ON THE PROPERTIES OF OXIDIZED AND REDUCED COPPER SAMPLES USED FOR ELECTRON IRRADIATION EXPERIMENTS IN THE kHz-RANGE

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Abstract - Undeformed oxidized and reduced samples are compared with respect to their pinning behaviour after electron-irradiation, to the existence of Bordoni peaks and to the amplitude dependence of internal friction.

I - INTRODUCTION

For copper it has been reported that the internal friction behaviour after cold-work depends strongly on the atmosphere used for the recrystallization anneal /1/. The oxidized and reduced state of copper had been obtained after anneals at 1173 K in corresponding atmospheres. For the investigation of internal friction in the Hz-range after electron-irradiation at 130 K such samples have been deformed and before irradiation the deformation-induced point defects and the Hasiguti peaks caused by them have been annealed at 400 K. Thus the irradiation effects could be increased /2/. However, for irradiations at 4.2 K a deformation-induced Bordoni-peak, which does not recover at 400 K, would make the quantitative evaluation of pinning experiments by the Granato-Lücke theory impossible. Therefore, first irradiation experiments with undeformed oxidized and reduced copper samples annealed at 1173 K will be reported here.

II - EXPERIMENTAL PROCEDURE

For the preparation of the samples in the first place rods of 99.999% ASARCO-copper with 9 mm diameter were rolled to a thickness of 3 mm. Then blocks of 21x6x3 mm were cut and 7 mm of the blocks were milled down to give a section 7 mm long, 2 mm broad and 0.15 mm thick. This milled section was the active part of the sample, a vibrating cantilever beam oscillating flexurally, the remaining thick portion was merely used as a clamping block. This preparation technique corresponds to that used by Sosin et al. /3/. The as-machined samples were annealed for 2 h at 1173 K and 1023 K in 0.13 Pa air (O-samples) or $1x10^5$ Pa CO (R-samples). Before and after the anneals the samples were etched electrolytically in 50% H_3PO_4. Then the thick portion of the sample, possessing two holes, was bolted to a sample holder, the temperature of which could be varied between 4.2 and 323 K. Opposite to the free end of the sample was an insulated electrode to detect the vibrations of the sample by frequency-modulation of a 120 MHz-oscillator. This was at 78 K to reduce the noise. To excite the vibrations of about 2 kHz an alternating voltage of the sample frequency and a polarizing voltage of 10 V were used. The alternating voltage was controlled automatically in a closed loop to maintain the amplitude of oscillation constant, thus representing a relative measure of decrement. The maximum strain amplitude was varied between $3x10^{-8}$ and $5x10^{-7}$. The polarizing voltage of 10 V caused a static strain amplitude of $3x10^{-8}$. With 300 V the static strain amplitude could be increased to $3x10^{-5}$ (used only for sample R1173). 3 MeV-electrons were used for the irradiations. A dose of $5x10^{15}$ electrons/cm² produced a Frenkel defect concentration of $3x10^{-7}$. After a dose of $5x10^{17}$ electrons/cm² the dislocations are pinned so strongly that they no longer contribute to internal friction (background dose).

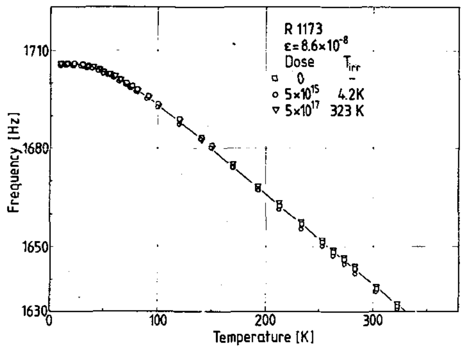

Fig.1: Temperature dependence of frequency for sample R.1173: before irradiation (squares), after $5x10^{15}$ electrons/cm² at 4.2 K (circles) and after the background dose of $5x10^{17}$ electrons/cm² (triangles).

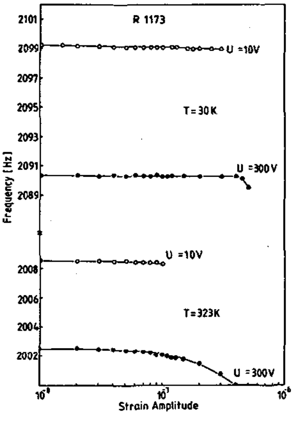

Fig.2: Amplitude dependence of frequency for sample R.1173 at 30 and 323 for polarizing voltages of 10 V (open symbols) and 300 V (full symbols).

III - EXPERIMENTAL RESULTS

The reduced sample R.1173 was annealed at 1173 K and during the measurements and irradiations a polarizing voltage of 300 V was used. Fig.1 depicts the temperature dependence of frequency for this sample: before irradiation (squares), after $5x10^{15}$ electrons/cm² (circles) and after the background dose of $5x10^{17}$ electrons/cm² (triangles). The coincidence of all three curves indicates that there is no irradiation effect. In Fig.2 the amplitude dependence of this sample is given for two temperatures and two polarizing voltages. At 30 K the static strain amplitude of $3x10^{-5}$ (300 V) decreases the modulus by 0.85% with respect to the 10 V-curves. For 323 K the effect is smaller because both measurements (10 V and 300 V) were performed at slightly different temperatures. So the temperature dependence of the modulus decreases the effect. The observed modulus decrease due to the bowing-out of the dislocations under the static stress indicates that there is a sufficient modulus defect under these conditions. Furthermore, one can conclude from the weak amplitude dependence, that for the statically small (10 V) and large (300 V) bow-outs of the dislocations their mean free loop length is rather small.

The temperature dependence of decrement for the oxidized sample 0.1173/2 (annealed at 1173 K) is depicted in Fig.3 (full symbols). One recognizes a marked Bordoni-peak at about 90 K. The reduction of the annealing temperature to 1023 K for sample 0.1023/2 (open symbols) gives a temperature dependence of decrement without a Bordoni-peak. For both annealing temperatures the oxidized samples show an irradiation effect /4/.

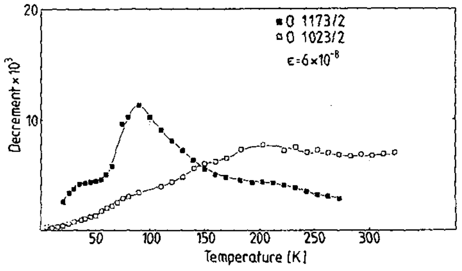

Fig.3: Temperature dependence of decrement for sample 0.1173/3 (full symbols) and for sample 0.1023/2 (open symbols).

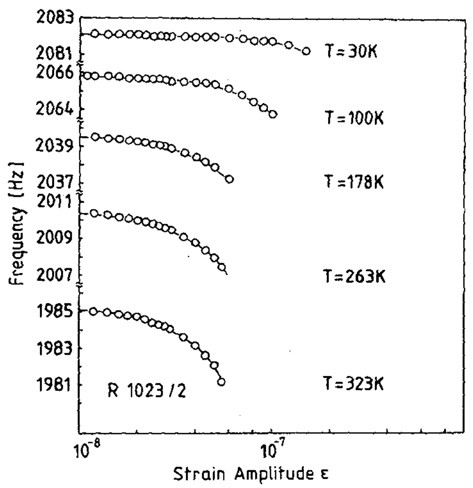

Fig.4: Amplitude dependence of frequency for sample R.1023/2 at different temperatures.

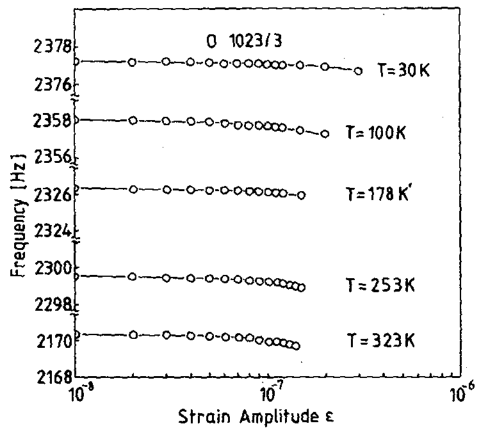

Fig.5: Amplitude dependence of frequency for sample 0.1023/3 at different temperatures.

For the reduced samples annealed at 1023 K dislocation pinning is observed after irradiation at 4.2 K /4/. The amplitude dependence of frequency for such a sample is shown for R.1023/2 in Fig.4. It can be seen that for low temperatures (T = 30 K) the amplitude dependence is very weak, but for higher temperatures (T = 323 K) it starts at amplitudes of about 1×10^{-8}. For the oxidized sample 0.1023/3 (annealed at 1023 K) the amplitude dependence of frequency is given in Fig.5. One recognizes that for all temperatures below about 6×10^{-8} the modulus is amplitude independent.

IV - DISCUSSION

The state of the sample R.1173 is characterized by a residual resistivity ratio RRR = 564, e.g. a high concentration of homogeneously dispersed single impurity atoms. However, the missing irradiation effect for this sample cannot be explained by a complete pinning of the dislocations by these impurity atoms. For the sample has been irradiated and measured in a statically bowed-out position of the dislocations corresponding to a maximum statical strain amplitude of

3×10^{-5} (300 V). In this state there exists a modulus defect of 0.85% with respect to a statical bow-out of 3×10^{-8} (10 V), indicating that there is a sufficient contribution of the dislocations to the modulus and dislocation pinning should be detectable after irradiation. However, the weak amplitude dependence of this sample corresponds to short loop lengths of the dislocations. To obtain a certain mean number of pinning points per loop more point defects are necessary than for longer loops. But the fact that even at the background dose no measurable pinning effect could be observed requires an additional assumption: The number of point defects arriving at the dislocations is too small. This reduced sample has the highest concentration of impurity atoms in the lattice, which must act as trapping centers for point defects. Thus this trapping of defects and the short loop length can account for the missing pinning effect. After an anneal at 1023 K the reduced samples show a value RRR = 816. Obviously, the smaller concentration of trapping centers and a longer loop length of the dislocations gives a pinning effect. However, this state of the sample is characterized by an amplitude dependence of internal frictions that starts at about 1×10^{-8} at 323 K. This means that an application of the amplitude-independent Granato-Lücke theory is only possible for measurements at very low amplitudes.

The oxidized sample (Fig.3) shows a Bordoni-peak after the recrystallization anneal at 1173 K. The existence of this peak is not due to accidental deformations during the handling of the samples, because it never appears in the reduced samples, which are handled in the same way. The Bordoni-peak should be due to surface oxidation effects during the anneals. Oxide islands have been observed on the surface of oxidized samples used for internal friction experiments /5/. There is a difference by a factor of 18 between the coefficients of thermal expansion of copper and cuprous oxide for instance /6/. Such a difference causes stresses under the oxide islands when the sample is cooled down from 1173 K. Plastic deformation will occur there and cause the Bordoni-peak. That not only stresses are responsible for the Bordoni-peak is evident, because after the anneal the samples were etched electrolytically and a surface layer including the oxyde islands was removed. For oxidizing anneals at 1023 K the surface oxidation seems to be reduced so far, that no Bordoni-peak appears (Fig.3).

The amplitude dependence of sample 0.1023/3 (Fig.5) is much less pronounced than that of R.1023/2 (Fig.4). This cannot be due to differences in loop length alone, because for the reduced sample with the lower residual resistivity ratio shorter loop lengths should be expected than for the oxidized sample. Thus the ratio of loop lengths should be just opposite to the observed behaviour of amplitude dependence. Therefore it is assumed, that different binding energies exist between the pinning points and dislocations for both states of the samples. In the reduced state one can expect a high concentration of single impurity atoms according to the low RRR-value. The pinning points that determine the mean free loop length in the reduced samples will be such single impurity atoms. In accordance with the observed difference in amplitude dependence their binding energy should be smaller than that of the pinning points in the oxidized state. In this state all oxidizable impurity atoms form impurity-oxide clusters, as can be seen from the higher RRR-value of oxidized copper. One can expect that impurity-oxides or small impurity-oxide-clusters will act as pinning points in these samples, having a higher binding energy as the pinning points in the reduced samples. Thus for temperatures up to 323 K the internal friction of sample 0.1023/3 is amplitude-independent for amplitudes $\leq 6\times10^{-8}$.

V - SUMMARY

The irradiation of undeformed samples showed that for the reduced state the recrystallization temperature must be decreased to 1023 K in order to obtain pinning effects after irradiation. However, then the amplitude dependence of internal friction begins at about 1×10^{-8} for 323 K. Also in the oxidized state the annealing temperature has to be decreased to 1023 K to avoid the existence of a Bordoni-peak. So both types of samples are suitable for irradiation experiments, but the reduced type must be measured at very low amplitudes.

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