

Crystallization, Thermal and Elastic Properties of Zr-Ti-Cu-Ni-Be-C Bulk Amorphous Alloy under High Pressure

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Abstract The crystallization, thermal, elastic and mechanical properties of bulk state $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ amorphous alloy (a-alloy) under ambient pressure and high pressure range have been investigated by means of x-ray diffraction, differential scanning calorimetry and ultrasonic technique. The results indicate that the crystallization, thermal properties and the density of the a-alloy are sensitive to the addition of carbon. The addition 1 at.% of carbon is effective for further extension of the wide supercooled liquid range and enhancement of the thermal stability of the alloy. The elastic constants as well as their pressure dependence of the a-alloy have been determined. High-pressure assisted crystallization is experimentally observed for the a-alloys, the crystallization induces no significant increase in density.

Introduction.

Bulk amorphous alloys (a-alloy) with complex multicomponent chemistry and excellent glass forming ability (GFA) have been recently developed [1-3]. These a-alloys reveal strong resistance to crystallization in the supercooled liquid state and exhibit many excellent physical properties. $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy represents one of these alloys [2-3]. The novel a-alloys are believed to have considerable potential as advanced engineering materials [1-2]. The previous work [2-4] showed that the dissolution of Be with smaller atomic size has a great effect on the formation of the a-alloys. However, not much information exists on the effects of the metalloid carbon on the alloys, and little work has been done about the pressure dependence of physical properties of these a-alloys. It may be expected that carbon with a small atomic size may tighten the alloy structure and thus stabilize the a-alloy against crystallization. In this work, X-ray diffraction (XRD), differential scanning calorimeter (DSC) are applied to study the effects of carbon on the formation, thermal stability of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy. The ultrasonic measurements and high pressure technique were used to study the elastic properties and crystallization of the addition obtained Zr-Ti-Cu-Ni-Be-C a-alloys. The purpose of the studies is to understand the glassy metallic state and the effects of HP on the microstructure and properties. An additional motivation for the study is to determine how the bulk a-alloy compares in elastic properties to other conventional a-alloy.

Experiments

Ni-C alloys were prepared by sintering pure Ni and C powder at 1500 K. Pure Ti, Zr, Cu, Be elements and the NiC alloy were induction melted together under a pure Ar atmosphere to form homogeneous alloy ingots of desired compositions. The ingots were remelted together in a silica tube and subsequently quenched in water, resulting a cylindrical rod with a diameter of 12 mm.

The nominal compositions are $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10-x}Be_{22.5}C_x$ ($x=0,1,3,4$). XRD was performed using a MAC M03XHF diffractometer with Cu K_{α} radiation. DSC measurements were carried out with a Netzsch DSC 404 under flowing pure Ar gas. The acoustic velocity, and their pressure dependence of the a-alloy were measured by using the pulse echo overlap method [5]. The amorphous rod was cut to a length of about 10 mm, and its ends were carefully polished flat and parallel. The travel time of ultrasonic waves propagating through the sample with a 10 MHz carrier frequency was measured using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. The HP measurements were performed using a piston-cylinder high-pressure apparatus. The pressure measurements were performed several times under cyclic load-unload conditions to examine the reproducibility. The density ρ was measured by the Archimedian method. The elastic constants (e.g. bulk modulus K , Young's modulus E , shear modulus G , and Poisson's ratio σ) of the alloy are derived from the acoustic velocity and density [5-7]. The HP was performed in an apparatus with six anvil tops. The pressure range of the apparatus is from ambient pressure to 8 GPa and the temperature range from room temperature to 1100 °C. The temperature is controlled by thermocouple with an error of ± 1.5 °C.

Results and Discussion

The amorphous natures as well as the homogeneity of the water quenched $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ and $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ alloys (referred to as alloy A and B respectively) was ascertained by XRD, DSC, high resolution transmission electron microscopy and small angle neutron scattering [4,9]. High carbon addition (>2%) induces the formation of ZrC crystalline phase, and the crystalline particles embedded in the amorphous matrix lead to an increased hardness of the a-alloy [4, 10]. Fig.1 shows a comparison of DSC traces for the alloy B [Fig.1(a)] and alloy A [Fig.1(b)]. For the alloy A, the glass transition temperature T_g is 623 K, the onset temperature of the first crystallization event T_{x1} is 683 K. $\Delta T = T_{x1} - T_g$, referred to as the supercooled liquid region, is 60 K. For alloy B, T_g is almost the same as that of alloy A. However, adding carbon raises T_{x1} to 712 K, and broadens the supercooled liquid region to 90 K. The results indicate that the thermal stability and the supercooled liquid region of the alloy B are significantly increased by carbon addition. The larger ΔT is of technological as well as scientific importance,

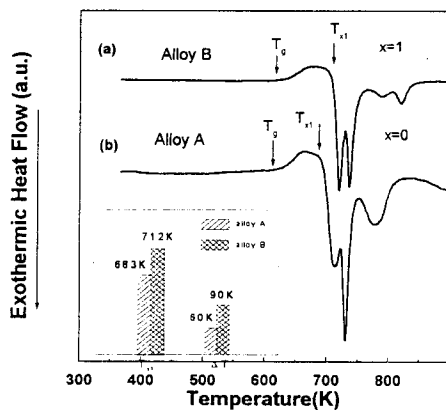


Fig.1. DSC traces of (a) a-alloy B and (b) a alloy A. Heating rate 10 K/min..

because the larger ΔT , the easier it is to prepare large sized bulk amorphous alloy sample by techniques such as injection moulding. A small amount of carbon addition can result in pronounced enhancement of the strength of the a-alloys [8]. The effect of carbon addition on the microhardness of the alloy may be attributed to the carbon addition resulting in more dense randomly packed structure of the alloy.

The values for the longitudinal, transverse velocities (v_l , v_s) and density at ambient conditions were 5.096 ± 0.001 km/s, 2.533 ± 0.003 km/s and 6.1608 ± 0.0001 g/m³ respectively. The E, G, K, σ , and K/G of the a-alloy at ambient conditions calculated from the acoustic data are 105.97 GPa, 39.54 GPa, 107.31 GPa, 0.34, and 2.71 respectively. The non-metallic glasses (e.g. oxide glass), whose values of σ

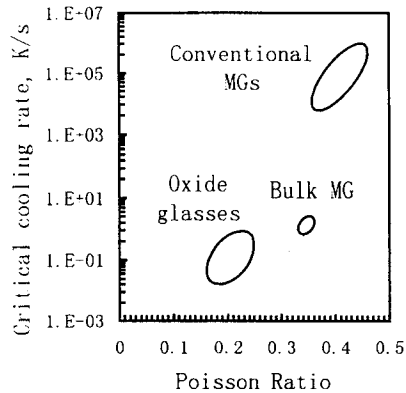


Fig.2. The relation of critical glass forming cooling rate and the Poisson's ratio σ for oxide glasses, conventional a-alloy and bulk a-alloy.

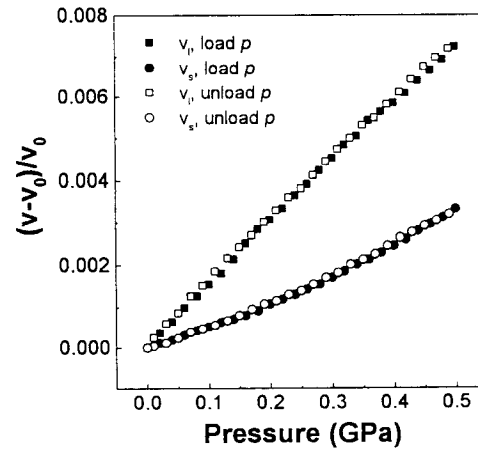


Fig.3. Variation of v_l , v_s of $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22}C_1$ a-alloy with pressure ($v=v_l, v_s$), v is normalized by $(v-v_0)/v_0$, where v_0 is a normal velocity at ambient pressure.

are less than 0.25, are brittle, since atoms or molecules can hardly rearrange themselves to shear strains without a drastic disturbance in bonding configurations [11]. In contrast, conventional a-alloys with poor GFA, have high value of $\sigma \approx 0.40$, indicating the ease of atomic rearrangement and consequently the ductile plastic deformation of these materials [12]. For bulk a-alloys with excellent GFA, their value of σ is between that of conventional a-alloy and oxide glasses. This is result from the atomic configuration in the bulk a-alloy. Previous studies showed that bulk a-alloys consist of mixture of atoms of different radii which lead to highly dense random packed structures compared to conventional a-alloys [13]. The closer packed structural characteristic of a-alloy makes redistribution of atoms extremely difficult, and leads to larger value of σ . On the other hand, bulk a-alloys have excellent GFA which is much better than conventional a-alloys and approaches that of oxide glass. The relation of σ and critical glass formation cooling rate for oxide glasses, bulk a-alloys and conventional a-alloys are shown in Fig.2. It can be seen that σ has a correlation with the GFA of the three kinds of glasses, the glass with small value of σ have good GFA. This indicates that the GFA has a close relation with the microstructure of a glass forming system. A decreasing σ may result in high GFA in a glass forming system. The nature of the chemical bond in a solid determines the microstructure of the solid, thus a difference in local structure will influence the mechanical properties of a solid, resulting in the variation of the acoustic parameters. For solid with covalent bonds such as silicate glasses, amorphous carbon, $K/G = (v_l/v_s)^2 - \frac{4}{3}$ is about 1.7 [14]. For conventional a-alloy K/G is about 5.2 [12], while the K/G of the Zr-based bulk a-alloy is 2.71, markedly different from the value for conventional a-alloys. This result also indicates the different microstructures between the two kinds of a-alloys. The relatively larger value of G for the bulk a-alloy compared to other a-alloys and glasses means that the bond-angle of the structure of the a-alloy can not be changed easily. The K/G of bulk a-alloys is similar to metals, such as Cu and steel

for which K/G is about 2.5. The results indicate that metallic bond is retained in the bulk a-alloy even though the a-alloy lacks long-range order. In fact, the a-alloy does have some isotropic metallic properties [2].

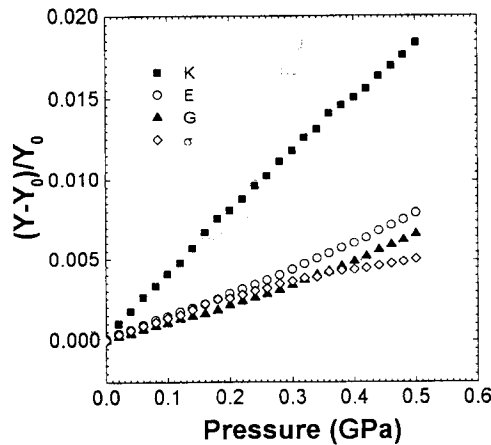


Fig. 4. Variation of elastic constants Y of $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ a-alloy ($Y=E, G, K, \sigma$) with pressure. Y is normalized by $(Y - Y_0)/Y_0$, where Y_0 is a normal modulus at ambient pressure.

unloading processes and show an approximately linear pressure dependence over a range of p_0 up to 0.5 GPa. v_s of the silicate glasses and amorphous carbon decrease with increasing of pressure [11]. The a-alloy has similar p dependence of sound velocities to steel and tungsten carbide [11].

The pressure variations $\delta Y(p)/Y(p_0) = [Y(p) - Y(p_0)]/Y(p_0)$ of the elastic constant E , G , K , and poisson ratio σ calculated from the ultrasonic velocities for $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ a-alloy are shown in Fig. 4. The elastic constants increase with increasing pressure. The increase in elastic constants is attributed to the denser packing of the a-alloy [12]. As shown in Fig. 4, dK/dp and dG/dp of the bulk a-alloy are positive, the elastic constants exhibit a positive deviation with pressure from linearity, showing that the modulus stiffness for the bulk a-alloy under hydrostatic pressure. The application of pressure does not induce acoustic mode softening for the bulk a-alloy.

The volume compression $V_0/V(p)$ and their hydrostatic-pressure dependence using an equation of state such as that of Murnaghan [15] which in logarithmic form is:

The pressure variations $\delta v(p)/v(p_0) = [v(p) - v(p_0)]/v(p_0)$ of the v_l and v_s , for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ a-alloy at room temperature are plotted in Fig. 3, where p_0 is the ambient pressure. The data are reproducible under pressure cycling and show no measurable hysteresis effects. It seems that there are no observable permanent changes in sound velocities with p up to 0.5 GPa. The changes in both v_l and v_s are reproducible for repeated compression as shown in Fig. 3. No density increase in the sample after testing was found within experimental error. These results indicate elastic behavior in the bulk a-alloy under hydrostatic compression up to 0.5 GPa. It is shown that both v_l and v_s increase smoothly with increasing pressure in loading and

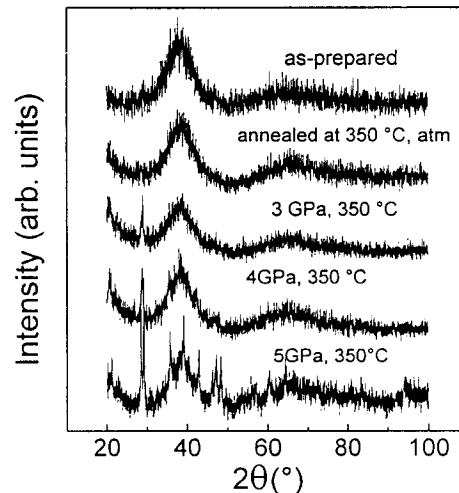


Fig. 5. XRD patterns for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ a-alloy annealed at 350 °C as indicated under different pressure.

$$\ln\left(\frac{V_0}{V(p)}\right) = \frac{1}{K_0'} \ln\left(\frac{K_0'}{K_0} p + 1\right). \quad (2)$$

where K_0 and K_0' are the bulk modulus and its pressure derivation at zero pressure respectively. On inspection of the data for K in Fig.4, we obtain $K=3.924p+107.37$ for the bulk a-alloy by assuming a linear relationship between K and p in the a-alloy. On substitution the data for K_0 and K_0' into Eq.(2), the equation of state obtained for the a-alloy in the non-phase transitional case is:

$$p = 27.35 \left[\left(\frac{V_0}{V(p)} \right)^{3.924} - 1 \right]. \quad (3)$$

Samples of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ a-alloy were isothermally compressed at of 623 K over the range of 2-5 GPa. The annealing temperature is equal to T_g and much lower than T_{x1} of the a-alloy. Each sample was heated to the desired temperature at a rate about 10 K/min. to ensure the same thermal history for all specimens. Figure 5 shows the XRD patterns for the specimens annealed under different pressures. No change was observed for the sample annealed at 623 K in vacuum for 20 h with zero applied pressure. Within the experimental error of the X-ray diffraction no crystallization occurs in the sample. However, when the a-alloy annealed at the same temperature under pressure for 4 h, partial crystallization of the a-alloy occurs progressively, starting at about 3 GPa. More crystalline peaks appear and the intensity of the crystalline peaks increase with increasing pressure as shown in Fig.5. This result indicates that applied pressure favours the crystallization in the bulk a-alloy, and that the crystalline fraction in the a-alloy increases with increasing pressure. The densities of $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ a in the as-prepared state and crystallized state at 5 GPa were measured to be 6.1608 g/cm³ and 6.1916 g/cm³ respectively. The increase in density due to high-pressure induced crystallization for the a-alloy is ~0.2-0.5% depending on the pressure. The density change is much smaller than that (~2-3%) for conventional a-alloys with poor GFA. This phenomenon has been also observed in Zr- and Pd-based bulk a-alloy [16]. The results further confirm that the bulk a-alloy has a more packed atomic configuration than conventional a-alloys. The microstructural characteristics lead to high GFA and high thermal stability of the alloy by decreasing the atomic mobility in the supercooled liquid region.

Summary

The formation, crystallization and mechanical behavior of the bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ a-alloy is sensitive to the addition of carbon. For such alloys with 1% carbon, a single amorphous phase exists with further extension of the wide supercooled liquid region, enhanced thermal stability and strength compared with an alloy without carbon. The elastic constants as well as the pressure dependence of the bulk a-alloy have been determined. The elastic properties of the bulk a-alloy have been correlated with its excellent glass forming ability and microstructural characteristics. The crystallization in bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ a-alloy is assisted by applied pressure larger than 3 GPa at 350 °C.

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