Role of interfaces on microstructure refinement and mechanical properties of severe plastically deformed copper and copper-silver eutectic

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Abstract. The process of microstructural refinement during deformation by high pressure torsion (HPT) of commercially pure copper (Cu-B), copper powders (Cu-P) and cast copper silver eutectic alloy (CuAg-E) were investigated. The presence of a surface oxide layer or of immiscible silver lamellae leads to much finer grain size. A saturation in microstructural refinement was attained in both Cu-B and Cu-P samples, while the CuAg-E sample showed a linear hardening propensity down to a 30 nm interlamellae spacing. The possible mechanisms for strengthening in the CuAg-E alloy are further discussed in view of the evolution of interlamellae spacing with applied shear strain.

1. Introduction
Design of suitable microstructure is key to the development of high strength advanced metals. In this regard, severe plastic deformation (SPD) techniques have played an important role for synthesis of bulk ultrafine grained, (100 nm < d < 1 µm) and nanocrystalline (NC; d < 100nm) metals [1]. During SPD of coarse grained metals different types of dislocation cell walls are generated. These cell walls can initially be characterized as incidental dislocation boundaries with lower misorientation angle (10°-5°) and geometrically necessary boundaries with higher misorientation angle (>5°) [2]. However, with increasing strain the misorientation between neighboring cells gradually increases until most of the boundaries (≥ 70%) have a misorientation angle >15° [2, 3]. In conjunction with the evolution of cell wall angle, the average dislocation cell size also reduces with increasing strain [4,5] until a saturated dynamic equilibrium size is attained. Generally, during high pressure torsion (HPT) of pure metals the saturated grain size is attained within a von Mises strain (εM) of 10-20 [3]. Several studies have shown that addition of secondary phases can significantly reduce the saturation grain size [3]. In addition to the grain refinement, the deformation processes and the mechanisms for hardening in NC metals have been the focus of many investigations [6-11].

It is the objective of present study to investigate the role of surface oxide layers and a secondary silver phase on grain refinement and their subsequent influence on the hardening of copper composites. For this study, samples were SPD-deformed by HPT. The shear strain (γ) and the von Mises strain (εM) in HPT samples are expressed as

\[ γ = \sqrt{3} \varepsilon_M = \frac{2πN}{t} \]  

(1)
where \( r \) is the radius, \( N \) represents the number of revolutions and \( t \) is the thickness of the disc. As the shear strain is linearly related with the radius (see equation (1)), a wide range of deformation states can be investigated from one sample.

2. Experimental Procedure
Commercially pure bulk copper (Cu-B), copper powder (Cu-P) with particle size ~30 - 50 \( \mu \)m from Alfa Aesar, and arc-melted Cu\textsubscript{30}Ag\textsubscript{70} (in wt %) eutectic alloys (CuAg-E) were processed by constrained HPT at room temperature (300 K) [3]. The bulk Cu-B and CuAg-E samples were first compressed and then deformed by torsion, while the Cu-P powders were first filled in a hollow copper tube, pressed to a solid lump and then deformed by torsion. A compressive stress of 4 GPa was applied during torsion of all the samples. The Cu-B and Cu-P samples were deformed by 10 revolutions and the CuAg-E sample was deformed by only 1 revolution. The final deformed samples were 30 mm in diameter and 2.5 mm in height.

Vickers hardness measurements of the HPT-deformed samples were carried out using a Buehler Micromet 5100 microindenter under a static load of 300 g applied for 10 seconds. The indents were made on the center half cross section of the deformed discs at four different positions for each radius (figure 1). A Carl Zeiss Leo 1525 FE scanning electron microscope (SEM) and a Philips CM-12 transmission electron microscope (TEM) operating at 120kV were used for microstructural analysis. Back-scatter SEM images were taken in both the radial and tangential direction, while selected TEM images were taken in the radial direction.

3. Results
3.1. Hardness
Figure 1 shows the evolution of hardness as a function of applied shear strain for all the materials. The hardness of the Cu-B and Cu-P samples was saturated after 10 revolutions. It is interesting to note that the Cu-P sample requires a higher strain (\( \gamma \approx 200 \)) in order to attain a saturation in hardness. In contrast, the CuAg-E alloy showed pronounced, nearly linear strain hardening, at significantly lower applied strains.

![Figure 1](image.png)

**Figure 1.** Evolution of Vickers hardness of Cu-B, Cu-P and CuAg-E with applied shear strain. A schematic showing the different sample coordinates is given in the inset.
3.2 Microstructure

Figure 2 shows example SEM and TEM micrographs in the radial direction for the deformed metals. Both the Cu-B and Cu-P samples show uniform microstructure with a saturation grain size of about 250 nm and 50 nm, respectively. Moreover, for the Cu-P sample several twins are visible inside the grains (marked with red circles). In contrast to the copper samples, the SEM image of the CuAg-E sample shows a non-uniform structure. Further high resolution SEM and TEM revealed a nano-lamellae structure with alternating Cu and Ag lamellae of 10 nm and 20 nm, respectively. Thus, the presence of surface oxides in the Cu-P sample and immiscible Ag in the CuAg-E alloy caused significant microstructural refinement. It is important to point out that unlike Cu-B and Cu-P (initial grain size, \(d_0 \sim 5-20 \mu m\)) the initial thickness of the Cu lamellae in the CuAg-E alloy was only \(\sim 100 \text{ nm}\).

In order to further understand the higher strain hardening characteristic of the CuAg-E alloy, figure 3 shows the evolution of microstructure with applied strain in tangential direction. In the as-cast state, the colonies of alternating Cu and Ag lamellae were oriented randomly. However, with increasing shear strain the Cu-Ag lamellae became aligned along the shear plane (perpendicular to the torsion axis). It is interesting to note that similar to the observations of rolling and wire drawing of eutectic alloys a gradient microstructure is developed during HPT of the Cu-Ag eutectic [12, 13]. Colonies of lamellae that were nearly parallel to the shear plane refined at a faster rate, while the lamellae that were oriented at larger angles were first bent and then aligned along the shear plane. This suggests that the Cu-Ag interphase boundary provides strong barrier for transfer of dislocation slip between neighboring phases. A linear intercept method was used to estimate the interlamellae spacing (\(\lambda\)) with increasing shear strain. Figure 3 (e) shows the evolution of the interlamellae spacing normalized by the initial interlamellae spacing (\(\lambda_0\)) in the as-cast state. The normalized lamellae spacing followed a nearly inverse relation with an exponent of (-0.9).

![Figure 2](image-url)"
4. Discussion

4.1. Microstructure refinement in Cu-B and Cu-P

Investigations of the correlation between structure and properties of HPT deformed metals have shown that the saturation grain size is strongly dependent on the deformation temperature and presence of alloying elements and secondary phases [3]. For pure metals, the saturation grain size reduces with decreasing deformation temperature [3, 14]. However, below a critical temperature the saturation grain size does not show any significant reduction. These observations clearly show that the structural recovery mechanisms at saturation have both thermal and athermal components for grain boundary (GB) and triple junction (TJ) migration. Evidence for deformation-assisted grain coarsening has also been observed during HPT deformation and indentation of NC nickel [15, 16].

A recent study by Renk et al. [17] has demonstrated that the balance between thermal driven and deformation-assisted GB and TJ motion can lead to a variety of microstructures ranging from elongated to equiaxed grains. For Cu-B deformed at 300 K, the dynamic equilibrium among various recovery processes led to a saturation grain size of 250 nm and an aspect ratio of 2-3. Most of the grain boundaries were high angle with dislocation debris inside the grains. However, for Cu-P the presence of surface oxides caused further grain refinement. A larger amount of shear strain was needed to attain the saturation grain size. The presence of oxide particles was confirmed by selected area diffraction and X-ray photoelectron spectroscopy. These results will be presented in a subsequent publication. It is well established that oxide particles can significantly reduce the thermal mobilities of GBs and TJs [18]. Thus, it appears that the presence of oxide particles can shift the dynamic equilibrium between the thermal- and deformation-induced GB and TJ motion to a more refined grain size.

Another interesting feature of the Cu-P microstructure is the presence of several deformation twins inside the grains. In a detailed analytical calculation, Zhu et al. [11] have suggested that the propensity for twinning in nanocrystalline metals follows an umbrella curve, with the number of twins first increasing and then decreasing with reduction of grain size. The optimum grain size for twinning in copper was estimated to be 46 nm, which is close to the grain size of Cu-P. Although these calculations

Figure 3. SEM micrographs of CuAg-E in tangential direction at (a) $\gamma = 0$, (b) $\gamma = 8.4$, (c) $\gamma = 16.8$, (d) $\gamma = 25.2$. (e) The evolution of normalized interlamellae spacing with applied shear strain. The blue curve shows the power law fit.
were made for pure metals and the influence of GB oxygen atoms is not clear, the presence of a significant number of grains with twins in Cu-P is noteworthy. It is also interesting to note that Cu-P develops a bulk crystallographic texture similar to low stacking fault Cu-15 wt% Zn brass. Thus, the twins in Cu-P grains appear to influence the deformation pattern significantly. A detailed comparison of the microstructural evolution of Cu-P will be presented in a subsequent paper.

4.2 Microstructure refinement and hardness correlation in CuAg-E

During HPT the grains are deformed in simple shear. Thus, at large strains ($\gamma>5$) the thickness of the grains can be correlated with the shear strain ($\gamma$) according to,

$$d \approx \frac{d_0}{\gamma}$$  (2)

Comparing equation (2) with figure 3 suggests that the individual lamellae of the Cu and Ag followed nearly perfect strain transfer between the individual phases without any significant slip (like GB sliding) at the interphase boundary. A similar correlation between the externally applied strain and interlamellae spacing was observed during drawing of eutectoid pearlitic steel [12, 19]. Under equilibrium conditions, the Cu and Ag phases show negligible solid solubility. However, as both Cu and Ag have face centered cubic structure and maintain a crystallographic correlation in the as-cast state, with their (111) planes parallel to the interphase boundary, dislocation pile-up in one phase can cause nucleation of dislocations in the neighboring phase [20-22]. In fact Wang et al. [20] have discussed the possibility for interface-facilitated deformation twinning in Cu lamellae and correlated this with the development of a Ag-type texture in Cu lamellae.

Further details about the deformation mechanisms can be obtained by comparing the hardness with the thickness of the Cu and Ag lamellae. In an early study, Frommeyer and Wassermann [23] have shown that the ratio of the thickness of Cu and Ag lamellae remains nearly constant, thus in this study we compare the hardness with the interlamellae spacing. Figure 4 shows the evolution of the hardness values with interlamellae spacing from both the previous [23, 24] and present study. It is interesting to note that although Frommeyer and Wassermann [23] used wire drawing of directionally cast CuAg eutectic alloys, their hardness and interlamellae spacing measurements correlate well with the present study. In contrast, the hardness values for vapor-deposited CuAg multilayers are higher [24]. One possible reason for this could be the difference in overall composition of vapor-deposited multilayers, where Cu and Ag layers of equal thickness were used, while for the CuAg-E alloy, the Cu to Ag layer thickness ratio is ~0.5.

In previous studies on multilayer composites, dislocation pile-up based Hall-Petch strengthening [25] and dislocation loop based Orowan strengthening [24, 26] were considered to be the primary possible deformation mechanisms. The Vickers hardness and the corresponding interlamellae spacing of CuAg-E (except the initial lamellae spacing) from the present study (figure 4) were plotted in different functional forms in order to check the possibilities for these mechanisms. Table 1 shows the various fitting parameters for these strengthening relations. In fact both Hall-Petch and Orowan strengthening mechanisms give reasonable fit. However, a logarithmic fit suggests a best fit exponent of -0.28. Thus, it appears that further quantitative structural analysis of Cu-Ag interfaces is required before ascertaining the primary deformation mechanism in CuAg-E alloys.
Figure 4. Evolution of hardness of CuAg multilayers with decreasing interlamellae spacing. For the vapor-deposited CuAg multilayers the nanoindentation hardness values were divided by 1.25 to get an equivalent Vickers microhardness [27].

Table 1. Fitting parameters for different hardening laws fitted with hardness in HV and λ in nm for CuAg-E. The initial interlamellae size is excluded in the fit. The error in the fitted parameter is given in parentheses (Err) and R represents the linear correlation coefficient.

| Fitted variables (Y-X)          | A (Err) | B (Err) | R     |
|---------------------------------|---------|---------|-------|
| Ln(H) – ln(λ)                   | 6.52 (0.08) | -0.28 (0.02) | 0.98  |
| H – (1/λ)                       | 155 (6)  | 3444 (268) | 0.97  |
| H – (1/λ)^0.5                   | 95 (9)   | 940 (63)  | 0.98  |

5. Conclusion
The microstructural refinement of commercially pure copper (Cu-B), copper powders (Cu-P) and cast CuAg eutectic alloy (CuAg-E) were investigated after high pressure torsion. The results show that a saturation microstructure with constant hardness can be achieved in the Cu-B and Cu-P samples. However, the presence of surface oxides in the Cu-P samples allows a reduction in the saturation grain size to 50 nm. At such finer grain size significant twinning activity commences, changing the deformation pattern towards that of low stacking fault energy metals such as CuZn alloys. The CuAg-E alloy, on the other hand, undergoes severe strain hardening with the CuAg interlamellae spacing reducing almost inversely with applied shear strain. The correlation of microhardness and interlamellae spacing suggest that both Hall-Petch and Orowan strengthening are equally possible and further in-depth microstructural analysis is necessary in order to understand the primary deformation mechanisms in such CuAg lamellar composites.

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6. References

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