Dual phase bulk metallic glasses fabricated by hot pressing using two different types of glassy alloy powder

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A new class of bulk metallic glasses (BMGs) the dual amorphous phased bulk metallic glass was studied with interest by researchers of materials science in the recent years, in order to bring together all the favorable properties for each amorphous phase. A dual phase bulk metallic glasses (DAPBMGs) fabricated by hot pressing using two different types of glassy alloy powder with the diameter of 10 mm and 5 mm in height were successfully achieved. The samples obtained were structural investigated by X-Ray diffraction (XRD), differential scanning calorimetry (DSC) and by scanning electron microscopy (SEM).

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Keywords: DAPBMGs, Amorphous ribbons, Glassy powders, Hot pressing

1. Introduction

In recent years, the dual amorphous phased bulk metallic glass (DAPBMGs) was studied with interest by researchers of materials science being a new class of bulk metallic glasses (BMGs).

These materials consist of several amorphous phases and are expecting to bring together all the favorable properties for each phase.

For example, the relatively brittle Fe-based BGAs can be improved by alloying it with high-toughness Zr-based BGAs [1].

The rules of glass-forming ability of this new class of advanced materials are different than the classics bulk metallic glasses (BMGs).

The requirements for the formation of a two-phase metallic glass alloy are on one hand a high glass forming ability, on the other hand a strong de-mixing tendency of some components, which is in contradiction with the high glass forming ability [2].

An alternative technique to prepare dual-phase metallic glasses would be via powder metallurgical methods, where the amorphous phases can be prepared individually and then consolidated by hot pressing in the supercooled liquid region of the amorphous phases or other appropriate processes and it was obtain a product with geometric shape like a disc [3].

The DAPBMGs can be obtained by powder metallurgy process using the following route: obtaining of the amorphous ribbons Zr and Fe-based corresponding to each phase by melt-spinning, the powders can be produced either by mechanical milling (MM), either by high-pressure gas atomization process (GA), mixing of this two glassy alloy powders by mechanical milling (MM) and compacting of the mixed glassy alloy powder using a hot-pressed technique (HP) or by spark plasma sintering (SPS) process. Thus it obtain this new advanced material called DAPBMGs [4-6]

2. Experimental

The aim of this study is to prepare a DAPBMGs by hot pressing in the supercooled liquid region using two different types of glassy alloy powder. Firstly there were obtained the glassy powders of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (Vitreloy105) and $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ which were used in this study.

For obtaining the glassy powders of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ was used a high-pressure gas atomization process (GA). The master alloy of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ that contains pure elements were remelted by induction heating via induction generator above the liquidus temperature, in an inert gas atmosphere and then it was applied a Ar gas pressure. The melt it was bottom casted through the atomization nozzle in a chamber and then it was lead by the Ar Gas in a cyclone separator and it was obtained the glassy powder. The structure of the Zr-based glassy powder was characterized by X-ray diffraction with CuKα radiation of the PANalytical X'PertPro device and by Perkin-Elmer 7 differential scanning calorimetry (DSC). The microstructure was characterized by scanning electron microscopy (SEM) using Hitachi Tabletop Microscope TM-1000.

A master alloy ingot of the nominal composition $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ was prepared by arc melting the mixture of pure elements under a Ti-gettered argon atmosphere. The master alloy was further crushed in small pieces of 5-6g and was used to produce six Fe-based amorphous ribbons in order to have enough material for

the hot pressing technological stage. All melt-spun ribbons with about 60 μm thickness and 2,5mm width were fabricated by a vacuum melt-spinning method using a Bühler equipment shows in Fig. 1. The surface velocity of the copper roller was 25 m/s. The structure of all six Fe-based melt-spun ribbons was characterized by X-ray diffraction with CuKα radiation of the PANalytical X'PertPro device and by Perkin-Elmer 7 differential scanning calorimetry (DSC). The microstructure was characterized by scanning electron microscopy (SEM) using Hitachi Tabletop Microscope TM-1000.

Milling of the amorphous ribbons Fe-based were performed using Retsch PM400 planetary ball mill and hardened stainless steel balls and vials. The milling was performed under Ar atmosphere and the handling of vials was done using LABstar glove box-MBRAUN. The ribbons were cut in the small pieces, by hand with scissors and put in the milling vial at a ball-to-powder mass ratio (BPMR) of 20:1.

The milling was performed at 150 rpm for 5h. The structure of the milled Fe-based glassy powder was characterized by X-ray diffraction with CuKα radiation of the PANalytical X'PertPro device and by Perkin-Elmer 7 differential scanning calorimetry (DSC). The microstructure was characterized by scanning electron microscopy (SEM) using Hitachi Tabletop Microscope TM-1000.

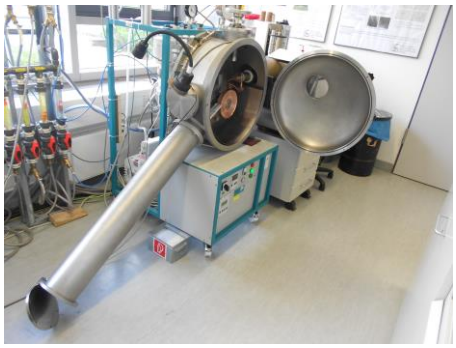

Fig. 1. Single-roller Bühler melt spinner device

The size of the glassy powders was determined by sieving. It was sieved the Fe-based glassy alloy powders and it was restrained only the powder which had the size below 90 μm and for Zr -based glassy alloy powders it was restrained only the powder which had the size below 20 μm. The Zr and Fe -based glassy alloy powder with the volume ratio $(Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5)$50%Vo $(Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2)$50% Vo were mixed using RETSCH PM400 planetary ball mill at 100 rpm for 10h with a ball-to-powder mass ratio (BPMR) of 10:1.

Secondly it was determined the temperature to realize the hot pressing and the time of maintaining of the loading. These parameters are very important because it must to avoid the recrystallization when the consolidation of the dual amorphous phased bulk metallic glass (DAPBMGs) is done.

DSC analyzes were performed in isothermal conditions, using Perkin-Elmer DSC7 under a continuous flow of purified argon. Have been taken 20g of glassy powders of each composition and placed in an Al crucible.

The heating was performed at different temperatures around the start point of supercooled liquid region (ΔTx) with 30 minute maintaining time at a constant heating rate of 20˚C /min. For Zr-based glassy powders the heating was performed at: 450˚C, 440˚C, 430˚C, 420˚C and for Fe-based glassy powders the heating was performed at: 480˚C, 460˚C, 450˚C.

The well-proportioned mixtures were put into Ni super-alloy die of the WEBER-PRESSEN device (Fig.2). The hot pressing was achieved at 420˚C in the supercooled liquid under applied pressure of 60 kN, for 600 s in an argon atmosphere.

Fig. 2. Hot pressing device

The heating was performed using a copper inductor with high frequency currents. As it can be seen from the Fig. 3, the hot pressed samples have a diameter of 10 mm and a height of 5 mm.

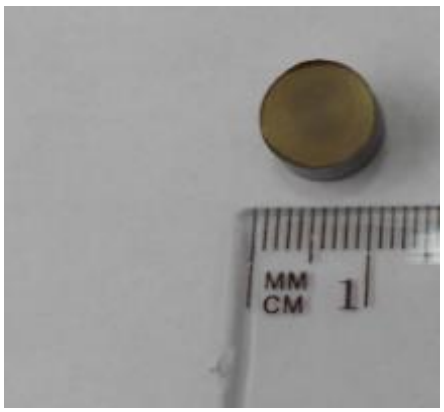

Fig. 3. The bulk consolidated samples with $(Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5)$ 50% Vo $(Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2)$50% Vo ratio

The structure of the DAPBMGs was characterized by X-ray diffraction with CuKα radiation of the PANalytical X'PertPro device. In order to check the thermal stability associated with glass transition, supercooled liquid and crystallization the samples was examined by Perkin-Elmer 7 differential scanning calorimetry (DSC) at a constant heating rate of 20˚C/min in a flowing argon atmosphere. The microstructure was characterized by scanning electron microscopy (SEM).

3. Results and discussion

Productions of six Fe-based ribbons were carried out in a single-roller Bühler melt spinner. In Fig. 4 it shows the amorphous structure of the ribbons that were produced, identified by X-ray and in Fig. 5 it shows the differential scanning calorimetry (DSC) analyses.

The ΔTx (Tx-Tg) of the ribbons which describes the supercooled liquid region is about 25˚C and the enthalpy of crystallization ΔH is 21J/g for each ribbon.

In Fig. 6 it shows the SEM morphologies of Fe-based glassy powder obtained by milling the amorphous ribbons and it can be observed that the geometry of the particles is irregular similar with flakes. The flakes glassy powders had the size below 90 μm.

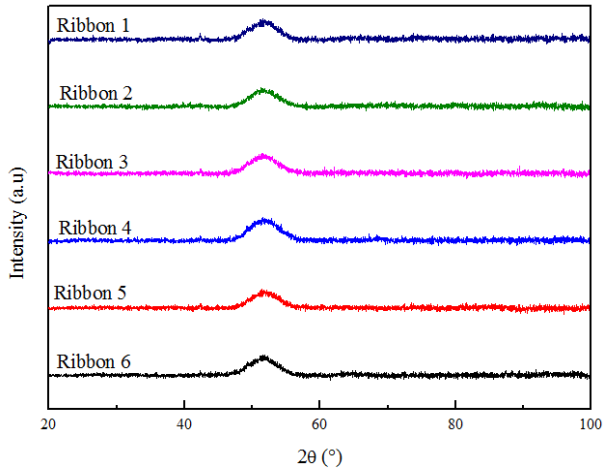

Fig. 4. XRD patterns of the $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ melt-spun ribbons

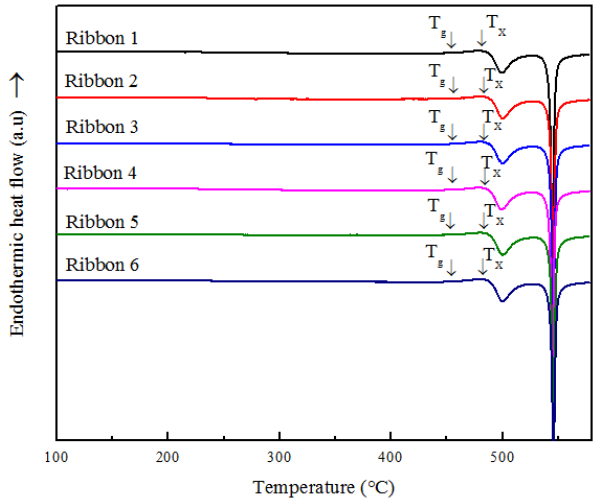

Fig. 5. DSC curves of the $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ melt-spun ribbons

The XRD patterns of the Fe-based powders are shown in Fig. 7 and indicate that these powders have amorphous structure.

In Fig. 8 it shows SEM morphologies of Zr-based glassy powder obtained by high-pressure gas atomization process.

It can be observed that the geometry of the particles is different comparing to the Fe-based powder, thus the particles are spherical. The spherical glassy powders had the size below 20 μm.

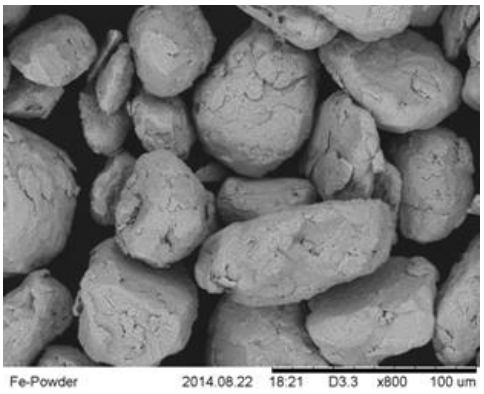

Fig. 6. SEM analyses of the $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ milled powders

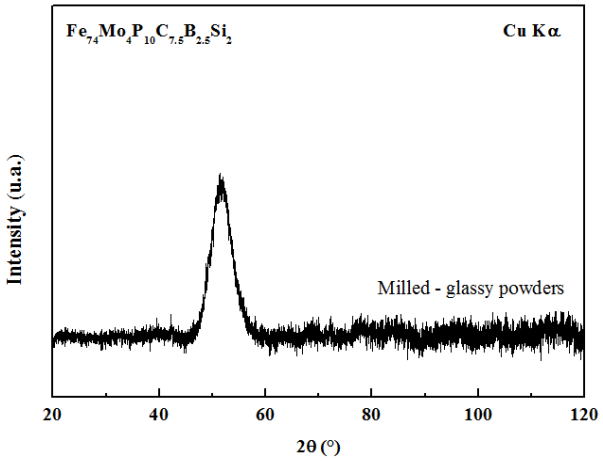

Fig. 7. XRD patterns of the $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ milled powders

The XRD patterns of the Zr-based powders which it shows in Fig. 9 indicate that these powders have amorphous structure.

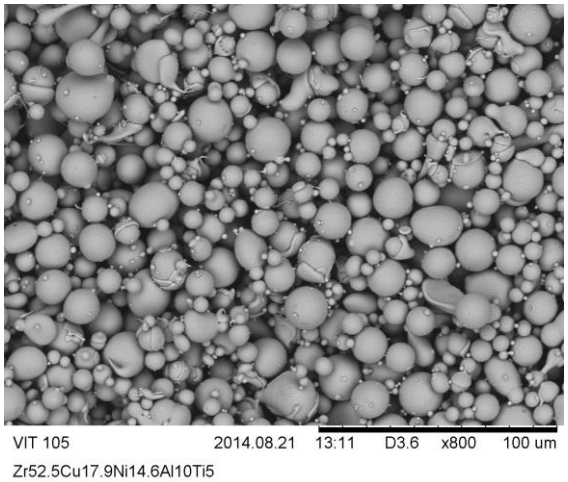

Fig. 8. SEM analyses of the $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ gas atomized powders

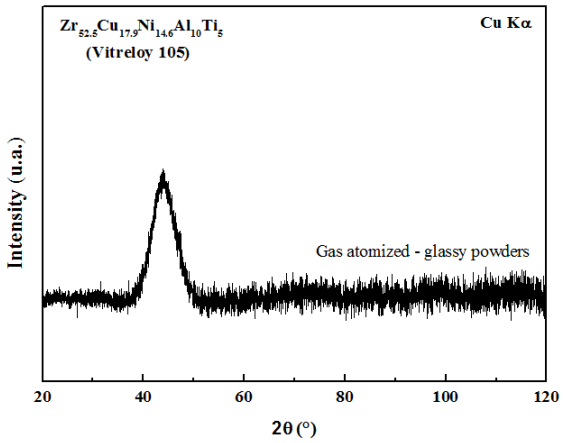

Fig. 9. XRD patterns of the $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ gas atomized powders

The mixtures of these two different types of glassy alloy powder with the composition ratio $(Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5)50\%Vo(Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2)50\%Vo$ for 2g were milled by RETSCH PM400 planetary ball mill device. In Fig. 10 (a) and (b) it shows SEM morphologies of mixed glassy powders and it can be observed that the smallest particles of Zr-based had adhered around the biggest particles of Fe-based. The XRD patterns from Fig. 11 shows that the amorphous structure of the mixed powders still remains after 10h mixing at 100 rpm.

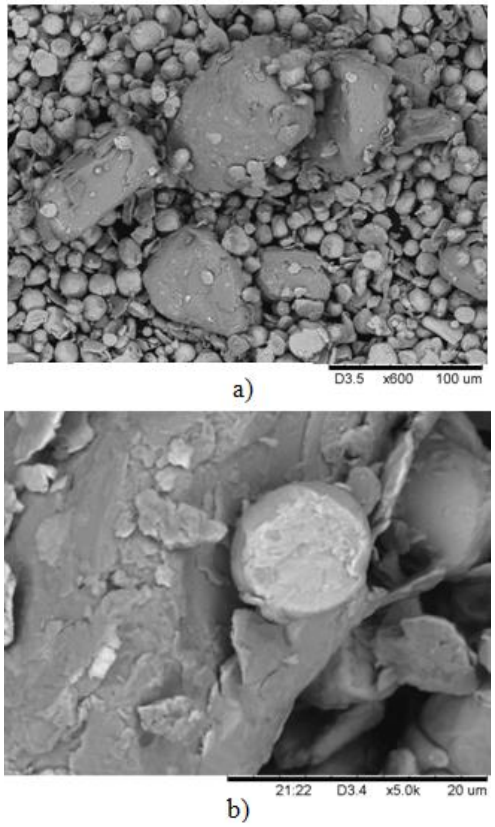

Fig. 10. SEM analyses of the mixed Fe and Zr-based glassy powders

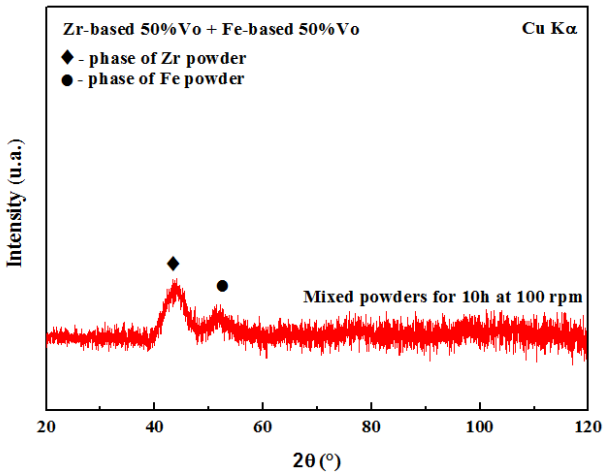

Fig. 11. XRD patterns of the mixed Zr and Fe-based glassy powders

The thermal stability it is shown by the differential scanning calorimetry (DSC) analyses. For the Fe–based and the Zr–based glassy powders, the DSC analyzes are shown in Fig. 12 and for both mixed glassy powders for 10h at 100 rpm they are shown in Fig.13.

The corresponding thermal stability data for Fe – based and Zr–based glassy powders are summarized in the Table 1. Where T_g is the onset of glass transition temperature, T_x is the crystallization temperature and $\Delta T_x=T_x-T_g$ describes the supercooled liquid region and ΔH is the enthalpy of crystallization.

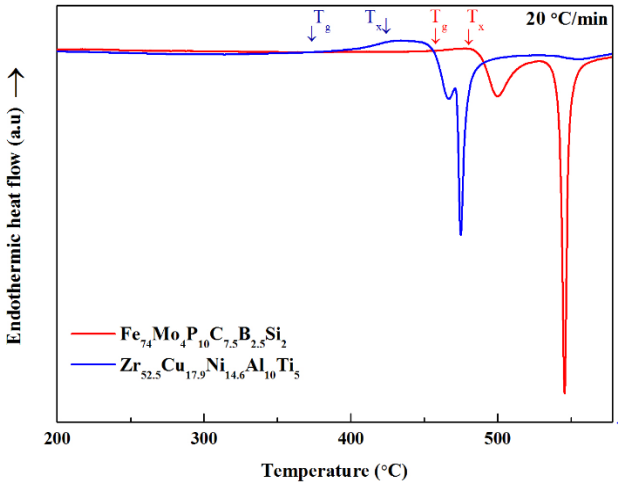

Fig. 12. DSC curves of the Zr and Fe–based glassy powders

In the case of the mixed Zr and Fe – based glassy powders it was observed continues curves which includes both glassy powders and the first onset of the glass transition temperature (T_g) and the first crystallization (T_x), dates which correspond with Zr–based glassy powders dates from Table 1.

It was observed that the supercooled liquid region given by ΔT_x for Zr–based glassy powders is larger than the supercooled liquid region of Fe–based glassy powders.

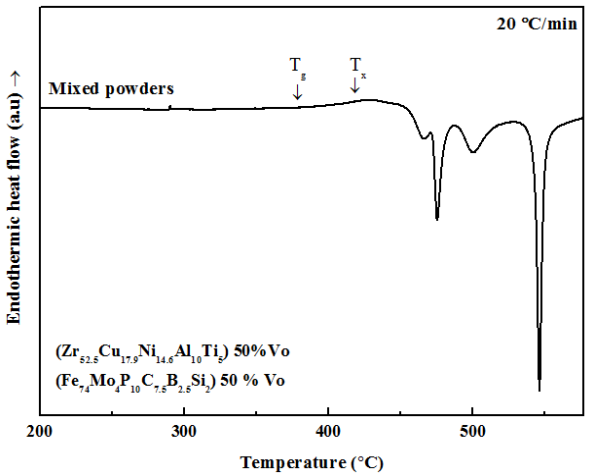

Fig. 13. DSC curves for mixed Zr and Fe–based glassy powders

As shown in Fig. 14 in the case of Fe-based glassy powders, the crystallization starts in the beginning of the glass transition temperature (Tg) at 450˚C after 1 minute of maintaining at this temperature and for Zr-based glassy powders the crystallization appears in the supercooled liquid region at 430˚C temperature after 2 minutes of maintaining at this temperature (Fig. 15).

Therefore to avoid the recrystallization of the Zr and Fe – based glassy, is recommended that the hot-pressed to be done at the temperature of 420˚C at 10 minutes of the maintaining time.

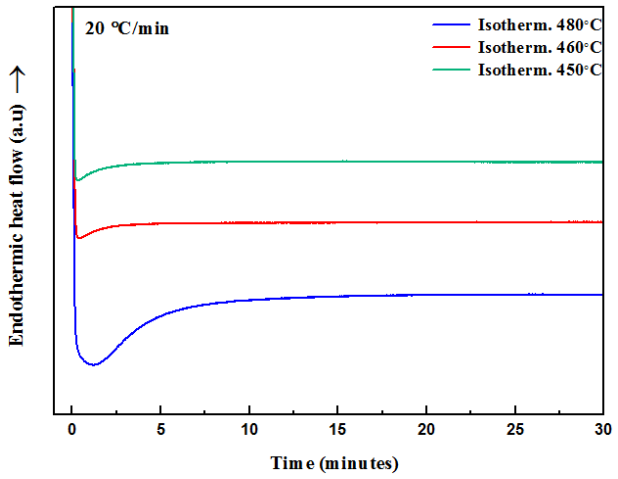

Fig. 14. Isotherms curves for Fe-based glassy powders, heating rate of 20˚C /min

In order to obtain a dual amorphous phased bulk metallic glass (DAPBMGs), for hot pressing of these two different types of glassy alloy powder was used the hot pressing device and the sample that was obtained has a diameter of 10 mm and a height of 5 mm.

The structural characterization of DAPBMGs obtained in the shape of disc was realized by X-ray diffraction (XRD), by differential scanning calorimetry (DSC) and by scanning electron microscopy (SEM).

The structural analysis by X-ray diffraction was realized with PANalytical X'PertPro device and the XRD pattern of the DAPBMGs from Fig. 16 it shows the dual amorphous structure. As it observed the DAPBMGs bring together the both Zr and Fe amorphous phases.

Fig. 17 shows the DSC curves for dual amorphous structure similar to DSC curves for mixed Zr and Fe – based glassy powders from figure 13.

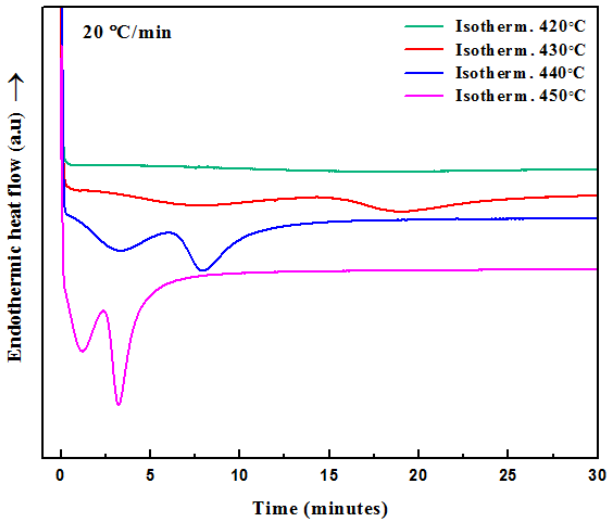

Fig. 15. Isotherms curves for Zr-based glassy powders, heating rate of 20˚C /min

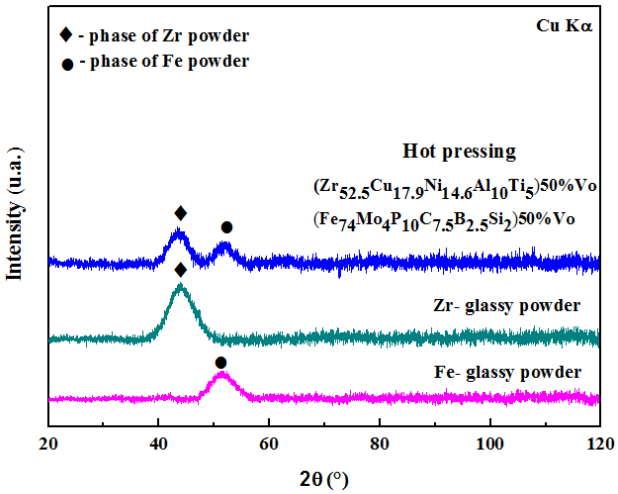

Fig. 16 XRD patterns of the DAPBMGs

Fig. 18 shows SEM morphologies of dual phase bulk metallic glasses fabricated by hot pressing using two different types of glassy alloy powder.

Table 1. Thermal stability

Millings	T_g [˚C]	T_x [˚C]	ΔT_x [˚C]	ΔH [J/g]
Zr-powder	408	459	51	42
Fe-powder	462	491	29	20

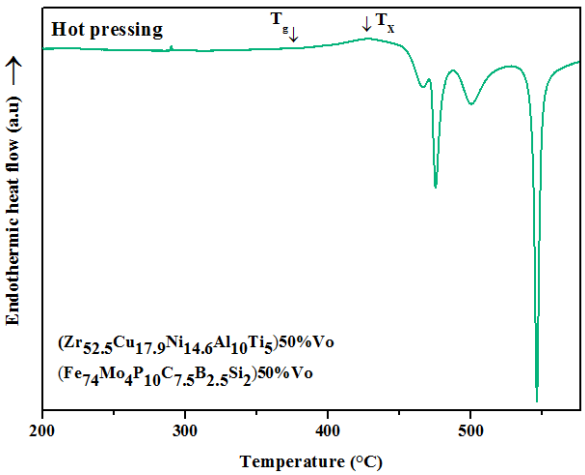

Fig. 17. DSC curves for hot pressing of the DAPBMGs

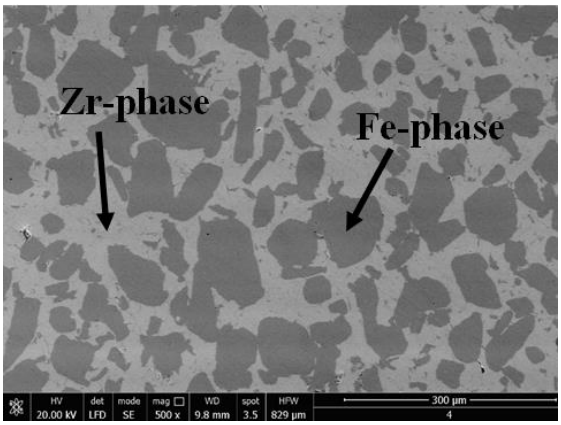

Fig. 18 SEM analyses of the DAPBMGs

4. Conclusions

Dual phase bulk metallic glasses (DAPBMGs) fabricated by hot pressing using two different types of glassy alloy powder with geometric shape like a disc of 10 mm diameter and a height of 5 mm have been successfully obtained by hot-pressing method.

By mechanical alloying, at 100 rpm for 10h, the smallest spherical particles of Zr-based glassy powder (below 20 µm) had adhered around the biggest particles of Fe-based glassy powders (below 90 µm). The pressing was achieved at the temperature of 420˚C at 10 minutes the maintaining time, with loading of 60 kN.

It was obtained a dens material without porosity and it was observed that the Zr-phase formed the matrix of these DAPBMGs with insertion of flakes particles of Fe-based similar to a composite material.

Acknowledgements

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