MICROSTRUCTURES OF SUBGRAIN AND GRAIN BOUNDARIES IN NANOMATERIALS

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Introduction

In the nineties of the last but one century, American Society for Testing and Materials attempted to propose rules for the quantitative comparison of materials, in particular steels, based on the metallographic analysis of their planar sections. Finally, two procedures have been recommended [1]. The *intersection count* N_L is the mean number of intersections between grain profile boundaries and unit lengths of random test lines; it was proposed by Emil Heyn in 1904. The *profile count* N_A proposed by Zay Jeffries in 1916 is the mean number of grain profiles per unit area of the observation window. Recently, the reciprocal value of N_L, namely the mean profile chord $\mu = 1/N_L$, is frequently used and called the *mean grain size*.
The both methods satisfactorily characterize also the 3D grain structures if the dispersion of grain sizes is moderate and their shapes are roughly equiaxial; then low values of N_L, N_A describe materials with coarse grains and, on the contrary, fine grain materials have high values of the both characteristics. Whenever a considerable anisotropy of the grain structure occurs, planar sections and test lines of different orientations must be examined.
A determination of spatial (3D) grain size by these methods is impossible because the sampling of grains by section planes and test lines is highly biased, namely the grains are sampled proportionally to their size. Consequently, a comparison of structures with great size dispersion of grains, such as frequently occur in nanomaterials, on the basis of the counting methods may give erroneous results if applied to grain size. As commented on the ASTM web page http://www.astm.org/: "These test methods cover the measurement of average grain size and include the comparison procedure, the planimetric (or Jeffries) procedure, and the intercept procedures. ... These test methods deal only with determination of planar grain size, that is, characterization of the two-dimensional grain sections revealed by the sectioning plane. Determination of spatial grain size, that is, measurement of the size of the three-dimensional grains in the specimen volume, is beyond the scope of these test methods... These test methods are used to determine the average grain size of specimens with a unimodal distribution of grain areas, diameters, or intercept lengths."

3D interpretation

However, already in 1860, the young French mathematician Joseph-Émile Barbier discovered that the intersection count correctly estimates the mean area per unit volume S_V of an arbitrary surface in 3D, namely

$$[S_V] = 2N_L,$$

where [] denotes the unbiased estimator. This formula was rediscovered and proved several times in the fifties of the last century. Hence the intercept count gives unbiased estimate of the 3D grain boundary surfaces. The profile count does not have such a simple interpretation; nevertheless, it can also be used under some assumptions. J.-É. Barbier also proposed that the mean length per unit volume L_V of a system of lines and curves in 3D can be estimated by the mean number P_A of its intersections with random planes, namely

$$[L_V] = 2P_A\,;$$

again no special assumptions are included. The multiconnected system of grain boundaries has a 1D subsystem of grain junctions (usually triple grain junctions are encountered) and its intersection with the section plane are profile vertices, hence *vertex count* has also 3D interpretation. Assuming that profiles create a random mosaic, then the mean number of vertices per profile must be 6 and if just 3 profile boundaries meet in a vertex (*i.e.* only triple grain junctions exist), then $P_A \approx 2N_A$ and also the profile count has a 3D interpretation, namely

$$[L_V] = 4N_A.$$

Combining these methods with the EBSD technique with variable lower limit of misorientation Δ produces a detailed quantitative and reliable description of the subgrain boundaries and grain boundaries which is applicable even to very complicated structures of nanomaterials. In particular, it should be remembered that also the "grain size" $\mu=1/N_L$ contains no information concerning 3D size of grains but relates exclusively to the grain boundary surfaces. In fact, this is perhaps more advantageous whenever the physical interpretation is searched of structural processes proceeding during various SPD techniques, mechanical tests, annealing etc. on the basis of data obtained by the area and lineal analysis of grain profiles in section planes. Some examples of such examinations will be shown in what follows (see also [4, 5, 6]).

Experimental

Materials

The starting materials were coarse-grained (~ 5 mm) high purity (99.99%) copper and aluminium (stacking fault energies are Al ≅ 200 mJ.m^{-2}, Cu ≅ 50 mJ.m^{-2}).

Procedures

The equal channel angular pressing (route B_C) was carried out at 293 K with a die having the internal angle of 90° between the two parts of the channel and an outer arc of curvature of approximately 20° at the external intersection of parts. The numbers of passes were N = 1, 2, 4, 8, 12, for details see [3]. As-pressed specimens, specimens after annealing and specimens after creep testing at the temperatures 473 K and 573 K at various stresses were examined by means of scanning electron microscope (SEM) equipped with an electron backscatter diffraction (EBSD) unit to determine the boundary disorientation distribution and the populations of high-angle grain boundaries; the images were generated at $\Delta \geq 2^o$, 5^o, 10^o and 15^o. The interception and profile counts have been carried out by a semiautomatic device in six systematically oriented directions in three mutually perpendicular sections planes. Two examples of EBSD images obtained from the same places at different choices of Δ show Fig's 1 and 2. Note the small grains scattered in the subgrains (in particular in Cu).

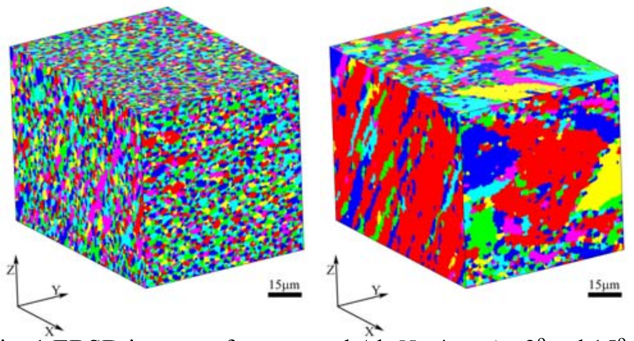

Fig. 1 EBSD images of as-pressed Al, N=4, at $\Delta \geq 2^o$and 15^o.

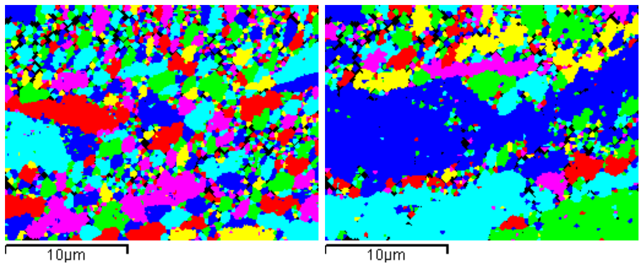

Fig. 2 EBSD images of as-pressed Cu, N=4, at $\Delta \geq 2^o$and 15^o.

Results and Discussion

Some results for as-pressed Al and Cu presents Tab 1. The values of S_V at $\Delta \geq 2^o$ are not substantially influenced by N: S_V(Al, $\Delta \geq 2^o$) ≈ 1.6 μm^{-1} and S_V(Cu, $\Delta \geq 2^o$) ≈ 2.9 μm^{-1}. The striking difference between Al and Cu is the systematic change of low angle boundaries into high angle boundaries during repeated passes, whereas in Cu are true grain developed already at N = 2, even when small and scattered within subgrains. After annealing during subsequent creep (Al: 473 K, 15 MPa, times to fracture t_f between 10^3 and 10 hours and Cu at 573 K, 50 MPa, t_f similar; the places near the specimens head with only small deformation were examined), a substantial grain coarsening occurred S_V(Al, $\Delta \geq 2^o$) ≈ 0.3 μm^{-1} and S_V(Cu, $\Delta \geq 2^o$) ≈ 0.8 μm^{-1}, but the fractions of S_V remained similar [6].

Table 1 Effect of the number of passes N on the fractions of S_V as-pressed materials.

Mater.	Range of Δ	N = 2	4	8	12
Al	$2^o \leq \Delta \leq 10^o$	87	48	36	26
	$15^o \leq \Delta$	6	36	64	64
Cu	$2^o \leq \Delta \leq 10^o$	25	38	23	-
	$15^o \leq \Delta$	73	57	72	-

Surprisingly it appears, that [7] heterogeneous specimens with partly conserved original coarse grain structure have better creep properties [7].

Conclusion

The 3D interpretation of the intercept and profile count based on the mathematical results 150 years old is recalled and its use demonstrated on the quantification of the subgrain and grain boundaries of ECAPed and also annealed creep loaded copper and aluminum.

Acknowledgements

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