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The influence of Mg and Ag on the precipitation kinetics and the formation of the T_1 phase in Al-Cu-Li alloys

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Abstract

Al-Cu-Li alloys are extensively used for aerospace applications. The main hardening phase is the T_1 phase that precipitates as thin platelets on $\{111\}_{Al}$ planes. To facilitate its nucleation, different minor alloying elements are added and dislocations are introduced by cold deformation before the ageing treatment. The impact of these additions in combination with the presence of dislocations on precipitate nucleation and growth needs a deeper understanding. In this work, we investigated the precipitation kinetics of the T_1 phase in alloys containing a common content of Cu and Li and different contents of minor solutes (Mg, Ag) where these elements are present either together or independently. A general overview on the precipitation kinetics was achieved by in-situ small-angle X-ray scattering and hardness measurements. The evaluation of precipitation kinetics reveals that magnesium plays an important role during precipitation by enhancing nucleation kinetics. Additionally, a smaller yet measureable effect of Ag, both in the presence and absence of Mg has been evidenced.

Introduction

Al-Cu-Li alloys are important alloys for aerospace application. Recently developed Al-Cu-Li alloys improve the weak points of the 1980s' alloy family; they possess low weight in combination with good corrosion resistance, improved toughness/strength behaviour and good thermal stability. The main difference is a significant lower Li content and in general a higher Cu/Li ratio [1]–[3]. Commercial Al-Cu-Li alloys contain additions of minor alloying elements such as Zr, Mg, Ag, Mn, etc. [4]. The main hardening phase that precipitates is the T_1 phase (Al_2CuLi), with an hexagonal structure, that precipitates on $\{111\}_{Al}$ planes [5]–[8] through a mechanism which probably involves nucleation on partial dislocations [9]–[12]. Other possible strengthening precipitates include phases from binary alloy systems, Al-Cu or Al-Li, that generate precipitation of θ'(Al_2Cu) [13], [14] or δ' (Al_3Li) [14]–[16] respectively. In the presence of Mg the S' phase from the Al-Cu-Mg system may also precipitate [15]. The effect of silver and magnesium has been already studied. Mg is reported to accelerate the hardening kinetics and favour a fine distribution of T_1 precipitates [12], [17], [18]. Ag is also reported to accelerate the kinetics but the effect is less pronounced [19]–[21]. Atom-

probe tomography characterization shows that Mg and Ag are found in the chemistry of the T_1 hardening phase [19].The objective of the present study is to further investigate the precipitation kinetics of Al-Cu-Li, with or without small amounts of Mg and/or Ag.

Materials and experimental procedure

The studied alloys were provided by Constellium and were produced on a laboratory scale. The purpose is to clearly separate the effect of the different minor alloying elements. Therefore a 'base' alloy containing 3.5 wt % Cu and 0.9 wt % Li was produced and different combinations of small additions of magnesium and silver were added. The compositions of the investigated materials are given in Table 1.

Table 1: Compositions in wt% of the investigated alloys

	Al	Cu	Li	Mg	Ag
AlCuLi (Base)	Bal	3.5	0.9		
AlCuLi Ag	Bal	3.5	0.9		0.35
AlCuLi Mg	Bal	3.5	0.9	0.35	
AlCuLi MgAg	Bal	3.5	0.9	0.35	0.35

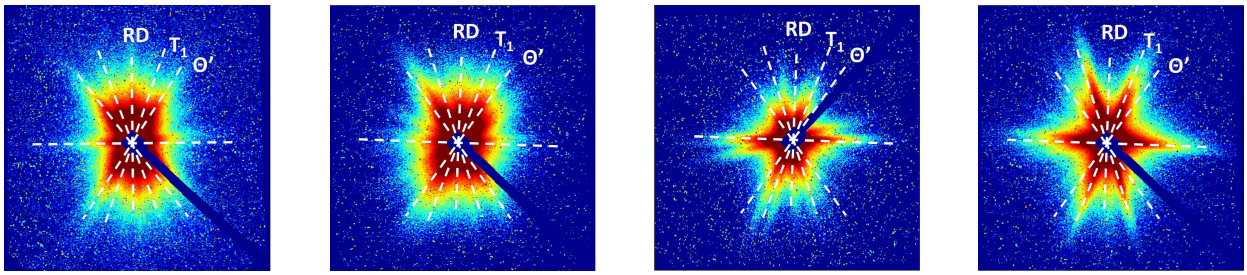
The cast ingots were homogenised, hot rolled and machined prior to the artificial aging heat treatment. Solution heat treatment was performed at 505 °C for 30 minutes in an air circulation furnace, followed by water quench. After 3-5 minutes of natural aging, a 4 % plastic deformation was introduced by stretching. Another 3-5 days of natural aging period were applied before artificial aging was performed. The latter combined a ramp heating with a heating rate of 20 °C/h up to 155°C and further isothermal ageing at 155°C. This heat treatment was done both ex-situ in oil bath and in in-situ during SAXS experiments. Micro-hardness samples were prepared by mirror polishing the surface. The hardness measurements were performed on a Tukon 1102 Wilson Hardness tester. The applied load was 500g. with an indentation time of 10 s. In total, 60 measurements per sample were performed. The samples for Small Angle X-ray Scattering (SAXS) were polished on both surfaces until a thickness of 70 to 100 µm was achieved. The measurements were performed on a laboratory setup (rotating Cu anode, energy 8.05 keV). The ageing heat treatment was performed in-situ and SAXS images were taken every 8 min. Platelet shaped precipitates appear as streaks in SAXS images. This is due to the reciprocity in diffraction between size and scattering angle. Due to the rolling texture, the orientation of the streaks can be analysed with respect to the rolling direction and provide information on the phases. Further kinetics can be determined by calculating the integrated intensity of each image, which is related to the volume fraction of precipitates. Further these values are normalized by the maximum value Q_{max} for each alloy at the end of the heat treatment and Q/Q_{max} is proportional to the volume fraction of precipitates. In order to get more information on the precipitates that formed during the ageing process, the thickness of the particles can be determined by fitting the experimental data as it is described in [22], [23].

Results

Indexing of phases for the different alloys. We have first compared the microstructure of the different alloys in peak-aged condition. As it will be seen later, this state corresponds to various ageing times depending on alloy composition. Fig. 1 shows the SAXS-images of peak aged conditions for AlCuLi (1a), AlCuLi-Ag (1b), AlCuLi-Mg (1c) and AlCuLi-MgAg (1d). The orientation of T_1 and θ' with respect to the rolling direction (RD) is indicated in the images. Two groups of alloys can clearly be distinguished. Images 1a and 1b are representative of non-Mg-

containing alloys and show that θ' is precipitating together with T_1. The scattering angle corresponding to T_1 does not show high intensity, which supports the assumption that it is not the dominant phase. Opposite observations were made for Mg-containing alloys, which are shown in Fig. 1c and 1d. It is very clear for AlCuLi-MgAg in Fig 1d that T_1 is the dominant phase and that θ' is hardly detectable. Similar observations were made for AlCuLi-Mg, shown in Fig. 1c. However, it appears less obviously, since 2 types of streaks are overlapping. This can be due to a non-ideal texture of the grains included in the analysed volume (1mm in diameter).

Analysis of the precipitation kinetics. A complete overview of precipitation kinetics is obtained by in-situ SAXS measurements, plotting the integrated intensity Q over time shown in Fig. 2 for AlCuLi, AlCuLi-Ag, AlCuLi-Mg and AlCuLi-MgAg alloys. Again, the main differences are seen between Mg and non-Mg containing alloys. For the AlCuLi-Mg alloy the increase in intensity is detected after approximately 3 hours of ageing at 155 °C. The addition of silver further enhances the kinetics; rise in intensity is detected after 1.5 hours. The plateau, which refers to a fully precipitated condition, is reached after 12 hours for AlCuLi-Mg and after 10 hours for AlCuLi-MgAg. This is the condition that was imaged in Fig. 1. Regarding the non - Mg containing alloys, the onset of precipitation is more difficult to detect. However, after 1.5 hours at 155 °C intensity increases slowly but continuously and the plateau is reached after 50 hours at 155 °C (condition imaged in Fig. 1a) and 1b).



a) AlCuLi after 50h at 155°C.

b) AlCuLiAg after 50h at 155°C

c) AlCuLiMg after 12.5h at 155 °C

d) AlCuLiMgAg after 10h at 155 °C.

Figure 1: SAXS images of the stabilised condition of AlCuLi (a), AlCuLi-Ag (b), AlCuLi-Mg (c), and AlCuLi-MgAg (d)

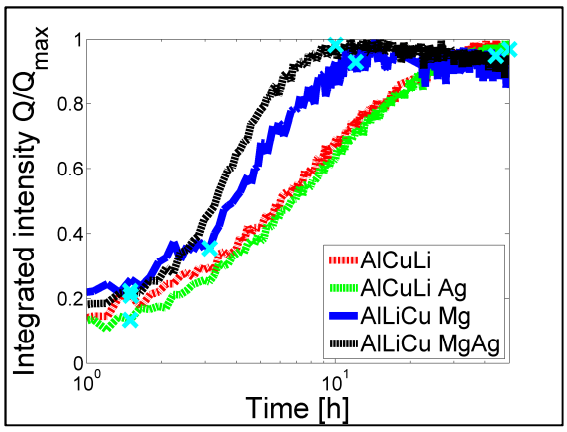


Figure 2: Integrated intensity over time for AlCuLi, AlCuLi 0.3Ag, AlCuLi Mg and AlCuLi MgAg, indicating precipitation kinetics

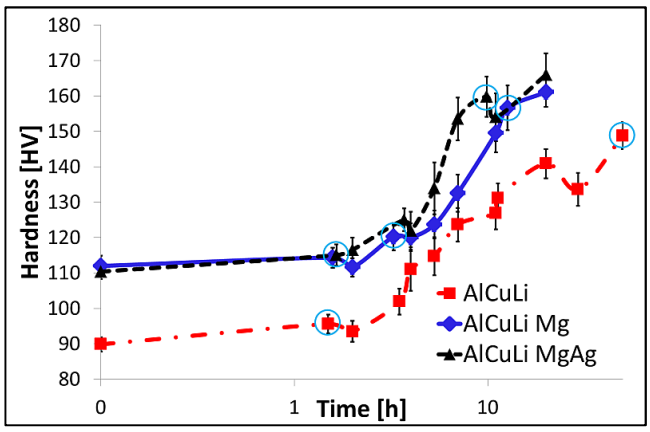


Figure 3: Hardness measurements for AlCuLi, AlCuLiMg and AlCuLiMgAg

The hardening kinetics of AlCuLi, AlCuLi-Mg and AlCuLi-MgAg alloys are presented in Fig. 3. Again Mg and non-Mg containing alloys are clearly distinguished. Alloys with Mg-additions lie around 20 HV above the base alloy AlCuLi throughout the whole ageing treatment. Similarly to what was seen in the precipitation kinetics determined by SAXS measurements, hardness increases for all alloys after 1.5 hours at 155 °C. Combined addition of Ag and Mg show highest hardness throughout the experiment and faster hardness increase compared to AlCuLi-Mg. More information on the precipitates is obtained by determining their thickness. The results of the thickness analysis over time are presented in Fig. 4. AlCuLi-MgAg shows a constant thickness over time that lies between 12 and 13 Å. This value is in good agreement with the measured thickness of a one-layer T_1 [7], [8]. The AlCuLi-Mg alloy has the same thickness in the beginning but for longer ageing times the thickness increases up to 16 Å.

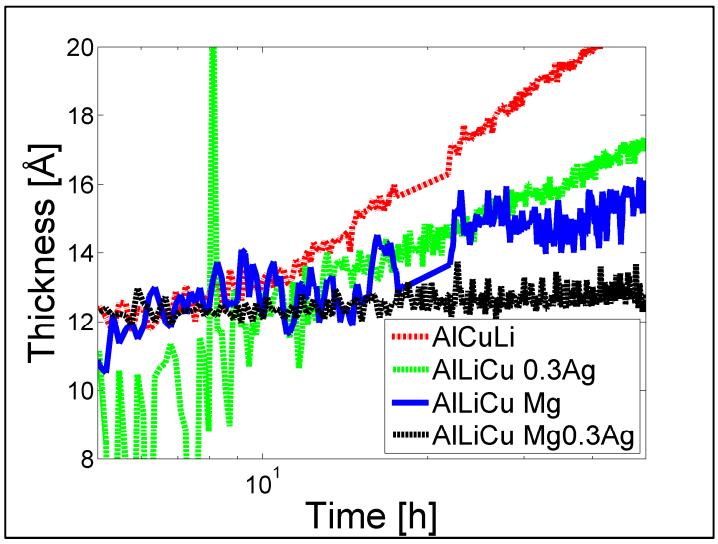


Figure 4: Thickness evolution of AlCuLi, AlCuLi Ag, AlCuLi Mg and AlCuLi MgAg over time.

Different behaviour is seen for the Mg free alloys. In both alloys, the thickness increases continuously during the whole heat treatment. This increase is more pronounced for the AlCuLi alloy, whereas the thickening rate for AlCuLi-Ag alloy is less important. It is not sure if the final thickness is reached after an ageing period of 50 hours. θ' being the dominant precipitating phase, it might be concluded that it grows and thickens during the whole ageing time.

Discussion

Precipitation kinetics was characterised by in-situ SAXS and hardness measurements. Both methods demonstrate a large influence of Mg-addition on the precipitation kinetics. Nucleation is detected between 1.5 to 3 hours ageing time for all alloys, but to reach a fully precipitated condition, ageing times for Mg-containing alloys were approximately 5 times shorter. However, due to the lack of absolute calibration of the integrated intensity, no information on the absolute value of volume fraction of precipitates can be extracted. Enhanced precipitation kinetics in non-deformed material was observed in earlier studies, in which the addition of Mg and especially the combination of Mg and Ag showed similar effects as in the present case. It was explained by the formation of additional nucleation sites such as voids and GP-zones in the presence of Mg [12]. In our case, hardness values for Mg containing alloys are higher throughout the heat treatment in pre-deformed materials. A similar effect was found for an Al-4.2%Cu-1.31%Li alloy with 0.5 % Mg-additions. Both enhanced precipitation kinetics and increased hardness were found [18]. Moreover, we have shown that an addition of Ag slightly enhances the nucleation kinetics. An earlier study investigating on Al-Cu-Li-Mg-Zr alloy showed that in non-deformed material the effect of Ag was remarkable, whereas the introduction of stretch prior to the artificial aging treatment cancelled out this effect [21]. In general, the role of pre-deformation plays an important role [10], [11] and the combined

effect of dislocations with minor alloying elements needs to be specifically investigated. However, comparisons to earlier studies have to be done carefully, since a wide range of investigations were performed on Al-Li-Cu alloys developed in the 80s which contained high levels of Li. Useful information was obtained in the present study by indexing SAXS-images of a fully precipitated condition, as seen in Fig. 1. Both precipitation kinetics and hardness differences might be explained by the predominant precipitating phases. It was pointed out that Mg-containing alloys predominantly form T_1 precipitates. The width of this phase is across 5 layers of {111} oriented Aluminium matrix planes and its thickness is then 14 Å [7], [8]. It can be argued, if it is correct to count the two Aluminium layers to the thickness of the precipitate, as it is done in [8]. The actual thickness, as measured by the SAXS experiments (which evaluate the dimension of the material with a different electron density as compared to the matrix), should therefore be slightly smaller, consistently with our measurements and other recently published data in similar [14], [24]. In the absence of Mg, θ' also precipitates and thickness measurements show a different behaviour: the ageing leads to larger thicknesses which is related to the formation of θ'-phases [16], [25], [26]. The effect of Ag additions on the thickness was remarkable. For both Mg and non-Mg containing alloys, the thickness remained smaller in the presence of Ag. It might indicate that Ag plays an important role during thickening. However, further studies have to be conducted in order to draw firm conclusions.

Conclusions

We have studied the influence of Mg and Ag on the precipitation kinetics in an AlCuLi base alloy during ageing at 155 °C. The biggest effect on precipitation kinetics was seen for Mg-additions, which are shown to favour T_1 precipitation, improving both strength and strengthening kinetics. In the absence of Mg the precipitation sequence is altered and θ' also precipitates; hardness and volume fraction of precipitates increased at a lower rate than in Mg-containing alloys. It is important to mention that the thickness of the precipitates in non-Mg containing alloys increased throughout the heat treatment, whereas it stayed nearly constant in Mg-containing alloys. The effect of Ag on the thickening behaviour should be studied more precisely in future studies, since it might play an important role, explaining differences on precipitation kinetics in the AlCuLi-MgAg alloy.

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