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Transmission electron microscope investigations on Cu-Ag alloys produced by high-pressure torsion

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Abstract. Cu-Ag alloys in three different compositions (Cu – 25/50/75wt% Ag) were produced by powder consolidation followed by high-pressure torsion. Deformation was performed till a saturation regime was reached. The generated microstructures were investigated by transmission electron microscopy and vary from ultra-fine grained to nanocrystalline to even partially amorphous structures. Vickers hardness measurements show a strong increase in hardness compared with the pure metals, annealing at 130°C leads to an additional increase in hardness.

1. Introduction

Severe plastic deformation (SPD) techniques like high-pressure torsion (HPT) are well-known methods to produce nanostructured alloys from all kind of materials [1,2]. The fabrication of nanocrystalline composite alloys from usually immiscible elements has attracted interest due to possible novel properties, for example high electrical and thermal conductivity [3, 4]. Particularly mechanical alloying was used in the past to obtain and study this new type of alloys and related phenomena such as supersaturation and amorphization [5–8].

Processing materials with HTP leads to dense bulk materials under controlled deformation states. Depending on material and process parameters (like temperature, pressure) a critical strain is limiting a period of continuous grain refinement (and associated hardening) followed by a saturation regime, where no further changes take place. In this also called steady state regime the material is ultrafine-grained (UFG) or even nanocrystalline (nc) and exhibits special microstructural features characteristic for SPD materials [9]. In this study the eutectic Cu-Ag system [10] was chosen as model material, which has a positive heat of mixing, very low room

temperature (RT) solubility, and a lattice mismatch of ~12%. The structural evolution in this system during ball milling has been investigated in few studies. Fcc supersaturated solid solutions have been reported over the whole composition range [11–13], and also amorphization occurred in some studies [7, 8]. One of the disadvantages of ball milling is the undefined applied strain, the effect of environment and an end product in powder form. In the present study the structural evolution during HPT after application of well-defined strains will be investigated.

2. Experimental

Due to the eutectic character of the CuAg system the microstructures strongly vary with the composition when produced by casting. Differences in the initial state of the material influence the deformation behavior and lead to a complex microstructural evolution of those alloys [16–18]. To avoid the influence of the initial microstructure elemental powders of Cu (purity: 99.7 %, particle size: 63 μm) and Ag (purity: 99.99 %, particle size: 54 μm) were mixed in three different compositions (Cu-25/50/75wt% Ag). Then the powders were consolidated directly in the HPT tool, followed by immediate processing. The generated bulk material is disk shaped with diameter of 8 mm and a thickness of 0.5 mm. For each composition samples were processed for 100 rotations at RT, thus to a shear strain of γ=4400 at a radius of 3.5 mm. For the Cu-50wt% Ag composition additionally samples were produced at a processing temperature of 200 °C for 75 rotations (γ=3300 at a radius of 3.5 mm) and samples processed to 200 and 300 rotations at RT (γ=8800 and γ=13200 at a radius of 3.5 mm, respectively). The applied pressure was between 5 and 7.5 GPa, with a rotational speed of 0.6 rotations per minute. The evolving microstructure was investigated by transmission electron microscopy (TEM). TEM samples were prepared by a standard procedure: material was glued into Ti holders, followed by grinding, dimple grinding and ion milling till perforation using a Gatan PIPS 691 with 4kV and cooled with liquid nitrogen. TEM images were recorded in radial direction at a radius of 3.5 mm unless otherwise specified. Bright-field (BF), dark-field (DF) and selected area diffraction (SAD) patterns were recorded on a Philips CM12. High-resolution TEM (HRTEM) was conducted on a JEOL TEM/STEM 2100F at 200 kV equipped with an image-side C_S-corrector (CEOS). Grain sizes were determined by measuring grain areas by hand in TEM DF images and calculating an equivalent circle diameter. Vickers microhardness measurements were performed on a Buehler Micromet 5100 using a load of 500 g and indents were placed in 0.25 mm distances along the cross-section of the 8 mm disk. Hardness measurements were done for all three compositions on the samples processed for 100

rotations; in the as-deformed state, as well as in annealed samples. Annealing was performed after the HPT process at 130 °C for 30 min in air.

3. Results and discussion

During the HPT process the initial μm-sized powder particles are strongly refined through a repeated shearing process. The material was deformed until a steady state is reached.

The generated microstructures of Cu-25/50/75wt% Ag alloys in or near this saturation regime are shown in BF and DF TEM micrographs (see Fig 1), the samples were processed for 100 rotations (a total shear strain of γ=4400 at a radius of 3.5 mm). All three specimens are homogenously refined (within the limits of TEM sample size). The Cu-25wt% Ag sample (see Fig 1a and d) shows the largest grain size of 100±37 nm, which is between the ultra-fine grained (UFG) and nanocrystalline regime. The grains are equi-axed with sharp grain boundaries, showing various twins and other defects displayed as contrast variations inside the grains. The microstructures of Cu–50wt% and 75wt% Ag can be defined as nanocrystalline. The grains are slightly elongated in the 75wt% Ag sample (visible from DF images in Fig 1f), and clearly elongated in the 50wt% Ag sample along the shear direction (see DF in Fig 1e). Twins were found occasionally in Cu-75wt% Ag (encircled in Fig 1c) and only rarely in the 50wt% Ag sample. Due to the very fine microstructure a clear identification of the grains and grain boundaries is difficult. A determination of the grain size of the Cu-50wt% Ag was not possible, for Cu-75wt% Ag a grain size of 31±10 nm was determined. It should be noted that grain sizes were measured from DF images with only few grains in favorable orientation, and therefore may not be representative. The trend however is evident from TEM micrographs. The strong grain refinement is also reflected in the SAD patterns. In the SAD pattern of the Cu-25wt% Ag sample (see inset in Fig 1a) single spots are still visible in the rings due to relatively large grains (aperture size: 200 μm). In comparison a broadening of the rings in the Cu-50wt% and 75wt% Ag samples (see insets in Fig 1b and c) demonstrates the very small grain size.

Vickers hardness measurements as a function of strain reveal for all three compositions a typical increase in hardness until a saturation level is reached (see Fig 2a). The maximum hardness is decreasing with increasing Ag-content: with 378±4.5 HV for Cu-25wt% Ag, 343±6 HV for Cu-50wt% Ag and 300±4 HV for Cu-75wt% Ag (mean values calculated from 5 indents at the edge of the disk). All alloys exhibited higher hardness than the pure metals (for reference: maximum hardness for Cu ~215 HV [19] and for Ag ~100 HV); coupled with a finer grain size in the alloys

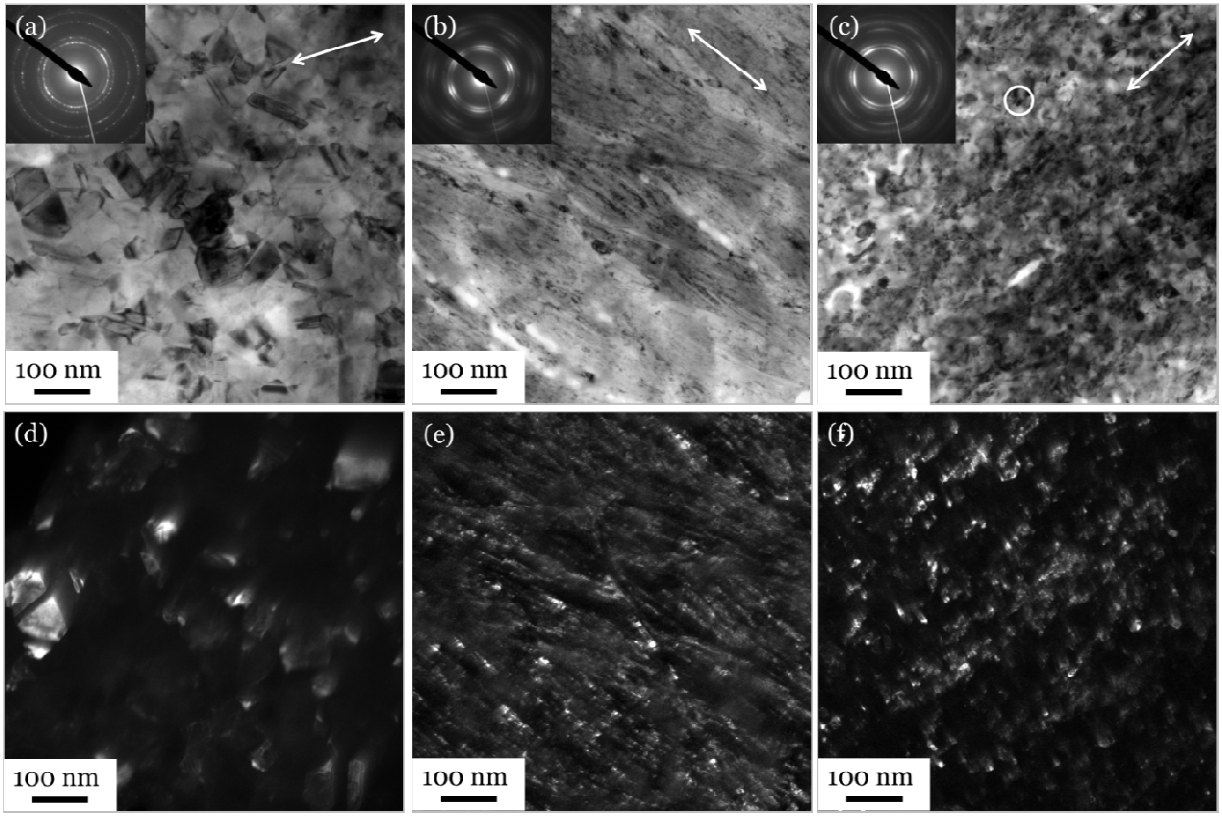

Figure 1: TEM BF and DF images of (a) and (d) Cu-25wt% Ag, (b) and (e) Cu-50wt% Ag and (c) and (f) Cu-75wt% Ag with corresponding SAD pattern (see insets), all alloys deformed at RT to a total shear strain of γ=4400; the shear plane is indicated with an arrow.

compared with the pure metals, which usually show grain sizes in the UFG regime. The highest hardness was obtained in the Cu-25wt% Ag alloy, although the grain size is significantly coarser than in the other samples. One reason is the higher Cu-content due to the higher hardness of pure Cu. Additionally the high amount of twins are lowering the actual structural dimension for dislocation motion and therefore influence the hardness.

In order to investigate the effect of sample preparation heating experiments were conducted. Annealing the samples at 130 °C for 30 min (which reflects the heat treatment in the sample preparation process) leads to a hardness increase (see Fig 2b), indicating that some "recovery" processes had taken place, but no grain growth occurred. Such a hardness increase after annealing has been reported in several systems, in alloys as well as in pure metals. Bachmaier et al. [20] produced alloys in the immiscible Cu-Fe system by HPT, they obtained complete supersaturated solid solutions at lower and higher Cu content. Annealing those samples led to

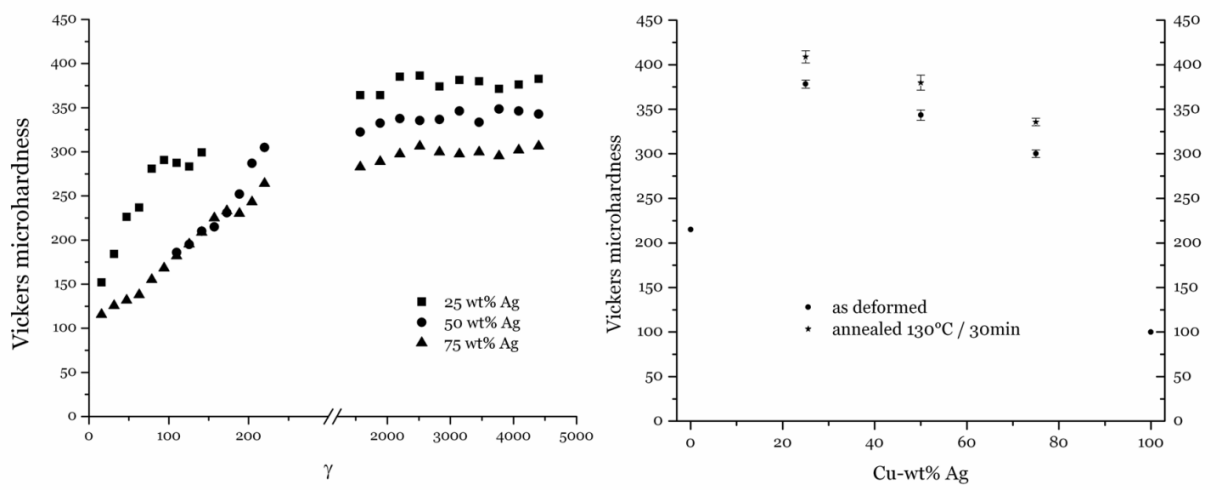

Figure 2: (a) Vickers microhardness evolution as a function of strain for Cu-25/50/75wt% Ag, (b) Vickers microhardness depending on composition in the as-deformed and annealed state with reference values for pure Cu and Ag.

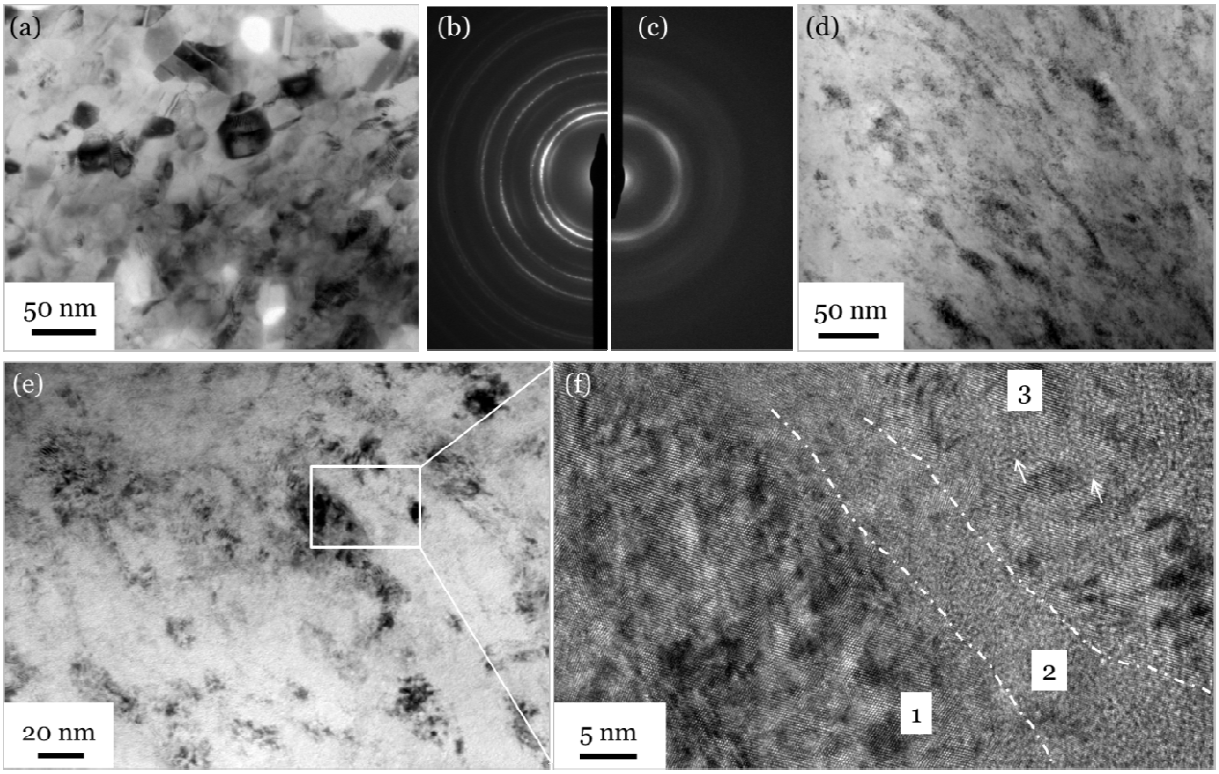

Figure 3: TEM BF images and related SAD pattern of Cu50wt%Ag alloy processed by HPT to a total shear strain of (a) and (b) γ=3300 (processed at 200°C), (c) and (d) γ=8800 (processed at 200°C till γ= 2000, then at RT till γ=8800) and (e) γ=13200 (RT, recorded in plan-view) with high resolution image in (f).

decomposition into the stable fcc Cu and bcc Fe phases, consequently to an increase in the fraction of interfaces in the material, which is causing the observed hardness increase. Anomalous hardening during annealing was also reported in pure Cu and Ni, caused by the formation of twins [21]. The distribution and type of twins, the grain size and morphology and type of grain boundaries are fundamental for an understanding of the behavior of SPD deformed materials. A systematically study on the microstructural characteristics in as-deformed and annealed samples is an issue of further investigations.

Because the Cu-50wt% Ag sample shows an extremely fine and unusual structure, additional investigations were made on this composition. In Fig 3a and d the microstructure of a sample processed at 200 °C is compared to a sample processed at RT (notice different applied shear strains of γ=3300 and γ=8800, respectively). The elevated processing temperature at 200 °C resulted in a coarser but still nanocrystalline microstructure with well-defined grains. The structure in Fig 3d shows that further deformation to a strain of γ=8800 at RT lead to marginal additional grain refinement of the lamellar structure and a changed appearance compared with Fig 1b. Structural elements are still elongated; contrast-rich darker grains are surrounded by bright featureless regions. The SAD pattern of the sample produced at 200 °C shows two sets of sharp diffraction rings including the Cu and Ag phase (see Fig 3b). In the RT deformed sample (Fig 3c) these rings broaden and merge into each other, pointing to a mixture of the two phases and extreme grain refinement. The change of the rings into diffuse halos indicates an amorphization of the structure.

Additional deformation to a strain of γ=13 200 brought no further refinement or amorphization of the microstructure (see Fig 3e, observations in plan-view at a radius of 3.5 mm). HRTEM imaging revealed that the dark contrast-rich regions are crystalline with a complex defect structure (referred as regions 1 and 3 in Fig 3f). Disordered regions (labelled as 2 in Fig 3f) are apparent in between the crystalline regions, confirming the amorphous nature of the bright featureless areas. The amorphization mainly occurs between grains (at former grain or phase boundaries), but also starts inside the grains (see grain 3, indicated with arrows), dividing them into smaller segments.

4. Conclusion

Cu-Ag alloys in three compositions with Cu-25/50/75wt% Ag were produced using elemental powders and HPT processing. Due to similar hardness and shear modulus of Cu and Ag both

phases are co-deformed uniformly. With evolving shearing and continuous refinement of the structural dimensions saturation in grain size and hardness is reached at very high strains. The obtained material characteristics are summarized in table 1.

Table 1: Summary of the obtained hardness values, grain sizes and microstructural characteristics.

	100% Cu	Cu-25wt%Ag	Cu-50wt%Ag	Cu-75wt%Ag	100% Ag
microhardness as-deformed HV	215 [19]	378±4.5	343±6	300±4.3	~ 100
microhardness annealed HV		409±7	380±8	335±4	
grain size [nm]	240 [19]	100 ± 37	-	31 ± 10	480 [22]
Microstructural features	UFG	UFG composite, numerous twins	nc, partial amorphization	nc composite, few twins	UFG

The resulting grain size and hardness depends strongly on composition. The Cu-25wt% Ag exhibited the largest grain size and surprisingly the highest hardness. With increasing Ag content the hardness is decreasing, despite a finer grain size of the alloys. In Cu-50wt% Ag samples a partial amorphous structure was obtained at very high strains, the disordering of crystallinity was not only observed at former grain or phase boundaries, but also appeared inside the grains, leading to further fragmentation.

HPT deformation at lower temperatures could lead to further amorphization. HPT processing and annealing experiments will be extended and properties of different material states will be studied systematically in further investigations.

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