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Loss of stress equivalence in solid-solution hardening

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Available data on the temperature, T, and concentration, c, dependence of the critical resolved shear stress, τ, of numerous copper- and silver-based solid solutions have been examined with special reference to the stress equivalence of solid-solution hardening, i.e. a common single curve for all alloy concentrations and solute types in a correlation of $\Delta\tau = \tau(78) - \tau(298)$ with $\tau(78)$, as first demonstrated by Basinski *et al.* in 1972. For solid solutions based on a given solvent metal, the stress equivalence is lost if the value of exponent r in the relation $\tau(T) \propto c^r$ varies with temperature. The critical concentration of the solute at which stress equivalence of solid-solution hardening is lost depends on the alloy system.

1. Introduction

In the early seventies some experiments with considerable potential implications in relation to solid-solution hardening theory were carried out by Basinski *et al.* [1] with copper- and silver-based alloy single crystals of high structural perfection and purity. They observed that if two solid solutions of different solutes in a given solvent had the same critical resolved shear stress (CRSS), τ, at any selected temperature in the range 4 to 400 K investigated by them, they had coincident values of the CRSS at all other temperatures. Moreover, on taking any of these two solvent metals, the difference between the CRSS at 78 K and 298 K, $\Delta\tau = \tau(78) - \tau(298)$, turned out to be a unique function of the CRSS at 78 K, independent of the alloy type and concentration. Basinski *et al.* concluded that the thermal behaviour of solid-solution hardening was stress equivalent, i.e. the $\Delta\tau$ data correlate well with the amount of solution hardening but do not correlate with the concentration of the solute.

The investigations of Basinski *et al.* [1] on the stress equivalence of the difference in CRSS between 78 K and 298 K in solution-hardened single crystals of copper (c = 0.01 to 11.0 at % Al, 0.05 to 0.19 at % Ag, 0.5 at % Si, 5.0 at % Ni) and silver (c = 0.01 to 2.5 at % In, 0.03 to 0.6 at % Sn, 10 to 20 at % Au) were extended [2–9] to several other binary solid solutions based on cadmium (c = 0.005 to 0.38 at % Zn, 0.01 to 0.2 at % Ag, 0.02 to 0.5 at % Mg) [2], magnesium (c = 0.006 to 0.45 at % Zn, 0.02 to 2.4 at % Cd, 0.24 to 1.63 at % Al, 0.49 to 4.0 at % In, 1.5 to 15 at % Li) [2, 3], titanium (c = 1 to 10 at % Al) [4], niobium (c = 5 to 16 at % Mo, 5 to 9 at % Re) [4], silver (c = 1 to 6 at % Al, 2.2 to 7.8 at % Zn) [5] and copper (c = 0.5 to 35 at % Zn, 0.5 to 7.3 at % Ge) [4, 6–8]. A straight line of slope one was shown [4] to pass through the experimental points denoting $\Delta\tau/\tau$ data plotted in log–log coordinates for all solid solutions referred to above. Nevertheless, rather small deviations from a unique straight line of slope $d \log(\Delta\tau)/d \log \tau = 1$ were apparent in some alloy systems.

In 1980 Schwink and Wille [9] compared the τ/T curves obtained by them for copper single crystals containing 1.5 to 7.7 at % Mn with that of Traub *et al.* [8] for copper single crystals alloyed with 0.5 to 7.3 at % Ge. They found that while for rather low solute concentrations the curves of the two alloy systems corresponding to a given level of solution hardening were nearly parallel, thus exhibiting stress equivalence, it no longer held for higher solute concentrations, i.e. the curves of Cu–Mn and Cu–Ge alloys intersected, demonstrating a departure from stress equivalence. Schwink and Wille [9] also expressed the difference in the CRSS between 78 K and 298 K as a function of the CRSS at 78 K for Cu–Mn alloys and compared their data with that appertaining to some other copper-based alloys, namely Cu–Al (c = 0.05 to 11 at % Al) [1] and Cu–Ge [8]. They obtained a single smooth $\Delta\tau/\tau$ curve for alloys with solute concentration $c < 2$ at %, irrespective of the type of alloying element, whereas the curves for Cu–Mn, Cu–Al and Cu–Ge alloys with solute concentration $c > 2$ at % markedly differed from one another. In their attempt to explain the loss of stress equivalence in solution hardening at rather high solute concentrations ($c > 2$ at %), Schwink and Wille plotted the τ/c data appertaining to Cu–Mn, Cu–Al and Cu–Ge alloys at 298 K in log–log coordinates and attributed the loss of stress equivalence to the marked changes in the slope of log τ–log c lines drawn through data points for these alloys in the vicinity of a solute concentration $c \approx 2$ at %. Nevertheless they did not consider the concentration dependence of the CRSS at the other temperature involved, i.e. 78 K. The analysis of experimental observations carried out by Schwink and Wille [9] in relation to loss of stress equivalence is therefore far from complete and an adequate explanation of the phenomenon is still outstanding, as remarked by Nabarro [10].

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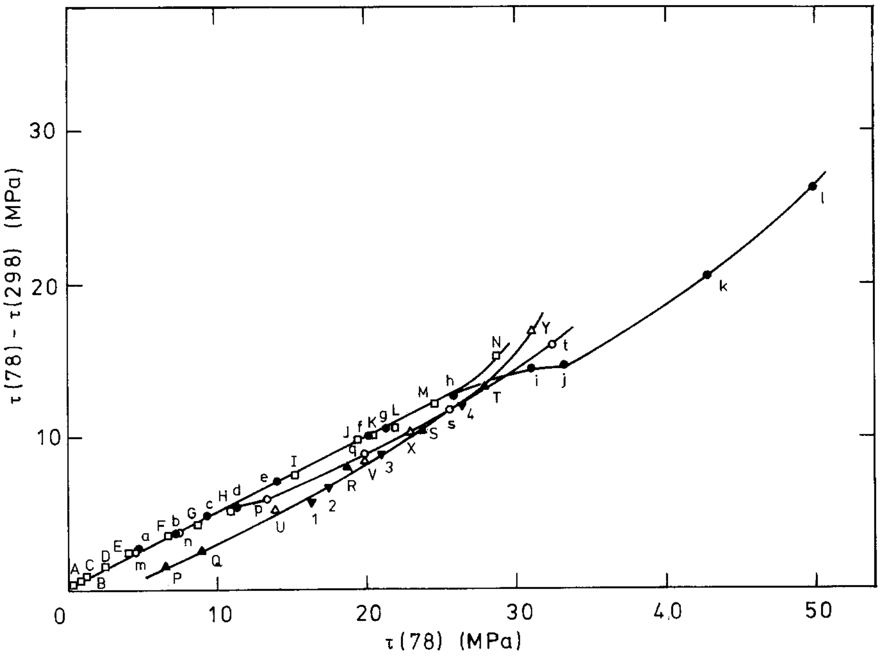

Figure 1 Relation between the difference in CRSS, τ(78) − τ(298), and τ(78) for copper-based alloys. Data points have been taken from the literature: □ Cu-Al [1] (A 0.01% Al, B 0.05% Al, C 0.1% Al, D 0.25% Al, E 0.5% Al, F 1.0% Al, G 1.4% Al, H 1.85% Al, I 2.8% Al, J 4.6% Al, K 5.6% Al, L 7.4% Al, M 9.2% Al, N 11.0% Al), ● Cu-Mn [9, 11] (a 0.11% Mn, b 0.21% Mn, c 0.42% Mn, d 0.44% Mn, e 0.96% Mn, f 1.5% Mn, g 1.83% Mn, h 2.2% Mn, i 3.3% Mn, j 3.8% Mn, k 5.5% Mn, l 7.7% Mn), ○ Cu-Ge [8] (m 0.5% Ge, n 1.0% Ge, p 2.0% Ge, q 3.8% Ge, s 5.6% Ge, t 7.3% Ge) and ▼ (1 10% Zn, 2 15% Zn, 3 20% Zn, 4 30% Zn), ▲ (P 0.5% Zn, Q 1.5% Zn, R 6.2% Zn, S 18% Zn, T 28% Zn), △ (U 5% Zn, V 10% Zn, X 20% Zn, Y 30% Zn) Cu-Zn [6, 12, 13].

The main object of the present work was to study in some detail the problem of the loss of stress equivalence in solid-solution hardening. Not only more data appertaining to copper-based alloys have been taken into account but also the investigations have been extended to numerous silver-based alloys. The loss of stress equivalence for the difference in CRSS between 78 K and 298 K in alloys based on a given solvent metal has been shown to be associated with the change in the value of exponent r in the relation $\tau(T) \propto c^r$ with temperature.

It should be noted that a small yield stress (CRSS) is also observed in crystals which are nominally solute free; impurities, the Peierls barrier, dislocation networks, etc. may determine its magnitude. This contribution may be encompassed by replacing c in the $\tau(T) \propto c^r$ relation by $(c + c_0)$, where c_0 is the "equivalent" concentration which is numerically equal to the intercept on the negative c-axis obtained on extrapolating isotherms representing the concentration dependence of the CRSS to $\tau = 0$. Since the use of c_0 is, in general, of significance only with alloys containing less than about 0.1 at % of solute [2], this semi-empirical correction can be ignored in the present work.

2. Analysis of data

For copper-based solid solutions, Fig. 1 illustrates the relationship between $\Delta\tau = \tau(78) - \tau(298)$ and $\tau(78)$ for Cu-Al [1], Cu-Mn [9, 11], Cu-Ge [8] and Cu-Zn [12, 13] alloy single crystals as well as that for Cu-Zn [6] polycrystals. The points represent the data taken from the literature. A Taylor factor of $\frac{1}{3}$ was used to obtain the mean shear stress in the active glide systems of the grains of polycrystalline brasses from the applied compressive stress. It is readily apparent that deviations from the $\Delta\tau/\tau$ line with a slope of about 0.5 for Cu-Ge, Cu-Mn and Cu-Al alloys set in at about 2.0 at % Ge, 2.0 at % Mn and 11 at % Al, respectively, whereas the data for mono, as well as polycrystalline Cu-Zn alloys fall on a separate $\Delta\tau/\tau$ curve. The concentration dependence of the CRSS of these alloys at 78 K and 298 K has been depicted in Figs 2–5. A

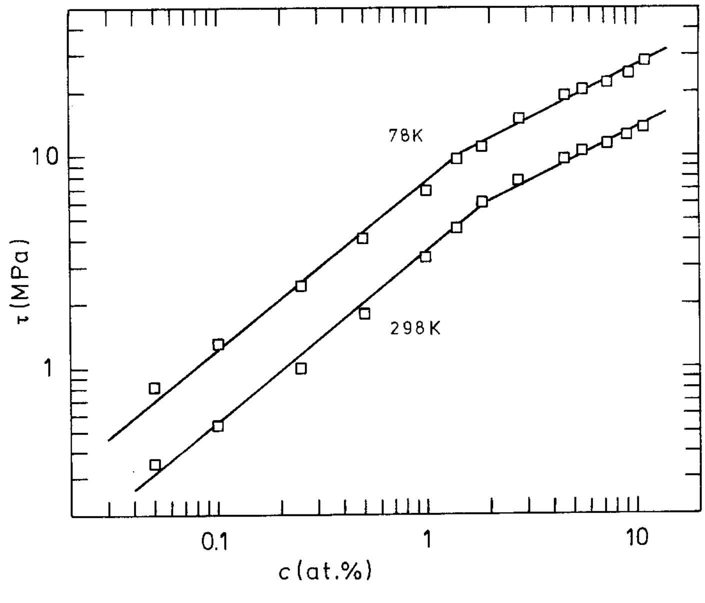

Figure 2 Concentration dependence of the CRSS of copper single crystals containing 0.05 to 11 at % aluminium. Data points are from [1].

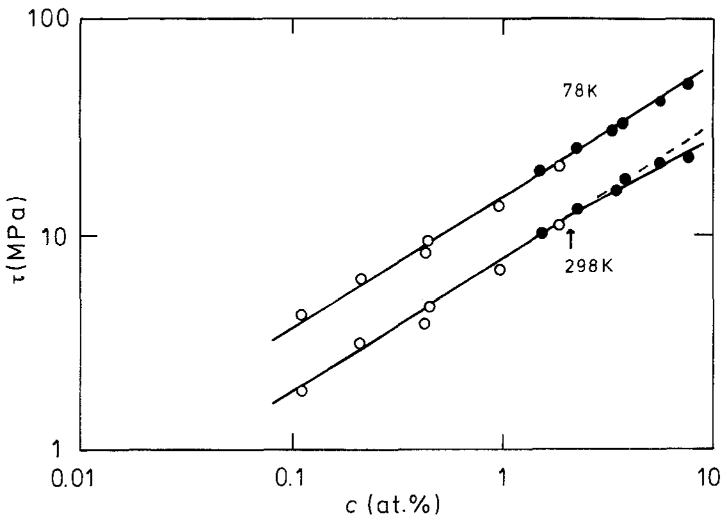

Figure 3 Concentration dependence of the CRSS of copper single crystals alloyed with 0.11 to 7.7 at % manganese. ● Schwink and Wille [9], ○ Wille *et al.* [11].

close study of Figs 2–5 in conjunction with Fig. 1 reveals the following information.

(i) The CRSS of Cu–Al alloys follow the concentration dependence $\tau \propto c^{0.81}$ and $\tau \propto c^{0.50}$ in the "low" and "high" concentration domains, respectively, at both 78 K and 298 K (Fig. 2). In spite of the change in τ/c dependence at $c \approx 2$ at % Al, the data, except that for Cu-11 at % Al, fall on a single straight $\Delta\tau/\tau$ line with slope of about 0.5 (Fig. 1).

(ii) Either Cu–Mn or Cu–Ge alloy system exhibits temperature independent τ/c dependence for $c <$ 2 at % (Figs 3 and 4), while the slope of the log τ–log c line drawn through the data points at 298 K for $c \geqslant 2$ at % is slightly less than that at 78 K (Table I). The difference in the τ/c dependence at 78 K and 298 K in the rather "high" solute concentration domain is accompanied by deviations from the unique $\Delta\tau/\tau$ line of slope ≈ 0.5 (Fig. 1).

(iii) The concentration dependence of the CRSS of Cu–Zn alloys at 298 K ($\tau \propto c^{0.28}$) is markedly different from that at 78 K ($\tau \propto c^{0.42}$) over the entire range of solute concentration i.e. 0.5 to 30 at % Zn. A unique $\Delta\tau/\tau$ curve for mono, as well as polycrystalline brasses is consequently quite different from that for the other copper alloys referred to.

Similarly the relationship between $\Delta\tau = \tau(78) - \tau(298)$ and $\tau(78)$ for some silver-based alloys, namely Ag–In [1, 14], Ag–Au [1], Ag–Sn [14, 15], Ag–Al [16] and Ag–Zn [17] has been shown in Fig. 6. The points have been obtained from the data given in the literature. Furthermore, Figs 7 and 8 depict the concentration dependence of the CRSS at 78 K and 298 K for the alloys referred to in Fig. 6; the τ/c data denoted by points have been plotted in log–log coordinates. The information available from Figs 6 to 8 can be summarized as follows.

(i) At both the temperatures involved, i.e. 78 K and 298 K, $\tau \propto c^{0.67}$ for Ag–In alloys (Fig. 7) and $\tau \propto c^{0.55}$ for Ag–Au alloys (Table I). However $\tau \propto c^{0.67}$ for Ag–Sn alloys at 78 K over the entire range of solute concentration (i.e. 0.03 to 2.0 at % Sn) whereas $\tau \propto c^{0.67}$ for $c \leqslant 0.25$ at % Sn and $\tau \propto c^{0.55}$ for $c > 0.25$ at % Sn at 298 K (Fig. 7). The deviation from the unique $\Delta\tau/\tau$ line of slope ≈ 0.5 for Ag–In, Ag–Au and Ag–Sn alloys occurs at $c \approx 0.25$ at % Sn

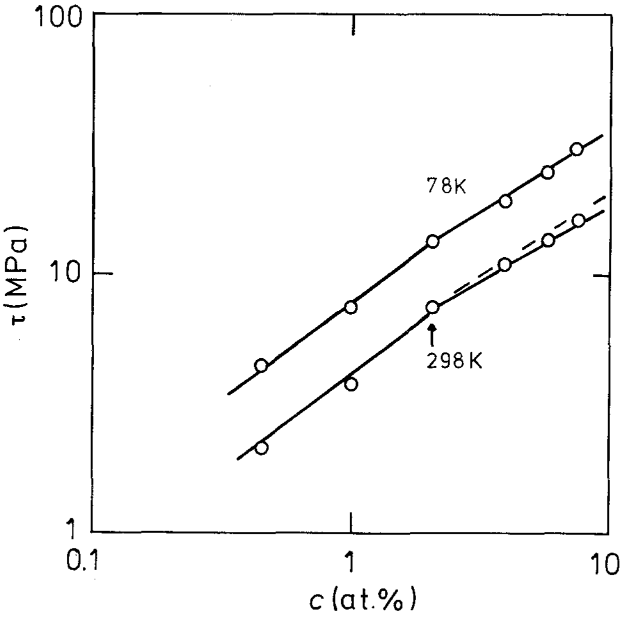

Figure 4 Concentration dependence of the CRSS of copper single crystals containing 0.5 to 7.3 at % germanium. Data points are from [8].

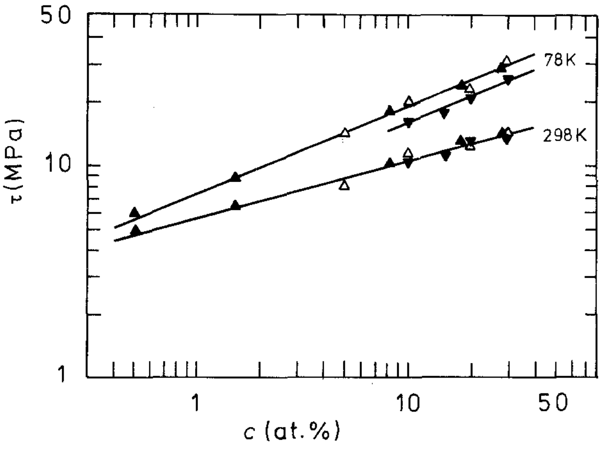

Figure 5 Concentration dependence of the CRSS of mono- and polycrystalline brasses (c = 0.5 to 30 at % Zn). ▲ Jamison and Sherrill [12], ▼ Butt and Feltham [6], △ Mitchell and Thornton [13].

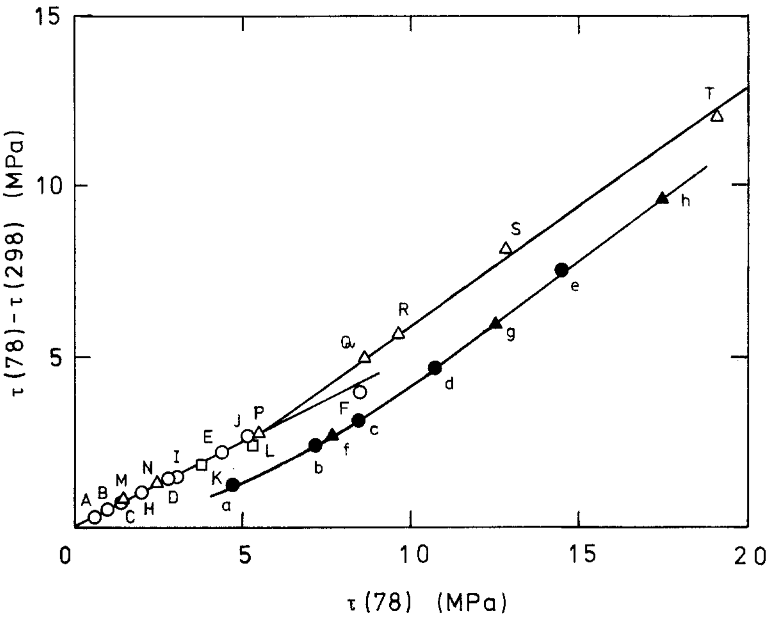

Figure 6 Relation between the difference in CRSS, $\tau(78) - \tau(298)$, and $\tau(78)$ for silver-based alloys. Data points have been taken from the literature: ○ Ag–In [1, 14], (A 0.05% In, B 0.1% In, C 0.2% In, D 0.5% In, E 1.0% In, F 2.5% In, H 0.28% In, I 0.45% In, J 0.95% In), □ Ag–Au [1] (K 10% Au, L 20% Au), △ Ag–Sn [14, 15] (M 0.03% Sn, N 0.08% Sn, P 0.25% Sn, Q 0.5% Sn, R 0.6% Sn, S 1.0% Sn, T 2.0% Sn), ● Ag–Al [16] (a 1% Al, b 2% Al, c 3% Al, d 4% Al, e 6% Al) and ▲ Ag–Zn [17] (f 2.2% Zn, g 5.6% Zn, h 7.8% Zn).

as a consequence of the change in the slope of the log τ–log c line at 298 K with respect to that at 78 K.

(ii) In the case of either Ag–Al or Ag–Zn alloys, values of the exponent r in the relation $\tau \propto c^r$ are 0.66 and 0.50 at 78 K and 298 K, respectively (Fig. 8). The data appertaining to these alloys fall on a unique $\Delta\tau/\tau$ curve, which is, however, different from that for the other silver alloys referred to.

3. Theoretical considerations and conclusions

It is clear from the above analysis that the loss of stress equivalence of the difference in CRSS between 78 K and 298 K cannot be explained in terms of the models of solid-solution hardening [18–23] which, unlike those given previously [2, 6, 24], do not take into account the effect of temperature on the concentration dependence of the CRSS of solid solutions. For instance, a common feature of Labushch's model [18, 19] as well as the kink-pair model [2, 6, 24] of solid-solution hardening is the involvement of groups of, rather than individual, atoms in the process of movement of dislocations. However, Labusch's model suggests that the CRSS of rather concentrated solid solutions is proportional to $c^{2/3}$ independent of temperature in the range 0 to $\frac{2}{3}$ T_{melt} [18, 19], whereas the kink-pair model predicts that for a given temperature the CRSS of solid solutions should be proportional to c^r with $\frac{1}{2} \leqslant r \leqslant 1$ [24], the larger r values occurring at higher temperatures. In fact, the kink-pair model remains valid up to temperatures e.g. 300 K for copper- and silver-based solid solutions, where no diffusional recovery processes occur in the crystal. The variation in the value of exponent r with temperature will therefore be rather small in the range 0 to $\frac{1}{3}$ T_{melt} for close-packed alloys. Furthermore, taking into account the concentration dependence of the parameters $U(< U_{\max})$, the mean binding energy between dislocations and solute atoms, as well as n, the number of interatomic spacings by which a kink-pair-like dislocation segment advances in an activated jump after breakaway from a row of closely-spaced solute–atom pinning points, the CRSS of dilute solid solutions ($c < 1$ at %) at 0 K should vary as $\tau_0 \propto c^{2/3}$ [2] instead of $\tau_0 \propto c^{1/2}$ envisaged for concentrated solid solutions ($c > 1$ at %) [6]. One can readily see from the numerical data (Table I) derived from Figs 2 to 5, 7 and 8 that, in general, the concentrated solid solutions

TABLE I The values of the exponent r in the relation $\tau(T) \propto c^r$ for copper- and silver-based alloys

Alloys	78 K		298 K	
	r	c (at %)	r	c (at %)
Cu-Al	0.81	0.01- 2.0	0.81	0.01- 2.0
	0.50	2.0 -11.0	0.50	2.0 -11.0
Cu-Mn	0.62	0.11- 7.7	0.62	0.11- 2.0
			0.53	2.0 - 7.7
Cu-Ge	0.76	0.5 - 2.0	0.76	0.5 - 2.0
	0.64	2.0 - 7.3	0.58	2.0 - 7.3
Cu-Zn	0.42	0.5 -30	0.28	0.5 -30
Ag-In	0.67	0.05- 2.5	0.67	0.05- 4.0
Ag-Sn	0.67	0.03- 2.0	0.67	0.03- 0.25
			0.55	0.25- 2.0
Ag-Au	0.55	10 -20	0.55	10 -20
Ag-Al	0.66	1.0 - 6.0	0.50	1.0 - 6.0
Ag-Zn	0.66	2.2 - 7.8	0.50	2.2 - 7.8

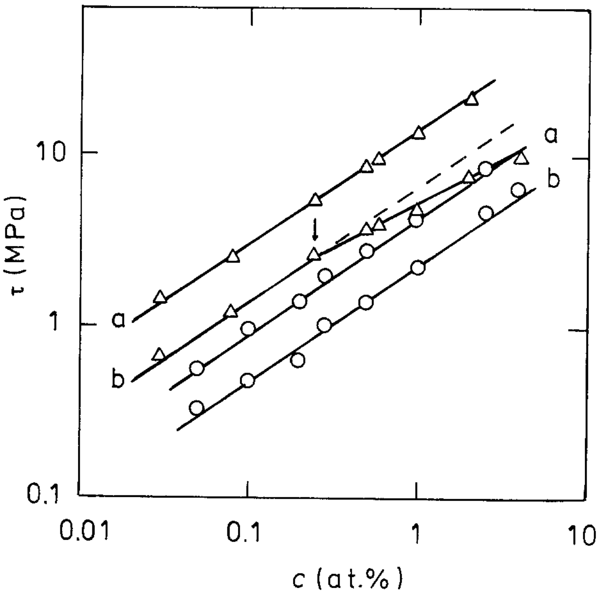

Figure 7 Concentration dependence of the CRSS of Ag–In (○) and Ag–Sn (△) single crystals referred to in Fig. 6. Data points are from [1, 14] and [14, 15], respectively. a 78 K, b 298 K.

follow $c^{1/2}$ law whereas the dilute alloys obey a $c^{2/3}$ law in accord with the kink-pair model of solid-solution hardening referred to above.

The main conclusions drawn from the preceding evidence are as follows.

(1) The $\Delta\tau/\tau$ data appertaining to solid solutions based on a given solvent metal fit to a single straight line of slope $d(\Delta\tau)/d\tau \approx 0.5$, irrespective of alloy concentration and solute type, if the value of exponent r in the relation $\tau(T) \propto c^r$ is independent of the temperature.

(2) Deviations from the unique $\Delta\tau/\tau$ line of slope ≈ 0.5 occur in the case of alloys for which the value of exponent r in the relation $\tau(T) \propto c^r$ varies with temperature.

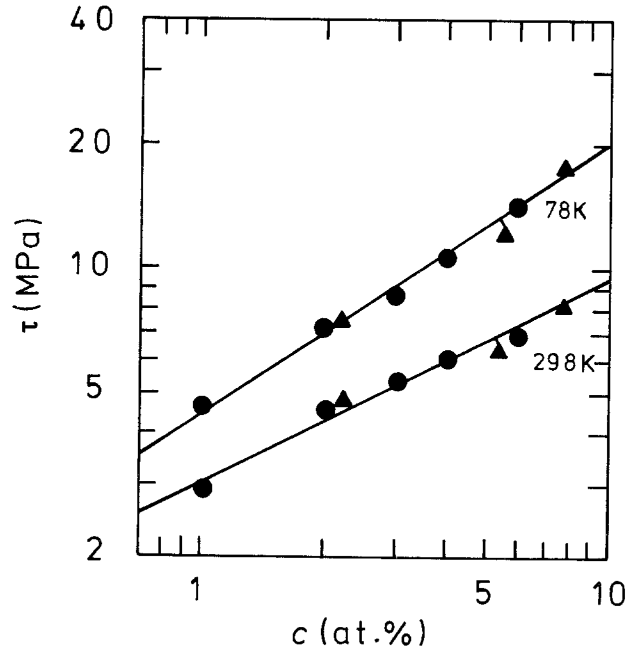

Figure 8 Concentration dependence of the CRSS of Ag–Al (●) and Ag–Zn (▲) single crystals referred to in Fig. 6. Data points are from [16] and [17], respectively.

(3) The critical concentration of the solute at which deviations from the unique $\Delta\tau/\tau$ line of slope ≈ 0.5 set in, i.e. stress equivalence is lost, depends on the alloy system, e.g. $c \approx 2$ at % Mn or Ge in copper alloys and $c \approx 0.25$ at % Sn in silver alloys.

(4) The data appertaining to solid solutions which exhibit identical τ/c dependence at a given temperature and the value of exponent r in the relation $\tau(T) \propto c^r$ varies with temperature in an identical manner fall on a single smooth $\Delta\tau/\tau$ curve, the value of the ratio $\Delta\tau/\tau$ being a function of τ.

(5) The observed concentration dependence of the CRSS of dilute as well as concentrated solid solutions correlates well with that predicted by the kink-pair model of solid solution hardening.

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