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Liquid-like platinum-rich glasses

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Bulk platinum-rich glasses exhibiting high bulk moduli and Poisson ratios are introduced. A bulk modulus of 217 GPa and a Poisson's ratio of 0.43 are measured, the highest values reported to date for a metallic glass. The present glasses demonstrate an unusual capacity for "liquid-like" deformation characterized by low resistance to shear flow and high resistance to cavitation, enabling extensive bending ductility in the absence of fracture. An indirect estimate of the fracture toughness yields a value of ~125 MPa m$^{1/2}$.

Keywords: Amorphous metal; Bulk metallic glass; Precious metals; Jewelry

Noble-metal glasses have been developed and studied extensively over the past few years [1–3]. Glass-forming alloys based on platinum, palladium and gold were sought owing to a demand for scratch-resistant precious metals for application in jewelry, watches and luxury goods. During their development it was inadvertently discovered that noble-metal glasses exhibit a very high Poisson's ratio v, along with a high bulk modulus B and a low shear modulus G. As v, which is directly related to B/G, approaches a value of 0.5, the glass would behave like an incompressible liquid (as implied by an infinite B and/or zero G). Poisson's ratio values as high as 0.42 have been reported for noble-metal glasses [4,5], higher than any other metallic glass alloy family. High values of B/G and v indicate a low resistance to shear flow (low G) together with a high resistance to cavitation (high B), and thus one can naturally anticipate a high resistance to fracture, i.e. a high fracture toughness [6]. Indeed, a high fracture toughness value of 200 MPa m$^{1/2}$ was recently reported for a palladium-rich glass [5]. The unusually high noble-metal content in that palladium glass (~80 at.% Pd) is believed to be responsible for its high Poisson's ratio and exceptionally high toughness.

Platinum glasses reported to date have been optimized to meet the "platinum alloy" jewelry hallmark, which certifies alloys comprising 85 wt.% platinum (Pt850) [1]. The atomic concentration of platinum required to meet this weight fraction criterion is typically below 60%. One example is alloy $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ (at.%), which comprises 85 wt.% platinum and is capable of forming glassy rods 16 mm in diameter. This alloy exhibits $B/G \approx 6$ and $v = 0.42$, along with a measured fracture toughness of ~80 MPa m$^{1/2}$ [4]. In the present work, platinum-rich glasses were sought with atomic fractions of platinum around 75%. Specifically, the glass-forming compositions developed in this work are designed to meet the "pure platinum" standard of fineness hallmark, which certifies alloys comprising 95 wt.% platinum (Pt950) [7]. Due to the very high Pt concentration, the present glasses demonstrate fairly "marginal" glass-forming ability (critical rod diameters up to ~2 mm), but exhibit $B/G \approx 7$ and $v = 0.43$, the highest values reported to date for a metallic glass. Consequently, the glasses demonstrate unusual "liquid-like" deformation characteristics exemplified by a large bending ductility accommodated by extensive shear banding without cracking.

To achieve bulk-glass formation at such a high Pt content, microalloying has been explored. The role of minor alloying additions on the structure and properties of metallic glass-forming systems is well documented [8]. Minority additions of <1 at.% have been reported to dramatically influence glass-forming ability, while kinetic, mechanical and magnetic properties of metallic glass formers are also found to be considerably affected [9]. The origin of this microalloying effect is believed not

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to be chemical but rather topological, relating to the structural organization of the glass at the atomic level. Interestingly, the enhancement in glass-forming ability by microalloying is found to correlate well with changes in the medium-range order of the atomic structure [10]. In the present study, the influence of minor additions of late-transition metals in a Pt-rich metal/metalloid system is explored. Dramatic improvements in glass formation with alloying additions of as little as 0.25 at.% are observed.

Alloy ingots were prepared by induction melting mixtures of the appropriate amounts of Pt of 99.95% purity and other elements of equal or better purity in quartz tubes sealed under high-purity argon. The ingots were fluxed with dehydrated boron oxide at ~800 °C under high-purity argon for about 1000 s. Glassy cylindrical rods were formed by remelting the ingots and injecting into thin-walled capillary quartz tubes (with wall thicknesses that are approximately 10% of the inner diameters) under high-purity argon and then quenching rapidly in water. The amorphous structure of the rods was verified by differential scanning calorimetry and X-ray diffraction with Cu K_α radiation.

To explore glass formation at very high Pt weight fractions, combinations of Pt with low atomic weight metalloids was investigated. Combining small fractions of P, B and Si with Pt was found to promote glass formation. Specifically, a glass-forming eutectic was found at composition $Pt_{76.5}P_{18}B_4Si_{1.5}$ (at.%). Alloy $Pt_{76.5}P_{18}B_4Si_{1.5}$ comprises 96.2 wt.% Pt, and is found capable of forming glassy rods 0.5 mm in diameter. The thermal scan of glassy $Pt_{76.5}P_{18}B_4Si_{1.5}$ is presented in Figure 1a, and the associated glass-transition, crystallization, solidus and liquidus temperatures, T_g, T_x, T_s, and T_l, are listed in Table 1. The quaternary Pt/metalloid composition allows for just 1.2 wt.% substitution of Pt by another element to enhance glass formation while satisfying the 95 wt.% constraint.

Elemental substitutions of 1.2 wt.% Pt by Ni and Cu were found to enhance glass formation. Specifically, Pt950 compositions $Pt_{74.4}Ni_{2.1}P_{18}B_4Si_{1.5}$ and $Pt_{74.5}Cu_2P_{18}B_4Si_{1.5}$ (at.%) were found capable of forming glassy rods 0.7 and 0.9 mm in diameter, respectively. The thermal scans are presented in Figure 1, and the associated T_g, T_x, T_s and T_l are listed in Table 1. Overall, the effect of Cu substitution in $Pt_{76.5}P_{18}B_4Si_{1.5}$ (at.%) on glass formation was more profound, as an increase in the critical rod diameter by nearly a factor of 2 is achieved. The effect of incorporating a second late-transition metal was further explored. Further improvements in glass formation were observed by substituting small fractions of Cu by Ni and Ag in Pt950 composition $Pt_{74.5}Cu_2P_{18}B_4Si_{1.5}$ (at.%). Specifically, Pt950 compositions $Pt_{74.5}Cu_{1.2}Ni_{0.8}P_{18}B_4Si_{1.5}$ and $Pt_{74.7}Cu_{1.5}Ag_{0.3}P_{18}B_4Si_{1.5}$ (at.%) were found capable of forming glassy rods 1.3 and 2.0 mm in diameter, respectively. The thermal scans are presented in Figure 2, and the associated T_g, T_x, T_s and T_l are listed in Table 1. Interestingly, incorporating just 0.3 at.% Ag in $Pt_{74.5}Cu_2P_{18}B_4Si_{1.5}$ (at.%) is shown to have a very dramatic effect on glass formation, as the critical rod diameter increases by more than a factor of 2.

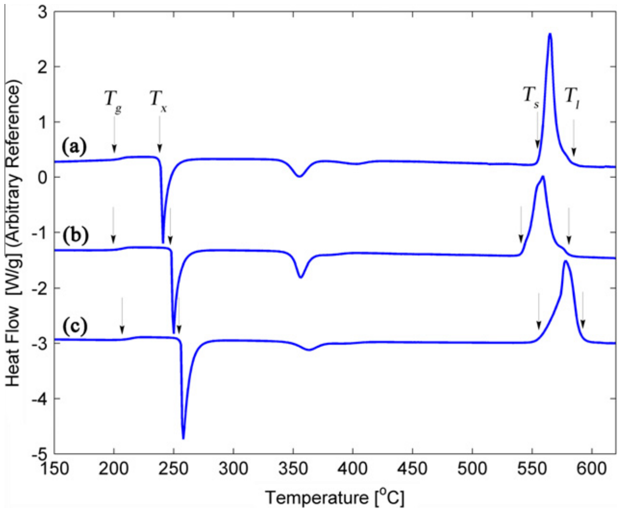

Figure 1. Differential scanning calorimetry at 20 K min^{-1} scan rate for (a) $Pt_{76.5}P_{18}B_4Si_{1.5}$, (b) $Pt_{74.4}Ni_{2.1}P_{18}B_4Si_{1.5}$ and (c) $Pt_{74.5}Cu_2P_{18}B_4Si_{1.5}$. Arrows designate T_g, T_x, T_s and T_l.

The capacity for "liquid-like" deformation of glassy $Pt_{74.7}Cu_{1.5}Ag_{0.3}P_{18}B_4Si_{1.5}$ (at.%) was assessed by measuring its elastic constants. The shear and longitudinal wave speeds were measured ultrasonically on an amorphous rod 1.5 mm in diameter and 3 mm in length using pulse-echo overlap with 25 MHz piezoelectric transducers. The density was measured by the Archimedes method, as given in the American Society for Testing and Materials standard C693-93. A density of 17.23 g cc^{-1} was measured, and the shear and bulk moduli were estimated to be 32.4 GPa and 216.7 GPa, respectively. The bulk modulus of the present glass is unusually high; it actually surpasses the bulk moduli of other, much stiffer, metallic glasses, like ferrous metal glasses. For example, this value exceeds that of amorphous $Fe_{49}Cr_{15}Mo_{14}C_{19}B_2Er_1$ of 207 GPa, one of the stiffest bulk metallic glasses known, having a strength in excess of 4 GPa [11]. Owing to such a high bulk modulus and a relatively low shear modulus, the glass exhibits $B/G = 6.7$ and $\nu = 0.43$, also the highest reported to date. The very high B, B/G and ν for this glass point to a large capacity for "liquid-like" deformation, associated with a tendency to preferentially accommodate stress by shear flow rather than cavitation and cracking.

The propensity for shear flow is evidenced by its capacity to deform plastically in bending under large strains without forming cracks. Bending is recognized to be the most suitable loading geometry to assess the ability of a glass to fail plastically under an opening stress without undergoing fracture. In uniaxial tension, uniform tensile loading gives rise to a flow instability within an operating shear band, which inevitably leads to incipient cavitation and spontaneous fracture irrespective of the toughness of the glass [5]. In bending, by contrast, the glass is subjected to tension only on one side of the neutral axis and the stress decreases linearly to zero as the neutral axis is approached, thereby providing flow stability as shear bands propagate towards the neutral axis. As presented in Figure 3a, a large plastic strain can be attained by bending a glassy $Pt_{74.7}Cu_{1.5}Ag_{0.3}P_{18}B_4Si_{1.5}$ rod about 1 mm in diameter.