Letters

Solid-solution hardening of metal crystals

On the basis of a statistical spectrum of obstacle strengths due to random distribution of solute atoms in a solid-solution Kratochvil *et al.* [1] formulated semi-empirical relations for the temperature dependence of the critical resolved shear stress (CRSS), τ, and of the activiation volume, v, defined by $v = (-\partial U/\partial \tau)_T$, where U is the activation energy (free enthalpy) of dislocation motion over an obstacle of strength U_0 which is "effective" at a given temperature. Attempts [2, 3] have been made to evaluate the strength of effective-obstacles to dislocation motion in some close-packed alloys by comparing the experimental $(\tau - T)$ relation with that proposed by Kratochvil *et al.* However, the U_0 value determined from the $(\tau - T)$ relation alone cannot be regarded as unique unless it proffers quantitative agreement between the experimental and the theoretical $(v - T)$ relation as well. It is thus of interest to examine to what extent, and with what prescription, the model of Kratochvil *et al.* [1] of solid solution hardening might be reconciled with experimental observations e.g. those of Basinski *et al.* [4] appertaining to copper- and silver-based alloy single crystals, for some unique value of the effective obstacle strength U_0.

According to Kratochvil *et al.* [1], the critical resolved shear stress, τ, of an alloy depends on temperature T and strain-rate $\dot\gamma$, as given by

$$\frac{\tau}{\tau_0} = 2\exp\left[-\frac{kT}{U_0}(\ln 2)\ln\left(\frac{\dot\gamma_0}{\dot\gamma}\right)\right] - 1. \qquad (1)$$

Here $\tau \to \tau_0$ as $T \to 0\,\mathrm{K}$ and $\dot\gamma_0$ is the pre-exponential factor in the Arrhenius relation for strain-rate,

$$\dot\gamma = \dot\gamma_0 \exp(-U/kT). \qquad (2)$$

Equation 1 remains valid as long as $T \leqslant T_c = U_0/k\ln(\dot\gamma_0/\dot\gamma)$, and is based on the empirical relation between U and τ

$$U = U_0 - \frac{U_0}{\ln 2}\ln\left(1 + \frac{\tau}{\tau_0}\right). \qquad (3)$$

The activation volume $v = (-\partial U/\partial \tau)_T$, as derived from Equation 3, is

$$v = \frac{U_0}{\ln 2}\left(\frac{1}{\tau + \tau_0}\right). \qquad (4)$$

Noting that $(-\partial U/\partial \tau)_T = (kT\,\partial \ln \dot\gamma/\partial \tau)_T$, one obtaines from Equation 1 the dependence of activation volume v on temperature T

$$v = \frac{U_0}{2(\ln 2)\tau_0}\exp\left[\frac{kT}{U_0}(\ln 2)\ln(\dot\gamma_0/\dot\gamma)\right]. \qquad (5)$$

Concerning the value of $\ln(\dot\gamma_0/\dot\gamma)$, Kratochvil [2] arbitrarily assumed it to be 15. Feltham [5], on the other hand, derived that $\ln(\dot\gamma_0/\dot\gamma) \approx 25$ if plastic deformation is to occur at rates most often studied. His assesment is based on the following considerations. Since $\dot\gamma_0$ is proportional to the Debye frequency ν_0 of the material, one can rewrite Equation 2 as

$$\nu = \nu_0 \exp(-U/kT), \qquad (6)$$

where ν is the time for the dislocations to overcome the obstacles. If ν is "observable", then, taking ν of the order of 1 sec as the criterion for observing deformation, Equation 6 with $\nu_0 = 10^{11}$ sec^{-1} implies that

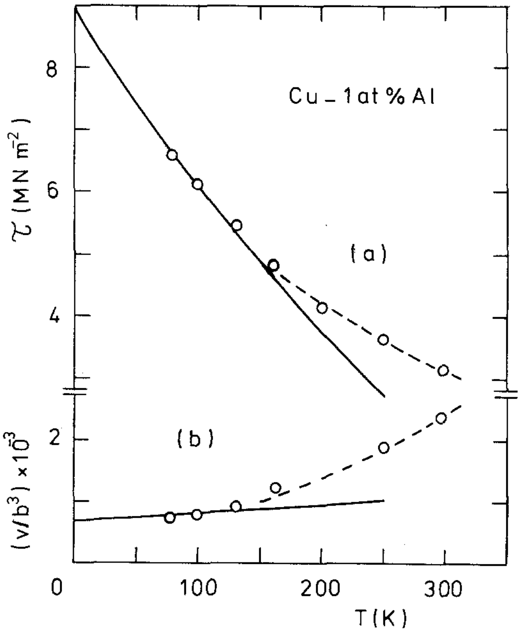

Figure 1 Temperature dependence of (a) the yield-stress and of (b) the activation volume in a Cu–1 at % Al alloy single crystal. Experimental values are denoted by circles; the full curves are computed by means of Equations 1 and 5 with $U_0 = 0.87$ eV, $\tau_0 = 9\,\mathrm{MN\,m^{-2}}$ and $\ln(\dot\gamma_0/\dot\gamma) \approx 25$.

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$$U = mkT. \qquad (7)$$

where $m = \ln(\nu_0/\nu) = \ln(\dot{\gamma}_0/\dot{\gamma}) \approx 25$.

It is readily seen that the value of m is not appreciably modified on taking other "reasonable" values of ν. In the present work, Feltham's flow criteria (Equation 7) has been used while correlating Equations 1 and 5 with experimental results.

Now, Fig. 1 refers to the temperature dependence of (a) the critical resolved shear stress (CRSS) and of (b) the activation volume for monocrystalline copper containing 1 at% aluminium. The points denote the experimental results of Basinski *et al.* [4] and disregarding for the present purposes "anomalies" below about 75 K, the full curves comply with Equations 1 and 5 for $U_0 = 0.87$ eV and $\tau_0 = 9\,\text{MN m}^{-2}$. Moreover, Fig. 2 shows the relationship between the activation volume and the CRSS of silver alloys at 78 K. The curve was drawn through the experimental data of Basinski *et al.* [4] and the points were obtained by

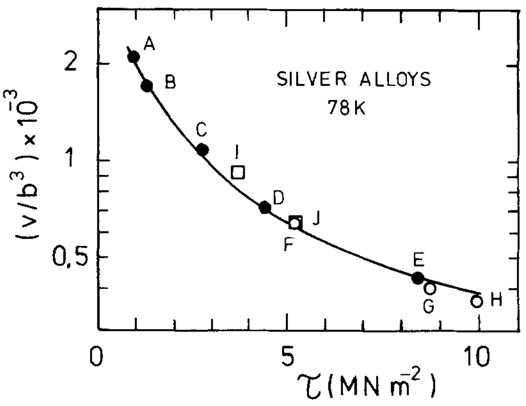

Figure 2 Stress dependence of the activation volume measured at the CRSS of silver alloys at 78 K. The curve was drawn through the experimental data of Basinski *et al.* [4] and the points were obtained by means of Equations 1 and 5 with the parameters given in Table I. Points A–E (full circles) refer to silver alloys, containing 0.1–2.5 at% In, points F–H (empty circles) refer to 0.25–0.6 at% Sn, and I–J (squares) refer to 10–20 at% Au.

TABLE I Values of U_0 and τ_0 used in Equations 1 and 5 to establish agreement with the experimental observations relating to copper- and silver-based alloys below about 150 K. τ_0 was obtained by extrapolation of the experimental $(\tau - T)$ curve (77–400 K) to the stress-axis [6, 7]. $\ln(\dot{\gamma}_0/\dot{\gamma}) \approx 25$.

Copper alloys			Silver alloys		
Solute content c (at%)	τ_0 (MN m^{-2})	U_0 (eV)	Solute content c (at%)	τ_0 (MN m^{-2})	U_0 (eV)
0.01 Al	0.68	0.48*	0.1 In	1.5	0.62
0.05	1.36	0.55	0.2	2.0	0.67
0.1	2.0	0.60	0.5	3.8	0.83
0.25	3.6	0.68	1.0	6.0	0.87
0.5	5.5	0.83	2.5	11.0	0.97
1.0	9.0	0.87			
1.4	11.6	0.92			
1.85	14.5	0.97	0.03 Sn	2.0	0.72
2.8	19.2	1.12	0.08	3.5	0.75
4.6	23.6	1.13	0.25	7.0	0.90
5.6	25.6	1.13	0.50	11.5	0.93
7.4	27.2	1.13	0.60	13.0	0.95
9.2	31.0	1.13			
11.0	37.0	1.10	10.0 Au	5.0	0.92
			20.0	7.0	0.90
0.05 Ag	4.0	0.75			
0.1	5.6	0.80			
0.19	9.6	0.87			
5.0 Ni	11.4	1.05			

* Comparing with the maximum interaction energy 0.13 eV between a solute atom and an edge dislocation in Cu–Al alloy [8, 9], the effective obstacle comprises about four solute atoms.

means of Equations 1 and 5 with the values of U_0 and τ_0 [6, 7] given in Table I. Agreement can be seen to be good at rather low temperature, i.e. below about 150 K.

It is therefore concluded from the foregoing evidence that the temperature dependence of the CRSS and of the activation volume in random alloys proposed by Kratochvíl *et al.*, agrees with experimental observations at low temperature for some unique value of the effective obstacle strength U_0, only if the flow criteria of Feltham (Equation 7) is taken into account. Further, the U_0 values (Table I) on comparison with the maximum binding energy between a solute atom and a dislocation [8, 9] show that even in dilute alloys the effective obstacles to dislocation motion are groups of solute atoms, and it is not therefore germane to consider as a model of yielding the break-away of dislocations from isolated solute atoms as, for example, in the well-known model proposed by Friedel.

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Dynamic mechanical properties of cross-linked poly(acrylic acid)–aluminum oxide composites

While extensive research has been conducted on polymer matrix composite materials, few studies have systematically examined the viscoelastic behaviour of cross-linked polymer composites. Recently, the effects of network formation on the physical and mechanical properties of poly(acrylic acid) (PAA) have been reported [1, 2]. The current study presents preliminary data on the changes in the dynamic mechanical properties which occur when cross-linked PAA is combined with Al_2O_3 particles. Whereas the absolute moduli of unfilled PAA decrease with the increasing mole fractions of cross-linking agent, X, [2], present results indicate that the relative modulus is proportional to the volume fraction of filler, ϕ_2, but remains approximately constants as X increases. In addition for each composition studied, the glass transition temperature, T_g, is shifted to higher values as either ϕ_2 or X is increased.

Mixtures of acrylic acid (AA)* and the tetrafunctional monomer, allyl acrylate (ALA)*, were prepared at four concentrations ($X = 0, 0.06, 0.13$ and 0.20). Each of these was subdivided into three batches: Two were combined with Al_2O_3 powder† of nominal particle size 0.05 or 1.0 μm, while the third remained unfilled. The resulting slurries were centrifuged (395 *g*) to obtain maximum packing of the powders, solidified via free radical polymerization (0.47 wt% benzoyl peroxide at 60° C for 24 h) and serially heat-treated to ensure complete conversion of the monomer (at 80, 100 and 120° C). The unfilled polymer was processed in identical fashion. Subsequent ash analyses indicated that $\phi_2 = 0.10$ and 0.17 for the composite materials containing the small and large filler particles, respectively. Cylindrical specimens with nominal dimensions $L = 38.1$ mm and $r = 1.5$ mm were heated under $N_{2(g)}$ at 10° C min^{-1} in a Du Pont 981 Dynamic Mechanical Analyser over a temperature range of -50 to 225° C. The operation of this instrument and the method for converting frequency and damping data to the corre-

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