



## Effect of vanadium substitution for zirconium on the glass forming ability and mechanical properties of a $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ bulk metallic glass

Nima Khademian<sup>a,\*</sup>, Reza Gholamipour<sup>b</sup>, Farzad Shahri<sup>c</sup>, Morteza Tamizifar<sup>c</sup>

<sup>a</sup> Department of Mechanics, Islamshahr Branch, Islamic Azad University (IAU), Tehran, Iran

<sup>b</sup> Iranian Research Organization for Science and Technology (IROST), Tehran, Iran

<sup>c</sup> Faculty of Engineering and High-Tech., Iran University of Industries and Mines (IUIM), Tehran, Iran

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### ABSTRACT

Effect of vanadium on the thermal and mechanical properties of the  $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$  bulk metallic glass has been studied. The vanadium substitution for zirconium in the bulk metallic glass leads to the decrease of the glass forming ability in constant cooling rate; as well as co-precipitation of  $Zr_2Ni$  and  $Zr_2Cu$  crystalline phases in amorphous matrix. The size of the crystallites are about 20–50 nm in amorphous matrix and they act as a barrier against of rapid propagation of shear bands. In fact, the nanocrystalline phases in amorphous matrix cause the increase of the strain and the quasi-static compression strength about 58% and 20%, respectively.

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### 1. Introduction

Bulk metallic glasses as relatively new materials are the most commonly candidates for structural applications, during the last two decades. These innovative materials open up unlimited possibilities for modern material science and development. Depend on the application; the characteristics of BMGs can be designed into a custom-made material. The properties of these new materials are basically determined by the properties of their components. The development objectives for BMGs are: an improvement in wear resistance, enhanced resistance to corrosion, high strength and large elastic limit, on the other hand, limited plasticity (0–2% plastic strain) prior to failure which constrains their applications as structural materials [1–8].

Zr-based bulk glassy alloys have attracted widespread interests because of their strong glass forming ability and wide supercooled liquid regions; however many studies are still focused on the development of new alloy compositions due to their attractive properties and technological applications [9–19].

In order to improve the ductility, heterogeneous microstructures have recently been designed by combining glassy matrix with crystalline second phase. The second phase in metallic glasses can be introduced by partial crystallization of the metallic glass,

especially during the solidification. The precipitation of crystalline phase in the glassy matrix may be induced by the addition of elements which cause partial crystallization during solidification [10,16–18,20].

This paper intends to present the effect of the substitution of a small amount of V for Zr on thermal and mechanical properties of  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 0, 1, 2, 3, 5$ ) bulk metallic glass. We report correlations among the elastic moduli, fracture strength, Vicker's hardness and glass transition for bulk metallic glasses. The clear correlations imply that the mechanical properties of BMGs would be better controlled by selection of elements and quantity of them.

### 2. Experimental

Zr-based alloy ingots with composition of  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 0, 1, 2, 3, 5$ ) prepared by arc melting using high purity elements in Ti-gettered Ar atmosphere on a water cooled copper crucible. Cylindrical rod alloys of about 30 mm in length and 4 mm in diameter were produced by a suction casting method. The structure of the samples was examined preliminarily by X-ray diffraction (XRD) using an X'Pert XRD-Philips diffractometer with  $Co-K\alpha$  radiation ( $\lambda = 0.178$  nm). Thermal analysis was carried out by differential scanning calorimetry (DSC) with heating rate of 20 K/min by a NETZSCH 449 DSC. Compressive tests were performed at the strain rate of  $10^{-4} s^{-1}$  by an INSTRON machine. Specimens for compression test with dimensions of 4 mm in diameter and 8 mm in height were machined from the suction casting samples. Fracture surfaces of compression tested samples were examined scanning electron microscopy by a VEGA//TSCAN. In addition, Vicker's hardness of the samples was carried out by applying a hardness indenter with a load of 10 kgf.

\* Corresponding author. Tel./fax: +98 2144435663.

E-mail address: [nkhademian@gmail.com](mailto:nkhademian@gmail.com) (N. Khademian).

### 3. Results and discussions

Fig. 1 shows a multiplot of XRD patterns of the as-cast 4 mm diameter  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 0, 1, 2, 3, 5$  at.%) alloys. As shown in Fig. 1, for the sample without vanadium and the sample with  $x = 1$ ; there are broad diffuse peaks between diffraction angles from  $35^\circ$  to  $50^\circ$  without detectable sharp diffraction peaks, indicating the glassy state of the samples. The increase of V concentration from 2 to 5% causes some diffraction peaks appear on the patterns corresponding to the precipitation of nanocrystalline phases. The size of them are about 20–50 nm according to the calculation by Scherer equation. The crystalline phases were indexed as the  $Zr_2Ni$  and  $Zr_2Cu$  phases in the as-cast rods.

Fig. 2 shows the DSC result of the as-cast  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 0, 1, 2, 3, 5$ ) glassy alloys. During heating; the alloy exhibits distinct glass transition, followed by supercooled liquid region (SLR) and finally an exothermic peak corresponding to a crystallization reaction. The arrows, pointing down, indicate the glass transition temperature  $T_g$  and the onset crystallization temperature  $T_x$ . Fig. 3 indicates that the onset temperature of crystallization  $T_x$  and  $\Delta T_x$  decrease; however, glass transition temperature increases with the increase of V content of the samples.

Therefore glass forming ability of  $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$  BMG is deteriorated with partial addition of V because though, there is a considerable difference between atomic radius of Zr and V; there are not large atomic size differences among Cu, Al, Ni and V as shown in Table 1 [21]. On the other hand, it was proposed that the addition of V more than 1 at.% can destabilize the melt of  $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$  alloy [13,17,19]. Therefore, the instability of the undercooled liquids leads to precipitation of nanocrystalline phases.

Fig. 4 shows the nominal compressive stress–strain curves of the as-cast  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 0, 1, 2, 3, 5$ ) alloys. In uniaxial compression,  $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$  bulk metallic glass exhibit fracture strength ( $\sigma_f$ ) about 1400 MPa but no plasticity. As V content of samples increases from 0 to 1 at.%, the strength as well as plasticity increases a little. Further increase of V content, from 1 to 2 at.%, causes ultimate strength ( $\sigma_u$ ), fracture strength and fracture strain to increase as indicated in the insert of Fig. 4. It is also shown that in the sample with  $x = 2$  the ultimate strength of 1690 MPa, the

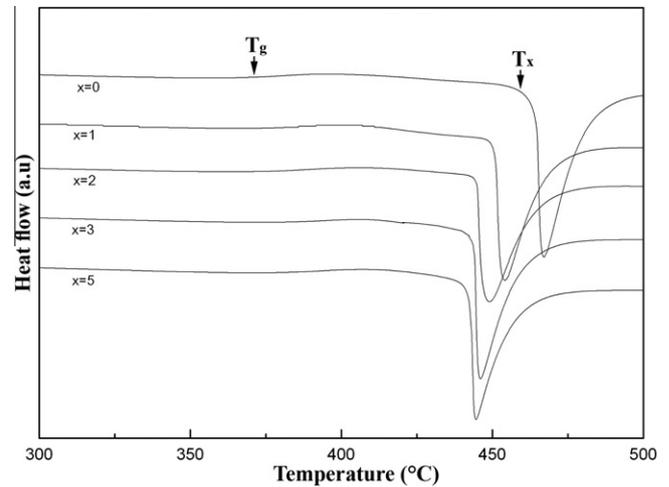


Fig. 2. DSC curves of as-cast  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 0, 1, 2, 3, 5$ ) alloys at a heating rate of 20 K/min.

fracture strength of 1674 MPa and fracture strain of 3% are the highest properties being reached among the samples. However, the increase of V content more than  $x = 2$  (i.e. 3 and 5) decreases fracture strength and strain simultaneously. The results, in the right inset of Fig. 4, show an increase in the elastic moduli of samples with increasing V contents.

Fig. 5 shows the fracture surfaces of the as-cast  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 0, 1, 2, 3, 5$ ) BMGs. The angle between the fracture surface and the compression axis for the samples with  $x = 0, 1, 2, 3$  is close to  $42^\circ$ ; however, there is a deviation of three degree at the end of the fracture as shown in Fig. 5a to Fig. 5d. In the sample with  $x = 5$  there are intersecting fracture planes with different angles without any shear band as indicated in Fig. 5(e). On the other hand in the sample with  $x = 2$  branching of shear bands has been occurred much more than that of in the other samples.

Fig. 6 exhibits the SEM micrographs of the fracture surface of the as-cast  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 1, 2, 3, 5$ ) alloys. The vein patterns (VP) and semi-liquid regions (SLR) were observed on the

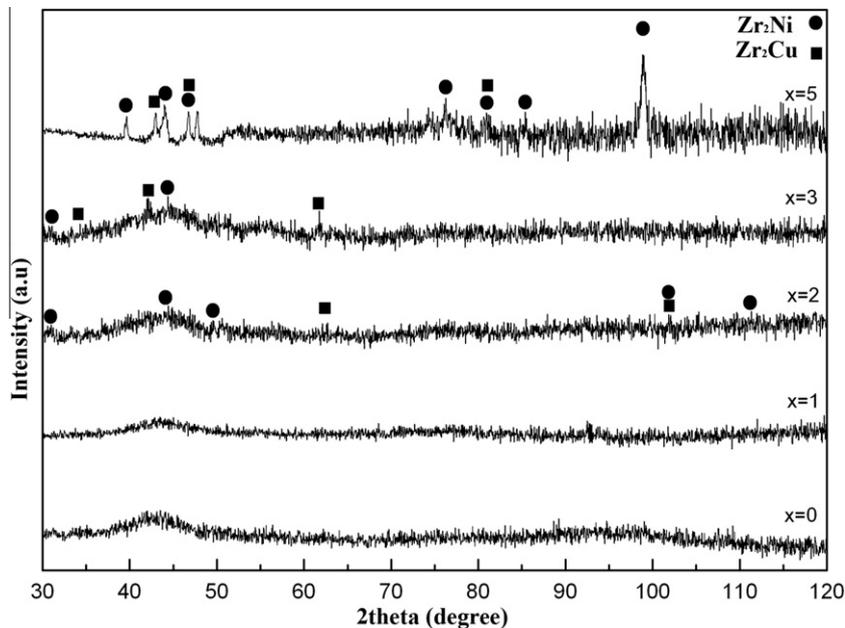


Fig. 1. X-ray diffraction patterns for the as-cast  $Zr_{65-x}Cu_{17.5}Ni_{10}Al_{7.5}V_x$  ( $x = 0, 1, 2, 3, 5$ ) alloys.

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