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Growth ledges on silver-segregated θ' (Al_2Cu) precipitates

Julian Rosalie[1], Laure Bourgeois[2]

[1] National Institute for Materials Science, Sengen 1-2-1, Tsukuba,Ibaraki, 305-0047, Japan.
[2]Monash Centre for Electron Microscopy, Monash University, Melbourne, Victoria, 3800, Australia.

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Abstract

The interfacial structure and composition of θ' (Al_2Cu) precipitates in Al-0.9at.%Cu-0.9at.%Ag alloys were examined using high resolution electron microscopy. High angle annular dark field scanning transmission electron microscope (HAADF-STEM) images showed the presence of a silver(Ag)-rich bi-layer on the coherent (100) θ'-Al interfaces of the precipitates (1). Despite the presence of this layer, growth ledges were observed on the θ' phase and thickening of the precipitates was able to proceed via ledges of step height $0.5c(\theta')$.

Introduction

Interface structure and energetics play a critical role in precipitation strengthening of aluminium alloys. Optimisation of precipitation strengthening in aluminium alloys depends on the ability to precipitate thin, high-aspect ratio precipitate plates. Such precipitates offer the most effective geometry for reducing the mean free path for dislocation glide and thus increasing resistance to plastic deformation (2). The formation of high-aspect ratio plates depends in turn on the existence of low-energy interfaces that are highly coherent with the matrix. This allows the lateral growth of the precipitate to proceed at much higher rates than thickening.

A classic example of the influence of interfaces on coarsening behaviour is the Ω phase formed in Al-Cu-Mg-Ag alloys. Initial studies found that the addition of Ag resulted in substantial improvements in the mechanical properties, particularly at high temperatures (3). It was later established that this was due to the precipitation of a phase termed Ω, with a structure related to the equilibrium θ phase, but with $\{111\}$ habit. Further studies determined that silver segregated to the coherent planar interfaces (4; 5), forming a bi-layer surrounding the precipitates (6). This layer is thought to not only stabilise the Ω phase, but to restrict ledge nucleation, leading to the high coarsening resistance of Ω phase precipitates(6).

In recent years the availability of improved experimental methods (in particular atomic resolution HAADF STEM and atom probe field ion microscopy) and computational methods has led to a renewed interest in the interfacial structure of precipitates. While the Ω phase provides a striking example of interfacial segregation, it has been shown that such segregation is not unique to this alloy. There are a growing number of examples in which interfacial segregation can result in deviation from the bulk composition and/or structure in the precipitate or matrix. It has been shown, for example, that Si segregates to the θ' phase in Al-Cu-(Si) where it substitutes for Cu atoms (7). Changes in the interface structure have also been reported in binary Al-Cu alloys, with Cu atoms occupying octahedral interstitial sites at the coherent θ'-Al interface and it is thought that this may affect the ledge-nucleation kinetics (8).

We have recently examined the interfacial structure of θ' precipitates in Al-Cu-Ag alloy. It was possible to show Cu segregation to the interface similar to that in binary Al-Cu. In addition Ag segregated to form a silver-rich layer surrounding the θ' precipitates (1). This Ag layer bore a remarkable similarity to the interfacial layers that formed around Ω precipitates in Al-Cu-Mg-Ag alloys (6), despite forming on the $\{100\}$ planes rather than $\{111\}$ planes.

The present work set out to determine whether growth ledges were present on the θ' precipitates in Al-Ag-Cu alloys and to determine whether silver-segregated θ' precipitates display similar resistance to coarsening as Ω phase precipitates.

Experimental

An aluminium alloy containing 0.90at.%Cu and 0.90at.%Ag (2.05wt.%Cu and Al-3.45wt.%Ag) was cast in air from high purity elements. The composition was verified via inductively coupled plasma-mass spectroscopy (ICP-MS). The alloy ingot was homogenised (525°C, 168 h). The ingot was then hot-rolled in a number of passes to a thickness of 2 mm thickness. It was then cold-rolled to form a sheet with thickness of 0.5 mm, from which discs (3mm diameter) were punched. These discs were solution-treated using a nitrate/nitrite salt pot at (525^{o}C, 0.5 h) and quenched in water. Previous studies of similarly aged Al-Cu-Ag alloys of this composition found that the micro-hardness reached a maximum after 64 h ageing (9). Solution treated discs were isothermally aged 200° for between 2 and 4 h in a silicone oil bath in order to study precipitate growth in the underaged condition, before Ostwald ripening became a significant influence.

The aged discs were manually ground to ∼0.2 mm and thinned to perforation by twin jet electropolishing at −20°C. The solution used was 1:2 nitric acid/methanol by volume. Discs were plasma-cleaned immediately prior to TEM examination.

High angle annular dark field (HAADF) scanning transmission electron microscope (STEM) images were obtained using a FEI Titan^3 80-300 microscope operating at 300 kV. The convergence semi-angle of 15 mrad provided a spatial resolution of $\approx$ 1.2 Å. The inner collection angle of 40 mrad yielded images dominated by atomic contrast. By default, images are presented adjusted only for brightness and contrast. Image analysis was performed using ImageJ software, version 1.44o.

Results

Silver enriched layers were present on all the θ' precipitates observed in foils aged for 2–4 h at 200°. HAADF-STEM images showed this Ag segregation as atomic layers with strong Z contrast on the coherent $001_{\theta'};001_{\mathrm{Al}}$ interfaces (1). Ag is strongly concentrated in two atomic layers on the upper and lower faces of the precipitate, with the HAADF-STEM intensity (and hence Ag concentration) decreasing to that of the Al matrix over 2–3 atomic planes.

Ledges were observed on many of the θ' precipitates, in spite of the existence of the Ag bi-layers and two to three ledges were frequently present on a single precipitate. Typical examples of such ledges on θ' precipitates are provided in Figure 1. Figure 1(a) shows a θ' precipitate with a thickness of $2c(\theta')$ and the incoherent edge and $3c(\theta')$ closer to the centre. Three ledges on the precipitate have have been indicated by asterisks, with the precipitate increasing in thickness by $0.5c(\theta')$ at each ledge. A similar situation can be seen in Figure 1(b), in which the precipitate has been imaged along the [001] direction. In this micrograph three ledges are present, each of riser height $0.5c(\theta')$ and the precipitate thickness increases from $2c$ at the edge to $3c$ towards the centre. All ledges observed on Ag-enriched θ' precipitate were of this same step height (0.29 nm). In addition the precipitate thickness is always less at the edges of the precipitate, implying that ledges form near the centre of the platelet and grow towards the edges.

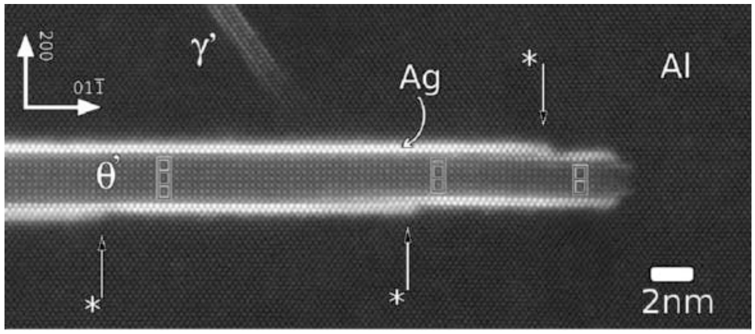
Growth ledges are shown in greater detail in Figure 2. In Figure 2(a) the precipitate (which is viewed along the [011] axis) has a thickness of $2c$ at the growing end, with a single ledge of rise height $0.5c$. The precipitate shown in Figure 2(b) (imaged along the [001] direction) has a thickness of only $1.5c$ at the semi-coherent edge, with the thickness increasing in 2 steps of $0.5c$ to $2.5c$ on the left. Additional Cu atomic columns were also present on the outermost layers of the θ' precipitates, as has been reported recently (8). When the precipitate is viewed along the [001] zone axis (Figure 2(b)) the additional Cu atoms are evident in additional atomic columns between the usual Cu columns. (labeled "Cu(B)"). The asterisked arrow indicated what appear to be additional Cu atoms at the growing edge of the θ' precipitates in both micrographs. Similar segregation of Cu atoms to semi-coherent interfaces has also been reported (17).

The thickness of the θ' precipitates was measured for as many examples as could be unambiguously determined. A frequency plot of the thickness in terms of the θ' c-lattice parameter is shown in Figure 3. It is quite striking that precipitates are present in half-integer multiples of the c lattice parameter and all thicknesses from 1–6c are represented, with no systematically missing thicknesses. There is also a slight increase in average thickness from $2.8c$ after ageing for 2 h to $3.5c$ after ageing for 4 h, indicating that thickening of the precipitates is proceeding.

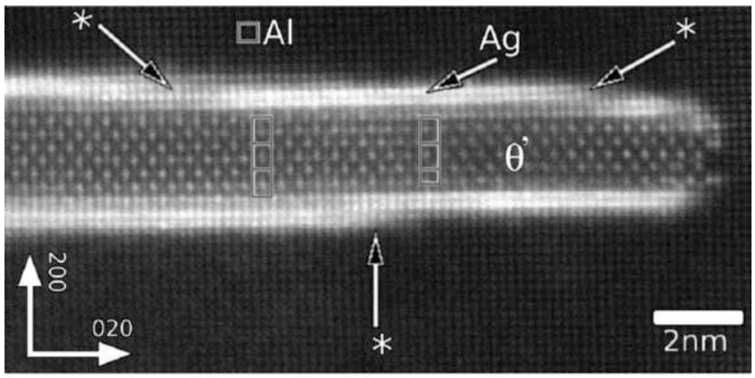
Discussion

Silver was found to segregate to all θ' precipitates formed in Al-Cu-Ag alloys. This segregation took the form of a Ag-rich bi-layer that formed primarily on the coherent {001} interfaces of the precipitates (1). The presence of this layer did not preclude thickening of the θ' phase, although the details of the ledge growth mechanism differed from other Al-Cu based alloys.

Ledgewise growth of θ' has been the subject of extensive study over many years (10–15). Ledges of riser height $0.5c$ ledge corresponded to the smallest spacing between Cu atomic planes normal to the c-axis and represent the smallest value permitted by



(a) [011]



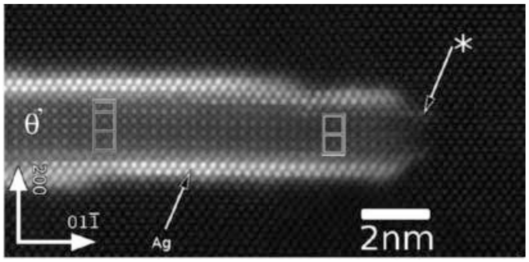
(b) [001]

Figure 1: Growth ledges on θ' precipitates with Ag enriched bi-layers. The figure shows HAADF-STEM images of growth ledges with riser height $0.5c(\theta')$ viewed along (a) [011] and (b) [001] directions. Three ledges (indicated by asterisked arrows) can be seen on each precipitate. The edge of a γ' ($AlAg_2$) precipitate can be seen in the upper region of (a).

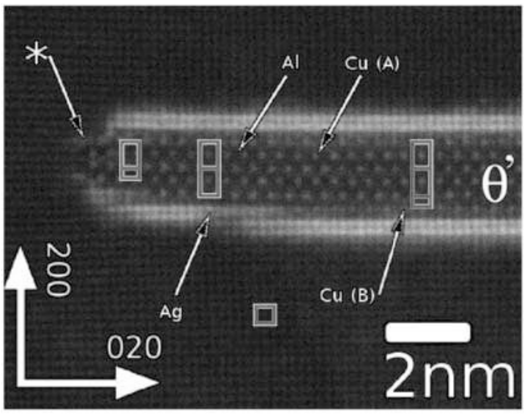
the θ' crystal structure (15). However, experimental studies reported ledges with step heights of several multiples of the c lattice parameter, in particular $2c$ and $3.5c(\theta')$ which provide the least misfit strain (10; 16). Ledges of 2-4c have been reported in Al-Cu(-Sn) alloys, with 2-3c being most common in the early stages of ageing (17). Purdy and Hirth have argued from structural and energetic grounds that the minimum step heights should be 1.16 nm and 2.03 nm, corresponding to $2c(\theta')$ and $3.5c(\theta')$ and ledges of this size have been reported by a number of authors (10; 16). Ledges with $0.5c(\theta')$ were ruled out on the basis of the high misfit strain (-44%) which would require extensive climb for the ledge to propagate. While the details remain to be clarified, it appears certain that the presence of ledges of height $0.5c$ is a consequence of the Ag interface layer restricting the formation and/or propagation of larger ledges.

Previous reports of θ' precipitates in Al-Cu (8) and Al-Cu-Sn (17) alloy noted that θ' precipitates showed a preference for specific thicknesses (aka. "magic thicknesses") that occupied local energy minima. Conversely thicknesses which occupied local energy maxima are unfavourable, giving rise to systematically absent thicknesses. While the number of precipitates examined herein is insufficient to draw firm conclusions, it appears that after 4 h ageing there is a slight preference for thicknesses of $2c$ and $3.5c$ (Figure 3), both of which represent local energy minima. However, the figure also shows no systematically absent thicknesses, as would be expected if growth was restricted to ledges steps of $0.5c$ in height.

In order to take advantage of the "magic thicknesses" it is necessary that ledge heights are such as to allow the precipitates to grow by progressing from one such thickness to another. However, thickening via ledges of $0.5c$ height, as is the case here, would not allow the precipitate to avoid passing though thickness with unfavourable strain energy values. It appears likely that a combination of (i) diffusion to the ledge riser being impeded by the Ag layer, (ii) the un-



(a) [011]



(b) [001]

Figure 2: HAADF-STEM images of growth ledges on silver-segregated θ' precipitates; viewed along (a) [011] and (b) [001] zone axes. The ledge height in each case is 0.5 of the c lattice parameter of the θ' phase.

favourable misfit strain for such ledges, (iii) the need for climb in order to propagate the ledge and (iv) the inability to avoid unfavourable thicknesses would tend to restrict the thickening of the θ' precipitates.

The existence of growth ledges is in striking contrast to Ag-segregated Ω precipitates in Al-Cu-Mg-Ag alloys. Coarsening of Ω phase precipitates is slow, due to the difficulty of nucleating growth ledges beneath the Ag interface layer. In contrast, while the Ag interface restricts the ledge riser height θ' precipitate and presumably the rate of growth, thickening is still able to proceed. The formation of ledges with step height $0.5c$ is energetically unfavourable due to the high misfit strain. It is probable that the formation of such ledge is due to the constraint provided by the Ag interface layer. Further investigations into the ledge structure and the thickening mechanism are underway.

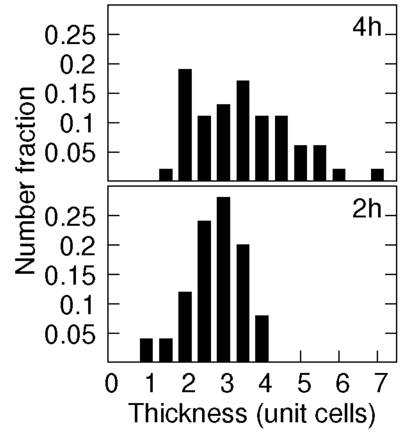


Figure 3: Thickness of θ' precipitates after ageing for 2–4 h at 200°C. Precipitates are present in half-integer multiples of the c-lattice parameter.

Conclusions

θ' (Al_2Cu) precipitates in Al-Cu-Ag alloys were examined using high resolution HAADF-STEM imaging.

1. Ag segregated to the coherent interfaces of the θ' precipitates, forming an Ag-rich bi-layer.
2. The average thickness of the precipitates increased when the ageing time was increased from 2 to 4 h indicating that the Ag layer did not prevent coarsening.
3. No systematically absent thicknesses were observed.
4. Growth ledges were observed on the θ' precipitates despite the presence of this Ag layer.
5. The step height of the growth ledges was always equal to half of the c-lattice parameter of the θ' structure (0.29 nm). This is an unfavourable, high-energy ledge height and this growth mechanism would not allow the precipitate to thicken solely by adopting preferred "magic thicknesses" with low interfacial and misfit strain.

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