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Bulk metallic glasses (BMGs) represent a viable alternative for replacing classic materials used in medical devices. This paper presents the research conducted in order to obtain copper based BMGs using two different chemical compositions: Cu₄₅Zr₂₇Al₅ and Cu₄₅Zr₃₅Al₁₅Ag₅. The samples were obtained by copper mold casting and their structure and properties were investigated using X-Ray diffraction (XRD), differential scanning calorimetry (DSC) and optical microscopy.

Keywords: Bulk metallic glasses, GFA, copper, medical devices

Biocompatible materials play a key role in the construction of medical devices currently used on a large scale [1-4]. Recent researches were focused on developing new materials that would not inherit the disadvantages of the classic materials (poor corrosion resistance, low deformability etc) [5-19]. Bulk metallic glasses (BMG) can be a viable alternative for replacing classic biocompatible materials [18, 19], due to their specific properties such as: good corrosion resistance in the absence of intercrystalline corrosion, excellent plastic deformability and good castability (absence of casting defects and voids that form when casting crystalline structure materials) even with complex geometries. This sum of properties makes the BMGs very appealing for medical devices.

After the first metallic glass of Au₃Si₃ was developed in the 1960’s [11], intensive research were conducted in order to obtain BMGs using different elements including Zr, Ni, Ti, Fe, Au, Pt, Cu as a base for these outstanding materials. Various methods of obtaining BMGs were developed, dealing with problems related to raw materials (their purity), complicated equipment and process, mechanical properties of the products (generally the BMGs are brittle) [5-19]. Recent studies are focused on discovering new alloying strategies including new materials combinations, processing methods, new structures (nanocrystalline or nanoquasicrystalline particles) as well as exploring new properties (such as magnetic, chemical or physical).

This study was aimed to assess the influence of silver on the structure and properties of bulk metallic glasses. Biocompatible properties from the Cu-Zr-Al respectively Cu-Zr-Al-Ag system. Also, since obtaining BMGs usually require special preparation conditions such as vacuum or controlled atmosphere, this study aims to develop a method to obtain them by air casting method, in the form of 3 mm rods, with no special conditions.

Experimental part

Pure elements Cu, Zr, Al and Ag were mixed together, than the mixture was melted using an Arc Melter AM 200 furnace, obtaining thus 10 grams batches of Cu₄₅Zr₂₇Al₅ and Cu₄₅Zr₃₅Al₁₅Ag₅ master alloys. Afterwards, the master alloys were re-melted and casted using a copper mold, obtaining rods with 3 mm diameter and 100 mm length. No special conditions were required during casting, as the process was conducted at room atmosphere.

The structure of the samples was investigated using SEM/EDAX and X-ray diffraction XRD. X-ray diffraction was conducted using an X’Pert³ Powder diffraction system, with the radiation of a Cu anode with a wavelength $\lambda = 1.54 \ \text{Å}$. Differential scanning calorimetry (DSC) was used to investigate the thermal stability, on a Netzsch STA 441 Jupiter apparatus under a flow of purified nitrogen. The glass transition temperature $T_g$, the crystallization temperature $T_c$ and the melting temperature $T_m$ were determined as the onset temperatures of the glass transition the crystallization and melting peak, respectively, and the liquidus temperature $T_l$ as the offset of the melting peak during heating with a constant rate of 0.33 K/s.

Vickers hardness HV was measured using a Wolpert Micro-Vickers Hardness Tester machine at room temperature using a 100 grams load. At least 10 measurements were conducted, in order to ensure the accuracy of the results. Olympus BX51M microscope with Analysis 5.0 software was used to microscopically analyze the alloys microstructure.

Results and discussions

In order to confirm the structural homogeneity of the master alloys, SEM analysis was conducted on both batches. The images are presented in figure 1.

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The Cu_{48}Zr_{47}Al_{5} alloy shows a casting structure with dendrites, specific to crystalline materials, while the Cu_{45}Zr_{45}Al_{5}Ag_{5} alloy exhibits only slight traces of dendrites embedded in an eutectic structure, indicating thus a higher amorphization susceptibility. X-ray diffraction shows the presence of high peaks for the Cu_{48}Zr_{47}Al_{5} master alloy (figure 2a), characteristic to crystalline materials, which together with the low eutectic quantity indicate a lower glass forming ability (GFA). The second X-ray diffraction (figure 2b) confirms the results given by the SEM image, that the alloy Cu_{45}Zr_{45}Al_{5}Ag_{5} is suitable for amorphization.

The rods casted in a copper mold (figure 3) were macroscopically analyzed. The examination emphasized the metallic luster and the absence of defects such as pores or cracks.

The presence of broad peaks in diffraction image (figure 4) confirms that the structure is amorphous only for the Cu_{45}Zr_{45}Al_{5}Ag_{5} alloy. The structure of the Cu_{48}Zr_{47}Al_{5} alloy is microcrystalline, with peaks corresponding to compounds such as CuZr, ZrCu, Zr_{2}Cu, Zr_{2}Al and Zr.
The DSC curves of the samples are showed in Figure 5.

In case of the Cu_{48}Zr_{47}Al_{5} alloy, the DSC curve shows an exothermic inflexion which marks the recrystallization of the microcrystalline metastable phase, obtaining as a result of the rapid cooling. Heating over $T_x = 472^\circ$C leads to obtaining a crystalline structure, similar to the master alloy.

In case of the Cu_{45}Zr_{45}Al_{5}Ag_{5} alloy the DSC curve exhibit s an exothermic peak which marks the crystallization event and an endothermic peak for the melting. The glass transition temperatures $T_g$, the crystallization temperatures $T_x$, and the $\Delta T_x = T_x - T_g$ parameter which estimates the glass forming ability was calculated for this alloy. The values are listed in table 1. For a good GFA the supercooled liquid region $\Delta T_x$ should be as large as possible [19], while a high $T_x$ means a higher stability of the glass.

| Sample          | $T_g$ [°C] | $T_x$ [°C] | $\Delta T_x$ | $T_m$ [°C] | HV0.1  |
|-----------------|------------|------------|--------------|------------|--------|
| Cu_{48}Zr_{47}Al_{5} | -       | 472        | -            | 807        | 423 ±5 |
| Cu_{45}Zr_{45}Al_{5}Ag_{5} | 430     | 487        | 57           | 804        | 396 ±6 |

It can be seen from table 1 that the addition of silver ensures the glass transition temperature $T_g$ of 430°C and a good the thermal stability, with crystallization temperature $T_x$ of 487°C. Meanwhile, the melting temperature slightly moves
to lower values, $\Delta T_x$, the most common parameter used to determine the GFA, is 57°C for the alloy that contains the Ag addition and it is well known that a high value for $\Delta T_x$ ensures a good GFA.

Regarding the mechanical properties, it was found that the alloys containing silver have a slightly lower microhardness than the Cu$_{45}$Zr$_{17}$Al$_3$ alloy.

Since silver tends to form eutectics with Cu, Zr, Al, according to the confusion principle, addition of silver to the chemical composition leads to the formation of a quaternary eutectic. As a result, the melting temperature decreases and it favors the transformation of the liquid into an amorphous solid. Meanwhile, it is well known that silver has low hardness and its tendency of forming solid solutions with Cu, Al, Zr can explain the decrease of hardness exhibit by the Cu$_{45}$Zr$_{17}$Al$_3$Ag$_5$ alloy [20].

The microscopic image of the arc melted Cu$_{45}$Zr$_{17}$Al$_3$Ag$_5$ alloy (Figure 6) presents two compounds with distinct shapes precipitated in the matrix. Different studies [5, 16] reported the presence of structures similar to those presented in this research. After casting, the structure is refining, but does not substantially change (Figure 7).

Conclusions

Cu$_{45}$Zr$_{17}$Al$_3$ and Cu$_{45}$Zr$_{45}$Al$_3$Ag$_5$ bulk metallic glasses were obtained in the shape of 3 mm diameter and 100 mm length rods using the copper mod casting method. The novelty consists of the fact that no special conditions were required during casting, as the process was conducted at room atmosphere.

It was found that the addition of silver in the chemical composition leads to a value for $\Delta T_x$ (the most common parameter used to determine the GFA) of 57°C. However, the hardness decreases slightly when adding silver in the chemical composition of the alloy. Considering the results, further investigations are required for these alloy class and future tests will include compression and corrosion tests.

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