Chapter 6

LIGHTWEIGHT TI-BASED BULK GLASSY ALLOYS EXCLUDING LATE TRANSITION METALS

Lightweight Ti-based bulk amorphous structural metals with more than double the specific strength of conventional titanium alloys have been discovered. Thermal, elastic, and mechanical properties of these metallic glasses were studied and are presented. These amorphous alloys exhibit good glass-forming ability, exceptional thermal stability, and high strength. The research results have important implications for designing and developing low-density bulk metallic glasses. The technological potential of this class of lightweight Ti-based glassy alloys as structural metals is very promising.

6.1. Introduction

Owing to their high glass-forming ability (GFA), good processing ability, and exceptional stability with respect to crystallization along with many promising properties such as high strength, elastic strain limit, wear resistance, fatigue resistance, and corrosion

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* Inspired by the light beers, we named this unique class of bulk metallic glasses the *Vit-Light* series.

resistance, bulk metallic glasses (BMGs) have been the focus of much study over the past 20 years [1, 2]. To date, families of binary and multi-component systems have been designed and characterized to be BMG formers, [3-15] among which the highly processable Zr-Ti-Cu-Ni-Be BMGs (Vitreloy series) have been used commercially for items such as sporting goods and electronic casings [3, 16].

Prior research results teach that Beryllium-bearing amorphous alloys (Vitreloy series) require the presence of at least one early transition metal (ETM) and at least one late transition metal (LTM) in order to form BMGs. It is believed that BMGs containing certain LTMs (e.g., Fe, Ni, Cu) have better glass forming-ability, higher strength and elastic modulus, and lower materials cost. However, because of the high density of LTMs, glassy alloys containing LTMs will have much higher densities than alloys excluding LTMs. Vitreloy alloys have typical densities of ~ 6 g/cc [17], and are therefore limited in applications requiring low density and high specific strength. The elimination of the LTMs would make this class of materials ideal for structural applications where specific strength and specific modulus are key figures of merit. We report in this chapter that Beryllium-bearing alloys excluding LTMs are excellent bulk-metallic-glass formers and have a 20% to 40% reduction of density compared to Vitreloy alloys, while still possessing high strength and high elastic modulus.

Conventional titanium alloys have been widely used in aerospace industries due to their resource availability, low density, and high specific strength. However no Ti-based BMGs with density comparable to that of pure titanium or Ti6Al4V alloy are yet known, although researchers have developed several Ti-based glass-forming systems [13, 18-20]. Recently, Ti-rich BMG forming alloys were reported in the Ti-Zr-Ni-Cu-Be system (Ref. 13). Fully glassy cast rods up to 14 mm diameter could be successfully produced. For a typical alloy, $Ti_{40}Zr_{25}Ni_{3}Cu_{12}Be_{20}$, a density of ~ 5.4 g/cc was obtained. In this chapter, we report a class of Ti-based bulk amorphous alloys with high GFA, exceptional thermal stability, low density of ~ 4.59 g/cc (comparable to that of pure titanium), and very high specific strength.

In early work, Tanner et al. [21-24] reported that amorphous ribbons (typically 30 μm thick) in the Ti-Be, Zr-Be, and Ti-Zr-Be systems could be prepared by splat quenching or melt spinning techniques at high cooling rates of ~ 10^6 K/s. However, no bulk glass formers have been identified in the ternary Ti-Zr-Be system. For the first time, we report ternary Ti-Zr-Be alloys excluding LTMs that form bulk glasses on cooling from the melt at rates less than 10^3 K/s.

6.2. Experimental

For a complete description of sample preparation and characterization details, please refer to Chapter 5.2. We evaluated the elastic properties of the samples using ultrasonic measurements along with density measurements. The pulse-echo overlap technique was used to measure the shear and longitudinal wave speeds at room temperature for each of the samples. 25 MHz piezoelectric transducers and a computer-controlled pulser/receiver were used to produce and measure the acoustic signal. The signal was measured using a Tektronix TDS 1012 oscilloscope. Sample density was measured by the Archimedean technique according to the American Society of Testing Materials standard C 693-93. Cylindrical rods (3 mm in diameter and 6 mm in height) were used to measure mechanical properties of these Ti-based bulk glassy alloys on an Instron testing machine at a strain rate of 1×10^{-4} s^{-1}. Before these mechanical tests, both ends of each specimen were examined with X-ray to confirm that the rods were fully amorphous.

6.3. Results and Discussions

It was recently found that the shear modulus, G, and Poisson's ratio, ν, of Cu(Ni)-Zr(Ti)-Be alloys are very sensitive to composition changes, where G decreases linearly with increasing total Zr+Ti concentration [25]. We initially studied the glass formation in the Ti-Zr-Be ternary system by fixing the Be content to be 35%. More extensive regions in the Ti-Zr-Be phase diagram were then subsequently examined. Surprisingly, the best glass forming region is located along the pseudo-binary line, $Ti_xZr_{(65-x)}Be_{35}$. Figure 6.1 shows pictures of three as-cast rods, $Ti_{45}Zr_{20}Be_{35}$ (S1), $Ti_{45}Zr_{20}Be_{30}Cr_5$ (S2), and $Ti_{40}Zr_{25}Be_{30}Cr_5$ (S3), having diameters of 6, 7, and 8 mm, respectively. Their as-cast surfaces appear smooth and mirror like. Cross-sectioned samples were used for X-ray studies. The X-ray diffraction patterns of S1, S2, and S3 are presented in Figure 6.2. S1 and S2 have X-ray patterns indicative of fully amorphous samples, while S3 has a small Bragg peak on an otherwise amorphous background, indicating that the critical casting diameter has been reached. Glassy rods up to 8 mm diameter are formed with the addition of 5% Cr to the ternary Ti-Zr-Be alloys.

Thermal behavior of these glassy alloys was measured using DSC at a constant heating rate of 0.33 K/s. The characteristic thermal parameters, including the variations of supercooled liquid region, ΔT, ($\Delta T = T_x - T_g$, where T_x is the onset temperature of the first crystallization event and T_g is the glass transition temperature), and the reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_l$, where T_l is the liquidus temperature) are evaluated and listed in Table 6.1. The DSC scans are shown in Figure 6.3. Upon heating, these amorphous alloys exhibit a clear endothermic glass transition followed by a series of exothermic events characteristic of crystallization. Apparently, Cr tends to delay the exothermic peaks, indicating a suppression of the kinetics of crystal nucleation and growth. In the Ti-Zr-Be ternary alloy system, the critical casting diameter of $Ti_{45}Zr_{20}Be_{35}$ and $Ti_{40}Zr_{25}Be_{35}$ is 6 mm (See Table 6.1). The addition of Cr increases the crystallization temperature, stabilizes the supercooled liquid, and consequently benefits the GFA. It is known already that the GFA of the present lightweight Ti-Zr-Be glassy alloys is dramatically improved with Ni and Cu additions as indicated in Ref. 13.

Table 6.1 also presents the density, critical casting diameter, thermal and elastic properties of representative glassy alloys in Zr-Cu-Be ternary systems and other Vitreloy type BMGs. The value of T_{rg} can be taken relatively as an indication of GFA. The newly developed low-density Ti-Zr-Be glassy alloys show very good thermal stability against crystallization. The best glass former, $Ti_{40}Zr_{25}Be_{30}Cr_5$, possesses a large supercooled liquid region of 93 K, among the highest for the known Ti-based BMGs. It is noted that the glass transition temperatures of Ti-Zr-Be amorphous alloys fall in the same range as those of Zr-Cu-Be glasses with similar total Zr+Ti concentration. For the elastic properties, we noticed that high-Ti-content alloys generally have high G values. Another interesting observation is that Zr-rich Zr-Ti-based Be-bearing glassy alloys exhibit a low G and a rather high ν.

We also obtained the typical compressive stress-strain curves for the lightest $Ti_{45}Zr_{20}Be_{35}$ and the best glass former $Ti_{40}Zr_{25}Be_{30}Cr_5$ obtained using 3 mm amorphous rods. Compressive tests indicate that $Ti_{45}Zr_{20}Be_{35}$ has fracture strength of ~ 1860 MPa, with total strain of ~ 2.2 % (mainly elastic). However, $Ti_{40}Zr_{25}Be_{30}Cr_5$ yields at ~ 1720 MPa, with an elastic strain limit of ~ 1.9 %, and finally fractures at a strength of ~ 1900 MPa, with a plastic strain of ~ 3.5 %.

Table 6.1. Density, thermal, and elastic properties of representative lightweight Ti-Zr-Be and Vitreloy-type glassy alloys.

Materials	ρ (g/cc)	d (mm)	T_g (K)	T_x (K)	T_l (K)	ΔT (K)	T_g/T_l	G (GPa)	B (GPa)	Y (GPa)	ν
$Ti_{45}Zr_{20}Be_{35}$	4.59	6	597	654	1123	57	0.531	35.7	111.4	96.8	0.36
$Ti_{40}Zr_{25}Be_{35}$	4.69	6	598	675	1125	76	0.532	37.2	102.7	99.6	0.34
$Ti_{45}Zr_{20}Be_{30}Cr_5$	4.76	7	602	678	1135	77	0.530	39.2	114.5	105.6	0.35
$Ti_{40}Zr_{25}Be_{30}Cr_5$	4.89	8	599	692	1101	93	0.544	35.2	103.1	94.8	0.35
$Ti_{30}Zr_{35}Be_{35}$	4.91	6	595	713	1201	118	0.495	36.4	111.5	98.5	0.35
$Zr_{65}Cu_{12.5}Be_{22.5}$	6.12	4	585	684	1098	99	0.533	27.5	111.9	76.3	0.39
$Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$	6.07	> 20	623	712	993	89	0.627	37.4	115.9	101.3	0.35
$Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$	6.00	> 20	625	738	1185	113	0.527	35.0	110.3	95.0	0.36

The current study has resulted in a new class of bulk amorphous alloys with high GFA, good processability, exceptional thermal stability, and mass densities significantly lower than those of the Vitreloy alloys and comparable to those of pure titanium and Ti6Al4V alloys (see Table I). $Ti_{45}Zr_{20}Be_{35}$ and $Ti_{40}Zr_{25}Be_{30}Cr_{5}$ show low densities of ~ 4.59 and ~ 4.76 g/cc respectively. A 20% to 40% advantage over Vitreloy alloys in specific strength is obtained. Furthermore, these lightweight Ti-based bulk amorphous alloys have very high specific strengths that considerably exceed those of conventional low-density Titanium alloys. For example, commercial Ti6Al4V exhibits a specific strength of 175 J/g, while bulk amorphous $Ti_{45}Zr_{20}Be_{35}$ is calculated to have a specific strength of 405 J/g. For comparison, the specific strength of Vitreloy 1 ($Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$) is about 305 J/g. Thus, this class of amorphous alloys is ideal for structural applications where specific strength and specific modulus are key figures of merit.

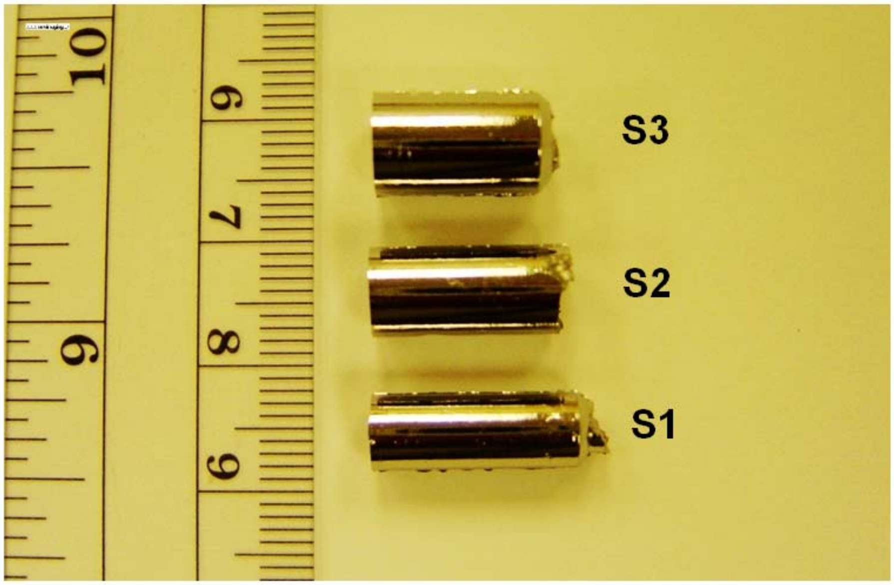

Figure 6.1. Pictures of amorphous 6 mm diameter rod of $Ti_{45}Zr_{20}Be_{35}$ (S1), 7 mm diameter rod of $Ti_{45}Zr_{20}Be_{30}Cr_5$ (S2), and 8 mm diameter rod of $Ti_{40}Zr_{25}Be_{30}Cr_5$ (S3) prepared by the copper mold casting method.

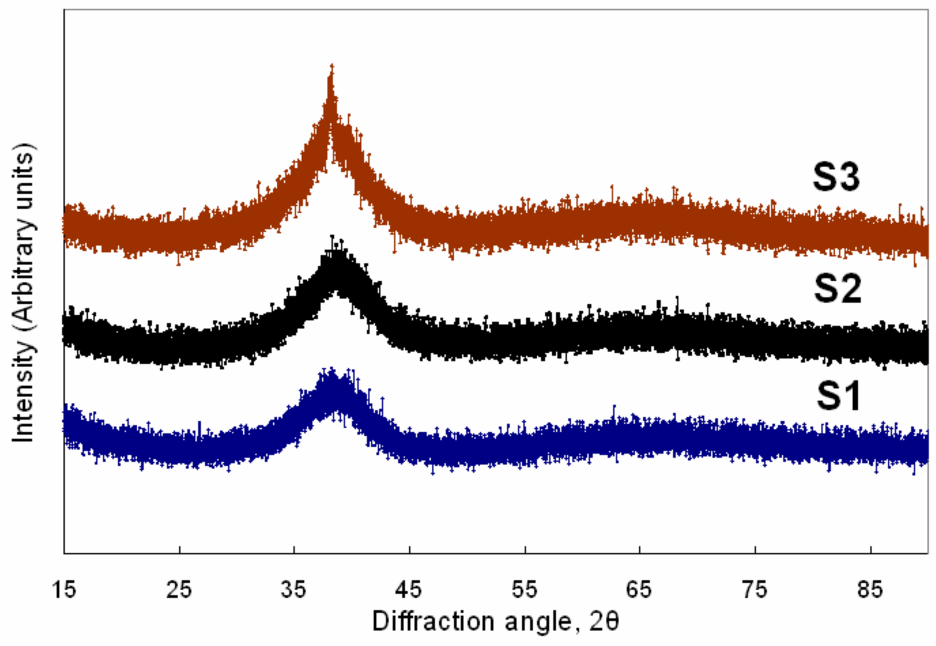

Figure 6.2. The x-ray diffraction patterns verify the amorphous nature of the corresponding samples: amorphous 6 mm diameter rod of $Ti_{45}Zr_{20}Be_{35}$ (S1), 7 mm diameter rod of $Ti_{45}Zr_{20}Be_{30}Cr_5$ (S2), and 8 mm diameter rod of $Ti_{40}Zr_{25}Be_{30}Cr_5$ (S3).

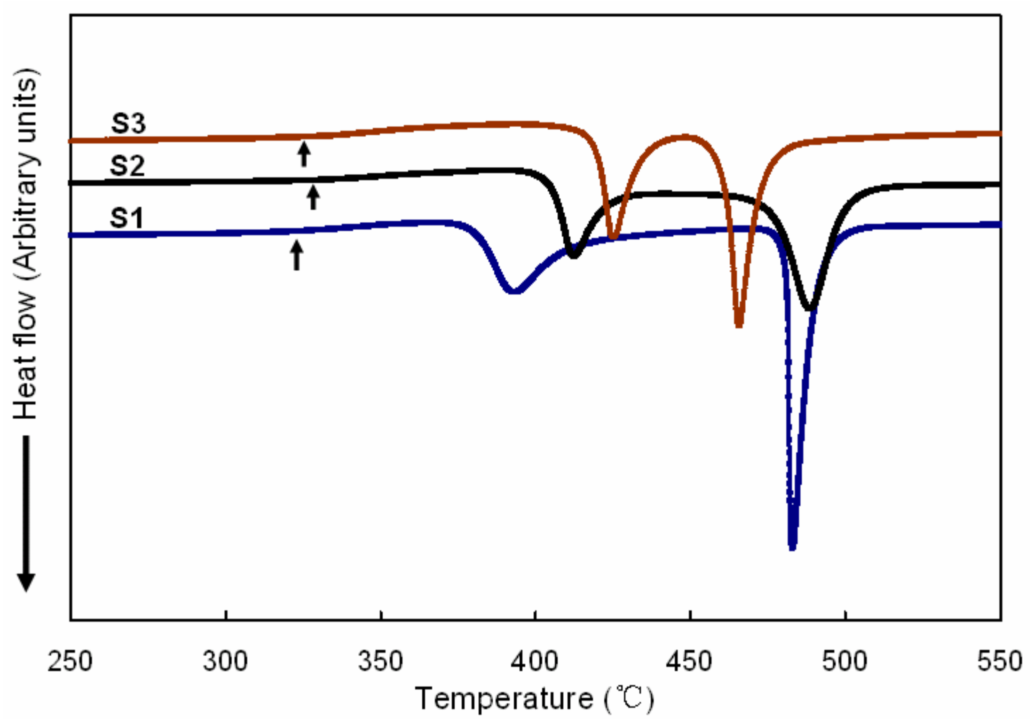

Figure 6.3. DSC scans of the amorphous $Ti_{45}Zr_{20}Be_{35}$ (S1), $Ti_{45}Zr_{20}Be_{30}Cr_5$ (S2), and $Ti_{40}Zr_{25}Be_{30}Cr_5$ (S3) alloys at a constant heating rate of 0.33 K/s. The marked arrows represent the glass transition temperatures.

6.4. Chapter Concluding Remarks

In summary, lightweight Ti-based bulk amorphous structural metals with mass density comparable to that of pure titanium have been discovered. These amorphous alloys exhibit high GFA, exceptional thermal stability, and very high specific strength. The technological potential of this class of glassy alloys is very promising.

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