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

R. Ivanov, A. Deschamps, F. De Geuser*

Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMAP, Grenoble, 38000, France

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ABSTRACT

Room temperature solute clustering in aluminium alloys, or natural ageing, despite its industrial relevance, is still subject to debate, mostly due to its experimentally challenging nature. To better understand the complex multi-constituents' interactions at play, we have studied ternary and quaternary subsystems based on the Al-Cu alloys, namely Al-Cu-Mg, Al-Cu-Li and Al-Cu-Li-Mg. We used a recently introduced correlative technique using small-angle neutrons and X-ray scattering (SANS and SAXS) to extract the chemically resolved kinetics of room temperature clustering in these alloys, which we completed with DSC and micro-hardness measurements. The comparison of the clustering behaviours of each subsystem allowed us to highlight the paramount role of Mg as a trigger for diffusion and clustering. Indeed, while a strong natural ageing was observed in the Al-Cu-Mg alloy, virtually none was shown for Al-Cu-Li. A very slight addition of Mg (0.4%) to this system, however, drastically changed the situation to a rapid formation of essentially Cu-rich hardening clusters, Mg only joining them later in the reaction. This diffusion enabling effect of Mg is discussed in terms of diffusion mechanism and complex interactions with the quenched-in vacancies.

1. Introduction

Natural ageing of Aluminium alloys encompasses the changes at room temperature to the microstructure and related properties after they have been quenched from solution treatment temperature. First observed by Wilm in 1906 [1] and later characterised by Guinier and Preston [2,3], the increase of hardness experienced during natural ageing at room temperature is related to the changes in solute distribution at the atomic scale. Solute clustering describes the initial stage of decomposition of a supersaturated solid solution into one with solute-rich domains retaining the host crystal structure. It results in measurable changes of the materials properties, in particular hardness, but also electrical resistivity, lattice parameter etc.

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 characterised and render necessary the combined use of several analytical techniques [4]. Most common experimental techniques based on global sample methods such as differential scanning calorimetry (DSC) [5–10], electrical resistivity [8,9] and of course hardness [11–14] provide evidence for the formation and evolution of clusters. Direct imaging of Cu-Mg "clusters" has been reported by Ralston et al. by high-resolution aberration-corrected TEM [15]; however this method has proven very difficult due to the small quantity and low Z-contrast of the solute species associated in individual clusters with large number density. Techniques based on positron annihilation spectroscopy [4,16–23], nuclear magnetic resonance [24,25] or X-ray absorption spectroscopy [18,26] provide more information about the local environment of solutes and can shine some light on solute-vacancy relationships. 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 or radial distribution functions (RDFs) to provide information on the correlation of solutes and size distributions of clustered domains [27–44]. Small angle scattering (SAS) techniques, providing a global view of the decomposition of the solid solution, have been until now only sparsely used to study clustering [4,25,45,46], despite them being used extensively to describe the degree of inhomogeneity of solute during spinodal decomposition, such as in the Fe-Cr system [47–52].

Since the diffusion of all major solute elements in Aluminium is

* Corresponding author.
E-mail address: frederic.de-geuser@simap.grenoble-inp.fr (F. De Geuser).

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substitutional, clustering kinetics depends on the presence of vacancies, their supersaturation resulting from the quench from the solution treatment temperature, and their interaction with the solutes they are conveying as well as with the clusters themselves. These interactions have been particularly studied in Al-Mg-Si alloys [4,8–10,12–14,17,20,21,23,31–33,36–40,53–55] owing for the prominent – generally negative – effect of clustering on the subsequent artificial ageing kinetics sought during paint baking cycles for automotive sheet. An extensive picture of clustering in this system has been reached by combining experimental observations, thermodynamic modelling [56], and more recently atomistic modelling [57]. These results show that clusters are generally present as early as the as-quenched state [21] and then evolve in number density, size but also chemistry, with several families of clusters involving several types of solutes coexisting in the microstructure. These characteristics depend of course on the alloy chemistry, with noticeable effects having been demonstrated by adding controlled amounts of minor solutes effective at trapping vacancies and thus delaying the natural ageing kinetics [12,13].

The other landmark system for clustering studies is Al-Cu-Mg, in which Mg and Cu co-segregate to form clusters that are very effective at increasing the alloy's strength. Only a few seconds at moderate artificial ageing temperatures (150–200 °C) are sufficient to obtain up to 70% of the maximum precipitation strengthening potential of such alloys, hence the name “rapid hardening” for this effect of clustering [5,27–29]. Clustering kinetics in this system has also been evaluated by combinations of APT, DSC, PALS, and modelling [6,7,11,16,18,26,35,41,42,58–62]. Despite a weakly attractive interaction between Cu and vacancies and a weak repulsion between Mg and vacancies [63], the addition of Mg to Al-Cu considerably accelerates the natural ageing process [11,26]. “Mg-vacancy complexes” (more on this expression in the discussion) have been claimed to already form during quenching [16,19,22]. However, clusters are mainly rich in Cu in the as-quenched state and incorporate Mg gradually during natural ageing [7,58]. Meanwhile, vacancies are surrounded by solute atoms and seem to become gradually trapped within clusters during ageing [18]. However, due to the low concentration of quenched-in vacancies (of the order of 10^{-5} according to [59]), most clusters are rapidly vacancy-free. A somewhat successful model for cluster growth has been developed considering that the limiting process was the detachment rate of vacancies trapped in these clusters [61]. The interaction of vacancies with solutes during the clustering process seem to be better described by non-trivial vacancy-clusters interactions rather than the sum of pairwise vacancy-solute bindings [42].

Al-Cu-Li-Mg alloys have been the object of intensive research in the last 10 years for aerospace applications [64,65]. Despite considerable work devoted to describing the precipitation sequence in these alloys as a function of thermo-mechanical history and alloy composition [45,66–80], the study of natural ageing has been so far quite limited. In the high Li-containing alloys developed initially, most of the low-temperature phenomena have been identified to precipitation of the δ'-Al_3Li phase [81,82]. However, in many of the recently developed Al-Cu-Li alloys, lower levels of Li do not result in appreciable amounts of this phase [45,83] and the natural ageing has been shown to involve Cu-rich clusters [45,84]. Recently, we have set up a correlative methodology for the quantitative evaluation of the quantity of solute atoms involved in clusters and the corresponding Mg/Cu ratio using X-ray and neutron small-angle scattering (SAXS & SANS), supplemented by atom probe tomography [46]. Using this methodology, it has been possible to demonstrate that a small addition of Mg to Al-Cu-Li profoundly changes the clustering behaviour, increasing drastically the clustering of Cu atoms [46]. The study of a compositionally graded Al-Cu-Li-(Mg) alloy with varying Mg concentration has shown that this positive effect of Mg on the clustering rate of Cu monotonically increases with Mg concentration [85].

In order to understand the respective roles of Li, Cu and Mg on clustering in this quaternary alloy, it is useful to evaluate separately the role of the different solutes and thus compare the different ternary alloys Al-Cu-Mg, Al-Cu-Li to the quaternary alloy Al-Cu-Li-Mg. Using the recently developed correlative SAXS/SANS methodology on three such alloys, the aim of the present paper is to provide a quantitative characterization of the chemistry (Mg/Cu ratio) and quantity of clusters continuously during natural ageing. These results will be supplemented by a more classical DSC evaluation, hence providing a better understanding of the heat events that have been already observed by previous studies.

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 100 gf Vickers indenter to generate mean hardness values based on 10 readings. 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).

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 h to represent steps along the ageing process. DSC experiments were carried out using a TA instruments Q200 DSC equipped with an 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 similarly to that used in Ref. [83]. 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 (step 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. Subtracting the signal of step 3 from step 1 generates accurate baseline corrected data for the clustering reactions taking place.

Small angle neutron scattering (SANS) experiments were carried out at the D11 instrument at the Institute Laue Langevin (ILL) in Grenoble, France under proposal 1-01-142 [86]. Samples from the 3 mm thick plate were solution treated, quenched and measured during natural ageing up to 12 h. Additional samples aged ex-situ were tested for the naturally aged condition (72 h of natural ageing). A wavelength of 5 Å was used, above the Bragg cut-off, ensuring that no double diffraction could bring additional noise. The sample to detector distance was kept constant at 1.2 m