished for micro-hardness observation using a 200 gf Vickers indenter. They were solution treated at 500 °C for 30 min, water quenched and tested. The measurements obtained within 5 min after quench correspond to the as quenched condition (AQ). Hardness evolution was monitored during the following 2 weeks. Samples aged for 72 h or longer are referred to as naturally aged (NA).

Table 7 Alloy compositions

Alloy	Cu at.% (wt. %)	Li at.% (wt. %)	Mg at.% (wt. %)	Al	Mg/Cu
Al-Cu-Mg	1.1 (2.5)	N/A	1.7 (1.5)	Bal.	1.55 (0.6)
Al-Cu-Li	1.5 (3.5)	3.5 (0.9)	N/A	Bal.	N/A
Al-Cu-Li-Mg	1.5 (3.5)	3.5 (0.9)	0.45 (0.4)	Bal.	0.3 (0.11)

Differential scanning calorimetry samples were prepared from the rolled plates by cutting 3 mm diameter discs at 0.5 mm thickness by a slow speed saw. The samples were batch solution treated at 500 °C for 30 min, water quenched with the as quenched (AQ) samples being tested within 2 min. Additional samples were left at room temperature after quench for 1, 2, 4, 6, 16 and 72 hours to represent steps along the ageing process. DSC experiments were carried out using a TA instruments Q200 DSC equipped with a RCS 90 cooling system allowing experiments to start at -50 °C. The experiments used pure Al crucibles and a 10 °C/min heating rate for all runs. As clustering reactions usually take place at room temperature, they are expected to generate formation and dissolution peaks at temperatures below 300 °C at the rate tested in the DSC. To focus on the low temperature clustering region and maximize the quality of the baseline correction so as to measure very weak clustering peaks, a three step DSC procedure was used. It consists of 1) heating ramp from -50 to 350 °C, 2) cooling segment down to -50 °C at 50 °C/min and 3) final re-heat up to 350 °C of a sample (versus an empty crucible). This procedure generates a sample specific baseline (run 3) which does not depend on estimates

of the heat capacity of the alloy, the reference used, the crucibles used or the sample vs reference position within the DSC as long as there is no reaction taking place (which is the case for up to at least 250°C). Subtracting run 3 from run 1 generated accurate baseline corrected data for the clustering reactions taking place. In order to check the validity of this procedure, a DSC scan in the full range until the single phase field (up to 550°C) was warried out using a Mettler Toledo DSC 3+ Star instrument, and standard polynomial baseline correction [9]. As shown in Figure 22, the low temperature data yields excellent agreement between the two instruments. For the low temperature range, the 2-ramp baseline correction is assumed to yield more stable results.



Figure 22 Typical heat flow profile for 10 °C/min ramp heating experiment on a naturally aged Al-Cu-Mg. The blue curve is a DSC scan on a full temperature range up to 550 °C typically carried out for precipitation studies. The red curve focuses on the low temperature range, -50 to 350 °C, where heat from clustering reactions occurs.

Small angle neutron scattering (SANS) experiments were carried out at the D11 instrument at the Institute Laue Langevin (ILL) in Grenoble, France. Samples from the 3 mm thick plate were solution treated, quenched and tested in situ up to 12 h. Additional samples aged ex situ were tested for the naturally aged condition. Bragg diffraction effects, including double diffraction, were removed by using a neutron wavelength of 5 Å. The sample to detector distance was kept constant at 1.2 m capturing scattering vectors from 0.07 to 0.6 Å⁻¹. All experiment data has been background corrected, normalized to absolute units and azimuthally averaged using the Graphical Reduction and Analysis SANS Program package (GRASP).

Small angle X-ray scattering samples were obtained by grinding and polishing the 3 mm plates down to \sim 300 µm, solution treating at 500 °C for 30 mins and water quenching. The final thickness reduction to 80 µm was achieved with in 15 mins after quench. These samples were

labelled as quenched (AQ) and their evolution was monitored in situ during 72h up to the fully naturally aged (NA) condition. X-rays were generated using a Rigaku MicroMax-007 HF rotating anode with Cu K_{α} X-ray source (λ =1.52Å) and scattering data was collected using a DECTRIS Pilatus 300K detector. The photon counting Pilatus detector, with its virtually zero noise, allows for excellent statistics even at low counting rates required by the present study. The collected data was background corrected and normalized to absolute units with a glassy carbon sample as a secondary calibration standard using in house scripts. For better comparison with neutron scattering, we chose to convert the X-ray intensities to cm⁻¹ rather than the more commonly reported # electrons² per Å³. The sample to detector distance was 0.6 m allowing for measurement of scattering vectors ranging between 0.02 and 0.5 Å⁻¹.

The scattering data from experiments with neutrons and X-rays has been interpreted using a recently proposed methodology described in Chapter 4. The radially averaged intensity of an isotropic systems with fluctuations around a scattering factor density $\bar{\rho}$ has been described by G. Porod as[26]:

$$I(q) = \int_0^\infty 4\pi r^2 \gamma(r) \frac{\sin(qr)}{qr} dr$$
(25)

where q is the scattering vector and $\gamma(r)$ is the so-called correlation function of scattering density fluctuation by Debye & Bueche [27]:

$$\gamma(r) = \langle \eta(\vec{r_1})\eta(\vec{r_2}) \rangle \text{ with } r = |\vec{r_1} - \vec{r_2}| = constant$$
(26)

By definition the mean square fluctuation of scattering factor density is $\gamma(0) = \overline{\eta^2}$. A Fourier transform relates the SAS intensity and the real space autocorrelation of scattering density fluctuations. When the intensity is known over a wide q range, the correlation function can be obtained by the inverse Fourier transform:

$$\gamma(r) = \frac{1}{2\pi^2} \int_0^\infty I(q) q^2 \frac{\sin(qr)}{qr} dq$$
(27)

and in particular, for r=0:

$$\overline{\eta^2} = \frac{1}{2\pi^2} \int_0^\infty I(q) q^2 \, dq \tag{28}$$

Because this integral (and $\gamma(0)$) is always equal to the mean square fluctuation of the scattering factor density, irrespective of the shape of the features, it is often called the *invariant*. The intensity in reciprocal space (I(q)) and a statistical description of the real space chemical fluctuations are hence related.

The model for the correlation function $\gamma(r)$ has been proposed by [25] and in Chapter 4.3.2 as:

$$\gamma(r) = \overline{\eta^2} \gamma_0(r) = \overline{\eta^2} \exp\left(-\frac{r}{\xi}\right) \cos\left(\frac{2\pi}{\lambda}r\right)$$
(29)

where the correlation length ξ is a measure of the scattering domain size and the modulation periodicity λ , can be related to the distance between domains. The mean square fluctuation of the scattering factor density, $\overline{\eta^2}$ is taken from Chapter 4.3.4 as:

$$\overline{\eta^{2}} = \frac{(f_{Al} - f_{Cu})^{2}}{\Omega^{2}} \overline{\Delta c_{Cu}^{2}} + \frac{(f_{Al} - f_{Cu})^{2}}{\Omega^{2}} \overline{\Delta c_{Mg}^{2}} + 2 \frac{(f_{Al} - f_{Cu})(f_{Al} - f_{Mg})}{\Omega^{2}} \overline{\Delta c_{CuMg}^{2}}$$
(30)

with $\overline{\Delta c_i^2}$, the mean square concentration fluctuation of element i and f_i the scattering factor for the considered radiation. Li is not considered in this interpretation as APT observations [28] (Chapter 4.4) reveal uniform distribution through the material resulting in no concentration fluctuations. Using this model, we simultaneously fit combined data from SAXS and SANS to gather the evolution of the 4 technique independent parameters describing the fluctuations due to solute clusters ($\overline{\Delta c_{cu}^2}, \overline{\Delta c_{Mg}^2}, \xi$ and λ). Finally, the mean square number of excess solute atoms

$$\overline{\Delta n_{Cu}^2} = \frac{8\pi\xi^3}{\Omega^2} \overline{\Delta c_{Cu}^2}$$
(31)

is used to represent the advance of a reaction as whenever it increases, it means that more solutes are involved in clusters. It is the sum of the square number of solutes in excess, per unit volume.

5.3 Results

The super saturated solid solution obtained after quenching from solution treatment temperatures contains the distribution of solutes closest to random. The evolution of solute distribution taking place at room temperature during natural ageing, were monitored using micro-hardness, differential scanning calorimetry (DSC), small angle scattering using X-rays (SAXS) and neutrons (SANS). Most of the evolution occurred during the first day (24 h) of ageing and measurements were found to plateau after 3 days (72 h) resulting in the naturally aged condition (NA). The details of this evolution are described in the following section.

5.3.1 Natural age hardening

The hardness evolution after quench depicts the undergoing changes to the distribution of solutes in the alloys studied. The hardness increase at room temperature with time, termed natural ageing, is shown in Figure 23. The Al-Cu-Li and Al-Cu-Li-Mg alloys start at 64 ± 2 HV. It is worth noting that the addition of 0.4 at. % Mg to the Al-Cu-Li system does not change the initial hardness significantly. The Al-Cu-Mg has higher as-quenched hardness at 74 ± 2 . These initial hardness values serve as an indication of the degree of solute in solution as only limited clustering or precipitation are expected this early after quench.

Alloys containing Mg show significant increase in hardness compared to the Mg free Al-Cu-Li alloy over the course of natural ageing. The as-quenched difference between Al-Cu-Mg and Al-Cu-Li-Mg alloys diminishes for longer ageing times. Hardening saturates after about 10h and for longer ageing times the hardness changes remain within experimental errors around the average naturally aged hardness. Ageing for 72 h after quench has been chosen as a point beyond which alloys are stable and can be termed 'naturally aged'. The naturally aged hardness values are 77 ± 3 , 117 ± 3 and 115 ± 3 HV for the Al-Cu-Li, Al-Cu-Mg and Al-Cu-Li-Mg alloys respectively. Exposure to room temperature after quench has on average resulted in a 20, 55 and

82 % hardness increase systems respectively. The vast change in behaviour of the Al-Cu-Li alloy by the addition of only 0.4 at. % Mg is clearly shown and highlights the importance of Mg solute atoms for the natural ageing processes. Furthermore, kinetic and quantitative similarity of the Al-Cu-Mg and Al-Cu-Li-Mg alloys during natural ageing suggests that only a small quantity of Mg is necessary to achieve hardening.



Figure 23 Natural age hardening curves for Al-Cu-Mg (green), Al-Cu-Li (blue) and Al-Cu-Li-Mg (red) alloys. Alloys containing Mg are shown to nearly double their hardness.

5.3.2 Differential scattering calorimetry

The heat flux vs temperature profiles for a selection of ageing times of Al-Cu-Mg alloy are shown in Figure 24. The profiles can be divided into two distinct regions with the first containing the exothermic peak between 50 and 125 °C and the second the endothermic peak between 150 and 260 °C. Within the first region, Cu-Mg clusters are forming during the DSC run and giving rise to the exothermic peak. The potential for cluster formation is expected to decrease with ageing time at room temperature together with the formation of cluster prior to the DSC scan; actually the integral of this region halves within 1h and continues to decrease during the first 6h. The formation of Cu-Mg clusters observed here is in line with previously reported DSC experiments on Al-Cu-Mg alloys [10,29]. The second region covers the dissolution of clusters previously formed in the sample. The area of the second region does not vary significantly with ageing time, meaning that the quantity of solute (Cu, Mg) involved in clusters formed at room temperature (during natural ageing) and that involved in cluster formation during the DSC experiment (in the as-quenched sample) is the same. The dissolution of clusters results in a characteristic double minima endothermic region which is consistently observed. Variation in

cluster chemistry, cluster size distribution, or even a complex dissolution-growth process may lead to such behaviour. The dissolution of Cu-Mg clusters liberates solute necessary for the rapid hardening reaction [30–33] which causes the profiles to group up at temperatures above $260 \,^{\circ}$ C.



Figure 24 DSC heat flux profiles for Al-Cu-Mg alloy carried out after various ageing times at room temperature with a heating rate of 10 °C/min. The as quenched (AQ) condition represents a case where all clusters are forming and dissolving in the DSC. The naturally aged (NA) condition represents the case where all clusters have formed at room temperature and are only dissolving in the DSC.

The temporal evolution of the heat flux profile for the Al-Cu-Li alloy is shown in Figure 25. The profiles remain flat with only a small magnitude endothermic region between 50 and 200 °C. No well-defined exothermic reactions are observed during the DSC experiments independent of the ageing time. However, for longer ageing times at room temperature, the increase of the endotherm indicates more dissolution, meaning that clustering reactions are too slow to occur during a DSC scan, but can occur during the course of a long natural ageing.



Figure 25 DSC heat flux profiles for Al-Cu-Li alloy carried out after various ageing times at room temperature with a heating rate of 10 °C/min.

Addition of 0.4 at% Mg to the Al-Cu-Li alloy vastly changes the heat flux profiles occurring in various states of ageing as shown in Figure 26. In general, the curves can be again divided in two regions, the reactions taking place between 50 and 135 °C and the reactions at temperatures above 135 °C up to 250 °C. Within the first region an exothermic peak appears for short ageing times and its magnitude is reduced with ageing up to 4h. This peak is in close proximity to that resulting from formation of Cu-Mg clusters in the Al-Cu-Mg alloy. Ageing for longer than 4h develops an endothermic peak in the first region. The proximity of the exothermic peak in the as quenched condition and the endothermic peak in the naturally aged condition make it unlikely that the solutes involved in these reactions are the same. The endothermic peak could be related to the disordering of short-range order involving Li [34]. Li ordering has been shown to be strongly influenced by the presence of Mg for the Al-Li-(Mg) system through changes to Li solubility in the alloy [34].

The profiles group up and remain in close proximity during the reactions in the second region, namely the temperature range between 135 and 250 °C. Dissolution of clusters is taking place independently from their formation at room temperature (naturally aged) or during the DSC experiment (as quenched). The shape of the endothermic peaks closely resembles those observed for the Al-Cu-Mg alloy where Cu-Mg clusters are reported to dissolve [10,15,35] albeit at a lower temperature. As the temperature increases, dissolution of clusters approaches completion and is followed by precipitation reactions at temperatures above 250 °C.



Figure 26 DSC heat flux profiles for Al-Cu-Li-Mg alloy carried out after various ageing times at room temperature with a heating rate of 10 °C/min. The as quenched (AQ) condition represents a case where clusters are forming and dissolving in the DSC. The naturally aged (NA) condition represent the case where clusters have formed at room temperature and are only dissolving in the DSC. The cluster reactions are significantly influenced by minor additions of Mg in comparison to Figure 25.

5.3.3 Small angle scattering

Combining small angle scattering measurements using X-rays and neutrons generates data which grant access to information about the length scale and chemistry of scattering domains [24]. These techniques provide excellent statistics, due to the large analysed volumes, and ability for in situ experiments reveals the temporal evolution of properties. The experimentally obtained SAS patterns are displayed in Figure 27 for the boundary conditions (AQ and NA) and one intermediate point. Natural ageing of 6h was selected for this point to match the ageing time for which no exothermic peaks are observed by DSC (Fig2-4). The scattering signals are isotropic indicating domains have near spherical shape and maintain it throughout the naturally ageing process. Diffuse scattering develops at intermediate angles clearly indicating evolution during naturally ageing. In the following sections, the radially averaged profiles are analysed to show the significant influence of Mg on clustering. The combination of time resolved X-ray and neutron scattering reveal quantitative morphological and chemical information about the clusters. The data, analysed by a recently proposed methodology for diffuse concentration fluctuations with contrast variation, reveal the chemical evolution of the clusters forming during natural ageing.

Al-Cu-Li



Figure 27 Evolution of small angle scattering 2D patterns during in situ natural ageing (masked area in black)

5.3.4 Temporal evolution of scattering intensity

The evolution of scattering intensity with ageing time after quench has been evaluated with in situ SAS using both X-rays and neutrons. Scattering profiles obtained during the first 10 h after quench and the naturally aged condition are shown in Figure 28. Data is obtained for the same

ageing times and the results are consistent for X-rays and neutrons. X-rays result in higher scattering intensity compared to neutrons due to the lower scattering cross section of neutron radiation. During the ageing period, the intensity increases in q range (0.1 - 0.4) Å⁻¹ corresponding to domains with average radii on the order of (10 - 2.5) Å. Scattering domains with solute concentration above average are solute clusters. Changes to the quantity and solute concentration of these clusters during ageing causes the evolution of intensity with time. Clusters are observed to develop in the Al-Cu-Mg and Al-Cu-Li-Mg alloys in agreement with the DSC and hardness results. The Cu rich clusters in Al-Cu-Li do not evolve in the absence of Mg as shown by SAS, DSC and hardness.

The scattering intensity observed by X-rays is predominantly due to Cu as this atom has the highest contrast variation with the Al matrix (Table 8). The formation of clusters with above matrix concentration of Cu is observed for the Al-Cu-Mg alloy in Figure 28b. X-ray scattering for the Al-Cu-Li alloy is possible due to Cu or Li clustering; however APT results strongly suggest that Li does not cluster [28]. Therefore, the small degree of scattering observed for this alloy (Figure 28a), suggests that any Cu rich cluster formed during quench. These clusters show little evolution after quenched. This is in agreement with the results of DSC and hardness and previous reports [36]. The addition of 0.4 at. % Mg to the Al-Cu-Li alloy drastically changes the scattering profile evolution despite the negligible contrast of Mg. The critical role of Mg for the clustering of Cu in the Al-Cu-Li system is evidenced.

Table 8. SAS elemental sensitivity in aluminium alloys as defined by $(f_i - f_{Al})/f_{Al}$, with f_i and f_{Al} the scattering factors of element i and Al, respectively

respectively							
	Cu	Mg	Li				
SAXS	1.23	-0.08	-0.77				
SANS	1.23	0.55	-1.55				

Additional and complimentary information can be derived from neutron scattering where all three alloying elements result in scattering. The clustering observed for the Al-Cu-Mg alloy involves both Cu and Mg resulting in more pronounced intensity changes subsequently to quench observed by neutrons over X-rays. No clustering is observed for the Al-Cu-Li alloy and the scattering profiles remain unchanged post quench in agreement with observations by DSC and hardness. From these finding and from atom probe tomography results on a similar alloy [28] (Chapter 4.4.1) it is possible to state that no clustering of Li is present. The critical role of Mg solute addition is again demonstrated with the dramatic change between the Al-Cu-Li and Al-Cu-Li-Mg alloy (Figure 28c). The evolution of Cu rich clusters is observed to be dependent on the presence of Mg in these alloys.

5.3.5 Temporal evolution of cluster properties

The model describing scattering intensity due to concentration fluctuations has been fitted to the in-situ scattering data using the methodology described in Chapter 4. The model successfully captures the evolution of intensity during natural ageing as shown by the solid lines in Figure 28. The simultaneous use of complimentary scattering from X-rays and neutrons grants access to chemical nature of domains and their evolution over the ageing period. In addition, the Mg/Cu

concentration ratio in clusters can be calculated and compared to the global alloy ratio to further evidence the chemistry of clusters.

The temporal evolution of mean square number of excess solute atoms for the Al-Cu-Mg alloy is shown in Figure 29a. Initially (AQ condition) the clusters are predominantly Cu rich. Throughout ageing the excess Cu in clusters remains relatively stable at 10 per nm³. During the first hour of ageing the excess Mg in clusters increases to match the Cu and surpass it as shown by the Mg/Cu ratio in Figure 29b. Initially clusters contain less Mg than the matrix concentration. When natural ageing progresses the Mg concentration increases with the naturally aged condition reaching 9.9 ±1 Cu and 34 ±11 Mg per nm³ and representing a ratio of 1.82.

The initial clusters formed in the Al-Cu-Li-Mg alloy are on average domains with excess Cu (Figure 30a). The content of Cu in clusters slowly increases from 10.7 ± 1.7 to 15.6 ± 1.6 during the first hour of ageing, and then increases up to 38.9 ± 0.6 over the course of naturally ageing. During this time the Mg/Cu ratio remains very low evidencing that Cu rich clusters have formed Figure 30b. The excess Mg within clusters remains negligible during the first couple hours of ageing. For ageing times above 2h, the Mg solute content is shown to increase in parallel with the increase of Cu content. The naturally aged clusters contain on average an excess of 38.9 ± 0.6 Cu and 9.0 ± 0.18 Mg per nm³ which grants Mg/Cu ratio of 0.48 and lies above the mean of the matrix.





Figure 28 Raw scattering data evolution for a) Al-Cu-Li, b) Al-Cu-Mg and c) Al-Cu-Li-Mg alloys during in-situ SAXS and SANS experiments. Solid lines are model fits for the data.



Figure 29 a) Evolution of mean squared excess solute number in clusters for the Al-Cu-Mg alloy during natural ageing. Cu rich clusters are observed in the AQ condition with a lower Mg content. The Cu number remains relatively stable while excess Mg increases for during ageing. The Mg/Cu ratio is compared to the alloy ratio in b). There is less Mg in cluster up to about 1h of natural ageing. The naturally aged value is 1.8.



Figure 30 a) Evolution of mean squared excess solute number of solute in clusters for Al-Cu-Li-Mg alloy during natural ageing. Cu rich clusters are observed from the AQ condition and increases several folds during ageing. The excess Mg increases only after 3h of ageing. The Mg/Cu ratio is compared to the alloy ratio to evidence that clusters contain less Mg than the mean during the first 7 hours of ageing.

5.4 Discussion

Clustering kinetics are effectively captured through the micro-hardness, changes to DSC thermograms and evolution of scattering intensity. The combined results demonstrate the profound positive effect of Mg on clustering of Cu atoms in Al-Cu-(Li, Mg) alloys. The formation of Cu rich clusters is particularly well shown by the Mg/Cu ratios (Figure 29b and Figure 30b) which contain less Mg than the matrix during the very early stages of ageing. Presence of only 0.45 at. % Mg in the Al-Cu-Li system enables drastic changes to clustering. The hardening rates observed for the Al-Cu-Mg and Al-Cu-Li-Mg are comparable despite large differences in Mg concentration.

When submitted to a DSC ramp the as-quenched samples give rise to exothermic peaks below 100 °C due to clustering. The progressive reduction of peak magnitude with longer exposure to room temperature after quench validates that cluster forming in DSC experiments are the same as those forming during natural ageing. Clustering is approaching completion after 16 hours at room temperature. The necessity of Mg for clustering is clearly evidenced when comparing the Al-Cu-Li and Al-Cu-Li-Mg alloys whose composition only varies by 0.45 at. % Mg, yet their DSC thermograms are vastly different. Furthermore, if the DSC thermograms of the Al-Cu-Mg and Al-Cu-Li-Mg alloys are normalised by the Mg concentration and compared they show striking similarity (Figure 31). Thus, the main chemical reaction underlying the exothermic peak during the temperature scan from the AQ state is likely to be the formation of Cu-Mg bonds. The small miss-match between the two alloys may arise from the different Cu content leading to formation of Cu-Cu bonds which would also contribute to the exothermic heat.



Figure 31 DSC thermograms normalized to the Mg concentration of the alloy to help evidence the variety of Cu-Mg clusters forming.

In the NA condition the presence of a few Cu rich clusters gives rise to a small endothermic peak for the Al-Cu-Li alloy which is confirmed by the low level of small-angle scattering. The thermograms for the NA condition in Mg containing alloys consistently reveal a two-peak endothermic region above 100 °C. When normalised by Mg concentration the endotherm is comparable for the two alloys; however, the higher Mg concentration alloy has more thermally stable clusters, i.e. they dissolve at higher temperature. The existence of two endothermic peaks during ramp heating experiments in DSC suggests a possibility for more than one type of clusters (or of chemical bonds), a wide size distribution or varying chemical content. A striking difference between the two Mg-containing alloys is the presence of a large endotherm at 100 °C for the quaternary alloy. The lack of a similar peak in the Mg free Al-Cu-Li alloy evidences a relationship between Mg and this peak. A possible hypothesis suggests the breaking of a Li short range order formed only when clusters are present in the alloy. Such ordering could lead to diffraction intensity at larger angles beyond the range studied here. If we compare the scattering intensity when no such endothermic peak is present (from the AQ state to 6h of natural ageing) to the fully NA condition no clear conclusion can be drawn. However, the presence or not of this peak yields no difference in the shape or magnitude of the higher temperature endothermic double peak as seen on the thermograms, suggesting that it is not related to Cu-Mg clustering.

The chemical nature of clusters during NA in the different alloys is effectively accessed when using the contrast variation method described in Chapter 4. A small quantity of Cu rich clusters is present immediately after quench for all alloys. In the case of Al-Cu-Mg, where more Mg than Cu is in solid solution, the clusters are initially Cu rich but contain some Mg. The Mg/Cu ratio of clusters at this stage is below that of the global alloy composition. During ageing, formation of Cu-Mg clusters progresses through a rapid increase of the mean squared excess Mg. The segregation Mg and Cu leads to clusters with Mg/Cu ratio of 1.82 in the naturally aged condition which lies above the solute ratio of the alloy. The development of clusters is accompanied by a significant increase in hardness.

When a limited amount of Mg is available (Al-Cu-Li-Mg alloy) clustering is predominantly Cu rich yet the increase of hardness during ageing is comparable. In the initial stages, the Cu rich clusters are not accompanied by any measurable clustering of Mg, and yet it does not happen in the absence of Mg (in the ternary Al-Cu-Li alloy). This drastic promotion of Cu rich clusters and their rapid formation kinetics in the presence of Mg points towards an increase of the excess vacancies available for diffusion. Nevertheless, excess Mg is measured in clusters only after 2h of ageing and the Mg/Cu ratio surpasses that of the alloy after 8h. These results suggest that the rate of Mg clustering is proportional to its concentration. For the Al-Cu-Li system, where Mg is not present to facilitate clustering, only the few Cu rich clusters from quench remain and do not evolve appreciably, with no significant increase of hardness either.

One last interesting point is related to the comparison between DSC and SAS results. Results show that the DSC thermograms almost coincide in the two Mg-containing alloys when the data is scaled by the Mg concentration. Therefore, the DSC signal is dominated by Mg clustering through formation of Cu-Mg bonds or their dissolution. However, the SAS results show that the clustering behaviour in the quaternary alloy of low Mg content is dominated by the Cu clustering. If two populations of clusters exist with one being Cu rich and the other Cu-Mg with

similar ratios to the ternary Al-Cu-Mg, it would mean that Cu clustering does not result in appreciable DSC signal, presumably due to a lower enthalpy change during the clustering / dissolution reaction. Yet the combination of these clusters yields an appreciable increase of hardness for the quaternary Al-Cu-Li-Mg alloy, similar to that of the ternary Al-Cu-Mg alloy.

5.5 Conclusion

Clustering kinetics during natural ageing post quench have been successfully characterised using a combination of differential scanning calorimetry and small angle scattering and complimented with micro-hardness evolution. The results clearly identify Mg as a solute necessary for clustering at room temperature in the Al-Cu-(Li, Mg) system. The small quantity of Cu rich clusters formed during quench from solution temperature does not evolve in the Mg free solid solution. When the Mg/Cu ratio of the alloy is high, Mg rapidly clusters with the initial Cu rich domains resulting in an increase of hardness due to the formation of strong Cu-Mg bonds. The Mg/Cu ratio of these clusters in the naturally aged condition is close to 2. For the Al-Cu-Li-Mg alloy, where the Mg/Cu ratio is low, clustering is dominated by formation of Cu rich domains. These domains contain Mg but in significantly lower concentrations with the Mg/Cu ratio remaining below 0.5 for the NA condition. The formation kinetics of clusters are the same for the Al-Cu-Mg and Al-Cu-Li-Mg alloy despite the difference in Mg concentration. The rate of clustering reactions taking place and giving rise to hardness evolution and decrease of the exothermic peak from DSC appears to be rather independent of Mg concentration in the alloy. The combination of these results provides strong evidence for Mg acting in a catalytic manner to effectively increase the concentration and/or the mobility of vacancies available for diffusion. These results also suggest that the composition of Cu-Mg clusters may vary significantly leading to clusters with different thermal stability.

5.6 References

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Thermal stability and post-reversion formation of solute clusters in Al-Cu-(Li, Mg) alloys

The characterisation and kinetics of solute clustering during natural ageing have been presented in the previous chapters. The co-existence of several solute cluster families including Mg is explored through heating in-situ SAS and DSC experiments. Cu rich clusters are found to dissolve at lower temperature followed by dissolution of clusters containing both Cu and Mg. We investigate the possibility to reform clusters after they have been isothermally reverted and use clustering kinetics to elucidate vacancy solute interactions. Dissolving the most stable Cu-Mg clusters at 250 °C in the quaternary alloy (Al-Cu-Li-Mg) forms a solid solution which can post reversion naturally aged at comparable kinetics to those obtained after quench from 500 °C. A strong link between Mg in solid solution and excess vacancies available for diffusion is confirmed.

6 Thermal stability and post-reversion formation of solute clusters in Al-Cu-(Li, Mg) alloys

6.1 Introduction

Solute clusters are known to exist in naturally aged aluminium alloys. The complex chemical composition of modern alloys provides a wide range of solute combinations possible to constitute clusters. When two or more solute species are involved, several cluster types of different chemistry can co-exist in the microstructure. These clusters may form with different kinetics and have different thermal stability, leaving a large variety of possible combinations when considering natural ageing and subsequent processing such as higher temperature treatments (reversion, pre-ageing). As an example, such co-existence of clusters is often reported for the Al-Si-Mg system [1–8]. The presence of predominantly Si rich clusters has an adverse effect on later precipitation kinetics [5,9–12]. Proposed pre-ageing treatment at ~ 80 °C circumvent the formation of Si rich clusters by forming more desirable Si-Mg clusters [13–17].

The most common 2xxx series alloys contain primarily Cu and Mg and in recent decades have seen additions of Li for its strong effect on precipitation strengthening. In these quaternary alloys a complex combination of clustering events may happen. In the former two chapters, we have studied the clustering behaviour during natural ageing of an Al-Cu-Li-Mg alloy and of two lower order alloys, namely an Al-Cu-Li and an Al-Cu-Mg alloy. We have shown that clustering mainly involved Cu and Mg, while Li was remaining in solid solution despite its abundance. The kinetics of cluster formation in the three alloys revealed the importance of the presence of Mg. In the Mg-free alloy, Cu was observed to show little clustering. With the addition of a small amount of Mg, Cu-rich clusters were observed to form rapidly in the Al-Cu-Li-Mg alloy, at a rate comparable to that of the ternary Al-Cu-Mg alloy which formed Cu-Mg clusters. The clusters formed have lower Mg/Cu ratio in the Al-Cu-Li-Mg alloy was highlighted by the similarity of the DSC signal of this alloy in the as-quenched (AQ) state with that of the Al-Cu-Mg alloy when scaled by the Mg concentration.

One of the important parameters of the effect of solutes on clustering which has been discussed in the literature is their ability to bind with the quenched-in vacancies[11,18–28]. In the most extreme case of a high binding energy between a solute and vacancies, the addition of this solute can effectively delay any diffusion-controlled clustering reaction by several orders of magnitude [11,18,28,29]. This is the case with Sn, whose addition to Al-Mg-Si alloys has been used to suppress clustering at room temperature. When vacancies are available for diffusion, clustering occurs. The question then arises as the rate of decay of these "free" vacancies during the natural ageing process. There is little experimental or theoretical evidence to understand if supersaturated vacancies become annihilated during natural ageing, if they become trapped at some microstructural features or if they are still available for diffusion in the clustered state.

These two important questions, namely the possibility of presence of multiple cluster types, and the behaviour of vacancies during the natural ageing process, can be tackled by studying the reversion behaviour of clusters and the subsequent natural ageing. Reversion is defined as the dissolution of precipitates or clusters by an increase of temperature. It has been thoroughly studied in the literature in relation to rapid temperature changes e.g. occurring during welding. By comparing the dissolution behaviour in differential scanning calorimetry and the evolution of cluster composition by correlative small-angle X-ray and neutron scattering, we will investigate in the three systems the thermal stability of the clusters in relation with their composition in the two main solutes (Mg and Cu). Reversion of the clusters results in an increased level of solid solution that would ideally be that of the as-quenched state. However, we will see that the extent of possible cluster reversion can be limited by the occurrence of higher precipitation reactions. Nonetheless, this renewed solid solution holds a different level of free vacancies than that of the as quenched solid solution, so that studying the rate of formation of new clusters after reversion will give indications about this level. This study of reversion behaviour and post-reversion natural ageing will be, similarly to that of the former chapter, carried out on three alloys. The Al-Cu-Li and Al-Cu-Mg alloys will serve as subsets of the more complex Al-Cu-Li-Mg alloy in order to better understand the interactions between the different solutes.

6.2 Materials and experimental methodology

The thermal stability and post-reversion formation of clusters was investigated in three Al-Cu based alloys with compositions shown in Table 1. Material was provided as 27 mm thick plates by Constellium-Voreppe C-TEC, France, where plates were homogenized at 500 °C for 24 h, quenched and subsequently hot rolled to 3 mm at 350 °C. All of the material was solution heat treated at 500 °C for 30 min, water quenched and aged at room temperature for 72 hours resulting in the naturally aged (NA) state. The solutes in this state are distributed in solute rich domains which have reached maturity and can be considered stable at room temperature as previously shown in Chapter 5. The dissolution of these solute rich domains during continuous heating was studied by applying ramp heating experiments in both small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC).

Table 9 Alloy compositions

Alloy	Cu at.% (wt. %)	Li at.% (wt. %)	Mg at.% (wt. %)	Al	Mg/Cu at.% (wt. %)
Al-Cu-Mg	1.1 (2.5)	N/A	1.7 (1.5)	Bal.	1.55 (0.6)
Al-Cu-Li	1.5 (3.5)	3.5 (0.9)	N/A	Bal.	N/A
Al-Cu-Li-Mg	1.5 (3.5)	3.5 (0.9)	0.45 (0.4)	Bal.	0.3 (0.11)

DSC samples were prepared by cutting $\sim 3 \times 0.5$ mm discs from the naturally aged starting material. DSC experiments were carried out using a TA instruments Q200 DSC equipped with a RCS 90 cooling system allowing scans to start at -50 °C. The experiments were carried out

using pure Al crucibles for the sample and as the reference. The data was baseline corrected in the same way as in Chapter 5.2 and is focused on low temperatures as all of the reactions concerning clusters in our alloys occur below 350 °C. Samples for SAXS were prepared by polishing 10 x 10 mm squares of the naturally aged material down to \sim 100 μ m. A Rigaku MicroMax-007 HF rotating anode equipped with a Cu K_{α} X-ray source (λ =0.154 nm) was used to generate X-rays. Data was collected using a photon counting DECTRIS Pilatus 300K detector providing excellent statistics with virtually zero noise. The sample was mounted in a resistance heating furnace capable of sustaining heating rates of 100 °C/min up to 500 °C. Sample to detector distance was measured and calibrated using an Ag behenate reference. Background correction and normalization to absolute units was carried out using a glassy carbon reference and in house scripts. Ramp heating experiments were performed in both DSC and SAXS. The heating rate was kept constant at 10 °C/min to allow for comparison and correlation between the two techniques with respect to temperature. Isothermal reversion was carried out using a Lauda oil bath where samples were dipped in the oil and held for the desired time (measured by a stopwatch). After isothermal reversion, samples were water quenched and stored in a freezer at -52 °C to avoid microstructural evolution, until they were further studied for post reversion room temperature ageing.

Small angle neutron scattering (SANS) experiments were performed on samples submitted to isothermal reversion and subsequent natural ageing. Experiments were carried out on the D11 instrument at the Institute Laue Langevin (ILL) in Grenoble, France. After reversion and quench, samples were transported to the beamline in liquid nitrogen to avoid ageing before exposure to the beam. The evolution of neutron scattering intensity was followed in-situ during the first 12 hours of natural ageing with additional ex situ samples for 72 hours and 480 hours of natural ageing. Neutron with a wavelength of 5 Å were used to avoid diffraction effects, including double diffraction. The sample to detector distance was set up to provide information in scattering vectors between 0.07 and 0.6 Å⁻¹. All experimental data has been background corrected, normalized to absolute units and azimuthally averaged using Graphical Reduction and Analysis SANS Program package (GRASP).

6.3 Results

6.3.1 Thermal stability of clusters

The dissolution of clusters was systematically studied using DSC and SAXS by following the evolution of heat flow signal and scattering intensity during heating respectively. At the start of all experiments presented below the material is in the naturally aged state and contains solute clusters. We choose to define clusters as domains where agglomeration of solute atoms results in above mean concentration of solute. Heat flux is a measure of the quantity and type of chemical bonds being broken or made during a heating ramp. It is sensitive to the chemistry of the clusters and the solution they are contained within. Clusters, as chemical fluctuations, will result in a mean square fluctuation in electron density and give rise to small angle scattering, whether measured by X-rays or neutrons [30] [page 45].

6.3.1.1 DSC

The heat flow traces obtained from ramps at 10 °C/ min carried out on naturally aged samples are shown in Figure 32. Dissolution of cluster during heating results in endothermic peaks as observed in all alloys. Clusters dissolve over a wide temperature range due to breaking of different chemical bonds and solubility change of the host matrix. The dissolution portion of heat profiles shows several minima for Mg containing alloys. The Al-Cu-Li thermogram is the simplest and contains a broad peak with a minimum at 130 °C. This peak corresponds to the dissolution of a small quantity of Cu rich domains as described by [pages 45 & 67]. Dissolution of these clusters is the only feature observed for this alloy. The reaction is complete by 200 °C and is subsequently followed by an exothermic peak due to precipitation of higher temperature phases. The complexity of curves increases when Mg is present in the alloy. They show a larger endothermic region with two local minima at 200 and 240 °C. These peaks represent the convoluted dissolution reactions involving Cu rich clusters with increasing Mg concentration. The first at 200 °C, is from Cu rich clusters and second, more stable Cu-Mg co-clusters as described by [31–34]. At temperatures above 250 °C the rapid increase in heat flow is due to the strong exothermic precipitation of GPB zones/S' phases [35] as observed during rapid hardening isothermal experiments. There is no region of zero heat flow between the endothermic and exothermic peaks which strongly indicates that precipitation of higher order phases and dissolution of clusters occur simultaneously.



Figure 32 The evolution of heat flow during 10 °C/min heating ramp of naturally aged alloys. Dissolution and precipitation are evidenced by endothermic and exothermic deviation in the curves.

Presence of only 0.45 at. % of Mg in the Al-Cu-Li alloy changes the heat flow curve drastically (Figure 32). The distribution of solute present in the Al-Cu-Li-Mg is shown to be stable only up to about 60 °C. The endothermic section of the curve is a convolution of 3 reactions with peaks at 105, 165 and 220 °C. The first at 105 °C, is suspected of being heat due to disordering of Li short range order similar to that observed for Al-Li and Al-Li-Mg alloys [36] and has been discussed in the previous chapter. The endothermic region above 150 °C contains a convolution of dissolution events with local minima at 165 and 220 °C. This dissolution region shows similarities in terms of shape, number of peaks and peak position with that observed for the Al-Cu-Mg. The dissolution of all clusters is shown to be complete up about 250 °C, and is followed by precipitation of higher temperature phases (mainly T_1 Al₂CuLi in this case [37]).

6.3.1.2 SAXS

Figure 33 shows small-angle X-ray scattering curves in the naturally aged state and for characteristic temperatures during a heating ramp performed in-situ at the same rate as for the DSC experiment (10°C/min). The initial curves illustrate the main features, which have been discussed in details in [pages 45 & 67]:

- In the three alloys the characteristic size of the clusters, which is qualitatively illustrated by the range of scattering vectors where a shoulder is observed, is similar and remains below 1 nm.
- The quaternary alloy, even though having a much lower DSC signal of clustering as compared to the ternary Al-Cu-Mg alloy, shows by far the strongest scattering intensity. This is due to a higher Cu concentration of clusters, resulting in a higher electron density contrast.



Figure 33 Scattering profiles at selected temperature during in-situ SAXS heating ramps at 10 °C/min

The dissolution curves illustrate that a significant decrease of intensity takes place during ramp heating, and therefore the clusters are being reverted (dissolved). Since these experiments were conducted only by SAXS, we do not have access to contrast variation as per the combination of SAXS and SANS. Instead, the mean square fluctuation of electron density will be used, as derived by model fitting of our results, to monitor the degree of clustering. The assumption of no contribution by Li, and Mg having an extremely low Z contrast with respect to Al, leads these fluctuations in electron density to be attributed mainly to Cu clustering.

The evolution of the mean square fluctuation in electron density from clusters versus the temperature during the heating ramp is shown in Figure 34. The Al-Cu-Li alloy shows a stable

scattering signal due to clusters up to 110 °C. For higher temperatures, clusters are dissolving and scattering is suppressed to a minimum by 180 °C. The Al-Cu-Mg alloy shows a somewhat different behaviour with cluster scattering first showing a slight increase up to 200 °C. Above this temperature, clusters are dissolving and their scattering decreases in two stages which correspond well with the two-peak dissolution region observed by DSC. Scattering from clusters reaches a minimum at 270 °C, immediately followed by the onset of precipitation which results in anisotropic scattering (observed on the original images, not shown here), characteristic from the elongated precipitates forming in this system [35,38].



Figure 34 Evolution of mean squared fluctuation in electron density during in-situ heating at 10 °C/min. Clusters in the Al-Cu-Li alloy are stable up to 140°C, in the Al-Cu-Mg up to 200 °C and in the Al-Cu-Li-Mg up to 130 °C.

In the Al-Cu-Li-Mg alloy, the scattering of clusters is significantly stronger and its magnitude has been scaled down by a factor 12 to compare with the other alloys (Figure 34) [page 67] in terms of kinetics and temperature ranges. The evolution during the heating ramp is more complex but holds features at the same temperature as to those observed by DSC. A curious feature is the increase of the mean square electron density difference from 90 to 125 °C corresponding well with the first endothermic (dissolution) peak observed by DSC. An increase of the matrix Li concentration will result in a lower electron density that may lead to a larger mean squared electron density difference between clusters and matrix causing this observation. The scattering due to clusters is drastically reduced for temperatures between 130 and 175 °C indicating the dissolution of the clusters. The remaining clusters are dissolving at higher temperature and lead to further decrease of scattering above 175 °C. Clusters are almost completely dissolved at temperatures above 240 °C. Precipitation of the T₁ phase begins at

temperatures above 250 $^{\circ}$ C and gives rise to anisotropic scattering when visualized in the 2D images (not shown here).

6.3.2 Isothermal reversion of clusters

After evaluating the reversion behaviour of the three alloys during ramp heating experiments, it is now possible to define reversion states appropriate for further study, namely for the evaluation of post-reversion natural ageing. The transient nature of heating ramp experiments makes it difficult to pinpoint the temperature at which dissolution reactions are complete. To address this difficulty naturally aged samples were reverted isothermally at a chosen temperature. The interplay between thermodynamics and kinetics is critical for these experiments as choosing a low temperature can result in very sluggish dissolution or none at all. Choosing a higher temperature speeds up the dissolution kinetics but may lead to the rapid precipitation of other phases. As such we choose to revert at temperatures in close proximity to peaks in DSC (highest rate) and control the dwell time to achieve as full dissolution of clusters as possible. In the ideal case, a reverted sample should contain no solute clusters or precipitates leading to no dissolution (endotherm) in the DSC profile and no scattering due to clusters in SAXS. The success of reversion is evaluated by comparing reverted samples to the starting naturally aged material.

For the Al-Cu-Li alloy, a reversion temperature of 200 °C was chosen as it lies above the dissolution range as observed by SAXS and DSC. At this temperature dissolution is expected to be rapid whereas precipitation of the higher temperature phases will be sluggish allowing for a sufficient time window to revert without precipitation taking place. Figure 35a shows the DSC thermograms of the Al-Cu-Li alloy in the naturally aged state and after different times of reversion at 200°C. For a very short dwell time of 5 seconds the cluster dissolution trace is not affected. The dissolution peak diminishes with increasing reversion times as early as 10 seconds. Successful dissolution of clusters is complete after 60 seconds at 200 °C, illustrated by the absence of cluster dissolution during the DSC scan. Small changes to the precipitation peak indicates possible nucleation of the T_1 phase; however, for dwell times under 60 seconds these effects seem negligible and are not expected to affect clustering. The time of 60s was thus chosen for further work.

In the Al-Cu-Mg alloy, the clusters are significantly more difficult to dissolve as shown in Figure 35b. Tests carried out at temperatures ranging from 200 to 240 °C with variable times were unsuccessful in fully dissolving clusters without strongly affecting the following precipitation. Reversion of the alloy in the temperature range between 200 and 235 °C results in a progressive reduction of the endotherm at 200 °C as a portion of clusters are dissolved. This reversion has virtually no effect on the remainder of clusters as the peak at 240 °C is not affected. These higher thermal stability clusters are not affected for very short dwell time (5 secs) at 240 °C. However, increasing the dwell time to 30 secs at 240°C results in a massive change to the heat flow signal, showing that clusters are no longer present in the alloy and solute has very rapidly formed precipitates (resulting in the absence of precipitation exothermic peak). The drastic change and very fast kinetics of this transformation are likely related to a short-range redistribution of solute rather than a diffusion controlled precipitation reaction. To study the

post reversion ageing we finally selected samples which were reverted for 60 seconds at 200 °C resulting in the disappearance of the lower temperature DSC endotherm.

The Al-Cu-Li-Mg alloy was reverted at two temperatures to mimic the dissolution events giving rise to the double endothermic region above 135 °C for this alloy as shown in Figure 35b. Reversion for 60 seconds at 120 °C is shown to dissolve the solute rich domains giving rise to the endothermic peak at 100 °C. The endothermic region at higher temperatures with peaks at 170 and 230 °C is not affected. The peak at 170 °C disappears when reversion is carried out at 200 °C for 60 seconds. The reactions at 100 °C and 170 °C are effectively suppressed after 60 seconds at 200 °C and do not influence the remainder of the thermogram, namely the remaining dissolution event at 230 °C, corresponding to most stable clusters.



Figure 35 DSC thermograms showing the effect of dwell time at reversion temperature for clusters in a) Al-Cu-Li at 200 °C, b) Al-Cu-Mg, and c) Al-Cu-Li-Mg alloys

When the reversion temperature is increased to 250°C, the DSC curves change significantly. Although the post-reversion thermogram is similar to that of lower temperature reversions, a new exothermic event appears at low temperatures. This peak is almost identical to that observed in the as-quenched material [pages 67]. This event means that, following reversion, a new population of clusters is able to form during the DSC scan, with kinetics similar to that observed in the as-quenched material. This formation of clusters is observed to be maximal at the reversion time of 30s at 250°C; for longer reversion times, precipitation of higher temperature phases occurs, evidenced by a modification of the high temperature exothermic precipitation peak, which reduces the amount of available solute. For the condition of 30s at 250°C, the area of the exothermic cluster peak and of the subsequent endothermic peak are similar, meaning that almost full cluster dissolution has been achieved after reversion.

The effect of isotherm reversion on the small-angle scattering intensity is captured in Figure 36 showing the results for AQ, NA and reverted samples in both SAXS and SANS [pages 67]. Reverting the Al-Cu-Li alloy for 60 seconds at 200 °C drives the scattering intensity due to clusters down as they are dissolved (Figure 36a). These changes are captured more effectively by SAXS compared to SANS as the clusters dissolving are Cu rich hence giving stronger contrast in SAXS. All of the clusters in the Al-Cu-Li alloy have been dissolved at 200 °C. Reverting the Al-Cu-Mg alloy for 60 seconds at 200 °C dissolves only a small portion of clusters as shown by DSC (Figure 35b). The scattering intensity after such reversion is not strongly affected in SAXS but has its amplitude decreased in SANS (Figure 36b). Thus small-angle scattering confirms that only a portion of the large quantity of clusters present in the NA state in this alloy have been dissolved at 200 °C for 60 seconds.

For the quaternary Al-Cu-Li-Mg alloy, there is a drastic difference between the scattering signal of the naturally aged state and that of the reverted samples at 200 °C for 60 seconds and 250 °C for 30s both for SAXS and SANS, as shown in Figure 36c. During both reversion, most of the scattering due to clusters is removed leaving the scattering curves below the AQ condition. Both reversion temperatures results in similar clustering states as measured by SAS.



Figure 36 SAXS profiles showing the effect of reversion on the scattering intensity due to clusters in a) Al-Cu-Li, b) Al-Cu-Mg, and c) Al-Cu-Li-Mg alloys

6.3.3 Post reversion behaviour

To investigate the cluster chemistry post reversion, we have employed the SAS contrast variation method as described in [pages 45 & 67]. It enables to separate the contribution of Cu and Mg. The mean squared excess solutes in as-reverted samples are discussed along with their evolution during subsequent natural ageing over the course of 10 h. DSC thermograms are presented alongside to emphasize the kinetics (or absence) of developing clusters during natural ageing post reversion. We compare the natural ageing kinetics after reversion with natural ageing in the as-quenched state from the solution treatment temperature [page 67] to evaluate the correlations between Cu-Mg clusters and vacancies.

Figure 37a shows the DSC curves in the as-quenched (AQ) state, after natural ageing (NA), after reversion (AR) of 60s at 200°C, and after 20 days (+480h) of natural ageing post reversion for the Al-Cu-Li alloy. Post reversion ageing of 480 hours results in no significant difference compared to the as reverted sample. In particular, the endothermic peak corresponding to the cluster dissolution that was present in the naturally aged material is absent even after long ageing post reversion and subsequent natural ageing, and compared to its evolution during the initial natural ageing following quenching from solutionizing temperature. The low value, during both evolutions, suggests that only a very low quantity of Cu is involved in clusters independently of the condition. The excess Cu shows hardly any detectable evolution when observed by SAS during natural ageing after quench and post reversion.



Figure 37 Natural ageing post reversion for the Al-Cu-Li alloy.

The Al-Cu-Mg alloy DSC curves in the AQ, NA, as-reverted (AR) states and for up to 480 hours of subsequent natural ageing, considering the reversion treatment of 60s at 200°C are shown in Figure 38a. Similarly, to the case of the Al-Cu-Li alloy, DSC curves show no evolution during post reversion natural ageing: the clusters that have dissolved during reversion (those whose dissolution were giving the DSC signal between 150°C and 230°C in the NA state) do not reprecipitate in this time range at room temperature. As shown in Figure 39, the combined SAS experiments (SAXS and SANS) provide the mean squared excess solute evolution for both Cu and Mg during natural ageing post reversion, which can be compared to that occurring during the initial natural ageing. From these graphs, it appears that the clusters dissolved after 60s at 200°C are only a fraction of the total present in the NA state. Namely, after reversion the mean squared excess Solute is subsequently very stable and does not evolve at room temperature confirming the stability of the solid solution resulting from reversion.



Figure 38 DSC thermograms showing the evolution of heat flow post reversion of Al-Cu-Mg for 60s at 200 $^{\circ}$ C



Figure 39 Mean excess a) Cu and b) Mg for the Al-Cu-Mg during evolution post reversion for 60s at 200 °C compared to natural ageing after quench ([page 45])

Now considering the quaternary alloy reverted for 60s at 200°C, the DSC curves in the AQ, NA, AR states and different times of natural ageing post reversion up to 72 hours, are shown in Figure 40a. The DSC curves show no evolution during post reversion natural ageing and behave similarly to those of the Al-Cu-Li and Al-Cu-Mg alloys. The signals remain flat up to 180°C, leaving only the highest temperature endothermic peak and illustrate the absence of cluster formation after reversion except for the most stable ones. The released solid solution does not form new clusters either during the DSC scan, or during the 3 days of natural ageing left after reversion. This behaviour is further captured by the mean squared excess solute evolutions, obtained from combined SAXS and SANS measurements and presented in Figure 41. Post reversion the Cu content of clusters is significantly reduced compared to that of the NA condition but is not zero. It is shown to remain stable during the first 12 hours of ageing. The mean squared excess Mg is strongly scattered throughout the ageing period studied; however, its values remain above zero. These observations suggest that the clusters remaining after reversion at 200°C in the Al-Cu-Li-Mg alloy contain less Cu compared to the NA condition but still contains Mg. These clusters do not evolve post reversion.

As already revealed by the as-reverted DSC curves presented in Figure 35, the behaviour is very different for the Al-Cu-Li-Mg alloy reverted at 250°C for 30s. The post reversion behaviour is captured by the evolution of the DSC thermograms during post reversion natural ageing shown in Figure 40b. The DSC thermogram in the as-reverted state is almost identical to that of the asquenched state, meaning that a complete solid solution equivalent to that following the solution heat treatment has been achieved and that the subsequent formation kinetics of clusters are identical in the two conditions (AQ and AR). At this position the mean squared excess Cu, shown in Figure 41, is close to that observed after reversion at 200°C, and lower when compared to the AQ condition (which might be attributed to difference in the quenching conditions from solution and reversion temperatures respectively). The excess Mg has been significantly reduced to almost 0 and is below its value after reversion for 60 s at 200 °C.



Figure 40 DSC thermograms showing the evolution of heat flow post reversion of Al-Cu-Li-Mg for a) 60s at 200 °C and b) Al-Cu-Li-Mg for 30s at 250 °C



Figure 41 Mean squared excess solute evolution after reversion of the Al-Cu-Li-Mg alloy. a) excess Cu, b) excess Mg.

The formation of clusters during post reversion natural ageing is effectively captured by DSC and SAS. The kinetics, as observed by both techniques, are very fast, with the majority of clustering occurring during the first 24 hours. In particular, the kinetics of Cu clustering post reversion are in close proximity to those during initial natural ageing. The mean squared excess Mg appears in contrast to be very low post reversion and during the first 10 hours of subsequent natural ageing. This involvement of Mg in the clustering during natural ageing is not observed post reversion. Longer ageing time allows for further development of the solute distribution as the endothermic region observed for R+72h resembles that of the naturally aged condition (Figure 40b), albeit the early peak position is shifted, which is most likely related to the difference in terms of Cu-Mg bonds. The clusters dissolving at 235 °C are always present independent of the condition of the alloy.

Reverting the different types of clusters present in the Al-Cu-Li-Mg alloy and subsequent evolution during natural ageing is also effectively shown by its effect on micro-hardness (Figure 42). Reversion for 60 seconds at 200 °C results in a loss of more than 60 % of the hardness from that of the naturally aged condition. The subsequent increase of hardness occurs only after more than 100h of natural ageing, showing that the clusters which have been dissolved can (at least

partially) reform but with much slower kinetics. After reversion at 250°C; the hardness is slightly further lowered as more clusters are dissolved, however the difference is small. The prominent feature is that the hardness evolution subsequent to reversion is extremely fast, in fact comparable and even slightly faster than that of initial natural ageing. The difference in hardness between initial and post-reversion natural ageing could be due to a small proportion of larger precipitates formed e.g. at dislocations during the reversion treatment, as suggested by the as-reverted SAXS curves (Figure 36c).



Figure 42 Evolution of micro-hardness for the Al-Cu-Li-Mg alloy

6.4 Discussion

The heating ramp experiments, both in DSC and SAS, show essentially 3 endothermic (dissolution) events occurring between 100°C and 250°C. The quaternary Al-Cu-Li-Mg shows the 3 events, while the Al-Cu-Mg alloys shows only the 2 higher temperature events (i.e. the most stable) and the Al-Cu-Li shows only a single moderate temperature peak.

The results for the Al-Cu-Li-Mg alloy support the hypothesis that the first least thermally stable peak corresponds to disappearance of Li short range order as the small-angle scattering intensity during ramp heating shows no evolution until this peak is over (up to 150 °C). When considering
the higher temperatures, the combination of SAXS and DSC helps confirming the dual nature of the clusters present. At 200°C, most of the SAXS intensity corresponding to clusters has disappeared, and the mean squared excess Cu has decreased to a value close to that of the asquenched state. The rate of decrease of SAXS intensity with temperature is actually qualitatively similar to that of the ternary Al-Cu-Li alloy (yet much more intense) further confirming that Curich clusters are the main objects dissolving in the range of reversion temperatures up to 200°C.

After 250°C isothermal reversion, the endothermic peak at 230°C that precedes the main exothermic precipitation peak in the DSC thermogram (corresponding to the dissolution of stable Mg-Cu clusters) is still present, but is compensated by the exothermic peak at low temperature which is similar to that of the as-quenched state, showing that Mg-Cu clusters are dissolved in this condition. This is confirmed by the mean squared excess Mg being zero after reversion at 250°C.

A more curious feature of this alloy is the increase of the mean square electron density difference from 90 to 125 °C corresponding well with the first endothermic peak observed by DSC. An increase of the matrix Li concentration may lead to a larger mean squared electron density difference between clusters and matrix causing this.

Decomposition of a super saturated solid solution after quench is a kinetic process. The rate is driven by the available vacancies for diffusion which in turn is strongly affected by Mg for the alloys explored [page 67]. During natural ageing, the amount of vacancies available for diffusion may change due to vacancy annihilation at sinks such as dislocations and grain boundaries, or their involvement with clusters. When the clusters are dissolved, a solid solution similar to that of the as-quenched state is made, however the question arises about the remaining vacancy concentration. Following the post reversion ageing kinetics helps to elucidate the effective vacancy concentration in the solution.

The 60 second dwell time at 200 °C for the Al-Cu-Li alloy successfully dissolves the low quantity of Cu rich clusters in the NA condition. The results of DSC and SAS show that this newly formed solid solution is stable up to 20 days at room temperature and therefore the effective vacancy concentration after reversion appears to be extremely low. One can conclude that the quenched-in vacancies that helped the formation of the clusters during initial natural ageing have either been annihilated during natural ageing, or trapped at sites which are stable until 200°C.

The 60 second dwell time at 200 °C for the Al-Cu-Mg alloy dissolves only a portion of the clusters present in the naturally aged state. The released solute does not cluster over 20 days at room temperature post reversion, which strongly suggests again that vacancies are not available for diffusion, either because they are trapped or because they have been annihilated during natural ageing. The attempts to apply a higher reversion temperature in order to dissolve all of the clusters in the Al-Cu-Mg alloy without precipitation proved unsuccessful with major precipitation occurring between 5 seconds and 30 seconds at 240 °C.

The situation is more favourable in the Al-Cu-Li-Mg alloy because of a higher temperature for precipitation of T_1 phase, allowing for reversion temperatures up to 250°C to be used without significant precipitation occurring. Isothermal reversion of the Al-Cu-Li-Mg alloys is shown at

two critical temperatures of 200 and 250 °C. At 200 °C the first two endothermic peaks are dissolved and result in a significant decrease in the mean squared excess Cu while the mean excess Mg is still present in clusters. This confirms that the most stable clusters for the quaternary alloy contain higher concentration of Mg. Reversion of these clusters is possible at 250 °C without precipitation. Both the mean excess Cu and Mg are significantly reduced as expected when all clusters are dissolved. The striking difference between reversion at 200°C and 250°C is that the kinetics of Cu clustering post reversion showing almost two orders of magnitude difference (whether observed in DSC or in hardness). While post-reversion clustering is extremely sluggish after reversion at 200°C, similarly to the behaviour of the two other alloys, it happens very fast after reversion at 250°C, in fact at the same rate as compared to the initial as-quenched condition.

We can bring this result in perspective with the fact that in the quaternary alloy, the addition of only 0.45 at% Mg strongly modifies the kinetics of Cu-rich cluster formation, meaning that there is a strong effect of Mg on the diffusion processes in the alloy, most likely via interaction with vacancies. These results suggest that when Mg is present in the solid solution it effectively amplifies the availability of vacancies for diffusion of Cu. Mg plays the role of a catalyst for clustering. Furthermore, these results reveal that vacancies can be made available for diffusion by dissolving the most stable Cu-Mg rich clusters.

An alternative explanation of the large difference in post-reversion clustering kinetics would be that during reversion, the equilibrium vacancy concentration (at the reversion temperature) is reached in the alloy, and that the difference in post-reversion kinetics illustrates the difference in vacancy concentration. In this case, the similarity of the clustering kinetics between the 250°C reverted state and the as-quenched state would mean that during initial quenching from the solutionizing treatment, a larger part of the vacancy concentration would have been lost to structural defects, leaving only the 250°C equilibrium concentration for clustering. However, if one assumes a vacancy enthalpy formation of 0.75 eV, the ratio of the equilibrium concentration between 200 and 250°C is only 6, which is significantly smaller than the ratio of the hardening kinetics. Moreover, the almost exact match between the DSC curves in the 250°C reverted and in the as-quenched states strongly suggest that both interpretations are at play. The release by reversion of solute and increase in vacancies due to elevated temperature results in a state comparable to that present after initial quenching.

6.5 Conclusions

In this paper we have evaluated the behaviour of clusters during dissolution and subsequent natural ageing, via their contribution to the DSC signal and their contribution to small-angle scattering. The comparison of the three alloys Al-Cu-Li, Al-Cu-Mg and Al-Cu-Li-Mg makes it possible to understand some of the complex interactions between solutes and vacancies in these systems.

Our results show that two types of clusters exist after natural ageing in these alloys, one type being mainly Cu-rich and the other containing Cu and Mg. The former is less thermally stable as it reverts at low temperature (200°C), whereas the Cu-Mg clusters do not revert before 250°C.

In the ternary Al-Cu-Li alloy, these Cu-rich clusters can be effectively reverted and do not form again appreciably when the alloy is naturally aged after reversion, meaning that the initial quenched-in vacancies are not available anymore.

In the ternary Al-Cu-Mg alloy, most clusters are of Cu-Mg type. Reversion can be studied independently of precipitation only up to 200°C. At this temperature only a small proportion of the clusters has been dissolved, which are mainly the Cu-rich ones. Similarly, to the Al-Cu-Li alloy, the partial solid solution after reversion does not form new clusters.

The quaternary Al-Cu-Li-Mg alloy, contains a majority of Cu-rich clusters and a minority of Mg-rich clusters. The Cu-rich clusters are considerably more present initial natural ageing than in the Al-Cu-Li alloy thanks to the presence of Mg. The effect of Mg on Cu clustering is further unravelled by the short isothermal reversions experiments. During reversion at 200°C the Cu-rich clusters are dissolved, and they form again during natural ageing but with a very sluggish kinetics, illustrating a very low mobility and/or availability of vacancies. During reversion at 250°C, both Cu-rich and Mg-rich clusters are dissolved, and the post-reversion clustering kinetics is remarkably similar to that of the as-quenched state. The release of Mg in solid solution appears to trigger the mobility of vacancies, which are shown to be present after reversion of natural aged in similar quantity compared to the as-quenched state.

6.6 References

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The effect of Mg concentration on clustering in Al-Cu-Li-Mg alloys

The previous chapters highlight the prominent role played by Mg for solute clustering in the Al-Cu-(Li, Mg). In this chapter, we investigate the influence of Mg concentration on the cluster formation by studying a compositionally graded material through time and space resolved insitu SAXS, DSC and micro-hardness. The close correlation between Mg concentration, smallangle scattering quantity and micro-hardness evidence that the addition of Mg to Al-Cu-Li, independently of concentration and without threshold, effectively translates in an increased presence of clusters after natural ageing. The immediate acceleration of kinetics when any Mg is present in solution suggests Mg act like a catalyst for excess vacancies necessary for the clustering of Cu in Al-Cu-(Li, Mg) alloys.

7 The effect of Mg concentration on clustering in Al-Cu-Li-Mg alloys

Al-Cu-Li alloys have become a staple of the aerospace industry with their high strength to weight ratio, good toughness and corrosion resistance [1]. The primary focus of research on these alloys has been around promoting of the T₁ (Al₂CuLi) phase through thermo-mechanical processing [2,3] and chemical alloving [4–7]. Dislocations were shown to dramatically promote the formation of high density T_1 [8–10] through heterogeneous nucleation. Mg additions above 0.2 wt. % strongly influence the precipitation pathway of the alloys through the formation of precursor phases rich in Cu-Mg during ageing, which promote subsequent formation of T_1 phase [7,11]. In our previous work, we have documented the large increase of room temperature formation of Cu rich solute cluster in the presence of Mg (Chapter 5). Through reversion experiments, the variable Mg content of Cu rich clusters has been evidenced and the strong link between Mg and vacancies in relation to Cu clustering has been confirmed (Chapter 6). In the present work, we aim at investigating if there is a minimum Mg concentration (i.e. threshold) necessary to allow for the formation of these clusters and explore the link between Mg concentration and cluster formation kinetics. The alloys investigated will be studied during the 3 days of natural ageing at room temperature following water quench from the solution temperature (naturally aged state).

We employ a combinatorial approach using composition gradient material in which the concentration of Cu and Li are kept constant and Mg varies [12,13]. Diffusion couples between Al-Cu-Li and Al-Cu-Li-Mg were elaborated by linear friction welding to alleviate presence of an oxide layer at the diffusion interface [14]. The narrow concentration gradient present after joining was enlarged by a diffusion heat treatment at 515 °C for 14 days. The gradient was further extended via hot rolling to a distance of about 10 mm, allowing for spatially resolved characterization by differential scanning calorimetry (DSC), micro-hardness and small-angle Xray scattering (SAXS) [15]. Slices parallel to the diffusion direction were prepared as shown in Figure 43. Entire samples were solution treated and the concentration of Cu and Mg across the diffusion couple was measured by a Cameca electron micro-probe analysis (EPMA) working at 20 keV and 300 nA. After ageing for 3 days at room temperature, the naturally aged microhardness was measured every 500 µm across the diffusion couple using a Buehler Tukon 1102 machine with a 25 gf load. SAXS measurements were carried out using the same spacing. The kinetics of clustering at room temperature was monitored in-situ during 3 days by SAXS. By displacing the diffusion couple continuously with respect to the X-ray beam during this monitoring, the kinetics were followed for all positions in the composition gradient. Scattering was achieved using a rotating Cu K_{α} anode with a wavelength 0.154 nm (8.048 keV) as a source. Scattering data was captured by a 2D Dectris Pilatus noiseless photon counting detector and the 2D information was radially averaged. Variation in the cluster formation as a function of alloy composition was further investigated by DSC using ramp heating at 10 °C/min with a sample thickness of the order of 500 µm and a TA Q200 instrument. More details about the baseline correction procedure can be found elsewhere (Chapter 3.4). The thickness of the DSC samples is about 1/20 of the extension of the diffusion couple. Therefore, although a small concentration gradient may exist within a given sample, it will be small in relative value, so that the approximation can be made that the clustering behaviour is representative of its average composition.



Figure 43 Diffusion couple sample real estate distribution for EPMA, micro-hardness, SAXS and DSC

The Mg content across the gradient follows a sigmoidal curve spanning 10 mm between 0 at. % Mg on the Al-Cu-Li end and 0.33 ± 0.02 at. % Mg on the Al-Cu-Li-Mg end. The variation has been normalized to its maximum value and presented in Figure 44. Micro-hardness is well known to show correlation with the presence of clusters [16]; hence it can be used to compare cluster contributions to strength across a diffusion gradient. In the naturally aged state, the micro-hardness increases from 90 \pm 3 HV at the Al-Cu-Li side to 123 \pm 2 at the Al-Cu-Li-Mg end of the diffusion couple. The normalized variation in hardness is shown in Figure 44 and spans 10 mm with the same sigmoidal shape as Mg concentration. The presence of clusters in the naturally aged sample is further confirmed by SAXS measurements. The Cu-rich clusters give rise to X-ray scattering which can be effectively quantified using a concentration fluctuation model as described elsewhere (Chapter 4). The quantity of clusters is shown to vary between 23 \pm 2 and 48 \pm 2 excess electrons per nm³ across the diffusion couple. Once again, the normalized change follows the same shape outlined by hardness and Mg concentration across the 10 mm as shown in Figure 44. The excellent correlation between Mg concentration, microhardness and scattering of clusters in the naturally aged state is clearly evidenced. Increasing the Mg concentration up to 0.33 at. % Mg for Al-Cu-Li-xMg alloy results in more clusters which in turn give higher hardness.



Figure 44 Variation of mean squared excess electrons, micro-hardness (HV) and Mg concentration (Mg) across the diffusion gradient in the naturally aged state

The clusters observed in the naturally aged material have formed during the decomposition of the solid solution from the as-quenched state, where the solutes are in solid solution alongside with excess vacancies. To investigate the relationship between Mg concentration and the clustering kinetics we analysed slices cut across the diffusion couples in the as-quenched state using DSC. In these experiments, the decomposition of the solid solution into clusters results in a re-organization of the solute which gives excess heat in the form of two exothermic peaks. Dissolution of the formed clusters happens subsequently at higher temperature. It requires heat and thus results in endothermic peaks. Figure 45 shows the thermograms across the diffusion couple in the as quenched state. They evolve with three distinct features as Mg concentration is increased. First, an exothermic peak develops at temperatures between 50 and 120 °C. The peak becomes evident at 0.09 at. % Mg and it continues to increase in magnitude with increasing Mg. This shows that more clusters are forming during the heating ramp with higher concentration of Mg. The second feature is the dissolution region at temperatures from 125 °C up to about 250 °C. Higher Mg concentrations cause the dissolution events to occupy wider temperature ranges. Additions of Mg from 0.09 up to 0.18 at. % result in a single dissolution peak at 175 °C with larger magnitude for higher Mg. Above 0.21 at. % Mg a new endothermic peak at 215 °C appears and is convoluted within the first dissolution region. The magnitude of the peak at 215 °C increases when more Mg is present in the sample. The third and final feature is the large exothermic peak at temperatures above 250 °C representing precipitation in the sample. The position of the precipitation peak shifts to lower temperatures when Mg is added to Al-Cu-Li with a notable step at around 0.18 at. % Mg. The precipitation peak corresponds to the formation of the T_1 (Al₂CuLi) phase which has a strong kinetic dependence on the concentration of Mg as previously reported [7].



Figure 45 DSC thermograms across the diffusion couple in the as quenched condition. Heat effects are increasing with increasing Mg concentration

In addition to the supersaturated solid solution, the material in the as quenched condition contains some degree of clusters as evidences by the scattering profiles in Figure 46a. The change from the AQ to the NA condition increases with increasing Mg concentration (Figure 46b) evidencing the positive effect Mg has on clustering. Nevertheless, excess vacancies are available for diffusion for all Mg concentrations in the sample and lead to changes. The kinetics of clustering depend on the solutes available and their diffusion; hence, they are directly correlated with the excess vacancies and the vacancy-solute interaction. Using time and space resolved in-situ SAXS on a sample with a concentration gradient, makes it possible to access both these factors. The clustering kinetics are effectively captured and shown in Figure 47. It is apparent that the cluster quantity, actually larger in the as-quenched state for the Mg-free alloy, increases faster when the Mg concentration is increased. The low scattering contrast of Mg in Al and the absence of Li clustering in the end members (Al-Cu-Li and Al-Cu-Li-Mg) allow for the assumption that the detected clusters forming are predominantly Cu rich [6,17] (Chapter 4.4.1). Using this assumption, the interaction between Mg and excess vacancies is confirmed by the fact that addition of Mg increases the kinetics of Cu clustering, so that with increasing Mg more (or more mobile) vacancies are available for Cu diffusion.

In conclusion, the influence of Mg concentration on cluster formation in Al-1.5Cu-3.5Li-xMg at. % alloy has been evaluated using a Mg diffusion couple. Analysis performed using differential scanning calorimetry (DSC), time and space resolved small-angle X-ray scattering and micro-hardness reveal strong changes to clustering behaviour across the concentration gradient. The quantity and complexity of clusters forming is shown to increase with increasing Mg concentration. An excellent correlation between the quantity of clusters, micro-hardness and

Mg concentration appears in the naturally aged condition. Clustering kinetics during the course of natural ageing are proportionally faster with increasing Mg concentration. The immediate increase of predominantly Cu clustering when Mg is present confirms the positive effect Mg has on clustering of Cu through vacancies available for diffusion.



Figure 46 Scattering profiles across the diffusion couple in a) As Quenched condition and b) Naturally Aged condition.



Figure 47 Evolution of Mg concentration on clustering kinetics during natural ageing measured by time and space-resolved SAXS.

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8 Discussion

The results described throughout this thesis are put in relation with each other to discuss the origin of the profound effect of Mg on the clustering of Cu in the Al-Cu-(Li, Mg) system. Decomposition of a solid solution is a process governed by a combination of thermodynamics and kinetics. The thermodynamic components describe the energetics of the system and frame driving forces as the difference between energy states. The kinetics, on the other hand, describes time dependent aspects and the path the solution follows between energy states. Ideally, the combination of these two theoretical fields could explain the experimentally observed results. First, the thermodynamic aspects will be discussed based on comparing states, such as the naturally aged vs. the as quenched condition as presented in Chapter 4. The kinetics aspects will then be considered and discussed in regards to the evolutions measured in Chapters 5 and 6. Finally, the results of this project will be discussed in light of these considerations.

8.1 Difference of clusters between naturally aged and as quenched condition

Solute clusters are present in the naturally aged state as evidenced by an elevated hardness (Figure 23 page 72), presence of endothermic heat regions signifying dissolution in DSC (Figure 32 on page 92), scattering signal from clusters with above matrix solute concentration (Figure 21 on page 55) and positive solute correlation from APT results (Figure 19 on page 54). Comparing this experimental evidence to the as-quenched condition reveals differences and therefore a thermodynamic driving force for clustering exists. Alloys containing Mg have the highest differences between AQ and NA conditions.

The equilibrium binary phase diagrams calculated using the FSlite FacSage database for the elements concerned are shown in Figure 48 [http://ptable.velp.info/]. Li has the highest solubility followed by Mg and finally Cu. Cu can be considered to have the highest driving force for leaving the solid solution. The Mg and Li are likely to remain in solution. This interpretation does not consider possible interactions when more than one solute is present. The combined effects are analysed using the Al-Cu-Mg and Al-Cu-Li systems in this work and the Al-Li-Mg system is reviews from literature.



Figure 48 Binary equilibrium diagrams for a) Al-Cu, b) Al-Mg, c) Al-Li. Adapted from http://ptable.velp.info/

The addition of more than 5 at. % Mg to the Al-Li system has been shown to affect Li solubility and push towards forming a large volume fraction of δ° (Al₃Li) phase [1]. The concentrations of Mg and Li used in the referenced alloy are ~10 and ~2 fold higher than the quaternary alloy we study respectively. We suspect that the Li solubility should not be significantly affected by the presence of 0.45 at. % Mg. Additionally, our results show no Li-Li or Li-X associated correlations (no Li clusters) in the naturally aged quaternary alloy as observed by APT (Figure 19 on page 54) and support Li remaining soluble during natural ageing when small quantities of Mg are added. Similar Li behaviours have been previously observed for artificially aged alloys [2,3]. By extension we suspect that there is no Li clustering in the lower order Al-Cu-Li alloy as it is unlikely for Li to show a higher tendency to cluster in the absence of Mg. Nevertheless, clustering of Cu in the Al-Cu-Li system may still be expected based on its low solubility and is supported by experimental observations of Cu rich GP zones found after natural ageing in similar Al-Cu-Li alloys [4].

The thermodynamics of the Al-Cu-Mg system have been the subject of research employing first principles calculations, quasi-chemical models and even a two atom co-cluster model based on interaction energy between Cu and Mg [5–7]. Despite widely varying experimental data, e.g. cluster sizes from 2 [7] atoms to hundreds [8] or specific Mg/Cu ratio with variations between 1 and 2, a multitude of Al-Cu-Mg and Al-Cu-Mg-X systems have been described. The models effectively explain the absence of observable precipitates by TEM despite the increase in hardness and decrease of heat detected by DSC [9,10] through presence of Cu-Mg clusters. Perhaps the most convincing evidence of these clusters comes from their direct observations using APT [9,11,8]. The popularity of the Al-Cu-Mg system makes it a good as a reference and guide when establishing a characterisation methodology.

Our results from SAS characterisation of clusters in the naturally aged Al-Cu-Mg material (Table 6 on page 56) show good agreement with the presence of clusters with Mg/Cu ratio of ~2 similarly to what has been observed by APT in the same alloy [8]. Similarly, the reduction in heat between the AQ and NA states has been reproduced in our DSC results supporting the strong interaction energy between Cu and Mg being a driving force for forming Cu-Mg coclusters after quench. The SAS technique presents the opportunity to access the very early stages post quench due to the short time required to prepare samples. In the AQ condition a significant amount of scattering due to Cu atoms is observed supporting the hypothesis that Cu is rejected from the solid solution due to its low solubility. The change to the NA condition is correlated with presence of Mg in the alloy evidencing the strong interaction between these solutes. However, the low number squared of excess Mg atoms involved in clusters in the AQ condition is very intriguing as it suggests that at this state Mg has not yet clustered with Cu. The solute-solute clustering exists but its extend is time dependent and thereby limited by diffusion. The time necessary to form Cu-Mg clusters highlights the importance of kinetics which are discussed further.

To summarize the thermodynamics considerations, there seems to be a strong driving force for Cu-Cu clustering as well as a driving force for Cu-Mg co-clustering.

8.2 Temporal evolution of solute clusters

The time it takes for a configuration between atoms to be established depends on the driving force, represented by the solute-solute bond strength, and the diffusion of each solute within the host. Diffusion in aluminium is a vacancy mediated process, with implications that will be discussed below. The total list of solute pairs possible for the alloys we are concerned with is: Cu-Cu, Cu-Li, Cu-Mg, Mg-Mg, Mg-Li and Li-Li. It should be noted that if the presence of an element expresses no effect on the other solutes then its binding energy with the solute is 0 and the probability of forming a cluster is random and depends solely on concentration and how quick the solutes move. As such, the presence of correlations between solutes shown by SAS and APT are good indication that non-zero binding energies are at play.

Figure 49a shows the influence of temperature on the diffusivity of solute elements in Al with diffusion pre-factor D_0 and activation energy Q summarised in Table 10 from literature [12–15]. Diffusivities appears to be in close proximity with a tendency for Mg \sim = Li > Cu. The diffusivity between Mg and Cu is compared in Figure 49b by taking the ratio which should remove effects of vacancies available for diffusion. Despite the large difference in experimentally summarised [12,14] and DFT calculations [15] diffusion of Mg is consistently faster than Cu. These tendencies mean that the most favored, Cu-Mg clusters, are also predicted to be the fastest forming which is not the case we observe for the evolution over natural ageing shown in Figure 29 on page 80.

Diffuser	$D_0 (m^2/s)$	D_0^{Sol}/D_0^{Al}	Q (kJ/mole)	Q^{Sol}/Q^{Al}	Reference
Cu	4.44 x 10 ⁻⁵	6.7	133.9	1.076	[14]
	1.00 x 10 ⁻⁵	1.5	127.6	1.025	[12]
	4.37 x 10 ⁻⁶	0.6	120.6	0.968	[15]
Mg	1.49 x 10 ⁻⁵	2.3	120.5	0.968	[14]
	1.00 x 10 ⁻⁶	0.15	110.0	0.884	[12]
	1.19 x 10 ⁻⁵	1.8	122.5	0.984	[15]
Li	1.55 x 10 ⁻⁵	2.3	119.2	0.957	[13]

Table 10 Summary of Arrhenius parameters for solute diffusion in Al ($D_0 = 6.6x10^{-6} Q = 124.5 kJ/mol$)



Figure 49 a) Diffusivities of Al (black), Cu (red), Mg (blue) and Li (green) in Aluminium, b) ratio between Mg and Cu in Aluminium.

Possible explanations for this apparent anomaly have to involve diffusion mechanism involving both solutes and the vacancies. Francis and Curtin [16] describe the controlled binding and release of vacancies via dilute concentration of solute additions to Al in relation to the possible design strategy to control precipitation [17]. Their proposed process is schematically shown in Figure 50 where the organisation of solute and vacancies is presented at the solution treatment temperature, room temperature and an elevated artificial ageing temperature which is outside the scope discussed here. Using a similar interpretation, Warinos et al. proposed that elements like Sn, with low solubility and very high solute-vacancy binding energies can be used to 'trap' and 'release' vacancies when needed [17].



Figure 50 Schematic of solute vacancy binding at a) effective solution treatment temperature with vacancies in thermal equilibrium, b) after quench to natural ageing temperature where solutes bind to vacancies and c) elevated artificial ageing temperature. Adapted from [16]

This interpretation suggests that Cu or Mg act as a vacancy trap in our alloys and during natural ageing vacancies are detached from such vacancy-solute clusters in order to transport different solute atoms to emerging vacancy-free clusters or that the vacancy-solute clusters themselves diffuse. The reported binding energies of solutes with vacancies are ~ 0.02 eV for Cu and -0.02 eV for Mg compared to 0.25 eV for Sn from first principles calculations [18]. The small binding energies with the vacancies are unlikely to be enough to trigger such a trapping mechanism.



Figure 51 Evolution of Mg/Cu ratio in the Al-Cu-Mg and Al-Cu-Li-Mg alloys compared to the ratio of solutes in the alloy composition.

It is nevertheless clear that, although Cu-Mg clusters seem to be the most stable type, and Mg is expected to be the fastest diffuser, the system always forms Cu clusters first which have a lower Mg/Cu ratio than that of the alloy (Figure 51). This ratio subsequently increases to reach a value which is higher than that of the alloy in line with the strong Cu-Mg pair energy. The low Cu-vacancy binding energy may be sufficient to make vacancies spend more time in the vicinity of Cu atoms. The mobility of such a vacancy would be reduced due to correlated 'useless' exchanges but it is not 'bound' like in the case of Sn additions to Al-Mg-Si alloys [17]. The quantity of 'free' vacancies available for diffusion is effectively reduced through Cu-vacancy clusters. Mg, on the other hand, has a low but negative (i.e. repulsive) binding with vacancies that may lead to uncorrelated (thus useful) exchanges with the vacancy making an active Mg-vacancy complex. Diffusion of such complexes leads to further clustering and growth by sweeping up other solutes. In the Al-Cu-Mg system, Cu and Mg are almost equally likely to be in such a clusters (similar concentrations); however, in the Al-Cu-Li-Mg system, Cu is more likely due to the higher concentration compared to Mg.

After isothermal reversion at 250°C for Al-Cu-Li-Mg, in addition to Cu, some Mg is put back into solution (Figure 52), resulting in retrieved clustering kinetics during the subsequent natural ageing. On the other hand, when reversion is performed at 200°C for Al-Cu-Mg or Al-Cu-Li-Mg, Mg remains in the clusters and the post reversion ageing kinetics is almost suppressed.



Time (h) Figure 52 Evolution of Mg/Cu ratios during natural and post reversion for the a) Al-Cu-Mg and b) Al-Cu-Li-Mg alloys

This could be explained by the fact that the equilibrium vacancy concentration is higher at 250°C than at 200°C (Figure 53) [19–21]. The difference in clustering kinetics seems to suggest that this quenched-in vacancy difference is not enough. The only way around this anomaly is to find a possible vacancy mediated diffusion mechanism which makes Mg slower in presence of Cu or Cu faster in presence of Mg.



Figure 53 Equilibrium vacancy concentrations in the alloys [19–21]

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9 Conclusion

The work presented in this thesis culminates to a deeper understanding of the behaviours of Cu, Mg and Li during the early stages of decomposition of super saturated solid solutions at room temperature. The distribution of solutes has been measured and interpreted through a combination of complimentary characterisation techniques as small angle scattering and atom probe tomography, and theoretical perspectives on solute clusters. Accessing the chemical nature of clusters at very early stages after quench has been made possible through contrast variation small angle scattering using neutrons and X-rays. The interpretation model developed has provided crucial information on clusters and their evolution with time and temperature. Reversion experiments have been used to show the significant effect Mg solute has on formation, thermal stability and possible reforming of solute clusters.

The main points can be summarised as follows:

- Cu rich clusters are present after quench in Al-Cu-Mg, Al-Cu-Li and Al-Cu-Li-Mg due to the low solubility of Cu.
- In the naturally aged state, Mg shows statistically significant involvement in clusters.
- Li has been shown to be homogeneously distributed after quench and in the naturally aged state by atom probe tomography and does not contribute to clustering.
- In the presence of Mg significant changes to hardness, scattering intensity and DSC heat signals occur over the course of natural ageing.
- In the absence of Mg, the initial Cu clusters formed do not evolve.
- The quantity and complexity of clusters forming is shown increase with increasing Mg concentration.
- Clustering kinetics during the course of natural ageing are faster with increasing Mg concentration.
- The clusters forming during natural ageing are shown to have evolving chemistry from Cu rich to more Cu-Mg rich clusters.
- Cu-Mg clusters are identified as the most stable due to the strong Cu-Mg bond.
- The drastic increases of Cu rich clusters by addition of Mg to Al-Cu-Li is strong evidence that Mg positively affects Cu clustering.
- Strong changes to the clustering behaviour of Cu in the presence of Mg are likely due to a vacancy-solute mediated process

1.1 Perspectives

These results may inspire for potential future research focused on improving the combination of small angle scattering and atom probe tomography. The challenges suspected to such projects would revolve around overcoming difficulties as gathering solute specific information and deciphering intensities arising from more than one type of clusters when analysing the global statistical small angle scattering data. Atom probe, with its solute specific information and ability to readily measure stoichiometry, may greatly help. Nevertheless, special resolution limitation, particularly in plane, make it very difficult for small clusters to be detected and may cause smearing which in turn is likely broaden RDFs from APT.

Another potential axis to explore may be focused on the complexity of vacancies and their surrounding environments during ageing. Positron annihilation studies may be a valuable tool for accessing such information. Overall, it would be ideal to establish a computational approach to solve the vacancy-solute interaction. A potential challenge along such a perspective would be the availability of accurate potentials validated by ab initio for the higher order systems in the presence of vacancies. Finally, the integration of time and temperature would be desired to model the complex kinetics experimentally observed and reported throughout this project.