JOURNAL OF MATERIALS SCIENCE 25 (1990) 4782–4784

Grain growth in copper and alpha-brasses

I. M. GHAURI, M. Z. BUTT
Nuclear Research Laboratory, P.O. Box 1750, Government College, Lahore 54000, Pakistan
S. M. RAZA
Department of Physics, University of Baluchistan, Quetta, Pakistan

The wires of 99.999% copper and alpha-brasses containing 12, 20, 30 and 35 at% Zn have been annealed in vacuum for 30 to 240 min at 873, 923, 973 and 1023 K. The grain-growth data obtained are well encompassed by the relation $D^2 - D_0^2 = Kt\exp(-H/kT)$, where D is the instantaneous mean grain diameter at the time, t, of isothermal anneal and D_0 refers to the initial mean grain diameter. In alpha-brasses the activation energy for grain-boundary self-diffusion, H, and the pre-exponential factor, K, depends on the zinc concentration, c, as $H = (H_0 - 1.1c)$ eV and $K = K_0\exp(-10.7c)\ \text{cm}^2\,\text{sec}^{-1}$. The values of H_0 and K_0, referred to the base metal are respectively 0.87 eV and $3.0 \times 10^{-4}\ \text{cm}^2\,\text{sec}^{-1}$, which are in good agreement with those (0.85 eV and $3.6 \times 10^{-4}\ \text{cm}^2\,\text{sec}^{-1}$) found for copper.

1. Introduction

In 1957 Feltham [1] developed a rather rigorous theory of isothermal grain growth in metals by using the grain diameters and grain-boundary curvatures as statistical variables, and by making allowance for the restrictive conditions imposed by surface tension and space-filling requirements. The initial and instantaneous mean grain diameters, D_0 and D, which have approximately the same respective values whether referred to planar or spatial distribution as recently confirmed by Pande [2], were then found to be related to the time of isothermal growth, t, by the equation

$$D^2 - D_0^2 = K_0 t\exp(-H_0/kT) \qquad (1)$$

where H_0 is the activation energy for grain-boundary self-diffusion and $K_0 = \lambda VGb^2/8h$, where V is the volume per atom, G the shear modulus, b the lattice parameter, h Planck's constant and λ is a constant of the order of unity. For copper with $V = 12 \times 10^{-30}\,\text{m}^3$, $b = 0.25$ nm, $G = 4.5 \times 10^4$ MPa and $\lambda = 1$, one finds $K_0 \approx 7 \times 10^{-2}\,\text{cm}^2\,\text{sec}^{-1}$. Also the activation energy for grain-boundary self-diffusion, involved in grain growth, would be somewhat less than the activation energy for vacancy migration in copper [3]. The latter, as given in the literature, is close to 1 eV. The validity of Equation 1 was checked by Butt and Feltham [4] using grain-growth data obtained by them with 99.99% copper rods of 1 cm diameter sealed in 13 kPa hydrogen at 937 to 1073 K.

Comparison of theoretical formalism with experiment yielded the values of H_0 and K_0 given in Table I. Feltham and Copley [3] expected that the grain growth in random substitutional solid-solutions would also be encompassed by an equation of the same functional form, namely

$$D^2 - D_0^2 = Kt\exp(-H/kT) \qquad (2)$$

However, as K and H depend on the various parameters of the crystal, and as these in turn depend on the concentration of the alloying element, both parameters should be a function of the composition of the alloy. Comparison of Equation 2 with experimental data appertaining to alpha-brasses [3, 5] shows that the dependence of H and K on the solute concentration, c, can be represented rather well by

$$H = H_0 - Hc^* \qquad (3)$$

$$K = K_0\exp(-K^*c) \qquad (4)$$

The values of various parameters of Equations 3 and 4 are given in Table II; these were used by Feltham and Copley [3] and Butt and Feltham [5] to accomplish agreement between Equation 2 and grain-growth

TABLE I The annealing conditions and values of various parameters of Equation 1 for grain growth in wires and rods of copper

Copper specimen specifications		Annealing conditions	H_0 (eV)	K_0 ($\text{cm}^2\,\text{sec}^{-1}$)	Reference
Purity (%)	Diameter (cm)				
99.99	1.0 (rods)	Hydrogen atmosphere of 13 kPa at 973 to 1073 K	0.87	1.6×10^{-2}	[4]
99.999	0.3 (wires)	Dynamic vacuum of 1.3 mPa at 873 to 1023 K	0.85	3.6×10^{-4}	Present work

0022-2461/90 $03.00 + .12

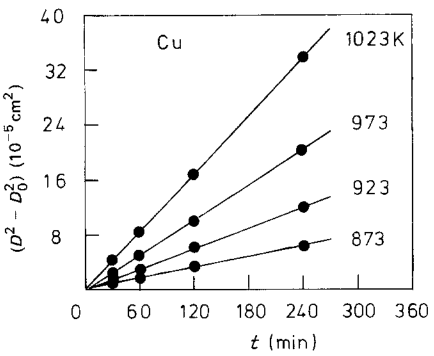

Figure 1 Grain-growth isotherms of 99.999% purity copper wires. $D_0 = 10\,\mu$m.

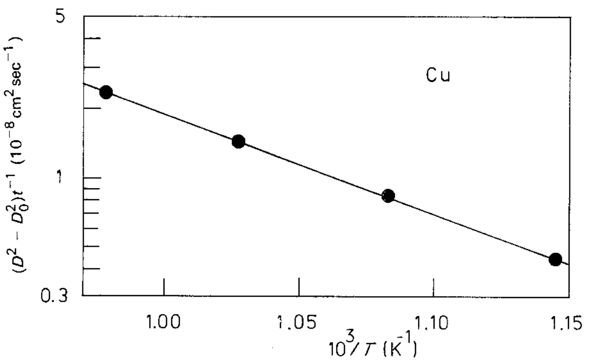

Figure 2 Temperature dependence of the slope of the grain-growth isotherms of 99.999% purity copper wires referred to in Fig. 1.

data for alpha-brasses in the form of wires and rods, respectively.

It is readily apparent from Tables I and II that the parameter H_0, whether obtained directly from the grain-growth measurements made with copper [4] (Table I) or indirectly derived from the grain-growth data appertaining to alpha-brasses [3, 5] (Table II) is independent of the specimen dimensions, purity and annealing conditions, etc.; its magnitude is also in accord with the expected value [3]. Similarly, H^* and K^* (Equations 3 and 4) remain invariant with the factors referred to above. However, the values of K_0 (Table II) derived from the experimental data obtained in the case of wires [3] and rods [5] of alpha-brasses differ markedly from each other indicating the influence of specimen dimensions. Also the experimental value of K_0 for copper rods [4] (Table I) annealed in a hydrogen atmosphere is ten times higher than that derived from the grain-growth studies made on alpha-brass rods [5] (Table II) annealed in an argon atmosphere. This discrepancy is most probably due to the diffusion of hydrogen into the copper specimens during heat treatment [4, 6]. The main object of the present work was to examine how far and with what limitations the set of Equations 1 to 4 can describe the grain growth in copper and alpha-brasses for a unique set of values of parameters H_0 and K_0.

2. Materials and methods

Polycrystalline wires of hard-drawn 99.999% purity copper (3 mm diameter) and of alpha-brasses of commercial origin (2, 3 and 4 mm diameter) were supplied by Johnson Matthy Chemical Ltd, London and Delta Metals Ltd, Birmingham, respectively. The zinc content of brasses were nominally 12, 20, 30 and 35 at. % and the main metallic impurities were iron (< 10 p.p.m.) and smaller amounts of tin, bismuth and silver. The wires were cut into specimen lengths of 12 cm prior to annealing. The 99.999% purity copper specimens were annealed in a dynamic vacuum of 1.3 mPa (10^{-5} torr) extending over periods of 30 to 240 min at 873, 923, 973 and 1023 K. The brass specimens were sealed separately into silica tubes part-lined with 70/30 brass sheet to minimize dezincification [5] and evacuated to 13 mPa (10^{-4} torr). Four such tubes containing specimens of a given composition were then placed side by side in a muffle furnace for isothermal heat-treatment in the temperature range 873 to 1073 K for different periods of time, as in the case of copper.

To facilitate the measurement of grain size, pieces 1 cm long, cut from annealed copper and brass wires, were embedded in bakelite moulds to yield transverse and longitudinal sections. These were polished and etched to reveal equi-axed grains. Mean grain-diameters were obtained by the line intercept method, as an average of values from at least ten diameters.

3. Results and discussion

Reference to Fig. 1 shows the grain-growth isotherms for 99.999% purity copper wires. A linear relationship between D^2–D_0^2 and annealing time, t, for each temperature can be seen to be consistent with the functional form of Equation 1. The straight line in Fig. 2 derived from the slopes of the isotherms (Fig. 1), yields $H_0 = 0.85$ eV. From this value of the activation energy for grain-boundary self-diffusion and the data

TABLE II The annealing conditions and values of various parameters of Equations 2 to 4 for grain growth in wires and rods of alpha-brasses

Alpha-brass specimen specifications		Annealing conditions	H_0 (eV)	H^* (eV)	K_0 (cm^2 sec^{-1})	K^*	Reference
Main metallic impurities	Diameter (cm)						
Fe (80 to 300 p.p.m.) Sn (20 to 30 p.p.m.) Pb (0 to 210 p.p.m.) Bi (30 to 60 p.p.m.)	0.2 (wires)	Unspecified vacuum at 748 to 973 K	0.87	1.1	3.0×10^{-4}	10.7	[3]
Traces of Fe (< 10 p.p.m.), Sn and Bi	1.0 (rods)	Argon atmosphere of 13 kPa at 973 to 1073 K	0.87	1.1	1.4×10^{-3}	10.7	[5]
Traces of Fe (< 10 p.p.m.) Sn, Bi and Ag	0.2 to 0.4 (wires)	Vacuum of 13 mPa at 873 to 1023 K	0.87	1.1	3.0×10^{-4}	10.7	Present work

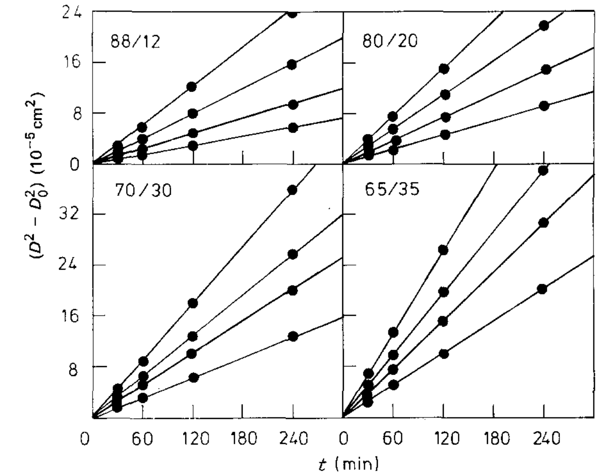

Figure 3 Grain-growth isotherms of alpha-brass wires. D_0 = 30, 15, 65 and 65 μm for 88/12, 80/20, 70/30 and 65/35 brass, respectively. For each composition, the annealing temperatures are, from top to bottom, 1023, 973, 923 and 873 K.

given in Fig. 1, one readily finds by means of Equation 1, that $K_0 = 3.6 \times 10^{-4}$ cm^2 sec^{-1}.

The linearity of the isotherms in Fig. 3 confirms the applicability of Equation 2 to the grain-growth in wires of alpha-brasses. Referring to Fig. 4, the straight lines drawn through the data points, derived from the slopes of the isotherms (Fig. 3) yield the values of H as a function of zinc concentration, c (Fig. 5). Using these H-values and the data given in Fig. 3, Equation 2 enables K to be evaluated (Fig. 6). It is apparent from Figs 5 and 6 that the dependence of H and K on the zinc concentration, c, can be represented well by Equations 3 and 4, respectively, with values of H_0, H^*, K_0 and K^* given in Table II.

It can be readily seen that the values of H_0 and K_0 (Table II) derived by extrapolation to $c = 0$ from the grain-growth data appertaining to wires of alpha brasses annealed in vacuum (Figs 5 and 6) is in excellent agreement with the corresponding ones measured experimentally with copper wires annealed in vacuum (Table I). In other words, Equations 1 to 4 can describe the grain-growth in vacuum-annealed wires of copper and alpha-brasses for a unique set of values of H_0 and K_0.

4. Conclusions

1. The grain growth in wires of copper and alpha-brasses annealed in vacuum is encompassed by Equations 1 to 4 for some unique values of H_0 ($\approx$0.87 eV) and K_0 ($\approx 3.0 \times 10^{-4}$ cm^2 sec^{-1}).

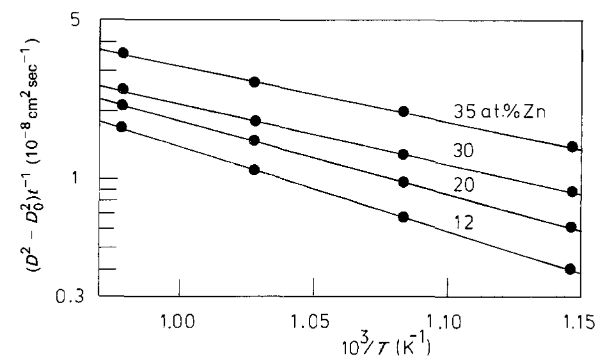

Figure 4 Temperature dependence of the slope of the grain-growth isotherms of alpha-brasses referred to in Fig. 3.

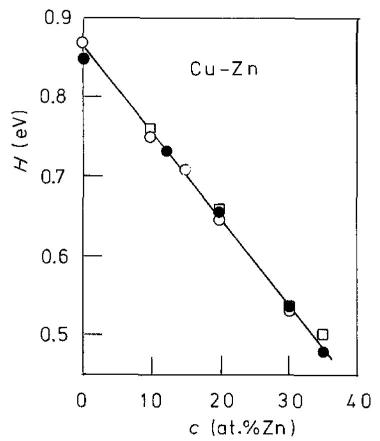

Figure 5 Relation between the activation energy for grain-boundary self-diffusion, H (Equation 2) and zinc content, c, in alpha-brasses: (○) rods [4, 5], (□) wires [3]. (●) Experimental values obtained in the present work with vacuum-annealed wires of copper and alpha-brasses.

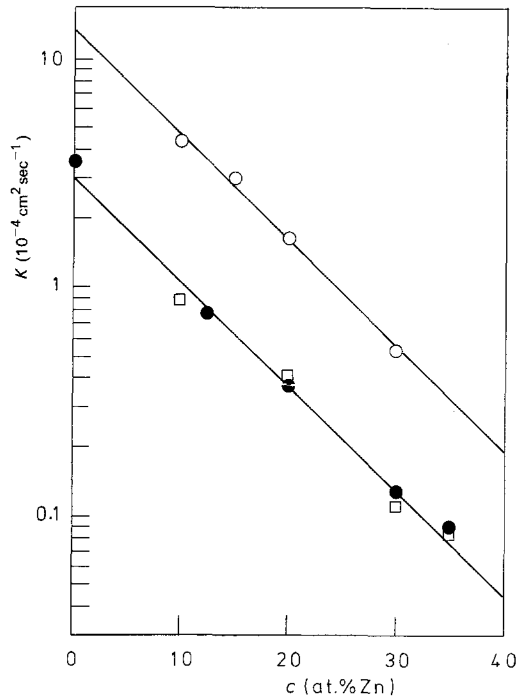

Figure 6 Dependence of the pre-exponential factor, K (Equation 2) on zinc content, c, in alpha-brasses: (○) rods [5], (□) wires [3]. (●) Experimental values obtained in the present work with vacuum-annealed wires of copper and alpha-brasses.

2. The activation energy for grain-boundary self-diffusion, H_0 (Equations 1 and 3), is independent of the specimen dimensions, annealing conditions, etc., whereas the pre-exponential factor, K_0 (Equations 1 and 4), strongly depends on these parameters.

3. The constants H^* and K^* (Equations 3 and 4) do not depend on alpha-brass purity, specimen dimensions or annealing conditions, etc.

References

1. P. FELTHAM, *Acta Metall.* **5** (1957) 97.
2. C. S. PANDE, *ibid.* **35** (1987) 2671.
3. P. FELTHAM and G. J. COPLEY, *ibid.* **6** (1958) 539.
4. M. Z. BUTT and P. FELTHAM, *Fizika* **14** (1982) 149.
5. *Idem, ibid.* **14** (1982) 113.
6. M. Z. BUTT, *J. Mater. Sci. Lett.* **2** (1983) 1.

Received 13 June and accepted 22 November 1989