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ULTRAFINE-GRAINED MATERIALS

Stored energy and recrystallization temperature in high purity copper after equal channel angular pressing

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Abstract Equal channel angular pressing (ECAP) was conducted at room temperature to impose high strain into high purity copper. Differential Scanning Calorimeter (DSC) was used to estimate the stored energy from ECAP and recrystallization temperature. It was found that the stored energy increases upon ECAP processing until a peak is reached at 12 passes of ECAP, and a slight decrease in stored energy was observed at higher ECAP passes. The recrystallization temperature decreases upon the increase of the stored energy up to ~50 J/mol, and reaches a stable valve of ~210 °C. Partial annealing of an ECAP processed (8 passes) sample by heating to ~185 °C at a heating rate of 20 °C/min released the stored energy from ~55 to ~18 J/mol, without substantial change on the recrystallization temperature of the sample. A two parameters model was used to help calculate stored energy of ultrafine-grained copper after high strain level processing.

Introduction

The stored energy of plastically strained metals, mostly in the form of their dislocation substructures, is one of the keys to control and improve the properties of metallic alloys. Apart from providing a direct strengthening effect, it also provides the driving force for subsequent microstructural evolution on heating by recovery and recrystallization, and thus, this generally results in lower recrystallization temperature in structures of higher stored energy [1].

In general, the stored energy and the related recrystallization temperature depend not only on deformation parameters such as strain extent, strain rate, and deformation mode, but also on structure factors of the material, such as grain size, grain boundary characters, chemical elements, second phase particles, crystal orientation, and stacking fault energy (SFE) [2–10]. Take strain effect, for example, stored energy increases as strain increases, and it usually reaches saturation, E_{sat}, after a critical strain level [2, 3]; the related recrystallization temperature decrease as strain increases. However, it did not lead to a further reduction on continuingly increasing strains in T_R once E_{sat} is attained [2, 4]; this reveals that T_R is independent of strain under a high strain level when E_{sat} is obtained, and the minimum recrystallization temperature is incidentally defined as T_{min} for convenience. It is generally found that at low strain levels ($\varepsilon < 0.5$), the stored energy (E_s) is greater for a small grain size than that for a coarse grain size, due to a greater grain boundary area per unit volume, and such difference in E_s becomes smaller as strain increases [3, 5, 6]. A fine-grained material will recrystallize more rapidly than a coarse-grained material, as grain boundaries are favored nucleation sites, and therefore the number of available nucleation sites is greater for a fine-grained material [1, 5, 6, 11, 12]. It is worth noting that in the investigations of Mandal and Baker [6] finer grain size results in higher E_{sat} and lower corresponding T_{min} in four different micro-grain sized samples.

This paper is dedicated to Ultrafine Grained Materials V.

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However, in the foretime, strains were obtained by conventional deformations, which have a limit on refining grain size. There is a lack of studies on stored energy and recrystallization temperature in structures with grain size below one micrometer, which are recently of more and more particular interest. By far, severe plastic deformation (SPD) is the one feasible method to impose high strains into materials and result in ultrafine grained-size (UFG, 100–1,000 nm) [13–15]; further investigations of stored energy and related recrystallization temperature need to be conducted in structures with grain size below one micrometer, on which rarely attentions have been paid until now.

In the present work, strain levels of 1–24 have been imposed on high purity copper (99.98%) by ECAP processing, and the stored energy and related recrystallization temperature at different strain levels have been observed. Also the relationship between stored energy and recrystallization temperature has been analyzed.

Experimental material and procedures

The experiments were conducted using hot-rolled high purity copper plate containing 99.98 wt% Cu. Samples with a grain size of $\sim$100 μm were cut along the longitudinal direction with a size of 12 × 12 × 80 mm^3 for ECAP processing. Square-shaped bar samples were used for the present investigation to permit easy rotation by 90° around the specimen axis between passes (Route Bc) and to prevent any undesirable rotations of the samples during ECAP. ECAP was conducted at room temperature using a die with the intersecting angle of 90° between the two equal channels, and an out angle of 20° at the channel intersection. With this die geometry, a true strain of $\sim$1 could be introduced into the material by each pass of ECAP.

To measure the grain size, TEM was used for observations on the transverse cross sections of the samples, by JCM-200CX and JEM-2100. A solution of 33% nitric acid with 67% methanol was used for twin-jet polishing before TEM. EBSD analysis was also conducted for static data of structure characters on FEI SIRION (200), with OIM 4000.

DSC was used to estimate the stored energy and recrystallization temperature of samples processed to different ECAP passes. The recrystallization temperature was defined as the temperature at which heat flow reaches a peak value of heat releasing, and stored energy was calculated as the area under the heat releasing peak. DSC was conducted on Shimadzu DSC-50 with nitrogen atmosphere. Heating rate of the sample was set to 20 °C/min, and the sample was heated from ambient temperature to 400 °C. For DSC experiments, the samples were cut into a disc with 3 mm in diameter and 1.2 mm in height. Additional tests were also conducted to guarantee the calorimeter stability during the experiments, and it was concluded that the sample preparation has an insignificant effect on its DSC behavior.

Experimental results and discussion

The grain size development of pure copper via ECAP strains are shown in Fig. 1. It is seen that ultrafine grain size was obtained just after 1 pass of ECAP processing, and further decreases in grain size were obtained as continuing ECAP strain increased until 8 passes, after which a minimum grain size, $\sim$260 nm, was achieved. Very little grain size increase was observed upon further ECAP to higher strain levels.

Evolutions of stored energy and recrystallization temperature with strain variety after ECAP processing are shown in Fig. 2. In general, stored energy evolution E_s

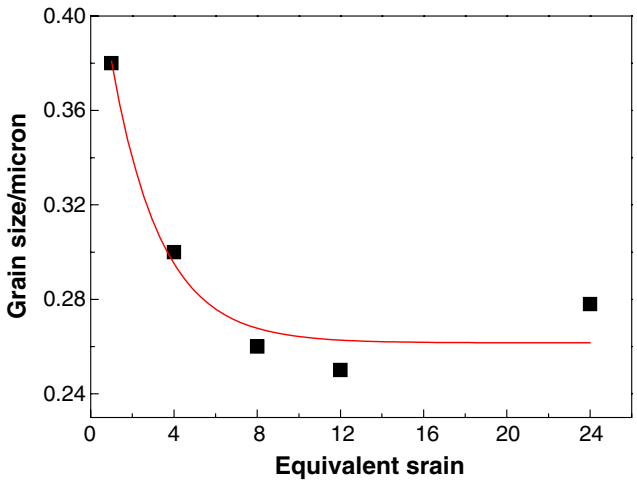

Fig. 1 Grain size dependence on ECAP strain

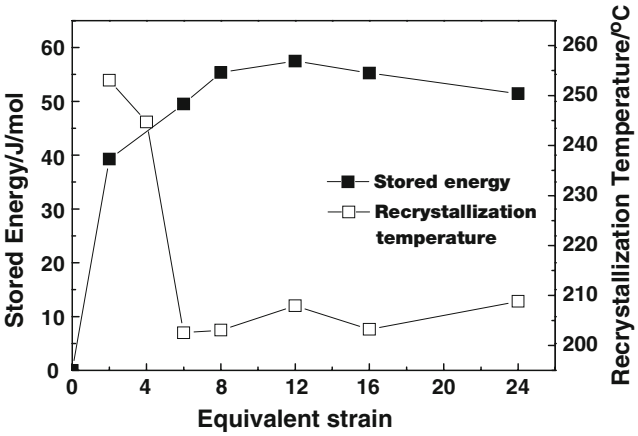

Fig. 2 Stored energy and recrystallization temperature in samples after different levels of ECAP processing

increases as ECAP strain increases, and reaches a maximum ($\sim$57 J/mol) at equivalent true strain of $\sim$12, after which stored energy appears to decrease slightly with further increases in strain. It is noticed that in the stage of increasing E_s, the increase rate of E_s is highest when $\varepsilon < 2$, and the increase rate of E_s decreases during ECAP passes from 2 to 12. It is of interest that E_s begins to decrease with increasing strains, after reaching its maximum at an equivalent true strain of $\sim$12. Such phenomenon is different from that acquired in structures of micrometer grains [2, 3], for which a saturation E_{sat} was achieved after some strain, as discussed above. However, in spite of a slight decrease appearing in E_s at higher strain levels, stored energy remains above $\sim$50 J/mol in the UFG structure after ECAP.

On the other hand, recrystallization temperature (T_R) of ECAP-processed copper decreases as strain increases (Fig. 2), and it seems to reach a constant after an equivalent strain of $\sim$8. It is obvious that T_R decreases with increasing strains at $\varepsilon < 8$, because of the higher stored energy with larger strain content. The minimum recrystallization temperature as obtained at strain levels which are higher than 8 is revealed to be independent of stored energy, which varies as strain increases, and may be related to the stable grain size as shown in Fig. 1. It could be indicated that the recrystallization kinetics are controlled by structure factors other than stored energy at high strain level in the UFG structure.

For a better description of grain size dependence on E_s and T_R, relevant data are plotted in Fig. 3 for both micrometer-grained structures and UFG structures. In the two kinds of structures, recrystallization temperature of materials decreased as stored energy increased with nearly a linear proportional relationship when E_s is lower than 50 J/mol, except that the slope for that in UFG structure is lower than that in micrometer-grained structure. This is in accordance with the effect of grain size observed in micrometer-grained structures [5, 6]. It is noticed that higher stored energy is preserved in UFG structure after SPD processing [16, 17], as shown in Fig. 3. Compared to the E_{sat} obtained in coarse grained copper with micrometers grain size [2, 4], which is no more than 50 J/mol, stored energy, E_s, preserved in UFG structure can be as high as 67 J/mol, as shown in Fig. 3. It is worth noting that T_R seemed to be independent of E_s when it is higher than 50 J/mol, and this fact reinforces the idea from Fig. 2 that recrystallization kinetics are controlled by structure factors other than stored energy at high strain level in UFG structure.

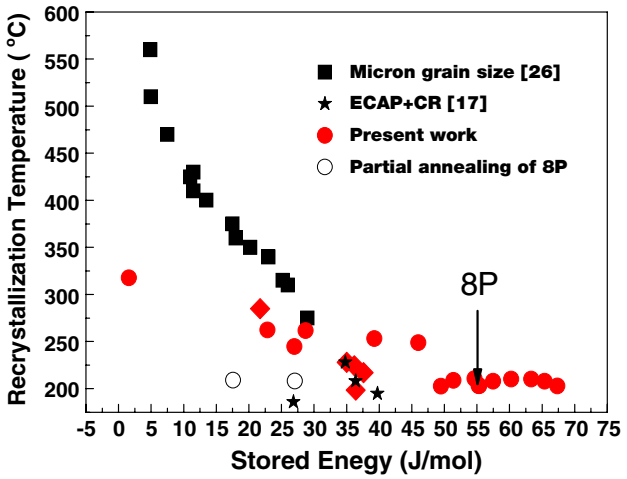

Fig. 3 Stored energy and recrystallization temperature for micron grain size and ultrafine grain size structures. It is shown that recrystallization temperature is proportional to stored energy; however, the slope of ultrafine grain size is lower than that in coarse micron grain size

To further investigate the recrystallization temperature dependence on stored energy in UFG structure, samples after 8 passes of ECAP processing (where E_s is $\sim$55 J/mol) are annealed partially, during which samples were first heated from ambient to a temperature of 180 or 185 °C at a heating rate of 20 °C/min in DSC unit, and then cooled down inside the stove with nitrogen gas blowing. Finally the samples were heated again from ambient temperature to 400 °C at the same rate of 20 °C/min, during which process E_s and T_R are measured. Stored energy in the samples with 8 passes of ECAP is decreased from 55 to 27 J/mol by partial annealing to 180 °C, and to only 18 J/mol by partial annealing to 185 °C. In contrast, the related recrystallization temperatures are still 208 °C and 209 °C, which is almost not changed from that of samples with 8 passes ECAP (210 °C). This shows that E_s has nothing to do with T_R in this case; the results are also shown in Fig. 3 as circles.

The temperatures of 180 and 185 °C are just a temperature around the onset temperature (183.8 °C) of the releasing peak for samples 8 passes of ECAP, and only recovery processes are believed to occur by dislocation rearrangement which results in initial decrease in dislocation density, but the UFG grain size formed during ECAP remains unchanged, as reported by Ungar et al. [18]. Additional separate annealing experiments of the same sample were conducted at 180 °C for 10 min; a well-recovered fine structure with low defects density was observed with $\sim$67% of grains with a size of 270 nm in average. This grain size means that there is almost no grain growth during this low temperature annealing. Therefore, it suggests that limited variety in T_R may be related to limited change in grain size, while the release of E_s from recovery of dislocation annihilation does not contribute much to the change in the recrystallization behavior.

Apart from grain size observations after ECAP processing, other microstructure features are also examined at

higher strain level where a steady grain size is achieved. According to TEM results, some grain boundaries evolve gradually into clearly defined sharper ones as strain increases over ~8, with grain interior becoming cleaner correspondingly and a gradual increase in mean misorientation, as revealed by select area diffraction pattern. These changes are similar to that observed after partial annealing of 8P samples. In other words, it could be inferred that when the steady refined grain size is obtained, which is 260 nm in the present work, increase or release in stored energy has very limited effect on recrystallization temperature, but affects structure rearrangement during recrystallization, e.g., misorientation adjustment and boundary structure rearrangement.

Although stored energy is generally accepted to be dependent on strain content and dislocation density at middle or low strain levels, it becomes independent on strains when a balance is achieved in dislocation storage and annihilation at large strain levels [19–22]. There is a rule given by Baker and his colleagues that the saturation value of the stored energy from geometrically necessary dislocations is inversely proportional to the grain size [5, 6]. So it is reasonable to describe stored energy with structure features, such as grain size and misorientation, under a high strain level. A model is introduced by Humphreys et al. [1] on the relationship between stored energy, grain size, and misorientation, with the hypothesis that the deformation microstructure consists of well-defined, equiaxed subgrains, which is reasonable under high strain level, and the stored energy may be estimated from the subgrain diameter (D) and the specific energy (γ_s) of the low angle boundaries which comprise the subgrain walls. The area of low angle boundary per unit volume is ~3/D and hence the energy per unit volume (E_D) is given approximately by [1]

$$E_D \approx \frac{3\gamma_s}{D} \approx \frac{\alpha\gamma_s}{R} \quad (1)$$

where α is a constant of value ~1.5.

The boundary energy (γ_s) is directly related to the misorientation (θ) across the boundary, and therefore Eq. 1 maybe expressed in terms of the parameters D and θ, both of which may be measured experimentally as

$$E_D = \frac{3\gamma_s\theta}{D\theta_m}\left(1 - \ln\frac{\theta}{\theta_m}\right) \approx \frac{K\theta}{D} \quad (2)$$

where θ_m is defined by the equation $\gamma = \gamma_m \frac{\theta}{\theta_m}\left(1 - \ln\frac{\theta}{\theta_m}\right)$, and K is a constant.

To inspect the validity of Eq. 2, E_s, instead of E_D, and mean misorientation θ_m, instead of θ, which are obtained by DSC and EBSD for samples after 12 and 16 passes of ECAP processing, are given in Table 1. Applying Eq. 2 yields a K value for each sample. The two values of K, for samples after 12 and 16 passes of ECAP processing, are almost same. This indicates that Eq. 2 is reasonably suitable for the high purity copper samples processed to high strain levels with high angle grain boundaries, although the model (Eq. 1) was initially developed for Al alloys with low angle grain boundaries [20, 23–25].

Table 1 Measured data of stored energy (E_s), mean misorientation (θ_m), and mean grain size ($\overline{D}$) in various processing states, and correspondingly calculated values of K from Eq. 2

True strain	E_s (J/mol)	θ_m (degree)	$\overline{D}$ (μm)	K
12	57.48	29.12	0.4874	0.9621
16	55.26	30.69	0.5353	0.9639

Conclusion

UFG copper was obtained after 1–24 passes ECAP processing, and the stored energy and recrystallization temperature were estimated correspondingly by DSC.

The stored energy increases as ECAP strain increases and reaches a maximum after 12 passes of ECAP, when the stored energy is ~57 J/mol. It then begins to decrease as ECAP strain increases further.

The recrystallization temperature decreases sharply with increase in strain when the stored energy is below ~55 J/mol. A nearly constant recrystallization temperature is observed after 8 passes of ECAP processing, when stored energy is higher than 50 J/mol, and a stable grain size is achieved. That is, recrystallization temperature seems to be independent of stored energy after steady grain size is achieved in samples after ECAP.

A two parameters model with grain size and mean misorientation is reasonable for estimating E_s after high strain level processing.

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