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Elastic and dissipative properties of metals with an ultrafine grain structure*

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Abstract

The sound wave velocity and internal friction were measured in samples of nanocrystalline silver and submicrocrystalline copper as functions of annealing temperatures by several acoustic techniques operating at different frequencies. It was found that at room temperature in the as-prepared samples the modulus defect is extremely large (up to 20%) and disappears only after annealing at temperatures above that of primary recrystallization. The effect does not depend on frequency. *In-situ* measurements demonstrated an internal friction peak and corresponding modulus change at the temperature of primary recrystallization. The suggestion is made that the observed anelastic behaviour is caused by structural rearrangement in the grain boundary region.

1. Introduction

Materials with an ultrafine grain structure exhibit a number of unusual mechanical properties that make them promising for industrial application. One of them is the 20–30% reduction in elastic constants of such materials in comparison with material of the same chemical composition but with a typical grain structure. One of the most wide spread explanations [1, 2] is based on the suggestion that the elastic moduli of grain boundary are much smaller than the corresponding elastic moduli of the bulk of the grain. In terms of the linear theory of elasticity for polycrystalline materials [3], the elastic constants (averaged over all crystal regions) are expected to be reduced by a fraction determined by the volume of grain boundaries. Because of the large number of crystallite interfaces (grain boundaries) in the materials with an ultrafine grain structure, they can strongly influence the value of the elastic moduli.

However, there is another viewpoint of this problem [4, 5], according to which the same effect is considered to be due to an anelastic phenomenon, caused by the peculiar state of a grain boundary region.

In order to test both interpretations, an investigation of the elastic and dissipative properties of metals with different grain size structures was carried out.

2. Experimental details

Two types of sample were used in the experiments.

Type I is nanocrystalline silver. We had only one sample of nanocrystalline silver, 12 mm in diameter and 0.7 mm thick, which was prepared by a well-known inert gas condensation process followed by consolidation at 2.3 GPa [6]. The sample density was 97% of the theoretical value. The sample was studied by the X-ray diffraction method [7] to estimate the grain size from the mean coherent scattering length normal to the diffraction plane and to estimate the mean strain in this direction. The mean grain size for this case was about 60 nm.

In order to change the grain size of the sample, subsequent sequential anneals at different temperatures in a vacuum of 10^{-4} Torr were carried out. The anneals were performed from 50 to 400 °C with 30 min holding at the fixed temperature.

Type II is submicrocrystalline copper. Copper samples, 99.997% and 99.98% pure, were used for the experiment. They were cut from the copper bar subjected to heavy deformation by a simple shear, using the equichannel angular pressing method [8]. The specimen microstructure was studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and the X-ray diffraction method. In as-prepared samples the mean grain size was about 200 nm. In order to obtain different structural states the samples were subjected to thermal treatments at different annealing temperatures from 100 to 500 °C, holding them at each temperature for 1 h.

The elastic and dissipative properties of the copper samples were measured by several well-known internal friction techniques operated at different frequencies: the inverted torsion pendulum method (f = 10–15 Hz), the composite vibration method (f = 100 kHz), the high

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frequency resonance method ($f=5$–10 MHz) and the echo-pulse method ($f=5$–10 MHz). The same properties for the silver sample were measured only at a frequency of 5 MHz.

Estimates of the effective elastic moduli of the samples were made on the basis of the sound wave velocity measurements, according to the well-known expressions $v_T=(G/\rho)^{1/2}$, $v_L=(C_L/\rho)^{1/2}$, $v_E=(E/\rho)^{1/2}$, where v_T, v_L and V_E are the transverse, the longitudinal and Young's velocities of sound respectively. Here ρ is the material density, G is the shear modulus, E is Young's modulus and $C_L=G(4G-E)/(3G-E)$ is the longitudinal modulus.

3. Results

3.1. Nanocrystalline silver

In Fig. 1 the X-ray diffraction data are presented for a nanocrystalline silver sample subjected to anneals at increasing temperature. The X-ray measurements were performed at room temperature. One can see that up to 100 °C the grain size does not change significantly; however, after annealing at 150 °C a drastic increase, of approximately 2.5 times, in grain size is observed.

A visible decrease in magnitude of the internal stresses is also observed only after annealing at 150 °C. It can be noted that a further increase in annealing temperature almost does not change the magnitude of internal stresses in spite of the essential growth of the grain size. This phenomenon can be attributed to the effect of a gas captured by the sample (into closed pores) during the process of sample preparation. Expansion of gas due to heating can lead to an increase in internal stresses and to compensation of a decrease in internal stresses due to structural rearrangement.

Figure 2 shows the dependences of the longitudinal and transverse sound velocities after subsequent anneals. The measurements were made at room temperature. One can see from the figure that the most significant change in sound velocity occurs only after annealing at 150 °C. This temperature, which we call T_0, as follows from the data in Fig. 1, is probably a characteristic temperature of the sample primary recrystallization. The velocity changes are irreversible.

3.2. Submicrocrystalline copper

Figure 3 shows the changes in the longitudinal sound velocity v_L and transverse sound velocity v_T (at 4 and 5 MHz) at room temperature with subsequent anneals for 1 h at different temperatures. The data are given for 99.997% Cu and 99.98% Cu samples. One can see a drastic increase in the velocities after the annealing temperatures are elevated above $T_0=125$ °C for the 99.997% Cu samples and above $T_0=175$ °C for the 99.98% Cu samples. The velocity changes are irreversible

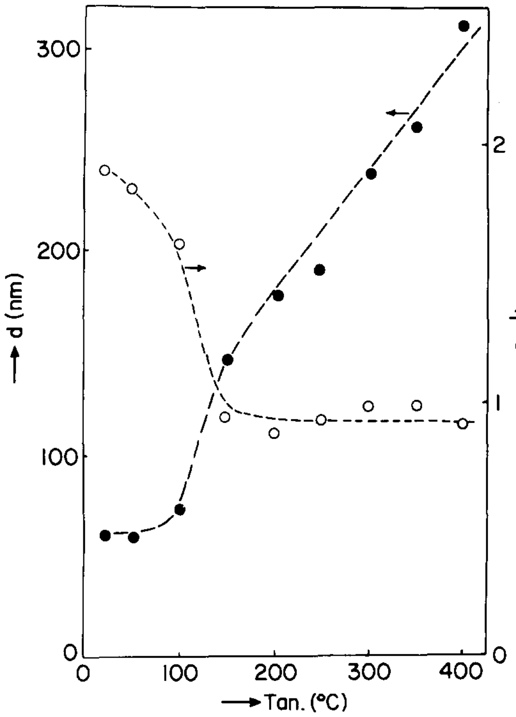

Fig. 1. Dependences of the mean grain size and the internal stresses of nanocrystalline silver on annealing temperature.

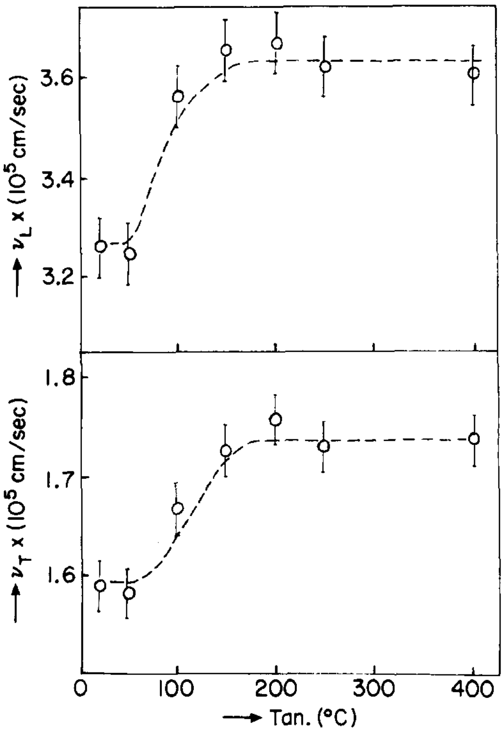

Fig. 2. Longitudinal ultrasound velocity v_L and transverse ultrasound velocity v_T of silver measured at $T=300$ K vs. the temperature of isochronal annealing for 0.5 h.

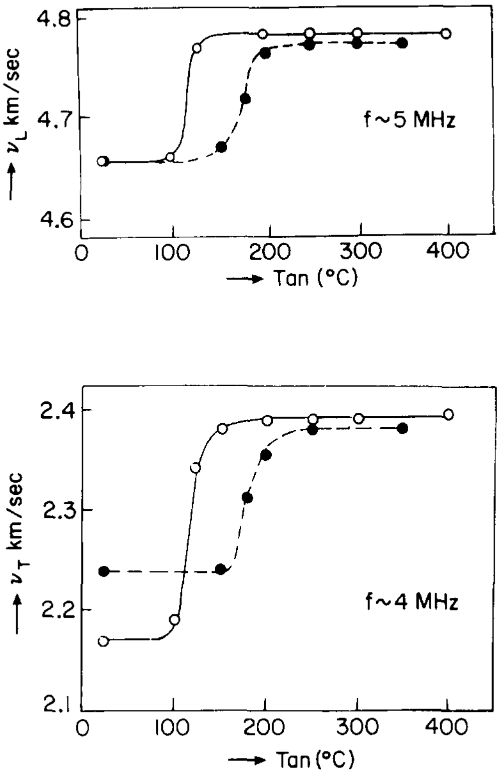

Fig. 3. Longitudinal ultrasound velocity v_L and transverse ultrasound velocity v_T measured at room temperature *vs.* the temperature of isochronal annealing for 1 h: ○, 99.997% Cu; ●, 99.98% Cu.

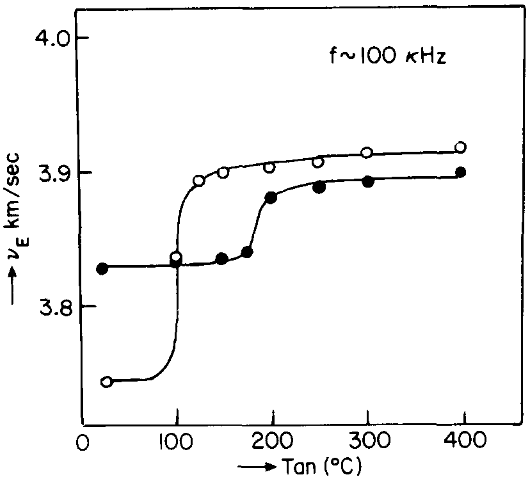

Fig. 4. Young's velocity v_E of ultrasound at room temperature *vs.* temperature of the isochronal annealing for 1 h: ○, 99.997% Cu; ●, 99.98% Cu.

just as for the nanocrystalline silver sample. A similar behaviour is observed for Young's velocity at the frequency of 100 kHz (Fig. 4).

Electron microscopy and X-ray diffraction measurements show that subsequent anneals of the copper sample lead to structural rearrangements. In an as-prepared sample a homogeneous submicrocrystalline structure with a mean grain size of 0.2 μm is formed. It is characterized by the absence of grain boundaries with specific striped contrast, indicating that the grain boundary structures are in a nonequilibrium state with large internal stresses in the grain boundary region. After anneals at temperatures above T_0 (the temperature of primary recrystallization) a uniform structure is formed with grain boundaries displaying typical striped contrast characteristic of the equilibrium state. The grain size growth via annealing temperatures is shown in Fig. 5 for 99.997% Cu samples. For 99.98% Cu samples the dependence is similar; however, $T_0 = 175$ °C.

Since in the case of submicrocrystalline copper we had more samples, we succeeded in measuring the elastic and dissipative (internal friction) properties during heating and cooling *in situ* at different frequencies. These measurements are presented in Fig. 6 (at a frequency of 15 Hz by the inverted torsion pendulum method) and in Fig. 7 (at a frequency of 5 MHz by the high frequency resonance method). At both frequencies, one can observe an internal friction peak and sharp increase in velocity at the peak temperature. The peak temperature coincides with the temperature T_0 of primary recrystallization. The anomalies in the sound wave velocity and in internal friction are irreversible and repeated measurements do not reveal them. It is very important to note that the temperature at which the internal friction peak was observed almost does not depend on the mode and frequency of sound oscillations, even if the frequency changes from 15 to

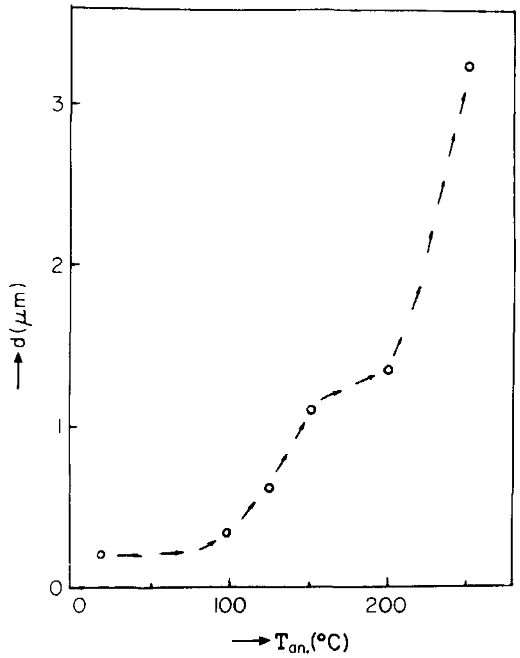

Fig. 5. Average grain size *vs.* annealing temperature (99.997% Cu).

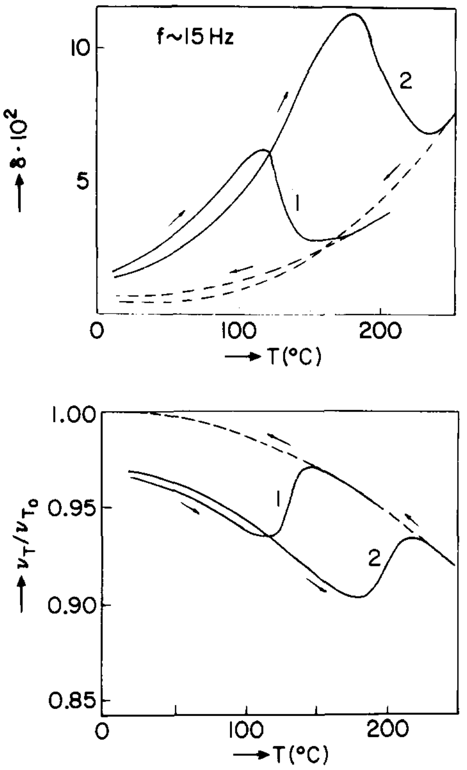

Fig. 6. Temperature dependences of the logarithmic decrement δ and transverse velocity change v_T/v_{T0} for copper measured on heating (——) and on cooling (- - -): curves 1, 99.997% Cu; curves 2, 99.98% Cu.

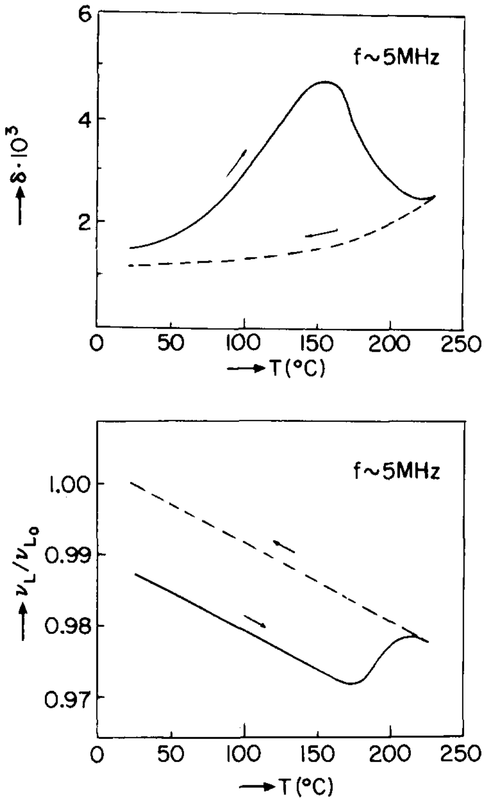

Fig. 7. Temperature dependences of the logarithmic decrement δ and longitudinal velocity change v_L/v_{L0} measured on heating (——) and on cooling (- - -) (99.98% Cu).

5 MHz. The sound velocity does not depend on the annealing temperature almost up to T_0 in the case of high frequencies, whereas at low frequencies a slight sound wave change is observed at temperatures below T_0.

4. Discussion

From the present data, one can conclude that the elastic and dissipative parameters of the as-prepared nanocrystalline silver and submicrocrystalline copper are essentially lower (by 10–20%) than those for the recrystallization state of these metals. It is known and also confirmed by our experiments that the primary recrystallization leads to a decrease in internal stresses, grain size growth and rearrangement of the grain boundary structure. Therefore, let us consider how these factors influence the elastic and dissipative properties of the metals investigated.

4.1. Elastic consideration

Suppose that the modulus of elasticity of the interfacial region is lower than that of the bulk material. Calculations show [9, 10] that the elastic modulus of the grain boundary region is between 0.5 and 0.7 of the bulk modulus. Then we can use the Reuss [3] approximation to estimate the averaged elastic modulus of the composite (grain boundary region bulk modulus):

$$C_1^{-1}=(1-\alpha)C_0^{-1}+\alpha C_{\rm gr}^{-1} \tag{1}$$

where C_0 is the matrix modulus, $C_{\rm gr}$ is the grain boundary region modulus, α is a relative volume of this region, $\alpha\approx 3x\ \Delta d/d$, where d is the grain size and Δd is the grain boundary width. Let us calculate for nanocrystalline silver what value of $C_{\rm gr}$ should satisfy the value of $C\approx 0.85C_0$ at present observed. Even if we take $\Delta d=2$ nm for $d=60$ nm and consider that C_0 is the value of silver modulus after recrystallization (after annealing at 400 °C), one obtains $C_{\rm gr}\approx 0.33C_0$, which seems to be unreasonable.

The same conclusion is obtained if this suggestion is applied to the results for submicrocrystalline copper, since from the experiments it follows that $C_1\approx 0.85C_0$ and $d\approx 200$ nm. Thus the contribution from the mechanism proposed to the effects observed can be significant only for grain sizes less than 10 nm.

4.2. Anelastic consideration

Let us try to explain the effect observed in terms of models describing anelastic behaviour of the material. One of the most effective mechanisms of that kind is grain boundary sliding which can lead to a significant change in elastic modulus. It was first proposed by Ke [11]. For oscillating stress the change $\Delta C/C$ in effective elastic modulus due to grain boundary sliding is described by an expression of the relaxation type

$$\frac{\Delta C}{C} = \frac{1}{1+(\omega\tau)^2} \qquad (2)$$

where ω is the angular frequency, $\tau = \tau_0 \exp(E/kT)$ with E being the activation energy of the relaxation process determining an intergrain sliding at τ_0 being a frequency factor. The grain boundary sliding is considered to be a diffusive process, and thus E is the activation energy of the diffusion. For silver the grain boundary diffusion is characterized by $E = 0.7$ eV [12] and in our experiment at $\omega \approx 10^7$ s^{-1} and $T = 300$ K we obtain $\omega\tau > 1$. This means that $\Delta C/C$ should be close to zero, in disagreement with the experimental results. The experimental results can be explained in terms of this model provided that $\omega\tau < 1$, which can be fulfilled at $E < 0.3$ eV. Since in the as-prepared samples of silver we observe a very high level of internal stresses, one can think that potential barriers in the grain boundary region can be reduced significantly owing to internal stresses. To test the validity of the explanation proposed, it is necessary to measure the temperature dependence of internal friction and modulus and to find anomalies in the low temperature region.

However, let us consider the experimental data for submicrocrystalline copper. We see from Figs. 2–4 that for as-prepared copper samples the modulus change $\Delta C/C$ at 300 K almost does not depend on frequency. This means that, if the suggestions made above are applied to nanocrystalline silver, it is impossible to explain the observed value of $\Delta C/C$. Indeed, if one takes $E = 0.3$ eV (the hypothetical potential barrier is the same as for silver), then at 300 K one will obtain $\omega\tau < 1$ for $\omega \approx 10^7$ s^{-1} and $\omega\tau > 1$ for $\omega \approx 10^2$ s^{-1}. This means that, for low frequency experiments at $T = 300$ K, one must obtain $\Delta C/C$ close to zero, in contrast with the results observed.

In situ measurements of the temperature dependences of the decrement and sound wave velocity reveal an internal friction peak and a drastic velocity increase at the temperature of primary crystallization of submicrocrystalline copper. They did not depend on the frequency and, as was shown previously in refs. 4 and 5, they could not be interpreted in terms of the models [13–15] based on the concept of the lattice dislocation mechanism.

In our opinion the most acceptable explanation is that in the as-prepared nanocrystalline and submicrocrystalline samples the grain boundary region structure is extremely disordered and is characterized by a high level of internal stresses [16]. Most probably this structure state determines the peculiar properties of the grain boundary region, including the easy grain boundary sliding. One can assure that under applied oscillating stresses the sliding can be realized by a very small atom displacement owing to cooperative effects. This easy sliding must lead to a frequency-independent modulus defect. At the temperature of the primary recrystallization, structural ordering occurs which leads to a decrease in internal stresses, to the appearance of equilibrium grain boundaries and to the transition to a conventional diffusive mechanism of grain boundary sliding. The modulus increase and internal friction peak are the results of the structural ordering in the grain boundary region.

Naturally, the structural ordering in the grain boundary region is only a hypothesis which needs further development and theoretical and experimental investigations.

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