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Preparation and characterization of Zr-based bulk metallic glasses in form of plate

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ABSTRACT

Zr-based bulk metallic glasses present an interesting combination of physical, chemical and mechanical properties. During the last decade, intensive progress has been made and a number of applications have been suggested for these materials. In order to successfully apply these materials, it is necessary to accurately characterize their structure, thermal stability and other properties accurately.

The aim of the presented work is the manufacturing, examination of the structure of selected Zr-based bulk metallic alloys and confirmation of an amorphous structure using X-ray analysis, microscopic observation and thermal analysis.

In this work, the Zr-based bulk metallic glasses in form of plate was successful produced by die pressure casting method. Designed scientific station for casting zirconium based amorphous alloys in the form of plates and rods with selected dimensions is in our university a comprehensive method for achieving amorphous materials which enables us to maintain repeatability of as-cast samples with the amorphous structure and the assumed dimensions range.

The diffraction pattern and exothermic reaction as well as the fracture surface morphology reveal that studied as-cast Zr-based alloy is in amorphous state. The calculated GFA parameters show that the alloy exhibits satisfactory glass-forming ability in form of studied plate. These obtained values can suggest that studied alloys are suitable materials for further planned practical application at welding process. The success of Zr-based bulk metallic glasses production in form of plate with obtained sizes is important for future progress in joining research of this group of materials.

1. Introduction

In the last years, a number of BMGs have been successfully developed and commercialized for engineering applications using their exceptional properties. Understanding the nature of glass formation and glass forming ability is the key to developing new BMGs with improved properties, manufacturing ability for industrial applications and larger dimensions [1,2].

Due to the special structure of amorphous materials, BMGs have different properties from crystalline alloys. They exhibit high strength, high fracture toughness, high hardness. Besides, they are characterized by corrosion, wear and radialization resistance [3,4]. BMGs in Zr-based alloys were first prepared in 1990s by the stabilization of supercooled liquid. Since then a lot of researches have been carried out to the development of BMGs. At first, researches concentrated on Zr-, Ti-, Hf-, Ln-, Mg-, Ca-, Pd-, and Pt-based systems because of their unique combination of properties [1,4].

In this paper, the structure and thermal properties of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy were studied. Zr-based alloys are attractive due to their good GFA and impressive mechanical properties. The bulk metallic glassy $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy possesses excellent mechanical properties such as high strength, high fatigue strength, high fracture toughness, high elastic strain and low Young's modulus [2,4,5]. These unique properties are a strong driving force for structural applications and they are important for engineering applications. This alloy has been suggested as a suitable material for applications for golf clubs, optical parts, microgeared motors and pressure sensors [4–6]. It is expected that Zr-based alloys may extend their application areas to astronautics, aeronautics and nuclear power industries [7].

Zr-based BMGs have reported low cooling rates less than 10 K/s. The maximum diameter of the fully glassy $Zr_{55}Cu_{30}Ni_5Al_{10}$ rod has been limited to about 16 mm. Although, Yokoyama et al. were able to produce a fully glassy rod 30 mm diameter in the Zr–Cu–Ni–Al system alloy using cap-cast technique [8,9].

Zirconium based alloys are very sensitive to the presence of impurities and oxygen. As examined, the high oxygen contents reduce the supercooled liquid region and change the crystallization behavior in the bulk metallic glasses [1].

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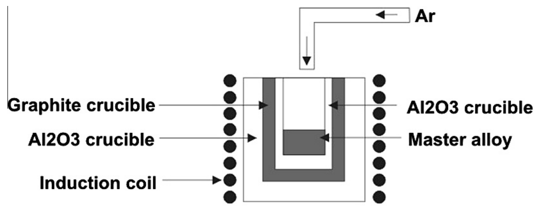

Fig. 1. Scheme of master alloy preparation.

From the analysis of literature data it can be concluded that the arc melting and suction casting method are the most popular and useful methods for production of Zr-based BMGs [5,6,9]. In this experiment, a homogeneous master alloy have been successfully prepared by induction melting. The new, simple arrangement of melting crucibles set have been used (Fig. 1). The success of producing the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy by the use of the elaborated master alloy preparation technique is very encouraging for the future preparation and production of BMGs. This simple preparation method is very useful for the prevention of oxidation of ingots.

The main aim of the presented work was the production attempt of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy by induction melting and pressure die casting method.

The additional purpose of this paper was examination of the structure of obtained $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG in the form of plate with thickness of 1 mm and confirmation of an amorphous structure using different methods.

A $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy was used in the present test because the alloy has a wide supercooled liquid region and could be used as tested materials for laser welding process planned in the future.

2. Experimental procedure

The preparation process of Zr-based bulk metallic glasses requires special technology to provide specific conditions for melting and casting process. Therefore, the preparation procedure of these alloys, which includes two stages was worked out. The first stage of casting consists the formation of a homogeneous master alloy by induction of high purity elements (Zr, Cu, Ni, Al) melting and of the appropriate atomic composition (Table 1). The master alloy was prepared in the protective atmosphere.

Scheme of melting crucibles with alloy ingot is presented in Fig. 1.

The second stage consists of the pressure injection process of molten alloy into copper mould in the argon atmosphere. Schematic illustration of the pressure die casting equipment used for casting bulk metallic glasses is presented in Fig. 2.

The plate with dimension of $1 \times 10 \times 20$ mm was investigated. The characterization of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic alloy using XRD, DTA, DSC, SEM and TEM methods was carried out.

The amorphous structure of as-cast plate was proved by X-ray diffraction using a Seifert – FPM XRD 7 diffractometer with Co Kα radiation at 35 kV. The data of diffraction lines were recorded by means of the stepwise method within the angular range of 20–100°.

The microscopic observation of the amorphous structure was executed by means of Titan 80–300 transmission electron microscope of FEI firm. The microscopic observation of the fracture morphology of studied glassy materials was carried out by means of the Supra 25 made by Zeiss factory scanning electron microscope as well.

The thermal properties: glass transition temperature (T_g), onset crystallization temperature (T_x) and peak crystallization temperature (T_p) of the as-cast alloy were examined by differential scanning calorimetry method using DSC822 Mettler Toledo at a constant heating rate of 40 K/min. In order to check the thermal stability of the cast sample, small slices of the inglot were heated up to a temperature of 1300 K under Ar flow in a TGA/SDTA 851 by Mettler Toledo factory thermal analyzer at a constant heating rate of 20 K/min. Afterwards, the samples were cooled at a constant cooling rate of 20 K/min too.

3. Results and discussions

The bulk metallic glass sample in plate form was successfully produced and investigated. At the beginning, the structure of as-cast Zr-based alloy was examined by X-ray diffraction method.

Table 1
Chemical composition, purity and shape of used elements.

No.	Elements	at. (%)	mass. (%)	Purity (%)	Shape
1	Zr	55	67.0141	99.9	Lump
2	Cu	30	25.4627	99.99	Globule
3	Ni	5	3.9195	99.9	Pieces
4	Al	10	3.6037	99.99	Lump

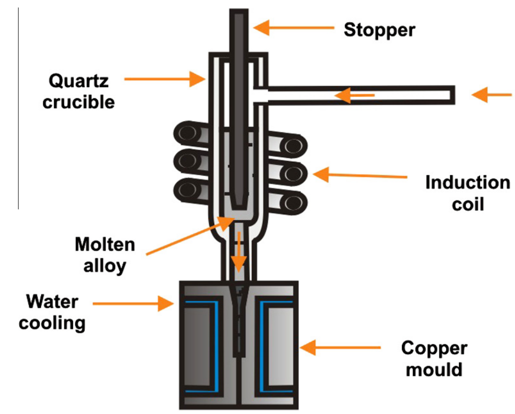

Fig. 2. Schematic illustration of the pressure die casting equipment.

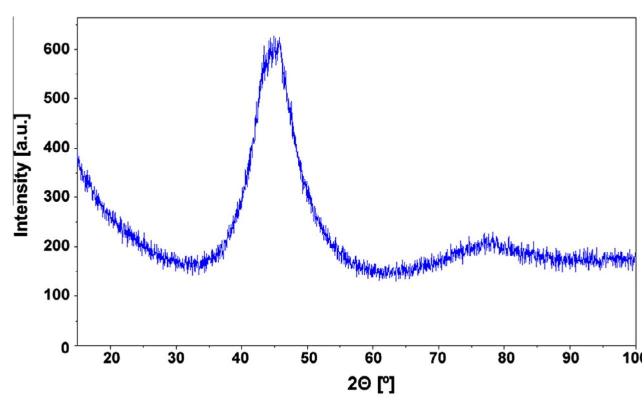

Fig. 3. X-ray diffraction pattern of the Zr–Cu–Ni–Al as-cast alloy.

The sample of determined chemical composition with a thickness of 1 mm consists of a single glassy phase as was evidenced from a main halo peak without crystalline peaks in their X-ray diffraction pattern. The diffraction record of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy plate is shown in Fig. 3.

To confirm the glassy structure of obtained Zr-based bulk metallic alloy more accurately, further and more precise analysis by transmission electron microscopy was carried out. The typical morphology of glassy alloy is shown in Fig. 4.

The fuzzy patterns without any crystalline fringe can be observed in Fig. 4 (b). These electron diffraction patterns are typical features of amorphous structure. No trace of phase separation is formed. The selected area electron diffraction pattern also indicates that the structure is amorphous.

The morphology of the fracture surface was investigated by SEM method. Fig. 5 shows SEM micrograph of selected areas of examined Zr–Cu–Ni–Al amorphous plate with thickness of 1 mm. The fracture surface (Fig. 5 (a)) appears to consists of small fracture zones. Probably, the occurrence of these different zones results from breaking of the sample into parts. The presented fracture surface could be classified as mixed type fractures with indicated