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Reduction of vacancy concentration during storage of severely deformed Cu

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ABSTRACT

A reduction of the stored energy in Cu processed by equal-channel angular pressing was observed after 4 years of storage at room temperature. It was found that the decrease of stored energy was most probably caused by the loss of excess vacancies.

1. Introduction

Severe plastic deformation (SPD) procedures are attractive methods for producing ultrafine-grained (UFG) metals in bulk form. One of the most frequently used method for processing bulk UFG metals by SPD is equal-channel angular pressing (ECAP) where it is possible to produce materials having dimensions of several centimeters in all directions [1]. The thermal stability of the UFG microstructure processed by SPD is a great importance from the point of view of practical applications of these materials. Previous studies [2–8] have shown that the UFG microstructure in Cu and Ag samples processed by ECAP or high-pressure torsion (HPT) at room temperature (RT) partially recovered and/or recrystallized during storage at the temperature of processing. For example, large recrystallized grains were observed in 99.96% purity Cu 8 years after processing by ECAP [4]. Experiments on 5N purity Cu showed that recrystallization occurred only 2 months after ECAP and the lower recrystallization time for the purer material was explained by the non-availability of the pinning effect of alloying elements on grain boundaries and dislocations [2]. Although these previous works have demonstrated the recrystallization of the ultrafine-grained structure in Cu samples during storage at RT, the effect of long-term storage on the lattice defect structure (dislocation density, vacancy concentration) in non-recrystallized UFG Cu is missing from the literature. In this paper, the stability of the defect structure in Cu samples processed by different number of ECAP passes is studied during storage for 4 years at RT.

2. Experimentals

Oxygen-free copper (99.98%) billets (M0b-grade corresponding to the Russian standard GOST 10988-75) having lengths of ~80 mm and diameters of ~20 mm were processed by ECAP following route B_C for 1, 3, 10 and 25 passes at RT. The ECAP die had an internal channel angle of 90° and an outer arc of curvature of ~0° at the intersection of the two parts of the channel. In this configuration, one pass corresponds to an equivalent strain of ~1.15 [9]. The microstructure was examined immediately after ECAP and 4 years storage by X-ray line profile analysis on transverse sections cut perpendicular to the axes of the billets. The measurements of the X-ray diffraction lines were performed using a special high-resolution diffractometer (Nonius FR591) with Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm). The line profiles were evaluated using the extended Convolutional Multiple Whole Profile (eCMWP) fitting procedure [10]. This method gives the crystallite size distribution as well as both the dislocation density and the twin boundary frequency with good statistics, where the latter quantity is defined as the relative fraction of twin boundaries in {1 1 1} planes along their normal vector. The stored energy in the ECAP-processed microstructure was investigated immediately after ECAP and 4 years storage by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC2 calorimeter at a heating rate of 40 K/min.

3. Results and discussion

Fig. 1 shows DSC thermograms taken at 40 K/min heating rate immediately after ECAP for the samples processed by 1 and 10 passes. For both samples, an exothermic peak was observed on the DSC curve which corresponds to the recovery and recrystallization of the microstructure as it has been shown in previous

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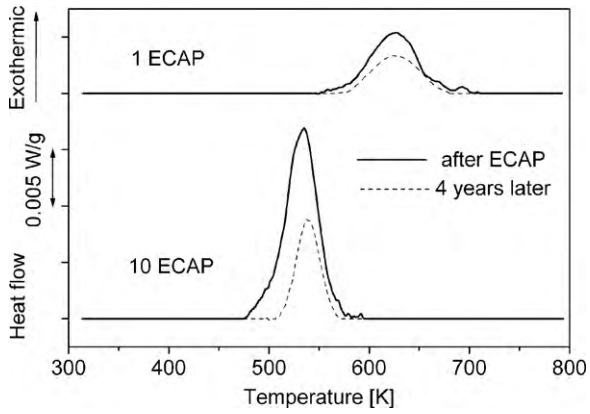

Fig. 1. DSC thermograms obtained immediately after ECAP and storage at room temperature for 4 years in the case of the samples processed by 1 and 10 passes. The heating rate was 40 K/min for all measurements.

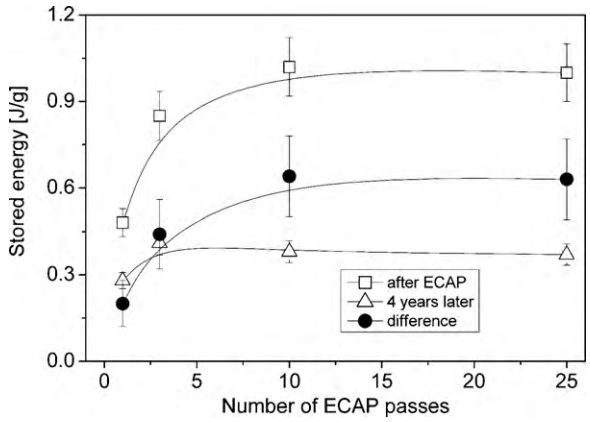

Fig. 2. The stored energy measured immediately after ECAP and storage at room temperature for 4 years as a function of number of ECAP passes. The change of stored energy during 4 years is also plotted.

studies [11–13]. As a consequence, the area under the peak gives the stored energy of the lattice defects (vacancies, dislocations and grain boundaries including twin boundaries). The DSC traces measured after 4 years storage of the samples are also shown in Fig. 1. It is evident that the area under the exothermic peak was reduced by a factor of 2–3 during the storage at RT indicating a decrease of the energy stored in the microstructure. Similar phenomenon was observed for the samples processed by 3 and 25 passes. The stored energies measured immediately after ECAP and storage for 4 years as a function of number of ECAP passes are listed in Table 1 and plotted in Fig. 2. The change of stored energy during 4 years is also plotted in this figure.

The average crystallite size, the dislocation density and the twin boundary frequency obtained by X-ray line profile analysis immediately after ECAP are listed in Table 1. The variation of these quantities as a function of number of ECAP passes has been discussed in a previous paper [14]. The twin boundary frequency for all

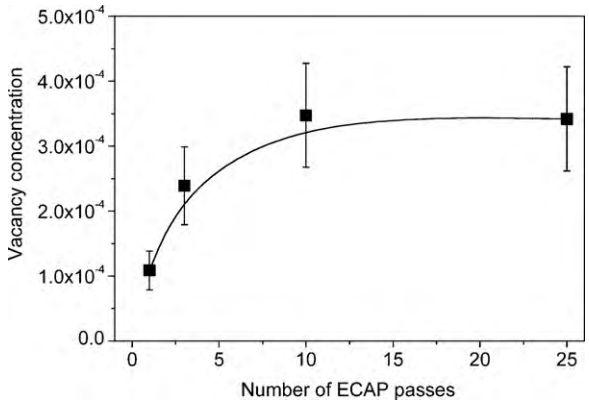

Fig. 3. The vacancy concentration determined from the change of stored energy as a function of number of ECAP passes.

the studied samples was relatively low ($0.1 \pm 0.1\%$) and this value is close to the detection limit of twin boundary frequency of X-ray line profile analysis for the applied experimental setup. After 4 years of storage the parameters of the microstructure determinable by X-ray line profile analysis (crystallite size, dislocation density, edge/screw character and arrangement of dislocations and twin boundary frequency) remained unchanged within the experimental error which indicate that recrystallization did not occur or it is marginal during storage for 4 years. If a significant amount of new, dislocation-free grains had been formed, the average dislocation density would have decreased. It should be noted that annihilation of dislocations and recrystallization may occur during longer storage of these Cu samples similarly as reported in previous studies, e.g. in Ref. [4].

The present results of X-ray line profile analysis show that the reduction of the stored energy during storage is most probably attributed to the annihilation of lattice defects which cannot be evaluated by line profile analysis. These defects may be point defects such as vacancies or vacancy agglomerates which form in a high concentration during severe plastic deformation as shown in previous papers [13,15,16]. The relation between the stored energy of vacancies (E_{vac}) per unit mass and the vacancy concentration (c_v) can be given as [15]:

$$E_{vac} = e_{vac} c_v \frac{N_A}{M}, \quad (1)$$

where e_{vac} is the formation energy of a vacancy (0.195×10^{-18} J [14]), N_A is the Avogadro's number (6×10^{23} mol^{-1}) and M is the molar mass for Cu (63.55 g mol^{-1}). Assuming that the reduction of the stored energy is attributed solely to the loss of vacancies, the decrease of vacancy concentration during the storage for 4 years was determined from the change of stored energy using Eq. (1). The change of c_v is plotted as a function of number of ECAP passes in Fig. 3. The loss of vacancy concentration ($\sim 1–3 \times 10^{-4}$) has similar value as the vacancy content determined previously for Cu samples immediately after ECAP by electrical resistivity measurement or a combination of X-ray line profile analysis and calorimetry [15]. Therefore, most probably the majority of vacancies formed during

Table 1
The crystallite size, the dislocation density (ρ) and the parameter q describing the edge/screw character of dislocations obtained by X-ray line profile analysis. The stored energy determined immediately after ECAP (E_{stored}) and storage for 4 years ($E_{stored,4y}$), the contribution of dislocations (E_{disl}) to the stored energy and the difference between $E_{stored,4y}$ and E_{disl}.

ECAP passes	Crystallite size [nm]	ρ [$\times 10^{14}$ m^{-2}]	q	E_{stored} [J/g]	$E_{stored,4y}$ [J/g]	E_{disl} [J/g]	$E_{stored,4y} - E_{disl}$ [J/g]
1	87 ± 9	15 ± 2	2.0 ± 0.1	0.48 ± 0.04	0.28 ± 0.03	0.23 ± 0.03	0.05 ± 0.05
3	75 ± 8	21 ± 2	2.0 ± 0.1	0.85 ± 0.09	0.41 ± 0.04	0.31 ± 0.04	0.10 ± 0.08
10	64 ± 7	20 ± 2	1.9 ± 0.1	1.0 ± 0.1	0.38 ± 0.04	0.31 ± 0.04	0.07 ± 0.07
25	101 ± 10	15 ± 2	1.7 ± 0.1	1.0 ± 0.1	0.37 ± 0.04	0.27 ± 0.04	0.10 ± 0.08

ECAP disappeared during storage for 4 years at RT. For supporting this assumption, the stored energy of dislocations (E_{disl}) was determined from the dislocation density listed in Table 1 using the following formula [15]:

$$E_{disl} = A\frac{Gb^2\rho}{\rho_m}\ln\frac{1}{b\sqrt{\rho}}, \quad (2)$$

where G is the shear modulus (47 GPa), b is the magnitude of Burgers vector (0.25 nm), ρ is the dislocation density, ρ_m is the mass density (8.96×10^6 g m^3 for Cu) and A stands for the factor depending on the edge/screw character of dislocations. The value of A equals to $(4\pi)^{-1}$ and $(4\pi(1-\nu))^{-1}$ for screw and edge dislocations, respectively, where ν is the Poisson's ratio (0.3 was taken). The parameter q determined from X-ray line profile analysis describes the edge/screw character of dislocations. The theoretically calculated values of q for pure edge and screw dislocations in Cu are 1.68 and 2.37, respectively [17]. The values of q obtained for the samples processed by different number of ECAP passes are listed in Table 1. In the case of mixed dislocations the value of A can be obtained from the experimentally determined q using a simple rule of mixture:

$$A = \frac{q-1.68}{0.69}\frac{1}{4\pi} + \frac{2.37-q}{0.69}\frac{1}{4\pi(1-\nu)} \quad (3)$$

The values of stored energy of dislocations (E_{disl}) calculated from Eqs. (2) and (3) are listed in Table 1. The values of E_{disl} are smaller than the stored energies measured after 4 years ($E_{stored,4y}$). The difference ($E_{stored,4y} - E_{disl}$) can be attributed to the grain boundaries and the remaining vacancies. As this difference is 4–9 times smaller than the stored energy of vacancies annihilated during 4 years ($E_{stored} - E_{stored,4y}$), therefore the remaining vacancy concentration should be much smaller than that of the vacancies disappeared during 4 years, i.e. the values of c_v plotted in Fig. 3 approximate well the concentrations of vacancies formed during ECAP.

Fig. 3 shows that the vacancy concentration increases with increasing the number of ECAP passes and saturates at about 10 passes. It is noted that the dislocation density saturates at smaller number of passes (at about 3 passes, see Table 1) in accordance with a previous report [15]. Future studies are needed to reveal why the vacancy concentration saturates at larger strain value than the dislocation density in ECAP-processed Cu samples. It is worth to note that the values of c_v obtained in this evaluation has the same order of magnitude as the equilibrium vacancy concentration near the melting point. Taking 1.28 eV as the value of vacancy formation energy and 12.2 as the pre-exponential factor in the Arrhenius-type formula of vacancy concentration [18], 4×10^{-21} and 2×10^{-4} are obtained for the equilibrium vacancy concentrations at RT and the melting point, respectively. This means that the vacancy concentration after ECAP at RT is 17 orders of magnitude larger than its equilibrium value. The very large excess of vacancies was most probably formed due to severe plastic deformation during ECAP. During storage of the ECAP-processed samples, the vacancy concentration might decrease by migration along the boundaries of UFG grains to the free surface and/or by sinking at small dislocation loops. In the latter case, the sink of vacancies is accompanied by the annihilation of dislocation loops. These small loops having a dimension of about 1–2 nm may be formed when mobile dislocations intersect immobile dislocation dipoles. These loops are also invisible by X-ray line profile analysis due to their strongly shielded strain fields and small dimensions. If a large number of loops act as sinks of vacancies, the annihilation of these loops also contributes to the decrease of the stored energy during storage of the samples, therefore the loss of vacancies may be lower than the values plotted in Fig. 3.

4. Conclusion

It was shown that the stored energy in Cu samples processed by ECAP at RT decreased by a factor of 2–3 during storage at RT for 4 years. At the same time, the crystallite size, the dislocation density and the twin boundary frequency remained unchanged indicating that the reduction of the stored energy was most probably resulted by the decrease of vacancy concentration. The loss of vacancy concentration calculated from the change of stored energy has very high value ($\sim 1–3 \times 10^{-4}$) which is in good agreement with the concentration of excess vacancies measured by other authors immediately after ECAP. This indicates that the majority of excess vacancies were annihilated during 4 years of storage. The vacancy content increased with increasing the number of ECAP passes and saturated at higher number of passes than the dislocation density.

Acknowledgements

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