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Sigma (σ) Phase Precipitation During Prolonged Ageing of an Al-Cu-Mg-Ag Alloy

R.N.Lumley[1], I.J. Polmear[2]

[1] CSIRO Manufacturing Science and Technology, Private Bag 33, Clayton South MDC, Victoria, 3169, Australia
[2] School of Physics and Materials Engineering, P.O. Box 69M, Monash University, Melbourne, Victoria, 3800, Australia.

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Abstract

Previous investigations have shown that the creep resistance of an Al-Cu-Mg-Ag alloy improves if it is underaged. Reasons for this behaviour have been sought by observing microstructural evolution during prolonged exposure at 130°C, with and without an applied load. Dynamic precipitation of θ' and S'(S) occurs on dislocations during creep whereas in the unloaded condition, the σ phase forms throughout the matrix. It appears that σ nucleates at sites where the Ω and θ' precipitates intersect. A mechanism is proposed for σ formation by interfacial diffusion when two Mg atoms replace two Al atoms in the crystal lattice of θ'.

1. Introduction

Al-Cu-Mg alloys containing small amounts (0.1at%) of Ag are attracting interest because they may exhibit creep properties superior to those of the commonly available, high strength aluminium alloys [1-3]. This behaviour is attributed to the fact that Ag stimulates nucleation of the finely dispersed and relatively stable phase Ω, which forms as thin hexagonal plates on the $\{111\}_\alpha$ planes [3,4]. It has also been shown that creep resistance may be further enhanced if the alloys are tested in the underaged (UA) condition, rather than the fully age-hardened (T6) condition [5,6]. This behaviour is attributed to the presence of "free solute" in solid solution in the UA alloys that is available to retard dislocation motion during creep [6].

Recent studies have shown that the alloy Al-5.6Cu-0.45Mg-0.45Ag-0.3Mn-0.18Zr in the UA condition exhibits zero secondary creep after prolonged exposure for 20000h at 130°C and a stress of 200MPa [7]. Reasons for this enhanced creep resistance have been sought by comparing changes in microstructure of the UA alloy after this prolonged exposure at 130°C, with and without the imposed stress.

The appearance of the microstructure of the alloy in the initial UA condition is shown in Figure 1. Two variants of thin plates of the uniformly dispersed Ω phase are present in the $[101]_\alpha$ orientation, together with one variant of the θ' phase (Figure 1a). In the $[001]_\alpha$ orientation

(Figure 1b), there are two variants of the θ' phase visible, together with occasional particles of a precipitate 15-25nm in size that electron diffraction confirmed to be the σ phase ($Al_5Cu_6Mg_2$) [8-13], and some of these σ particles appeared to be co-incidental with a θ' plate (Figure 1b).

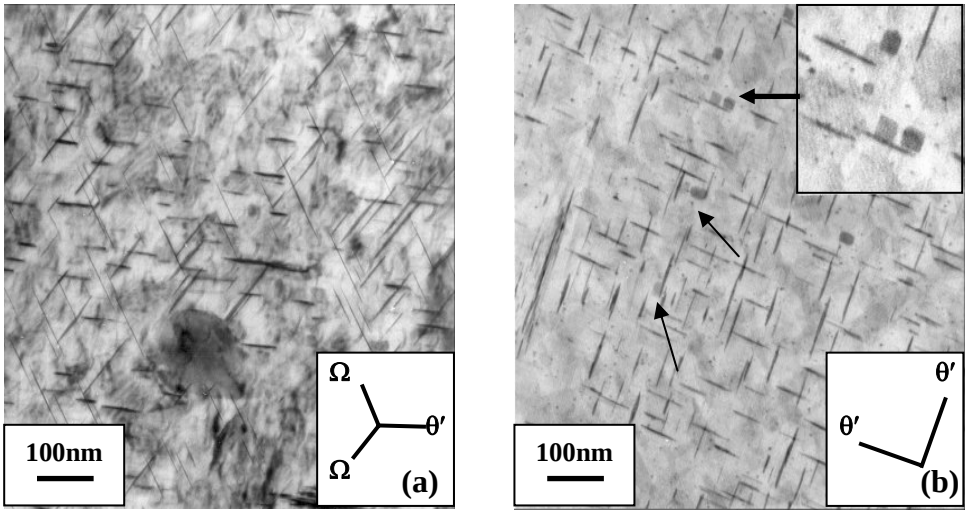

Figure 1: Microstructures of the starting UA alloy; (a) $[101]_\alpha$ orientation showing two variants of the Ω phase and one variant of the θ' phase, and (b), $[001]_\alpha$ orientation showing two variants of the θ' phase and occasional cuboids of σ phase. In b), examples of co-incidence between the σ phase and θ' phases are arrowed, and shown in the inset.

During prolonged exposure of the alloy at 130°C under creep conditions, the Ω phase was retained and the density of θ' in the matrix much reduced. Instead, dynamic precipitation of parallel plates of this phase (θ') occurred along dislocation lines, together with laths of the S'(S) phase [14]. With the unloaded alloy, the amount of Ω in the matrix decreased and the density of θ' increased. However the most significant change was a large increase in the density of the σ cuboids. The purpose of the present study was to provide an explanation for the enhanced nucleation and growth of this σ phase.

1.1 Sigma (σ) Phase

The σ phase has been described as cube-shaped, or as cuboids, but careful examination has revealed that the edges of the cuboids are truncated or chamfered [eg.10,11]. It is known to have a complex cubic structure with 39 atoms per unit cell and a lattice parameter of 0.831nm [8]. It has been reported to be semi-coherent with a misfit of 2.8%, and to be co-planar with the aluminium matrix so that $\{001\}_\sigma$ // $\{001\}_\alpha$ and $<010>_\sigma$ // $<010>_\alpha$ [15]. Sigma (σ) has been observed in several Al-Cu-Mg alloys, and is thought to require a minimum concentration of Si to act as a nucleant [10-16], although other workers have suggested that Ag may have a similar effect [17].

2. Experimental

The Al-Cu-Mg-Ag alloy was prepared as 70.6×27.6mm extruded bar, which was solution treated 5.5h at 525°C, cold water quenched and underaged (UA) 2.5h at 185°C in an oil bath. This treatment compares with 10h at 185°C for the fully hardened, T6 condition. The specimen was then exposed at 130°C for 20000h. Samples for transmission electron microscopy (TEM) were prepared by spark machining disks parallel to the longitudinal direction of the extruded bars that were electropolished at 15V in a solution of 33% HNO_3 in

methanol. The resulting thin foils were examined in a JEOL 2000EX electron microscope operating at 200kV, close to (<4°) the relevant zone axis.

3. Results and Discussion

The microstructure of the unloaded alloy after exposure for 20000h at 130°C is shown in Figure 2. Two variants of the Ω phase were again observed in the $[101]_\alpha$ orientation although the density had decreased (Figure 2a). On the other hand, it is clear that the density of θ' had increased (Figure 2b). The most significant change, however, was the large increase in the density of the σ cuboids, which was an unexpected result since the Si content of this alloy is so low (0.07%), and there was little σ present in the starting microstructure. Their size had also increased to 30-50nm. The σ cuboids were observed often to be bounded on one or more edges by θ' plates, and a more detailed analysis revealed that they were often located at sites where θ' and Ω plates appeared to intersect. This suggested that a close relationship may exist between these three precipitates.

A schematic representation of the σ cuboids is shown in Figure 3 (a&b), along with a higher magnification image of a $[001]_\alpha$ orientation, and it is to be noted that the truncated faces all display {111} orientations. The complete orientation relationship of σ with the Ω and θ' precipitates, and with the α aluminium matrix are:

$$\{001\}_\alpha \,//\, \{001\}_\sigma,\ \{111\}_\alpha \,//\, \{111\}_\sigma,\ \{001\}_\alpha \,//\, \{001\}_{\theta'},\ \{111\}_\alpha \,//\, \{001\}_\Omega,\ \{001\}_\Omega \,//\, \{111\}_\sigma;$$
$$[010]_\Omega \,//\, [10\bar{1}]_\alpha \,//\, [10\bar{1}]_\sigma, \text{ and } \{010\}_\alpha \,//\, \langle 010\rangle_{\theta'}$$

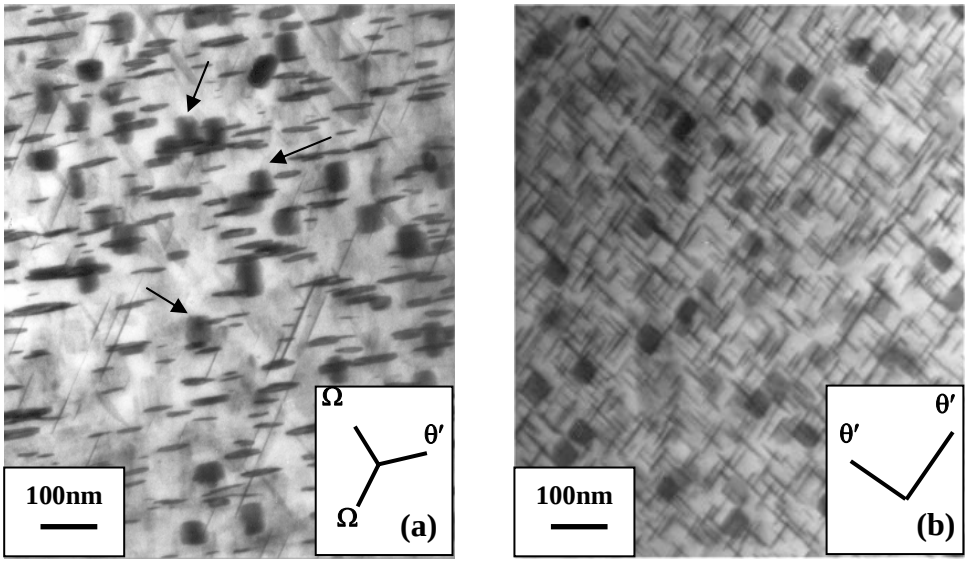

Figure 2: Microstructures of the UA alloy subsequently exposed for 20000h at 130°C. (a) $[101]_\alpha$ orientation showing two variants of the Ω phase and one variant of each of the θ' phase and the σ phase (examples arrowed). (b), $[001]_\alpha$ orientation showing the σ phase and two variants of the θ' phase.

For the case of C, the relationship between Ω and θ' suggests that these precipitate plates may cross, if viewed edge on from the appropriate $[101]_\alpha$ orientation. For a particular $[101]_\alpha$ orientation one or other of these four relationships was observed in approximately 50% of the σ particles examined (157 out of 302). For the remainder of σ particles, it seemed that these

relationships were again evident when viewed from other $[101]_\alpha$ orientations. These observations suggest that the proposed interactions are real rather than apparent, and do not arise because of random groupings of precipitates, or from overlapping as they are viewed through the foil specimen thickness.

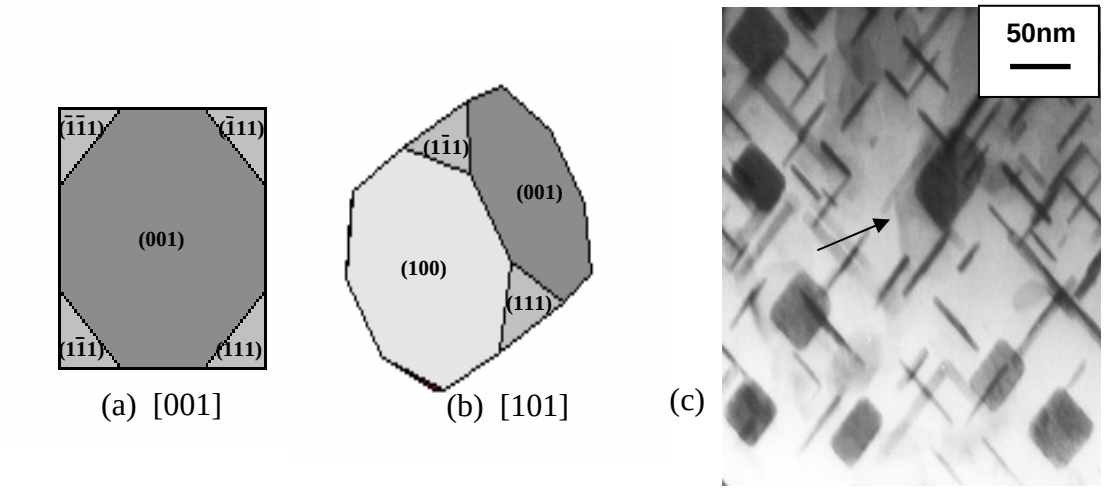

Figure 3: Truncated cube morphology of the σ phase, viewed from the (a) [001] and (b) [101] directions; c) shows the $[001]_\alpha$orientation showing truncated corners of σ and two θ' variants on the $\{001\}_\alpha$ planes. Arrowed in c) is an Ω plate on a $\{111\}_\alpha$ incline plane.

As the composition of σ is $Al_5Cu_6Mg_2$, both Cu and Mg atoms are required for nucleation and growth to occur. Copper atoms are available from residual solute in the underaged matrix, the Ω precipitate and possibly from θ'. Since neither Ω nor θ' contain Mg in their crystal structures [18], this element will be available in the solid solution. It should also be noted that Mg segregates to, and is available at, the surfaces of the Ω plates which themselves are parallel to the $\{111\}_\alpha$ planes [18-20].

Growth of precipitates can occur by ledge formation involving vacancy assisted lattice diffusion, or by interfacial diffusion along surfaces [21], the latter of which will occur in the absence of residual solute or vacancies within the matrix. This condition may be expected during prolonged ageing such as has been examined here. In simplified terms, if it is assumed that growth is indeed occurring by surface diffusion along the precipitate interface, and a mono-layer of Cu atoms (atomic radius 1.28Å) is deposited at a surface, the succeeding layer in the structure to form will comprise Al atoms (atomic radius 1.43Å).

This situation is depicted in Figure 5. In order to nucleate σ at this site, it is proposed that two of the relatively large Mg atoms (atomic radius 1.6 Å) that are already available at the Ω surface, will substitute for two of the Al atoms in this layer. The result of such a modification will be to displace the other central Al atoms outwards from their normal positions. Any Ag (atomic radius 1.44 Å) that is present may substitute for the displaced Al atoms in this layer. Deposition of the relatively small copper atoms may then occur at a rate controlled by interfacial surface diffusion which will allow the tetrahedral structure of Cu atoms (present in the σ phase) to form across the interface so that the crystal structure of σ will be developed as proposed by Samson [8].

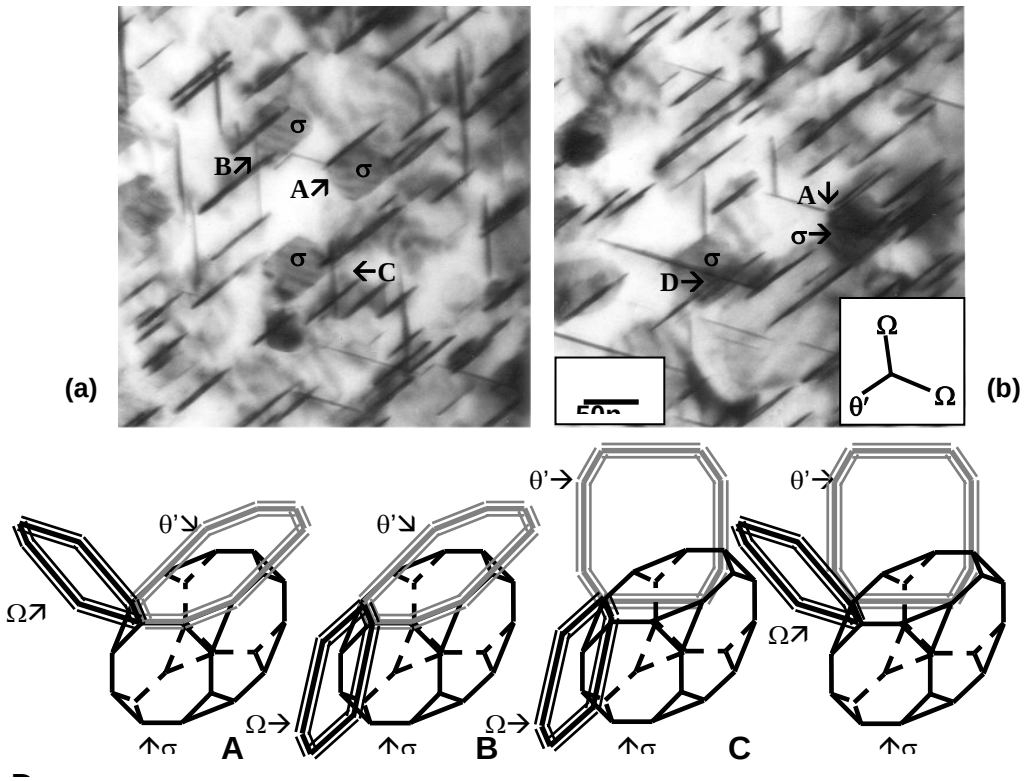

Figure 4: Observed relationship between the σ, Ω and θ' phases, as viewed from a [101]α orientation. (a)& (b) show examples of the 4 relationships. A,B,C&D show the equivalent 3 dimensional representations noted in (a) and (b). The Ω and θ' plates either lie parallel or normal to the equivalent faces of the σ particle.

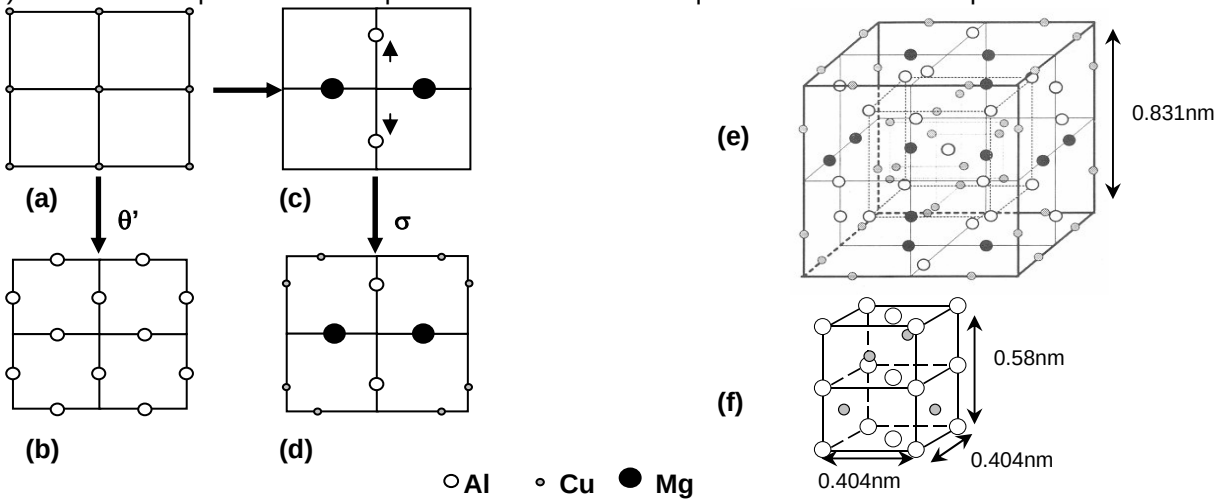

Figure 5: Proposed mechanism of σ formation by interface controlled diffusion. σ grows when 2 Mg atoms and 2 Al atoms (or Ag atoms) attach to the (mono-layer of Cu atoms) at the interface of θ' instead of 4 Al atoms. The progression (a) to (b) shows a simplified model of the proposed continued formation of θ' by diffusion of atoms along the precipitate surface, as viewed from the [001] direction. The progression (a) to (c) to (d) shows a simplified model of the proposed substitution of two Mg atoms (c) that may facilitate the formation of the first layer of the [001] face of σ (d), which will then provide the basis for further growth of the σ phase. The presence of the larger Mg atoms forces the Al into modified locations, and the σ phase may form. To further grow the σ phase, Cu is consumed from the Ω and θ'. For comparison, (e) and (f) show the unit cell for each of the σ [22] and θ' phases respectively.

4. Conclusions

1. The Ω and θ' precipitates that were present in the microstructure of the unloaded UA alloy coarsened during prolonged exposure at 130°C. The amount of Ω decreased whereas the density of θ' increased. In addition, continued formation of σ cuboids occurred throughout the matrix.
2. σ cuboids are known to have truncated corners which have {111} orientations. During prolonged exposure at 130°C of the Al-Cu-Mg-Ag alloy, it is proposed that σ nucleates at the sites where Ω and θ' precipitates intersect.
3. Mechanistically, it is proposed that the essential condition required for σ to form is the substitution of two Mg atoms to sites in the θ' lattice that would normally be occupied by two Al atoms.
4. Although Ag has indirectly facilitated nucleation of σ, it is clear that this phase can form in an Al-Cu-Mg-Ag alloy without the presence of a critical amount of Si.

5. Acknowledgements

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