Production and properties of high strength Ni free Zr-based BMGs

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Abstract. Bulk metallic glasses (BMGs) are well known for very attractive physical, mechanical and thermal properties. Zr-based BMGs are used as structural materials in sports goods, electronics, jewelry, medical and aerospace applications. Ni free Zr_{48}Cu_{36}Al_{8}M_{8} (M = Nb, Ti and Ta) BMGs are successfully synthesized by Cu mold casting technique. Differential scanning calorimetry (DSC) results show that the Zr_{48}Cu_{36}Al_{8}Nb_{8} BMG have good thermal stability, wide supercooled liquid region of 80 K and contain the double stage crystallization. The alloy has fracture strength of 1.953 GPa. Shear angle was measured to be in the range of 43.5±5° for the alloy studied. Vicker’s hardness of the BMGs was found to be over 500 HV for the as cast alloy which enhanced about 11 % more by annealing up to 600 °C/20 min. Intersected shear bands were observed. The observed promising mechanical and thermal properties showed that BMG studied can be used for industrial applications.

1. Introduction
Bulk amorphous materials are new class of materials having better physical, mechanical and thermal properties over their crystalline counter parts [1-3]. Bulk metallic glasses (BMGs) are super cooled liquids having disorder random non-equilibrium structure [4-5]. Zr-based BMGs especially Zr-Cu-Al-Ni quaternary and Zr-Cu-Al-Ni-M (M is a metal) pentanary alloys are widely studied due to their technical importance and are being used for structural and medical applications [6-8]. Ni and Cu are used in Zr based alloys for certain purposes such as to enhance mechanical strength and thermal stability of the super cooled liquid as well as competitive resistance to crystallization during casting process. As enthalpy of mixing (ΔH_{mix}) of Ni-Zr is very high (-44 kJ/mol) as compared to ΔH_{mix} of Cu-Zr phase (-23 kJ/mol) so Ni is avoided to prevent and stop the fast nucleation and rapid growth of Ni-Zr phases. Although a few Ni free Zr-based BMGs have been reported [9-11] but there is no report available on mechanical and thermal properties of Zr_{48}Cu_{36}Al_{8}M_{8} (M = Nb, Ti and Ta) BMGs. In this manuscript, results on mechanical and thermal properties of Zr_{48}Cu_{36}Al_{8}Nb_{8} BMG synthesized by Cu mold casting technique are reported.

2. Experimental
Alloy buttons of Zr_{48}Cu_{36}Al_{8}M_{8} (M = Nb, Ti and Ta) alloys were prepared by using arc melting furnace by taking 50 grams mixtures of 3-4N pure metals of the alloy constituents. Alloy buttons were repeatedly melted at least four times to get the extended chemical homogeneity. Pieces of homogenized alloy buttons were further used for casting of alloy ingots of 1-5 mm thick rods of 70 mm length and sheets of size ~70x10x2 mm³. Cu mold casting technique was used for materials
preparation under pressure of $2 \times 10^{-3}$ Pa. The samples taken from the center of the alloy ingots were characterized by XRD (RIGAKU Diffractometer using Cu $K_{\alpha 1}$ radiation with wavelength $\lambda = 1.54056$ Å) and DSC (Perkin Elmer 7/Pyris DSC and NETZSCH DSC 404 systems). Compression tests were applied on the samples with aspect ratio of ~2 under strain rate of $4 \times 10^{-4}$/sec. Fractures studies were conducted by using scanning electron microscope (SEM) Leo 440i. Analysis of samples was done by energy dispersive x-ray analyzer (EDAX) attached with SEM. For high resolution images, filed emission scanning electron microscope (FESEM) was employed. Density was measured by using the “Archimedes principle” at room temperature of ~20 °C. Acoustic studies were conducted and elastic moduli were calculated from the data collected. Low and high temperature differential scanning calorimetry (DSC) was conducted at various heating rates “r” of 5, 10, 20 and 40 K/min. Activation energy was calculated by using Kissinger equation. In order to study crystallization and phase formation, annealing of the samples was done at 350, 450, 550 and 600 °C for 20 minutes in PC controlled tubular furnace with maximum temperature variation of ±1° C by sealing the samples in quartz capsules under high purity Argon. Vicker’s hardness of the as cast and annealed samples was measured by using “Everone hardness tester” under appropriate load. Here, results on Zr$_{48}$Cu$_{36}$Al$_8$Nb$_8$ BMG are presented.

3. Results and discussion

XRD results of as cast Zr$_{48}$Cu$_{36}$Al$_8$Nb$_8$ alloy ingot of 5 mm diameter and 70 mm length and sheet of size 70x10x2 mm$^3$ are shown in figure 1(a). The broad band without any diffraction peaks indicates the amorphous nature of the alloy. Similar patterns were observed for rod samples of 1-4 mm diameter. Average density of as cast samples was found to be 6.9794 g/cm$^3$ which is comparable with other Zr-based alloys [1]. XRD of the samples annealed at 350 to 550 °C results in the nucleation of CuZr$_2$ phase. XRD pattern of the sample annealed at 600 °C is shown in figure 1(b) which confirmed the formation of Cu$_{10}$Zr$_7$ stable phase. Atomic radii $R_a$ (in nm) [12] and $\Delta H_{mix}$ [13] of the alloy constituents are presented in table 1. It is interesting that no other phase other than CuZr$_2$ was observed. The CuZr$_2$ phase nucleated due to strong interaction of Cu and Zr atoms as enthalpy of mixing of Zr-Cu pair is -23 kJ/mol while $\Delta H_{mix}$ of Cu-Al pair is only -1 kJ/mol. The Nb-Zr pair has positive heat of mixing (4 kJ/mol) so Zr and Nb don’t react chemically. Actually Nb is added to enhance the mechanical properties. Diffraction peaks in XRD patterns of the samples annealed at 350 to 600 °C indicating the presence of crystalline phases. XRD results confirmed the formation of CuZr$_2$ metastable phase at temperature ≤ 550 °C and stable phase Cu$_{10}$Zr$_7$ at 600 °C. It is interesting to note that solute atoms (Al and Nb) are not more reactive to solvent atoms (Zr) than Cu atoms because atomic radius of Cu is smaller than all other atoms. So, Cu atoms are more reactive to Zr than Al and Nb atoms. As a result, CuZr$_2$ metastable and Cu$_{10}$Zr$_7$ stable phases are observed. Al and Cu atoms have positive role in increasing the thermal stability of the Zr-based alloys.

Figure 2(a, b) shows low and high temperature DSC traces of the Zr$_{48}$Cu$_{36}$Al$_8$Nb$_8$ BMG. Low temperature DSC at 10 and 40 K/min shows single stage crystallization while high temperature DSC at 20 K/min shows double stage crystallization at temperature ≥ 600 °C which is in agreement with the XRD results. Exothermic and endothermic reactions occurred are clear in DSC traces.


**Figure 1(a-b)** XRD patterns of the as cast rod of 5 mm thick and 70 mm long as well as sheet of 70x10x2 mm³ size (a) XRD of a sample annealed at 600 °C containing Cu₉₀Zr₇ stable phase (b)

**Figure 2(a-c)** Low (a) and high temperature DSC (b) plus Kissinger plot (c) of the alloy studied

| Table 1. Mixing enthalpies and atomic radii of alloy constituents |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Alloy constituents               | Atomic radii Rₐ (nm) | Zr               | Al              | Cu              | Nb              |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Zr                              | 0.16025         | -44             | 0.12780         | 0.14290         |
| Al                              | 0.14317         | -18             | -1              | -               |
| Cu                              | 0.12780         | -23             | -1              | -               |
| Nb                              | 0.14290         | 4               | -18             | 3               |

Thermal parameters like glass transition temperature Tₓ, crystallization temperature Tₓ, peak temperature Tₓ, melting temperature Tₘ and liquidus temperature T₁, a key parameter known as “reduced glass transition temperature” Tᵧ = Tₓ/Tₘ and Tᵧ = Tₓ/(T₁+Tₓ) [14], β = Tₓ/(T₁-Tₓ) [15], γ = Tₓ/(Tₓ+T₁) [16] and ω = Tₓ/Tₘ - 2Tₓ/(Tₓ+T₁) [17] are also deduced and the results are presented in table 2(a) and table 2(b). In addition some more thermal parameters such as Hruby parameter Kᵩ = ΔTₓ/(Tₘ-Tₓ) [18], Thermal parameter proposed by Saad and Poulain Kₛₚ = (Tₓ-Tₓ)/(ΔTₓ/Tₓ) [19], Weinberg parameter Kₚ = ΔTₓ/Tₘ, Kₓₐ = Tₓ/(Tₘ+Tₓ) [20], Kₐ = Tₘ-Tₓ, K₁ = ΔTₓ, K₂ = ΔTₓ, K₃ = Tₓ/Tₘ and K₄ = (Tₓ-Tₓ)/(ΔTₓ/Tₘ) [21] were also calculated and the results are presented in table 2(c). These thermal parameters showed good thermal stability and complete thermal behavior of the alloy studied. The values of thermal parameters of the presently reported Zr₉₀Cu₅₆Al₈Nb₈ BMG is better than the results reported by Zhang et al. [9, 10] for Ni free Zr-Fe-Al-Cu, Zr-Cu-Al-Ag and Jiang et al. [11] for Zr₁₀₀ₓ₋₉(Cu₅₆Ag₁₆ₓ)ₐₓ BMGs. The reason is substitution of Nb with Fe and Ag. The activation energy “Eₐc” required for crystallization of an alloy is an important kinetic parameter to
determine the thermal stability of amorphous phase. The dependency of crystallization temperature on heating rate was used to determine the associated activation energy ($E_{ac}$) by means of Kissinger’s equation $\ln \left( \frac{r}{T_p^2} \right) = -\frac{E_{ac}}{R}T_p + \text{constant}$. Here “$r$” stands for the heating rate, $T_p$ is the peak temperature in DSC scans, $R$ is the gas constant ~8.3145 J/mol K, with slope $-\frac{E_{ac}}{R} = B$, where $B$ is a constant [22]. Kissinger plot is shown in figure 2(c). The activation energy was calculated to be 392 kJ/mol.

Table 2(a). Thermal parameters (in K) evaluated from low temperature DSC done at various heating rates

| $r$ (K/sec) | $T_g$ | $T_x$ | $\Delta T_x$ | $T_p$ | $E_{ac}$ (kJ/mol) |
|------------|-------|-------|-------------|-------|------------------|
| 5          | 660   | 740   | 80          | 746.5 | 392              |
| 10         | 670   | 750   | 80          | 755.0 |                  |
| 40         | 680   | 765   | 80          | 771.0 |                  |

Table 2(b). Various thermal parameters (in K) evaluated from high temperature DSC conducted at heating rate of 20 K/min

| $r$ | $T_g$ | $T_x$ | $\Delta T_x$ | $T_p$ | $T_{m}$ | $T_1$ | $T_{rg1}$ | $T_{rg2}$ | $\gamma$ | $\beta$ | $\delta$ | $\omega$ |
|-----|-------|-------|-------------|-------|--------|-------|-----------|-----------|---------|--------|---------|--------|
| 20  | 670   | 750   | 80          | 756.5 | 1119   | 1175  | 0.599     | 0.57      | 0.407   | 2.72   | 1.49    | 0.17   |

Table 2(c). Some more thermal parameters (in K) deduced for the alloy studied

| $r$ | $K_{H}$ | $K_{W}$ | $K_{LL}$ | $K_{SP}$ | $K_1$ | $K_{2 - \Delta T_x}$ | $K_3$ | $K_4$ |
|-----|---------|---------|----------|----------|-------|----------------------|-------|-------|
| 20  | 0.2168  | 0.714   | 0.4192   | 0.0776   | 449   | 80                   | 0.67  | 0.465 |

Average Vicker’s hardness of the as cast and samples annealed at 350, 450, 550 and 600 °C was found to be 524, 542, 570 and 580 HV respectively. The maximum variation is ±10 HV. Maximum increase in hardness was found to be ~11 %. The enhancement in hardness is due to nucleation of crystalline phases CuZr$_2$ (metastable) and Cu$_{16}$Zr$_7$. The hardness at temperature ≥ 550 °C is almost same due to nucleation of stable phase Cu$_{10}$Zr$_7$. Elastic moduli $E$, shear modulus $G$ and bulk modulus $K$ were calculated by measuring the acoustic properties of the alloy using the relations, $E = \rho V_s^2[(3V_s^2 - 4V_l^2)/(V_l^2 - V_s^2)]$, $K = \rho(V_s^2 - 4/3 V_l^2)$ and $G = \rho V_l^2$. Propagation of longitude and transverse acoustic waves are shown in figure 3(a). Time calculated Cal$_t1$ and Cal$_t2$ for longitudinal and sound waves are fond to be 6.997 and 3.128 µsec with longitudinal acoustic velocity $V_l = 4.747$ Km/sec and transverse acoustic velocity $V_s = 2.122$ Km/sec respectively. Length and diameter of the samples taken was 5 mm and 7.4 mm respectively having density 6.979 g/cm$^3$ at 20 °C. The values of elastic modulus $E$, shear modulus $G$ (modulus of rigidity), bulk modulus $K$ (modulus of compression) and Poisson’s ration were found to be 86.434 GPa, 31.43 GPa, 115.37 GPa and 0.375 respectively. The data shows excellent properties of the alloy studied. Compression tests were applied and stress strain curves (SS curves) of Zr$_{48}$Cu$_{36}$Al$_{8}$M$_{8}$ (M = Nb, Ti and Ta) are plotted in figure 3(b). Maximum fracture stress “$\sigma_f$” was found to be 1.953 GPa for Zr$_{48}$Cu$_{36}$Al$_{8}$Nb$_{8}$ BMG which is higher than fracture stress of Zr$_{48}$Cu$_{36}$Al$_{8}$Ta alloy (1.540 GPa) and Zr$_{48}$Cu$_{36}$Al$_{8}$Ti$_{8}$ (1.086 GPa) alloys as well as previously reported BMGs [1]. It means Nb addition has beneficial role for the improvement of fracture strength. The lower fracture strengths of the alloys containing Ta and Ti are due to their partially crystalline nature. The observed properties are comparable or better than many well-known Zr-based BMGs [2-3].
Figure 3(a-b) Propagation of longitudinal/transverse waves for measurement of acoustic properties of Zr\textsubscript{48}Cu\textsubscript{36}Al\textsubscript{8}Nb\textsubscript{8} BMG (a) SS curves of Zr\textsubscript{48}Cu\textsubscript{36}Al\textsubscript{8}M\textsubscript{8} (M = Nb, Ti, Ta) BMGs (b)

Figure 4(a-c) SEM images of compression tested samples at low (a) and high magnifications (b)

Secondary electron images (SEI) taken by SEM/FESEM of Zr\textsubscript{48}Cu\textsubscript{36}Al\textsubscript{8}Nb\textsubscript{8} BMG of the compression tested fractured samples are shown in figure 4(a-c) at low and high magnifications. Figure 4(a) shows shear angle of 43.5° was observed. But the common observation is 45° for compression tested BMGs. Observation of shear angle less than 45° is in agreement with the previous studies [1, 5, 23]. Low shear angles show deviations from Tresca or Von Mises criterion [24]. Intersected shear bands over the cylindrical plain surface were examined. A shear band is usually initiated at a local region where the viscosity or the resistance of the materials to deformation is greatly reduced [25, 26]. Multiple shear bands were usually observed before fracture. There are two hypotheses about the local change in viscosity within the shear bands. The first suggests that the reduction of viscosity within the shear bands is resulted from the generation and coalescence of free volume and localized heating [25-27]. It may be due to diffusion annihilation of free volume. The second hypothesis is that the local adiabatic heating beyond the glass transition temperature \( T_g \), or even the melting temperature, thus leading to the deformation softening, is the main cause for formation of shear bands in BMGs. Many studies including the present results support this hypothesis. However, the precise physical nature of the formation, initiation and propagation of shear bands as well as the possible mechanism for enhancing the plasticity in BMGs is still unclear [25, 26]. Plastic deformation of BMGs occurs in the form of shear bands due to lack of dislocation systems and grain structures. Shear band evolution process is critical to understand the failure mechanism, determining the ductility and improving the reliability of BMGs [27, 28]. The formation of shear band is rate-dependent process and shear banding instability in BMGs has not previously been identified [29]. The density of shear bands in Zr-based alloys increased with strain rate. Strain rate not only affects the strength but also exerts a significant influence on the formation of shear bands in BMGs [25-27]. Figure 4(b, c) shows FESEM images of veins patterns, plain facets of veins, their propagation and formation of liquid droplets within the veins. Veins branching and localized melting was observed in fractured areas. The compressive force is uniaxial and shear is opposite to veins propagation direction. Failure of materials catastrophically is not evident. Mostly the failure is ductile. The promising properties suggest that Zr\textsubscript{48}Cu\textsubscript{36}Al\textsubscript{8}Nb\textsubscript{8} BMG can be used for structural and medical applications. However, further investigations are still needed to improve the ductility of the presently studied BMGs.
4. Conclusions
The Zr₄₈Cu₃₆Al₈Nb₈ BMG has good thermal stability and better GFA than the Zr₄₈Cu₃₆Al₈Ta₈ and Zr₄₈Cu₃₆Al₈Ti₈ metallic glasses. Supercooled liquid region of 80 K and fracture stress of 1953 MPa indicate that the alloy studied has better thermal and mechanical properties than other similar quaternary Zr-based alloys. Veins patterns, liquid droplets, low shear angle (43°) and serrated flow observed in fractured samples indicate ductile behavior in Zr-based BMGs containing Nb. The addition of Nb in Zr-based BMGs is beneficial for achieving high fracture strength. Hardness increases due to nucleation of Cu-Zr phases. Activation energy of 392 kJ/mol shows high resistance to crystallization of metastable and stable phases in Zr-base alloys. Wide supercooled region shows good thermal stability of the alloy. XRD, DSC and SEM results are well agreed. The excellent properties indicate that Zr₄₈Cu₃₆Al₈Nb₈ BMG is suitable for structural, medical and jewelry applications.

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