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# Optimization for toughness in metalloid-free Ni-based bulk metallic glasses

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The toughness of metalloid-free Ni-based bulk metallic glasses (BMGs) manifests a concentration dependency. In terms of measured notch toughness, $Ni_{40}Cu_2Pd_2Zr_{27.6}Ti_{18.4}Al_{10}$ BMG exhibits the optimal toughness among the six investigated alloys. Its fracture energy is comparable to Fe-based BMGs with optimal toughness. In contrast to the Poisson's ratio, the shear modulus is much more sensitive to composition change in the Ni-based BMGs. Improvement in toughness of Ni-based BMGs roughly scales with reducing the shear modulus or glass transition temperature.


*Keywords:* Bulk amorphous materials; Metallic glasses; Toughness; Nickel alloys; Elastic property

Over the past decade, a variety of new alloys have been discovered for bulk metallic glass (BMG) formation [1]. Among the BMG classes, Ni-based BMGs manifest advantages in several aspects, such as ultrahigh strength (up to ∼3 GPa), high thermal stability due to their high glass transition temperature, $T_g$, and excellent corrosion resistance [2–6]. However, in comparison with Zr-, Cu-, Mg- and Fe-based alloys, the glass-forming ability (GFA) of the Ni-based BMGs remains unsatisfactory [7–9], unless incorporating a noble element such as Pd (as in Ni–Pd–P alloys) [10], which limits its dimensions as a desirable bulk material.

As is well known, BMGs fail without global plasticity under loading in the absence of geometrical confinement [11]. Nonetheless, some BMGs, such as Zr- [12–15] and Ti-based [16] alloys, exhibit high fracture toughness ($K_{IC} > 50$ MPa $m^{1/2}$), even comparable to the conventional engineering alloys in crystalline form. The high toughness of a BMG is associated with the formation of a high density of shear bands at the crack tip, as an extended plastic zone. Recently, it has been suggested that the intrinsic toughness/ductility of BMGs correlates with the Poisson's ratio $\nu$, the ratio of the shear modulus $\mu$ to bulk modulus $B$ owing to a relation of $\mu/B = (3/2)(1 - 2\nu)/(1 + \nu)$, and even the single shear modulus [17–19]. In other words, it is expected that the $\nu$ (or $\mu/B$) or $\mu$ alone can be used as the indicator in the search for tough/ductile BMG alloys. Furthermore, the toughness of metallic glasses (MGs) has a significant concentration dependency, depending not only on the host constituent elements [15,17,18,20–23] but also on the micro-alloying [13]. This implies that toughness improvement in BMGs is potentially possible by virtue of chemistry optimization (or alloy design). In fact, such improvements have been made in some alloy systems [20–23].

As indicated in Ref. [24], the $\nu$ value of Ni-based BMGs is around 0.36, which is comparable to that of tough Zr- and Ti-based glasses ($\nu = 0.35$–$0.37$) [13,15,16,24]. Note that this level considerably exceeds the previously suggested critical value of $\nu$, in the range of ∼0.31–0.32, for brittle-to-tough transition in MGs [18,20]. However, to our knowledge, there are no data available to date on the toughness of Ni-based BMGs, let alone the optimization of alloys for toughness. It is therefore of interest to justify the toughness of Ni-based BMGs and its correlation with the elastic moduli as well as glass transition temperature. As we have noted previously [2–4,7–9], a major challenge for toughness assessment lies in the inadaptability of GFA for testing. For most of the currently developed Ni-based BMGs, the critical diameter ($D_c$) for as-cast glassy rods is limited to less than half a centimeter.

In this work, we are concerned with several metalloid-free Ni-based BMGs with enough GFA to fabricate cylindrical samples 2 mm in diameter, including

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$Ni_{40}Cu_5Zr_{28.5}Ti_{16.5}Al_{10}$ [7], $Ni_{59}Zr_{19}Ti_{11}Nb_6Si_3Sn_2$ [8] and $Ni_{56}Co_3Nb_{28}Hf_8Sn_5$ [9], without consideration for metalloid-containing alloys, such as Ni–P-based alloys, due to their high cost. $Ni_{44}Zr_{27.6}Ti_{18.4}Al_{10}$ alloy, with the optimal GFA of a quaternary Ni–Zr–Ti–Al system as determined by our composition pinpointing [25], is also selected. Based on this alloy, Ni was partially substituted with Cu and Pd to examine the effects of alloying on toughness. The toughness of the investigated BMGs is assessed with notch toughness, $K_Q$, under mode I conditions, measured using single edge-notched bend (SENB) tests. As shown in previous work [18,21–23], such $K_Q$ data are not standard $K_{IC}$ (plane-strain fracture toughness), but they are meaningful in distinguishing the variation in toughness of materials under identical testing conditions. Furthermore, correlations between the toughness, the $\nu$ and $\mu$, and the $T_g$ are discussed with regard to Ni-based BMGs.

Samples for notch toughness measurement were taken from as-cast 2-mm-diameter rods, fabricated by suction casting of arc-melted master alloys. Their amorphous nature was confirmed using X-ray diffraction and thermal analysis. The $T_g$ of the glassy alloys was determined at a heating rate of 20 K $min^{-1}$ in a Perkin-Elmer differential scanning calorimeter (DSC-diamond). Notches with a root radius of 150 μm were made to a depth of 0.45–0.55 of the rod diameter by using a low-speed diamond wire saw. Three-point bend (3 PB) tests for notched samples with a span of 20 mm were carried out in an Instron 5848 instrument under displacement control at 0.1 mm $min^{-1}$. At least seven samples were tested for each alloy. The toughness values were calculated using standard references for this geometry [18,21–23]. Elastic constants, including Young's modulus $E$, bulk modulus $B$ and shear modulus $\mu$, were measured using resonant ultrasound spectroscopy. Cylindrical as-cast rods of 2 mm diameter with an aspect ratio of 0.8–1 were used. Two independent elastic variables, $C_{11}$ and $C_{44}$, were obtained to calculate the elastic constants. For each alloy, three samples taken from different cast rods were measured to ensure the reproducibility of the data. The uncertainty of the measured $B$, $\mu$ and $\nu$ is less than 0.3%, 0.1% and 0.3%, respectively. Compression tests at room temperature were conducted on a Shimadzu AG-1/500 kN testing machine using cylindrical samples of 2 mm diameter with an aspect ratio of ~2. For a given BMG, compression tests were repeated on at least five samples. A strain rate of $\sim 10^{-4}$ $s^{-1}$ was used.

Subjected to 3 PB testing (under mode I loading), overall BMGs fail in the form of complete linear-elastic deformation. For the alloys assessed, the measured $K_Q$, elastic constants, $T_g$ and compressive fracture strength $\sigma_f$, as well as the $D_c$ of BMGs, are listed in Table 1 for comparison. The fracture energy, $G_Q$, of the BMG is calculated using the relationship $G_Q = K_Q^2(1-\nu^2)/E$. As shown in Table 1, the $K_Q$ of the investigated BMGs with different chemistry varies between 26 and 43 MPa $m^{1/2}$. As examples, plastic zone size ($r_p$) in the plane-strain state of $Ni_{56}Co_3Nb_{28}Hf_8Sn_5$ and $Ni_{40}Cu_2Pd_2Zr_{27.6}Ti_{18.4}Al_{10}$ is roughly estimated to be about 4 and 18 μm, respectively, in terms of $r_p = 1/6\pi\cdot(K_Q/\sigma_y)^2$. Such small plastic zone sizes mean that only very-small-scale plastic deformation is involved during crack propagation in the BMGs, which is far inferior to the Zr- [15] and Ti-based [16] BMGs, with $r_p \approx 200$ μm. Moreover, it is noteworthy that substitution of 2 at.% Cu and Pd for Ni in the $Ni_{44}Zr_{27.6}Ti_{18.4}Al_{10}$ glass gives rise to a significant improvement in toughness. The $K_Q$ increases from 26 MPa $m^{1/2}$ for $Ni_{44}Zr_{27.6}Ti_{18.4}Al_{10}$ up to 43 MPa $m^{1/2}$ for $Ni_{40}Cu_2Pd_2Zr_{27.6}Ti_{18.4}Al_{10}$. In addition, as indicated, the Ni–Nb–Sn-based glasses are markedly more brittle than the Ni–Zr–Al-based ones.

In Figure 1, $K_Q$ is plotted against $\nu$ for the six Ni-based BMGs. Although $\nu$ varies by only ~0.5% (0.362–0.364), a tendency for the toughness to increase as $\nu$ increases is shown. Based on the cooperative shear model (CSM) for MGs [24], a relationship was proposed between the shear-flow energy barrier $W$ and $\mu$ for a frozen-in atomic configuration at $T_g$, given by $W(T_g) \propto \mu(T_g)V_m(T_g)$, where $V_m$ is the molar volume. According to this relationship, the toughness of MGs may be expected to scale inversely with $W$. As seen in Table 1, in contrast to $\nu$, $\mu$ is much more sensitive to the chemistry changes of Ni-based BMGs, and varies in the range of 39–53 GPa, with a maximum change of ~36%. Such a strong chemical dependence can be understood in terms of $\mu$ being strongly correlated with an atomic configuration trapped in a potential energy megabasin [26]. Figure 2 shows a plot of $K_Q$ vs. the product of $\mu$ and $V_m$ for the current Ni-based BMGs. As expected, $K_Q$ indeed scales inversely with $\mu V_m$, i.e. a tougher BMG corresponds to a lower shear modulus. Similar correlations and trends are also observed in Fe- [22] and Zr-based [15] BMGs.

As indicated elsewhere [11], the energy of a shear transformation zone in an MG is related to the $T_g$. For transition metals, it is usually on the order of ~20–120$kT_g$, with $k$ the Boltzmann constant. According to the CSM, the $T_g$ is also a measure of $W(T_g)$, since the requirement for the liquid viscosity at $T_g$ ($10^{12}$ Pa s) gives $W(T_g) \approx 37RT_g$ ($R$ is the gas constant) [27]. In other words, both $\mu V_m$ and $RT_g$ are independent measures of $W$, implying that the high $\mu$ or $T_g$ reflects a high

**Table 1.** Critical diameter for glass formation, glass transition temperature, elastic modulus, fracture strength, notch toughness and fracture energy of Ni-based BMGs.

| Alloy | $D_c$ (mm) | $T_g$ (K) | $E$ (GPa) | $B$ (GPa) | $\mu$ (GPa) | $\nu$ | $\sigma_f$ (MPa) | $K_Q$ (MPa $m^{1/2}$) | $G_Q$ (kJ $m^{-2}$) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| $Ni_{56}Co_3Nb_{28}Hf_8Sn_5$ | 4 | 864 | 144.1 | 173.8 | 52.9 | 0.362 | 3050 ± 80 | 26 ± 3 | 4 ± 1 | This work |
| $Ni_{59}Zr_{19}Ti_{11}Nb_6Si_3Sn_2$ | 5 | 845 | | | | | | | | [8] |
| | 2 | 840 | 129.6 | 159.2 | 47.5 | 0.364 | | 33 ± 3 | 7 ± 1 | This work |
| $Ni_{40}Cu_5Zr_{28.5}Ti_{16.5}Al_{10}$ | 5 | 763 | 122.0 | 140.2 | 45.2 | 0.355 | 2300 | | | [7] |
| | 2 | 742 | 108.6 | 132.2 | 39.8 | 0.363 | | 38 ± 7 | 12 ± 4 | This work |
| $Ni_{44}Zr_{27.6}Ti_{18.4}Al_{10}$ | 2 | 754 | 107.6 | 130.4 | 39.5 | 0.362 | 2280 ± 25 | 26 ± 3 | 6 ± 1 | This work |
| $Ni_{40}Cu_4Zr_{27.6}Ti_{18.4}Al_{10}$ | 2 | 738 | 107.9 | 132.3 | 39.6 | 0.364 | 2250 ± 40 | 35 ± 3 | 9 ± 1.5 | This work |
| $Ni_{40}Cu_2Pd_2Zr_{27.6}Ti_{18.4}Al_{10}$ | 2 | 750 | 108.4 | 131.2 | 39.8 | 0.363 | 2330 ± 40 | 43 ± 8 | 16 ± 6 | This work |