USE OF THE INTERNAL FRICTION TECHNIQUE TO MEASURE RATES OF GRAIN BOUNDARY SLIDING*

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Since boundaries are usually non-planar (the bamboo structure is an exception), sliding at boundaries must be accompanied by an accommodation process. Small amounts of total sliding (~100 Å or strains $\sim 10^{-4}$) can be accommodated by elastic strains in the neighboring grains; this sliding is recoverable and hence the sliding strain is "anelastic." The relaxation time associated with the elastically accommodated sliding can be measured by the internal friction technique. This relaxation time has been calculated when inclusions of size "p" are present in the boundaries of a polycrystal of grain size "d" where $p \ll d$. It is assumed that sliding across the inclusions is accommodated by boundary diffusion of vacancies, whereas the total overall sliding is determined by the elastic deformation of the grains. Results from the internal friction measurements in polycrystalline copper (with SiO_2 or GeO_2 inclusions) are shown to be in agreement with the theoretical relaxation times.

MESURE PAR FROTTEMENT INTERIEUR DE LA VITESSE DE GLISSEMENT AUX JOINTS DE GRAINS

Les joints n'étant généralement pas plans (la structure en bambou est une exeption), le glissement aux joints doit être accompagné d'un processus d'accommodation. Une petite partie du glissement total (~100 Å, ou déformation de $\sim 10^{-4}$) peut être accommodée par des contraintes élastiques dans les grains voisins; ce glissement est récupérable et la déformation de glissement est donc "anélastique." On peut mesurer par la technique du frottement intérieur le temps de relaxation associé au glissement accommodé élastiquement. Ce temps de relaxation a été calculé lorsque des inclusions de taille "p" sont présentes dans les joints d'un polycristal dont la taille des grains est "d," avec $p \ll d$. On suppose que le glissement à travers les inclusions est accommodé par la diffusion intergranulaire de lacunes, alors que le glissement total est déterminé par la déformation élastique des grains. On montre que les résultats des mesures de frottement intérieur dans du cuivre polycristallin (avec des inclusions de SiO_2 ou de GeO_2) sont en accord avec les temps de relaxation théoriques.

UNTERSUCHUNG DES KORNGRENZENGLEITENS DURCH MESSUNG DER INNEREN REIBUNG

Da Korngrenzen normalerweise nicht-planar sind (die Bambusstruktur ist eine Ausnahme) muß mit der Gleitung an Korngrenzen ein Akkommodationsprozeß verbunden sein. Kleine Abgleitungen (~100 Å oder $\sim 10^{-4}$) können durch elastische Spannungen in den benachbarten Körnern akkomodiert werden. Diese Gleitung kann sich erholen und die Dehnung ist somit "anelastisch." Die mit der elastisch akkommodierten Gleitung verbundene Relaxationszeitka nn durch Messung der inneren Reibung bestimmt werden. Diese Relaxationszeit wurde für die Anwesenheit von Einschlüssen der Größe "p" in den Korngrenzen eines Vielkristalls der Korngröße "d" ($p \ll d$) berechnet. Es wird angenommen, daß Gleitung durch die Einschlüsse durch Grenzflächendiffusion von Leerstellen akkommodiert wird, während die Gesamtgleitung durch die elastische Verformung von Körnern bestimmt wird. Die Ergebnisse aus Messungen der inneren Reibung von polykristallinem Kupfer (mit SiO_2-oder GeO_2-Einschlüssen) sind in Übereinstimmung mit den theoretischen Relaxationszeiten.

1. INTRODUCTION

Although large numbers of observations of grain boundary damping in internal friction experiments have been reported since the identification by Kê(1,2) of the phenomenon, details of the basic mechanisms are yet to be adequately documented. Among the suggested models have been grain boundary sliding,(1–4) the migration of grain boundary protrusions,(5) damping by dislocations in grain boundaries(6) and grain boundary migration.(7,8) The present paper presents evidence in support of the grain boundary sliding model.

In a polycrystal, grain boundary sliding can be accommodated by elastic deformation of the grains. Such sliding leads to an apparently lower shear modulus of the polycrystal; this has been calculated.(3,4) The additional strain due to sliding is anelastic since it is recoverable upon the removal of the applied stress and since it is accumulated and discharged with a characteristic relaxation time which is a function of the viscosity of grain boundary sliding. This relaxation time can be measured in an internal friction experiment.

This paper presents the results of an investigation in which grain boundary sliding viscosity was controlled by introducing GeO_2 or SiO_2 particles into the grain boundaries of a copper polycrystal. The viscosity was calculated using the procedure of Raj and Ashby(4) which has been tested in an earlier experiment.(9) In the calculation sliding across the particles is assumed to be accommodated by the diffusive flux of copper. Next the relaxation time was calculated using a procedure described herein. Internal friction experiments were performed to measure these relaxation times. Satisfactory agreement was obtained with the analytical results. The measurements also confirmed the theoretically predicted dependence of boundary sliding viscosity upon the particle size, particle spacing and the grain size.

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2. THEORY

2.1 *Analysis of the relaxation time*

Consider a polycrystal containing inclusions in the grain boundaries as shown in Fig. 1. When a stress (lower than the yield stress) is applied to the polycrystal the following happens: First there is an instantaneous elastic deformation. As grain boundaries begin to slide, further elastic deformation of the grains occurs, back stresses opposing the sliding build up and the sliding comes to a halt; this is sliding by elastic accommodation. The rate at which this sliding occurs is dependent upon the intrinsic viscosity of the boundary, and the rate at which sliding across the particles is accommodated. The latter is controlled by the diffusion flux of copper atoms around the particles.(4,9) If we wait longer the entire polycrystal can deform in a viscous manner by the diffusion of copper atoms across the grains; this is described as the deformation of the polycrystal due to diffusion-accommodated sliding.(4)

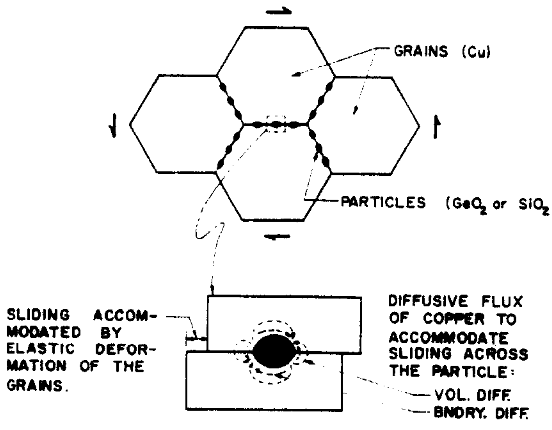

FIG. 1. Sliding by elastic accommodation results in anelasticity. The rate of sliding is controlled by diffusive accommodation of sliding across the particles.

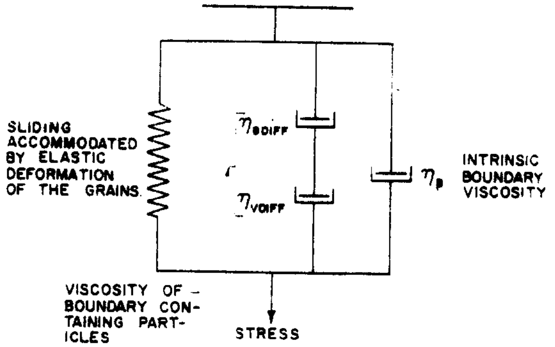

FIG. 2. A spring–dashpot in a polycrystal due to sliding. η_B is the sliding viscosity of a planar boundary. η_{BDIFF} and η_{VDIFF} are the sliding viscosities of a boundary containing particles where the sliding across the particles is accommodated by boundary diffusion (η_{BDIFF}) or volume diffusion (η_{VDIFF}). Usually η_{BDIFF} or $\eta_{VDIFF} \gg \eta_B$.

Here we are concerned only with the anelastic deformation of the polycrystal; i.e. sliding accommodated by elastic deformation of the grains. A spring–dashpot model, Fig. 2, describes the various parameters which are relevant in the problem. The spring stiffness describes the total sliding strain available at a given applied stress. The three dashpots describe the viscosities which control the rate at which the sliding can accumulate. η_B is the intrinsic viscosity of a particle-free, planar boundary. η_{BDIFF} and η_{VDIFF} are the additional resistances to sliding introduced by the necessity of accommodating sliding across the particles by diffusion of copper atoms. Kê, in his experiments with polycrystals of pure metals, measured η_B. More recently η_{BDIFF} and η_{VDIFF} have been calculated(4) and shown to be valid in sliding experiments with bicrystals.(9) For particles impermeable to diffusion, of dia p and with interparticle spacing λ, the sliding viscosities are given by:

$$\eta_{BDIFF} = \frac{\delta}{8} \cdot \frac{kT}{\Omega} \cdot \frac{p^4}{\lambda^2} \cdot \frac{1}{\delta D_B} \tag{1}$$

$$\eta_{VDIFF} = \frac{\delta}{1.6} \cdot \frac{kT}{\Omega} \cdot \frac{p^3}{\lambda^2} \cdot \frac{1}{D_V} \tag{2}$$

where the sliding viscosity obeys the relation.

$$\tau_a = \frac{\dot{U}}{\delta} \cdot \eta. \tag{3}$$

Here τ_a is the average shear stress across the boundary, $\dot{U}$ is the rate of sliding, δ is the grain boundary thickness, Ω is the atomic volume and D_B and D_V are the self-diffusion coefficients for grain boundary and volume diffusion.

The problem of total sliding from elastic accommodation has also been solved.(4) In this approach the boundary was considered to be of a periodic undulating shape. In the general case the shape was described by a Fourier series:

$$x = \sum_{n=1}^{\infty} h_n \cos \frac{2\pi}{L} ny \tag{4}$$

where L is the periodicity, and the results were expressed in terms of the Fourier coefficients $h_n{}^s$. In the Appendix to this paper the equivalent solution for the transient problem is given. For a boundary of a general sliding viscosity η, the result is:

$$U(t) = \frac{\tau_a}{\beta}(1 - e^{-t/\tau}), \tag{5}$$

where the relaxation time

$$\tau = \frac{\eta}{\delta\beta}, \tag{6}$$

and

$$\beta = \frac{E}{(1-\nu^2)}\frac{\pi^3}{L^3}\sum_{n=1}^{\infty} n^3 h_n^{\,2}. \tag{7}$$

Here $U(t)$ is the time dependent sliding, while E and ν are Young's Modulus and Poisson's Ratio, respectively.

For an equiaxed grain structure, considering both possible sliding modes (Fig. 2.3, ref. 4), β is given by:

$$\beta_{EQUIAXED} = \frac{1}{1.14}\cdot\frac{E}{(1-\nu^2)}\cdot\frac{1}{d}, \tag{8}$$

where d is the grain size of the polycrystal. The relaxation time τ can now be calculated from equations (1–3, 6 and 8). In our experiments we expect boundary diffusion to be the rate controlling mechanism for accommodation of sliding across the inclusion; the relaxation time for this case is given by:

$$\tau = 0.14\cdot\frac{kT(1-\nu^2)}{E\Omega}\cdot\frac{p^4 d}{\lambda^2}\cdot\frac{1}{\delta D_B}. \tag{9}$$

2.2 *Calculation of sliding viscosities*

We will now show that, in the presence of particles, the rate controlling viscosity for the model in Fig. 2 is η_{BDIFF}. First we calculate the intrinsic viscosity η_B using the data of Weinig and Machlin(13) from their experiments with pure copper. They observed a peak at 300°C for a frequency of 1.2 Hz and a grain size of 0.06 mm, and determined an activation energy of 33 kcal/mole for the relaxation. Substituting the above data in equation (6), along with the following physical constants for copper: Young's modulus 12.7×10^{11} dyn/cm², Poisson's ratio 0.35 and atomic volume 1.1×10^{-23} cm³, we obtain

$$\frac{\eta_B}{\delta} = 7.1 \exp(\Delta H/RT)\ \mathrm{P/cm} \tag{10}$$

where $\Delta H = 33$ kcal/mole. Since δ is an arbitrary parameter in all calculations involving the sliding viscosity, we have normalized the viscosity to viscosity per unit thickness of boundary.

In boundaries containing particles, the viscosity is calculated via equations (6 and 9). A lower bound of this viscosity in our experiments can be calculated using the smallest particle size (p) and the largest interparticle spacing (λ) observed for our specimens. For $p = 0.2\ \mu$, $\lambda/p = 10$ and diffusion coefficients $D = D_0 \exp(-\Delta H/RT)$, where $D_{0B} = 0.1$ cm²/sec†, $\Delta H_B = 24.8$ kcal/mole†, $D_{0V} = 0.62$ cm²/sec and $\Delta H_V = 49.6$ kcal/mole, we obtain:

$$\frac{\eta_{BDIFF}}{\delta} = 1.6 \times 10^6 e^{\Delta H_{B}/RT}\ \mathrm{P/cm} \tag{11a}$$

$$\frac{\eta_{VDIFF}}{\delta} = 2.5 \times 10^3 e^{\Delta H_{V}/RT}\ \mathrm{P/cm}. \tag{11b}$$

Consideration of Fig. 2 with the above values for boundary viscosities leads to the conclusion that in the presence of particles the viscosity in equation [11a] will be rate controlling. We would expect the peak to occur at a higher temperature than the pure metal peak (corresponding to η_B), to have an activation energy equal to that for boundary diffusion, and to shift with particle size, particle spacing and grain size in accordance with equation (9). Results for such experiments are now described.

3. EXPERIMENTAL METHOD

3.1 *Specimen preparation*

Cu–Ge and Cu–Si alloys were prepared by vacuum melting high purity (99.999% or better) components in a high frequency induction furnace. The Cu–Ge alloys ranged in composition from approx 0.1 wt% to 0.2 wt% of Ge, while the Cu–Si alloy contained approx 0.1 wt% Si. These were all cold drawn into 0.031 in. dia wires. Appropriate lengths were internally oxidized by heating them in a mixture of alumina, cuprous oxide and copper powders (equal parts) at 850°C for 24 hr. Grain size and the size and distribution of particles in the grain boundaries (Fig. 3 is a representative structure) were determined metallographically following the internal friction measurements. Grain size was measured by the intercept technique (intercepting at least 20 gr); averages of at least 50 particles were used to characterize their size and spacing. The measurements for all samples are listed in Table 1.

3.2 *Internal friction measurements*

5½ in. long specimens were tested in an inverted torsional pendulum as described elsewhere,(10) except that a tubular stainless steel radiation heater was used for specimen heating. Specimen temperatures were deduced from the condition of equality between grip temperatures and that of the radiation heater. Specimens were given a slight axial strain after installation in the apparatus to assure straightness, followed by annealing *in situ* for 1 hr at 900°C to stabilize the structure. Careful counterbalancing of the pendulum bob was necessary to avoid axial creep. Damping measurements were made at frequencies in the range 0.3–2 Hz at maximum strain amplitudes

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† The self diffusion coefficient for boundary diffusion in copper has not been measured. It was derived by analogy with silver where direct measurements have been made.(12)

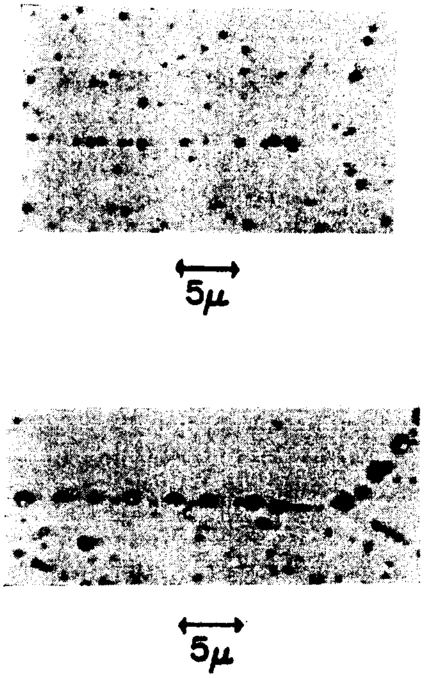

FIG. 3. Representative microstructures of Cu–SiO$_2$ (upper) and Cu–GeO$_2$ (lower) alloys. Samples were electropolished in a solution of 2 parts CH$_3$OH and 1 part HNO$_3$ at −20°C.

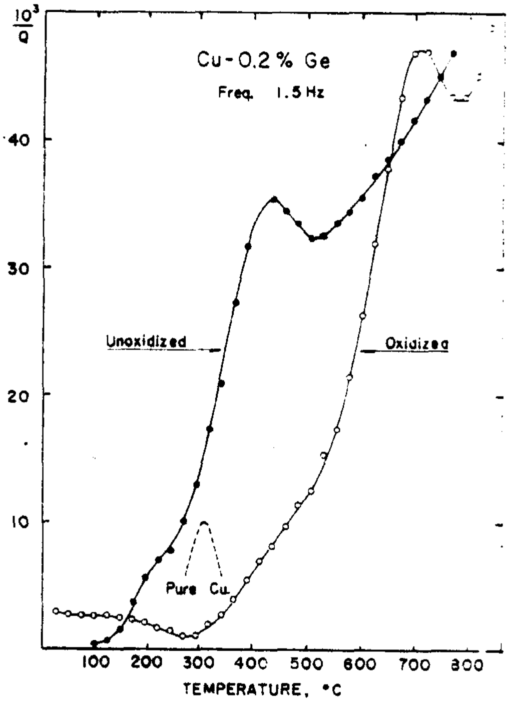

FIG. 4. Damping spectra of Cu–0.2% Ge before and after internal oxidation. Boundary sliding-viscosities are increased by the introduction of GeO$_2$ particles, displacing the damping peak to higher temperatures.

of less than 10^{-4} over the temperature range from room temperature to about 900°C.

4. RESULTS AND DISCUSSION

4.1 *The damping spectra*

A comparison of the damping spectra of the solid solution alloys (Cu–Ge and Cu–Si) and the internally oxidized alloys containing particles (Cu–GeO$_2$ and Cu–SiO$_2$) is given in Figs. 4 and 5. Since the solute peak† in the solid solution alloys suppresses the pure metal peak (both peaks have been observed at low solute concentration), the approximate position of the pure metal peak has been indicated for comparison. As expected, the peak for the grain boundaries with particles occurs at a temperature higher than that for the pure metal. Disappearance of the solute peak is attributed to removal of solute from the grain boundaries by oxidation.

4.2 *Comparison of results with equation* (9)

In order to determine if equation (9) is a valid description of the grain boundary sliding peak in the presence of particles, experiments were performed with different distributions of particle size and spacing in the grain boundary. The complete results are tabulated in Table 1. The relaxation time τ for comparison

TABLE 1. Summary of experimental data

Sample	Symbol	Grain size (cm)	Particle size (μm)	Particle spacing (μm)	Freq. (Hz)	Peak temp. (°C)
Cu–GeO$_2$	△	0.035	0.60	2.87	1.48	685
					0.34	633
Cu–GeO$_2$	○	0.010	0.68	3.19	0.36	583
					0.95	621
					1.80	654
Cu–GeO$_2$	□	0.075	0.58	2.25	2.05	631
					1.10	567
					0.35	538
Cu–GeO$_2$	◇	0.014	0.60	6.28	2.25	579
					0.33	485
					1.71	532
Cu–SiO$_2$	●	0.021	0.82	2.53	1.45	649
					0.34	595

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† The solute peaks observed by us are in agreement with the findings of Rotherham and Pearson.(11)

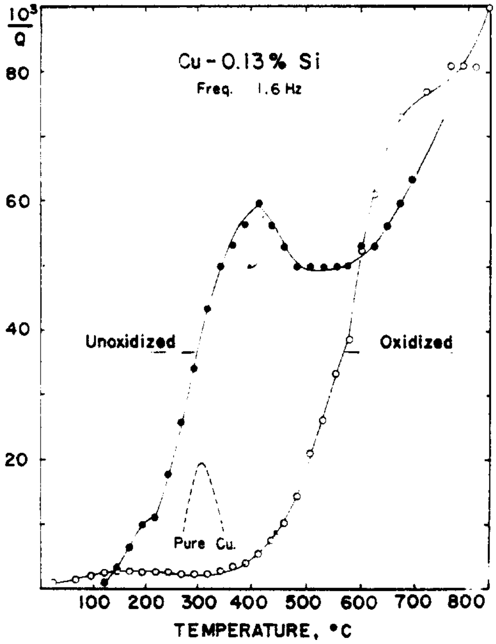

FIG. 5. Damping spectra of Cu–0.13% Si before and after internal oxidation. Boundary sliding-viscosities are increased by the introduction of SiO_2 particles, displacing the damping peak to higher temperatures.

with equation (9) was calculated from the condition $\omega\tau = 1$ where $\omega = 2\pi f$ is the frequency of oscillation at the damping maximum.

In all, five samples were tested. Relaxation times for the various tests are plotted logarithmically against reciprocal absolute temperature in Fig. 6, where it may be noted that the activation energies range from 25 to 37 kcal/mole.

Comparison of the experimental results with theoretical results from equation (9) is shown on the master curve in Fig. 7. Normalization of the relaxation time for the variables of the experiment (excepting temperature), leads to the following modification of the equation (9):

$$\tau \cdot \frac{\lambda^2}{p^4 d} = 0.14\,\frac{kT(1-\nu^2)}{E\Omega}\cdot\frac{1}{\delta D_B}.^{\dagger} \qquad (12)$$

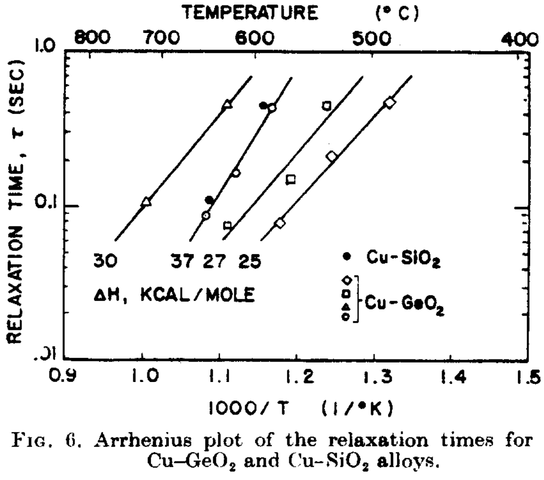

FIG. 6. Arrhenius plot of the relaxation times for the $Cu–GeO_2$ and $Cu–SiO_2$ alloys.

The theoretically calculated curve for the right hand side of the equation and the experimental measurements of the left hand side of the equation are plotted in Fig. 7. The values of the constants in the above equation have been given in Section 2.2.

Figure 7 demonstrates that the normalization reduces the spread in relaxation times from a factor of 10 (Fig. 6) to a factor of 2, and gives an average activation energy of 28 kcal/mole, which is about the value expected for boundary diffusion of copper. The vertical shift between the experimental and the theoretical lines can be attributed to error in the pre-exponential factor for D_B in equation (12).

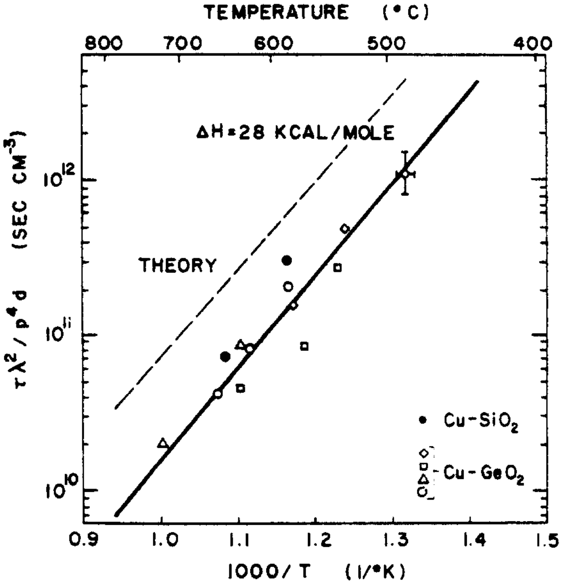

FIG. 7. Arrhenius plot of the relaxation times normalized with respect to grain size (d), particle size (p) and interparticle spacing (λ). The theory line represents the result predicted according to equation (12).

We interpret this to mean that the grain boundary damping peaks observed in $Cu–GeO_2$ and $Cu–SiO_2$ alloys result from grain bounday sliding accommodated by elastic deformation of the grains. The rate of sliding is controlled by the rate at which boundary diffusion of copper can accommodate sliding across the GeO_2 and SiO_2 particles.

5. SUMMARY AND CONCLUSIONS

Grain boundary damping peaks in solid solution Cu–Ge and Cu–Si alloys and in $Cu–GeO_2$ and $Cu–SiO_2$

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† The validity of equation (12) has been demonstrated in an earlier experimental study on sliding in bicrystals.[19]

alloys (containing particles) were measured. The peaks were attributed to grain boundary sliding with elastic accommodation because:

(a) Introduction of particles into the boundaries caused the peaks to shift to a higher temperature, which is indicative of a decrease in sliding rate.

(b) The relaxation time for sliding in alloys with particles varies with particle size and spacing and with grain size in accordance with the model of Raj and Ashby,(4) the validity of which has been verified in an earlier experiment.(9)

(c) The activation energy of the relaxation is in agreement with that for boundary diffusion of copper. This supports the model in which the sliding rate is controlled by diffusive accommodation around the particles.

We further conclude that internal friction measurements provide a useful method for measuring rates of grain boundary sliding with elastic accommodation.

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APPENDIX

An analysis is presented here for the time dependent rate of sliding which is accommodated elastically. The shape of the grain boundary is given by equation (4). From equations (2 and 3) in reference,(4) the total sliding $\bar{U}$ and the normal stress at the boundary σ_n as a result of an applied stress τ_a are given by:

$$\bar{U} = \frac{(1-\nu^2)}{3}\cdot L^3 \frac{1}{\sum_{n=1}^{\infty} n^3 h_n^2}\cdot\frac{\tau_a}{E}, \qquad \text{(A1)}$$

and

$$\sigma_n = -\frac{\tau_a L}{\pi}\frac{\sum_1^{\infty} n^2 h_n \sin(2\pi/L)ny}{\sum_1^{\infty} n^3 h_n^2} \qquad \text{(A2)}$$

where L is the periodicity and h_n are Fourier coefficients of the boundary shape. E and ν are the Young's Modulus and the Poisson's Ratio. The relation between U and σ_n at any instant is obtained by eliminating τ_n from the above two equations:

$$\sigma_n(t) = -\frac{E}{(1-\nu^2)}\frac{\pi^2}{L^2}\sum_1^{\infty} n^3 h_n^2 \sin\frac{2\pi}{L}ny\cdot U(t). \qquad \text{(A3)}$$

The shear stress across the boundary at time t, $\tau_B(t)$ will be given by:

$$\tau_B(t) = \tau_a - \frac{2}{L}\int_0^{L/2}\sigma_n(t)\cdot\tan\theta\cdot \mathrm{d}y \qquad \text{(A4)}$$

where $\tan\theta$ is the slope of the boundary and is given by:

$$\tan\theta = \frac{\mathrm{d}x}{\mathrm{d}y} = -\frac{2\pi}{L}\sum_1^{\infty} nh_n \sin\frac{2\pi}{L}ny. \qquad \text{(A5)}$$

Substituting for $\sigma_n(t)$ and using the integral:

$$\frac{2}{L}\int_0^L \sin\frac{2\pi}{L}ny \sin\frac{2\pi}{L}my\,\mathrm{d}y = \begin{matrix} 0 & m \neq n \\ \frac{1}{2} & m = n \end{matrix}$$

we obtain

$$\tau_B(t) = \tau_a - \beta U(t), \qquad \text{(A6)}$$

where

$$\beta = \frac{E}{(1-\nu^2)}\cdot\frac{\pi^3}{L^3}\sum n^3 h_n^2. \qquad \text{(A7)}$$

Using the equation for boundary viscosity η and taking δ as the boundary thickness

$$\frac{\dot{U}(t)}{\delta} = \frac{\tau_B(t)}{\eta}$$

and combining it with (A7) leads to

$$\dot{U} = \left[U - \frac{\tau_a}{\beta}\right]\frac{\delta\beta}{\eta}, \qquad \text{(A8)}$$

the solution to which is given in the text.