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Solid solution hardening of copper crystals

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The effect of Mg, Si, In and Cd solute atoms on the critical resolved shear stress of Cu single crystals has been studied in the "plateau" region in order to complete data on the solid solution hardening of Cu base alloys. Labusch's equation is obeyed both for the concentration dependences and for the dependence of $d\tau_p/dc^{2/3}$ on $\epsilon^{4/3}$. Edge dislocation/solute atoms interaction dominates in Cu as in Au and Ag base alloys.

1. Introduction

The effect of substitutional solute atoms on the flow stress of fcc metal crystals has been studied recently by many authors (see [1] or [2] for a review). The present paper reports further results obtained by the authors in copper alloys which may be useful for detailed understanding of the solid solution hardening in the so-called plateau region. The "plateau" is the temperature independent region which exists in the temperature dependence of the critical resolved shear stress (CRSS) of substitutional alloy crystals.

Labusch [3] has shown that the plateau stress (CRSS at the plateau temperature) satisfies the following equation:

$$\tau_p = G \,.\, Z \,.\, \epsilon^{4/3} c^{2/3} + \tau_{00} \qquad (1)$$

where τ_{00} is the CRSS of the pure metal, Z a numerical factor equal to 1.3×10^{-3}, G the shear modulus, c the solute atom concentration (in atomic fractions) and ϵ the misfit parameter. ϵ accounts for the size and modulus misfit in the neighbourhood of the foreign atom:

$$\epsilon = \sqrt{(\eta'^2 + \alpha^2\delta^2)} \qquad (2)$$

where η' is the modulus misfit depending on $\eta = (1/G)\,(dG/dc)$ and δ is the size misfit parameter equal to $(1/a)\,(da/dc)$ where a is the lattice constant. Parameter α describes the difference of the interaction forces between the screw and edge dislocations, respectively, and the foreign atom.

Labusch [3] used the fact that $d\tau_p/dc^{2/3}$ was linearly proportional to $\epsilon^{4/3}$ as a proof of the solid solution hardening theory. Equation 1 is only valid at $T = 0$ K or for values of CRSS extrapolated to this temperature [4]. The experiments at high temperatures (plateau region) can be justified by the fact that the dependence of CRSS on temperature runs in the same way for different values of the interaction force between the obstacle and dislocation, for different solute atom concentrations and for different dislocation line tensions. If only one type of obstacle exists, i.e. individual atoms, the CRSS should fall with increasing temperature [5, 6].

The solid solution hardening of copper crystals has been studied by many authors [7-12]. It is the purpose of the present paper to summarize the cited data together with some new data obtained for *Cu*–In, *Cu*–Cd, *Cu*–Mg and *Cu*–Si* alloys. Thus the verification of the theoretical models will again be possible (the recent critical evaluation of the results was given by *Jax et al.* [14]).

2. Experimental procedure and results

The original alloys were prepared in vacuum from high purity Johnson and Mathey metals.

*The data obtained by Evans and Flanagan [13] for this alloy are not reliable as they are based on two points at 5 and 7 at. % respectively which are very near to the solubility limit.

The ingots were then annealed at 700°C in hydrogen and finally rolled and die drawn to a diameter of 3.5 mm.

The crystals were grown by the modified Bridgman method. The seed crystals were used to grow single crystals in graphite moulds in argon at the rate of 0.8 cm h^{-1}.

The samples (15 mm long and 4 mm in diameter) were spark cut from larger single crystal pieces and then annealed at 800°C in pure argon for 48 h and then cooled to room temperature. All crystals had identical orientation (Fig. 1). The deformation was carried out

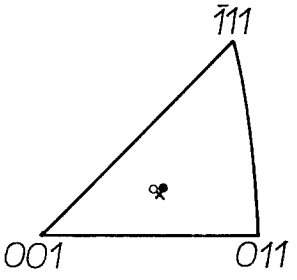


Figure 1 The orientation of seed grown Cu-alloy single crystals.

in a TT-BM Intron at constant deformation rate corresponding to the initial strain-rate $\dot{a} = 3 \times 10^{-4}$ sec^{-1} in compression. All crystals were deformed at 235 to 250°C, i.e. in the plateau region. The solute concentration of each sample was determined after deformation with an accuracy of $\pm$ 0.05 at. %.

A summary of the results evaluated with respect to the $c^{2/3}$-dependence is given in Table I. The corresponding plots are shown in Fig. 2. The slope of the *Cu*–Mg curve changes: this may be due to the limited solubility especially at either the testing or room temperature.

During the solidification of copper alloys, redistribution of solute took place. The redistribution of Cd is, nevertheless, so intensive that it is not possible to explain it on the basis of the corresponding phase diagram [15]. The original concentration of 0.94 at. % Cd was lowered after the solidification process to $\sim 2.0 \times 10^{-3}$ at. %. Therefore, it was not possible to prepare samples with different concentrations of Cd. The effect of Cd atoms on the CRSS is very strong: the addition of $2.0 \pm 0.8 \times 10^{-3}$ at. % Cd increases the value of

TABLE I

	c (at. fractions)	$c^{2/3}$	τ_p (gf mm^{-2})	Number of crystals
Cu–Mg	0.0005	0.006	130	1
	0.0024	0.018	310	3
	0.0044	0.027	442	1
	0.0065	0.035	662	2
	0.0087	0.042	822	2
	0.0104	0.048	1030	2
	0.0133	0.056	1180	2
Cu–Si	0.0037	0.041	160	4
	0.0085	0.060	204	4
	0.0270	0.194	535	1
	0.0450	0.273	684	2
	0.0560	0.318	790	1
	0.0650	0.348	894	1
Cu–In	0.0003	0.004	230	2
	0.0062	0.034	1080	3
	0.0106	0.048	1700	1
	0.0160	0.063	2150	1
	0.0211	0.076	2690	4

τ_p by 24 gf mm^{-2}. The value of $d\tau_p/dc^{2/3}$ given in Table II is approximate: this value, as well as the scatter of concentration, were obtained from an average of seven samples.

The typical effect of the solute concentration on the stress-strain curve is illustrated in Fig. 3 where the stress-strain curves are given for the *Cu*–In system.

3. Discussion

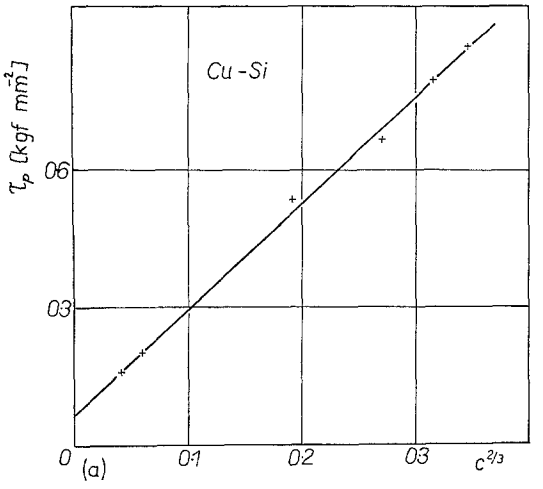
The basic results are summarized in Table II together with those of the other authors, and the

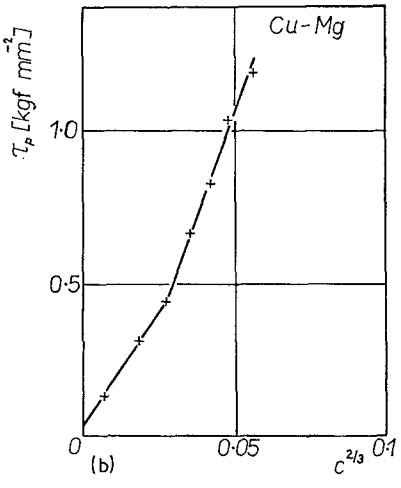
TABLE II

System	ϵ	$d\tau_p/dc^{2/3}$ (kgf mm^{-2})	Ref.
Cu–Ge	1.78	6.3	[7]
Cu–Ga	1.51	4.6	[7]
Cu–Au	2.47	10.0	[9]
Cu–Ni	0.66	2.3	[12]
Cu–Zn	1.06	3.9	[7]
Cu–In	4.31	33.7	this paper
Cu–Cd	3.55	35.0	this paper
Cu–Al	1.20	4.0	[10, 11]
Cu–Si	0.81	2.2	this paper
Cu–Mg	2.94	15.1	this paper

corresponding log-log plots are given in Fig. 4.

The points for *Cu*–In and *Cu*–Cd deviate slightly from the linear proportionality between log $(d\tau_p/dc^{2/3})$ and log ϵ (see Fig. 4). This was





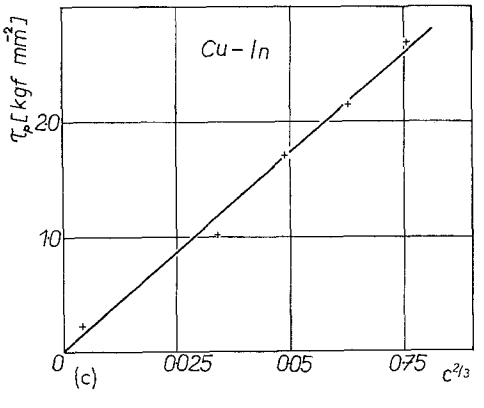


Figure 2 The dependence of τ_p on $c^{2/3}$ (a) for Cu–Si, (b) for Cu–Mg, (c) for Cu–In at 523 K.

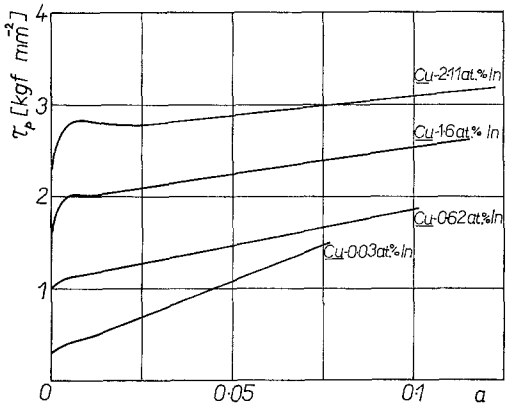


Figure 3 The effect of In concentration on the stress-strain curve at the plateau temperature, 523 K. The τ_p value is the extrapolated value of τ for $a = 0$.

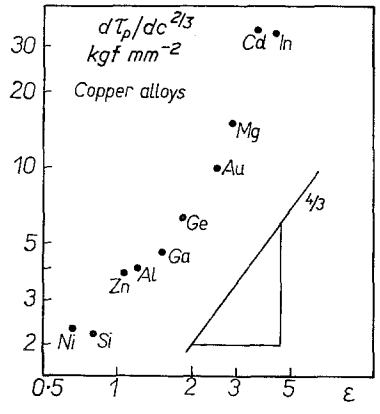


Figure 4 The linear relationship between log $(d\tau_p/dc^{2/3})$ and log $\epsilon^{4/3}$.

recently connected with the appearance of second phase particles or zones [16]; however, a detailed study using transmission electron microscopy will be necessary in future.

The τ_p-$c^{2/3}$ dependence can be said to describe the solid solution hardening for copper single crystals as well as for silver and gold single crystals [14]. Also, the 4/3 dependence of ϵ fits the experimental data. The most important parameter is the solubility limit. It was shown that, as with the Au–Ge [17] and *Cu*–Mg systems, the slope of τ_p versus $c^{2/3}$ changes near the solubility limit.

The numerical value of Z can be obtained from a plot of $(d\tau_p/dc^{2/3})$ versus $\epsilon^{4/3}$ when $Z \approx 0.9 \times 10^{-3}$: this is in good agreement with Equation 1. For the experiments with copper

single crystals the value of α which fits Equation 2 was 16, as were the values for silver and gold alloys [14]. The major interaction is, therefore, the edge dislocation/obstacle interaction. This assumption is verified by electron microscopic observation of dislocation arrangement in deformed copper-base solid solutions [18-20], where practically the only observed dislocation braids are the group of edge dipoles similar to those observed in pure crystals (see e.g. [21, 22]).

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