

## Research Article

# A Centimeter-Sized Quaternary Ti-Zr-Be-Ag Bulk Metallic Glass

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A novel centimeter-sized Ti-based bulk metallic glass (BMG) was developed by the addition of Ag in the ternary  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  glassy alloy. By replacing Be with Ag, the glass forming ability (GFA), the yield strength, and the supercooled liquid temperature of the quaternary  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) glassy alloys have been obviously enhanced. Among the developed Ti-Zr-Be-Ag alloy systems, the  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$  alloy possesses the largest critical diameter ( $D_{\text{max}}$ ) of 10 mm, while the yield strength is also enhanced to 1961 MPa, which is much larger than that of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  (1755 MPa) alloy. The experimental results show that Ag is an effective element for improving the GFA and the yield strength of Ti-Zr-Be glassy alloy.

## 1. Introduction

Ti-based BMGs have been under intense investigation for many years, owing to their excellent properties, such as low density, high strength, high specific strength, low elastic modulus, and strong corrosion resistance [1–4]. Moreover, the low cost makes the Ti-based BMGs a profound application prospect. Up to date, a number of Ti-based BMGs have been synthesized by the copper mold casting method [5–7]. However, compared with other alloy systems, the GFA of most Ti-based BMGs is relatively low [8, 9]. Therefore, it should be of scientific and technological interest to develop Ti-based BMGs with large GFA, together with good mechanical properties. Furthermore, introducing new elements, or so-called “alloying,” is proved to be an effective method to improve the GFA of alloys [8, 9], which makes the developing of Ti-based BMGs with better GFA and less components more challenging.

It is known that  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  ternary BMG possesses a critical size of 5 mm which is larger than other Ti-Zr-Be ternary alloys [6, 10]. In the previous work, it shows that its GFA and mechanical properties could be improved through alloying with suitable elements [11, 12]. In this paper, Ag element has been selected as an addition element in the Ti-Zr-Be alloy system. By replacing Be with Ag, a series of BMGs with the composition of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$ ), which have improved GFA and mechanical properties, have been obtained.

## 2. Experimental Procedure

The master alloy ingots with nominal compositions of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) were prepared by arc-melting the mixtures of high-purity Ti, Zr, Be, and Ag metals in a Ti-gettered high-purity Ar atmosphere. The purity of Be and Ag metals is over 99.99% in weight, while that of Ti and Zr metals is 99.4% and 99.7% in weight, respectively. Each ingot was flipped and remelted four times to ensure the homogeneity. Cylindrical rods with different diameters were prepared by copper mold casting method.

The structure of the as-prepared samples was examined by X-ray diffraction (XRD) using  $\text{Cu K}\alpha$  radiation. The thermal stability of the glassy samples was evaluated by differential scanning calorimeter (DSC) at a heating rate of 20 K/min. Compression tests were carried out on a WDW-100 testing machine under a strain rate of  $4.2 \times 10^{-4} \text{ s}^{-1}$ . The test samples were cut out from the as-cast  $\Phi 2$  mm rods with gage aspect ratio of 2:1. For the compression tests, at least 3 samples of each glassy alloy were tested. The density  $\rho$  of each glassy alloy was measured by Archimedes' principle in the deionized water.

## 3. Results

Figure 1 presents X-ray diffraction spectra of the as-cast  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  BMG samples ( $x = 2, 4, 6, 8$  at.%) with the critical diameters. The typical broad halo patterns for

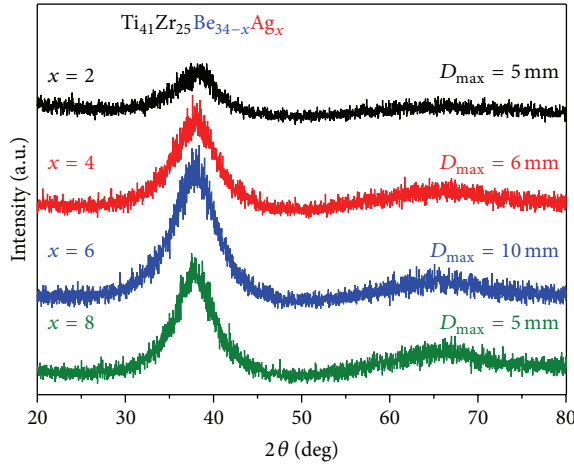


FIGURE 1: XRD patterns for the  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) glassy alloy system with their critical diameters.

the amorphous phases were observed in each XRD spectrum, and no sharp diffraction peaks corresponding to the crystalline phases could be observed. Figure 1 indicates that, with the proper addition of Ag, the GFA of the  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  alloy has been obviously improved. Meanwhile, the optimized addition content of Ag is about 6 at.%, since its critical diameter for forming fully amorphous structure is 10 mm. As the content of Ag increased to 8 at.%, the critical diameter of the  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{26}\text{Ag}_8$  alloy returns to 5 mm, which is the same as that of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  alloy [6]. The experimental results indicate that Ag is an effective alloying element for improving the GFA of Ti-Zr-Be alloys. In present work, a new centimeter scale quaternary BMG with the nominal composition  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$  has been developed. According to some reported results [13, 14], this is the second quaternary centimeter-diameter Ti-based BMG.

Figure 2 shows the DSC curves of the sample cut out from the as-cast fully glassy  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) rods with a diameter of 2 mm. Thermodynamic parameters were measured from the DSC scans, while the glass transition temperature  $T_g$ , initial crystallization temperature  $T_x$ , and liquidus temperature  $T_l$  were marked with arrows in Figure 2. In addition, for evaluating the GFA of the  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  alloys, the supercooled liquid region  $\Delta T_x$  (defined as  $T_x - T_g$ ),  $\gamma$  parameter (defined as  $T_x/(T_g + T_l)$ ), and reduced glass transition temperature  $T_{rg}$  (defined as  $T_g/T_l$ ) [15] were calculated as listed in Table 1.

From Figure 2, it can be found that, with the addition of Ag,  $T_g$  decreases from 607 K for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  [6] alloy to 589 K for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{30}\text{Ag}_2$  and  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{30}\text{Ag}_4$  alloy and then slightly increases to 597 K for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$  alloy and 593 K for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{26}\text{Ag}_8$  alloy, respectively.  $T_x$  increases from 656 K for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  [6] alloy to 670 K for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$  alloy and then decreases to 654 K for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{26}\text{Ag}_8$  alloy. It should be noted that, with Ag addition, the value of  $\Delta T_x$  has been obviously enlarged; especially,  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{30}\text{Ag}_4$  glass alloy has the largest supercooled liquid region of 81 K in the Ti-Zr-Be-Ag alloy system.  $\Delta T_x$

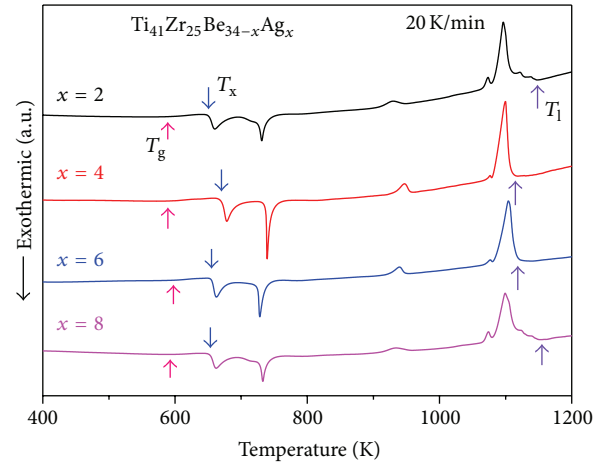


FIGURE 2: DSC curves of the  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) glassy alloys.

is considered as a measure to evaluate the thermal stability related to supercooled liquid stability against crystallization [16]; thus Ag addition can effectively improve the thermal stability of the Ti-Zr-Be-Ag glassy alloy. Moreover, the variation tendency of  $T_{rg}$  and  $\gamma$  with the Ag content in the alloy is roughly the same. The value of  $T_{rg}$  for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$  alloy is the largest among all the Ti-Zr-Be-Ag alloys, and  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{30}\text{Ag}_4$  alloy possesses the largest  $\gamma$  value and the lowest  $T_l$  value. It is suggested that these two alloys may possess relatively good GFA [16], which is in accordance with the experimental results.

Figure 3 shows the compressive stress-strain curves of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) at room temperature. The yield strength  $\sigma_{0.2}$ , the maximum compression stress  $\sigma_{max}$ , and the plastic strain  $\epsilon_p$  of the  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  BMGs were listed in Table 2. In the present work, the addition of Ag enhances the density of Ti-Zr-Be alloy, while the value of the specific strength (defined as yield strength/density) of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 5, 6, 8$ ) BMGs does not change a lot. According to the reported results, the Ag-free alloy exhibits a yield strength  $\sigma_{0.2}$  of 1755 MPa, a maximum compressive strength  $\sigma_{max}$  of 1914 MPa, and a plastic strain  $\epsilon_p$  of 2.9% [6]. As shown in Figure 3, Ag addition can greatly increase the yield strength of the BMGs.

For the glassy alloy with optimum Ag content of 6 at.%, the yield strength  $\sigma_{0.2}$  is 1964 MPa, while with 8 at.% of Ag, the maximum compression stress  $\sigma_{max}$  and plastic strain  $\epsilon_p$  are 2054 MPa and 4.8%, respectively. The present results indicate that Ag addition could effectively improve the mechanical properties of Ti-Zr-Be glassy alloys.

It shows that, among the quaternary Ti-Zr-Be-Ag alloy system,  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$  glassy alloy possesses not only the largest GFA, but also high strength and good compressive plastic strain.

#### 4. Discussion

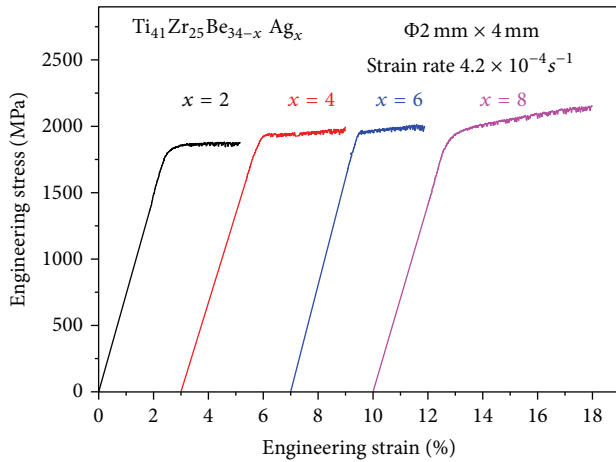
It is known that the mixing enthalpies  $\Delta H_{mix}$  between Ti-Ag, Ti-Zr, Zr-Ag, Ti-Be, Ag-Be, and Zr-Be are  $-2$  kJ/mol,

TABLE 1: Thermal parameters of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) BMGs. The error of the temperature values is  $\pm 1$  K.

Composition (at.%)	$T_g$ (K)	$T_x$ (K)	$\Delta T_x$ (K)	$T_l$ (K)	$T_{rg} = T_g / T_l$	$\gamma$	$D_{\max}$ (mm)
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$ [6]	607	656	49	1123	0.5405	0.3792	$\Phi 5$
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{32}\text{Ag}_2$	589	651	62	1148	0.5131	0.3748	$\Phi 5$
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{30}\text{Ag}_4$	589	670	81	1107	0.5321	0.3950	$\Phi 6$
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$	597	655	58	1118	0.5340	0.3819	$\Phi 10$
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{26}\text{Ag}_8$	593	654	61	1153	0.5143	0.3746	$\Phi 5$

TABLE 2: Densities and mechanical properties of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) BMGs.

Composition (at.%)	Density ( $\text{g}/\text{cm}^3$ )	$\sigma_{0.2}$ (MPa)	$\sigma_{\max}$ (MPa)	$\varepsilon_p$ (%)	Specific strength (Nm/Kg)
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$ [6]	4.76	1755	1914	$2.9 \pm 0.1$	$3.69 \times 10^5$
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{32}\text{Ag}_2$	5.01	1808	1882	$2.4 \pm 0.1$	$3.61 \times 10^5$
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{30}\text{Ag}_4$	5.13	1931	1995	$2.9 \pm 0.1$	$3.76 \times 10^5$
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$	5.27	1961	2013	$2.3 \pm 0.1$	$3.73 \times 10^5$
$\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{26}\text{Ag}_8$	5.42	1946	2054	$4.8 \pm 0.1$	$3.59 \times 10^5$

FIGURE 3: Compressive stress-strain curves at room temperature for  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) glassy samples.

0 kJ/mol, -20 kJ/mol, -30 kJ/mol, 2 kJ/mol, and -43 kJ/mol, respectively [17]. Thus, in the Ti-Zr-Be-Ag alloy system, the strong chemical short-range order clusters or medium-range order clusters would be expected [18], which may restrain the diffusion of the atoms, and could suppress crystallization during the solidification. Meanwhile, the addition of Ag increases the number of the components in the alloy, which could generate more types of local ordering clusters and stabilize the liquid phase [18].

In addition, the electronegativity difference  $\Delta x$  and the atomic size difference parameter  $\delta$ , the two parameters that related to the GFA of the glassy alloy, have been applied to evaluate the effect of Ag addition on the GFA of Ti-Zr-Be glassy alloy [19].  $\delta$  is defined as  $\delta = \sqrt{\sum_{i=1}^n c_i(1 - r_i/\bar{r})}$ ,  $\Delta x$  is defined as  $\Delta x = \sqrt{\sum_{i=1}^n c_i \times (x_i - \bar{x})^2}$ , where  $\bar{r} = \sum_{i=1}^N c_i r_i$ ,  $\bar{x} = \sum_{i=1}^N c_i x_i$ ,  $c_i$  is the atomic fraction,  $r_i$  and  $x_i$  are atomic radius and electronegativity of  $i$ th element, and  $N$  is the number

of alloying elements [20, 21].  $\Delta x$  and  $\delta$  of Ti-Zr-Be-Ag glassy alloys were calculated and summarized in Figure 4.

According to the Hume-Rothery rules and Inoue's three empirical rules [20, 21], the alloys with larger value of  $\delta$  and  $\Delta x$  could form amorphous phase readily. As shown in Figure 4, because Ag possesses larger Pauling electronegativity (1.91) than Ti (1.54), Zr (1.33), and Be (1.57), the addition of Ag would increase the value of  $\Delta x$  in the Ti-Zr-Be alloys, which effectively enhance the GFA. However, the value of  $\delta$  would decrease as the content of Ag increase, which is not beneficial to improve the GFA [22]. When the content of Ag is relatively low, the beneficial effect of  $\Delta x$  dominates the alloying effect on GFA. So the critical size increases with Ag content and reached the maximum value of 10 mm at 6 at.%. When increasing Ag content again, the effect from  $\delta$  would significantly reduce the beneficial effect from  $\Delta x$ , resulting in the decrease of GFA. Similar effects have also been observed in Ti-Zr-Be-Al [8] and Ti-Zr-Be-Fe [6] quaternary BMGs, too. Due to the efforts of these two factors, there would exist an optimized Ag content in the Ti-Zr-Be alloy system, which is 6 at.%.

## 5. Conclusion

In summary, Ag addition could significantly improve the GFA, thermal stability, and mechanical properties of the Ti-Zr-Be glassy alloys. By replacing Be with Ag, it has been found that the developed  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Ag}_6$  alloy possesses much better GFA; the critical diameter of the quaternary BMG has been increased to 10 mm, while that of ternary  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  [6] alloy is only 5 mm. This alloy also exhibits a yield strength of 1961 MPa, 10% higher than that of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  BMG [6]. Furthermore, The Ti-Zr-Be-Ag glassy alloys have a wider supercooled liquid temperature range than that of the  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34}$  glassy alloys, indicating a higher thermal stability of the glassy alloys. The enhanced GFA is supposed to be related to the improved atomic packing efficiency and high electronegativity difference, which can retard the atomic diffusion due to the addition of Ag.

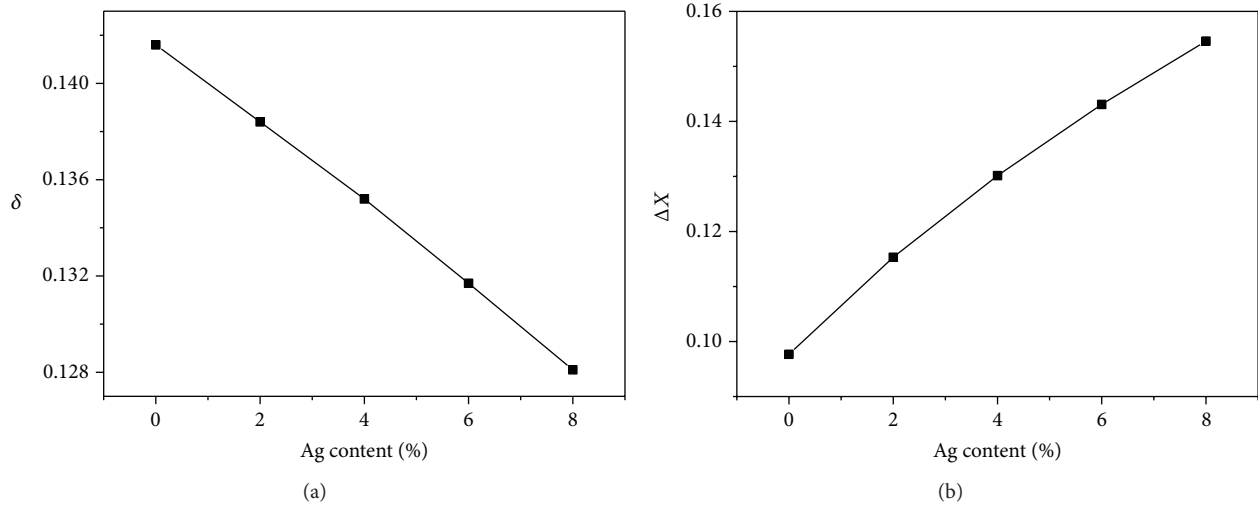


FIGURE 4: The atomic size parameter  $\delta$  (a) and the electronegativity difference  $\Delta x$  (b) of  $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{34-x}\text{Ag}_x$  ( $x = 2, 4, 6, 8$  at.%) glassy alloys.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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