Glassy steel optimized for glass-forming ability and toughness

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An alloy development strategy coupled with toughness assessments and ultrasonic measurements is implemented to design a series of iron-based glass-forming alloys that demonstrate improved glass-forming ability and toughness. The combination of good glass-forming ability and high toughness demonstrated by the present alloys is uncommon in Fe-based systems, and is attributed to the ability of these compositions to form stable glass configurations associated with low activation barriers for shear flow, which tend to promote plastic flow and give rise to a toughness higher than other known Fe-based bulk-glass-forming systems. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3184792]

The remarkably high strength, modulus, and hardness of iron-based glasses, combined with their low cost, prompted an effort over the past five years to design amorphous steel suitable for structural applications. The development effort yielded glasses with critical rod diameters as large as 12 mm [1,2] and strengths in excess of 4 GPa.[3] These low-cost ultrastrong materials however exhibit fracture toughness values as low as 3 MPa m$^{1/2}$,[4] well below acceptable toughness limits for structural materials. The low toughness has been linked to their elastic constants, specifically their high shear modulus,[5] which for some compositions exceeds 80 GPa.[3] Recent efforts to toughen these alloys by altering their composition yielded glasses with lower shear moduli (below 70 GPa), which exhibit improved notch toughness (as high as 50 MPa m$^{1/2}$) but compromised glass-forming ability (critical rod diameters less than 3 mm).[5,6] In this study, we implement an alloy development strategy coupled with toughness assessment and ultrasonic measurements to design glassy steel alloys with particularly low shear moduli (below 60 GPa) that demonstrate high toughness (notch toughness in excess of 50 MPa m$^{1/2}$) yet adequate glass-forming ability (critical rod diameters as large as 6 mm).

The link between the high shear modulus and the low toughness of Fe-based glasses rests on the argument that a high shear modulus implies a high resistance to relax stress by shear flow. In turn, this promotes cavitation and early fracture and thus limits toughness. Using a Frenkel-like analysis to study cooperative shearing, Johnson and Samwer[7] arrived at a quantitative expression for the activation energy for shear flow, that is, the energy barrier to initiate plastic flow. Specifically, a relationship was proposed between the shear-flow barrier W and the shear modulus G for a frozen-in atomic configuration at the glass transition temperature T_g, given by $W(T_g) \propto G(T_g) v_m(T_g)$,[7] where v_m is the molar volume, which usually varies little within an alloy family. Aside from their high G, the brittle behavior of these glasses can also be predicted by their high T_g, which for some compositions exceeds 600 °C.[1,2] The glass transition temperature is also a measure of $W(T_g)$, since the requirement for the liquid viscosity at $T_g(10^{12}$ Pa s) gives $W(T_g) \approx 37RT_g$.[7–9] Such high G and T_g therefore imply a high barrier for shear flow, which explains the high resistance of these glasses to relax stress by undergoing shear flow.

In this study, bulk glasses derived from the classic $Fe_{80}P_{12.5}C_{7.5}$ glass-forming system are considered. This system was introduced by Duwez and Lin[10] in 1967, who reported formation of glassy foils 50 μm in thickness. Subsequent investigations revealed that glassy Fe–P–C microwires exhibit a rather high bending ductility.[11] The ductility is associated with a relatively low T_g, reported to be ~400 °C,[10] and a relatively low G. Using the uniaxial yield strength of Fe–P–C of ~3000 MPa and the universal shear elastic limit for metallic glasses of 0.0267,[7] a shear modulus of ~56 GPa can be expected. Owing to such low G and T_g, one would expect the Fe–P–C glass to also exhibit high toughness. The plane-stress fracture toughness of glassy Fe–P–C ribbons was measured to be 32 MPa m$^{1/2}$,[12] a value substantially higher than that of the bulk glasses in Refs. 1 and 2. In 1999, Shen and Schwarz[13] reported development of bulk glassy alloys derived from the Fe–P–C system. Specifically, they demonstrated that alloys in the system (Fe,Co,Cr,Mo,Ga)–P–(C,B) form glassy rods with diameters up to 4 mm. More recently, the alloy systems of (Fe,Mo)–P–(C,B),[5,14] (Fe,Mo)–(P,Si)–(C,B),[15] (Fe,Cr,Mo)–P–(C,B),[5] (Fe,Ni,Mo)–P–(C,B),[16] and (Fe,Co,Mo)–(P,Si)–(C,B) (Ref. 17) have been explored, all of which were found to form bulk glasses with critical rod diameters between 2 and 6 mm. The glass-transition temperatures and shear moduli of these alloys, however, are not particularly low, with T_g as high as 470 °C (Ref. 17) and G of nearly 70 GPa (Ref. 5) reported.

The aim of the present approach was to develop bulk-glassy alloys with T_g and G not much higher than $Fe_{80}P_{12.5}C_{7.5}$, such that a favorable glass-forming ability–toughness relationship is attained. The compositions[18] and critical rod diameters are listed in Table I. Thermal scans are presented in Fig. 1 and T_g's are listed in Table I. The elastic constants of the bulk glasses were evaluated using ultrasonic tests with 25-MHz transducers along with density measurements. The results of the development strategy can be summarized as follows: substitution of 2.5% C by B in $Fe_{80}P_{12.5}C_{7.5}$ yielded glassy rods 0.5 mm in diameter; further substitution of 5.5% Fe by Mo in $Fe_{80}P_{12.5}(C_5B_{2.5})$ yielded 3

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TABLE I. Glass-transition temperature T_g, critical rod diameter d_c, molar volume v_m, shear modulus G, bulk modulus B, and notch toughness K_Q for (Fe,Cr,Ni,Mo)–P–(C,B) glassy alloys.

Composition	T_g (°C)	d_c (mm)	v_m (m^3/mol)	G (GPa)	B (GPa)	K_Q (MPa $m^{1/2}$)
$Fe_{80}P_{12.5}C_{7.5}$	405	0.05[a]	⋯	56[b]	⋯	32[c]
$Fe_{80}P_{12.5}(C_5B_{2.5})$	412	0.5	⋯	⋯	⋯	⋯
$(Fe_{74.5}Mo_{5.5})P_{12.5}(C_5B_{2.5})$	429	3	6.85×10^{-6}	56.94 ± 0.09	145.0 ± 0.3	53.1 ± 2.4
$(Fe_{70}Mo_5Ni_5)P_{12.5}(C_5B_{2.5})$	423	4	6.89×10^{-6}	57.31 ± 0.08	150.1 ± 0.4	49.8 ± 4.2
$(Fe_{68}Mo_5Ni_5Cr_2)P_{12.5}(C_5B_{2.5})$	426	6	6.87×10^{-6}	57.94 ± 0.07	149.7 ± 0.3	44.2 ± 4.6

[a]Critical foil thickness attainable by splat quenching or melt spinning (Ref. 10).
[b]Estimated using the uniaxial yield strength of ~3000 MPa and the universal shear elastic limit of 0.0267 (Ref. 7).
[c]Plane-stress fracture toughness value measured by Kimura and Masumoto using "trouser-leg" type shear tests (Ref. 12).

mm diameter glassy rods; substitution of 10% Fe by 5% Mo and 5% Ni in $Fe_{80}P_{12.5}(C_5B_{2.5})$ yielded 4 mm diameter glassy rods; finally substitution of 12% Fe by 5% Mo, 5% Ni, and 2% Cr in $Fe_{80}P_{12.5}(C_5B_{2.5})$ yielded 6 mm diameter glassy rods. As shown in Table I, glass-forming ability improves dramatically while T_g and G increase only slightly on going from the parent $Fe_{80}P_{12.5}C_{7.5}$ to the bulk-glass compositions.

For the notch toughness tests, 2 mm diameter glassy rods of $(Fe_{74.5}Mo_{5.5})P_{12.5}(C_5B_{2.5})$, $(Fe_{70}Mo_5Ni_5)P_{12.5}(C_5B_{2.5})$, and $(Fe_{68}Mo_5Ni_5Cr_2)P_{12.5}(C_5B_{2.5})$ were utilized.[19] The stress intensity factor for the cylindrical configuration was evaluated using the analysis by Murakami.[20] Considering that the average ligament size in the present specimens was ~1 mm, and taking the yield strength for this family of glasses to be ~3200 MPa,[5,14,16,17] nominally plane strain conditions can be assumed for fracture toughness measurements of <60 MPa $m^{1/2}$, as obtained here. Nevertheless, since sharp precracks ahead of the notches were not introduced in the present specimens the measured stress intensity factors are not standard K_{IC} values. Thus, direct comparison of the notch toughness, K_Q, evaluated in this study with standard K_{IC} values for conventional metals is inappropriate. Nonetheless, K_Q data provide useful information about the variation in the resistance to fracture within a set of uniformly tested materials. Due to inherent critical-casting-thickness limitations, notch toughness measurements using cylindrical specimens with no pre-existing cracks are often reported for amorphous metals.[21,22] More specifically, the notch toughness measurements performed recently for Fe-based glasses by Lewandowski and co-workers[6,23] using specimens with configurations and dimensions similar to the present work are suitable for direct comparison.

The measured notch toughness K_Q, along with the quoted errors representing standard deviations in values, is presented in Table I. Despite the relatively large uncertainty (attributed to processing defects often exceeding the small plastic zone size of these glasses)[23] the data reveal a monotonically decreasing trend in K_Q in going from the least to the best glass former. In Fig. 2 we display this trend by plotting K_Q against the critical rod diameter d_c The plot reveals a roughly linear trend. On the same plot we present K_Q versus d_c for Fe-based glassy alloys developed by Poon and co-workers[2,3,5,24] and tested by Lewandowski and co-workers.[6,23] Although the data for those glasses are more scattered, linear regression reveals a toughness versus glass-forming ability correlation of similar slope but lying well below the correlation shown by the present data.

According to arguments presented earlier, K_Q can be expected to scale inversely with W. Since W is understood to be linearly dependent on Gv_m,[7] one can expect K_Q to decrease with Gv_m. In Fig. 3(a) we plot K_Q against the product of the measured G and v_m for the present alloys. As shown in the plot, K_Q decreases roughly linearly with Gv_m. When d_c is plotted against Gv_m, however [Fig. 3(b)], a near-linear increasing trend is revealed which points to a scaling tendency between d_c and Gv_m, or more precisely, between d_c and W. This scaling tendency suggests that glass-forming ability is

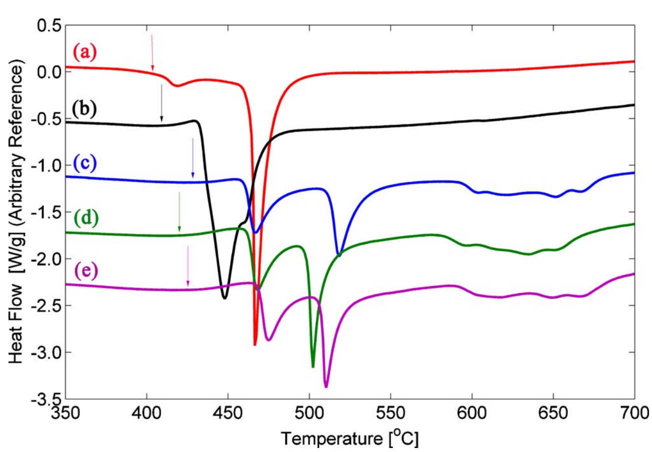

FIG. 1. (Color online) Differential scanning calorimetry at 20 K/min scan rate for (a) $Fe_{80}P_{12.5}C_{7.5}$ (b) $Fe_{80}P_{12.5}(C_5B_{2.5})$, (c) $(Fe_{74.5}Mo_{5.5})P_{12.5}(C_5B_{2.5})$, (d) $(Fe_{70}Mo_5Ni_5)P_{12.5}(C_5B_{2.5})$, and (e) $(Fe_{68}Mo_5Ni_5Cr_2)P_{12.5}(C_5B_{2.5})$. Arrows designate the glass transition onsets.

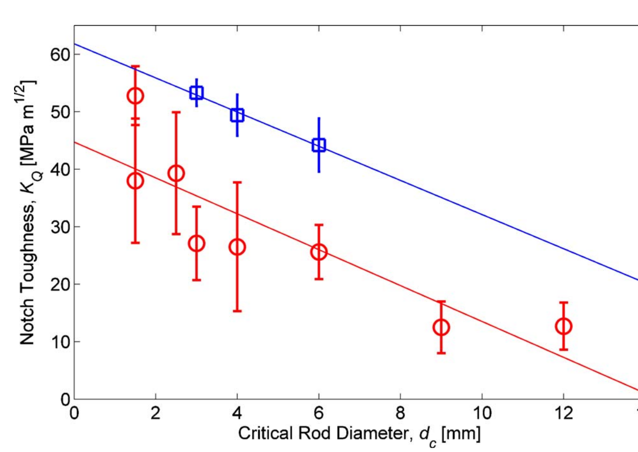

FIG. 2. (Color online) Notch toughness vs critical rod diameter for $(Fe_{74.5}Mo_{5.5})P_{12.5}(C_5B_{2.5})$, $(Fe_{70}Mo_5Ni_5)P_{12.5}(C_5B_{2.5})$, and $(Fe_{68}Mo_5Ni_5Cr_2)P_{12.5}(C_5B_{2.5})$ (□), and for the Fe-based glasses in Refs. 2, 3, 5, and 24 and tested in Refs. 6 and 23 (○). Lines are regressions to data.

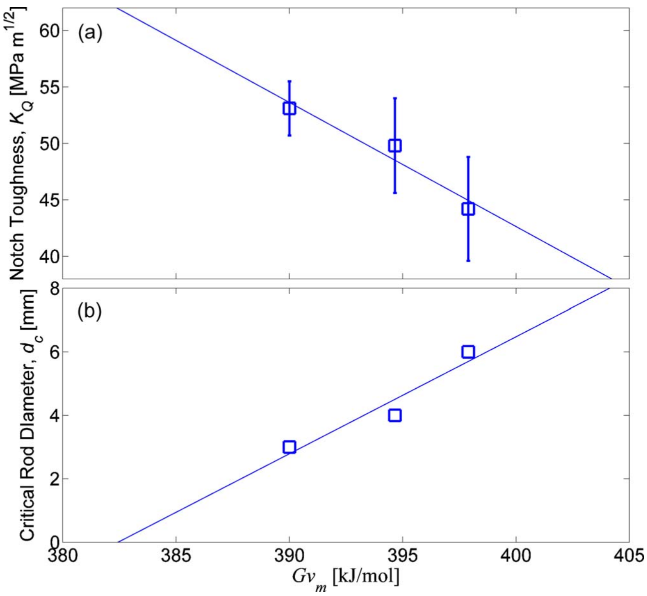

FIG. 3. (Color online) (a) Notch toughness vs Gv_m (b) and critical rod diameter vs Gv_m for $(Fe_{74.5}Mo_{5.5})P_{12.5}(C_5B_{2.5})$, $(Fe_{70}Mo_5Ni_5)P_{12.5}(C_5B_{2.5})$, and $(Fe_{68}Mo_5Ni_5Cr_2)P_{12.5}(C_5B_{2.5})$ (□). Lines are regressions to data.

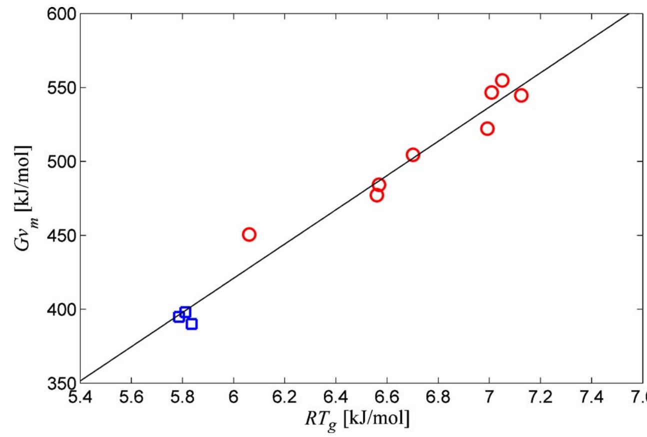

FIG. 4. (Color online) Gv_m vs RT_g for $(Fe_{74.5}Mo_{5.5})P_{12.5}(C_5B_{2.5})$, $(Fe_{70}Mo_5Ni_5)P_{12.5}(C_5B_{2.5})$, and $(Fe_{68}Mo_5Ni_5Cr_2)P_{12.5}(C_5B_{2.5})$ (□), and for the Fe-based glasses in Refs. 2, 3, 5, and 24 tested in Refs. 6 and 23 (○). The line is a regression to all data.

enhanced by increasing W. The interdependence of glass-forming ability and toughness through W explains the trend of monotonically and near-linearly decreasing K_Q with increasing d_c (Fig. 2). Furthermore, the relatively low K_Q for a given d_c demonstrated by the previously developed alloys suggests that their glass-forming ability arises from increasing W to levels that considerably degrade toughness.

As discussed by Ponnambalam *et al.*,[25] the alloy development strategy that led to the bulk-glasses in Refs. 1 and 2 relied on attaining structurally rigid liquid configurations through heavy alloying. Structural reinforcement of the equilibrium liquid, they argue, is associated with the formation of a "backbone" liquid structure which gives rise to higher T_g and higher isoconfigurational G. Ponnambalam *et al.*[25] therefore imply that such alloy development strategy relies on dramatically increasing W. In the present approach, bulk-glass-forming compositions were derived directly from $Fe_{80}P_{12.5}C_{7.5}$, a tough yet marginal glass former exhibiting a rather low T_g and G. As shown in Table I, the present compositions are designed to improve glass-forming ability with respect to the parent $Fe_{80}P_{12.5}C_{7.5}$ without raising T_g and G. To put this argument into perspective, in Fig. 4 we plot Gv_m versus RT_g data[26] for the present and previously developed Fe-based glasses. The combined data reveal a one-to-one correspondence between Gv_m and RT_g that extends over a broad range. Such correspondence is expected, since both Gv_m and RT_g are independent measures of W. Interestingly though, the data for the present glasses lie at the low-end of the correlation, supporting that the configurations formed by the present glasses are indeed associated with lower W.

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