Recovery of Young's Modulus During Annealing of Submicrocrystalline Cu and Cu: ZrO2 Composite

A. A. Lebedev, Yu. Burenkov, S. Pulnev, V. Vetrov, V. Kopylov

JOURNAL DE PHYSIQUE IV
Colloque C8, supplément au Journal de Physique III, Volume 6, décembre 1996

Recovery of Young's Modulus During Annealing of Submicrocrystalline Cu and Cu: ZrO_2 Composite

A.B. Lebedev, Yu.A. Burenkov, S.A. Pulnev, V.V. Vetrov and V.I. Kopylov*

Solid State Physics Division, A.F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, Polytekhnicheskaya 26, 194021 St. Petersburg, Russia
** Physico-Technical Institute, Belorussian Academy of Sciences, Zhodinskaya 4, 220730 Minsk, Belorussia*

Abstract. Young's modulus of pure Cu (99.98%) and precipitate hardened Cu:ZrO_2 polycrystals with an ultrafine-grained (UFG) structure has been investigated at temperatures 20-600°C. Nanoparticles of ZrO_2 with a size of about 10nm have been formed by an internal oxidation of Cu-Zr solid solution. The polycrystals have been produced by a heavy plastic deformation using the equichannel angular pressing technique, which yields an average size of grains *d* of about 200nm. Young's modulus *E* has been measured as a function of temperature *T* and of the annealing temperature T_a. The dependence $E(T_a)$ in Cu-ZrO_2 demonstrates a recovery stage near 200-250°C (4-6% increase in *E*). Structural investigations show that *d* practically does not change during 2 hours annealing up to 500°C. Such a structural stability was observed only in the composite material. Pure copper with the same type of initial structure (*d*=200nm) shows approximately the same recovery in *E* at T near 200-250°C, however, this recovery corresponds to a steep (an order of magnitude) increase in *d*. This fact is a direct experimental proof that the softening of the Young's modulus in UFG materials is due to not only the smallness of grains but also the structure of grain boundaries and, in particularly, the mobility of grain boundary dislocations.

1. INTRODUCTION

In recent years, ultrafine-grained (UFG) materials (both nanocrystals and polycrystals with submicron-sized grains) have become the subjects of intensive theoretical and experimental studies (see, for example, review papers by Gleiter [1], Gryasnov and Trusov [2] and Valiev [3]). These materials exhibit a number of unusual physical and mechanical properties. In particular, a high value of the microhardness [4] and yield stress [5-7] and a softening of the elastic modulus [8-13] have been reported for UFG copper produced by heavy plastic deformation techniques. However, these properties are not thermostable: annealing at temperatures of about 150-250^{0}C for 20-120 min. leads to the primary recrystallization, which considerably increases the grain size [4,5,7-11,13], reduces the yield stress [5,7] and microhardness [4] and causes a recovery stage of the elastic constants [8-13]. It has been shown recently by Lebedev et al. [14] that the grain size and yield stress thermostability is much more better in heavily deformed UFG Cu with nanoparticles of ZrO_2. Fig.1 demonstrates the effect of annealing temperature on the yield stress and grain size for heavily deformed (HD) pure copper and Cu: ZrO_2 composite. In the present communication, we pay attention to Young's modulus.

2. EXPERIMENTAL

Submicrocrystalline Cu (99.98%) and Cu: ZrO_2 composition were produced by a simple shear plastic deformation using the equichannel angular pressing technique suggested by Segal et al. [15,16]. The deformation was carried out at room temperature up to true logarithmic strain $e \approx 3$, which leads to an average grain size of about 200 nm [4,8,11]. After the deformation, the specimens had the following dimensions: 30x14x14 mm^3 (for HD Cu) and 30x8x8 mm^3 (for HD Cu: ZrO_2).

Initial Cu: ZrO_2 composition with 0.3 vol.% of zirconia nanoparticles having a size of about 10 nm has been produced by the internal oxidation method [17] from Cu-0.15wt.%Zr solid solution.

For ultrasonic measurements, several rod-shape samples with dimensions about 2.5x2.5x20 mm^3 were cut by electrospark machining from the initial bulk specimens. Standard electrostatic excitation of longitudinal vibrations has been used. Measurements were carried out in a helium atmosphere. Detailed description of the experimental setup is given elsewhere [18].

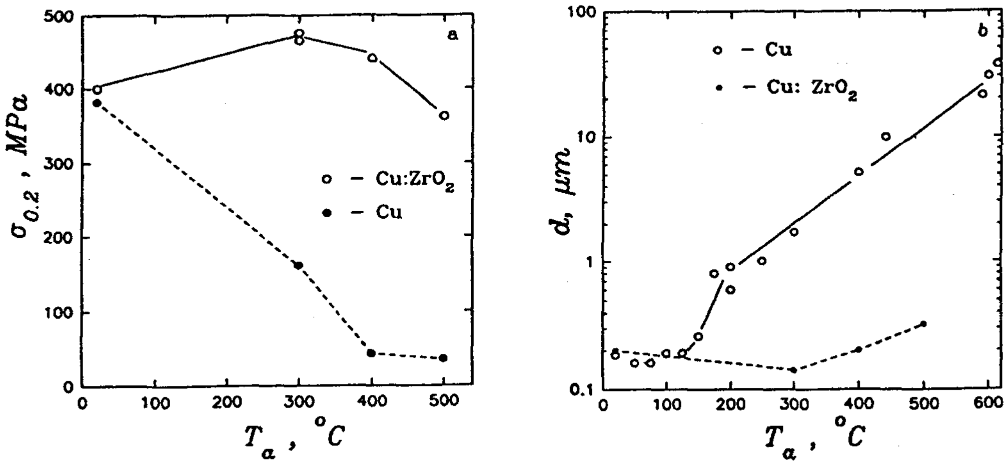

Figure 1. Effect of annealing temperature on the yield stress (a) and grain size (b) of HD Cu and Cu:0.3vol.%ZrO_2 [14].

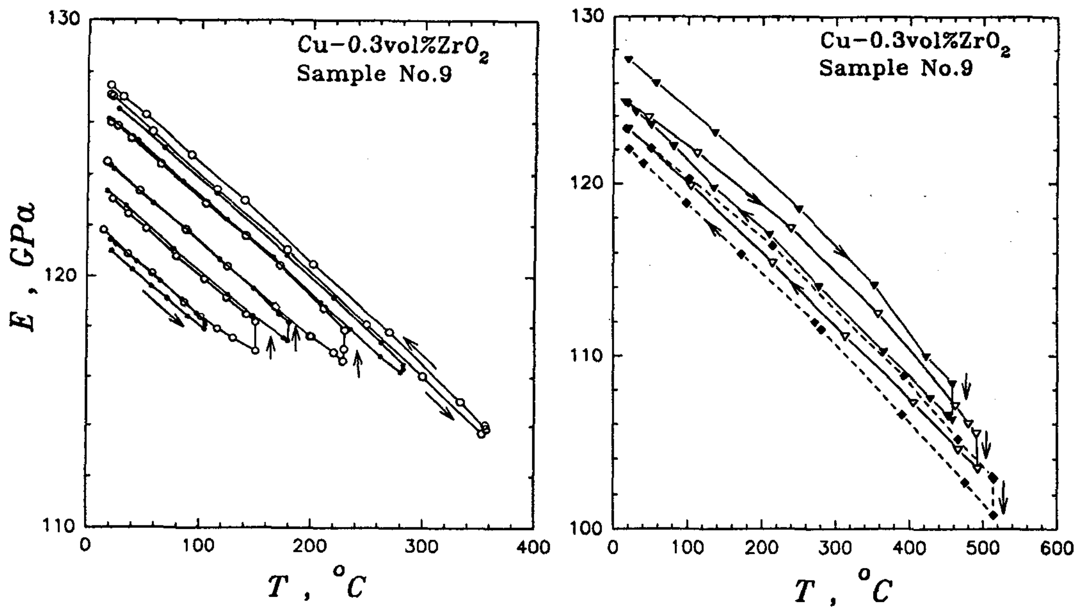

Figure 2. Young's modulus as a function of temperature for one of the HD Cu:ZrO_2 samples measured during "heating-annealing for 2 hours at T=T_a-cooling" runs with successive increase of T_a.

3. RESULTS

Fig.1 shows the effect of two hours annealing at various temperatures on the yield stress and grain size in pure Cu and Cu:ZrO_2 composite. It is clear that in pure HD copper, UFG structure is not thermostable, as was reported earlier (see Section 1), whereas in Cu:ZrO_2 composition both the yield stress and grain size are practically stable up to 500^0C. One would expect the stability of Young's modulus either.

Fig.2 shows Young's modulus E as a function of temperature T for one of the HD Cu:ZrO_2 samples measured during successive heating-cooling runs with different maximum temperature T_a. During each run, the sample was heated up to $T=T_a$, then annealed for 2 h and then cooled down to room temperature. At $T_a < 400^0$C, Young's modulus increases during holding the temperature equal to T_a and the curve $E(T)$ measured during the next heating coincides well with that obtained on the previous cooling (like in pure HD copper [11-13]). At $400^0\mathrm{C} < T_a < 500^0$C, the modulus decreases during annealing.

Fig.3 shows Young's modulus measured at room temperature as a function of T_a for one of the samples of pure HD Cu and three samples of Cu: ZrO_2 . The dashed line in Fig.3 corresponds to the curve plotted from the data of Fig.2. In spite of some minor quantitative difference in absolute values of E, all the samples of Cu: ZrO_2 exhibit a good agreement and show the stage of recovery at 170-250^0C (like in pure HD copper). The curves for Cu: ZrO_2 differ from those for pure Cu at T > 400^0C. A softening effect near T=500^0C was observed only in the composite material. The softening takes place in all Cu: ZrO_2 samples but differs from sample to sample quantitatively.

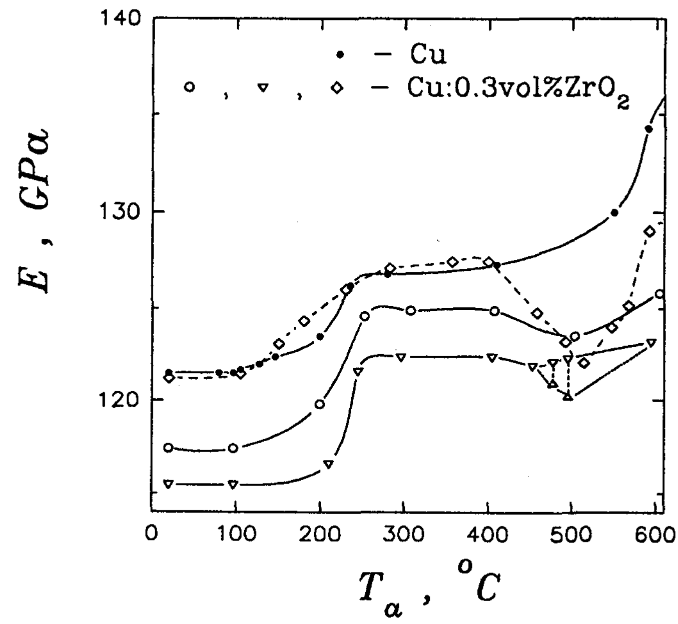

Figure 3. Young's modulus at room temperature vs. annealing temperature for HD Cu and Cu: ZrO_2. The dashed line represents the data taken from Fig.2.

4. DISCUSSION

The nature of the Young's modulus softening and the recovery stage at T≈200^0C in heavily deformed UFG copper have been discussed by Akhmadeev et al. [8,9], Soifer [10] and Lebedev et al. [11,13]. All the authors (after discussing several mechanisms) considered mobile defects in interface region to be the most reasonable cause for the softening (and recovery). It should be noted that the same recovery stage was observed in ordinary polycrystals after plastic deformation (see, for example, [19] and references in [11]). Lebedev et al. [11] suggested that the recovery stage is due to redistribution of glissile grain boundary (GB) dislocations and their pinning by point defects. The result of the present work confirms this conclusion, because the recovery stage is observed in Cu: ZrO_2 composite, when the primary recrystallization does not increase the grain size, but it should lead to relaxation of internal stresses. The presence of long-range internal stress fields in UFG polycrystals is the main feature of the so-called non-equilibrium state of GBs [3]. It is natural to consider that after annealing at 300-500^{0}C, GBs become equilibrium. Thus, the state of GBs does not influence plastic properties of UFG polycrystals, it influences, however, the modulus defect related to mobile GB dislocations. Thus, a high value of the yield stress in UFG polycrystals is due only to the smallness of grains.

The modulus softening effect after annealing at $T_a \approx 500^0$C in HD Cu:ZrO_2 might be due to the phase transformation (tetragonal-monoclinic) in zirconia particles. According to Winterer et al. [20], the critical size for low temperature stabilization of tetragonal phase is 7 nm, which is close to a size of zirconia particles in our samples (10 nm) estimated by TEM.

Acknowledgments

The work was supported in part by the International Science Foundation (ISF R51300). One of the authors (A.B.L.) wishes also to thank NATO for Linkage Grant 930838. The authors wish to thank Dr. G.D. Motovilina for TEM research, Mr. O.V. Vylegzhanin for his help during sample preparation and also Dr. A.E. Romanov and Dr. V.G. Gryaznov (with the PGPT Foundation) for valuable discussions.

References

1. Gleiter H., *Progress in Materials Science* **33** (1989) 223-301.
2. Gryaznov V.G., Trusov L.I., *Progress in Materials Science* **37** (1993) 289-401.
3. Valiev R.Z., *Nanostruct. Materials* **6** (1993) 73-82.
4. Akhmadeev N.A., Valiev R.Z., Kopylov V.I., Mulyukov R.R., *Metally* No.5 (1992) 96-101. [Engl. transl.: *Russian Metallurgy* No.5 (1992) 86-91].
5. Gertsman V.Y., Birringer R., Valiev R.Z., Glieter H., *Scripta metall. matter.* **30** (1994) 229-234.
6. Valiev R.Z., Kozlov E.V., Ivanov Yu.F., Lian J., Nazarov A.A., Baudelet B., *Acta metall. mater.* **42** (1994) 2467-2475.
7. Gertsman V.Y., Birringer R., Valiev R.Z., *Phys. Stat. Solidi (a)* **149** (1995) 243-252.
8. Akhmadeev N.A., Valiev R.Z., Kobelev N.P., Mulyukov R.R., Soifer Ya.M., *Fiz. Tverd. Tela* **34** 1992) 3155-3160 [Engl. transl.: *Sov. Phys. Sol. State* **34** (1992) 1687-1690].
9. Akhmadeev N.A., Kobelev N.P., Mulyukov R.R., Soifer Ya.M., Valiev R.Z., *Acta metall. mater.* **41** (1993) 1041-1046.
10. Soifer Ya.M., *J. Alloys Comp.* **211-212** (1994) 475-479.
11. Lebedev A.B., Burenkov Yu.A., Romanov A.E., Kopylov V.I., Filonenko V.P., Gryaznov V.G., *Mater. Sci. Engng. A* **203** (1995) 165-170.
12. Lebedev A.B., Burenkov Yu.A., Kopylov V.I., Romanov A.E., Gryaznov V.G., *Phil. Mag. Letters,* **73** (1996) 241-246.
13. Lebedev A.B., Burenkov Yu.A., Kopylov V.I., Filonenko V.P., Romanov A.E., Gryaznov V.G., *Fiz. Tverd. Tela* **38** (1996) 1775-1783 [Engl. transl.: *Phys. Sol. State* **38** (1996) 978-982].
14. Lebedev A.B., Pulnev S.A., Kopylov V.I., Burenkov Yu.A., Vetrov V.V., Vylegzhanin O.V., *Scripta Materialia* **35** (1996) (in print).
15. Segal V.M., Reznikov V.I., Drobyshevski A.E., Kopylov V.I., *Izv. Acad. Sci. SSSR. Metally* No.1 (1981) 115-123 [Engl. transl.: *Russian Metallurgy,* No.1 (1981) 99- 107].
16. Segal V.M., Reznikov V.I., Kopylov V.I., Pavlik D.A., Malyshev V.F., Processes of Plastic Structural Formation of Metals (Nauka i Technika, Minsk, 1994) (in Russian).
17. Chen I.-W., Chiao Y.-H., *Acta metall.* **31** (1983) 1627-1638.
18. Burenkov Yu.A., Nikanorov S.P., Stepanov A.V., *Izv. Acad. Nauk SSSR. Ser.Fiz.,* **35** (1971) 525-528 [Engl. transl.: *Bull. Acad. Sci. USSR. Phys. Ser.,* **35**, (1971) 479-482].
19. Kobelev N.P., Soifer Ya.M. *Scripta Metal. Mater.* **27** (1992) 13-18.
20. Winterer M, Nitsche R., Redfern S.A., Schmahl W.W., Hahn H., *Nanostruct. Mater.* **5** (1995) 679-688.