# Mechanical behaviors of partially devitrified ti-based bulk metallic glass

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The fabrication of bulk metallic glasses (BMGs) has received attention due to their unique properties and potential applicability [1–3]. The beneficial characteristics of composite systems that allow controlling mechanical properties of BMGs has led to the fabrication of *in-situ* composite systems or partially devitrified BMGs and thus to the prevention of catastrophic fracture of BMGs [4, 5]. The composite has shown improved mechanical properties compared with monolithic BMGs. It has been proposed that the enhanced strength and ductility of the composite is due to the high strength of devitrified nano-sized particles, stable interfaces, or enhanced multiple shear band formation, inferring that the devitrification process and selection of nanoparticles significantly affects the mechanical properties of the composite [6, 7]. Also, when enhanced mechanical properties of the composites are observed, a specific amount of volume fraction of nanoparticle embedded in amorphous matrix has been reported [6, 7]. In order to control the volume fractions of nanocrystals in amorphous matrix, a devitrification process of BMG via controlled thermal process has been exercised in several BMG systems. While the mechanical properties of the composites sensitively react to the volume fraction of nanocrystalline phase, the effect of mechanical properties upon heat treatment temperatures (and heating rate) has rarely focused in the previous studies.

In this study, we have carefully selected a BMG with a composition of $Ti_{55}Zr_{18}Ni_6Cu_7Be_{14}$ (at.%) that shows $\alpha$-Ti as a primary phase after partial devitrification process. Following investigation of continuous differential scanning calorimetry (DSC) trace with different heating rates and crystallization onset temperatures of the BMG, we were able to obtain an optimized $\alpha$-Ti (hexagonal close packed structure) volume fraction. Also, the mechanical behaviors of various $\alpha$-Ti volume fraction at various heat treatment temperatures have been investigated in order to provide a guideline for optimized crystallization volume fractions and the temperature effects.

Thirty grams of alloy ingots with a composition of $Ti_{55}Zr_{18}Ni_6Cu_7Be_{14}$ (at.%) have been made by arc melting pure elements and Ni-Cu-Be alloys for Be additions. The ribbons were produced by melt spinning of the alloy in an Ar atmosphere with a surface wheel speed of 40 m/s. The extents of crystallization were monitored by DSC (Perkin DSC-7) and the crystallized phases were identified by X-ray Diffractometer (XRD) (Ricaku 98)). In order to monitor the effect of devitrification temperature of the amorphous alloy, three heating rates (5, 40 and 80 K/min) were selected. From DSC measurements, three temperatures (310, 320 and 330 °C) below crystallization onset temperature (Tx) were determined corresponding to the selected heating rates. The $Ti_{55}Zr_{18}Ni_6Cu_7Be_{14}$ alloys were isothermally annealed for various times from 1 to 60 min in DSC. The heat-treatment conditions are shown in Fig. 1. Following an identification of the extents of crystallization, compression tests have been carried out with a rod type 1 mm (in diameter) and 2.5 mm (in height) BMG produced by injection casting process. The compression tests were performed using an Instron–type multitester (Hounsfield H25KT) at room temperature with a strain rate of $1 \times 10^{-4}$ $sec^{-1}$. The fractured surface was examined by secondary electron microscope (SEM) (Hitachi S-2700)). The microstructures of the specimen were investigated by transmission electron microscope (TEM (JEOL2000E)) and high resolution transmission electron microscope (HREM (JEM4010)).

Fig. 2(a) shows the continuous DSC curve of the BMG. The DSC trace shows three exothermic peaks, among which the first peak was identified as the formation of $\alpha$-Ti phase (hexagonal close packed structure) formation after identification of XRD of the heat-treated specimen at 425 °C (Fig. 2b). Here we focus on the first peak that was identified as $\alpha$-Ti phase upon XRD. From DSC measurements, the enthalpy of $\alpha$-Ti phase was estimated about 60% of the total crystallization heat. Therefore, the $\alpha$-Ti volume percent (vol.%) was estimated from the first peak ($X_{Ti}= 0.6$ $(\Delta H_{\alpha-Ti}$-$\Delta H_x)/\Delta H_{\alpha-Ti}$) following devitrification process. The estimated crystallization volume fraction is shown in

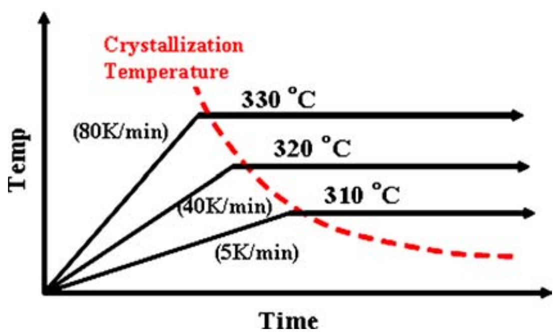


*Figure 1* Schematics of heat treatment cycles.

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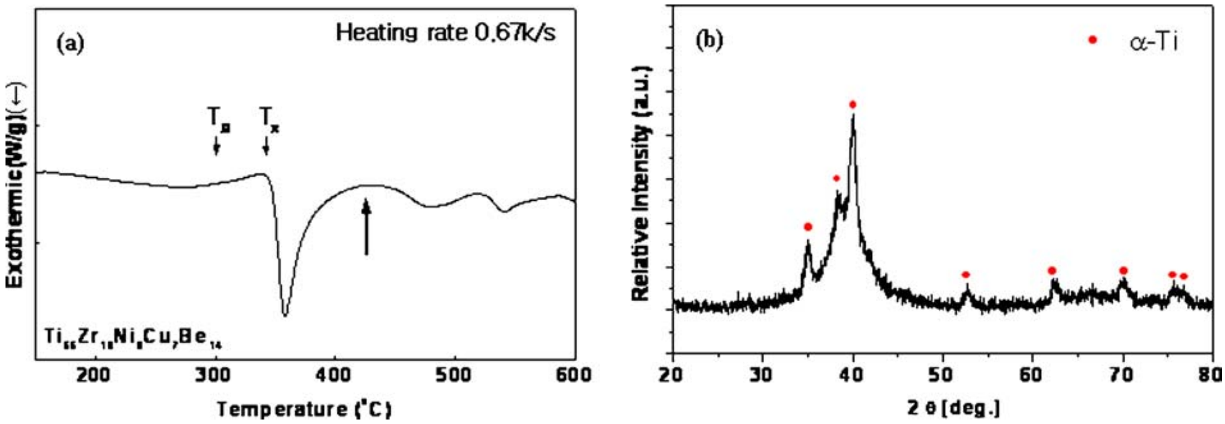


*Figure 2* XRD and DSC results showing primary crystallization of (α-Ti phase in amorphous $Ti_{55}Zr_{18}Ni_6Cu_7Be_{14}$ alloy.

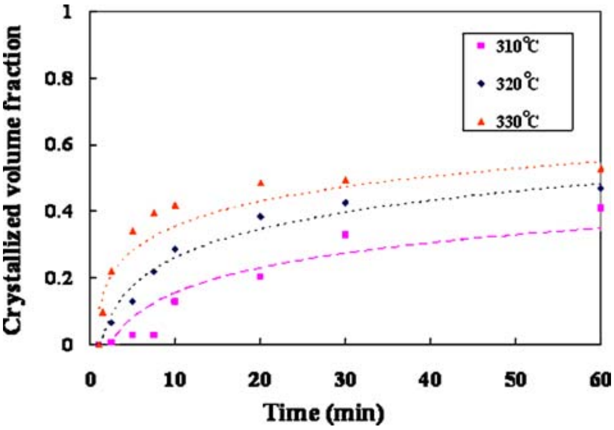


*Figure 3* The crystallization volume fractions upon isothermal heating at selected temperatures.

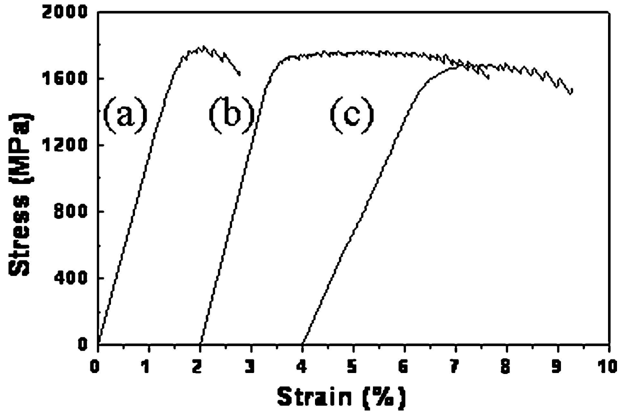


*Figure 4* Compression test results of BMGs (a) annealed at 330 °C for 2.5 min (22 volume percent of α-Ti), (b) at 330 °C for 1.5 min (10 volume percent of α-Ti), and (c) as-cast BMG.

Fig. 3. It is clear that the fraction of α-Ti drastically increased upon increasing the isothermal heating time, and the heat-treatment temperature appeared very sensitive to the precipitation of α-Ti. For example, compared with the specimens annealed for 20 min, the volume fraction of α-Ti significantly increased from about 20% (310 °C) to 40% (330 °C).

Fig. 4 shows the mechanical properties of (a) 10 vol.% and (b) 22 vol.% of α-Ti annealed at 330 °C and (c) as-cast. The ultimate compressive strength (UCS) was obtained as 1670, 1740 and 1780 MPa of the as-cast, 10% and 22 vol.% of α-Ti, respectively. Upon an increase of α-Ti vol.% up to 22%, the strength increased from 1670 to 1780 MPa. It is noted that when the BMG was partially crystallized, the elastic modulus is increased (the elastic range is decreased), which is a typical observation for partially devitrified BMG alloys [5]. At the same time, the plastic strain exhibited as 2.5, 1.5 and 4% for as-cast BMG, 10 vol.% and 22 vol.% of α-Ti, respectively. Since the specimen annealed at 330 °C for 1.5 min showed a strength and ductility increase, further structural identification has been performed. Fig. 5 shows HREM image of the BMG annealed at 330 °C for 1.5 min (10 vol.% of α-Ti). The size of the α-Ti about 3 nm was observed through the amorphous matrix.

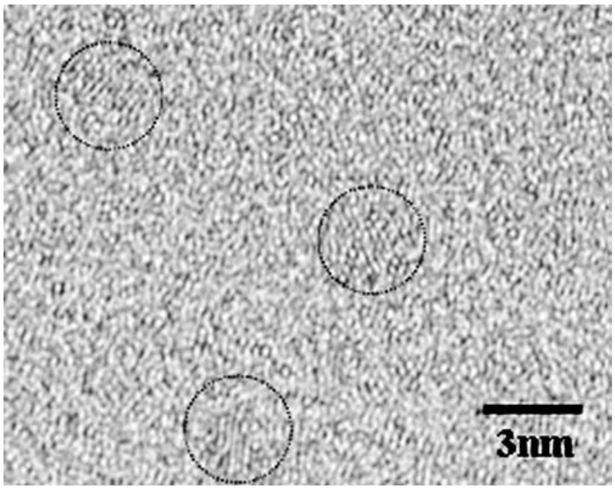


*Figure 5* HREM of the $Ti_{55}Zr_{18}Ni_6Cu_7Be_{14}$ alloy annealed at 330 °C for 1.5 min (10 volume percent of α-Ti).

Fig. 6 shows the fractured surface of the specimen annealed at 330 °C for 1.5 min. The fractured surface showed a typical vein-like pattern of BMGs. Also, it clearly indicates that shear bands were developed along the specimen surface. The development of large density of shear bands has been an indication of large ductility for BMG, which prevents the catastrophic fracture of BMG [8].

The increase of strength and ductility at a specific volume fraction of ductile primary phase has been reported in previous studies [6, 7]. When icosahedral phase was selected as a primary phase, the stable interface between amorphous matrix and the icosahedral

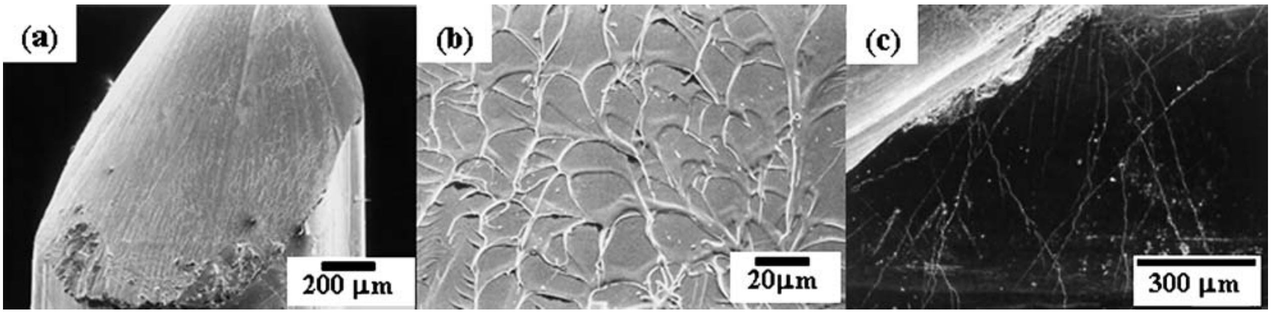


*Figure 6* SEM of (a) the sample shape, (b) fractured surface and (c) surface morphology after compression tests.

phase has appeared to be the main reason for strength and ductility increase at a 7 vol.% of icosahedral phase [7]. In a similar manner, the increase of toughness in Zr-Ti-Ni-Cu-Al system was considered as a multiple shear band formation along the devitrified phase at the 16 vol.% of primary phase [6]. For the present results, when a partial devitrification has been made, both the strength and ductility increased at 17 vol.% $\alpha$-Ti, which can be characterized as the optimum volume percent of $Ti_{55}Zr_{18}Ni_6Cu_7Be_{14}$. While the large increase of the toughness at a specific volume percent is not clear at present stage, it is probable that the increase of toughness appears due to the homogeneous distribution of nanocrystals and thus development of large density of shear band formation along the ductile crystalline phase, providing more homogeneous deformation and thus showing a larger macroscopic deformation (Fig. 7), compared to the as-cast specimen [8].

In summary, the effect of various volume fraction of nano-size $\alpha$-Ti embedded $Ti_{55}Zr_{18}Ni_6Cu_7Be_{14}$ BMG on mechanical property has been examined. The volume fraction of the primary $\alpha$-Ti phase was controlled via annealing temperatures and times. When the $\alpha$-Ti volume percent (about 3 nm in diameter) reached at 17% annealed at 330 °C for 1.5 min, the ductility is increased as a factor of 2 times compared with the as-cast BMG, and a large number of shear bands at the surface of the specimen were observed. The compressive strength exhibited the largest value when the BMG annealed at 330 °C for 2.5 min. It appears that the increase of the strength is mainly related to the recovery of amorphous matrix during annealing process.

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## References

1. W. L. JOHNSON, *MRS Bull.* **24** (1999) 42.
2. A. INOUE, *Acta Mater.* **48** (2000) 279.
3. W. B. KIM, B. J. YE and S. YI, *Metals Mater. Int.* 10 (2004) 1.
4. F. SZUECS, C. P. KIM and W. L. JOHNSON, *Acta Mater.* **49** (2001) 1507.
5. C. FAN, C. LI and A. INOUE, *Phys. Rev.* B **61** (2000) R3761.
6. G. HE, J. ECKERT, W. LÖSER and M. HAJIWARA, *Acta Mater.* **52** (2004) 3035.
7. Y. C. KIM, J. H. NA, J. M. PARK, D. H. KIM. J. K. LEE and W. T. KIM, *Appl. Phys. Let.* **83** (2003) 3093.
8. H. KATO, T. HIRANO, A. MATSUO, Y. KAWAMURA and A. INOUE, *Scripta Mater.* **43** (2000) 503.

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