The Mechanism of Anneal Hardening in Dilute Copper Alloys

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Copper alloys containing 4 at. pct of a solute (Al, Au, Ga, Ni, Pd, Rh, and Zn) were cold worked and annealed below the recrystallization temperature to study the effect of different solute species on the anneal hardening. By measuring the flow stress at small bending strains, it was found that anneal hardening occurs with all solutes and that the magnitude increases with the misfit of the solute atoms. This indicates that solute segregation to dislocations and the resulting binding force is the primary cause of anneal hardening.

COPPER alloys are widely used as spring contact materials because of their conductivity, corrosion resistance, formability, nonmagnetic behavior, and large yield strength to elastic modulus ratio. One of the mechanisms employed to improve the mechanical properties of single-phase copper alloys is anneal hardening whereby considerable strengthening is attained when alloys in the cold rolled state are annealed at 425 to 575 K. However, the mechanism responsible for this hardening effect is incompletely understood.[1] The effect has been investigated mainly in copper base alloys[2-9] and some observations have been interpreted as indicating that atomic ordering is primarily responsible for the hardening effect.[7,8] On the other hand, in a recent detailed investigation of anneal hardening in Cu-Al alloys,[9] it was concluded that solute segregation to dislocations gives rise to the predominant hardening mechanism. If this is the case, dilute alloys should also show anneal hardening, and the magnitude should be related to those properties of the solute atoms which determine the extent and effectiveness of their segregation to dislocations. In order to test the validity of this conclusion, the present study was undertaken in which the anneal hardening behavior of a series of copper alloy solid solutions with constant solute content was investigated.

EXPERIMENTAL PROCEDURE

Seven binary copper alloys, each weighing approximately 0.2 kg and containing nominally 4 at. pct of a solute (Al, Au, Ga, Ni, Pd, Rh, Zn) were melted in an induction furnace and cast in chilled copper molds. Chemical analyses of the samples are given in Table I. The cast alloys were homogenized at 1123 K for six days in an evacuated quartz tube and subsequently cold rolled with intermediate anneals at 773 K, from 10 mm to approximately 0.5 mm; in order to obtain a comparable initial state in all specimens, a heat treatment of 723 K for 2 h followed by an ice-water quench was given. A final 50 pct reduction through rolling was then performed.

Mechanical properties were measured on punched-out foil strips. The samples were tested in four different conditions: 50 pct cold worked and 50 pct cold worked followed by a one h anneal at either 473, 523, or 573 K. Five samples were tested in each of these states. It has been shown that cold worked Cu-Zn[10] and Cu-Al[9] alloys exhibit property changes during storage at room temperature. These effects have been ignored in the present experiments since their magnitude can be considered negligible in comparison to effects arising from heat treatments at 473 K and higher.

The spring bending limit σ_{bE} was chosen to follow the anneal hardening behavior. This proof stress at small bending strains involves little plastic deformation and is, therefore, particularly suited to study the effect of dislocation unlocking while the contribution of the initial rate of work hardening is small. The σ_{bE} was measured according to the German standard DIN 50 151: a strip sample, 10 mm wide and approximately 0.25 mm thick, is loaded under three point bending; the load is increased in steps of equal magnitude; after removing the load, the residual deflection is determined; σ_{bE} is defined as the outer fiber stress causing a residual deflection which corresponds to an outer fiber strain under elastic conditions of $\epsilon_{el} = 3.75 \times 10^{-5}$. Due to the internal stresses within the bent foil, this residual strain is smaller than the total plastic strain induced during the test. The true plastic strain at the outer fiber has been estimated to be about 0.02 pct. Thus, the spring bending limit is determined by a

Table I. Chemical Analyses of Experimental Alloys

Solute	Concentration At. Pct	 Wt Pct
Al	3.97 ± 0.01	1.73
Au	3.99 ± 0.05	11.40
Ga	4.02 ± 0.05	4.40
Ni	3.75 ± 0.10	3.48
Pd	4.08 ± 0.02	6.64
Rh	*	
Zn	3.70 ± 0.20	3.80

*The rhodium content could not be analyzed. The mode of alloy preparation should ensure a concentration of (4.0 ± 0.1) at. pct.

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plastic strain varying from 0 in the neutral fiber to approximately 0.02 pct in the outer fiber. Consequently, σ_{bE} is found to be lower than $\sigma_{0.2}$ for identical samples,[1,11] with the ratio $\sigma_{bE}/\sigma_{0.2}$ depending on the rate of work hardening. In calculating σ_{bE}, the elastic modulus is needed, and this is determined for each sample, again under bending conditions.

In addition to the mechanical property measurements, some limited studies were undertaken using calorimetry, light microscopy, and transmission electron microscopy. The calorimetry was carried out on 50 pct cold worked samples using a differential scanning calorimeter. The samples, weighing approximately 100 mg, were heated at 30 K/min from 298 K to approximately 773 K, quenched to room temperature and reheated. Both light microscopy and electron microscopy samples were taken from strip samples already tested for their bending limit.

RESULTS

The values of the spring bending limit after cold working 50 pct and annealing for one h at different temperatures T_a are listed in Table II. The variation of σ_{bE} with annealing temperature is shown in Fig. 1. Each data point is the average of five measurements, with the standard deviation also given in the table. In the last two columns the maximum absolute and relative increase in σ_{bE} is listed; $\Delta\sigma_{bE}$ is defined as the difference between the maximum value of σ_{bE} observed and the initial value, σ_{bE}^{o}, in the cold worked state. Although a maximum in σ_{bE} *vs* annealing time is not reached in the Cu-Au, Cu-Pd, and Cu-Rh specimens, based on the recrystallization temperatures of the different alloys, a maximum in σ_{bE} is expected to occur below 623 K. This fact, combined with the relatively flat peaks of σ_{bE} *vs* annealing temperature, indicates the values chosen for σ_{bE} at 573 K are probably not significantly different from the true maximum of σ_{bE}.

For comparison, samples quenched from 723 K and annealed in the undeformed state were also measured. However, they were too soft to permit an exact measurement of their spring bending limit. A slight increase was noticed upon annealing.

The calorimetric tests indicated a heat release above 623 K corresponding to recrystallization. In addition, a small heat release at lower temperatures was observed in most alloys. Light microscopy and transmission microscopy were employed in order to detect the beginning of recrystallization in samples annealed at 573 K. Only in the Cu-Ga alloy was any evidence of recrystallization found by light microscopy. Transmission electron microscopy proved fruitless in detecting any early stages of recrystallization.

DISCUSSION

The hypothesis that led to the present experiments was that solute segregation to dislocations, analogous to the formation of Cottrell atmospheres in interstitial solid solutions, is primarily responsible for the anneal hardening phenomenon. If this is the case, the flow stress should be determined by the binding of solute atoms to dislocations. The interaction free energy $\Delta G(r)$ is given by the change in Gibbs free energy of a solid when a solute atom migrates from the "undistorted" crystal to a site at the termination of position vector r in a plane perpendicular to the dislocation line. The maximum interaction is given by $\Delta G(0) = G_B$, *i.e.* by the binding free energy of a solute atom at the dislocation core. An amount of work, proportional to G_B, is required to unlock the dislocation from the solute atom such that G_B is a measure of the increase in flow stress due to solute segregation to dislocations.

The solutes studied in the present experiments were chosen based on their differences in atomic radius, in

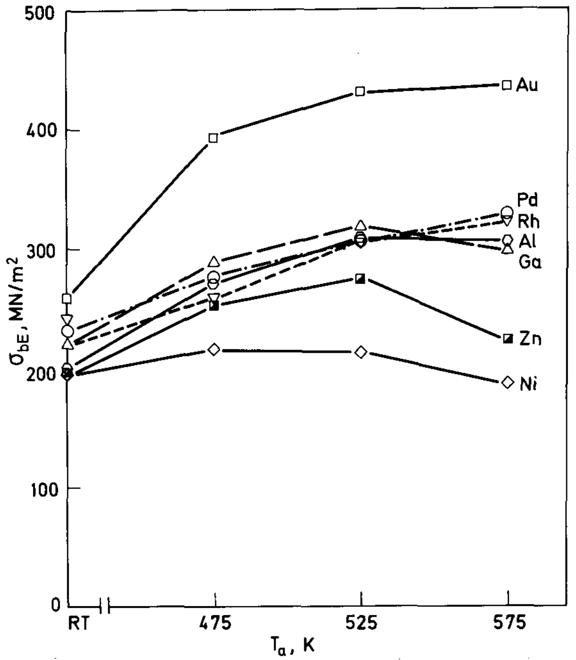

Fig. 1—Spring bending limit, σ_{bE}, *vs* annealing temperature, T_a, for the alloys investigated.

Table II. Spring Bending Limit σ_{bE}(MN/m^2) after Cold Working 50 Pct and Subsequently Annealing for 1 h

	As-Cold Worked		T_a = 473 K		T_a = 523 K		T_a = 573 K		Maximum Increase	Maximum Relative Increase
Solute	σ_{bE}^{o}	Standard Deviation	σ_{bE}	Standard Deviation	σ_{bE}	Standard Deviation	σ_{bE}	Standard Deviation	$\Delta\sigma_{bE}$	$\Delta\sigma_{bE}/\sigma_{bE}^{o}$
Al	200	11	271	17	309	5	306	15	109	0.55
Au	259	14	393	20	431	21	436	11	177	0.68
Ga	220	7	288	12	319	11	298	1	99	0.45
Ni	195	11	216	19	213	23	187	42	21	0.11
Pd	232	27	277	17	307	16	329	9	97	0.42
Rh	241	21	258	16	306	11	323	10	82	0.34
Zn	196	5	252	5	274	6	224	34	78	0.40

elastic moduli and in valence electron concentration because these are expected to yield the main contributions to G_B. Since,

$$G_B = H_B - TS_B \qquad [1]$$

where H_B and S_B are the binding enthalpy and binding entropy, respectively, a complete and exact treatment would require analysis of all contributions to both H_B and S_B. However, a review of the subject[12] shows that only the major contributions to H_B are tractable with reasonable accuracy and that the magnitude of S_B is comparatively small. In the present context we have considered the following three major contributions to the binding enthalpy H_B; elastic interaction due to the size misfit of the solute atoms, H_B^s; elastic interaction due to the modulus effect of the solute atoms, H_B^m; electrical interaction of the electrical field of the dislocation with the net effective charge of solute atoms, H_B^e.

For edge dislocations, the elastic interaction is given by:

$$H_B^s = -4\mu r_o^3 \kappa_a \qquad [2]$$

where μ = shear modulus, r_o = solvent radius, r_{eff} = effective solute radius, and $\kappa_a = (r_{\mathrm{eff}} - r_o)/r_o$. Using the shear modulus data of Hopkin *et al*[13] and the effective solute radii from King,[14] the values for H_B^s (edge) were calculated. A plot of $\Delta\sigma_{bE}$ *vs* H_B^s is presented in Fig. 2. The data show that to a good approximation the change in flow stress is proportional to the size misfit contribution to H_B.

In terms of the relations compiled by Fiore and Bauer,[12] we have also computed H_B^m for edge and screw dislocations. However, the absolute magnitude of this contribution is about one order of magnitude smaller than that of H_B^s. In view of the experimental error in determining σ_{bE} and the uncertainties in the calculation of H_B^m, the resulting slight improvement of the linear relation between $\Delta\sigma_{bE}$ and H_B was not considered significant.

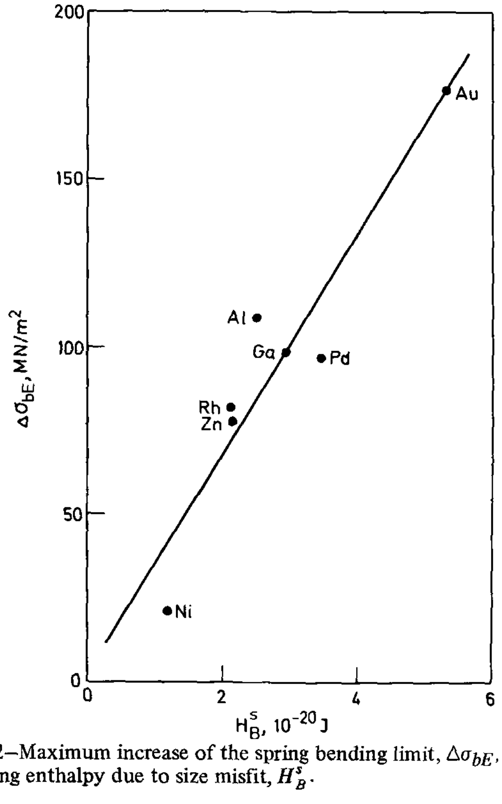

Fig. 2—Maximum increase of the spring bending limit, $\Delta\sigma_{bE}$, *vs* binding enthalpy due to size misfit, H_B^s.

The electrostatic contribution H_B^e cannot be assessed in a simple manner because it is proportional to the effective charge difference between the solute and solvent atoms in the vicinity of a dislocation. Moreover, the electrical and size misfit interactions may attract a solute atom to different positions (compression or tension side) around an edge dislocation. The estimated magnitude of the contribution is once again small compared to the size misfit term. Nonetheless, it is interesting to note that the sign of the charge difference, Δq, of a solute with respect to copper, given by its relative position in the periodic system (Rh: –2; Ni, Pd: –1; Au: 0; Zn: 1; Al, Ga: 2) is in general related to the sign of the deviation of the data points from a straight line in Fig. 2.

From these considerations it may be concluded that the unlocking stress, measured as $\Delta\sigma_{bE}$, which is caused by solute segregation to dislocations is the origin of anneal hardening. The unlocking stress was found to be determined by the binding enthalpy H_B at temperatures where solute diffusion is negligible. The dominant contribution to H_B is due to the solute size misfit in the host lattice. Ordering effects do not appear to be a major contribution since this study has shown that anneal hardening occurs at the 4 at. pct solute level where ordering effects are absent or negligibly small. Since the present results are based on alloys of constant solute content and degree of deformation, $\Delta\sigma_{bE}$ could be related directly to H_B. In alloys of different solute concentration and deformation, the magnitude of anneal hardening would have to be corrected accordingly, as suggested in an earlier paper.[9]

Apart from the increase in σ_{bE} caused by anneal hardening, there is also an increase in $\sigma_{0.2}$, but it is smaller by about an order of magnitude.[4,9,11] Considering that σ_{bE} represents a proof stress of the order of $\sigma_{0.02}$ in the outer fiber only (and a still lower average proof strain for the total cross-section), it is obvious that this stress is associated with the processes determining the onset of flow to a much larger degree than $\sigma_{0.2}$ which is the stress required after 0.2 pct tensile plastic strain has occurred in the entire specimen volume. Therefore, σ_{bE} will be dominated by the unlocking stress whereas a tensile proof stress such as $\sigma_{0.2}$ and those measured at still higher proof strains will represent, increasingly, the interactions of unlocked and newly formed dislocations with the dislocation forest, *i.e.* the initial rate of work hardening. Therefore, σ_{bE} is a very suitable measure of the effect of anneal hardening. This conclusion was corroborated while this paper was under review through an investigation of the anneal hardening of nickel alloys by both σ_{bE} and tensile measurements. These showed that proof stress values such as $\sigma_{0.01}$ and $\sigma_{0.02}$ are indeed increased by anneal hardening much more than $\sigma_{0.2}$ or even $\sigma_{0.5}$ and $\sigma_{1.0}$.[20]

An upper and lower yield point, the classical indication of dislocation locking, has not been observed in anneal hardened specimens so far. This absence of a yield drop is not surprising since the initial cold worked state of the sample and the concentration gradients established by the annealing treatment result in a broad spectrum of internal stresses such that the local yield stresses vary accordingly. Moreover, the formation of highly localized slip bands and corresponding large displacements should be suppressed by the preexisting dense dislocation structure.

Further evidence for the effect of solute segregation on the deformation behavior of Cu base solid solutions is provided by stress relaxation[11] and creep[16] data. A number of experimental and commercial cold worked copper alloys were tested for their stress relaxation behavior in the as-cold worked and in cold worked plus annealed conditions. It was observed that the amount of stress relaxation was reduced considerably in the annealed condition; the reduction is related to the species and concentration of the alloying elements. The steady state creep rate in Cu solid solutions can be described by:[16]

$$\dot{\epsilon}_{s,T} = A\,(\sigma - \sigma_0)^n \qquad [3]$$

with a common stress exponent $n \simeq 4$ if a friction stress σ_0 is introduced which depends on the solute species and which can be correlated with the dislocation/solute interaction. It should be noted, however, that thermally activated processes determine these time dependent deformation effects such that they do not depend on H_B by a simple, linear relationship.

Finally, some property changes other than hardening response during annealing may be considered in support of solute segregation to dislocations. In the previous investigation of anneal hardening of a Cu-Al alloy,[9] it was shown that the major decrease in electrical resistivity during annealing cannot be accounted for by short range ordering. It was concluded that segregation to dislocations is the only consistent interpretation for the major portion of the change in resistivity. A similar conclusion was drawn by Klimanek[17] regarding analogous investigations of α-Cu-Zn alloys. In both systems the segregation effect was found to be predominant while additional ordering as a secondary contribution could not be excluded. Similarly, the exothermic heat effect of deformed specimens of Cu-Al upon heating[7] was found to be considerably higher than the effect expected from short range ordering.[9] Moreover, exothermic heat effects were found even in 4 and 6 at. pct Al specimens which should not show any significant ordering. The limited calorimetric measurements on the present alloys are consistent with those findings. All solutes, with the possible exception of Ni, gave rise to a heat evolution below the recrystallization peak attributable to the segregation effect. The effects were rather broad and weak and did not allow for quantitative evaluations. Lattice parameter changes of cold worked α-Cu-Zn during annealing[18] have also led to the conclusion that solute clustering at dislocations should be one of the major causes of the observed changes.

The anneal hardening effect is well known for Cu-base solid solution alloys. This is due to the fact that these alloys are widely used as spring contact materials where strength in the elastic/plastic limit is of primary significance and has, therefore, been investigated intensively. Anneal hardening has also been found in the Al-Cr system[19] where a size misfit of about 5 pct exists, similar to the magnitude of the misfit in the Cu-Rh system.

CONCLUSIONS

1) The anneal hardening effect of a number of Cu alloys at the 4 at. pct solute level is found to be proportional to the binding enthalpy of misfitting solute atoms to dislocations.

2) It is concluded that solute segregation to dislocations and the ensuing unlocking stress is the primary cause of the anneal hardening effect.

3) The contribution of anneal hardening to the flow stress appears to decrease rapidly with increasing plastic strain.

4) Ordering effects are not a primary cause of anneal hardening but may contribute to it.

5) Anneal hardening may be considered as a genuine hardening mechanism in analogy to other basic hardening mechanisms such as work, grain size, solid solution, or dispersion hardening.

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