



EFFECT OF MINOR ALLOYING ADDITION ON PROPERTIES OF Zr-BASED BULK METALLIC GLASS

*M. IQBAL and J.I. AKHTER

Physics Division, Directorate of Science, PINSTECH, P.O. Nilore, Islamabad, Pakistan

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An alloy with composition $Zr_{64}Ni_{17}Al_{11.5}Cu_{7.5}$ was designed using the criterion of valence electron-atom ratio (1.38) and average atomic size R_a (0.1498 nm). Addition of 2 at. % Ti, V and Pd was carried out in the base alloy. All the alloys were synthesized by Cu mold casting and characterized by SEM, EDS, FESEM, DSC and XRD techniques. Effect of additives on mechanical and thermal properties was studied. The alloys showed good mechanical properties. All the alloys have high fracture strength. Improvement in ductility was achieved with the elemental addition of Ti and V which produced intersecting shear bands in the alloy during compression tests. The calculated thermal parameters indicate good glass-forming ability (GFA) and high thermal stability. Nucleation of liquid droplets within the vein patterns verifies the adiabatic heating theory of BMGs.

Keywords: Bulk metallic glasses, Amorphous alloys, Shearing, Glass-forming ability, Mechanical and thermal properties

1. Introduction

The designing and synthesis of high strength and ductile bulk metallic glasses (BMGs) has been subject of considerable research for the past few years. BMGs are the most important class of advanced materials with unique mechanical properties such as high fracture strength, promising hardness, low Young's modulus and good glass-forming ability (GFA) [1-3]. The BMGs have found industrial applications as structural materials, golf clubs, jewelry applications and high strain-sensing devices [1-5]. However their commercial applications are still limited due to lack of ductility, which results in catastrophic failure along the shear plane. Therefore one of the major challenges in the field of amorphous alloys is to enhance the ductility while retaining good mechanical and thermal properties. Attempts have been made to improve the ductility by designing new compositions. The alloy compositions are usually designed following the Inoue's rules [6], Greer's confusion principle [7] and Dong's criterion for BMGs [8, 9]. The criterion of valence electron-atom ratio (e/a ratio) and average atomic radius R_a for Zr-based alloys [10-12] has also been widely used to design alloy composition having good

thermal and mechanical properties. Following these criteria, Zr-Cu-Al-Ni alloys have been synthesized which showed promising mechanical properties, useful thermal properties, good GFA and high thermal stability [10-15].

Kumar et al. [4] have reported that a small variation in the alloy composition has marked effect on mechanical properties. The technique of minor alloying [16] has also been found very effective for the enhancement of ductility and other mechanical properties. In this case, elements with atomic size greater than or less than the alloy constituents are being added in small quantities to produce disordered structure. Minor alloying of additional elements such as Nb, Ti, Y, W, Er, Si and Ta etc. has been reported to be useful and effective for enhancing properties of Zr-based alloys [12, 14]. The addition of Ti, Nb and Pd in Zr-Cu-Al-Ni alloys played beneficial role for the suppression of the growth of the crystalline nuclei [6]. Recently, Chen et al. [3] have reported much improvement of compression plastic deformation of Cu-Zr-Al alloy by 2 at. % addition of Ti. The outstanding plastic deformation was attributed to the randomly distributed free volume that resulted in extensive shear band formation. In the present study, an alloy

* Corresponding author : miqbalchishti@yahoo.com

having composition $Zr_{64}Ni_{17}Al_{11.5}Cu_{7.5}$ with e/a ratio 1.38 and R_a 0.1498 nm was designed, synthesized and characterized. The influence of Ti, V and Pd elemental addition on the thermal and mechanical properties in the $Zr_{64}Ni_{17}Al_{11.5}Cu_{7.5}$ off eutectic alloy was investigated.

2. Experimental

The alloy buttons having composition $(Zr_{0.64}Ni_{0.17}Al_{0.115}Cu_{0.075})_{100-x}M_x$ ($M = Ti, V$ and Pd and $x = 0, 2$ at. %) were prepared by melting the mixtures of 2-4N pure elements (Zr, Cu, Al, Ni are 4N and Ti is 2N pure) in an arc furnace under Ti gettered atmosphere of high purity Ar at pressure of 4.5×10^{-4} Pa. The alloys are designated as A1, A2, A3 and A4 for base alloy and alloys containing 2 at. % Ti, V and Pd respectively. Bulk samples having at least 3 mm diameter and 60 mm length and sheets of size $60 \times 5 \times 2.5$ mm³ were synthesized in an induction furnace under Ar atmosphere by Cu mold casting technique at pressure by diffraction (XRD) was conducted by Rigaku D/Max-2500 diffractometer using $CuK_{\alpha 1}$ ($\lambda = 1.54056$ Å) radiation. For thermal analysis, high temperature differential scanning calorimetry (DSC) measurements were conducted using DSC 404 C NETZSCH apparatus at different heating rates "r" under Ar atmosphere. Compression tests were conducted at room temperature under uniaxial compressive quasistatic loading at a constant strain rate of 4.2×10^{-4} /s using cylindrical samples with aspect ratio approximately 2. Microstructure of samples was examined by scanning electron microscope (SEM) and high resolution field emission scanning electron microscope (FESEM) and elemental analysis was carried out by energy dispersive system (EDS) attached with SEM. Vicker's microhardness (H_V) of all as cast alloy samples was measured and average of eight to ten measurements was taken.

3. Results and Discussion

Figure 1 shows the XRD patterns of the as cast alloys A1-A4. Broad bands were observed for all the alloys which indicate their amorphous structure. SEM examination of fine polished bulk samples of the alloys revealed featureless surface, which confirmed the amorphous structure of the alloys. High temperature DSC scans conducted at 40 K/min are shown in Figure 2 for alloys which revealed that alloy A2 undergoes multi-stage crystallization while alloys A1, A3 and A4 have single-stage crystallization. Different parameters

like the glass transition temperature T_g , crystallization temperature T_x , peak temperature T_p , melting and liquidus temperatures T_m and T_l were obtained from the DSC scans. Using these values, a number of thermal parameters such as supercooled liquid region $\Delta T_x = T_x - T_g$, reduced glass transition temperature $T_{rg1} = T_g/T_m$ and $T_{rg2} = T_g/T_l$, parameter $\gamma = T_x/(T_l + T_g)$ [17], parameter $\delta = T_x/(T_l - T_g)$ [18], parameter $\beta = T_g \cdot T_x/(T_l - T_x)^2$ [19] and the parameter $\omega = T_g/T_x - 2T_g/(T_g + T_l)$ [20] were evaluated and summarized in Table 1. The results show that alloy A1 have maximum ΔT_x of 100 K. T_{rg} and ω increases with additives Ti, V and Pd. Maximum T_{rg} was found to be 0.61 for alloy A4. Addition of V enhanced T_{rg} , δ , β and ω considerably. The results indicate that Ti, V and Pd addition have positive effect on GFA. Present alloys have better thermal behavior than many BMGs [14, 21, 22].

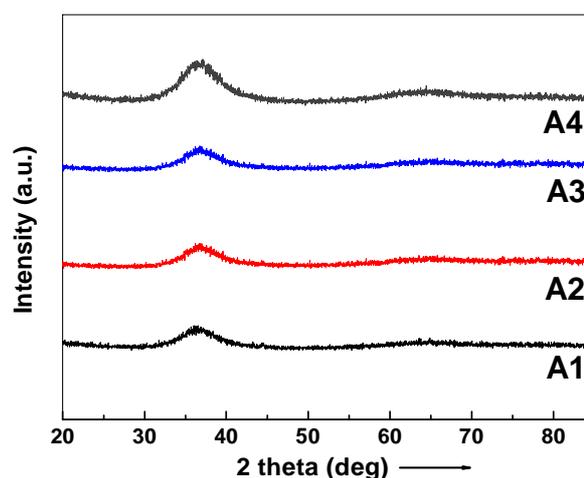


Figure 1. XRD patterns of the as cast alloys A1-A4.

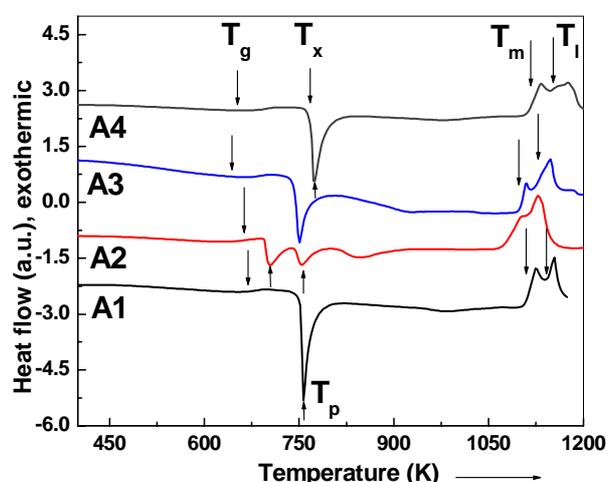


Figure 2. DSC scans of as-cast alloys studied at 40 K/min.

Table 1. Thermal properties (in K) of alloys studied at heating rate of 40 K/min.

Alloy	T_g	T_x	ΔT_x	T_m	T_l	T_{rg1}	T_{rg2}	γ	δ	β	ω
A1	652	752	100	1101	1139	0.592	0.572	0.420	1.544	3.27	0.139
A2	626	696	70	1064	1103	0.588	0.568	0.403	1.459	2.60	0.175
A3	661	743	82	1094	1118	0.604	0.591	0.418	1.626	3.49	0.149
A4	668	760	92	1098	1148	0.608	0.582	0.419	1.584	3.38	0.143

Table 2. Average Vicker's hardness H_v , fracture strength σ_f , strain ϵ_{max} and plastic strain ϵ_p of the alloys.

Alloy designations	H_v	σ_f (GPa)	ϵ_{max} (%)	ϵ_p (%)
A1	438	1.590	6.44	-
A2	442	1.700	10.34	3.9
A3	404	1.956	10.11	3.0
A4	452	1.767	6.26	-

The mechanical properties like Vicker's hardness " H_v " and fracture strength " σ_f ", were measured and the results are summarized in Table 2. Compression testes were conducted at room temperature and the stress strain curves for the alloys A1-A4 are shown in Figure 3. The fracture stress " σ_f " was found to be 1590 MPa with limited plastic strain for the base alloy. It is important to note that fracture strength of alloys A2 is 1700 MPa with highest plastic strain of 3.9 %. It means that Ti has considerable effect on the fracture strength as well as plasticity. Similar effect of Ti addition was observed in a Zr-based alloy [12]. Improvement of plasticity by Ti addition is in agreement with the results previously reported by Jiang et al. [23]. However, Qiang et al. [21] did not find plasticity before fracture in alloys containing 7-10 at. % Ti. The most striking feature of the present study is that addition of V gives the highest fracture stress of 1956 MPa with 3 % plastic strain. Liu et al. [24] reported improvement of plasticity of Zr-Cu-Ni-Al BMG by Nb addition and attributed this phenomenon to the existence of structural inhomogeneity or short range order clusters in the amorphous phase that affects the formation and propagation of shear bands. According to Zhang et al. [25] plastic deformation is mainly dominated by a single major shear band. Pd addition in the alloy A1 enhanced fracture strength from 1590 to 1767 MPa but with limited plasticity. The measured values of the strength are much higher than the alloys reported by Yoshimi et al. [26]. The

compressive shear angles " θ_c " for the present alloys was found to be $\leq 40^\circ$ which are in agreement with previous studies [10-12, 14].

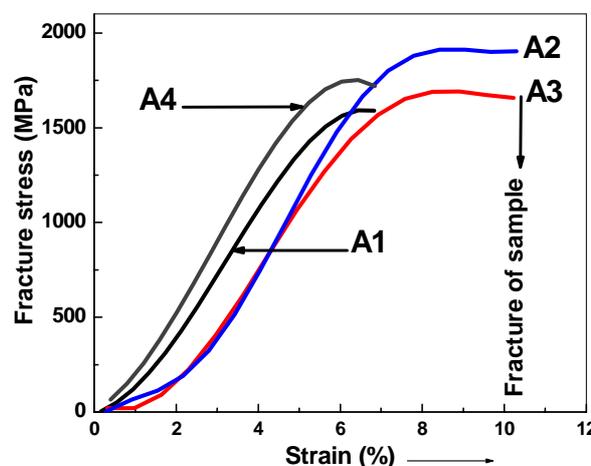


Figure 3. Room temperature stress strain curves for the four alloys A1-A4.

The microstructure of the fractured surfaces, as well as the side views of the plain surfaces of compression tested samples were examined in SEM. Development of intersected, branched, parallel and wavy shear bands were observed over the fractured surfaces of alloy A2 as shown in Figure 4. The presence of intersected shear bands indicates plasticity in alloy A2 and A3. The shear bands in alloys A1 and A4 were mostly parallel in

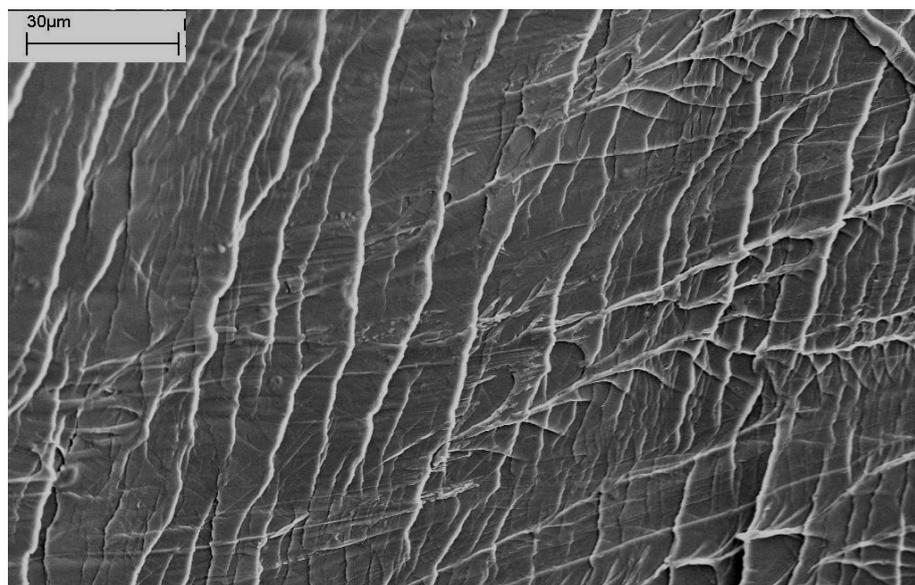


Figure 4. SEM viewgraphs showing shear bands in compression test samples over fracture surface of alloy A2.

Table 3. Estimation of rise in temperature (in K) within shear bands.

Alloy	σ_{f-avg} (MPa)	ε (%)	ρ (g/cm ³)	C_p (J/(kg-K))	ΔT (K)
A1	779.8	3.22	6.630	379.6	898
A2	1143.9	5.10	6.597	382.4	2081
A3	712.7	3.22	6.644	381.8	814
A4	905.0	3.12	6.746	376.8	1000

stead of intersecting and the alloys do not show any plasticity. Another interesting observation was the formation of semicircular shear bands after indentation without any diagonal cracking on fine polished surface of as cast alloy A2 and A3, which also indicate ductility in the alloys. The presence of a large number of shear bands in the alloys A2 and A3 indicate the occurrence of free volumes in the alloys after minor alloying [3]. Veins patterns and liquid droplets within the veins were observed in all the alloys which are the characteristics of BMGs. The increase in the size of the veins and presence of liquid droplets within the veins suggest that the temperature rises considerably during the final adiabatic deformation [14]. Liquid droplets and localized melting in compression tested samples are often linked with the rise in temperature within the shear bands. Estimation of rise in temperature ΔT within shear bands was calculated using the relation $\Delta T = \kappa \sigma_f \varepsilon / \rho C_p$, and the results are summarized in Table 3. Here $\kappa \sim 0.9$ is the heat transfer coefficient, σ_f and ε are the average shear

stress and strain respectively, ρ is the density and C_p is the specific heat of the alloys [27]. The formation of liquid droplets within veins patterns and rise in temperature support adiabatic heat theory of BMGs.

4. Conclusions

The designed base alloy $Zr_{64}Ni_{17}Al_{11.5}Cu_{7.5}$ showed a wide supercooled liquid region of 100 K. Minor alloying with Ti and V enhanced the mechanical properties considerably. Alloying with Ti and V has marked effect as compared to Pd addition and produced plastic strain of 3-4 %. The maximum fracture strength approximately 2 GPa was achieved by V addition. The vein patterns, high density of liquid droplets and localized melting verify instantaneous rise in temperature in compression tested fractured samples. The alloys $(Zr_{0.64}Ni_{0.17}Al_{0.115}Cu_{0.075})_{98}Ti_2$ and $(Zr_{0.64}Ni_{0.17}Al_{0.115}Cu_{0.075})_{98}V_2$ show enhanced plasticity due to intersected shear band formation.

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