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Bulk metallic dual phase glasses by severe plastic deformation

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ABSTRACT

Two different metallic glass powders were consolidated and deformed via high-pressure torsion to synthesize amorphous dual phase composites. The influence of volume fraction of the two amorphous phases and the applied shear strain was investigated. By varying the applied strain, the dimensions of the phases could be systematically varied from the micro- to the nanometer regime and at the highest applied strain even a transition to a single phase state could be observed. The study illustrates the potential of producing novel bulk metallic glasses by deformation-induced mixing which are not accessible by the classical casting route.

1. Introduction

Bulk metallic glasses (BMGs) engage the science communities since their discovery in 1960 [1]. Besides studies on single phase BMGs, efforts are made to control the properties by producing bulk metallic glass composites (BMGCs) [2,3]. Different combinations are possible such as amorphous/crystalline, amorphous/quasicrystalline and amorphous/amorphous [2]. The shape of the second phase can also vary from particles over dendrites to wires and even more complex forms [4–9]. One way to produce amorphous/amorphous composites is by exploiting phase separations, which can occur during annealing in the supercooled liquid region or of the undercooled melt. This chemical demixing is caused by a positive enthalpy of mixing or as pre-stage to primary crystallization. Some well studied compositions for BMGs show this behavior as Vit105, but also Cu-, Ni-, Pd-, Zr- and Mg- based BMGs [2]. Another technique is to use two targets with different chemical composition for inert gas condensation and to produce bulk samples by in-situ compaction [10]. High-pressure torsion (HPT) was used in the past to produce and deform various materials and composites. The advantages of this technique are the high flexibility as the starting material can be either in bulk or powder form and the large variation in applied strain by simply changing the number of rotations. Due to the high, nearly hydrostatic pressure, also brittle materials [11,12] are deformable and the applied strain can go up to shear strains as high as $\gamma = 20000$ and more. This gives the possibility to produce supersaturated solid solutions [13,14] and amorphization of crystalline phases. BMGs and BMGCs can be produced by HPT [15–26] and furthermore, it can be used for adjusting the microstructure of the composites [27] or rejuvenation of BMGs [28–33].

The aim of this study was to produce amorphous/amorphous BMGCs via HPT and to investigate the evolving microstructures. Main questions addressed are: How does the applied shear strain affect the microstructure? How do the mechanical properties change with refining of the phases? What happens if the applied shear strain goes to very high values? For this purpose, two different compositions (Ni-MG 30 wt% Zr-MG and Ni-MG 50 wt% Zr-MG) were produced as well as single phase Ni-MG and Zr-MG samples as reference. The influences of shear strain and ratio of the two phases were investigated with scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), nanoindentation, and hardness measurements.

2. Materials and methods

The metallic glass powders ($Zr_{57}Cu_{20}Al_{10}Ni_8Ti_5$ and $Ni_{53}Nb_{20}Ti_{10}Zn_8Co_6Cu_3$, spherical particles with diameters between 1 μm and 40 μm) were fabricated via high pressure gas atomization [3] and were blended in the respective composition by hand. The mixtures were then filled into the gap between two grooved steel anvils and compacted by HPT (4 GPa and 10° rotation). The main

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deformation was applied at higher pressures (8–9 GPa) at room temperature and the rotations were varied from 2 to 100. The thickness varied from 0.45 to 0.6 mm due to the anvil preparation, but the diameter of the specimens were constant with 6 mm. The applied shear strain γ can be estimated with

$$\gamma = 2\pi\ r\ N/t \quad (1)$$

where r is the radius of the disk, N is the number of rotations and t is the thickness after deformation. SEM and hardness measurements were performed on the cross sections of the HPT disks, which were produced by wire saw cutting and further grinding and polishing. For TEM samples, small pieces at larger radius (about 2.5 mm) were cut from the disks and the samples were prepared via a standard procedure with dimple grinding and subsequent ion milling (to avoid heating, samples were cooled with liquid nitrogen) in radial direction. Structural analysis were conducted in Carl Zeiss Leo 1525 field emission scanning electron microscope using the back-scatter and inlens detector and in a Cs-corrected JEOL JEM-2100F operated at 200 kV transmission electron microscope.

Vickers hardness was measured along the diameter on the cross section with a load of 0.5 kg and 1 kg. An error of 2% for the measured hardness values is assumed and the standard deviation errors of the fitted curve were calculated and used for the error bars in the inlet of Fig. 3.

For the nanoindentation property map, a platform nanoindenter G200 (Keysight Tec) was used and the experiments were conducted under constant indentation strain rate (0.05 s^{-1}) to a maximal indentation depth of 100 nm with a diamond Berkovich tip (Synton-MDP Inc.). Hardness and Young's modulus were measured over indentation depth with a continuous stiffness measurement unit. All data were evaluated according to Oliver and Pharr [34] using a Poisson ration of 0.37 for the modulus and were averaged between indentation depths from 80 to 95 nm. To estimate the phase fraction for each indent, SEM micrographs with very high resolution were taken and the free software ImageJ was used to mark the Ni-MG lamellae by hand (due to the edge effect of the indents an automatic approach was not feasible) and only the regions inside the indents were evaluated. The lamellae thickness was determined by evaluating the intersections with a circle (also in the region of the respective indent), which was performed with an ImageJ plugin called “Oval Profile Plot” by Bill O'Connell [35]. Determining phase fraction and thickness with this methods leads to several errors. One is the lack of information, as the volume beneath the indent is unknown. Another is inaccurate marking of the Ni-MG phase by the author as subjective perception will distort the results (repeating the phase analysis for one indent showed a difference of 4 vol%).

A 5-circle X-ray diffractometer equipped with a source for Cu-K_α radiation was used for reflection XRD phase analysis of the Zr-MG and the Ni-MG 50 wt% Zr-MG with lower applied deformation. Only pieces from the outer part of samples were used to exclude the nearly undeformed material in the center of the disks. Additionally, the surface was ground to remove any impurities from the HPT process. The other samples were investigated with Synchrotron X-ray diffraction performed at the PETRA III P07 beamline at the DESY Photon Science facility (Hamburg) using a beam energy of 111 keV. The primary and secondary slit of 1 × 0.25 mm^2 and 1.2 × 0.3 mm^2, respectively, were used to measure in a small strain range. The measured transmission diffraction patterns were analyzed with FIT 2D software. The theta angles were converted to scattering vector q with

$$q = 4\pi\ \sin(\theta)/\lambda \quad (2)$$

where θ is the reflection angle and λ is the wavelength of the rays. This conversion allows plotting data from the synchrotron and lab diffractometer measurement in one figure.

3. Results and discussion

3.1. Microstructural evolution as function of strain

The evolution of the microstructure was investigated by SEM, TEM, and XRD. In Fig. 1a and b, SEM micrographs of two different composites (Ni-MG 30 wt% Zr-MG and Ni-MG 50 wt% Zr-MG) are shown for different applied strains. The micrographs in the second row are taken from the same position as the micrograph above but at higher magnifications and the shear direction is indicated with an arrow on the right side. As the starting materials were powders, a deformation and consolidation of the powder particles takes place in the beginning. Due to the lower hardness, this consolidation is carried mainly by the Zr-MG (light grey), while the Ni-MG particles (darker grey) show hardly any deformation and the material is hold together by the deformed softer phase (see first micrographs on the left side). The welding of the particles is not completed and the boundaries of the initial powder particles are still visible. As the two powders had similar sizes and forms, no problems regarding agglomeration was expected and at low deformations, good mixing of the two materials was observed. Regions with higher contents of Ni-MG result from the higher volume fraction of Ni-MG particles in Ni-MG 30 wt% Zr-MG, but subsequent deformation ensures a homogeneous distribution of both phases. With higher deformation, both phases are forced to deform and a lamellar structure evolves. This structure refines with increased strain and the lamella length decreases from tens of micrometers to 1 μm and the width from 10 μm below 10 nm. TEM micrographs in Fig. 1c, show the fine microstructure of Ni-MG 30 wt% Zr-MG at γ = 1200. Thin and long lamellae are sometimes disrupted by shear bands, which cause steps and further refine the phases. At very high shear strains, a saturation is reached, where only one phase is detectable in the micrographs. A single phase microstructure imaged by SEM can be explained by a refinement of the lamellae below the resolution limit or mixing of the two MGs into a new phase. Changing the ratio of the two MGs, leads to a slightly different microstructure evolution. Ni-MG 50 wt% Zr-MG shows a fast consolidation at the beginning as the fraction of the softer phase is relatively high and it can act as glue to the harder Ni-MG particles. Therefore, no cracks are detectable even at low strains as γ = 60 (see Fig. 1b). On the other hand, the high fraction of the softer Zr-MG can carry most of the applied strain and the Ni-MG is not forced to deform. This leads to an inhomogeneous deformation behavior, where large Ni-MG lamellae can still be found even at very high strains (γ = 2700). If the fraction of the harder phase is higher, strains higher than γ = 590 must be applied to achieve fully dense samples without cracks along the phase boundaries (see Fig. 1a). The delay of the consolidation is caused by the lower fraction of the glue-like phase, which cannot hold all Ni-MG particles together, and by the hardness of the Ni-MG, which impedes fast welding of the Ni-MG particles. The lower fraction of the softer phase forces the Ni-MG to carry more of the deformation and this causes a more homogenous deformation. The lamellae thickness is more evenly distributed and the saturation is reached at lower strains compared to Ni-MG 50 wt% Zr-MG.

In Fig. 2a, XRD profiles of the two single phase BMGs and the two composites are shown with intensity as a function of the scattering vector q. For Ni-MG + 50 wt% Zr-MG, profiles of two different samples are shown. For one profile, an intermediate microstructure was chosen. In this state, two overlapping amorphous peaks from the two initial MGs can be seen. The second profile is acquired at higher applied shear strains; only one amorphous peak is detectable and its position lays between the positions of the amorphous peaks of the initial two metallic glasses. This can be explained by generating a new amorphous phase by mixing of the two initial MGs. Generating a single phased MG consists with SEM-micrographs, where also only one phase is detectable at high applied shear strains (see Fig. 1). For Ni-MG + 30 wt% Zr-MG, only the profile at saturation is shown, where a single amorphous peak is