Chapter 2 - Lightweight Ti-based Bulk Glassy Alloys Excluding Late Transition Metals

This chapter draws heavily on the article, "Lightweight Ti-based Bulk Glassy Alloys Excluding Late Transition Metals," published in Scripta Materialia [G. Duan, A. Wiest, M.L. Lind, A. Kahl, W.L. Johnson, Scripta Mater. 58 (2008) 465]. It discusses lightweight Ti based bulk amorphous metals with more than double the specific strength of conventional titanium alloys discovered in the course of alloy development in the ZrTiBe system. Thermal, elastic, and mechanical properties of these metallic glasses were studied and presented. These amorphous alloys exhibit good glass forming ability, exceptional thermal stability, and high strength. The research results have important implications on designing and developing bulk metallic glasses (BMG). The technological potential of this class of lightweight Ti based glassy alloys as structural metals is very promising.

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 resistance, BMG have garnered considerable attention in the past 20 years scientifically and technically [1-2]. To date, families of binary and multi-component systems have been designed and characterized to be BMG formers [3-15] among which highly processable ZrTiCuNiBe BMG (Vitreloy series) have been used commercially for items such as sporting goods and electronic casings [3, 16].

Prior research results teach that Be 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 BMG. It is believed that BMG containing certain LTM (e.g., Fe, Ni, Cu) have potential advantages including better glass forming ability, higher strength and elastic modulus, and lower materials cost. However, because of the high density of LTM, glassy alloys containing LTM will have higher densities than alloys excluding LTM. Vitreloy alloys have densities of about ~ 6 g/cc [17] and are therefore limited in their uses in structural applications requiring low density and high specific strength materials. The elimination of LTM would make this class of materials ideal for structural applications where specific strength and specific modulus are key figures of merit. We discovered that Be bearing alloys excluding LTM are excellent bulk metallic glass formers and have a 20% to 40% advantage over Vitreloy alloys in density while still possessing high strength and high elastic modulus.

Conventional titanium alloys have been widely used in the aerospace industry due to their resource availability, low density and high specific strength. However no Ti based BMG with density comparable to that of pure titanium or Ti-6Al-4V alloy have been discovered yet, although researchers have developed several Ti based glass forming systems [13, 18-20]. Recently BMG forming alloys in the form of glassy ingots were discovered in TiZrNiCuBe system [13]. Up to 14mm amorphous rods could be successfully produced. For a typical $Ti_{40}Zr_{25}Ni_3Cu_{12}Be_{20}$ alloy, 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, and low density (~ 4.59 g/cc) comparable to that of pure titanium, as well as very high specific strength.

Tanner reported that some TiBe, ZrBe and TiZrBe compositions could be made amorphous at very high cooling rates of ~ 10^6 K/s [21-24]. These cooling rates are achievable using splat quenching or melt spinning techniques, which limits the thickness of the alloys to 30 - 100μm. However, no bulk glass formers have been identified in the ternary TiZrBe system. This research discovered that TiZrBe compositions are not limited to 30 - 100μm thick foils, but many compositions can be cast into bulk samples of 1 - 6mm thickness. This discovery reveals alloys can be cooled amorphous 1000 times slower than reported by Tanner [21-24].

Mixtures of elements of purity ranging from 99.9% to 99.99% were alloyed in an arc melter with a water cooled copper plate under a Ti-gettered argon atmosphere. Each ingot was flipped over and remelted at least three times in order to obtain chemical homogeneity. After the alloys were prepared, the materials were cast into machined copper molds under high vacuum. These copper molds have internal cylindrical cavities of diameters ranging from 1 - 10mm. A Philips X'Pert Pro X-ray Diffractometer and a Netzsch 404C Pegasus Differential Scanning Calorimeter (DSC) with graphite crucibles performed at a constant heating rate 20 K/min were utilized to verify the amorphous natures and to examine the thermal behavior of these alloys. 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 3mm in diameter x 6mm in height were used to measure mechanical properties of the lightweight 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 diffraction to make sure that the rod was fully amorphous and that no crystallization occurred due to unexpected factors.

It was recently found that in the CuZrBe alloy system, the shear modulus, G, and Poisson's ratio, ν, are very sensitive to composition changes, where G decreases linearly with the increasing total Zr concentration [25]. Extensive regions in the TiZrBe phase diagram were systematically examined. The best glass forming region was found along the pseudo-binary line, $Ti_xZr_{(65-x)}Be_{35}$. Figure 2.1(a) 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 8mm, respectively. Their as-cast surfaces appear smooth and no apparent volume reductions can be recognized on their surfaces. The X-ray diffraction patterns of S1, S2, and S3 are presented in Figure 2.1(b). S1 and S2 have X-ray patterns indicative of fully amorphous samples and S3 has a very small Bragg peak on an otherwise amorphous background indicating that the critical casting diameter has been reached. Glassy rods up to 8mm diameter are formed by the addition of 5% Cr into the ternary TiZrBe alloys.

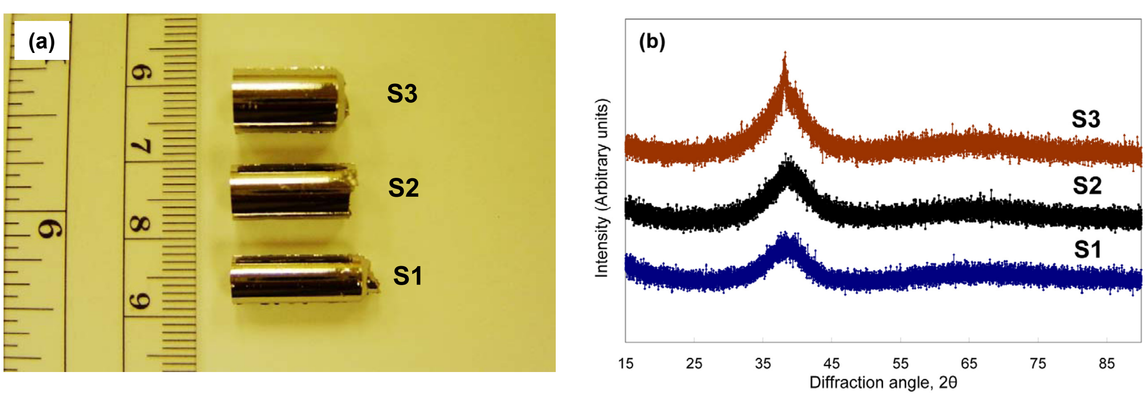

Figure 2.1: Pictures of amorphous 6mm diameter rod of $Ti_{45}Zr_{20}Be_{35}$ (S1), 7mm diameter rod of $Ti_{45}Zr_{20}Be_{30}Cr_5$ (S2) and 8mm diameter rod of $Ti_{40}Zr_{25}Be_{30}Cr_5$ (S3) prepared by the copper mold casting method are presented in (a). The X-ray diffraction patterns (b) verify the amorphous nature of the corresponding samples.

Thermal behavior of these glassy alloys was measured using DSC at a constant heating rate of 20 K/min. The characteristic thermal parameters including the variations of supercooled liquid region, ΔT, ($\Delta T = T_x - T_g$, in which T_x is the onset temperature of the first crystallization event and T_g is the glass transition temperature) and 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 2.1. The DSC scans are shown in Figure 2.2.

Table 2.1: Density, thermal and elastic properties of representative lightweight TiZrBe and Vitreloy type glassy alloys.

Materials	ρ [g/cm^3]	d [mm]	T_g [K]	T_x [K]	T_L [K]	ΔT [K]	T_g/T_L	G [Gpa]	B [Gpa]	Y [Gpa]	υ
$Ti_{45}Zr_{20}Be_{35}$	4.59	6	597	654	1123	57	0.53	35.7	111.4	96.8	0.36
$Ti_{40}Zr_{25}Be_{35}$	4.69	6	598	675	1125	76	0.53	37.2	102.7	99.6	0.34
$Ti_{45}Zr_{20}Be_{30}Cr_5$	5.76	7	602	678	1135	77	0.53	39.2	114.5	105.6	0.35
$Ti_{40}Zr_{25}Be_{30}Cr_5$	4.89	8	599	692	1101	93	0.54	35.2	103.1	94.8	0.35
$Zr_{65}Cu_{12.5}Be_{22.5}$	6.12	4	585	684	1098	99	0.53	27.5	111.9	76.3	0.39
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	6.07	>20	623	712	993	89	0.63	37.4	115.9	101.3	0.35
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	6.00	>20	625	738	1185	113	0.53	35.0	110.3	95.0	0.36

Upon heating, these amorphous alloys exhibit a clear endothermic glass transition followed by a series of exothermic events characteristic of crystallization. It appears that Cr delays the exothermic peaks, indicating a suppression of the kinetics of crystal nucleation and growth. In the TiZrBe ternary alloy system, the critical casting diameter of $Ti_{45}Zr_{20}Be_{35}$ and $Ti_{40}Zr_{25}Be_{35}$ is 6mm (see Table 2.1). The addition of Cr increases the crystallization temperature, stabilizes the supercooled liquid, thereby increasing the GFA. It is known that the GFA of the present lightweight TiZrBe glassy alloys would be dramatically improved with Ni and Cu additions as indicated in [13].

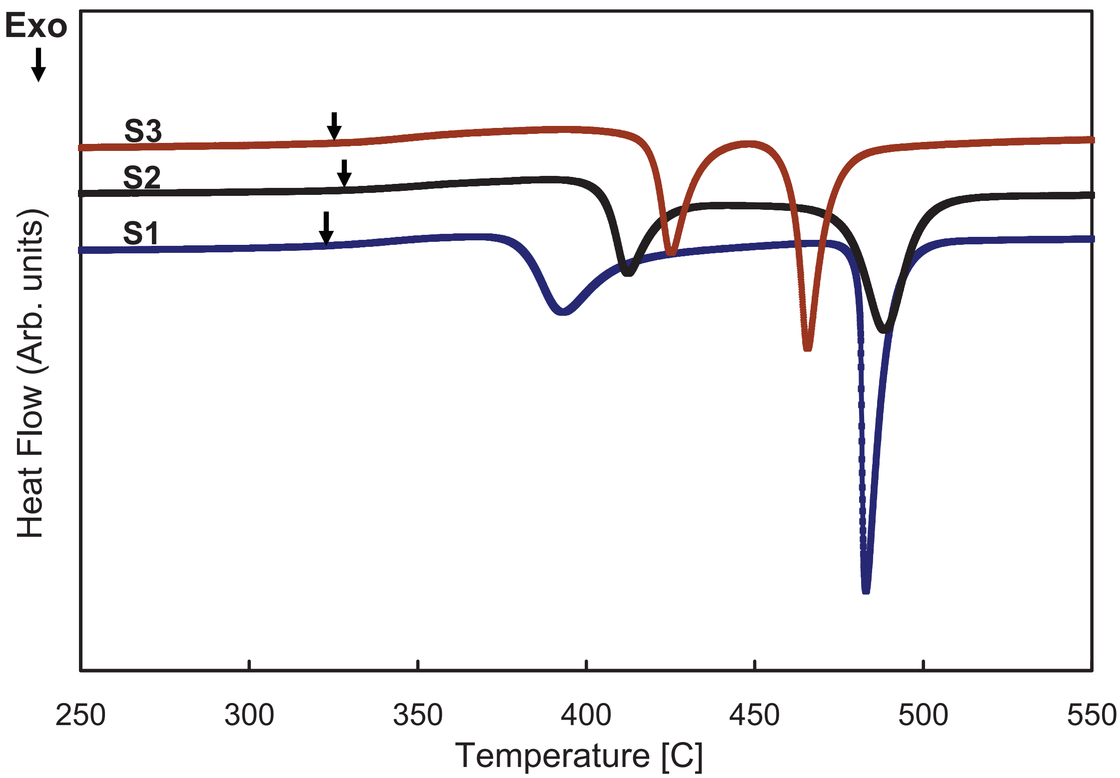

Figure 2.2: DSC scans of the amorphous $Ti_{45}Zr_{20}Be_{35}$ (S1), $Ti_{45}Zr_{20}Be_{30}Cr_5$ (S2), and $Ti_{40}Zr_{25}Be_{30}Cr_5$ (S3) alloys at a constant heating rate of 0.33 K/s. The marked arrows represent the glass transition temperatures.

Table 2.1 also presents the density, thermal and elastic properties of representative glassy alloys in ZrCuBe ternary systems and other Vitreloy type BMG. The value of T_{rg} gives a good first order approximation of GFA. The newly developed low density TiZrBe 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 in the known Ti based BMG. It is noted that the glass transition temperatures of TiZrBe amorphous alloys fall into the same range as those of ZrCuBe glasses with the same total Zr + Ti concentration. High Ti content alloys exhibited higher G values than are typical for Vitreloy type alloys. Another interesting observation is that ZrTi based Be bearing glassy alloys have to be Zr rich to exhibit a low G and a high ν.

Figure 2.3 presents typical compressive stress-strain curves for 3mm diameter amorphous rods of the lowest density alloy, $Ti_{45}Zr_{20}Be_{35}$, and the best glass former, $Ti_{40}Zr_{25}Be_{30}Cr_5$. Compression tests indicate that $Ti_{45}Zr_{20}Be_{35}$ shows fracture strength of ~ 1860 MPa, with total strain of ~ 2.2% (mainly elastic). $Ti_{40}Zr_{25}Be_{30}Cr_5$ yields at ~ 1720 MPa, with an elastic strain limit of ~ 1.9%, and ultimately fractures at a strength of ~ 1900 MPa, with a plastic strain of ~ 3.5%.

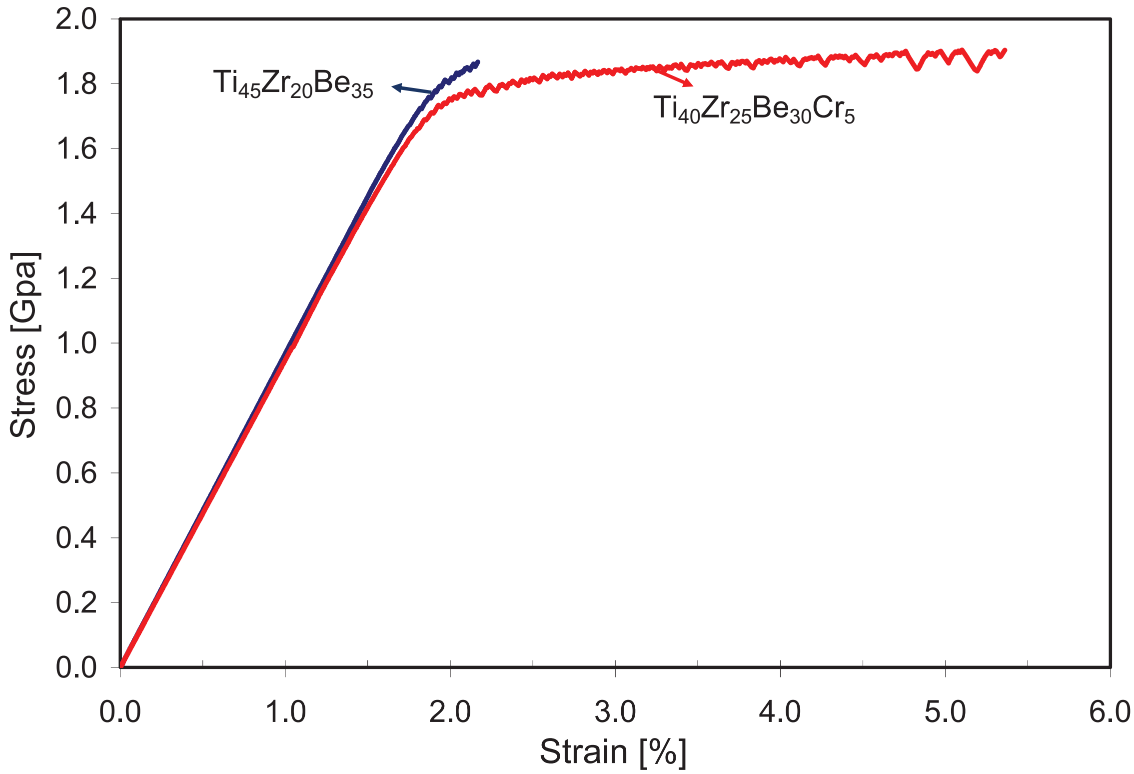

Figure 2.3: Compressive stress-strain curves for the $Ti_{45}Zr_{20}Be_{35}$ and $Ti_{40}Zr_{25}Be_{30}Cr_5$ 3mm amorphous rods.

The current study resulted in a class of bulk amorphous alloys with high GFA, good processing ability and exceptional thermal stability with mass densities significantly lower than those of the Vitreloy alloys and comparable to those of pure titanium and Ti-6Al-4V alloy (see Table 2.1). $Ti_{45}Zr_{20}Be_{35}$ and $Ti_{40}Zr_{25}Be_{30}Cr_5$ show low densities of ~ 4.59 and ~ 4.76 g/cc respectively. Compared to Vitreloy alloys, a 20 - 40% higher specific strength is observed in the lightweight TiZrBe compositions. These lightweight Ti based bulk amorphous alloys also exhibit higher specific strengths than crystalline Ti alloys. For example, commercial Ti-6Al-4V 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. 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.

In summary, lightweight Ti based bulk amorphous structural metals with low 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 research results have important implications on designing and developing bulk metallic glasses.

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