

# Effect of small amounts of B and C additions on glass formation and mechanical properties of a Zr-base alloy

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## Abstract

The effect of B and C additions up to 0.4 at. % on glass formation and mechanical properties of a Zr-base alloy Vitreloy 105 was studied using various techniques. All alloys were prepared by arc melting and drop casting. Boron additions increase the glass forming ability by lowering  $T_m$  and increasing  $T_g$ . Carbon additions only lower  $T_m$ , but do not affect  $T_g$ . B and C additions occupy free space and do not harden the glass phase.

## Introduction

Metallic glasses in amorphous states possess many attractive properties for structural and functional use [1]. Recent studies show that it is possible to produce the glass state in bulk metallic glass (BMG) alloys containing multiple components at critical cooling rates of 1 to  $10^2$  K/s [2-6]. In comparison, high critical cooling rates of  $10^5$  to  $10^6$  K/s are generally required for formation of the glass state in metallic elements or simple binary alloys. These observations demonstrate that BMG alloys have a much superior glass forming ability. In the recent review paper, Inoue [5] pointed out that the high glass forming ability of BMG alloys can be simply rationalized by three empirical rules: (1) BMGs contain multiple elements,  $\geq 3$ , (2) constituent elements have a large difference in atomic size, usually  $\geq 12$  %, and (3) these elements possess negative heats of mixing. It should be pointed out that no single intermetallic phase is stable with the multi-component composition. In view of these rules, it may be possible to further stabilize BMG alloys by adding small amounts (within solubility limits) of elements with small atomic sizes, such as boron and carbon. Boron and carbon could easily occupy open space in the amorphous states, resulting in enhancement of random packing density and stabilization of the supercooled liquid state. Also, the formation of strong Zr-B or Zr-C atom pairs in Zr-base BMG alloys is expected to further lower the heat of mixing and increase the glass forming ability [6,7]. On the other hand, excessive amounts of B and C additions may cause the formation of Zr boride and carbide embryos, which may serve as nuclei for crystallization.

In this study, a Zr-base alloy, Zr-10Al-5Ti-17.9Cu-14.6Ni alloy (Vitreloy 105) was selected as the base composition [8,9], where additions of B and C up to 0.4 at. % were added to the base alloy. The B- and C-doped alloys were prepared by arc melting and drop casting, and their metallurgical and mechanical properties were characterized using various techniques. The addition of 0.3 % B or C lowers the melting by  $\sim 6^\circ\text{K}$  and causes no significant hardening of the base alloy.

## Experimental procedures

Three series of BAM alloys were prepared based on Vitreloy 105, with their compositions listed in Table 1. The first and second series were doped with up to 0.4 at. % B and C, respectively, and the third was doped with equal amounts of B and C up to a total of 0.3 %. All the alloys were synthesized by arc melting in an inert gas, followed by drop casting into 6.2 mm diam. Cu molds chilled with water. Zone-refined Zr bars (containing 12 appm O and 10 appm Hf) together with pure metal elements, electron-grade boron, and pyrolytic graphite were used as charge materials. Cast alloy ingots were then sectioned for microstructural analyses and property evaluation. Metallographic specimens were polished on a syntron machine and etched in a

solution of 40-ml HNO<sub>3</sub> plus 10 drops of HF. The microstructure and phase compositions were analyzed by wavelength dispersive spectroscopy and energy dispersive spectroscopy using an electron microprobe. The phase transformation behavior was studied at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC).

Table 1. Nominal Compositions

Composition (at. %)	0	0.05	0.1	0.2	0.3	0.4
Alloy number			<u>B-Doped</u>			
	BAM-11	BAM-31	BAM-23	BAM-24	BAM-25	BAM-26
			<u>C-Doped</u>			
	BAM-11	BAM-32	BAM-27	BAM-28	BAM-29	BAM-30
			<u>(B+C)-Doped*</u>			
	BAM-11		BAM-33	BAM-34	BAM-35	

\*Equal amounts of B and C.

Tensile specimens with a 3.19-mm gage diameter were fabricated by centerless grinding. Tensile tests were all conducted on an Instron testing machine at room temperature at a strain rate of  $3.3 \times 10^{-3} \text{ s}^{-1}$ . Microhardness was measured on metallographic samples using 25 to 200 g, dependent on the size of alloy phases. Sectioned alloy ingots were crushed in a hydraulic press to produce coarse powder for bulk density measurements. The density was measured using a helium pycnometer with an accuracy of approximately 0.01 vol. %. The use of powdered samples is intended to eliminate microporosities in alloy ingots, resulting in more accurate density measurements.

## Results

The microstructure of BAM alloys was examined by both metallography and electron microprobe analysis. Figure 1 shows a back-scattered electron image (BSEC) of BAM-35 containing 0.15 B and 0.15 C. No microstructural features were detected in the matrix, indicating the formation of the glass phase in the alloy [9]. In contrast, massive crystalline phases are observed in BAM-30 doped with 0.4 C (Fig. 2), and their amount increases steadily with the distance away from the ingot surface. This increase is due to a continuous decrease in cooling rate from ingot surface to center. Unmelted B (dark contrast) was observed in BAM-26 containing 0.4 B, which was surrounded by crystalline phases (light gray) and B-rich phase particles (dark gray) in Fig. 3a. In comparison, unmelted C (dark contrast) was first detected in 0.3 C alloy (BAM-29), with no observation of carbon-containing phases around it. A particle of unmelted carbon and its surrounding structure in BAM-30 containing 0.4 C is shown in Fig. 3b.

Since the BMG alloys were produced by drop casting that induced turbulent flows, oxide particles (dark contrast) and isolated crystalline phase particles (gray contrast) were occasionally observed in turbulent-flow regions in cast ingots, as shown in Fig. 4 at a high magnification. The dendritic growth of large oxide particles is also visible in Fig. 4. Table 2 summarizes the composition of phases in BAM-35 by electron microprobe analyses. The glass matrix has its composition similar to the nominal alloy composition. Crystalline particles are enriched slightly with Ni and depleted with Al. On the other hand, oxide particles are enriched with Al and oxygen, indicating the formation of aluminum oxide particles. Since the volume ( $\sim 2 \mu\text{m}$ ) excited by the electron beam is larger than the size of oxide particles in dendritic shapes, the exact oxide composition can not be determined here.

100µm



Fig.2 BSEI of BAM-30

Fig. 1 BSEI of BAM-35



(a)



(b)

Fig. 3 BSEI of (a) BAM-26 showing unmelted B, and (b) BAM-30 showing unmelted C

10µm



Fig. 4 BSEI of BAM-35

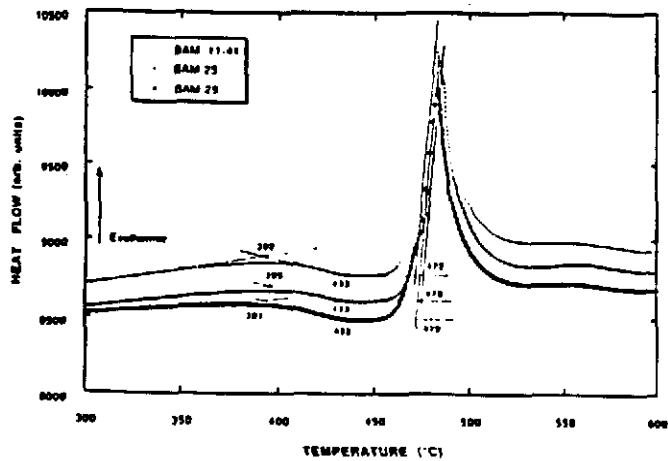


Fig. 5 DSC curves of BAM-11, -25, and 29

The Glass transition ( $T_g$ ) and crystallization temperatures ( $T_x$ ) of BAM-25 containing 0.3 B and BAM-29 with 0.3 C together with the base alloy BAM-11-41 were determined by DSC, and the results are shown in Fig. 5. Noticeably, the B addition increases  $T_g$  and  $T_x$  by 3°K, whereas these temperatures are not affected by the C addition. Figure 6 shows the effect of B and C additions on the melting point of the base alloy. As indicated in the figure, both B and C lower the melting point,  $T_m$ , of the base by 5- 6°K.

Table 2. Phase Compositions in BAM-25 (Containing 0.3 at. % B) Determined by Electron Microprobe Analyses

Phase	Compositions (at. %)				
	Cu	Ni	Al	Ti	O
Alloy nominal	17.9	14.7	10.0	5.0	
Glass matrix	18.0	14.7	10.0	5.4	
Crystalline phase	18.2	15.2	9.6	5.2	
Oxide particle	16.6	9.5	17.0	4.0	7.2

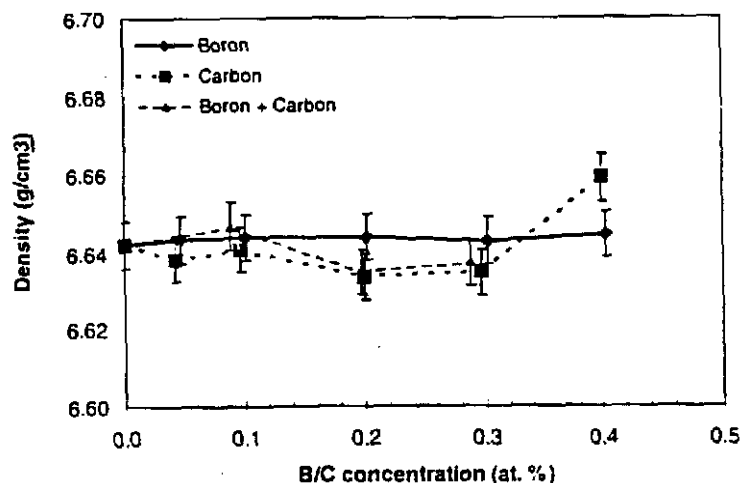
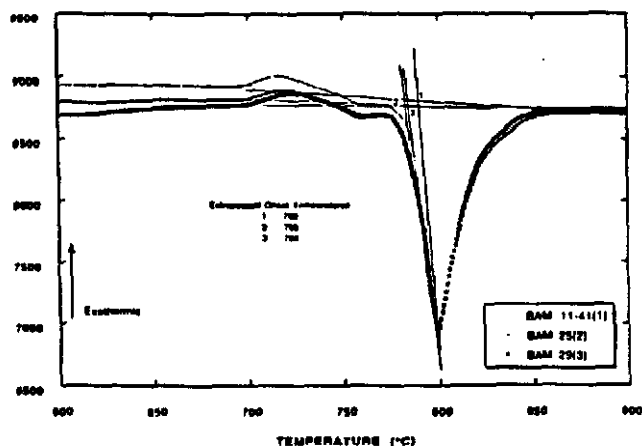


Fig. 6 DSC curves for BAM-11, -25, -29 Fig. 7 Plot of density vs B/C concentration

The measured density of BAM alloys is plotted as functions of B and C concentrations in Fig. 7. The density of the alloy in the glass state is essentially not affected by B and C additions at levels to 0.4 %. For the C and (B+C) doped alloys, their density exhibits a small decrease at 0.2-0.3 %. A relatively sharp increase in density is observed for 0.4 C alloy, mainly due to the massive formation of crystalline phases (see Fig. 2).

The mechanical properties of BAM alloys were determined by hardness and tensile testing at room temperature. Figure 8 shows that the hardness is essentially not sensitive to B and C additions. Note that the hardness measurements reported here were all made on the glass matrix. The fracture strength determined by tensile testing at room temperature is shown in Fig. 9. The strength of the base alloy is as high as 1650 MPa. Adding with a combination of B and C up to 0.3 % does not affect the tensile fracture strength. The strength is not sensitive to B or C at levels up to 0.2 %, and above that level it decreases with increasing B or C addition. A sharp decrease

in strength at the C level above 0.3 % is due to a massive formation of crystalline phases, as observed in BAM-30 doped with 0.4 C (Fig. 2).

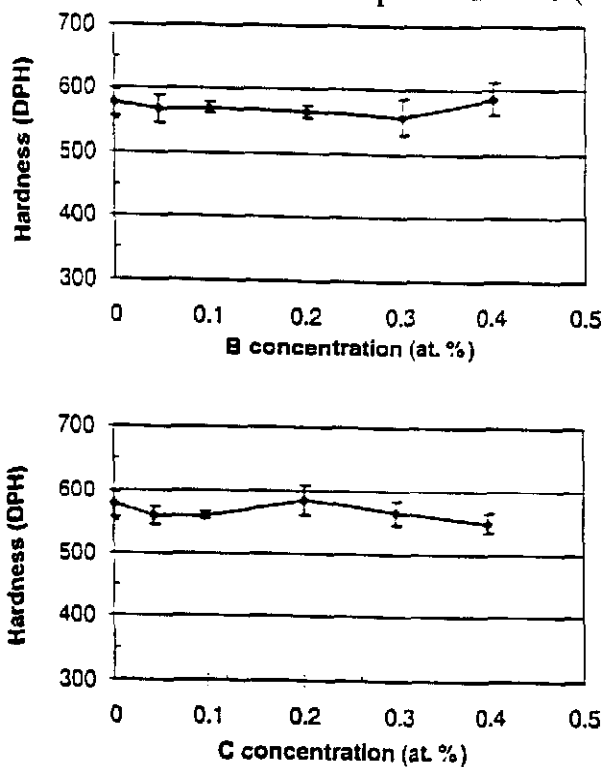


Fig. 8 Plot of hardness as functions of B & C Concentrations

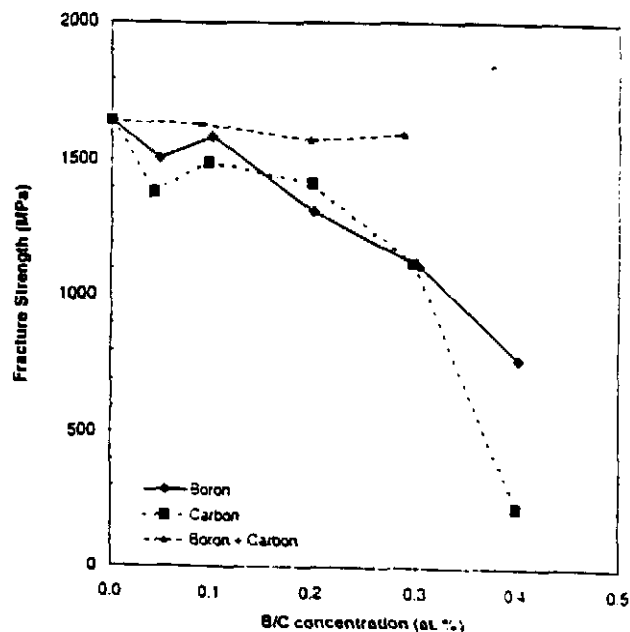


Fig. 9 Plot of tensile fracture strength vs dopant concentration

## Discussion

Recently, Inoue et al. [6,7] found that additions of B significantly increase the thermal stability of the supercooled liquid region in Zr- and Pd-base alloys prepared by melt spinning. The addition of 3 at. % B extends the supercooled liquid region,  $T_{Xg}$  ( $=T_X - T_g$ ), of Pd-6Cu-18Si alloy from 47 to 70 K [6]. In this case, the increase in  $T_{Xg}$  is due to a combination of a small increase in  $T_X$  and a large decrease in  $T_g$ . For the Zr-base BMG alloy, Zr-27.5Cu-7.5Al, the addition of 4 % B extends  $T_{Xg}$  from 72 to 100 K, and this increase is mainly due to a significant increase in  $T_X$  [7]. In the present study, all BAM alloys were prepared by arc melting and drop casting, and their molten states could not be superheated and soaked extensively above  $T_m$ . The finding of unmelted elements suggests that the solubility of B and C appears to be ~0.4 % for B and ~0.3 % for C in drop-cast BAM ingots. These small amounts apparently do not extend the supercooled liquid region ( $\approx 80$  K) of Vitreloy 105. Boron at 0.3 % increases both  $T_X$  and  $T_g$  by 3 K, resulting in no change of  $T_{Xg}$ . Carbon at 0.3 % virtually does not alter  $T_X$  and  $T_g$ . However, in terms of the reduced glass transition temperature ( $T_g/T_X$ ), the 0.3 % C and B additions increase the value from 0.626 to 0.633 for B and 0.626 to 0.628 for C.

Small atoms such as boron enhance the stability of glass forming ability; however, oxygen, on the other hand, lowers the glass forming ability and dramatically increases the critical cooling rate required for glass forming in Vitreloy 105. Lin et al. reported that the increase in the oxygen level from 0.025 to 0.525 at. % increases the critical cooling rate by several orders of magnitude [8]. Their study suggests that oxygen-induced precipitates are catalytic sites for heterogeneous nucleation for intermetallic phases and control the crystallization behavior of the glass forming alloy. It has been reported that small silicon additions between 0.5 to 1 % enhance the glass forming ability of Cu- and Ni-base alloys [10,11]. Choi-Yim et al. [10] suggest that the

beneficial effect of silicon comes mainly from passivating oxygen impurities that promote heterogeneous nucleation in the molten state.

It is interesting to examine the hardening behavior of the glass state by B and C additions. As shown in Fig. 8, the addition of up to 0.4 % B and C causes no significant hardening in the glass matrix. This is very different from interstitial hardening in crystalline phases [12,13]. For instance, doping with 0.2 % of B results in a twofold increase in the yield strength of Ni<sub>3</sub>Al [12]. This suggests that B and C with small atomic sizes mainly occupy free space, resulting in no significant increase in lattice strain and hardness in the glass state. Adding 0.4 % C produces massive crystalline phases in BAM-30, whose hardness is 695 DPH as compared with 545 DPH for the glass phase. The tensile fracture strength, similar to the hardness, showed no increase with B and C additions. The significant decrease in fracture strength of BAM alloys with  $\geq 0.3$  % B or C is due to the existence of defects, such as unmelted B/C elements and crystalline phases. In this Zr-base alloy, the formation of crystalline phases causes severe embrittlement [14].

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