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The effect of particle size and spacing on the retardation of recrystallization in two-phase copper crystals

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The effect of stable dispersion of Al_2O_3 in copper crystals upon recrystallization kinetics has been studied in three alloys, termed L1, L2 and H2, and in pure copper. L1 and L2 contained particles of similar size (0.028 μm), but of differing interparticle spacing, and L1 and H2 contained particles of similar spacing (0.05 μm) but of differing size. After a cold-rolling reduction of 50%, alloys L1 and L2 showed retarded recrystallization at 700° C compared with pure copper, there being greater retardation in L2, which had the smaller inter-particle spacing. Extensive recovery prior to recrystallization was observed and this led to deviations from the Avrami equation in describing the recrystallization kinetics. Calculations show that the retardation cannot be due to grain-boundary or sub-boundary pinning by the dispersed phase, and it is concluded that the effect is due to the homogenization of dislocation distribution by the particles suppressing nucleation. Alloy H2 contained larger particles (0.041 μm), and exhibited accelerated recrystallization compared with pure copper. This indicates that a very delicate balance must exist between the factors tending to retard and those tending to accelerate recrystallization in these materials. It is suggested that the acceleration arises from an increased misorientation developing within the transition bands.

1. Introduction

It has been well-established that a material containing a dispersed second phase may exhibit either acceleration or retardation of recrystallization compared with the dispersion-free material (e.g. [1–3]). In the case of accelerated recrystallization, the recent work of Humphreys [4] and Porter and Humphreys [5] has demonstrated that nucleation of recrystallization may occur in the vicinity of large second-phase particles (i.e. particles of the order of 1 μm diameter). It is clear that there is a critical partical size for this "particle-stimulated nucleation" (PSN), which is found to decrease as the deformation is increased, and the recrystallization process is associated with the large local lattice rotations observed in the vicinity of these large particles.

The present study is concerned with the effect of particles deliberately chosen to be much smaller than those required to produce PSN, and the work is an attempt to identify the factors leading to retardation of recrystallization. Its aim has been to separate the effects of inter-particle spacing and particle size in this context, and to explore whether recrystallization inhibition by the particles arises from a pinning effect upon grain boundaries or through tendency to homogenize the dislocation distribution [6].

In view of the long-term annealing necessary when recrystallization is retarded, it is important that a dispersed-phase of stable particle size is chosen. In the present work, dispersions of Al_2O_3 in copper single crystals provided by internal oxidation fulfil this requirement [7]. Single crystals were chosen so that discontinuous recrystallization at grain boundaries could not occur.

2. Experimental materials and methods

Two alloys of copper containing different amounts of aluminium were used: alloy 1, 0.10 wt% Al;

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alloy 2, 0.19 wt% Al. Both were in the form of single crystals (20 mm x 2.5 mm x 12 mm) grown by a modified Bridgeman technique. A series of crystals of pure copper were also prepared for comparison purposes.

The alloy crystals were internally oxidized throughout their thickness by the method due to Rhines *et al.* [8], one series (L1 and L2) being oxidized at 900° C and a second series (H2) were oxidized at 1000° C. In order to reduce the variation in particle size of the Al_2O_3 dispersions, the outer one third of the specimen thickness was removed by chemical polishing, so that the final thickness of each specimen was 1.70 mm.

2.1. Particle-size analysis

Al_2O_3 particles formed in copper by internal oxidation are in the form of crystalline plates lying on $\{111\}$ matrix planes with edges parallel to $\langle 110 \rangle$ matrix directions, with $(110)_{Cu}//(110)_{Al_2O_3}$ and $(111)_{Cu}//(111)_{Al_2O_3}$. The particle sizes were measured directly from extraction replicas observed in the transmission electron microscope, the largest particle dimension being measured from micrographs. The results are shown in the histograms of Fig. 1a to c. By plotting the cumulative frequency against the upper group limit of the largest particle dimension, using log-probability graph paper, the arithmetic mean of this value was obtained for each dispersion and the values are shown in Table I, together with the average aspect ratio of the Al_2O_3 plates, and the volume fraction, f, of the dispersion.

In order to define an average inter-particle spacing, it is first necessary to calculate an equivalent particle diameter, D_s. Although this has no physical meaning, D_s can be defined in terms of t, the plate thickness, and $\bar{x}_A$ arithmetic mean value of the largest particle dimension, as follows [9]:

$$D_s = \left(\frac{3.18\bar{x}_A t + 3\bar{x}_A^2}{4\pi}\right)^{1/2}.$$

Values of D_s for the three dispersions are also shown in Table I. The values of Δ_3, the nearest-neighbour inter-particle centre-to-centre spacing and of Z_3 the corresponding edge-to-edge nearest neighbour distances are also given in Table I, calculated according to Corti *et al.* [10]. It may be

TABLE I Dispersion parameters of the Al_2O_3 particles

Alloy	Largest particle dimension (μm)	Aspect ratio	D_s (μm)	Vol. fraction $\times 10^3$	Δ_3 (μm)	Z_3 (μm)
L1	0.055	2.2:1	0.028	4.25	0.077	0.049
L2	0.057	2.4:1	0.028	8.08	0.062	0.034
H2	0.087	3:1	0.041	8.08	0.091	0.050

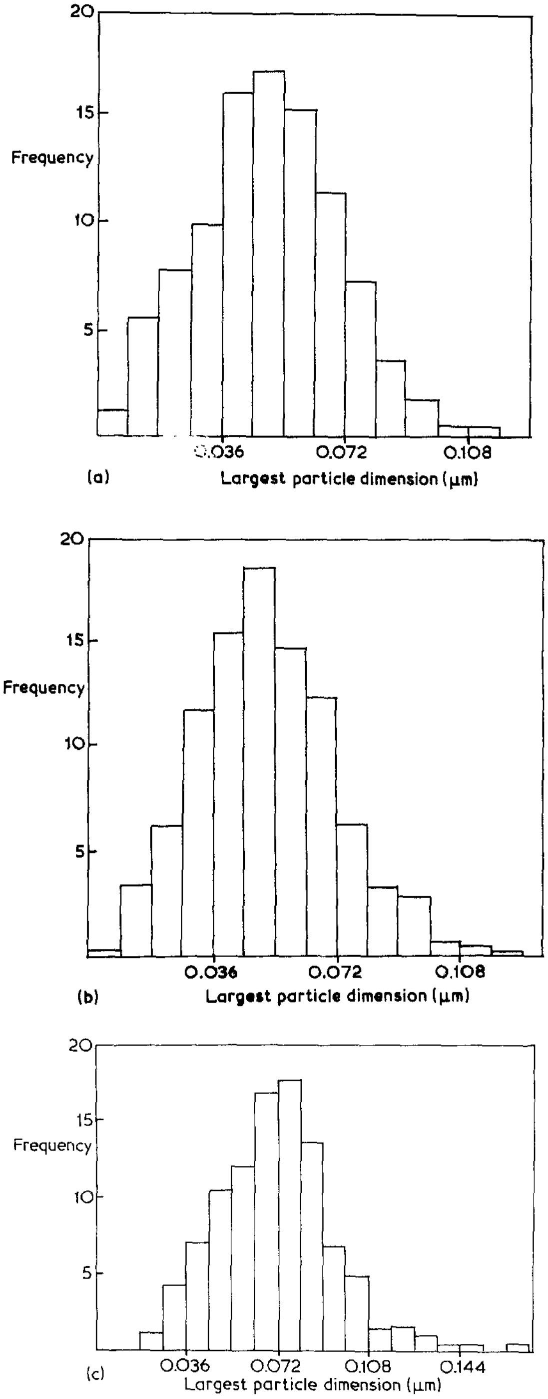

Figure 1 Particle-size distribution in alloys (a) L1, (b) L2 and (c) H2.

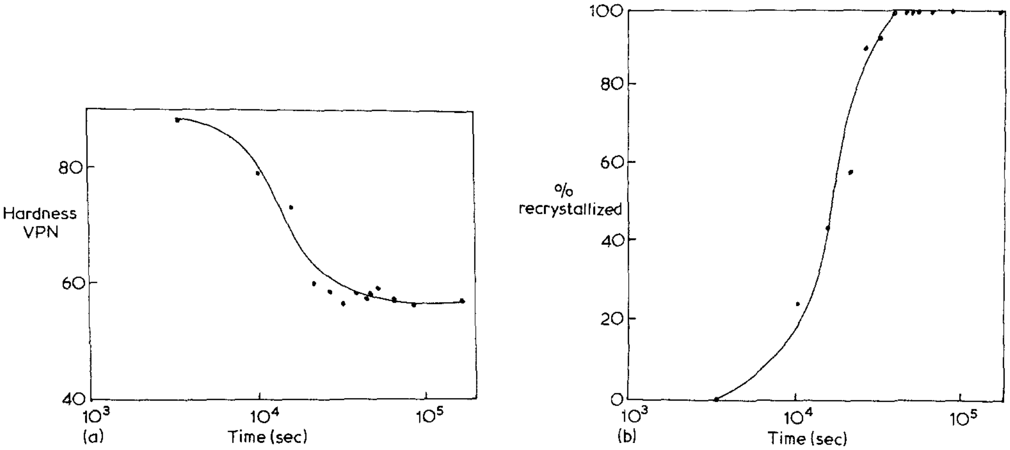

Figure 2 Recrystallization kinetics of alloy L1 at 700° C followed (a) by changes in hardness, and (b) by optical microscopy.

seen that the dispersions studied have been selected such that the value of D_S is the same in L1 and L2, and the values of Z_3 are closely similar in L1 and H2.

2.2. Recrystallization experiments

Crystals were deformed 50% by cold rolling, using a 2in. hand mill, and 10mm square specimens were cut from the material. Microstructures of high dislocation densities, of the order $10^{16}\,m^{-2}$ were observed by transmission electron microscopy of the specimens. After chemical removal of any spark-machining damage, specimens were annealed in a salt bath (for short annealing periods) or a resistance furnace (for long anneals). The progress of recrystallization was followed both by hardness measurements and by means of optical metallography.

3. Experimental results

A temperature of 700° C was selected for the recrystallization of material L1 and L2, both of which exhibited retarded recrystallization. Figs. 2 and 3 illustrate the recrystallization kinetics of these two materials as revealed by both hardness and optical metallographic measurements.

At 700° C material H2 was fully recrystallized in less than 2 sec, and the pure copper crystals were fully recrystallized in less than 3 sec. These times are obviously comparable with the heating-up time of the specimens in the salt bath, and so, in order to compare the recrystallization rates of H2 and pure copper an annealing temperature of 425° C was chosen. The results are shown in Fig. 4, where it may be seen that H2 exhibits accelerated recrystallization in comparison with pure copper. L1 and L2 obviously exhibit severly retarded recrystallization in comparison with pure copper, L2 showing greater retardation than L1. Fig. 5 shows the results as plots of $\ln(1-X_v)^{-1}$ versus ln (time), where X_v is the fraction recrystallized as identified metallographically. These relationships should be linear if the Avrami equation is obeyed, and this appears not to be the case with L2.

The grain size of the fully recrystallized alloys increased with increasing time of recrystallization. The final grain sizes of the retarded alloys were larger than those of the pure copper, whilst those of the accelerated alloy were smaller than those of pure copper. For the fast recrystallizing alloy, some specimens were annealed for 48h at 425° C to establish if secondary recrystallization would occur, but no such coarsening of the grain size was observed.

Transmission electron microscopy of thin foils prepared from the as-deformed and partially recrystallized materials was carried out. The as-deformed crystals exhibited a dislocation "cell" structure, which became smaller and less well-defined as the interparticle spacing decreased. Particles were seen usually to be situated in the cell walls. In partially recrystallized specimens of H2, which showed accelerated recrystallization, the dislocation density and configuration within the unrecrystallized regions appears to be little different from the as-deformed state. This was in contrast to the retarded alloys, L1 and L2, in which the dislocations were arranged in networks (Fig. 6).

Several completely recrystallized specimens

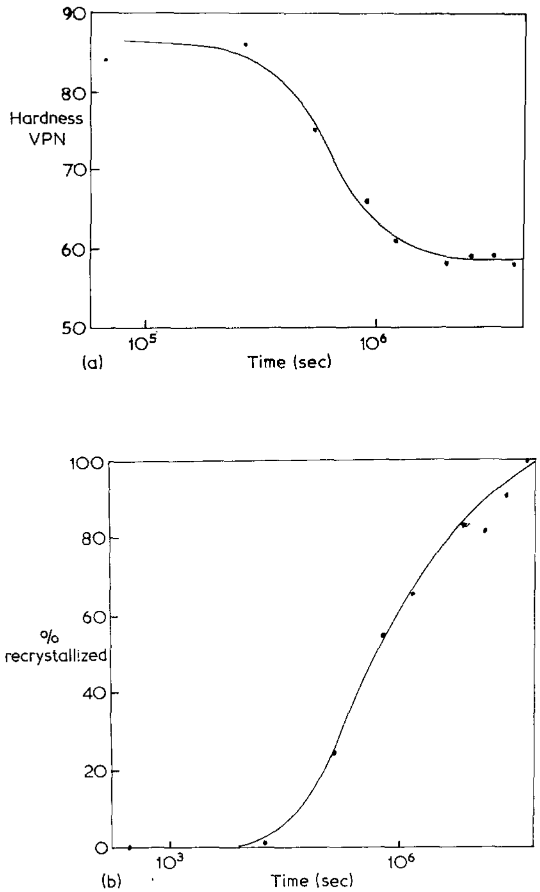

Figure 3 Recrystallization kinetics of alloy L2 at 700° copy.

were observed and compared with foil from specimens prior to any deformation. No rearrangement of particles could be detected.

4. Discussion

Alloys L1 and L2 have been shown to exhibit extensive recovery before the start of recrystallization, in contrast to the accelerated alloy, H2. This recovery is apparent not only metallographically (e.g. Fig. 6) but also from the large drop in hardness observed prior to the onset of recrystallization (c.f. Figs 2 and 3 with Fig. 4). This also accounts for the failure of L2 to obey an Avrami relationship (Fig. 5), since this assumes a constant driving force. It is seen that the rate at which the alloys recrystallized decreased with a decrease in interparticle spacing, which is in agreement with previous work [1, 2], and the question arises as to whether this can be ascribed to particle-pinning effects, or whether it is predominantly due to the particles having the effect of homogenizing the distribution of dislocations during the cold-working stage.

It is possible to estimate the pinning forces exerted by the dispersion on the grain boundaries and upon the sub-boundaries. The maximum pinning force per unit area of grain boundary is [11]

$$F^{\mathrm{gb}}_{\mathrm{max}} = 3f\sigma_{\mathrm{gb}}/D_{\mathrm{s}},$$

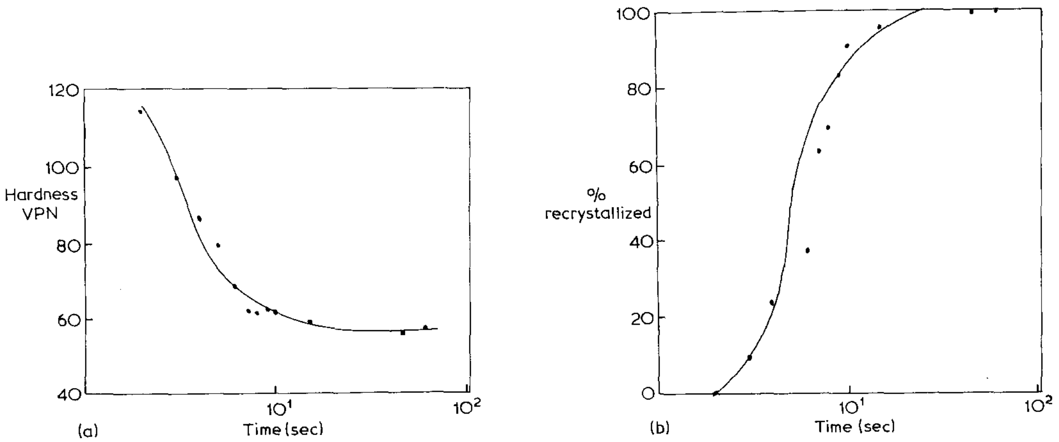

Figure 4 Recrystallization kinetics of alloy H2 at 425° C followed (a) by changes in hardness and (b) by optical microscopy.

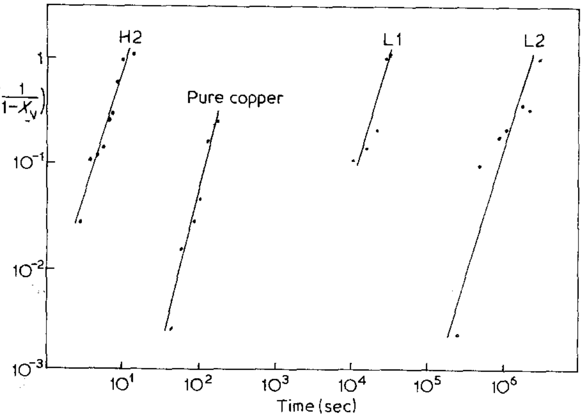

Figure 5 Fraction recrystallized (X_v) as a function of annealing time for the four materials plotted according to the Avrami relationship.

where σ_{gb} is the energy per unit area of a grain boundary. In the present alloys it may be shown that this force is of the order 10^5 Pa, which is clearly sufficient to inhibit secondary recrystallization, as is observed. Duggan and Hutchinson [12] have extended the above approach to obtain an estimate of the pinning force by particles upon sub-boundaries, giving

$$F^{sb}_{max} = 6f\sigma_{sb}/AD_s^2,$$

where A is the area of sub-boundary per unit volume, and σ_{sb} is the energy per unit area of a sub-boundary. Assuming the reasonable values of $0.1\,\mathrm{J\,m^{-2}}$ for σ_{sb}, and $6 \times 10^6\,\mathrm{m^{-1}}$ for A, a force of the order 1 MPa is obtained.

The driving force for primary recrystallization in these alloys, F_{rex}, may also be estimated readily, since the change in dislocation density upon recrystallization $\Delta\rho$ is of the order $10^{16}\,\mathrm{m^{-2}}$, and the driving force will be given approximately by

$$F_{rex} = \Delta\rho G b^2,$$

where G is the shear modulus of the matrix and b the Burgers vector. Substitution yields a value of 100 MPa for F_{rex}, so it is clear that the pinning forces upon both grain boundaries and dislocation sub-boundaries are negligible compared with the driving force for recrystallization, so that theories of particle pinning cannot be invoked to account for the retardation of recrystallization in alloys L1 and L2.

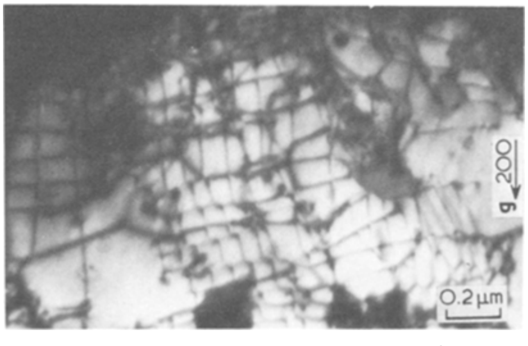

Figure 6 Alloy L2 annealed for 3 days at 700° C (corresponding to the 1% recrystallized condition), showing recovered dislocation distribution.

The alternative explanation of the retardation of recrystallization is therefore that the particles affect the state of deformation during cold work by causing homogenization of distribution of the dislocations. This effect has been reported by Humphreys and Martin [6] in deformed copper crystals containing SiO_2 particles: slip distances and the number of dislocations per slip line are smaller in two-phase alloys than in single-phase alloys for equivalent stresses, so the structure is less inhomogeneous in two-phase crystals, and lattice misorientations are lower. Such dislocation distributions have been shown to be inhertently stable and resistant to recrystallization.

It is concluded, therefore, that the retardation of recrystallization arises from this homogeneity of dislocation distribution favouring the process of recovery rather than recrystallization. The degree of homogenization will increase as the volume fraction of particles increases: L1 and L2 contain particles of similar size, but of about double the volume fraction in the latter material which has given rise to a further retardation of recrystallization.

In alloy H2 there appears to have been little recovery preceding recrystallization. The particle size, though larger than in L1 and L2, is apparently too small to give rise to the high local lattice rotations associated with particle-stimulated nucleation as defined by Humphreys [4]. It is very striking that the change in particle size on passing from

L1 to H2 (the particle spacing being closely similar) has caused an acceleration of recrystallization by a factor of about 10^4. Again, the change in particle distribution between L2 and H2 has changed to time of recrystallization by a factor of 10^5 at 700° C. These observations suggest that a very delicate balance must exist between the factors tending to retard and those tending to accelerate recrystallization. Although in H2 the larger particle size will give rise to an increased dislocation density on cold working, this effect cannot be significant, since there is very little difference in hardness between the various cold-rolled materials. The increased nucleation rate in H2 presumably arises from an increased misorientation within the transition bands; the increase in particle size has thus critically changed the inherently stable dislocation array present in L1 and L2. Further, and more detailed, work would be necessary to identify this transition in deformation behaviour.

5. Conclusions

(1) The two alloys showing retarded recrystallization, and containing particles of similar size showed increasing retardation as the inter-particle spacing decreased.

(2) Calculations suggest that the retardation cannot be due to grain-boundary or sub-boundary pinning by the dispersed phase, so it is concluded that the retardation is due to the homogenization of dislocation distribution by the particles.

(3) In the retarded alloy L2, a decrease in the driving force for recrystallization by extensive recovery during annealing leads to deviations from the Avrami equation in describing the recrystallization kinetics.

(4) An increase in particle size, for a given inter-particle spacing, can lead to a dramatic acceleration of recrystallization (alloy H2), although the size is too small to cause 'particle-stimulated nucleation' through local lattice rotation [4]. The effect may arise through an increased misorientation developing within the transition bands.

(5) The grain size of the fully recrystallized alloys increased with increasing time of recrystallization, so that the second phase appears to affect the nucleation of recrystallization more than the growth of these nuclei.

(6) Secondary recrystallization was inhibited in all the two-phase materials, and this may be ascribed to particle pinning effects.

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