Effect of back pressure on the thermal stability of severely deformed copper

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Abstract. The effect of back pressure during equal channel angular pressing on thermal stability of Electrolytic Tough Pitch (ETP) copper was studied. The thermal behavior was assessed by means of microhardness measurements and microstructure characterization of the deformed samples at various stages of annealing. The assessment of the variation of the recrystallized fraction of the material with annealing was also carried out using a relatively new method based on internal misorientation measurements by EBSD technique. A higher stored energy and lower activation energy for recrystallization in the case of a back pressure of 100 MPa was obtained by means of DSC analysis. As a main outcome of this work, it was found that application of back pressure reduces thermal stability of the UFG microstructure. However, the effect is relatively small and does not negate the advantages of processing with back pressure in terms of the degree of grain refinement and strength enhancement.

1. Introduction
Production of bulk nanomaterials by severe plastic deformation (SPD) has been a subject of intensive research over the past three decades. These materials are already finding their way into manufacturing industries. For example, high-purity copper obtained by industry-scale equal-channel angular pressing (ECAP) was used in manufacturing better-quality sputtering targets [1, 2]. However, thermal stability of ultrafine grain (UFG) copper becomes an important issue in maintaining the enhanced mechanical properties resulting from SPD processing. Microstructure restoration in copper can be significant even at room temperature (RT) due to the accumulation of a large amount of stored energy during SPD processing.

It is widely accepted that application of back pressure during ECAP leads to more pronounced grain refinement and attendant improvement in mechanical properties [3]. However, the effect of back pressure on the thermal stability of UFG copper processed by ECAP has not been investigated to date. This paper aims at exploring the back pressure-dependent thermal behavior on the UFG copper. Considering the application of back pressure would bring about the difference in the extent of recrystallization of UFG structures, it is also of great interest to quantify the volume fraction of recrystallized...
material. A new method based on grain orientation spread (GOS) was employed to analyze recrystallization in annealed UFG structures.

2. Experimental

Electrolytic Tough Pitch (ETP) copper with 99.9 wt. % purity was chosen for ECAP processing. The billets were annealed at 600°C for 2 h prior to deformation and the average grain size obtained was ~28 µm. A back pressure of 100 MPa was applied during ECAP deformation at RT via Route Bc (90° clockwise rotation around the long axis of the billet after each pass) using a 90° die with a zero outer angle of curvature. Similar processing, but without back pressure, was used as a reference. The samples were then subjected to annealing under various conditions using an oil bath immediately followed by water quenching.

Electron backscattering diffraction (EBSD) measurements were conducted by scanning electron microscopy (SEM, Jeol JSM-7001F) with HKL Channel 5 software package. At least two EBSD maps for different locations were obtained for each condition to truly reflect the microstructure and each of them contained at least 10,000 (sub)grains. The Vickers microhardness was measured by means of Duramin A-300 hardness tester with a load force of 300 gf. For each condition, the measurements were carried out over a rectilinear grid comprising 16 points with the spacing of 0.5 mm between the points. All examinations were performed on a transverse section of the middle parts of the billets. Thermal stability of ECAP-induced microstructures was also monitored by means of differential scanning calorimetry (DSC) using a Perkin Elmer Pyris 1 DSC device. A sample about 6 mm in diameter with a weight of about 70 mg was used for each DSC experiment.

3. The method for estimation of recrystallized volume fraction

To determine the volume fraction of recrystallized material, various approaches have been used in the past, such as the microhardness-based softening estimation [4, 5], the point counting method on the basis of microstructure imaging [6, 7], and new efficient statistical methodologies based on the EBSD map partitioning, including image quality (IQ) [5, 8], grain average misorientation (GAM) [8, 9] and grain orientation spread (GOS) [4, 8] analysis. Recently, Gazder and coworkers [4] proposed a new methodology for quantifying recrystallization based on GOS technique for partially recrystallized steel processed by rolling, where GOS values were calculated by averaging the deviation of the orientation of individual points in a grain from the average orientation of the grain [8]. In their investigations, the fractions of the deformed, recovered, newly nucleated and growing grains were identified by using a cut-off value, θc, determined by the change in slope of the normalized cumulative distribution versus internal misorientation (GOS criterion) and other morphology-based threshold filters.

In the present work, this GOS criterion was applied for the first time to characterize the annealing behavior of ultrafine-grained copper obtained by ECAP with and without back pressure. With the aid of the GOS cut-off criterion, two subsets of grains within an EBSD maps were initially identified, where one with internal misorientation exceeding θc was
classified as the deformed grains; the other, with the misorientation angles below $\theta_c$, was considered as a combination of recrystallized and recovered grains. Considering the recovered grains are smaller than the recrystallized ones, a meaningful cut-off value could be defined. The corresponding threshold was applied to the matrix with the internal misorientation below $\theta_c$ via tracking the slope change of the normalized cumulative distribution vs. grain size, which is similar to the GOS cut-off criterion.

However, when the GOS method is employed, twins are unavoidably identified as single grains, and thus classified as recovered grains due to their internal misorientation being below the critical value. A possible way to avoid this artefact is to consider the relatively large deviation of the grain shape aspect ratio from unity or low internal misorientation within the twins and place them in the recrystallized subset of the partition on that basis. In the present work, the latter method was adopted. The fraction of twins was counted as part of the recrystallized fraction.

The results of this analysis were compared with those derived from the softening obtained by microhardness measurements conducted after annealing at different temperatures. In all tests reported here, the annealing time of 10 min was used.

4. Results

4.1 As-fabricated microstructure

Typical microstructures of coarse grained and as-deformed Cu with and without back pressure are illustrated in Fig. 1. In all the EBSD maps, black lines denote high angle grain boundaries (HAGBs) with misorientation greater than 15°, while low angle boundaries (LAGBs) with the misorientation between 2° and 15° are marked as grey lines. Irrespective of the level of back pressure, similar grain morphologies were observed in ECAP-processed samples: both microstructures shown in Fig. 1 exhibited approximately equiaxed grains. However, more significant refinement from the initial grain size of approximately 28 µm is evident in the material ECAP-processed under back pressure of 100 MPa. The average grain size of ~0.32 µm in the case of back pressure should be compared with the grain size of ~0.34 µm in the case when no back pressure was applied. Another marked feature was the prevalence of high angle grain boundaries in both conditions after deformation. The presence of back pressure induced a marginally higher fraction of HAGBs of ~61.7% to be compared with ~60.9% in the absence of back pressure. These findings are consistent with the earlier results for pure Cu [10, 11] and a variety of Al alloys [3, 12, 13] and Mg alloys [14] processed under back pressure.

After ECAP deformation, microhardness values trebled compared with those for as-received Cu, rising from ~44 to ~137 kgf/mm² in the absence of back pressure and to ~138 kgf/mm² when a back pressure of 100 MPa was applied. This lack of sensitivity of Vickers hardness to back pressure is at variance with the results on the yield strength data of Raab et al. [10], considering scaling between hardness and yield strength. The authors of [10] reported an increase of yield strength of the ECAP-processed pure copper by ~5% when back pressure was applied.
4.2 Microhardness evolution during annealing
The annealing temperature and back pressure dependence of microhardness of copper subjected to 12 passes of ECAP is illustrated in Fig. 2, where error bars represent the scatter in the hardness values. Both hardness curves versus annealing temperature exhibited similar trends in softening. Detailed study indicated that the onset of a softening stage in the back pressure case began at an annealing temperature about 10 °C lower than for the case of zero back pressure. After the onset of softening, irrespective of the level of back pressure, a sharp drop of microhardness within a narrow temperature internal of ~35 °C occurred. The largest scatter in the data observed within this range is ascribed to bimodality of the grain structure due to recrystallization. The hardness plateaus at both ends of the diagrams were found to lie slightly higher in the case of 100 MPa of back pressure.

Fig. 2 Microhardness dependence on the annealing temperature for samples subjected to ECAP with and without back pressure (BP)
4.3 Microstructure development during annealing

Regardless of whether back pressure was applied or not, a significant duplex microstructure consisting of large and small grains was detected upon annealing (Fig. 3). The emergence of new larger grains at the expense of the deformed microstructure was enhanced with increasing annealing temperature (Fig. 3(b)). Similar microstructure evolution with annealing associated with discontinuous recrystallization was also observed for Cu processed by 12 passes of ECAP [15]. A comparison of annealed microstructures (see Fig. 3(c) and (d)) revealed that for a certain annealing temperature the area occupied by bigger grains was larger for the samples in the back pressure case, suggesting that the restoration processes were faster in that condition.

![Microstructures for samples processed with a back pressure of zero (LHS) and 100 MPa (RHS) annealed at 142°C (a), 157°C (b) and 150°C (c and d) for 10 min.](image)

Fig. 3 Microstructures for samples processed with a back pressure of zero (LHS) and 100 MPa (RHS) annealed at 142°C (a), 157°C (b) and 150°C (c and d) for 10 min.

To account for this significant difference in grain structure, the extent of recrystallization was studied by misorientation-based EBSD analysis and microhardness measurements. Based on the former method described in Section 3, an example of sub-division of microstructures into the deformed, recovered and recrystallized parts was drawn in Fig. 4. The recrystallized fraction versus annealing temperature is plotted in Fig. 5 along with the microhardness curve. The application of back pressure was seen to rise to consistently higher values of the recrystallized fraction. The values obtained by both methods used are in reasonable agreement, particularly in the high temperature range (above 142 °C).
Fig. 4 Inverse pole figure maps of the partially recrystallized microstructures annealed at 150 °C for 10 min in the absence of back pressure sub-divided into (a) deformed, (b) recovered, (c) recrystallized fractions.

Fig. 5 Recrystallized volume fractions estimated by the misorientation-based EBSD method (GOS) and by HV measurements.
4.4 Thermal analysis by DSC
The influence of back pressure on thermal stability of copper was also investigated using DSC analysis. As seen in Fig. 6, the temperature DSC scans of UFG copper at a heating rate of 10 °C/min showed that the application of back pressure led to a small shift of the peak to a lower temperature: from 175.0 °C for the back pressure case to 168.7 °C for that of zero back pressure. Contrary to this trend, the stored energy (obtained by integration of the curve over the peak area) increased slightly: from 1.05 ± 0.03 J/g in the absence of back pressure to 1.12 ± 0.03 J/g for the case when back pressure was applied. These values are close to those reported for copper processed by ECAP to a similar level of strain [16]. However, compared to the stored energy values found in the work by Sarkar et al. [17] for Cu after four ECAP passes using routes A, Bc and C, our results show a higher magnitude of the stored energy. Clearly, the larger number of ECAP passes in our work gave rise to a higher dislocation density and a larger grain boundary area, both contributing to a higher stored energy [18]. Based on the dependence of peak temperature \( T_p \) on the heating rate \( v \) proposed by Kissinger [19], the apparent activation energy was obtained from the slope of a fitted straight line in the \( \ln(v/T_p^2) \) vs. \( 1/T_p \) plot, as shown in Fig. 7. The activation energies for the samples processed without back pressure and under a back pressure of 100 MPa were calculated to be ~88.1 kJ/mol and ~79.2 kJ/mol, respectively. Recent measurements of the activation energy by means of DSC for copper after ECAP for large numbers of passes obtained similar results (75.3 kJ mol\(^{-1}\) and 62.7 kJ mol\(^{-1}\) after 8 and 16 passes, respectively) [20]. DSC results suggest that the restoration processes are slightly more sluggish for zero back pressure, which is consistent with a lower stored energy in this case.

Fig. 6 (a) DSC scans of copper processed by 12 passes of ECAP without back pressure and with a back pressure of 100 MPa at a heating rate of 10 °C/min. (b) Linear fit of the \( \ln(v/T_p^2) \) vs. \( 1/T_p \) diagrams.

5. Discussion
The results obtained demonstrate that the thermal stability of UFG ECAP processed copper decreases upon application of back pressure of 100 MPa during ECAP. However, as shown above, this decrease of stability is pretty insignificant. A measure of this change in thermal stability is an about 7 °C shift observed in both the microhardness softening curves and the
DSC thermal scanning curves. Two different methods used for quantifying the fraction of recrystallized grains in the microstructures produced by annealing produced very close results clearly identifying a mild loss in thermal stability. The stored energy as the driving force for the microstructure restoration plays a great role in the thermal behavior. While recrystallization is driven by the energy stored in dislocation structure, recovery and grain growth are mainly governed by grain boundary energy [21]. In this study, the overall stored energy comprised by the contributions from the dislocation structure, \( P_d \), and the grain boundaries, \( P_b \), was measured directly by means of DSC analysis. It was found that in the non-zero back pressure case this energy was higher than in the absence of back pressure.

During ECAP process the microstructure of copper evolves basically from a banded to an equiaxed cellular structure of predominantly HAGBs [18]. The resultant average cell diameter is well known to be inversely proportional to the square root of the dislocation density, thus the smaller average grain size obtained in back pressure case is associated with a higher dislocation density. This is a result of back pressure, which raises the vacancy migration enthalpy, thus retarding the diffusion controlled annihilation of dislocations via dislocation climb [22]. Hence, in the non-zero back pressure case, a larger contribution to the total stored energy is provided by the dislocation ensemble. As mentioned before, back pressure also gives rise to a larger fraction of HAGBs. According to [23], the energy per unit volume associated with high angle grain boundaries is given by:

\[
P_b = \frac{2 \gamma}{D} F_{HAB}
\]

where \( \gamma \) is the grain boundary energy, \( D \) is the (sub)grain size, and \( F_{HAB} \) is the fraction of high angle grain boundaries. Thus, a smaller grain size achieved by ECAP under imposed back pressure leads to a higher contribution of grain boundaries to the stored energy. The opposite trends in the effect of back pressure on the dislocation and grain boundary contributions are thus obvious. The fact that the overall stored energy in the non-zero back pressure case was found to be larger than for zero back-pressure indicates the prevalence of the dislocation structure related contribution.

The results of the quantification of the fraction of recrystallization by the misorientation (GOS) and microhardness based methods are consistent with the annealing response during DSC scanning. All three methods indicate a reduction of thermal stability of the UFG structure if a back pressure is applied. A careful inspection of Fig. 5 shows that a loss of stability sets in at an annealing temperature above a critical value of \( \sim 150 \) °C. We note a difference between the results of the GOS and HV analyses in Fig. 5, particularly in the early stages of temperature ramping. Here the GOS method tends to over predict the fraction of recrystallized material. This result is opposite to the observations in Ref. [24, 25] on recrystallization in IF steel and an Al alloy deformed by cold rolling. This discrepancy may be associated with the specifics of the UFG structures of the kind involved in the present case as opposed to microstructures with conventional grain size as in [23,24].
grains in the UFG microstructure tend to be relatively uniform in terms of the dislocation density, as they cannot develop a dislocation substructure [26, 27]. Thus, they are likely to be considered as the ones with a low internal misorientation falling below the critical value, \( \theta_c \). Hence, they will be counted into the fraction of recrystallized grains even though recrystallization may not have happened. This drawback of the method seems to be unavoidable at this stage and distinguishing the grains inherited from the ECAP deformation from those resulting from static annealing requires further in-depth studies. Despite this discrepancy between two methods in the range of low annealing temperatures, they are largely in a reasonably good agreement, and both can be applied to quantify recrystallization.

6. Conclusion
Thermal stability of ultrafine grained microstructure produced by ECAP was investigated for the case when a back pressure was applied during processing as opposed to the case of no back pressure. Through systematic microhardness measurements, microstructure observations and differential scanning calorimetry, it was shown that copper samples fabricated by ECAP with back pressure of 100 MPa had a lower thermal stability than the reference material processed in the absence of back pressure. The effect was found to be minor, though. It does not negate the benefits of processing with back pressure, which leads to a more refined microstructure with a higher proportion of high angle grain boundaries and ensuing improvement of strength characteristics. The kinetics of recrystallization was characterized quantitatively in terms of the activation energy. Thus, this work provides a reference for assessing thermal stability of ECAP processed copper. An additional outcome of this study is the demonstration of the advantages of quantitative characterization of recrystallization by means of a misorientation-based EBSD method (GOS), which can complement the microhardness-based method.

7. Acknowledgements
The authors acknowledge the use of facilities in the Monash Centre for Electron Microscopy (MCEM). One of our authors (Y Wang) is grateful for the financial support of the China Scholarship Council.

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