Microstructure of severely deformed metals determined by X-ray peak profile analysis

J. Gubicza a,b,*, N.H. Nam b, L. Balogh a, R.J. Hellmig c, V.V. Stolyarov d, Y. Estrin c, T. Ungár a

a Department of General Physics, Eötvös University, Pazmany P.s. 1/A, H-1117, Budapest 1518, Hungary
b Department of Solid State Physics, Eötvös University, Pazmany P.s. 1/A, H-1117, Budapest 1518, Hungary
c Institute for Materials Engineering and Technology, Clausthal University of Technology, Clausthal, Germany
d Institute of Physics of Perspective Materials, Ufa State Aviation Technical University, Ufa, Russia

Received 1 September 2003; accepted 5 November 2003

Abstract

Two essentially different metals, fcc copper and hexagonal titanium, were deformed by equal channel angular pressing (ECAP) up to eight passes. The microstructure developed as a result of severe plastic deformation (SPD) was studied by X-ray peak profile analysis. The formation of submicron grain sized structures was studied as a function of the number of ECAP passes. Thermal stability of the microstructure in both copper and titanium was examined by differential scanning calorimetry (DSC). During the isothermal heat-treatment of copper a bi-modal microstructure was formed, as manifested in a special shape of the peak profiles. In titanium, a considerable fraction of dislocations gets annihilated at temperatures well below the exothermic peak in the DSC curve.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Metals; Dislocations; X-ray diffraction

1. Introduction

Severe plastic deformation (SPD) is an effective tool for producing bulk ultrafine grained (submicron grain sized or nanostructured) metals [1]. One of the most common SPD methods is equal channel angular pressing (ECAP)—a technique that results in a homogeneous submicron grain structure of the workpiece [2,3]. X-ray diffraction peak profile analysis is a widely used method for studying the microstructure of materials [4,5]. In SPD processed materials where the lattice distortions are primarily caused by dislocations the strain broadening of X-ray peak profiles can be expressed in terms of the characteristic parameters of the dislocation structure [6,7]. In these formulas, the anisotropic strain broadening is taken into account by the contrast factors of dislocations [8–10]. Since the values of the dislocation contrast factors depend on the dislocation slip systems present in the crystal, the evaluation of X-ray profiles for the contrast factors permits the determination of the dislocation structure. In the last few years, a fast development in computing made it possible to work out procedures for determining the parameters of the microstructure by fitting the whole diffraction profiles [11–14]. In the recently elaborated multiple whole profile (MWP) fitting method, the measured intensity profiles are fitted by theoretical functions calculated on the basis of a model of the microstructure [13,14]. This procedure makes it possible to determine both the crystallite size distribution and the dislocation structure in ultrafine grained materials.

In this work, the microstructure formed due to ECAP deformation in copper and titanium was studied by X-ray peak profile analysis. The development of the submicron grained structure was investigated as a function of ECAP passes. Thermal stability of the ultrafine grained microstructures was also studied.

2. Experimental

Technical purity copper specimens were annealed at 450 °C for 2 h prior to ECA pressing to obtain a
defined initial state. They were subsequently deformed by 1, 2, 4, or 8 ECAP passes at room temperature using a 90° die following route C. This means that after each pass the billet was rotated around its longitudinal axis through the angle 180°. An ultratine grained commercial pure (CP) titanium specimen was also produced by eight ECAP passes at 400–450 °C with B1 route (the billet was rotated around its longitudinal axis through the angle 90° between intermediate passes). Thermal stability of ultratine structures produced by severe plastic deformation was investigated by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC2 calorimeter.

The X-ray diffraction profiles were measured on the cross-section of the billets. The X-ray diffraction experiments were performed by a special double-crystal diffractometer (Nonius FR591) with negligible instrumental broadening using Cu Ka1 radiation (λ = 0.15406 nm). The X-ray peak profiles were recorded by a linear position sensitive gas-flow detector (OED 50 Braun, Munich). The peak profiles were evaluated by the MWP fitting procedure described in detail in Refs. [13,14]. In this method, the experimental profiles are fitted by the theoretical intensity peak profiles calculated on the basis of a microstructural model. In this model, the crystallites have a spherical shape and a log-normal size distribution, and the lattice strains are assumed to be caused by dislocations. The procedure has five and six fitting parameters for cubic and hexagonal crystals, respectively: (i) the median and the variance, m and σ, of the log-normal size distribution function; (ii) the density and the arrangement parameter of dislocations, ρ and M; and (iii) the q (cubic crystals) or q1 and q2 (hexagonal crystals) parameters in the contrast factors of dislocations. The arithmetic, the area- and the volume-weighted mean crystallite sizes can be calculated from m and σ using formulas given in Ref. [6]. In this paper only the volume-weighted mean crystallite size is presented. The magnitude of M gives the strength of the dipole character of dislocations: a higher M value corresponds to a weaker dipole character and weaker screening of the displacement fields of dislocations. The q or q1 and q2 parameters describe the dislocation types (e.g. edge or screw) present in the specimen. The copper specimens deformed by ECAP were subjected to DSC scan from 300 to 650 K at the heating rate of 40 K/min. A broad exothermic peak was observed on the DSC curve which corresponds to the release of the stored strain energy during the recovery of the microstructure. The maximum of the peak and the evolved heat are listed in Table 1. The peak profiles were evaluated by the MWP fitting procedure described in detail in Refs. [13,14]. In this method, the experimental profiles are fitted by the theoretical intensity peak profiles calculated on the basis of a microstructural model. In this model, the crystallites have a spherical shape and a log-normal size distribution, and the lattice strains are assumed to be caused by dislocations. The procedure has five and six fitting parameters for cubic and hexagonal crystals, respectively: (i) the median and the variance, m and σ, of the log-normal size distribution function; (ii) the density and the arrangement parameter of dislocations, ρ and M; and (iii) the q (cubic crystals) or q1 and q2 (hexagonal crystals) parameters in the contrast factors of dislocations. The arithmetic, the area- and the volume-weighted mean crystallite sizes can be calculated from m and σ using formulas given in Ref. [6]. In this paper only the volume-weighted mean crystallite size is presented. The magnitude of M gives the strength of the dipole character of dislocations: a higher M value corresponds to a weaker dipole character and weaker screening of the displacement fields of dislocations. The q or q1 and q2 parameters describe the dislocation types (e.g. edge or screw) present in the specimen.

### Table 1

<table>
<thead>
<tr>
<th>Number of ECAP passes</th>
<th>m (nm)</th>
<th>σ</th>
<th>⟨ΔV_cr⟩ (mm)</th>
<th>ρ (×10²⁴ m⁻²)</th>
<th>M</th>
<th>q</th>
<th>T_peak (K)</th>
<th>H (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35(3)</td>
<td>0.28(2)</td>
<td>71(9)</td>
<td>12(2)</td>
<td>1.9(1)</td>
<td>2.9(3)</td>
<td>581(1)</td>
<td>0.54(4)</td>
</tr>
<tr>
<td>2</td>
<td>40(4)</td>
<td>0.43(3)</td>
<td>85(9)</td>
<td>22(2)</td>
<td>1.6(1)</td>
<td>1.9(1)</td>
<td>556(1)</td>
<td>0.83(6)</td>
</tr>
<tr>
<td>4</td>
<td>45(5)</td>
<td>0.34(3)</td>
<td>67(9)</td>
<td>28(2)</td>
<td>1.1(1)</td>
<td>1.9(1)</td>
<td>536(1)</td>
<td>0.84(6)</td>
</tr>
<tr>
<td>8</td>
<td>50(5)</td>
<td>0.31(3)</td>
<td>70(8)</td>
<td>26(2)</td>
<td>1.1(1)</td>
<td>2.0(3)</td>
<td>534(1)</td>
<td>0.57(7)</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. ECA pressed Cu

The median and the variance of the size distribution function, the volume-weighted mean crystallite size values, the dislocation density, the dislocation arrangement parameter and the q parameter obtained for the copper specimens ECA pressed by one to eight passes are listed in Table 1. The mean crystallite size has been reduced from several tens of microns to 71 nm already after a single ECAP pass. The crystallite size does not change significantly by further ECAP deformation. The dislocation density increases from 12 × 10¹⁴ to 28 × 10¹⁴ m⁻² when the number of ECAP passes increases from 1 to 4. The dislocation density does not change significantly with further deformation. The experimental value of the q parameter is 2.0 ± 0.1 for all samples. The q parameter values for copper corresponding to pure screw and edge dislocations in the {110} {111} slip system were determined by detailed numerical calculations using the equations from [15] and the elastic constants from [16]. This yielded the q values of 2.4 and 1.7 for pure screw and pure edge dislocations, respectively. The experimental value of q for ECA pressed Cu agrees well with the arithmetic average of the values calculated for pure edge and screw dislocations, which means that the character of dislocations is half edge-half screw. The M parameter decreases with the increase of the number of ECAP passes. This indicates that with increasing deformation the dipole character of the dislocation structure becomes stronger. It can be established that after four passes there are no substantial changes in the microstructure.

The copper specimens deformed by ECAP were subjected to DSC scan from 300 to 650 K at the heating rate of 40 K/min. A broad exothermic peak was observed on the DSC curve which corresponds to the release of the stored strain energy during the recovery of the microstructure. The maximum of the peak and the evolved heat are listed in Table 1. The maximum of the exothermic peak in the DSC curve was shifted to lower temperatures and the released heat increased with the increase of deformation up to four ECAP passes. These changes can be explained by a rise of the dislocation density with increasing number of ECAP passes.
Table 2

<table>
<thead>
<tr>
<th>Duration of heat-treatment (min)</th>
<th>m (nm)</th>
<th>σ</th>
<th>⟨x⟩_{vol} (nm)</th>
<th>ρ (× 10^{14} m^{-2})</th>
<th>Mq</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>45(5)</td>
<td>0.50(4)</td>
<td>108(8)</td>
<td>26(2)</td>
<td>1.3(1)</td>
</tr>
<tr>
<td>20</td>
<td>38(4)</td>
<td>0.54(5)</td>
<td>105(9)</td>
<td>26(2)</td>
<td>1.2(1)</td>
</tr>
<tr>
<td>40</td>
<td>290(10)</td>
<td>0.40(4)</td>
<td>510(20)</td>
<td>0.3(2)</td>
<td>1.1(1)</td>
</tr>
</tbody>
</table>

To study the recovery of the microstructure of ECA pressed Cu, the sample deformed by eight passes was annealed at 453 K for 10, 20, 30, and 40 min. The microstructure of the heat-treated specimens was also investigated by X-ray peak profile analysis. The microstructural parameters obtained for 10, 20, and 40 min annealing are listed in Table 2. It can be established that during the heat-treatment of 10 or 20 min there are only slight changes in the microstructure. The parameters of the microstructure for the sample annealed for 30 min are not given in Table 2. In this case none of the peaks could be fitted by a single theoretical profile and each peak seems to be the sum of a narrow and a broad peak. This special shape of the diffraction peaks has already been observed by Kuzel et al. [17] for the Cu sample deformed by torsion under 6 GPa pressure and annealed at 250°C for 100 min. Fig. 1 shows the 3 1 1 peak (circles) for a specimen annealed for 30 min in double logarithmic plot. In this plot the intensity goes through a well defined inflection point around ΔK = 0.006 nm^{-1}, indicating that the diffraction profile consists of two peaks, indeed. After dividing the intensity by an appropriate factor, the profile for the non-annealed specimen (the solid line in Fig. 1) matches perfectly the tail part of the peak recorded after annealing (open circles in Fig. 1). This indicates that the broad peak component of the profile obtained after annealing can be well approximated by the profile measured before the heat-treatment. The difference between the two profiles (the solid line and the open circles in Fig. 1) gives a sharp peak which corresponds to the recovered volume of the material.

The mean crystallite size was evaluated from the integral breadth of these peaks by the modified Williamson-Hall plot [10]. In Fig. 2a the integral breadth values in the conventional Williamson-Hall plot show a typical strain anisotropy which is characteristic of dislocation-rich copper [10]. In the modified Williamson-Hall plot (Fig. 2b) the data points are arranged along a quadratic polynomial, from the intercept of which at K = 0 the volume-weighted mean crystallite size was determined to be 600 ± 80 nm. The coefficient of the quadratic term equals to πAb^2/2, where b is the Burgers vector of dislocations (0.256 nm) and A is a constant. The value of A was determined for the specimen annealed for 40 min by determining the dislocation density from the MWP fitting and the coefficient of the second term in the modified Williamson-Hall relation.
It was obtained that $A = 49$. Assuming the same value of $A$ for the specimen annealed for 30 min, the dislocation density is obtained to be $5 \times 10^{13} \text{m}^{-2}$. This means that the recovery of the microstructure starts inhomogeneously in the volume of the ECA pressed specimen. In some volumes of the material the recovery occurs even after 30 min which gives a sharp peak, in other parts of the sample the distorted microstructure remains unchanged which results in a broad peak. The bi-modal microstructure in copper results in high strength as well as high ductility of the material \[18\]. After the heat-treatment for 40 min the microstructure becomes more homogeneous, the mean crystallite size is about 510 nm and the dislocation density is $3 \times 10^{13} \text{m}^{-2}$.

3.2. Ti deformed by ECAP

The titanium sample deformed by eight ECAP passes has a very fine microstructure with the mean crystallite size of about 60 nm and dislocation density of $44 \times 10^{13} \text{m}^{-2}$. The deformed specimen was subjected to DSC scan from 300 to 1000 K at heating rate of 40 K/min. An exothermic peak is observed which starts at 800 K and ends at 900 K. The released heat corresponding to this peak is 0.72 J/g. The recovery of the microstructure was studied on the samples quenched from different temperatures of the DSC scan (400, 500, 600, 700, 750, 800, 820, and 850 K) to room temperature. The volume-weighted mean crystallite size and the dislocation density as a function of temperature are shown in Fig. 3. It can be established that the recovery of the microstructure starts before the appearance of the DSC peak. At 800 K, where the DSC peak starts, the dislocation density has already decreased from $44 \times 10^{13}$ to $9 \times 10^{13} \text{m}^{-2}$. The increase of the crystallite size is accelerated only after 800 K and it reaches 164 nm at 850 K. The dislocation density decreases further after 800 K and at 850 K it has a value of $8 \times 10^{13} \text{m}^{-2}$.

The $q_1$ and $q_2$ parameters of the contrast factors depend on the character of dislocations, and therefore, enable the determination of the prevailing dislocation slip systems in the sample. The $q_1$ and $q_2$ values for the 11 possible slip systems in Ti according to Kuzel and Klimanek \[9\] have been calculated and listed in Table 2 in Ref. \[19\]. The 11 dislocation slip systems can be classified into three groups based on their Burgers vectors: $b_1 = \frac{1}{3}(1 \ 1 \ 2 \ 0)$ (⟨a⟩ type), $b_2 = (0 \ 0 \ 0 \ 1)$ (⟨c⟩ type), and $b_3 = \frac{1}{3}(1 \ 1 \ 2)$ (⟨c+a⟩ type). A computer program was elaborated to determine the Burgers vector population from the experimental values of $q_1$ and $q_2$ \[20\]. There are 4, 2, and 5 slip systems in the ⟨a⟩, ⟨c⟩, and ⟨c+a⟩ Burgers vector groups, respectively. The program selects some slip systems from each group and averages their calculated $q_1$ and $q_2$ values with equal weights. The relative fractions of the Burgers vectors were calculated by making the measured and the weighted averaged theoretical values of $q_1$ and $q_2$ equal. If the weights have positive values the program stores them as one of the possible solutions. After examining all possible solutions, ranges of the three weights are obtained as the final solution. In the ECAP deformed sample the relative fractions of the ⟨a⟩, ⟨c⟩, and ⟨c+a⟩ Burgers vectors are 62, 0–4, and 32–36%, respectively. The abundance of ⟨a⟩-type dislocations besides the ⟨c⟩- and ⟨c+a⟩-type dislocations is in agreement with previous X-ray diffraction \[19\] and transmission electron microscopy results \[21,22\]. As the temperature increases the relative fraction of the ⟨c+a⟩-type dislocations decreases down to between 0 and 4%, indicating that these dislocations disappear faster than the ⟨a⟩ or ⟨c⟩-type ones. This can be explained by the fact that the ⟨c+a⟩-type dislocations have larger Burgers vectors and consequently higher formation energies than the other two types.

4. Conclusions

The microstructure of ECA pressed copper and titanium specimens was investigated by X-ray diffraction profile analysis. It was found that in copper the crystallite size is several tens of nanometer even after one ECAP pass and further refinement cannot be achieved by increasing the number of passes. At the same time the dislocation density increases up to four ECAP passes. The recovery of the microstructure was studied at 453 K. After 30 min a part of the sample has been recrystallized with about 600 nm crystallite size while the other part of the volume did not change. This bi-modal microstructure results in a line profile, which consists of a narrow and a broad peak. After 40 min the bi-modal microstructure disappeared, the crystallite size and the dislocation density were 510 nm and $3 \times 10^{13} \text{m}^{-2}$, respectively.

During annealing of the severely deformed titanium a considerable portion of dislocations was annihilated before the appearance of the exothermic peak in the DSC scan. The significant increase of the crystallite size (recrystallization) is correlated to the exothermic peak. The ⟨c+a⟩-type dislocations disappeared faster than the ⟨a⟩ or ⟨c⟩-types because of their higher self-energy.
Acknowledgements

This work was supported by the Hungarian Scientific Research Fund, OTKA, Grant Nos. F-047057, T-046990 and T-042714.

References