Composite Materials Fabricated of Amorphous and Nanocrystalline Metallic Powders

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The bulk metallic glasses composites are a new class of bulk metallic glasses (BMGs), containing an amorphous metal matrix and reinforcing materials of metallic or ceramic nature in order to obtaining the desired combination of mechanical properties including strength, hardness, ductility and toughness. Composite materials of cylindrical form with the diameter of 10 mm and 5 mm in height were successfully prepared by hot-pressing of Zr – based glassy alloy powder and Fe – based nanocrystalline alloy powder in different volume fraction. The samples obtained were structural investigated by scanning electron microscopy and X-Ray diffraction and mechanically characterized by hardness and compression tests. It was found that increasing the volume ratio of the Fe-based nanocrystalline alloy up to a certain value leads to an increase in hardness and mechanical compressive strength.

Keywords: metallic glasses, composites, microstructures, hardness, compressive strength

The rapid pace of industrial development has led the specialists, in the technical fields of research and production, to create new materials (composites, ceramic powders, amorphous and nanocrystalline alloys, etc.). If ceramic composite and powder materials are old application [1-9], bulk amorphous and nanocrystalline alloys begin to outperform them, in terms of research and practical application, due to their unique physico-chemical and mechanical properties. The researchers have focused mainly on the discovery of new types of metallic glasses with excellent glass forming ability (GFA) so as to allow the production of bulk materials at low cooling rate by conventional casting methods.

Multicomponent zirconium based alloys with a wide supercooled liquid region before crystallization and excellent glass forming ability have been discovered [10-15]. Among these, Zr-Al-TM (TM = transition metals) [13,14] alloy system is known to be one of the best glass formers. They are easier to process than Fe-based alloys, but their tensile strength at room temperature of about 1500...2000 MPa [10, 16-18] is inferior to that achieved by the Fe-based bulk amorphous alloy which can exceed 4000 MPa [19, 20].

In order to improve this mechanical propertie, bulk metallic glasses composites reinforced by ceramics particles have been synthesized and characterized so far. Kato et al. have found that bulk glassy Zr-Al-Ni-Cu composite materials containing ZrC particles, which have been added to liquid BMG matrix, exhibit higher fracture strength and larger plastic strain as compared with the Zr-Al-Ni-Cu single phase [21, 22].

Another method of obtaining bulk metallic glasses composites is through partial crystallization of the molten during solidification. The composites is formed during cooling of the melt by nucleation and growth of the crystalline phase, followed by the solidification of the remaining liquid alloy. Inoue et al. [23] were found that the addition of special elements such as Ag, Pd, Au, Pt or Nb in Zr–Al–Ni–Cu alloys lead to new mixed structures consisting of the amorphous phase containing nanocrystalline or quasicrystallline particles. The mechanical strength and ductility of these *in situ* BMG matrix composites, prepared by the copper mold casting and squeeze casting methods, are significantly improved by the formation of the nanostructures as compared with the corresponding amorphous single phase alloys. Qiao et al. [24] have reported fabrication of $Zr_{60.0}Ti_{14.7}Nb_{5.3}Cu_{5.6}Ni_{4.4}Be_{10.0}$ *in situ* BMG matrix composites by copper-mould suction casting method. In this case a significant increase in plasticity has been achieved detrimental the yielding strength comparing to bulk amorphous alloys.

Taking into account the effects on mechanical properties of partial crystallization of a zirconium based bulk amorphous alloy, Gravier et al. [25] revealed the BMG ability to produce nanocomposite materials after heat treatments nearby the glass transition temperature T_g. Indeed, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk nanocomposites were produced by appropriate heat treatments at temperatures higher than the glass transition temperature. It was found that the degree of crystallization remains limited (less than 20%), the fracture stress is slightly higher than for the amorphous alloy and for large degrees of crystallization the fracture stress is sharply reduced.

An alternative technique to prepare bulk metallic glasses composites is based on powder metallurgy using amorphous and nanocrystalline metallic powders [26]. It involves the following steps [26-29]: (i) obtaining amorphous and

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nanocrystalline metal powders by atomization or milling; (ii) mixing of this two alloy powders by mechanical milling for homogenization; (iii) compacting of the mixed alloy powder in the supercooled liquid region of the amorphous component, using hot- pressing technique.

In this paper, has been studied the possibility of obtaining bulk metallic glasses composites by hot-pressing of Zr – based glassy alloy powder and Fe – based nanocrystalline alloy powder in different volume fraction. The influence of the volume ratio of the Fe-based nanocrystalline phase on the mechanical properties of a bulk composite material was analyzed.

Experimental part

The glassy powders of the $Zr_{48}Cu_{36}Al_8Ag_8$ and $Fe_{65.4}C_{7.1}Si_{3.3}B_{5.5}P_{8.7}Cr_8Al_2$, with an average diameter of 20 μm were obtained by high-pressure gas atomization process. Nanocrystalline structure of Fe – based alloy powder was obtained by heating the amorphous powder at 540°C for 30 minutes in argon atmosphere.

Zr – based glassy alloy powder and Fe – based nanocrystalline alloy powder were mixed in different volume fraction using RETSCH PM400 planetary ball mill at 100 rpm for 1h with a ball-to-powder mass ratio of 10:1. Subsequently, the powders were compacted by hot pressing in the WEBER-PRESSEN pressing device. The hot pressing was performed in the supercooled liquid region of Zr – based glassy alloy, at 420°C, under applied pressure of 60 kN, for 10 minutes.

The structure of Zr – based alloy powder, Fe – based alloy powder and the composite material was identified by X-ray diffraction with a X'Pert³ Powder diffraction system, with the radiation of a Cu anode with a wavelength λ = 1.54 Å. The microscopic structure of the composite material was examined by means of FEI Inspect S scanning electron microscope.

In order to set the temperatures for Fe-based alloy nanocrystallization and for hot pressing of amorphous and nanocrystalline metal powders, the glass transition temperature T_g and the crystallization temperature T_x were determined by differential scanning calorimetry (DSC) using a Netzsch STA 441 Jupiter, under a flow of purified nitrogen and with a constant heating rate of 20°C/min.

The mechanical properties were determined by Vickers method hardness test and compressive test. The hardness tests were performed using Volpert Micro - Vickers Hardness Tester with a 0.1 kgf load. The compressive tests were done at room temperature, at a loading speed of 1mm/min on a Zwick/Roell- machine.

Results and discussions

Fe – based glassy alloy powder obtained by the gas atomization method were subjected to DSC analysis, to determine the crystallization temperature, T_x, in order to establish the optimum temperature for the heat treatment applied to obtain the nanocrystalline structure.

DSC curve of amorphous metal powders shown in Figure 1, indicates a crystallization process of the amorphous phase, with a strong exothermic effect, that starts at a temperature of 550°C. Also, the glass transition temperature, T_g, can be highlighted, being of 513°C. Consequently, the $\Delta T_x = T_x - T_g$ of the Fe – based glassy alloy powder, which describes the supercooled liquid region, is of 37°C.

In order to avoid a significant increase of the crystalline phase resulting from the devitrification of the amorphous phase, the heating temperature of 540°C was chosen for the nanocrystallization of Fe – based glassy alloy powder.

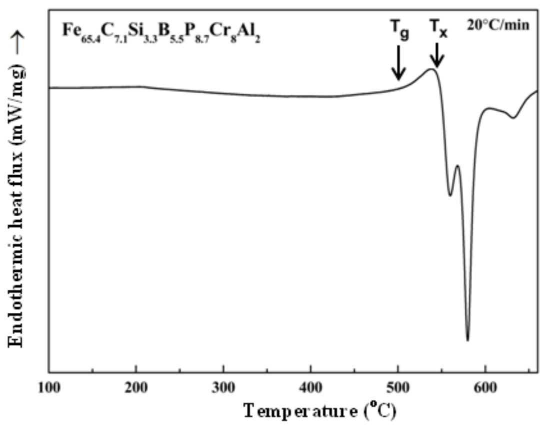


Fig. 1. DSC curve of the $Fe_{65.4}C_{7.1}Si_{3.3}B_{5.5}P_{8.7}Cr_8Al_2$ glassy alloy powder

Both Zr – based glassy alloy powders, obtained by the gas atomization method, and Fe – based nanocrystalline alloy powder were subjected to structural analysis by X-ray diffraction. The XRD patterns (Figure 2) show the amorphous structure of the $Zr_{48}Cu_{36}Al_8Ag_8$ alloy and a structure with nanocrystalline phases distributed in an amorphous matrix in the case of the $Fe_{65.4}C_{7.1}Si_{3.3}B_{5.5}P_{8.7}Cr_8Al_2$ alloy.

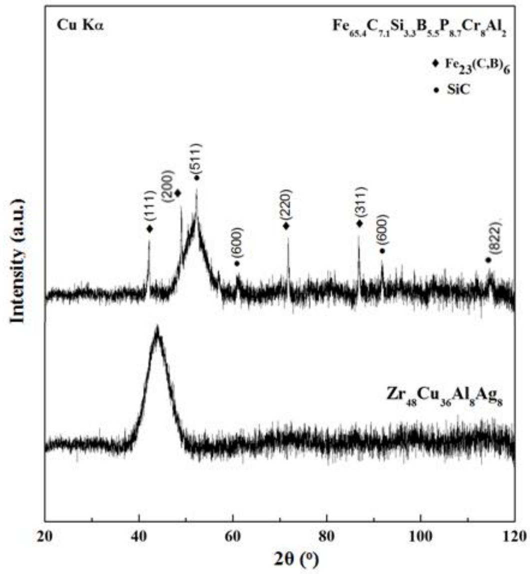


Fig. 2. XRD patterns of the glassy and nanocrystalline powders

Zr – based glassy alloy powder were also subjected to DSC analysis. DSC curve from Figure 3 shows a crystallization temperature, T_x, of 458°C and a glass transition temperature, T_g, of 407°C. So, the supercooled liquid region $\Delta T_x = T_x - T_g$ is of 51°C. One can observed that ΔT_x of Zr – based glassy alloy powder is higher than ΔT_x of Fe – based glassy alloy powder, and consequently, the Zr based glassy alloy powder has a better glass forming ability.

Taking into account the values of T_g and T_x and to avoid crystallization of the Zr based alloy during the hot pressing process, the temperature of 420°C was chosen to obtain the composite material.

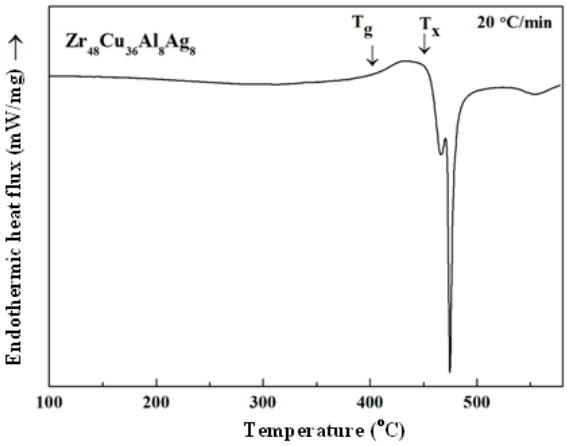


Fig. 3. DSC curve of the $Zr_{48}Cu_{36}Al_8Ag_8$ glassy alloy powder

The hot pressed samples having a diameter of 10 mm and heights of 5 mm are shown in Figure 4. The samples containing 65 % Zr – based alloy powder and 35% Fe – based alloy powder were marked with **S1**, the samples containing 60 % Zr – based alloy powder and 40% Fe – based alloy powder were marked with **S2**, the samples containing 55 % Zr – based alloy powder and 45% Fe – based alloy powder were marked with **S3** and the samples containing 50 % Zr – based alloy powder and 50% Fe – based alloy powder were marked with **S4**.

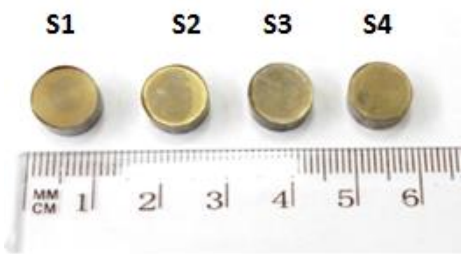


Fig. 4. The hot pressed samples mixed with different volume fraction of Fe– based alloy powder

They were subjected to structural analysis by X-ray diffraction. The XRD patterns (Figure 5) show that the amorphous structure of Zr –based alloy is preserved also in compacted powders for all samples. It is also observed the nanocrystalline phases which are identical to those highlighted in the case of nanocrystalline Fe-based alloy powders.

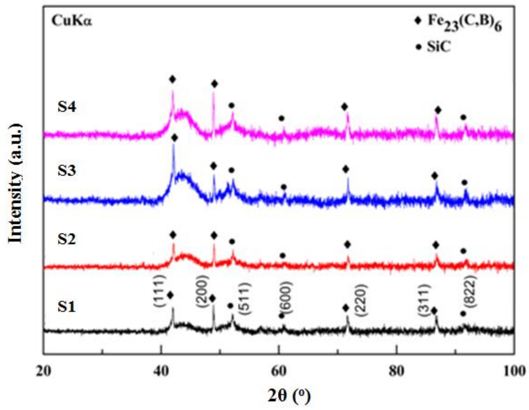
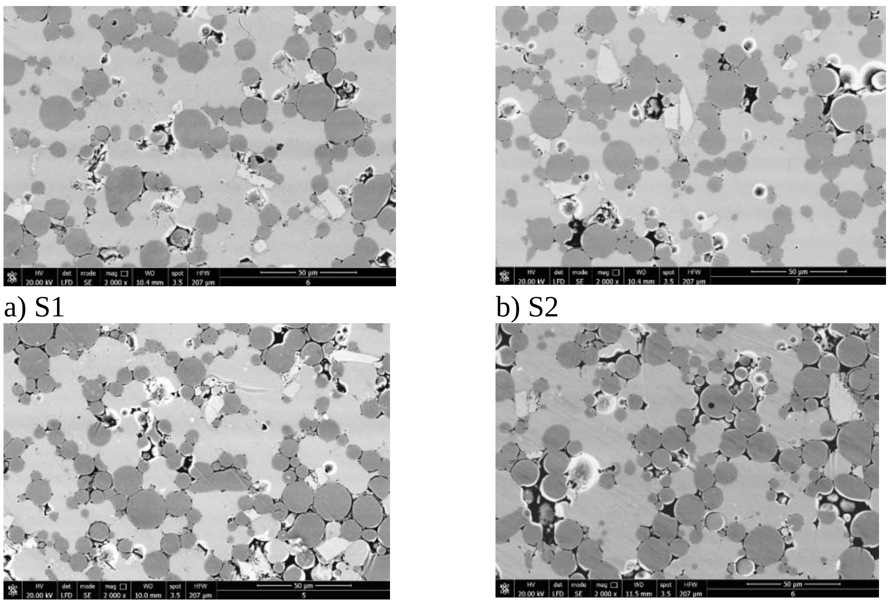


Fig. 5. XRD patterns of the hot pressed samples

Therefore, X-ray diffraction analysis certifies the obtaining of a composite material, which combines a distinct metallic amorphous phase with metallic nanocrystalline phases.

Figure 6 shows SEM morphologies of the hot pressed samples. One can be seen that the lighter color Zr – based alloy had adhered around the particles of Fe – based alloy. It is also remarked the presence of pores whose size and proportion increase with increasing the volumetric ratio of Fe – based nanocrystalline powders.

In the case of samples with a lower content of Fe – based alloy the particles of Fe – based nanocrystalline alloy are more uniform distributed and better embedded in the Zr – based alloy matrix.



a) S1 b) S2 c) S3 d) S4

Fig. 6. SEM morphologies of the hot pressed samples

The hardness test was performed both on the Fe phase and on the Zr phase and the hardness of the sample was determined as the average of the hardnesses measured on the two metallic phases. Ten tests were performed on each sample and the averages of the resulting values are shown in Table 1.

Figure 7 presents the compressive stress-strain curves of the hot pressed samples. One can notice some plastic strain just before the final fracture of the samples. The results of the five compression tests performed on each sample are shown in Table 1.

It can be seen that with increasing of the Fe – based nanocrystalline powders volume fraction the hardness of the composite material increases. This can be explained by the fact that the Fe – based nanocrystalline alloy has a much higher hardness than Zr – based alloy. It is also found that the composite material with the smallest volume ratio of Fe

– based alloy has a higher hardness (689 HV0.1) than the Zr – based bulk metallic glass with the same chemical composition as that of the Zr – based alloy matrix (614 HV0.1) [30].

The compression test showed that with increasing of Fe – based alloy volume ratio up to 40% the fracture strength increases from 1800 MPa corresponding to the Zr – based bulk metallic glass with the same chemical composition as that of the Zr – based alloy matrix [30] to 2369 MPa. Therefore, the presence of the nanocrystalline phase with higher compressive strength than the Zr – based alloy matrix, contributes to the increased compressive strength of the composite material.

It can also be observed that a volume fraction of Fe – based nanocrystalline powders greater than 40% leads to a decrease of the compressive strength. This can be explained by the presence of a high proportion of pores, highlighted in the microscopic structure of the composite material, which lead to the formation of micro-cracks. Also, the SEM images of the composite material show that at proportions greater than 40% of the nanocrystalline phase, the Zr- based alloy matrix can no longer incorporate all the Fe – based alloy particles.

Consequently, due to these structural inhomogeneities, although the average hardness of the composite reaches a maximum value of 715 HV0.1 for a volume ratio of 50% Fe – based nanocrystalline powders, the compressive strength reaches the lowest value of 1968 MPa.

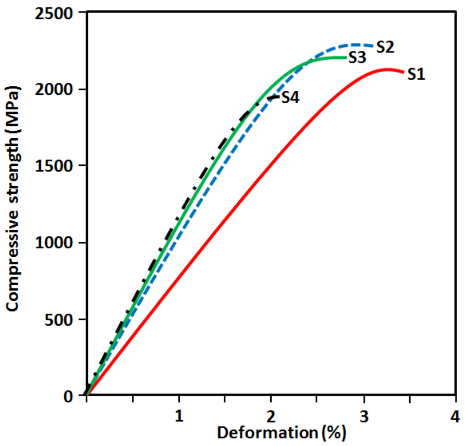


Fig. 7. The stress-strain curve of the hot pressed samples

Table 1
THE HARDNESS AND THE COMPRESSIVE STRENGTH OF THE HOT PRESSED SAMPLES

Sample	**HV0.1**	**Compressive strength, σ_f [MPa]**	**Total deformation ε_t [%]**
S1	689 ± 9	2180 ± 12	3.4 ± 0.1
S2	693 ± 12	2369 ± 15	3.1 ± 0.1
S3	712 ± 10	2238 ± 16	2.8 ± 0.1
S4	715 ± 13	1968 ± 19	2.2 ± 0.2

Conclusions

Bulk metallic glasses composites of Zr – based glassy alloy powder and Fe – based nanocrystalline alloy powder of cylindrical form with the diameter of 10 mm and 5 mm in high have been successfully obtained by hot-pressing method.

The hardness and the compressive strength of the obtained composite material are superior to the Zr – based bulk metallic glass with the same chemical composition as that of the Zr – based alloy matrix.

With increasing the volume ratio of Fe – based nanocrystalline powders the hardness of bulk metallic glasses composites increases. At the same time, a volume ratio of Fe – based alloy greater than 40% leads to structural inhomogeneities and to the appearance of pores and micro-cracks that affect the compressive strength.

Therefore, the parameters of the hot pressing process, in order to obtain the bulk metallic glasses composites, can be optimized so that, on the one hand to preserve the amorphous structure of the matrix and on the other hand to obtain the desired mechanical properties.

Acknowledgements: Acknowledgements to Leibniz-Institute for Solid State and Materials Research (IFW) Dresden, Institute for Complex Materials which has provided the raw materials and required equipment for this research.

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Manuscript received: 11.11.2019