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Influence of heat-treatment and solute content on repeated precipitation at dislocations in Al-Cu alloys

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The influence of heat-treating parameters and Cu content on repeated precipitation of the θ' phase which occurs at climbing dislocations during quenching dilute Al–Cu alloys has been studied by transmission electron microscopy. In Al–3.85 wt % Cu the process occurs during quenching from all temperatures within the solid solution range to all temperatures in the range from room temperature to at least 300° C. It also occurs over a wide range of quench rates. Depending on the quench rate, it can occur at a variety of dislocation geometries, including climb sources, glide dislocations which climb off their slip planes, and collapsed vacancy loops. Quenching directly to the ageing temperature establishes the distribution of almost the entire volume fraction of θ' by repeated precipitation during the quench. This process does not occur in alloys with Cu content below 1.5 ± 0.5 wt %.

1. Introduction

It has been recognized since 1964 [1] that precipitates can be nucleated repeatedly at climbing dislocations. Recently [2] the authors described the repeated precipitation of the metastable θ' phase in Al–3.85 wt % Cu as it occurs during direct-quenching from the solid solution range to the ageing temperature. θ' colonies are generated at both dislocation climb sources and glide dislocations which climb off their slip planes. The dislocation climb sources operate to produce concentric, pure-edge dislocation loops on {1 1 0} habits with $a/2\langle 1\,1\,0\rangle$ Burgers vectors. Consequently, the θ' colonies nucleated at these climb sources are disc-shaped, being bounded by the outermost source loops. The glide dislocations are $a/2\langle 1\,1\,0\rangle$ type initially on {1 1 1} prior to climbing during quenching. These nucleate sheet-like colonies of θ' along their climb paths. When viewed in the electron microscope, such colonies are gnerally truncated by the foil surfaces. The mechanism for repeated precipitation of θ' differs from mechanisms proposed for the process in other alloy systems [1, 3]. For θ' there is no co-operative vacancy flux between growing precipitates and climbing dislocations. The latter climb during quenching by vacancy annihilation, the vacancies being supplied from the quenched-in supersaturation, while θ' forms by repeated heterogeneous nucleation at the dislocations as they climb through the lattice.

The present investigation was undertaken to determine the range of experimental heat-treating variables for which repeated precipitation of θ' will occur in dilute Al–Cu alloys. Investigated separately were the effects of: (1) isothermal ageing following direct-quenching; (2) solution treatment temperature; (3) temperature of the quenching medium (for direct-quenches), (4) quench rate; (5) solute concentration.

2. Experimental

The Al–Cu alloys were prepared by double-melting in an induction furnace, then alternately cold-rolled and annealed to reduce to 0.1 mm sheet. Fig. 1 shows the applicable portion of the Al–Cu

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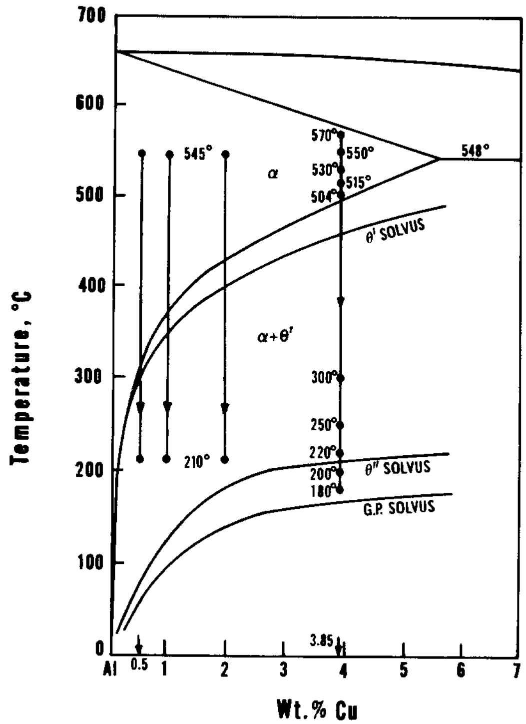


Figure 1 Aluminium-rich end of the Al–Cu phase diagram showing heat-treating temperatures for the various alloys.

phase diagram on which are plotted the metastable solvus lines for θ' and θ'' [4], and for GP zones [5]. Solution treatments were conducted for 1 h in a vertical furnace in air. All heat-treatments involved direct-quenches to the ageing temperature except those employed in investigating the effects of quenching rates. Direct-quenching was accomplished by dropping the sample into a constant temperature oil bath maintained at the ageing temperature. For investigating quenching rates (Section 3.4), samples were quenched into a container of a low temperature medium, then immediately up-quenched into the oil bath at the ageing temperature and appropriately aged. Finally, all samples were quenched from the ageing bath into water at room temperature. They were then electropolished in a solution of 5% perchloric acid in methyl alcohol at -50° C and examined in a Phillips EM 200 electron microscope at 100 kV.

For clarity, the temperatures and times employed in each experiment are given in each section of the Results with reference to the appropriate portion of Fig. 1.

3. Results and discussion

All experiments reported below were conducted on the 3.85 wt %Cu alloy except those where the influence of solute content was investigated (Section 3.5).

3.1. Isothermal ageing

Samples were solution treated at 550° C, quenched to 220° C (see Fig. 1) and aged for increasing times. The microstructures after ageing 8 sec, 5 min, 30 min, and 2 h, respectively, are shown at low magnification in Fig. 2. After ageing 8 sec, a random distribution of climb sources and glide dislocations are present. The precipitate colonies have already been nucleated by these dislocations during quenching but remain unresolved for short ageing times [2]. After ageing 5 min, sufficient growth has occurred so that the interiors of the colonies are seen to be densely precipitated. These precipitates were identified as θ' by electron diffraction. After 30 min at 220° C, the precipitates have grown further and have begun to coalesce, but precipitation is still localized within the boundaries of the original colonies. After 2 h at 220° C, some scattered precipitates are observed outside the colonies, but the vast majority are still associated with the original colonies.

Thus the precipitate density generated by repeated nucleation during quenching is sufficiently large that ageing for long times results almost entirely in precipitate growth alone. Since there was no evidence for bands of precipitates spreading out from the original colonies, the driving force for any autocatalytic nucleation mechanism [6] following direct-quenching must be small. Hence, the distribution of nearly the entire volume fraction of θ' is established by nucleation during the quenching step ($\leqslant 0.1$ sec).

3.2. Solution treatment temperature

Five samples were solution treated for 1 h at various temperatures over the solid solution range, then quenched to 220° C and aged for 5 min. These temperatures (570, 550, 530, 515 and 504° C) covered the range from just below the solidus temperature to just above the θ solvus temperature for the 3.85 wt %Cu alloy (Fig. 1). The major difference between samples was the quenched-in vacancy supersaturation, the magnitude of which is unknown in Al–Cu, but is estimated to vary by about a factor of 2.5 between 504 and 570° C (based on the equilibrium vacancy concentrations at these temperatures in pure aluminium [7, 8]). Selected microstructures for 570 and 504° C are shown in Fig. 3. The microstructure for quenching from 550° C was shown in Fig. 2b.

We conclude that repeated precipitation occurs during quenching from all temperatures in the solid solution range as indicated by the association of θ' colonies with all dislocations in every sample. Therefore, the process depends on the degree of vacancy supersaturation only insofar as it is sufficient for the dislocation climb during quenching to make repeated precipitation possible. Furthermore, both climb sources and glide dislocations which subsequently climbed were present in all samples, although their relative densities varied.

Two further observations were made about the influence of solution treatment temperature on the operation of climb sources in this alloy (which in turn influences the size and density of θ' precipitate colonies formed):

(1) The average diameter of the source loops increased with increasing solution treatment temperature. In samples quenched from the lowest temperatures (504, 515° C), the climb sources were small, with few exceptions. In the sample quenched from 570° C, both small and very large sources ($\simeq 5$ to 6 μm diameter) were observed, but the average size was the largest of all samples.

(2) The number density of active climb sources was lowest for quenching from 504° C, increased with solution treatment temperature to a maximum at 550° C, then decreased to an intermediate value at 570° C. Quantitative measurements of these densities were not made.

These observations may be explained plausibly as follows. The vacancy supersaturation increases exponentially with solution treatment temperature and thereby the average distance a source loop will climb increases proportionately. However, the source particle* solubility also increases with solution treatment temperature. The trade-off between increasing vacancy supersaturation and decreasing source particle density leads to the maximum active source density in the sample quenched from 550° C.

In the sample quenched from 570° C, repeated precipitation occurred only within a limited band (about $\frac{1}{2}$ to 1 μm wide) during the last stage of dislocation climb. (Note the climb sources in Fig. 3a produced several concentric loops tending to mask this effect.) Apparently appreciable dislocation climb occurred at temperatures above which θ' could not nucleate. The well-defined boundary where precipitation begins indicates that a θ' solvus temperature exists for precipitation during quenching and is an effective barrier to nucleation above it.

3.3. Temperature of the quenching medium

Five samples were solution treated at 550° C, quenched directly to various temperatures above the GP zone solvus, and aged. The temperature to which each sample was quenched shall be denoted T_a. The temperatures selected were (see Fig. 1): $T_a = 180°$ C, just above the GP solvus; 200 and 220° C, just below and above the θ'' solvus; and 250 and 300° C, increasing temperatures in the $\alpha + \theta'$ region. With decreasing T_a, the ageing time was increased so that the θ' colonies would be visible. Selected microstructures for $T_a = 300$, 250 and 180° C are shown in Fig. 4. (The microstructure for $T_a = 220°$ C appears in Fig. 2b.)

It was found that θ' precipitated repeatedly in all these samples, although only to a small degree in the sample quenched to 300° C (Fig. 4a). Furthermore, both glide dislocations which climbed and climb sources nucleated precipitates in all samples. The density of glide dislocations varied little from sample to sample but the density of climb sources varied greatly. Fig. 4 illustrates that decreasing T_a increased the number of active climb sources and decreased the averaged source loop diameter. The maximum active source density occurred at $T_a = 180°$ C and was about 6×10^6 per grain (grain diameter $\simeq 0.25$ mm). This trend may be explained by the time-at-temperature histories during the respective quenches, and hence by the respective vacancy diffusion distance. Decreasing T_a lowers the diffusion distance so that more sources must operate to reduce the excess vacancy concentration.

In the samples quenched to 200 and 180° C, θ'' did not form as predicted by Fig. 1. However, this is in agreement with observations that θ'' nucleates only on previously formed GP zones [6, 9].

3.4. Quenching rate

In general, direct-quenching into oil at elevated temperatures is a rather slow quench. To determine if repeated nucleation of θ' could be eliminated by faster quenches, the quenching medium

* Climb sources are thought to operate by vacancy condensation onto small, undissolved inclusions known as the source particles.

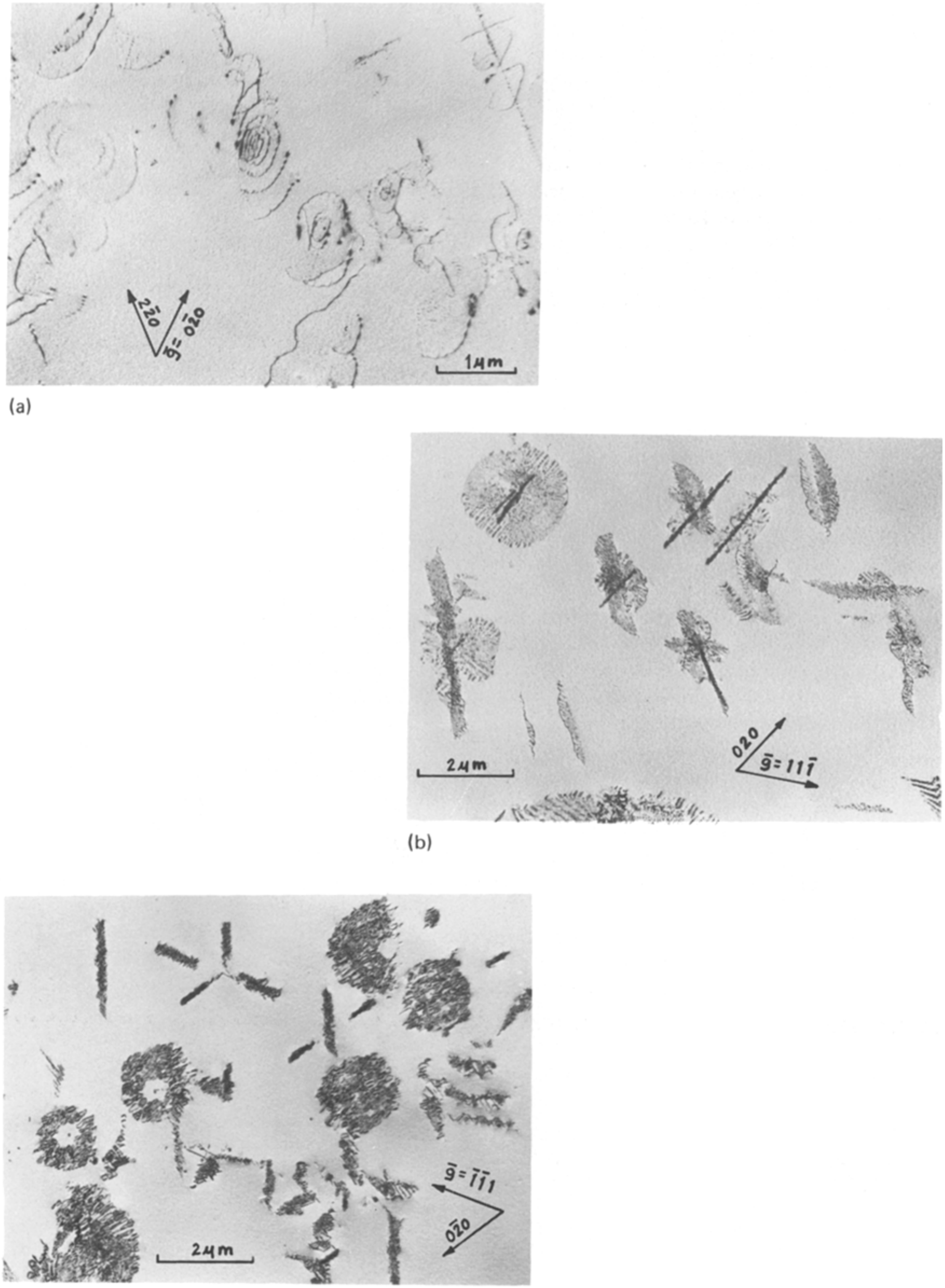
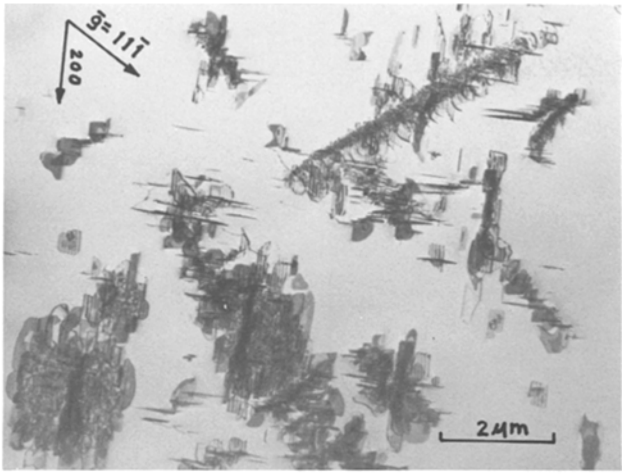


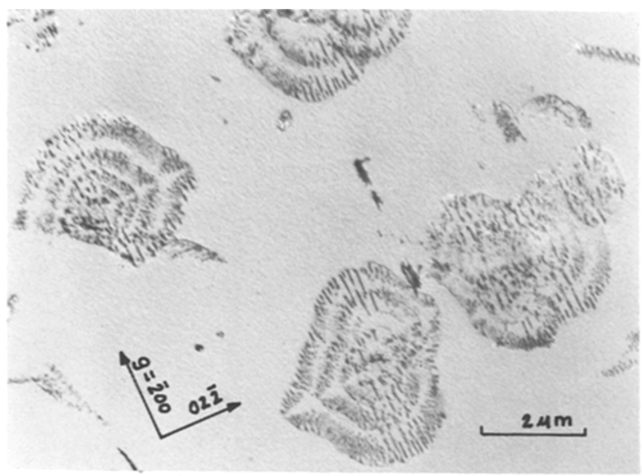
Figure 2 Illustrating the effect of isothermal ageing on θ' colony growth. Ageing time: (a) 8 sec, (b) 5 min, (c) 30 min, (d) 2 h.



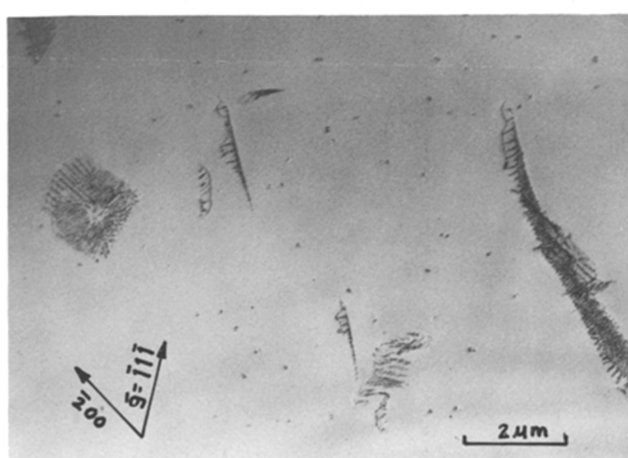
(d)

Figure 2 continued.

Figure 3 Illustrating the influence of solution treatment temperature on microstructure of the 3.85 wt %Cu alloy. (a) 570° C, (b) 504° C. Samples were direct-quenched to 220° C and aged 5 min.

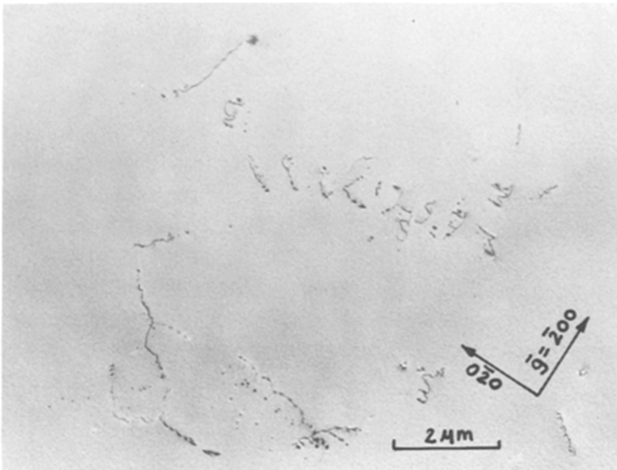


(a)

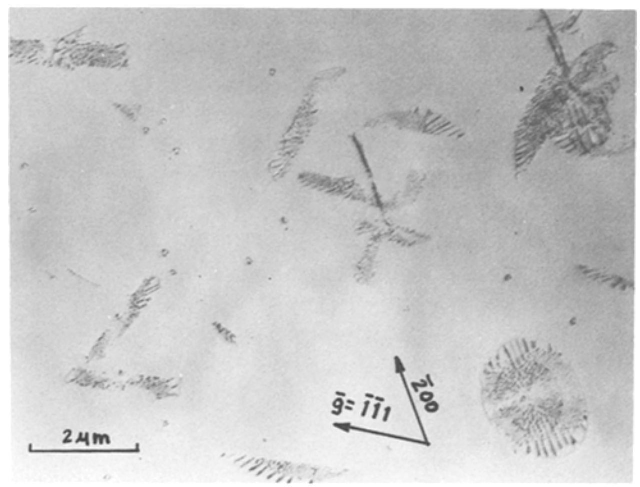


(b)

Figure 4 Illustrating the influence of T_a, the temperature to which samples were direct-quenched. T_a and ageing time: (a) 300° C, 15 sec, (b) 250° C, 1 min, (c) 180° C, 1 h.



(a)



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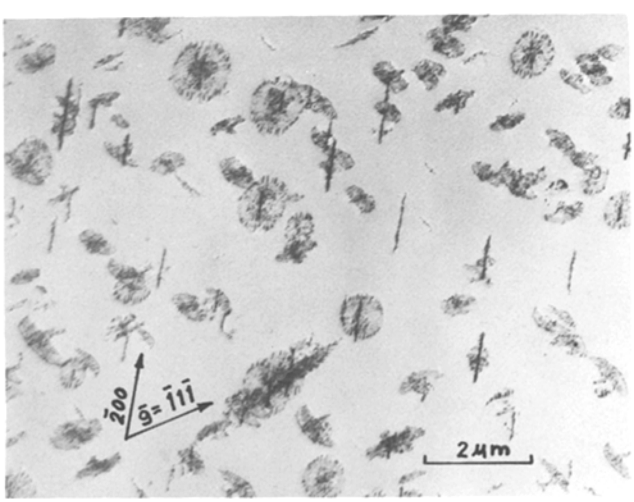

(c)

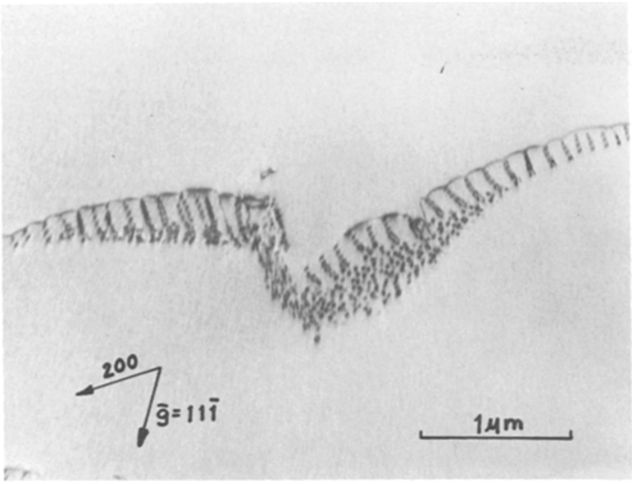

Figure 5 θ' colony in Al–3.85 wt % Cu air-quenched from 550° C, then up-quenched to 220° C and aged 5 min.

was varied as follows: (1) ambient air, (2) liquid nitrogen, (3) room-temperature oil, (4) room-temperature water. The quench rates were not measured but they should increase in the order given. After quenching from 550° C, all samples were up-quenched to 220° C and aged 5 min.

3.4.1. Air quench

Air quenching generated approximately the same density of glide dislocations as did direct-quenching into oil. These climbed during quenching and nucleated precipitate colonies (Fig. 5). Climb sources were observed only occasionally but they nucleated precipitate colonies within the same general appearance as those in direct-quenched specimens.

3.4.2. Liquid nitrogen quench

The microstructure of this sample was similar to that of the air-cooled sample. The density of glide dislocations which climbed and nucleated θ' colonies was approximately twice that of the air-cooled sample (attributed to somewhat higher quenching stresses). Both small and large climb sources were present and all sources nucleated precipitate colonies during quenching.

3.4.3. Room-temperature oil quench

The dislocation structure changed abruptly in going to a room-temperature oil quench. The resulting microstructure is full of small dislocation loops (Fig. 6). There were also isolated glide dislocations present which had climbed during quenching and had nucleated precipitate colonies. The density of small loops was reduced in the vicinity of the glide dislocations. Some climb sources were observed, but their density was much lower than in the samples quenched directly

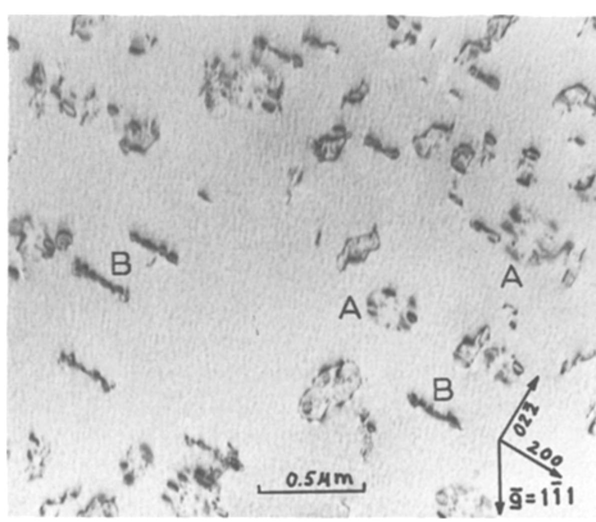

Figure 6 Microstructure of Al–3.85 wt % Cu quenched from 550° C into room-temperature oil, then up-quenched to 220° C and aged 5 min.

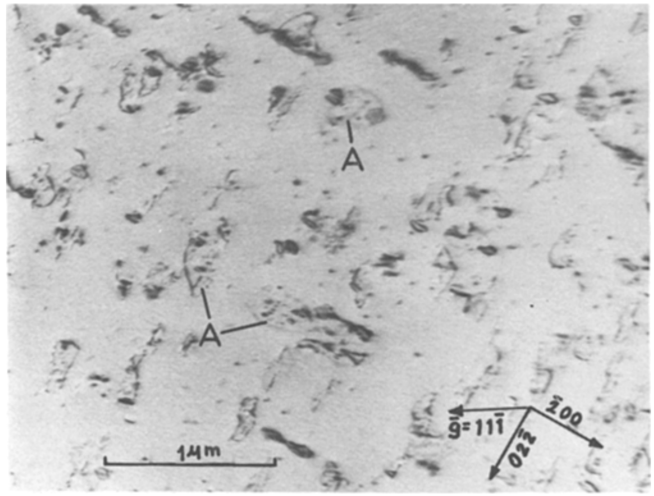

Figure 7 Microstructure of Al–3.85 wt % Cu quenched from 550° C into room-temperature water, then up-quenched to 220° C and aged 5 min. Loops around precipitate colonies marked A lie in the foil plane and are out of contrast.

into oil at the ageing temperature. The density of small loops was also low in the regions adjacent to climb sources.

As seen in Fig. 6, the interiors of the small loops are precipitated with θ' in much the same manner as the interior of the climb source loops shown in previous micrographs. The loops around precipitate colonies at points A are out of contrast.

The small loops lie on $\{1\,1\,0\}$ planes as illustrated by the edge-on habits at B. Their Burgers vectors were determined to be $a/2\langle 1\,1\,0\rangle$ normal to the loop planes. Thus, they are prismatic edge-loops. It is assumed that these loops were formed by collapse of vacancy clusters onto $\{1\,1\,0\}$ planes. Similar prismatic loops on $\{1\,1\,0\}$ have been observed in quenched Al–2.5 wt % Cu [10] and in quenched Al–Mg alloys [11]. Once the loops form, they grow during quenching from further vacancy condensation. In so doing, they nucleate the small precipitate colonies. In fact, apart from their origin and size, there is probably no difference between repeated precipitation of θ' during the growth of these small loops and during the growth of the large climb source loops.

The measured loop density was 2.2×10^{13} cm^{-3} and the average loop diameter was approximately 0.25 μm. Assuming the removal of two adjacent $\{1\,1\,0\}$ planes during climb [12], the vacancy concentration necessary to generate these loops was calculated to be 3×10^{-4}. This is almost identical with the equilibrium vacancy concentration in aluminium ($\sim 2.5 \times 10^{-4}$) at the 550° C solution treatment temperature [7, 8].

3.4.4. Room-temperature water quench

This sample also contained a high density of small loops (Fig. 7). The loops were very irregular and were seldom planar indicating appreciable climb or glide off their habit planes. Loops which were approximately planar were found to have $\{1\,1\,0\}$ habits with Burgers vectors $a/2\langle 1\,1\,0\rangle$ normal to their habit planes. Hence these are prismatic edge-loops as in the samples quenched into room-temperature oil. Upon close examination, colonies of small θ' precipitates can be detected within the loops, e.g. at points A, indicating that repeated nucleation occurred during the growth of these loops as well. Prolonged ageing of such a structure at temperatures within the $\alpha + \theta'$ field should create an approximately random distribution of large θ' platelets. Indeed such microstructures have been illustrated numerous times in studies of the θ' phase where samples were water-quenched and then aged for long times in the $\alpha + \theta'$ field. It has generally been assumed that the θ' nucleates during the ageing treatment. The present results would indicate that an appreciable fraction of these precipitates (if not all) nucleate during the quench.

Occasional glide dislocations were also observed which had climbed and nucleated precipitate colonies. Helical dislocations were observed in isolated areas of the foil.

3.5. Copper concentration

Samples with decreasing copper content were investigated to determine if solute concentration played an important role in the repeated precipi-

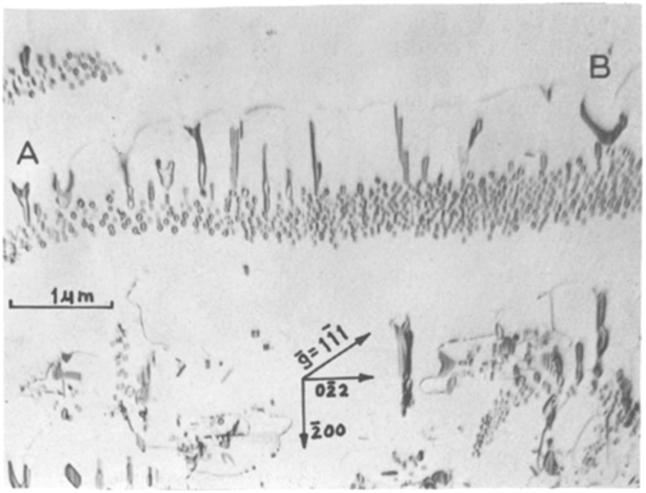

Figure 8 θ' colony nucleated by an initial glide dislocation (out of contrast between AB) in 1.96 wt % Cu alloy.

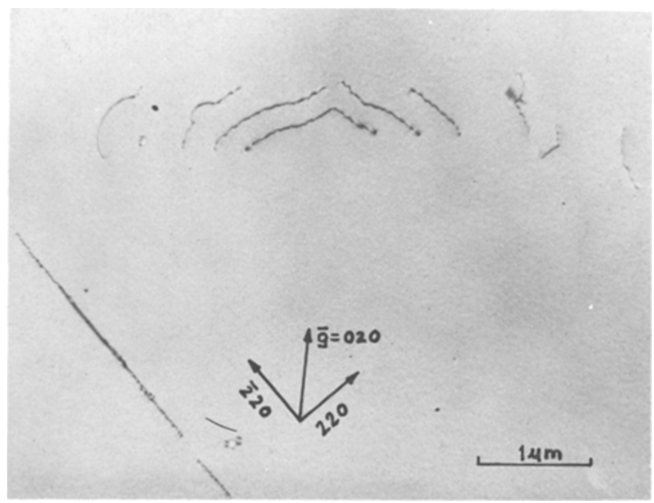

Figure 9 Illustrating the absence of θ' colonies at dislocation climb sources in 1.0 wt % Cu alloys aged 1 h after direct-quenching to 210° C.

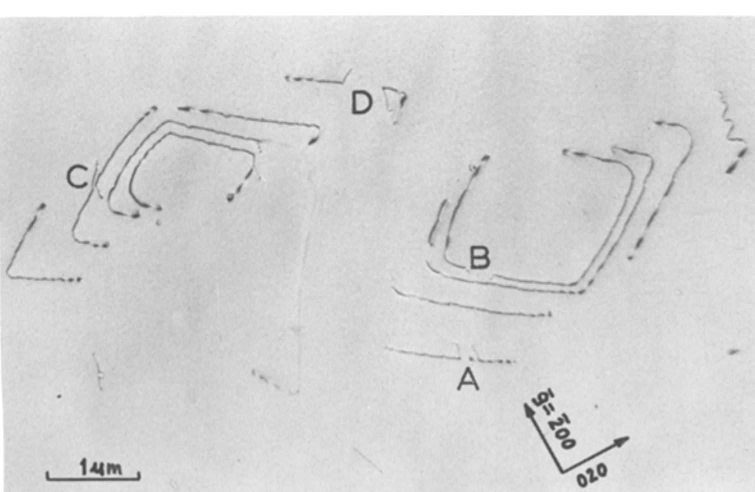

Figure 10 Rhombus-shaped dislocation climb sources in the 0.5 wt % Cu alloy aged 1 h after direct-quenching to 210° C. Note absence of θ' colonies.

tation of θ'. The alloys were nominally 1.96, 1.0, and 0.5 wt % Cu, respectively. The samples were solution treated at 545° C, direct-quenched to 210° C (see Fig. 1), and aged from 3 sec up to 24 h.

It was found that repeated precipitation of θ' occurred extensively in the 1.96 wt % alloy (Fig. 8), but not at all in the 1.0 and 0.5 wt % Cu alloys (Figs. 9 and 10), even though appreciable dislocations climb of both sources and glide dislocations occurred during quenching in all three alloys. Thus, the degree of copper supersaturation is vital to the repeated precipitation process, tending to suppress the mechanism altogether below some concentration between 1.96 and 1 wt % Cu.

Fig. 10 illustrates that climb source loops in the 0.5 wt % Cu alloy are rhombus-shaped. They were found to have the same geometry as climb sources observed in Al–Mg alloys [11]. Breaks in the loops at points A–D in Fig. 10 suggest that local dislocation segments had slipped off their climb plane.

4. Conclusions

(1) The range of repeated θ' precipitation over various heat-treatment variables is very large, and the mechanism is quite general in these alloys.

(2) Repeated θ' precipitation occurs on a variety of geometries of climbing dislocations, i.e. climb sources, initial glide dislocations, and small prismatic loops, all of which climb during quenching from the solid solution region.

(3) Repeated precipitation establishes the distribution of almost the entire volume fraction of θ' in direct-quenched Al–Cu alloys which are subsequently aged in the $\alpha + \theta'$ field.

(4) Repeated precipitation of θ' is suppressed in alloys with Cu content below some value between 1.96 and 1.0 wt %. Considerable supersaturation is thus an essential requirement.

(5) Conclusions 1 and 2 suggest that repeated precipitation might occur under specific heat-treating conditions in other aluminium alloys in which metastable precipitates nucleate at dislocations, but is as yet undiscovered.

Acknowledgements

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