Microstructural evolution in immiscible alloys processed by High-Pressure Torsion

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Abstract. The application of High-Pressure Torsion (HPT) to two different Co-Cu alloys permits the generation of materials with nanocrystalline grain sizes. The evolution of the microstructure with increasing strain and the resulting microstructure are investigated by scanning electron microscopy. The final attainable grain sizes are significantly smaller than in corresponding pure metals deformed by HPT. Special attention is given on microstructural evolution and deformation behavior of the Cu and Co phases revealing the importance of nature, morphology and deformation behavior of the single phases on the formation of nanocrystalline structures during HPT processing.

1. Introduction
A multitude of studies on initial coarse grained single phase materials deformed by High-Pressure Torsion (HPT) show that the formation of ultrafine grained or even nanocrystalline grained structures is possible [1, 2]. The minimum size of the structural elements which can be achieved during HPT at very large strain depends on the HPT processing parameters and the material itself. Typical grain sizes are between 150–300 nm if single phase materials are deformed [3, 4].

One possibility to overcome the grain size limit is the deformation of two or three phase microcrystalline or ultrafine grained metals which can lead to nanocomposites with a grain size in the order of ~ 10 nm (an overview is given, for example, in [5]). HPT of corresponding single phase metals used in these composites lead to a much larger grain size [6–8]. Contrary to HPT deformed single phase materials and alloys, HPT deformed multiphase materials have not been intensively investigated until now [5,9,10]. The microstructural evolution in multiphase materials might be considerably different. A classical composite consists of two or more distinct phases or constituents with different physical or chemical properties which are separated by an interface. An alloy with a microstructure consisting of two phases is usually not denoted a true composite material. However, the Co-Cu alloys investigated in this study are labeled as composite materials because their behavior is the same.

In this study, two different types of Co-Cu composites- one predominantly consisting of a Cu matrix containing Co-particles, the other has a Co matrix containing Cu-particles- were HPT deformed and the structural evolution in both cases is investigated.

2. Experimental
The investigated materials were Co-Cu composites fabricated by RHP-Technology (Seibersdorf, Austria). Co powders (purity 99.8%) and Cu powders (purity 99.9%) were mixed with two different ratios and subsequently precompacted into samples with cylindrical shape. In this work, Cu powder mixtures containing 25 wt. % and 75 wt. % Co powder are denoted as Co25Cu75 and Co75Cu25 composites, respectively. The samples in the as-fabricated condition had a diameter of 20 mm and a thickness of 11 mm. From the as-fabricated material, rods with a diameter of 8 mm were turned and subsequently cut into disks with a thickness (t) of 0.60 mm.
The disks were HPT deformed at room temperature at a pressure of 5.0 GPa for 5 and 25 rotations \((n)\). A detailed description of the HPT equipment used in this work is given in [11]. Different shear strains \((\gamma)\) across the radius \((r)\) of the HPT disk were attained which can be calculated by the relation [12]

\[
\gamma = \frac{2\pi n r}{r^2}.
\]  

Investigated strains for the samples deformed for 5 and 25 rotations are summarized in Table 1. Microstructures in the as-fabricated and deformed condition were characterized in a scanning electron microscope (SEM) type ZEISS SIGMA VP using back scattered electrons. All micrographs were taken in tangential direction at selected positions across the radii of the HPT deformed samples.

| n  | r(mm) | \(\gamma(-)\) |
|----|-------|---------------|
| 5  | 1     | 52            |
|    | 2     | 105           |
|    | 3     | 157           |
| 25 | 1     | 262           |
|    | 2     | 524           |
|    | 3     | 785           |

Table 1. Shear strains at certain radii of the HPT samples.

Vickers microhardness measurements were performed using a load of 500 g (HV0.5) across the radii of the disks (3 indents at each position) with a spacing of 0.25 mm between the individual indents. To measure the hardness of the individual phases in the as-fabricated condition, indentations on the as-fabricated samples were performed with a nanoindenter (ASMEC UNAT-SEM2) fitted with a Berkovich Indenter. 20 indentation measurements in each phase were done with a load of 2 mN. For the purpose of comparison, the Vickers hardness is calculated using the measured indentation hardness. In [13] it was shown that mean difference between conventional Vickers hardness and indentation hardness is below 10% using the InspectorX software package.

3. Results and Discussion

The microstructure of the as-fabricated composites is shown in Fig.1a and b, which consists of a Cu or Co matrix with Co or Cu particles, respectively. The Co and Cu particles are inhomogeneously distributed and strongly clustered. The cluster size of the Co particles is strongly varying and about 3-50 µm. The Cu particles exhibit a larger cluster size of about 20-150 µm. In Fig.1c and d, the microstructures of the Cu region (labelled A in Fig.1b) and the Co-region (labelled B in Fig.1a) is shown in SEM images with a higher magnification. From these micrographs, an ultrafine grained structure with an average grain size of about 200-1000 nm for the Cu phase and an ultrafine grained structure with an average grain size around 100 nm for the Co phases can be estimated. In the Co-phase, only single grains have a grain size above the nanometer range.
Fig. 1 SEM images of the microstructure of the as-fabricated, undeformed Co-Cu composites: a) Co75Cu25 composite, b) Co25Cu75 composite, c) Cu region (labelled A) and d) Co-rich region (labelled B). Please note the large difference in magnification.

In Fig. 2, the microstructures of the Co25Cu75 composite HPT deformed to a shear strain of 52, 105, 262 and 785 is shown, which illustrates the Co particle distribution in the Cu matrix with increasing strain. The Co and Cu phases in the micrographs can be easily distinguished by their different brightness levels (Cu rich regions appear brighter, Co rich regions darker). At strains of 50 to 260 (Fig.2a-2c), a very inhomogeneous microstructure is observed. Co particles, which are elongated in the shearing direction and which have aspect ratios up to 10, are randomly distributed in the Cu matrix. The size of the Co particles becomes significantly finer with increasing strain level, although the aspect ratio is not significantly changing. The cluster size of the Co-particles is about 0.5-8 µm at a strain of 52. The size at a strain of 105 varies between 0.5-6 µm, the size at a strain of 262 is about 0.5 – 2.8 µm. Only the sample deformed to a strain of 785 appears to be free of micro-particles (Fig.2d). A detailed analysis revealed that even at the highest amount of applied strain, single Co-particles can be still detected in the micrograph (marked with arrows in Fig.2d). The size of these Co particles is still about 1 µm at a strain of 785. One example of such a Co particle is shown in the inset of Fig. 2d.

Fig. 3 shows the microstructure of the Co75Cu25 composite HPT deformed to the same amounts of strain as used before. At a strain of 52 (Fig.3a) and 105 (Fig.3b), bands of Cu regions are embedded in the Co matrix. The distance between the Cu bands and the thickness is strongly varying at both deformation strains, which can be seen in the insets with a higher magnification. The thickness of the Cu bands at a strain of 52 is varying between 0.5-6.5 µm. The thickness at a strain of 105 becomes somewhat reduced (0.2-2.5 µm), which is in both cases significantly smaller than the size of the Cu phase in the Co matrix in the as-fabricated condition. After applying a strain of 262, a homogeneous microstructure is observed (Fig. 3c). A further increase of the strain does not alter the microstructure: No difference between the microstructure of the samples deformed to a strain of 262 and to a strain of 785 (Fig. 3d) is visible and the Cu and Co phase cannot be longer distinguished from each other.
In Fig. 4, the microhardness for the Co75Cu25 and Co25Cu75 composites after 5 and 25 rotations, which was measured from the center to the edge (i.e. increasing applied strain) of the disks, is plotted. After 5 rotations, the microhardness of the Co25Cu75 composite is steadily increasing along the radius of the disk with values ranging from 180 to 250 HV (Fig.4a). After 25 rotations, the hardness increases in the center of the disk (r<1.5 mm or γ<400), but a constant hardness of 279±8 HV is finally reached above an applied strain of 400.

Fig. 2: Representative SEM micrographs taken at different positions i.e. different strain across the radii of the Co25Cu75 composite sample: a) γ=52, b) γ=105, c) γ=262 and d) γ=785. Please note the difference in magnification. The shearing direction for all micrographs is indicated by the arrow in a).
Fig. 3 Representative SEM micrographs taken at different positions i.e. different strain across the radii of the Co75Cu25 composite sample: a) $\gamma=52$, b) $\gamma=105$, c) $\gamma=262$ and d) $\gamma=785$. Please note the difference in magnification. The shearing direction for all micrographs is indicated by the arrow in a).

Fig. 4 Microhardness plotted along the radius of the HPT disk: a) Co25Cu75 composite after 5 and 25 rotations (n=5, n=25) and b) Co75Cu25 composite after 5 and 25 rotations (n=5, n=25).

In Fig. 4b, the microhardness of the Co75Cu25 composite is plotted. In the center, the hardness starts with a value of 325 HV and increases continuously to a hardness of 384 HV after 5 rotations. After 25 rotations, constant hardness values (439±7 HV) are reached almost entirely.
across the radii of the HPT disk. Only directly in the center, a lower hardness is measured \((r< 1 \text{ mm or } \gamma<150)\). These findings fit well with the observed microstructure. After 5 rotations (Fig. 3a and b), the microstructure is still inhomogeneous and bands of Cu are embedded in the Co matrix. After 25 rotations, saturation and the final state, a homogeneous microstructure is reached (Fig. 3c and d). A saturation in hardness, which corresponds to a saturation in the refinement process, is not achieved as long as both phases are present in the Co75Cu25 composite.

In Fig. 5, the microstructure of both composites at the highest degree of deformation \((\gamma=785)\) in the saturation regime is shown. It is not possible to distinguish between the phases due to the small grain size and lack in contrast. An apparent homogeneous microstructure is reached in both cases. The grain size in the Co25Cu75 composite in the saturation regime is about 100 nm and slightly above, whereas grain sizes well below 100 nm in the Co75Cu25 composite are obtained. A significant refinement could be achieved in the Cu-phase during HPT deformation if the final and as-fabricated microstructure is compared. In the Co75Cu25 composite, the grain size is also reduced. The grain sizes obtained in the composites in the saturation regime are significantly smaller compared to HPT deformed pure Co and Cu. HPT of bulk Cu leads to a much larger grain size, which is about 200 nm in the saturation regime (depending on purity of Cu) and a hardness of 130-150 HV \([14,15]\). During HPT deformation of bulk Co, an ultrafine grained structure with a final grain size of 120 nm and a hardness of 360 HV can be reached \([16]\).

The thickness \(d\) of individual components or phases in a composite during HPT deformation at a certain shear strain \(\gamma\) can be calculated under the assumption of ideal co-deformation and volume conservation of both phases \([5, 7]\):

\[
\frac{d}{r} = \frac{d_i}{r_i}
\]

(2)

In the formula, \(d_i\) are the initial phase dimensions or the cluster size of the different components in the composite \([5, 7]\).
Assuming a Co25Cu75 composite structure with the largest initial cluster size \((d_0 = 50 \, \mu m)\) comparable to the maximum observed Co cluster size in the as-fabricated condition, a strain of 785 should lead to a maximum particle size of only 0.06 \(\mu m\) if the assumptions given above are fulfilled (see Table 2). Nevertheless, the observed size of the Co particles in the micrographs recorded at strain of 785 is still about 1 \(\mu m\) in few cases, which is significantly higher than the calculated value. In general, the observed maximum particle size is always larger than the calculated one in case of the Co25Cu75 composite.

| Initial particle cluster size | \(\gamma=52\) | \(\gamma=105\) | \(\gamma=262\) | \(\gamma=785\) |
|------------------------------|---------------|---------------|---------------|---------------|
| 150 \(\mu m\)               | 2.88          | 1.43          | 0.57          | 0.19          |
| 100 \(\mu m\)               | 1.92          | 0.95          | 0.38          | 0.13          |
| 50 \(\mu m\)                | 0.96          | 0.48          | 0.19          | 0.06          |
| 10 \(\mu m\)                | 0.19          | 0.10          | 0.04          | 0.01          |

Table 2. Calculated particle size/phase dimensions for different assumed initial particle cluster sizes.

The hardness of the individual Co particles in the as-fabricated condition is 394±21 HV, the hardness of the Cu phase is 103HV±12. Both, the Cu matrix and the Co particles are deformed at least in the beginning of the deformation in the Co25Cu75 composite. This causes the observed reduction of the grain size in the Cu matrix and the observed elongation of the Co particles in the early stages of deformation. At higher strains, HPT deformation has no significant effect on the shape, but the size of the Co particles. It can be assumed that during HPT deformation of such an inhomogeneous material (softer Cu matrix containing hard Co particles), a localization of the plastic deformation easily occurs. The plastic deformation mainly localizes in the Cu matrix. Ideal co-deformation does not occur, which lead to the large deviation of the observed size of the Co particles from the calculated particle size.

In case of the Co75Cu25 composite \((d_0 = 20-150 \, \mu m)\), a strain of 52 and 105 should lead to Cu phase dimensions with a maximum size of about 2.9 and 1.4 \(\mu m\), respectively (see Table 2). The size of the Cu phase in the micrographs recorded at strain of 52 and 105 is about 0.5-6.5 \(\mu m\) and 0.2-2.5 \(\mu m\) (Fig. 3b), which is only twice as high as the calculated values. At higher amounts of strain, the thickness of the Cu phase seems to decrease more quickly. Although the maximum size of the Cu phase at a strain of 262 and 785 should be around 0.57 and 0.19 \(\mu m\), an apparent homogeneous microstructure is observed. Possible reasons are the small phase dimensions of the Cu phase in the Co-matrix, which cannot be resolved by SEM. The saturation regime during HPT deformation (no further grain size reduction, no further increase in hardness) is reached faster, if a hard Co matrix with soft Cu as a second phase is combined. Furthermore, the assumption of ideal co-deformation of both phases seems to be fulfilled to a greater extent in this case.

4. Conclusion
Two different types of Co-Cu composites were subjected to HPT to different strain levels at room temperature. At low strains, deformation of both phases occurred in the Co25Cu75 composite at
least to some extent. The grain size in the Cu-phase could be reduced and an ultrafine grained structure with a grain size about 100 nm is finally reached. Above a certain strain, the plastic deformation is mainly localized in the Cu phase. Entirely homogeneous microstructures could not be observed even in the sample deformed to the highest amount of strain. In contrast, homogeneous microstructures with a grain size below 100 nm could be reached in the Co75Cu25 composite in which both phases are deformed over the whole strain range. Furthermore, the saturation regime is reached in shorter time in this composite type. The higher hardness of the Co75Cu25 composite compared to the Co25Cu75 composite in the saturation regime is mainly attributed to strengthening from this significantly smaller grain size.

In summary, it was shown that the production of Co-Cu composites with ultrafine grained or even truly nanocrystalline structure is possible by HPT. The focus of this work is on the structural evolution during the deformation of the composites. Further investigations will include analysis of possible formation of supersaturated solid solutions in this Co-Cu system and the evaluation of the thermal stability.

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