Microstructure changes in HPT-processed copper occurring at room temperature

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Abstract

In the present work the long-term stability of ultrafine-grained (UFG) copper at room temperature was investigated. The pure copper specimen was processed by 10 revolutions of high-pressure torsion (HPT) at room temperature. This procedure imposes an equivalent strain of about 30000% on the material sample. In the region of these large strains a saturation in grain size refinement occurs. UFG copper, deformed up to the region of microstructure saturation, was subsequently annealed at room temperature for several years. Microstructure changes of HPT-processed copper were investigated by means of 2D and 3D electron back scatter diffraction (EBSD) and also by transmission electron microscopy.

It was found that the UFG microstructure of copper with saturated HPT-grain sizes coarsens significantly during long-term storage at room temperature. The analysis of grain volumes showed that the boundaries of coarse grains often contain flat segments with the coincidence site lattices (CSL) Σ3 and Σ9. The misorientation distributions revealed that most boundaries in the annealed microstructure are low energy grain boundaries of these kinds. However, groups of fine grains that are surrounded by random boundaries can also be found in the microstructure. Furthermore, 3D EBSD data were analysed in order to obtain a statistical microstructural information. The microstructure contains a high number of fine grains, but they form only a minority of the investigated volume. Quantitative geometrical characteristics of grain boundaries including CSL were described and interpreted.
Keywords: high-pressure torsion (HPT); ultrafine-grained microstructure; microstructure stability; 3D – electron back scatter diffraction; statistical image analysis.

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1. Introduction

It is generally accepted that ultrafine-grained (UFG) or even nanocrystalline materials can be prepared in large volumes using methods of severe plastic deformation (SPD) [1-4]. The most effective technique for the production of UFG materials with a large amount of imposed plastic strain is probably high-pressure torsion (HPT). This method allows to introduce extremely large strains in a material even at cryogenic temperatures [5]. However, SPD-processed materials have a microstructure with low thermal stability and grains can coarsen even at room temperature (RT) [1,5]. So far, most of the existing literature has addressed the thermal stability of SPD materials after applying relatively small amounts of plastic strains.

It was shown in [6-9] that UFG microstructures of pure metals with plastic strains up to about 1200% coarsen significantly during annealing at RT. The pure metals that were deformed up to the region of grain size saturation (i.e., plastic strain more than 1000-3000%) [10,11] exhibited UFG microstructures that are resistant against grain coarsening at room temperature [5,7].

Thus, the aim of the present work is the characterization of microstructure changes in pure copper deformed up to the region of grain size saturation after long-term annealing at RT using 2D and 3D – electron back scatter diffraction (EBSD). The quantitative description of the microstructure extends the results presented in [12].
2. Experimental material and procedures

The experimental material used in present work was ultrafine-grained Cu. The 20 mm diameter discs with 1 mm thickness were manufactured from an ingot of cast Cu with a purity of 99.99% and a mean grain size of about 1.2 mm. The specimens were subjected to 10 HPT revolutions at room temperature under a pressure of 4 GPa. The equivalent strain imposed by the HPT processing can be calculated according to the following equation:

\[ \varepsilon_{eq} = \left( \frac{2 \pi r N}{\sqrt{3} t} \right) 100 \% \]

where \( r \) is the distance from the torsion axis, \( N \) is the number of turns, and \( t \) is the thickness of the disc.

The Cu samples were subsequently annealed at room temperature for about 6 years. Their microstructure was examined in 2D and 3D by a FIB/SEM Tescan Lyra 3 equipped with an EBSD detector manufactured by Oxford Instruments. The 3D scans were performed fully automatically using a focused ion beam (FIB) for milling and EBSD for microstructure analysis without the necessity of specimen repositioning, see [13,14]. The EBSD analyses were performed in the sections of the torsion axis. The microstructure in 2D and 3D was investigated in areas of about 20×15 μm² with a step size for the EBSD mapping of 80 nm. The reconstruction of the 3D structures from the individual 2D slices and the determination of grains and their characteristics was performed using the software DREAM-3D, see [15]. Grains were characterized as the volumes (areas in 2D) completely surrounded by boundaries with misorientation angles \( \theta > 15^\circ \).

Additional microstructure investigations were performed by transmission electron microscopy (TEM). The TEM studies were carried out on thin foils using a JEOL 2100 F microscope operating at 200 kV.
3. Results

3.1. Microstructure of pure Cu after HPT

Fig. 1 shows the microstructure of a Cu sample processed by 10 HPT revolutions. One can see that the microstructure is more or less homogeneous. The grain size distribution revealed that most grains had a size of about 0.4 \( \mu \text{m} \) (Fig. 2) but there were also grains whose sizes exceeded the 1 \( \mu \text{m} \) mark.

The misorientation distribution shows that the microstructure contains predominantly high-angle grain boundaries (HAGB) (Fig. 3). Approximately 78% of grain boundaries in the microstructure are HAGBs. These are distributed similar to the Mackenzie plot of the misorientation distribution for a sample with a random texture. However, in the interior of a few larger grains, there were observed low-angle grain boundaries with misorientation lower than 15° (Fig. 3).

Fig. 4 shows the distribution of the strains in the HPT-processed Cu using local changes of misorientation. It can be seen that the distribution of local misorientation is heterogeneous not only in the microstructure, but also in the interior of the individual grains. The results demonstrate that predominantly grains with high values of local misorientation can be observed in the microstructure. The highest values of local misorientation were often detected near boundaries and triple points. However, grains with local misorientation values, which are small compared to the local misorientation values of neighbouring grains, can be found in the microstructure, too.

3.2. Microstructure of pure Cu after HPT and long-term annealing

Fig. 5 shows the microstructure of HPT-processed Cu after long-term annealing at room temperature. The results demonstrate the significant coarsening of grains, resulting in the
duplex microstructure containing large and fine grains in comparison with the microstructure before annealing. The large grains reached sizes of about 3 μm (Fig. 6).

The misorientation distribution (Fig. 7) demonstrates that the microstructure after long-term annealing contains predominantly HAGBs. The majority of HAGBs are formed by special boundaries Σ3 (111/60°) and Σ9 (110/38.94°). These boundaries form the prevalent part of large grain boundaries. However, fine grains are predominantly surrounded by random boundaries. The distribution of local orientation changes in the microstructure (Fig. 8) revealed a significant decrease of areas with high values of local misorientation in comparison to the microstructure before annealing. The majority of areas (more than 90%) exhibits the local misorientation up to 0.5°.

Fig. 9 shows that large grains exceeding 1 μm are predominantly surrounded by straight segments of different lengths. The results demonstrate that the boundaries of large grains can have step-like character. Groups of small grains with rounded boundaries can also be seen in the microstructure (Fig. 9b).

3.3. 3D EBSD results

In order to obtain more information on microstructure changes and the distribution of boundaries, the microstructure was investigated in 3D. We use a specimen of the size 8x8x2.88 μm - (Fig. 10). Fig. 11 demonstrates selected individual slices of the 3D EBSD map from Fig. 10a.

Detailed investigation of microstructure changes in 2D slices of the 3D EBSD map revealed that separated fine grains (denoted A,B) are situated in the interior of a large (blue) grain, marked by 1, see Fig. 11a,b. It is seen that the fine grain A in Fig. 11a is surrounded by Σ3 boundary, but the fine grain B visualized in Fig. 11b has a random boundary. Further 2D slices (Fig. 11 c,d) showed that the grains are not situated in the interior of the large grain volume,
but they are also connected with other grains. The results demonstrate that the boundaries of these grains change their misorientation in transition from one neighbouring grain to another one (e.g. grain A in Fig. 11a,b). The Σ3 boundaries enclosing the grain A are partially transformed into the boundary Σ9 (Fig. 11b). The random boundary of grain B is partially transformed into the special boundary Σ3 (Fig. 11c,d). Similar misorientation changes (denoted by white arrows) in parts of the grain boundaries can be observed in other selected slices, too (Fig. 11a-d).

The 2D slices show that the large blue grain 1 in Fig. 11a,b is replaced by several finer grains, see Fig. 11c,d. However, the 3D EBSD map reconstructed from 2D slices revealed that the large blue grain 1 has a very rugged surface, so that in some 2D slices it can be seen as several finer grains (Fig. 11,12).

3.4. Quantitative characteristics of the microstructure

The 3D EBSD map was analysed separately, using the software DREAM3D, see [15]. Besides the local phenomena described in the previous sections, this approach allows us to obtain global statistical information about the specimen. For this purpose, we work with a larger specimen than in the preview section, more precisely with a specimen of the size 18.88x14x5.88 μm. For detection of individual grains, we use the filter ‘Segment Features (Misorientation)’ in DREAM.3D with misorientation tolerance of 2 degree, see Fig. 13. In this section we present some quantitative geometrical characteristics of the specimen with an emphasis on grain boundaries.

There are 2265 grains in the sample (edge effects are not corrected), the majority of them is very fine, so that the 95 biggest grains form 75% of the overall volume. In Fig. 14, histograms of various grain characteristics are shown: volume (Vol), sphericity (Sph) and number of neighbouring grains (Nng). The number of neighbouring grains is equal to the number of faces
of the grain under consideration. Note that the faces of a grain form the grain boundary. The empirical correlation coefficients between Vol-Sph, Vol-Nng and Sph-Nng are -0.29 (i.e., the bigger grains are less likely spherical), 0.76 (i.e., the bigger the grain is the more neighbours it has), -0.44 (i.e., the more spherical grains have smaller numbers of neighbours), respectively. Further analysis concerns the grain faces and their misorientations. There is 11513 faces in the sample, among them 1458 faces with the largest surface areas form 75% of the total surface area.

For a face we define its volume neighbour ratio (VNR) by the formula

\[
VNR = \left( \frac{\max(|C_1|,|C_2|)}{\min(|C_1|,|C_2|)} - 1 \right)^{1/2},
\]

where \(C_1, C_2\) are the neighbouring grains of the considered (common) face and \(|C|\) denotes the volume of set \(C\). Note that the VNR encounters interactions between the volumes of neighbouring grains, where it is equal to zero when the volumes are equal, otherwise it is positive. In Fig. 15 we present histograms of misorientation, surface area and VNR for all faces and the largest ones, respectively. As seen from the figure, many of the faces with largest surface are \(\Sigma 3\) boundaries (approximately 30%). On the other hand, misorientation of all faces together is distributed more uniformly. In this case, only 10% of the boundaries are \(\Sigma 3\). As in Fig. 7, the misorientation histograms reveal peaks corresponding to \(\Sigma 3\) and \(\Sigma 9\) boundaries. Our aim is to classify their spatial distribution. For this purpose, we assign a location to each face, i.e. we consider the point

\[
\left[ x_1 + \frac{ed_1}{ed_1 + ed_2}(x_2 - x_1), y_1 + \frac{ed_1}{ed_1 + ed_2}(y_2 - y_1), z_1 + \frac{ed_1}{ed_1 + ed_2}(z_2 - z_1) \right],
\]

where \([x_1, y_1, z_1]\) are the coordinates of the centroid of the face and \(ed_i\) denotes the volume-equivalent diameter, \(i = 1, 2\), of the neighbouring grains. In this way, a point pattern is formed in 3D.
The faces with misorientations lower than 15 degrees are omitted. Those with higher misorientation are split into 3 groups: $\Sigma 3$ (I) and $\Sigma 9$ (II) boundaries, and the rest creates the third group (III). $\Sigma 3$ boundaries are considered as those with misorientations of $60 \pm 2$ degrees, and $\Sigma 9$ boundaries those with misorientations of $39 \pm 2$ degrees. Thus, we obtain three point patterns: (I), (II), (III), where the number of points is equal to 1508, 1289, 7795, respectively. Plots of these three point patterns are shown in Fig. 16.

We now investigate the spatial distributions of the special boundaries $\Sigma 3$ and $\Sigma 9$. In Fig. 17, three characteristics of the point patterns (I), (II), and (III) are considered, namely the empty-space function (called F-function for brevity), the nearest-neighbour distance distribution function (briefly called G-Function), and the pair correlation function (briefly called g-function), cf. [16]. The empty-space function is the cumulative distribution function (cdf) of the radius of a randomly located sphere, when it first hit a point of the considered point pattern. Similarly, the nearest-neighbour distance distribution function is the cdf of the distance between a randomly selected point of the considered point pattern and its nearest neighbor in the pattern. The pair correlation function describes the (normalized) frequencies of distances between pairs of points, where values higher/smaller than one indicate that the considered distance is more/less likely than in the model of complete spatial randomness. These three characteristics are estimated for each point pattern (I), (II), (III) and plotted together with the corresponding (theoretical) characteristics for the Poisson point process, which represents complete spatial randomness (CSR). The graphs reveal some clustering in all three point patterns, in particular, this means that special boundaries are clustered. The points are not scattered completely at random in the 3D space which is caused by the presence of large grains (there are no points in their interior). Comparing the integrated distance between both (solid and dashed) curves in the plots for the F-function and the G-function in Fig. 17, we observe that the clustering is slightly
weaker for point pattern (I) than for point pattern (II), which, in addition, is confirmed by comparing the maximum values of the g-functions for (I) and (II).

This is confirmed by Fig. 18, histograms I-II and II-I, where the distances taken from a point of one pattern to the nearest neighbour of the other pattern are considered.

Note that the present statistical 3D analysis of grain boundaries is more comprehensive than that one performed in [12].

4. Discussion

In the present work, Cu of 99.99% purity was processed by 10 HPT revolutions at room temperature so that a large strain of about 30000% was introduced into the material. The grain refinement of pure metals after so large strains usually reaches a saturation in grain size refinement and further increase of strain does not contribute to an additional reduction of grain sizes in pure metals [10,11]. Thus, the coarse-grained microstructure of the initial Cu was transformed into the ultrafine-grained one. The mean grain size of HPT-processed Cu was about 0.42 μm. This value is quite consistent with previously published results [1].

Furthermore, previous studies [5,7,9] revealed that the microstructure of pure SPD-processed Cu is unstable even at room temperature. It has been found that the largest changes of hardness and microstructure occur up to equivalent strain about 1000%. This observation can be related to the formation of UFG microstructure during the application of SPD. At very low equivalent strain, the microstructure contains predominantly LAGBs and the dislocation density is high. The value of LAGBs and dislocation density decreases with further increase of equivalent strain. Subgrains are subsequently transformed into grains and dislocations moved from their interiors to boundaries. Strains higher than about 1000% lead to an equilibrium between the generation and annihilation of defects and the microstructure characteristics (such as grain size and number of HAGBs) saturate at a certain value [10,11]. It was observed that the
The microstructure of Cu processed by HPT up to region of refinement saturation was relatively stable and exhibited only minor changes of microstructure and hardness even after long-term annealing at RT [5,7].

The formation of UFG microstructure occurs under high external stresses, which cause plastic strain. The high stress and strain applied in the region of saturation leads to the strain-induced boundary migration [10,17]. The results obtained in the present work show that internal microstrain, indicated by changes in local misorientation, is distributed heterogeneously in the microstructure. The largest values of local misorientation were found near grain boundaries, which can be caused by pileups of dislocations and by unrecovered dislocation entering into the boundaries. In the microstructure, also grains with low values of local misorientation were observed. The regions with different values of local misorientation may serve as nucleation places for grain coarsening during long-term annealing at room temperature. It is generally accepted that the heterogeneity of strain plays an important role in grain coarsening. It was found that in the specimens processed by equal-channel angular pressing (ECAP), the grains predominantly coarsen only in certain areas of the ECAP specimen [9,8,18]. However, the plastic strain is not fully homogeneous, also in specimens processed by HPT, because the strain depends on the radius according to Eq. (1). For this reason, the same microheterogeneity of strain may be expected in HPT processed specimens.

The results obtained in the present work demonstrate that long-term annealing at room temperature of HPT-processed Cu led to the formation of large grains with low values of local misorientation i.e. with low density of geometrically necessary dislocations. The increase of area with low local misorientation is caused by the boundary migration from low into the high dislocation region. Thus, the deformed microstructure formed during the HPT process is replaced by a recrystallized one.
The comparison of misorientation distributions before and after annealing revealed that random boundaries are replaced by low energy boundaries, predominantly by $\Sigma 3$ and $\Sigma 9$. Furthermore, the results demonstrate that the replacement of random boundaries by special ones led to a reduction in the overall boundary curvature because special boundaries are formed by straight segments. The special boundaries $\Sigma 3$ and $\Sigma 9$ are very often combined with each other. The boundary $\Sigma 9$ is often split into two $\Sigma 3$ boundaries, but in the whole space of the specimen, the locations of $\Sigma 9$ boundaries are slightly more clustered than the locations of $\Sigma 3$ boundaries. It can be suggested that the transformation of curved grain boundaries into flat areas is a consequence of reducing the energy of deformed microstructure [19,20], when the original boundaries may even be in a non-equilibrium state [1].

The 3D EBSD results show that the annealed microstructure contains quite large grains with significantly irregular shapes. The irregular surface of coarse grains in the annealed microstructure is probably influenced by the heterogeneous distribution of local misorientation created during HPT. For this reason the grains grow in various deformed volumes at different rates.

It was found that less than 5% of all grains occupy about 75% of the whole volume. The rest of volume is formed by very fine grains, which were probably inherited from the initial HPT microstructure. The 3D plot of point patterns shown in Fig. 16 demonstrates that grain faces are distributed inhomogeneously in the volume, which implies an inhomogeneous distribution of fine grains. This can influence the local strength of the annealed specimen. Fig. 19 shows results of the measurements of hardness from the centre to the edge of the annealed disc. It can be seen that the hardness exhibited a significant scattering of the measured values. Previous works showed that the hardness of pure Cu deformed up to the region of microstructure saturation is unchanged after short-term annealing at RT, in comparison to the hardness of the specimens processed by a lower number of HPT revolutions [7]. The comparison of hardness measured in
the present work with the results published in previous works [5,7] demonstrates the systematic decrease of hardness with increasing annealing time. The present results suggest that the increasing value of plastic strain imposed into pure Cu shifts room temperature stability of UFG microstructure to longer times.

5. Conclusion

The microstructure of UFG pure Cu processed by HPT up to the region of grain size saturation is not stable and grains can coarsen even at room temperature. The large grains are surrounded by segments of special boundaries. 3D EBSD analyses revealed that the annealed microstructure can contain a high number of fine grains, but the coarse grains occupy the majority of the investigated volume. The statistical analysis of the 3D microstructure performed in this work provided additional information about the microstructure and, in this way, clarified some experimental observations of the microstructure changes.

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References


Figure captions

Fig. 1 Microstructure of pure Cu processed by 10 HPT revolutions.

Fig. 2 Distribution of grain sizes in the HPT-processed Cu.

Fig. 3 Misorientation distribution of boundaries measured in the microstructure processed by 10 HPT revolutions.

Fig. 4 Local misorientation map for HPT-processed Cu. The colour scale is in degrees.

Fig. 5 Microstructure of HPT-processed Cu after annealing at RT, special boundaries \(\Sigma 3\) (white) and \(\Sigma 9\) (brown) and random boundaries (black).

Fig. 6 Distribution of grain sizes in the HPT-processed Cu after long-term RT annealing.

Fig. 7 Misorientation distribution of boundaries measured in the HPT-processed microstructure after long-term annealing.

Fig. 8 Local misorientation map for annealed HPT-processed Cu. The colour scale is in degrees.

Fig. 9 TEM micrographs of annealed Cu a) segmented boundary of large grains, b) duplex microstructure of large faceted grains and fine grains.

Fig. 10 3D EBSD reconstruction of an RT annealed microstructure

Fig. 11 Selected 2D slices from a 3D EBSD map (Fig. 10). Coloured boundaries indicate special boundaries (\(\Sigma 3\) white, \(\Sigma 9\) brown), black boundaries indicate random boundaries.

Fig. 12 Grain 1 from the 3D EBSD map reconstructed from 2D slices

Fig. 13 3D microstructure of pure Cu after HPT and long-term annealing (grains coloured at random).

Fig. 14 Histograms of 3D grain characteristics of the sample shown in Fig. 13: volume [\(\mu m^3\)], sphericity, number of neighbours.

Fig. 15 Histograms of 3D characteristics of grain boundaries (faces) of the sample shown in Fig. 13: misorientation [degrees], surface area [\(\mu m^2\)], VNR defined in (2). The histograms are computed a) from all 11513 faces, and b) from the 1458 faces with the biggest surface areas. The largest surface is 67.83 \(\mu m^2\), but only 40 faces have surface area larger than 10 \(\mu m^2\). Therefore histograms of face area do not display 0.35 % of faces in the case a) and 2.74 % of faces in the case b).
**Fig. 16** 3D plots of the point patterns (I) – red, (II) – green and (III)-black, corresponding to the locations of grain faces.

**Fig. 17** Spatial distribution of grain boundaries: F-function, G-function and g-function of the point patterns (I), (II), and (III) (estimated with correction of edge effects, solid lines) and of the completely random model (dashed lines).

**Fig. 18** Histograms of cross-nearest-neighbour distances, for pairs of points from (I), (II), and (III). The heavier tail in histogram I-II in comparison to histogram II-I indicates that pattern (II) is slightly more clustered than (I). Note that the histograms regarding pattern (III) are influenced by a larger difference between the number of points of the respective pairs of point patterns.

**Fig. 19** Comparison of microhardness measured in the present work with results published in previous works.
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