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Amorphous phase stability and the interplay between electronic structure and topology

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ABSTRACT

It is well-known that the stability of Pd-Si amorphous alloys can be improved substantially by minor additions of alloying elements such as Cu and Ag. Such improvement in stability is explained herein, whereby microscopic models based on efficient atomic packing and electronic structure were applied to the results of first principles simulations of $Pd_{82}Si_{18}$, $Pd_{77.5}Si_{16.5}Cu_8$ and $Pd_{75}Si_{15}Cu_7Ag_3$ metallic glasses. It was revealed that while the atomic packing model fails to unequivocally explain the stabilizing effect of the binary Pd-Si alloy due to minor additions of Cu and/or Ag, the contribution of electronic states with lower energies to the stability of the amorphous structure is increased markedly. Further, the observed enhancement in the compressive ductility as a result of the addition of Ag to the $Pd_{77.5}Si_{16.5}Cu_8$ alloy can be correlated to the combined effects of an increased heterogeneity in the local topology, weakened covalency and, hence, reduced directionality of Pd-Pd bonds as well as enhanced metallicity in the $Pd_{75}Si_{15}Cu_7Ag_3$ amorphous alloy. The analysis was further expanded to amorphous alloys where their characteristic binary prototypes are synthesised from late transition metals and non-metals as well as those comprising early transition metals and late transition metals. The findings shed light on the effects of minor alloying on the cooperative and competitive relationship between the topological and electronic structure of amorphous alloys.

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1. Introduction

It is well-known that certain metallic liquids can be undercooled to form a glass via the suppression of nucleation and growth of crystalline phases. It is generally accepted that an enhancement in glass forming ability (GFA) correlates well with a major thermodynamic criterion termed the reduced glass transition temperature T_{rg}, defined as the ratio of glass transition temperature T_g to liquidus temperature T_l [1]. As T_{rg} increases, the thermal window for crystal nucleation becomes narrower, thereby reducing the tendency of the metallic liquid to crystallize. Since the discovery of the first metallic glass in 1960, various empirical rules have been proposed for explaining the stabilization of supercooled liquids leading to an improvement in GFA, such as opting for multicomponent alloys comprising constituents that have significantly different atomic sizes and a negative enthalpy of mixing [2]. While the microscopic mechanisms underlying such rules are not fully understood, they may, in-part, be attributed to an efficient packing of

the local topology achieved for specific radius ratios between solute and solvent atoms (increasing alloy viscosity, hence hindering nucleation kinetics) [3], chemical bonding due to strong interactions between unlike atoms [4] or electronic structure [5,6]. Using a nearly-free-electron model, Nagel and Tauc [7] proposed that the stability of metallic glass is due to the contribution of electronic structure, whereby a Mott's pseudogap emerges at the Fermi energy (E_F) if the diameter of the Fermi sphere ($2K_F$) equals the wave vector at which the structure factor is maximum (k_p). The development of the pseudogap at E_F decreases the electronic energy and stabilizes the amorphous phase over allowing nucleation to occur in the supercooled liquid. This model was used to explain the improved GFA of a number of metallic glasses. For example, $Pd_{40}Ni_{40}P_{20}$ forms a bulk metallic glass (BMG) with a critical casting diameter (d_c) of 3 mm. However, a significant increase in d_c (>40 mm) was achieved by simply replacing Ni in this alloy with 30 at.% Cu and 2.5 at.% Pd (i.e. $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$) [8,9]. While the total density of states of both alloys showed similar pseudogaps at slightly higher energy than E_F, the partial 4d orbital of Pd in the latter was suppressed more markedly than the former near E_F, supporting this nearly-free electron model [9]. Moreover, in

contrast to $Pd_{40}Ni_{40}P_{20}$, the 4d band of Pd in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, possesses a large structure in lower energy regions which is also reflected in the total density of states (DOS) [9] and, along with the more suppressed pseudogap near E_F, is recognized as the source of higher phase stability and better GFA in the latter. However, while $Pd_{40}Ni_{40}P_{20}$ remains a superior glass-former compared to the slightly modified composition of $Pd_{40.5}Cu_{40.5}P_{19}$ [10], the DOS of the latter shows a markedly deeper pseudogap at the E_F. This result demonstrates that the nearly-free electron model cannot be applied in this case and neither can the efficient packing model as the atomic radii of Ni and Cu are almost the same. In contrast, the greater amorphous phase stability of $Pd_{40}Ni_{40}P_{20}$ over $Pd_{40.5}Cu_{40.5}P_{19}$ can only be explained by the appearance of a shoulder at the lower energies in the DOS of the latter indicating the existence of a higher number of bonding states at lower energies, whereby the electronic contribution to the total energy of the glass is reduced and a greater stability is achieved [10].

Further, the first avenue generally adopted for improving the stability of the supercooled liquid and GFA of an alloy is by the minor addition of other elements [11]. For example, the addition of 1.5 at.% H to a ZrCuAl alloy resulted in an increase in d_c from 2.8 to 5.1 mm [12]. This improvement in amorphous phase stability was also accompanied by a 40% increase in the strain to failure in uniaxial compression of the hydrogenated alloy. For this H-doped BMG, an atomic-scale insight into the underlying local topology, dynamics, electronic structure and chemical bonding was obtained by first principles molecular dynamics (MD), which revealed that while the addition of 1.5 at.% H decreases the icosahedral order of the supercooled liquid over the entire temperature range, it also decreases the diffusivity of the metallic constituents over the temperature range where heterogeneous nucleation is expected to occur. In this tradeoff between local structural stability and depressed crystal nucleation dynamics, the latter dominates in the H-doped alloy and the capacity for glass formation is enhanced. In addition, H was found to increase iconicity of the base glassy alloy, promote heterogeneity in the local structure and increase metallicity. In the competition between these opposing tendencies of chemical bonding and local structure to determine mechanical properties, the latter prevails and explains the experimentally-observed improvement in compressive ductility [13].

Recently, Zhang et al. [14] reported a range of P-free BMGs based on the $Pd_{82}Si_{18}$ binary composition, whereby the addition of Cu ($Pd_{77.5}Si_{16.5}Cu_6$) followed by further addition of Ag ($Pd_{75}Si_{15}Cu_7Ag_3$) increased d_c from less than 1 mm to 3 and 10 mm, respectively. The reported T_{rg} also increased from 0.556 for the binary alloy to 0.578 and 0.604, respectively. Here, the minor addition of Ag appears to be of particular significance, where improved GFA, accompanied by enhanced compressive strength and ductility, were observed. The aim of the present work is to carry out first principles molecular dynamics (MD) to better understand the influence of local atomic order, diffusivity and electronic structure on the notable improvement in both GFA and compressive ductility of the Pd-Si glass-forming binary alloy due to the addition of Cu and Ag [14].

2. Method

The atomic configuration of the $Pd_{82}Si_{18}$, $Pd_{77.5}Si_{16.5}Cu_6$ and $Pd_{75}Si_{15}Cu_7Ag_3$ glass forming alloys were simulated using ab initio MD. The software of choice was VASP [15] implementing the projector augmented wave method [16]. The exchange and correlation energies were approximated as a generalized gradient functional [17]. Γ point was used to sample the Brillouin Zone in the simulation of melting and quenching processes and to calculate the electronic structure, the k-point sampling was increased to $2 \times 2 \times 2$. The Fourier transform grids were reduced to ¾ during the

simulations whereas, for electronic structure calculations, a full grid was adopted. A cubic cell was considered with periodic boundary conditions and dimensions of order 15 Å containing 200 atoms. Each system was equilibrated at 1300 K and quenched to room temperature with a cooling rate of 0.66×10^{13} K/s at 3000 time steps per 100 K [18,19]. The equilibrium volume at any given temperature was found by implementing Parrinello-Rahman dynamics [20] with Langevin thermostat [21] at zero pressure for up to 2 ps followed by maintaining constant volume and temperature using Nose thermostat [22] in a canonical ensemble [13]. Simulations were also carried out on the Pd77Si32Cu5.5H1.5 alloy for understanding the effects of H doping in Pd-Si-Cu alloys and other alloy systems [12,13].

3. Results

3.1. Structure: mean packing density and local structural fragmentation

Fig. 1 shows the partial pair distribution functions ($g_{\alpha\beta}$) averaged over the last one thousand simulation steps at 300 K. The most abundant bond length ($r_{mode}^{\alpha\beta}$) between a central α atom and β atoms located in the first shell around the former, is represented by the abscissa of the first peak of $g_{\alpha\beta}$ and given in Table 1. To evaluate the symmetry of the distribution, the mean weighted bond length ($r_{mean}^{\alpha\beta}$) by $g_{\alpha\beta}$ and bounded by its first minimum ($r_{cutoff}^{\alpha\beta}$) is also listed in Table 1. Throughout the text, bond length refers to the mode ($r_{mode}^{\alpha\beta}$) of the bond between two atoms.

It is found that Pd-Pd and Si-Si modes in the base alloy, as well as the Cu- and (Cu + Ag)- containing alloys, are shorter than the means, illustrating non-Gaussian and slightly left-skewed bond length distributions. However, the Pd-Si bond length, which is larger than its mean in the base alloy (right-skewed), becomes shorter than its mean due to the addition of Cu and Ag. While the most common Pd-Pd bond length ($r_{mode}^{\alpha\beta}$) remains essentially unchanged with the addition of Cu and Ag, the Pd-Si bond length is decreased (much closer to the accepted atomic radii of Pd and Si) and that of Si-Si is increased well beyond that expected of the atomic radius of Si, indicating that true Si-Si atomic contact has likely been diminished in the Cu- and (Cu + Ag)-containing alloys and the atomic packing of these structures is more dense/efficient with respect to the majority elements, Pd and Si. Compared to the ternary $Pd_{77.5}Si_{16.5}Cu_8$ alloy, the Pd-Cu and Si-Cu bond lengths in the $Pd_{75}Si_{15}Cu_7Ag_3$ quaternary alloy do not change. In the hydrogenated Pd77Si32Cu5.5H1.5 alloy, the Pd-Si and Pd-Cu bond lengths are decreased and increased, respectively, and the Si-Si bond length remains essentially unchanged.

The structure of each of the alloys was analyzed further based on coordination numbers (CN), which are proportional to the area under the first peaks and represent the local packing density around a given atomic species. The calculated CNs listed in Table 2 indicate that the addition of Cu to the $Pd_{82}Si_{18}$ base alloy does not significantly change the total CN around Pd and Si. The addition of Ag relative to the $Pd_{77.5}Si_{16.5}Cu_8$ alloy results in a minor decrease in the total CN around Pd by 3.8% and an increase around Si by 4.6%.

As an alternative approach to analyzing the topology of the amorphous systems, the distribution of Voronoi polyhedral [23] formed by the nearest neighbors of a central atom is calculated via tessellation of the atomic configuration. Such polyhedra are identified by a Voronoi signature given as $< v_3, v_4, v_5, v_6 >$ where v_n is the number of faces having n edges. The summation of all v_n is an alternative way of expressing CN ($= v_3 + v_4 + v_5 + v_6$). Surfaces having an area less than 1% of the total area of the Voronoi cell