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A scanning force microscopy study of grain boundary energy in copper subjected to equal channel angular pressing

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Abstract

We employed a scanning force microscopy technique to determine the ratio of grain boundary and surface energies in copper using the thermal grooving method. Samples of ultrafine grain copper obtained by four passes of equal channel angular pressing were heat treated in a reducing atmosphere at 400 °C for 15 min and at 800 °C for 2 h. The average dihedral angles of the grain boundary grooves after the former and the latter heat treatments were $152.4 \pm 6.3°$ and $164.2 \pm 4.3°$, respectively, which can be translated into the difference by a factor of 1.8 in average grain boundary energies. This difference implies that the grain boundaries in ultrafine grain copper produced by equal channel angular pressing are in a state of high non-equilibrium that cannot be fully relaxed after a short annealing at 400 °C, but that undergoes significant relaxation after annealing at 800 °C.

Keywords: Equal channel angular pressing (ECAP); Grain boundaries (GBs); Grain boundary energy; Scanning force microscopy (SFM); Copper alloys

1. Introduction

The reduction of average grain size represents a traditional way of improving mechanical properties of polycrystalline metals and alloys. Severe plastic deformation (SPD) methods developed during the last three decades offer one of the most efficient ways to produce bulk ultrafine-grained (UFG) metals and alloys with the average grain size in the sub-micrometer range. Equal channel angular pressing (ECAP) is a sub-group of the SPD techniques which is most suitable for industrial scale-up [1–6]. Its main principle is repetitive pressing of a metal billet through a bent channel. Shear bands formed during pressing constitute preferential sites for the nucleation of dislocations. Thus, the sub-division of grains into cells results in grain refinement. Subsequent cycles of pressing together with the rotation of the billet between the passes cause the accumulation of more dislocations in the cell walls, increase the misorientation angles between the cells and, therefore, promote the formation of high-angle grain boundaries (HAGBs) [2].

In addition to the UFG microstructure, alloys produced by ECAP exhibit many unusual functional properties, which have been attributed to the special state of grain boundaries (GBs) in these alloys. The term "non-equilibrium GBs" has been applied to GBs in a highly strained, energetically metastable state [1]. These GBs exhibit a higher interfacial energy, higher intensity of strain fields, higher diffusivity and larger free volume than their relaxed counterparts.

The modification of GB properties due to the accumulation of lattice dislocations has been reported by Grabski and Korski [7]. They observed an increase of GB energy in Cu due to absorption of lattice dislocations during the migration of GBs, and concluded that these GBs transform into a non-equilibrium state. Based on this approach, Nazarov [8–11] has developed a structural model that describes both the formation mechanism of non-equilibrium GBs during plastic deformation and their properties. The

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starting point for the model is a low-angle GB (LAGB), which can be described as a periodic dislocation array in the framework of classical Read–Shockley model [12,13]. Hence, all GB properties are expressed as the sum of contributions of individual dislocations forming the GB. In particular, the elastic strain field in the vicinity of GB is the sum of the elastic strain fields of individual dislocations. Because of the periodicity in distribution of dislocations, the elastic fields of individual dislocations cancel each other out at large distances from the LAGB, so that only a short-range strain field near the GB remains. This periodicity in distribution of dislocations is lost in non-equilibrium GBs which evolve during plastic deformation by absorbing a large number of lattice dislocations. These trapped dislocations dissociate into two different components with the Burgers vectors normal ($\pm b_n$) and tangential (b_t) to the GB plane. While the tangential components are glissile and form pile-ups at triple lines, the normal ones are sessile. Both dislocation populations (pile-ups of glissile extrinsic GB dislocations and disordered networks of sessile GB dislocations) contribute to the increase in energy and changes in the properties of these non-equilibrium GBs. In the framework of this dislocation model the following properties of non-equilibrium GBs can be quantified: the root-mean-square (RMS) strain in the vicinity of GBs, the GB excess energy γ_b, and the GB excess volume. For example, the total elastic energy, E_{el}, associated with a non-equilibrium GB can be calculated as the volume (V) integral of all stress (σ_{ij}) and strain (ε_{ij}) components associated with the disordered array of GB dislocations:

$$E_{el} = \frac{1}{2}\int\int\int \sigma_{ij}\cdot\varepsilon_{ij}\,dV \tag{1}$$

The resulting expression for the GB energy, γ, is then:

$$\gamma_b = \frac{Gb^2\cdot\rho_v d}{12\pi(1-v)}\ln\left(\frac{d}{b}\right) \tag{2}$$

where ρ_v is the density of dislocations in the bulk ECAP-ed material, b is the Burgers vector, d is the grain size, and G and v are the shear and Poisson's moduli, respectively. Eq. (2) predicts that for Cu produced by ECAP with common values of $\rho_v \approx 6\times10^{15}\ m^{-2}$ and $d \approx 200$ nm the energy of non-equilibrium GBs should be about $1.2\ J\ m^{-2}$ [8–11], i.e. nearly twice its equilibrium value [14].

Although the concept of non-equilibrium GBs is widely employed for describing the properties of UFG materials produced by SPD, its experimental foundations are still controversial. First, the measurements of GB properties requiring heat treatments at elevated temperatures (i.e. GB energy and diffusivity) are difficult because of insufficient thermal stability of the microstructure of SPD-processed alloys. For example, while several researchers reported significantly enhanced GB diffusivity in UFG materials produced by SPD [15–18], in some other studies the measured GB diffusivities were consistent with the known data for coarse-grained materials [19,20]. Secondly, most of the experimental support presented so far in favor of the hypothesis of non-equilibrium GBs is indirect in nature (i.e. the GB properties are extracted from kinetics of grain growth or magnetic properties). A critical review of the available experimental evidence for the non-equilibrium GB character in UFG materials produced by SPD is given elsewhere [21].

The GB energy, γ_b, is the most direct indicator of the degree of GB non-equilibrium. The GB energy can be measured in UFG materials employing differential scanning calorimetry (DSC). For instance, Huang et al. [22] measured the enthalpy released during grain growth in nanocrystalline copper (with an initial average grain size of 8.5 nm) produced by compaction of particles. The value of γ_b extracted from the enthalpy release was $0.7\ J\ m^{-2}$, about the same as the well-known value for pure copper ($0.6\ J\ m^{-2}$) [14]. Concerning the effect of plastic deformation, it was shown that UFG copper exhibits a higher exothermal peak with respect to cold-rolled copper due to the higher values of elastic and capillary energy stored in the former [23]. It should be noted that the DSC results alone are too indirect, and for a better understanding of the physical processes in the UFG alloys they should be combined with the results obtained by other characterization techniques. For example, the comparison of the DSC peak integral intensity of ball-milled metals with the X-ray diffraction (XRD) peak broadening shows that the heat released is proportional to the square of the RMS strain [24]. The energy released is, therefore, associated with strain relaxation.

In spite of the fact that DSC measurements provide a quantitative estimation of GB energy, this technique suffers from several drawbacks. First, the heat released (ΔH) during grain growth characterizes some average value of GB energy; it is impossible to determine the differences in energies between individual GBs or the parameters of GB energy distribution using this method. Secondly, the relaxation of some other defects (i.e. dislocations) can contribute to ΔH values measured by DSC, so that only the upper limit of γ_b can be obtained. Another drawback of this method is that it can be employed for GB energy measurements in fine-grained polycrystals only. As grain size increases, the total area of interfaces decreases and the intensity of the DSC peak associated with grain growth drops below the detection limit of the technique.

In the view of the above problems in quantifying the degree of GB non-equilibrium, it is very attractive to implement the method of scanning force microscopy (SFM) to measure the ratio of GB and surface energies for individual GBs using the thermal grooving technique [25–31]. Among the advantages of this method are its simplicity, the capability of measuring the relative energies of individual GBs and the possibility of conducting the measurements in polycrystals with very different grain sizes. The goal of this work was to quantify the degree of GB non-equilibrium in ECAP-processed Cu employing the SFM and thermal grooving techniques. To achieve this goal we compared the GB energies in the UFG Cu obtained by ECAP with