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IMPURITY EFFECTS ON THE RECOVERY OF COPPER STUDIED BY ULTRASONIC ATTENUATION MEASUREMENTS UNDER CYCLIC BIAS STRESS

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Abstract. - High purity Cu single crystals doped with Mg, Ag, Pb, Sb, Bi (20-50 ppm) were isochronally annealed between 373 K and 923 K after 0.12% deformation at room temperature. After each annealing step the dependence of sound attenuation on frequency (10 - 200 MHz) and bias stress (cyclic compression/tension; peak amplitudes below plastic yield) was measured. From the latter experiment specific information on the solute diffusion towards the dislocations and their pinning strength is obtained. From the frequency dependence of attenuation the dislocation pinning point density and the recovery of dislocation density as a function of temperature and type of solute is derived.

I. INTRODUCTION

Measurements of MHz ultrasonic attenuation $\alpha$ as function of external stress $\sigma$ (s.c. cyclic bias-stress (CBS) measurements) are informative with respect to dislocation/point defect interactions $/I/$. During annealing foreign atoms (FA) tend to segregate at the dislocations into "Cottrell Clouds". In copper these FA pinning points (PP) are immobile at room temperature (RT) (in contrast to e.g. Al $/2/$), i.e. after the dislocations are broken away by the bias stress the PP do not diffuse away or along with the dislocations. Thus under CBS the dislocations move back and forth through their Cottrell clouds. The accompanying changes in loop length $L$ give rise to symmetrical "butterfly"-shaped $\alpha(\sigma)$ curves which are stable in time and yield information with respect to (i) the binding energy between dislocations and PP, (ii) the concentration difference of FA in the Cottrell clouds and the lattice, (iii) the build-up of Cottrell clouds, e.g. during annealing after plastic deformation. To study the interaction between dislocations and different kinds of FA, copper single crystals were doped with 20 to 50 atppm of Mg, Ag, Pb, Sb, Bi which elements cover a broad range of dislocation interaction due to different atomic size and solubility. After preparation the samples were slightly plastically deformed at RT (0.12% compression) to about $10^8$ cm$^{-2}$ dislocation density (DD) initially free of Cottrell clouds. During the subsequent annealing treatments (1h: $\Delta T$=100 K) first the deformation induced vacancies (V) anneal out at the dislocations forming PP. With increasing T these PP then become unstable and disappear. At higher T FA Cottrell clouds are formed, i.e. FA PP are generated. In this temperature range also the DD starts to decrease. The influence of the different FA on these effects was investigated by CBS measurements.
II.- EXPERIMENTAL PROCEDURE

Ultrasonic attenuation measurements: A commercial apparatus (Matec Mod.6000) was used for measuring Ultrasonic attenuation (UA) by the pulse-echo-technique with 10 MHz x-cut quartz-transducers and "Nonaq" bonds.

Samples: For all specimens the matrix was vacuum melted cathode copper (ELMORE-kabelmetal, Osnabrück) with a Residual-Resistance-Ratio (RRR) of ≈2000. From this material 6 single crystals were grown, 5 were doped with nominally 20 atppm Mg, Ag, Pb, Bi, and Sb. Fig.1 shows size and orientation of the Bridgeman single crystals and the samples. The undoped single crystal served as a reference for the behaviour of a pure sample and for comparison with earlier measurements /3/. After Laue x-ray orientation control the crystals were spark-erosion cut into sample size (Fig.1) and then carefully ground and lapped to surface planparallelity and flatness within 10⁻⁶ cm/cm. The remaining deformed surface layer (thickness ≈10μm) was chemically etched away. Finally the samples were annealed for 4 hours at 923 K in a vacuum (1.3⋅10⁻⁹ Pa).

FA concentration: To obtain the FA concentration in solid solution (given in the sample label, e.g. #Ag96 = Cu+96atppmAg) the RRR of the UA samples themselves was measured by the contactless eddy current method /4/. The sample #Mg18 shows a concentration (18ppm) in the intended range. The very low concentrations in #Pb4 and #Bi2 point to almost zero solubility in solid copper. Nevertheless, strong CBS effects can be expected in these cases if precipitation at dislocations takes place.

Because of the extremely low resistivity contribution of Ag we believe that in #Ag96 the presence of residual matrix impurities considerably masks the Ag concentration (e.g. 1ppm of Fe is electrically equivalent to 100ppm of Ag). In #Sb44 a high concentration of micropores was found, which to a minor degree contribute to RRR.

Non-dislocation UA background: All samples were heavily irradiated by 3 MeV Van de Graaff γ-Bremsstrahlung and then annealed for 1 hour at 373 K. After such treatment the dislocations are completely pinned by irradiation induced point defects (PD), i.e. the attenuation in Fig.2 is caused by non-dislocation effects (α=α bg=background). It is seen that α(f) is independent of solute type (as to be expected), except for #Sb44 showing strongly increased values. Since metallographical inspection revealed porosity the surplus attenuation of #Sb44 was evaluated with respect to the sound scattering at micropores /5/ yielding 4.3⋅10³ pores/cm³ with a mean diameter of 42±5 μm /6/.

Bias-stress measurements /7/: The γ-irradiated samples were annealed for 4 hours in vacuum at 923 K which treatment results in complete reestablishment of the pre-irradiation state of the samples /8/. Subsequently the samples were plastically deformed 0.12% by compression and annealed for 1h at 373 K prior to the first CBS measurement (by this...
anneal, time dependent $\alpha(\sigma)$ curves due to V recovery at RT are avoided). The samples then were annealed for 1h at 473, 573, 673, 773, 823, and 923 K, resp. and after each anneal mounted in the compression/tension apparatus using the technique described in /7/ to avoid any unwanted stressing of the samples prior to CBS. Under CBS ($\sigma_{\text{MAX}}=+100$ N/cm²) $\alpha$ was measured at 30 MHz. Furthermore $\alpha(f)$ was measured under zero stress and after completion of the 1st CBS cycle under peak stress.

Evaluation of measurements: The Granato–Lücke (GL) theory of dislocation resonance /9/ was used to evaluate dislocation loop length $L$ and density $\Lambda$ as described earlier in more detail /10/. According to this theory the dislocation logarithmic decrement $\delta(Np) = 1.15 \cdot 10^{-5}(\alpha-\alpha_0)/f$ (in dB/$\mu$s) runs through a broad maximum as a function of frequency $f$ which for the case of overdamped resonance in a double logarithmic plot leads to a universal $\delta(f)$ master curve describing the frequency dependence of dislocation damping for all values of $\Lambda$ or $L$ /10/. For random pinning (i.e. exponential loop length distribution /11/) the position of the maximum is given by

$$\delta_{\text{max}} = \frac{8GB^2}{\sigma^2\cdot\Lambda}$$.  \hspace{0.5cm} (1)

$$f_{\text{max}} = \frac{0.113 \cdot C}{(L^2-B)}$$

where $G$ is the shear modulus, $B$ is the damping constant and $C$ is the line tension of the dislocations. From the equations (1) $L(\sigma)$ is derived. However, since the UA under CBS was measured at a single fixed frequency (30 MHz) the shift of the maximum coordinates of the GL master curve during the stress cycle had to be calculated numerically starting from the $\delta(f, \sigma=0)$ frequency dependence. This procedure is justified if no change in dislocation density under CBS takes place. Such changes are excluded (i) by plastic predeformation ensuring that $\sigma < \sigma(\text{yield})$; (ii) by evaluation of $\delta(f)$ measurements under $\sigma = \sigma_{\text{MAX}}$; (iii) by analysis of the $\alpha(\sigma)$ curves themselves, which strongly change (i.e. lose their butterfly shape) if fresh dislocations without Cottrell clouds come into play. Thus for the present measurements $L = L(\sigma)$ and $\Lambda = \text{const.}$ holds, i.e. during the compression/tension cycles the $\delta(f)$ master curve moves forth and back across the shaded area in Fig.3 along a $-45^\circ$ direction. This figure proves that indeed $\Lambda = \text{const.}$ during the CBS since the $\delta(f)$ data measured under peak stress can be fitted by a GL curve of same HF asymptote (which is independent of $L$ but $-\Lambda$). In this case the GL master curve measured under zero stress and $\alpha(\sigma)$ measured at a single arbitrary frequency (mostly 30 MHz) can be used to derive the $L(\sigma)$ dependence /6/.

Fig. 3: Shift of the GL-master curve under bias stress

We point out that this evaluation depends on the assumption that $\Lambda$, $L$, and $L(\sigma)$ are the same on all 12 glide systems. However, for the presently used samples the longitudinal ultrasonic pulse propagating along [111] monitors ("sees") only 6 slip systems which is taken into account by the appropriate orientation factor $O$ in Eq.(1). For the bias stress along the [112] direction 4 of these slip systems have the same Schmid factor but the remaining 2 experience only 1/2 of this shear stress. Thus principally $L(\sigma)$ is different for the two groups of glide systems. However, careful measurements and analysis of $\delta(f)$ curves show that, due to the smallness of the $L$ changes and the very broad $L$ distribution and the 4:2 ratio of glide systems (with 4 showing the larger $L$ changes) the resulting influences on the GL master curve are too small to be experimentally observed /6/. This is shown in Fig.3 where the $\delta(f)$ data measured under zero load and maximum load, resp. are equally well fitted by the GL master curve derived from the exponential $L$-distribution /10,11/.
Fig. 4a: Ultrasonic attenuation in Bi$_2$ after 0.12% plastic deformation under cyclic compression/tension measured at RT after annealing at temperature $T_A$.

Fig. 4b: The loop length dependence derived from Fig. 4a.

Fig. 5: Mean loop length vers. bias stress and annealing temperature of pure sample #RP.

Fig. 6: Mean loop length vers. bias stress and annealing temperature of the Pb-doped sample #Pb4.

Fig. 7: Mean loop length vers. bias stress and annealing temperature of the Mg-doped sample #Mg18.

Fig. 8: Mean loop length vers. bias stress and annealing temperature of the Ag-doped sample #Ag96.
III.- RESULTS

As an example Fig.4a shows the annealing behaviour of $a(\sigma)$ curves measured at RT on $\#Bi2$ after 0.12% deformation at RT. The curves are plotted with their zero stress starting values (solid squares) at their respective annealing temperatures $T_A$ and refer to the stress scale indicated in the figure. It is to be seen that the strong deformation induced increase in attenuation anneals out in two distinct $T$ ranges (373-573 K and 773-923 K); simultaneously the $a(\sigma)$ loop first grows to maximum amplitude then becomes reduced. After $T_A=373$ K a strong irreversible $a(\sigma)$ effect is found during the first loading. This effect becomes more and more reduced after higher $T_A$. From the $a(\sigma)$ data in Fig.4a the $L(\sigma)$ behaviour is derived (Fig.4b; c.f. also Fig.5-8 for the other alloys). One recognizes that in the 373-573 K annealing stage $L$-shortening takes place. However, the 773-923 K effect which is very pronounced in the $a(\sigma)$ curves (Fig.4a) is not due to $L$ changes but is caused (as Fig.9 shows) by the recovery of dislocation density. The very different $a(\sigma)$ and $L(\sigma)$ behaviour indicates that it is most important to simultaneously measure $a(\sigma)$ in order to separate $L(T_A)$-effects. Fig.9, furthermore, shows that the increase in $A$ for the same amount of deformation (0.12%) is considerably reduced by doping due to solution hardening ($\#Bi2$, $\#Hg18$, $\#Ag96$). Furthermore, $\#Pb4$ behaves very similar to pure Cu which indicates that very little Pb is in solution. In all samples $A$ stays constant up to 673 K. Bi and Pb tend to accelerate $A$ recovery presumably by trapping of matrix impurities, whereas Mg tends to slow down $A$ recovery more than the other FA.

IV.- DISCUSSION

In addition to Fig.4b ($\#Bi2$) Figs.5-8 show the $L(\sigma)$ butterflies for the other alloys, except $\#Sb4$. This sample behaved very different: (i) irradiation resulted in no $a$ decrease, (ii) plastic deformation and subsequent anneal at 473 K resulted in no $a$ increase, (iii) under CBS no increase in $a$ was observed. These observations show that Sb very strongly pins the dislocations (no break-away under CBS) to the non-dislocation background (no irradiation pinning) and that only 40ppm Sb are sufficient to keep the attenuation close to background during deformation and to bring it back to the background already by 1h, 473 K annealing.

The $L(T_A)$ behaviour of pure Cu ($\#RP$, Fig.5) first shows pinning in recovery stage IV (RT-400K) by the deformation induced V which at these temperatures escape from vacancy clusters and/or impurity traps. These V pinning points then disappear from the dislocations in the T range 450-650K indicated by the increase in $L$. At still higher T the dislocations become pinned by thermally diffusing residual impurities. This type of pinning behaviour is also observed in $\#Hg18$ (Fig.6) and less pronounced in $\#Pb4$ (Fig.7). In contrast $\#Ag96$ (Fig.8) shows only very slight V effects up to 600K (explained by the comparatively large number of Ag atoms) but considerable pinning at high temperatures. Sample $\#Bi2$ (Fig.4b) exhibits strong pinning but no depinning up to 700 K. This can be best explained if the deformation induced V are strongly bound to Bi and cause Bi transport towards the dislocations already at $T < 700$ K.

Considering the $L(\sigma)$ results in Figs. 4b-8 several interesting features are observed: (i) In all samples part of the pinning points of stage IV (RT - 400K) are instable with respect to stress. This is seen by the large difference between L
measured before stressing (solid circles) and $L(\sigma=0)$ during the CBS experiment. This means either that these PP diffuse away after breaking away from the dislocation or that the bowing dislocation forces these PP to diffuse along the line until they become trapped at some other PP. This leads to the conclusion that in both cases the PP involved consist of a single atom or a simple V complex (e.g. a double vacancy or a strongly bound vacancy/impurity pair). (ii) At medium temperatures (550-700K) the $L(\sigma)$ "butterflies" considerably increase in amplitude and significantly reduce their hysteresis. Since at these $T$ the dislocations become depinned from vacancy PP as known from irradiation experiments /7/ and the remaining V clusters in the lattice anneal out the steep and narrow $L(\sigma)$ loops are attributed to FA PP. The unexpected reduction of hysteresis can only be explained by reduced point defect/dislocation interaction (weak pinning). However, this PP softening is a transient effect and the CBS hysteresis width reappears after annealing at $T_A>750K$. Thus we attribute the effect to trapping of vacancies at FA which causes a reduction of the FA stress field and thus dislocation interaction. This V trapping takes place both at FA in the lattice (observable for those FA which are encountered by the dislocations moving under CBS) and at FA PP on the dislocations which are easy to reach traps for vacancy PP disappearing above 500 K. (iii) At $T_A>750K$ the broader $L(\sigma)$ hysteresis becomes visible again. According to (ii) this is explained by final annealing-out of the V after break-up of FA/V pairs and restoration of the stronger "naked" FA/dislocation interaction. At these higher $T$ also thermal FA diffusion leads to an increase in number of FA PP (decrease in $L$). In all samples the $L(\sigma)$ amplitude increases (most pronounced after $T_A=930K$). This effect is most easily explained by the loss in overall dislocation density which results in a reduction of long-range internal stress opposing the CBS stress.

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REFERENCES


[7] C. Becker, D. Lenz, K. Lücke; this conference


