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Grain growth in the two-phase Al–Cu alloys

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Grain and phase growth in the two-phase Al–Cu alloys containing 6, 11, 17, 24 and 33 wt% Cu were investigated by annealing at 535 °C for 0.5–100 h. The grain and phase sizes of the κ phase are seen to be larger than that of the θ phase. The size of κ phase decreases whereas the size of θ phase increases with increasing copper content in the alloy. As such, the κ phase- and grain-size distributions are broader than the θ phase- and grain-size distributions, but the size range depends on annealing time and alloy composition. The grain sizes of the κ, d_κ, and θ, d_θ, phases can be related to the volume fraction of the θ phase, f_θ, according to the equation $d_\kappa = 0.497\ d_\theta/f_\theta$.

1. Introduction

The grain size influences several mechanical properties. While smaller grains are recommended for better properties at low temperatures, coarse grains improve creep properties at elevated temperatures. It has also been established that superplasticity can be achieved if fine equiaxed grains of size $\leqslant 10$ μm can be produced in a material [1]. In view of the importance of grain size, grain growth has been extensively studied in pure metals and alloys. However, studies on grain growth in two-phase alloys, despite their wider uses, are rather indicative of a recent interest.

Grain growth in quasi-single-phase as well as two-phase systems is restricted by pinning the grain boundaries with fine particles and by having neighbouring grains of dissimilar phases, respectively. Unlike in pure metals, grain growth in two-phase systems requires diffusion of the specific type of atoms from one grain to another grain of the same phase, but through the surrounding phase of a different composition. During annealing, both the phases in the two-phase systems, or the particles as well as the matrix in the quasi-single-phase systems, undergo grain growth. According to theory [2], grain growth obeys the relationship $d \propto t^{0.25}$ in two-phase systems, whereas in the particle-containing systems, the matrix grows according to $d \propto t^{0.33}$, where d is the grain size at time t. However, the experimental results show some variations. In Ti–6Al–4V [3], α/β brass [4] and Ti–V [5] alloys, the values of time exponent, n, in the relation $d \propto t^n$, have been reported to be ≈ 0.25, whereas in the Al–Cu eutectic alloy [6] it was noted to be much smaller (≈ 0.1).

The aim of the present work is to investigate the grain- and phase-growth behaviour of the component phases in the Al–Cu alloys containing different proportions of the κ and θ phases. The Al–Cu system was selected because of its importance in precipitation strengthening in the lower copper-content alloys and its ability to exhibit superplasticity under the eutectic microduplex structural state. For both these properties, grain size plays vital roles.

2. Experimental procedure

2.1. Materials

Aluminium and copper of the compositions given in Table I were melted in air in an alumina crucible kept in a tubular furnace at 755 °C. First, a master alloy of 50 wt % Al and 50 wt % Cu was prepared. Then, this alloy was added, in appropriate quantity, into molten aluminium, melted as above, to prepare the Al–Cu alloys of five selected compositions. The melts were chill-cast in the form of slabs of size 80 mm × 40 mm × 20 mm in a mild steel mould. The chemical compositions of the alloys thus prepared are listed in Table II.

2.2. Mechanical working and annealing

As-cast slabs were homogenized at 520 °C for 48 h. They were then rolled unidirectionally at 520 °C to 1.8 mm thick sheets in several passes with intermittent soaking at the same temperature for 10 or 30 min. Small pieces were cut from the rolled sheets for annealing and metallography. In order to study grain growth, these pieces were annealed at 535 ± 2 °C for 0.5, 1, 4, 10, 24 and 100 h. Following the rolling and annealing for grain growth, the samples were quenched in water and stored in a refrigerator.

2.3. Metallography

Metallographic specimens were prepared by mechanical polishing finishing with diamond paste of size 0.25 μm. Etching was done with a modified Keller's

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TABLE I Chemical compositions (wt %) of commercial purity aluminium and copper used for making Al–Cu alloys

Material	Cu	Fe	Ni	Mn	Mg	Zn	Si	Al
Commercial Al	< 0.1	0.15	< 0.05	< 0.05	< 0.05	< 0.05	< 0.1	Bal.
Commercial Cu	Bal.	0.16	< 0.002	< 0.001	–	0.0011	0.006	< 0.5

TABLE II Chemical compositions (wt %) of the Al–Cu alloys

Alloy	Designation	Cu	Fe	Si	Zn	Ni	Mn	Mg	Pb	Al
1	Al–6Cu	5.6	0.13	0.05	0.01	< 0.002	0.002	0.004	< 0.005	Bal.
2	Al–11Cu	11.0	0.12	0.05	0.006	< 0.002	0.002	0.0023	< 0.005	Bal.
3	Al–17Cu	17.03	0.11	0.052	0.006	< 0.002	0.0011	0.0033	< 0.005	Bal.
4	Al–24Cu	24.38	0.29	0.05	0.023	< 0.002	0.006	0.003	< 0.005	Bal.
5	Al–33Cu	33.39	0.09	0.048	0.006	< 0.002	0.0018	0.0024	< 0.005	Bal.

reagent composed of 20 ml HF, 30 ml HCl, 50 ml HNO_3 and 190 ml H_2O. The aluminium-rich phase, κ, appeared bright, whereas the θ-phase appeared dark. With this etchant, κ/κ and θ/θ grain boundaries could be revealed.

The volume fractions of the κ and θ phases in the specimens were measured by the point-counting method. The sizes of individual grains and phases were measured directly from the specimens with the help of a graduated and calibrated eye piece mounted in an optical microscope. More than 300 grains were considered for each average grain-size data reported here. The grain sizes of κ and θ phases are denoted d_κ and d_θ, whereas the phase sizes are denoted P_κ and P_θ, respectively. The errors in the grain-size values were within ± 10% at a confidence limit of 95%. In the as-rolled state, the grains were observed to be equiaxed on three mutually perpendicular sections of a sample. Therefore, detailed microstructural observations were made on only one section (longitudinal) of each specimen.

3. Results

With increasing copper content in the Al–Cu alloys the proportion of θ phase is seen to increase, Table III. The volume fractions of κ and θ phases, determined from the phase diagram of the Al–Cu system [7], at an annealing temperature of 535 °C and at room temperature, are also given in this table. The proportion of θ phase is higher at room temperature.

The Al–Cu alloys of different compositions were annealed at 535 °C to follow the grain and phase growth in the κ and θ phases as a function of time; the results are presented below.

3.1. Variation in mean grain and phase sizes

With an increase in annealing time, grain growth occurred in both the κ and θ phases. Fig. 1 shows the microstructures of all five alloys after annealing for 0.5 and 100 h. The θ phase is seen to be dispersed in a globular form, even after the long annealing time.

The grain and phase sizes of both the κ and θ phases increase with time to varying extents, depending on composition, Fig. 2. Because more than one grain was often present within any phase, the phase size is noted to be greater than the grain size. In the Al–6Cu, Al–11Cu and Al–17Cu alloys, the κ-phase and grain sizes are seen to be much larger than the θ-phase and grain sizes. In addition, the rates of grain and phase growth in the former phase are noted to be higher. However, the difference between the sizes of the two phases becomes narrower with increasing copper content, approaching comparable sizes in Al–33Cu alloy.

On examining the effect of composition on the sizes of κ and θ grains and phases, it is seen that while the grain and phase sizes of κ phase decrease with increasing copper content, the grain and phase sizes of θ phase increase. This is illustrated by replotting the variation in the κ- and θ-phase sizes as a function of time for alloys of the five compositions shown in Fig. 3.

TABLE III Volume fractions (%) of κ and θ phases in the Al–Cu alloys of different compositions

Source	Al–6Cu		Al–11Cu		Al–17Cu		Al–24Cu		Al–33Cu	
	κ	θ	κ	θ	κ	θ	κ	θ	κ	θ
Experiment (RT)	93.3	6.7	77.8	22.2	68.1	31.9	56.1	43.9	48.1	51.9
Phase diagram (535 °C)	99.5	0.5	87.8	12.2	75.7	24.3	60.5	39.5	41.9	58.1
Phase diagram (RT)	90.4	9.6	82.3	17.7	69.2	30.8	55.5	44.5	38.5	61.5

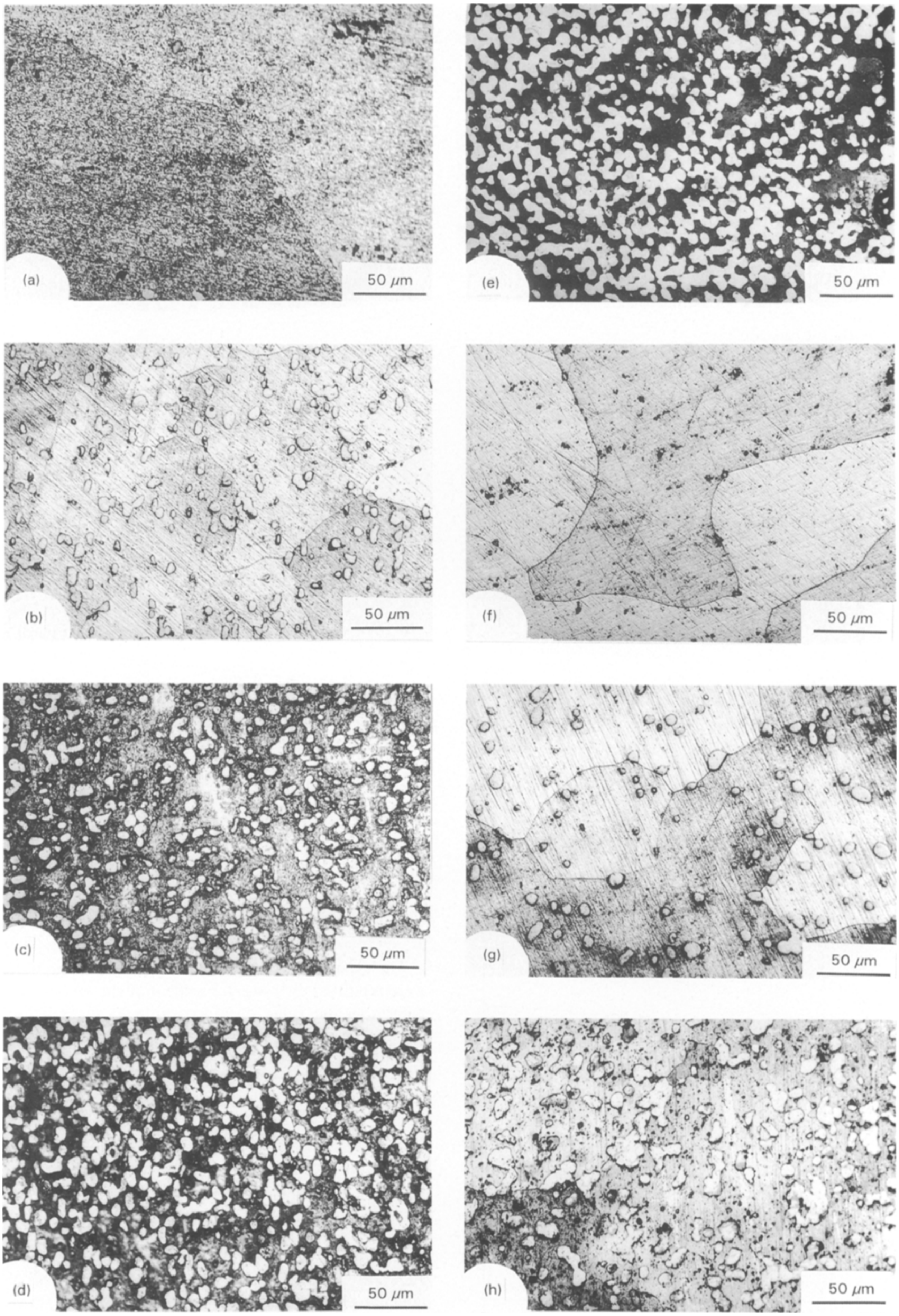


Figure 1 Microstructure of the Al–Cu alloys of various compositions upon annealing for (a–e) 0.5 h and (f–j) 100 h: (a, f) Al–6Cu; (b, g) Al–11Cu; (c, h) Al–17Cu; (d, i) Al–24Cu; (e, j) Al–33Cu. Volume fraction and size of θ phase increase with copper content. The grain sizes are larger upon 100 h annealing.

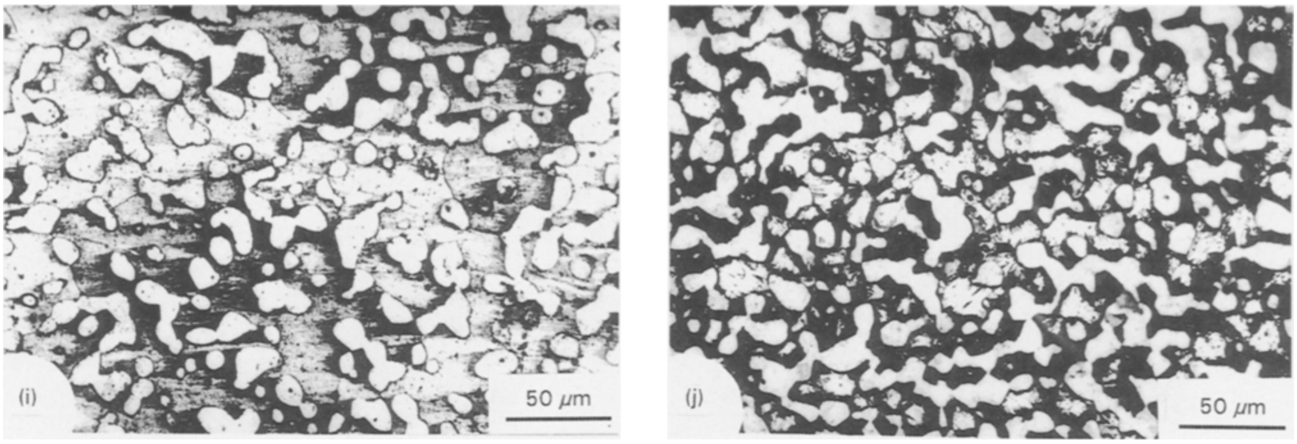
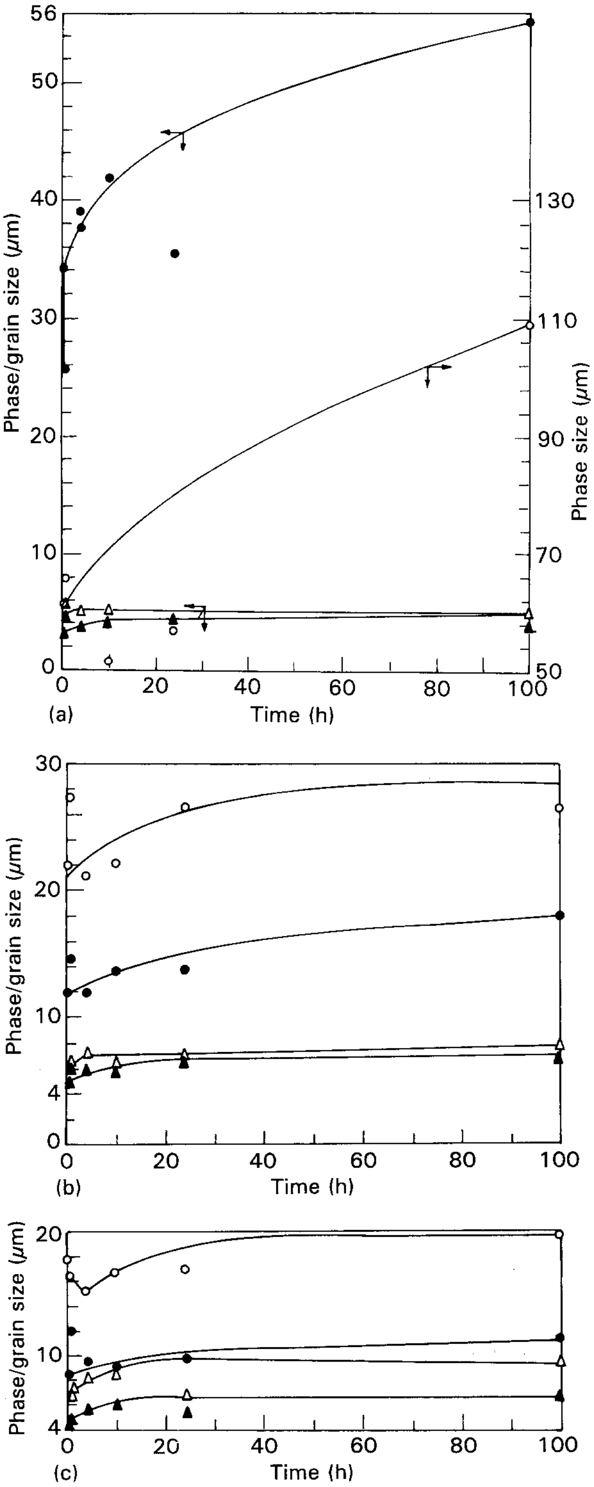


Figure 1 (Continued)



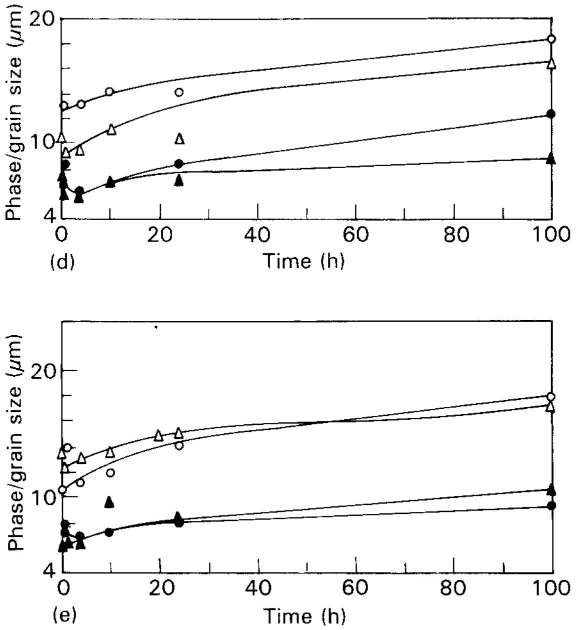


Figure 2 Variation in the (●, ▲) grain and (○, △) phase sizes of (○, ●) κ and (△, ▲) θ phases as a function of annealing time: (a) Al–6Cu, (b) Al–11Cu, (c) Al–17Cu, (d) Al–24Cu, and (e) Al–33Cu alloys.

The grain-size data as a function of annealing time were replotted on a log–log scale (not shown here) to determine the value of n according to the relation $d \propto t^n$. The values of n for the grains of κ and θ phases, obtained from the regression analysis, are listed for different alloys in Table IV.

3.2. Relation between κ- and θ-grain sizes

As described above, both the κ- and θ-grain sizes increase with time. Fig. 4 shows the effect of the proportion of θ phase on the ratio d_κ/d_θ on a log–log scale. With increasing volume fraction of θ phase, f_θ, the ratio d_κ/d_θ decreases through an increase in d_θ and a decrease in d_κ. The trend is seen to be independent of annealing time. The relation between d_κ, d_θ and f_θ can be expressed by

$$d_\kappa = C \frac{d_\theta}{f_\theta^m} \qquad (1)$$

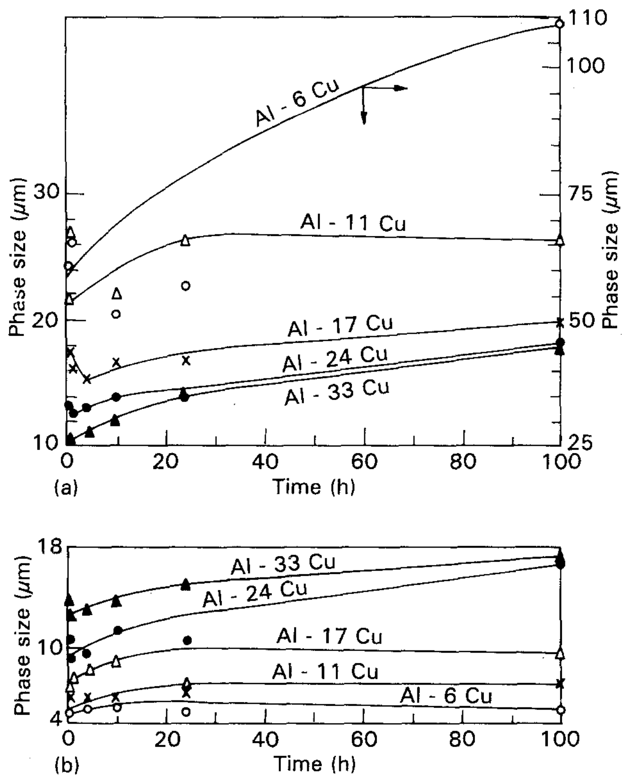


Figure 3 Effect of copper content on the growth behaviour of (a) κ and (b) θ phases. Whereas the κ-phase size decreases, the θ-phase size increases with increasing copper content.

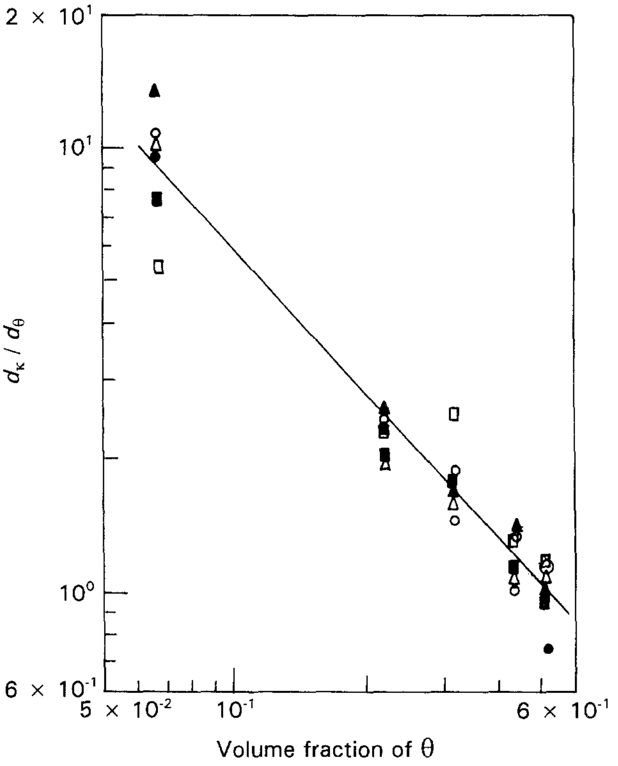


Figure 4 Log–Log plot of d_κ/d_θ versus f_θ, where d_κ is the grain size of κ phase, d_θ the grain size of θ phase, and f_θ the volume fraction of θ phase. T = 535 °C. d_κ/d_θ decreases with increasing f_θ. t(h): (○) 0.5, (□) 1.0, (△) 4.0, (●) 10.0, (■) 24.0, (▲) 100.0.

TABLE IV Values of time exponent n according to the relation $d \propto t^n$ for κ and θ grains in different alloys

Phase	Al–6Cu	Al–11Cu	Al–17Cu	Al–24Cu	Al–33Cu
κ	0.10	0.01	0.02	0.07	0.08
θ	0.01	0.06	0.10	0.05	0.09

The values of C and m for different annealing times, as obtained from the regression analysis of the data points in Fig. 4, are given in Table V. The regression coefficients, r^2, were generally 0.99.

By considering the average value of d_κ/d_θ for various annealing times for each alloy composition, the values of C and m were estimated to be 0.497 and 1.08, respectively. These values represent the line drawn in Fig. 4.

3.3. Grain-size distribution

Histograms showing the per cent frequency (number of grains) as a function of d_κ, d_θ, P_κ and P_θ were obtained for all the specimens from the individually measured values. As illustrated for the Al–24Cu alloy, Fig. 5, the grain sizes of both the κ and θ phases have a higher frequency in the smaller size range. The phase sizes exhibit broader distributions than those of the grain sizes. With increasing annealing time, phase and grain coarsening occur, but the phase-size distribution remains broader than the grain-size distribution, Fig. 5b. Comparison of the histograms for κ and θ phases, in general, suggests that the κ phase-size distribution is wider than the θ phase-size distribution. Also, the θ phase has a higher frequency in the smaller grain-size range than that of the κ phase for the various annealing times, Fig. 5, and compositions, Fig. 6. Towards the larger grain-size range, on the other hand, κ phase shows a higher frequency.

With increasing copper content in the alloy, the distribution of κ phase size becomes narrower with a simultaneous increase in the frequency of the smaller size range. This is illustrated in Fig. 6a by the histograms for alloys of different compositions upon annealing for 24 h. The reverse is true when the θ-phase size is considered, Fig. 6b.

4. Discussion

In the Al–Cu alloys with different amounts of copper, both the κ and θ phases and grains coarsen with time at 535 °C . However, at room temperature, at which the grain sizes were measured, the equilibrium proportion of θ phase is more than that at the annealing temperature, Table III. Therefore, some precipitation of θ phase, probably may occur at room temperature during the time elapsed in specimen preparation for metallography and grain-size measurement. Thus, one may expect that the θ grain/phase size may be different from that produced at the annealing temperature. However, by following the same region of a well-annealed metallographic specimen of the Al–Cu eutectic alloy, it was noted [8] that the grain-boundary positions remained unaltered on subsequent annealing/ageing. Therefore, the grain-size data at room

TABLE V Values of C and m in Equation 1 for different annealing times

Parameter	Annealing time (h)					
	0.5	1.0	4.0	10.0	24.0	100.0
C	0.526	0.825	0.437	0.350	0.512	0.449
m	1.10 ± 0.05	0.72 ± 0.12	1.13 ± 0.09	1.24 ± 0.03	1.00 ± 0.07	1.24 ± 0.08

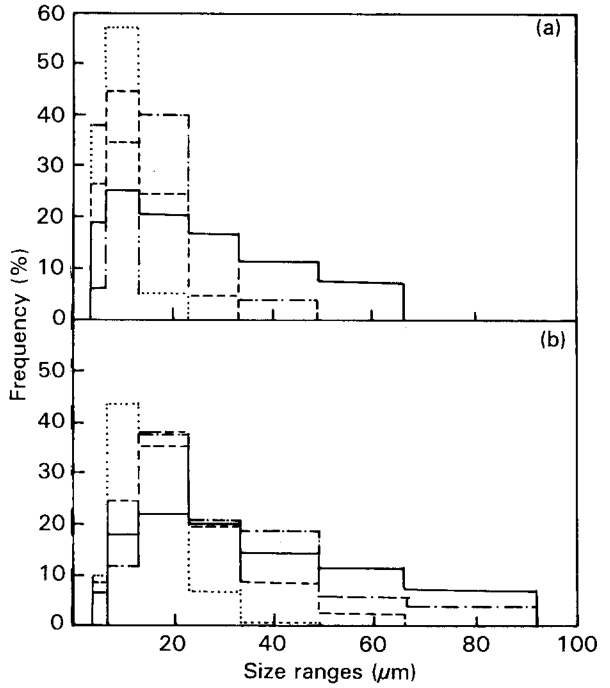


Figure 5 Histograms showing the distribution of the sizes of κ and θ phases and grains in the Al–24Cu alloy upon annealing for (a) 0.5 h and (b) 100 h. (–·–) θ phase, (···) θ grain, (——) κ phase, (– – –) κ grain.

temperature in the present study are considered to represent a stable structure developed at 535 °C.

For pure metals, the instantaneous grain size, d, is suggested [9] to increase with time according to the relationship

$$d^2 - d_0^2 = Kt \qquad (2)$$

where d_0 is the initial grain size at $t = 0$ and K is a constant. For the negligibly small initial grain size, Equation 2 may be written as $d = Kt^{1/2}$ where 1/2 is the value of the time exponent, n. Experimental values of n are, however, seen to be much smaller [10]. For a zone-refined aluminium, n has been reported to be 0.25.

The grain size in the particle-containing systems varies with time according to the relation $d \propto t^{1/3}$ [2]. In the present study, the alloys containing less copper may be considered to represent such a system. The values of n for the growth of both κ and θ phases are seen to be much smaller (0.01–0.10) than the expected value of 0.33. The observed values are also much smaller than $n = 0.25$, suggested [2] for grain growth in the duplex structure; although the Al–24Cu and Al–33Cu alloys represent such structure. The very sluggish grain growth in the Al–Cu alloys may be ascribed to the inherently lower value of n in pure aluminium. In addition, grain-boundary migration may be retarded by the dragging effect [11] of solutes and other impurity elements in the alloys.

According to the Cahn [12] and Lücke–Stüwe [13] theories of solute drag effect on grain-boundary migration, a partition coefficient of less than 1, as in the Al–Cu alloys of the present composition range (hypo-eutectic), creates a trailing atmosphere of solute. As

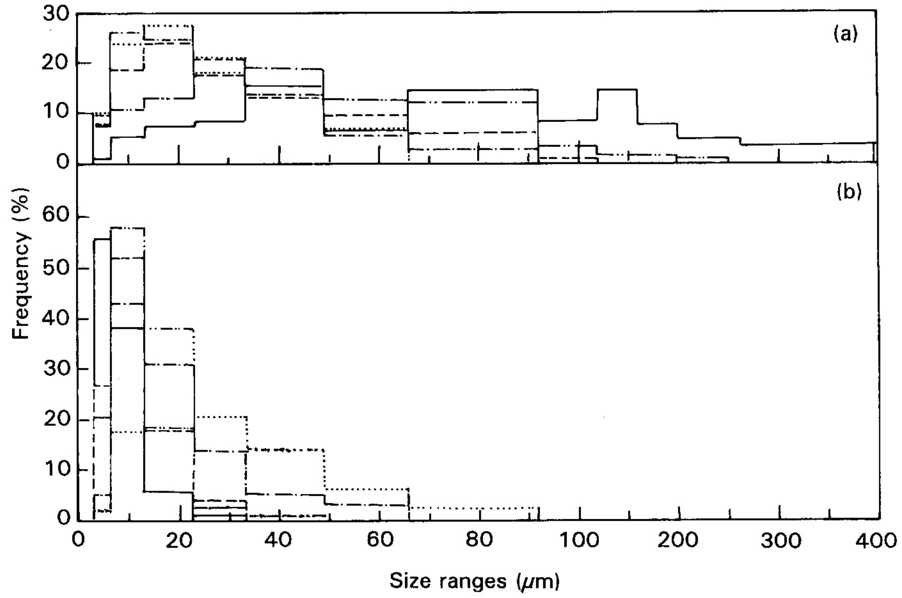


Figure 6 Histograms showing the distribution of (a) κ-phase size and (b) θ-phase size in Al–Cu alloys of different compositions after annealing for 24 h at 535 °C. (···) Al–33Cu, (—·—) Al–24Cu, (– – –) Al–17Cu, (—··—) Al–11Cu, (——) Al–6Cu.

the grain-boundary migration rate is observed to be low (i.e. sluggish grain growth), the slowly diffusing solutes may exert a greater drag on the grain boundary. The activation energies for diffusion of impurities such as copper, magnesium, zinc, silicon, nickel and lead in aluminium are less than or equal to that for self diffusion of aluminium (142 kJ mol^{-1}) [14] , in which case, these impurities might not exert much drag on the grain boundary. However, an impurity such as iron has a much higher activation energy for diffusion in Al (192–258 kJ mol^{-1}) [14] which may contribute to the retardation of grain growth. Under such conditions, the value of n may become much smaller, suggesting a deviation from normal grain growth.

In the lower copper-content alloys, the κ-phase and grain sizes are much larger than the θ-phase and grain sizes, Fig. 2a and b. This may be due to the smaller volume fractions of θ phase seen as dispersoids. The growth of θ phase may be limited during annealing by the larger interparticle spacing, whereas κ phase may grow more due to the lower pinning provided by these θ particles. As the volume fraction and size of θ phase increase with increasing copper content, a larger proportion of κ phase boundaries comes into contact with the θ phase. This may restrict the growth of κ phase due to the greater number of κ–θ phase neighbours. Thus, the decrease in κ-phase size, Fig. 3a, and increase in θ-phase size, Fig. 3b, with increasing copper content in the Al–Cu alloys can be understood. Consequently, a decrease in d_κ/d_θ with increasing volume fraction of the θ phase, Fig. 4, should be expected.

A theoretical study of the retardation of grain growth by the second-phase particles was made for the first time by Zener [15]. He gave the retarding force as

$$P = 3/4 f\frac{\gamma}{r} \tag{3}$$

under the assumption that the particles are uniformly distributed and the grain boundary moves in a rigid way without changing its shape. Here P is the retardation pressure, f the volume fraction of second-phase pinning particles, γ the grain-boundary interfacial energy, and r the mean radius of the second-phase pinning particles. Subsequently, several refinements of this theory were made [16–19] but they all give the values of the retardation pressure closer to Zener's original estimate. According to the various models [15, 20, 21] for inhibition of grain growth by second-phase particles, relations similar to Equation 1 were proposed. The predicted values of C and m, according to Smith and Zener [15], are 0.67 and 1, respectively. These are supported by the present experimental values. Hillert [21] has recently refined the Smith and Zener model and he obtained $C = 0.44$ and $m = 0.93$, which are not very different from the original values. However, Hillert proposed the values of C and m to be 3.6 and 0.33, respectively, when the volume fraction of second-phase particles exceeds 0.1. In the present investigation, except for the Al–6Cu alloy, $f > 0.1$ but the values of C and m are in variance with these predicted values. Instead, they are comparable to that predicted by the Smith and Zener model.

During grain growth, the coarser grains increase in size at the expense of smaller grains. By following the growth of individual θ precipitates in an Al–Cu alloy at 469 °C, Brown [22] noted that only the largest 8% precipitates increased in size whereas all other precipitates shrank on ageing. This may then result in the broadening of the grain-size range and a shift in the mean grain size towards a larger value with an increase in annealing time, Fig. 5. The distribution of κ-phase size is seen to be broader than that of the θ-phase size, Fig. 6. Also, the κ-size range decreases with increase in copper content. This effect may be ascribed to the increasingly greater deviation from the single-phase nature of the κ phase towards particle-containing or duplex-type structures with increasing proportion of θ phase. The increase in the θ-phase size range with increasing copper content in the alloys can also be ascribed to the increasing amount of θ phase available for its growth. The increased frequency of θ phase in the lower size range is suggested to be the result of its lower volume fraction and a longer interparticle diffusion path for grain growth.

Thus, grain and phase growth in the two-phase alloys depend on the volume fractions and relative sizes of the constituent phases. The grain- and phase-size distributions extend over broader size ranges for that phase which has a larger volume fraction; they also decrease with an increase in the volume fraction of the second phase.

5. Conclusions

1. The phase size, P_κ, and grain size, d_κ, of κ phase are larger than the phase size, P_θ, and grain size, d_θ, of θ phase, respectively. The phase sizes are larger than the respective grain sizes due to the presence of more than one grain within a phase.

2. Rapid grain growth occurs in the κ phase in comparison to that in the θ phase, especially in alloys with lower copper contents. The faster growth of the κ phase is explained by the limited number of pinning contacts of the κ phase boundaries by θ particles. An increase in copper content leads to a decrease in the size of κ phase and an increase in the size of θ phase.

3. The κ-phase size range is broader than the θ-phase size range, but the θ phase exhibits a higher frequency in the lower size range. With an increase in copper, the range of θ-phase sizes broadens, whereas the range of κ-phase sizes reduces.

4. The grain sizes of the κ and θ phases can be related to the volume fraction of θ phase, f_θ, according to the equation, $d_\kappa = 0.497\ d_\theta/f_\theta$, which is in agreement with the theory of Smith and Zener for the inhibition of grain growth by second-phase particles.

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