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Designing aluminum-rich bulk metallic glasses via electronic-structure-guided microalloying

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ABSTRACT

Aluminum-based bulk metallic glasses (BMGs) are notoriously difficult to make, owing to the relatively low glass forming ability (GFA) of Al-rich alloys. As a result, the search for Al-rich BMGs has resorted to adjusting the alloy composition through minor additions of alloying elements. But such a "microalloying" strategy faces yet another challenge well known to the BMG community: GFA often shows a strong composition dependence but the underlying reason remains poorly understood. Here we tackle these two problems using an electronic-structure-informed approach, in lieu of relying solely on trial and error. Co and La are introduced into the Al–Ni–Y base alloy to partially substitute for Ni and Y, respectively, and their effects on the Fermi level and Brillouin zone size are monitored using spectroscopy experiments. The Co and La contents are tailored to approach a favorable condition that minimizes the electronic density of states at the Fermi level, a recipe to elevate the stability of the amorphous phase. This approach guided us to land an optimal composition in the quinary alloy system, $Al_{86}Ni_{6.75-}Co_{2.25}Y_{3.25}La_{1.75}$, where fully glassy rods reached a record size of 1.5 mm in diameter via copper mold casting. The electronic structure perspective thus appears to be a useful knob to turn to push the envelope of GFA accessible to Al-rich BMGs.

1. Introduction

Aluminum-based metallic glasses represent an important family of amorphous metals. Of particular interest is their light weight, and correspondingly their exceptional specific strength, which is twice that of conventional crystalline aluminum alloys [1–3]. Their good corrosion resistance is also attractive for many engineering applications [4,5]. As a result, there has been a relentless pursuit of Al-rich bulk metallic glasses (BMGs) ever since the discovery of melt-spun Al-based metallic glass ribbons in 1988 [4,6]. Unfortunately, Al-based BMGs have turned out to be the most difficult to find, lagging far behind those based on other engineering metals such as Cu, Fe, Mg and Zr, for which the diameter of fully glassy cast rods is now easily of the order of 10 mm. In comparison, the largest diameter obtained so far for Al-rich glasses is merely ~1 mm [7], barely reaching the borderline that qualifies them as BMGs.

A large number of studies [8–11] have aimed at overcoming this bottleneck problem of low glass-forming ability (GFA), only to discover that the various empirical guidelines [12–14] learnt from prior experience with other BMG alloy systems are of limited use in Al-rich alloys. Generally speaking, minor alloying addition (often dubbed as "micro-alloying" [15]) is left as the primary approach to elevate the GFA [7,16–24]. For example, ~2 at% replacement of Ni or Y by Co or La in $Al_{86}Ni_8Y_6$ provided a two-fold increment in GFA, leading to the recent discovery of Al–Ni–Y–Co–La MGs approaching 1 mm in size [7,16]. It was also reported that the addition of as little as 0.5 at% of Ti or V dramatically improves the GFA in $Al_{88}Y_7Fe_5$ alloys [24]. The marked GFA improvement could be related to the beneficial effects of microalloying on increasing liquid phase stability and/or suppressing crystalline phase formation [15,25,26]. A specific rationalization purports that there may be an extraordinarily efficient atomic packing structure in the glass [27,11] at some specific compositions. However, the effect of this atomic packing rationale is difficult to quantify. For example, adding a small amount of Co (and La) atoms into the $Al_{86}Ni_8Y_6$ alloy [28] did not change the short-range order around Ni (and Y) in terms of coordination number and bond distance, as measured by X-ray absorption spectroscopy (XAS). For the $Al_{88}Y_7Fe_5$ metallic

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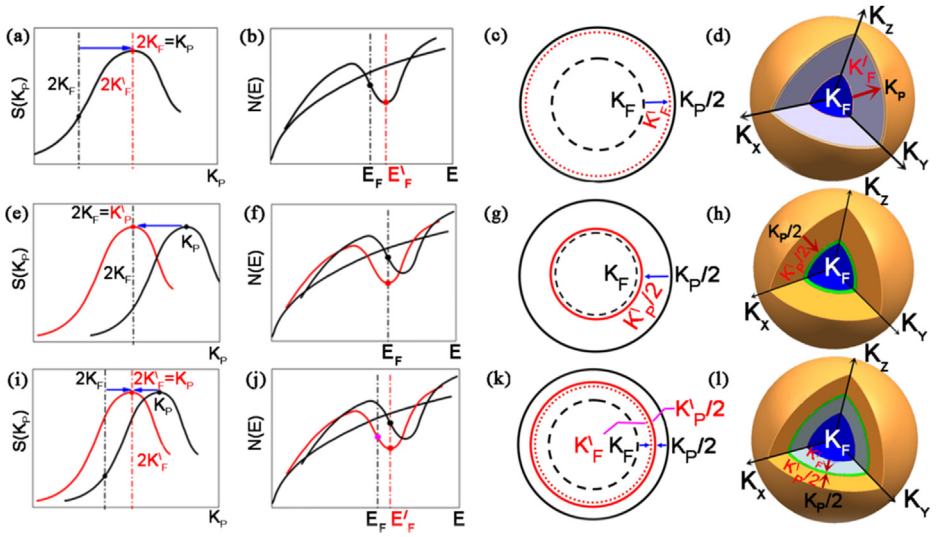

Fig. 1. Fermi sphere - Brillouin zone interactions. Schematic diagrams of the structure factor as a function of wave number, for three cases before and after substitutional alloying: (a) K_P remains constant, K_F changes; (e) K_F is constant, K_P changes; (i) K_P and K_F simultaneously change. The direction of change is marked with the blue arrow. The change of K_F (black to red dashed vertical line in (a)) by adding TM atoms, or of K_P (in (e)) by adding RE atoms, or of both (in (i)) by adding TM and RE atoms, eventually establishes $2K_F=K_P$. (b) (f) (j) Schematic diagram of the density of states, $N(E)$ at the Fermi level, corresponding to each of the above three scenarios. (c) (g) (k) Two-dimensional schematic diagram of Fermi sphere-Brillouin zone interaction. Dashed lines mark the value of K_F whereas the solid lines the value of $K_P/2$; black for the Al-TM-RE ternary system and the red for the RE(TM)-alloying Al-TM-RE system. (d) (h) (l) Three-dimensional schematic diagram of Fermi sphere-Brillouin zone interaction. The yellow ball indicates the quasi-Brillouin zone while the blue ball represents the Fermi surface.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

glass, extended X-ray absorption fine structure (EXAFS) data were also insensitive to the small amounts of Zr and Hf (0.53%) addition that changed the GFA [22]. The lack of quantitative guidelines prompted us to ponder from a different angle: can the glass stability and GFA be further optimized from the perspective of electronic structure changes, which can be monitored through experiments?

The role of electronic structure in the stability of MGs has long been recognized, dating back to the 1970's. For instance, Nagel and Tauc [29] proposed a Hume-Rothery stabilization mechanism based upon the Fermi sphere - Brillouin zone interaction: extra stability arises when the Fermi sphere with a diameter of $2K_F$ is in touch with the boundary of the pseudo-Brillouin zone, which has a diameter of K_P in reciprocal space. This means that when $2K_F=K_P$, the phase stability is enhanced, which coincides with a minimum of the electronic density of states at the Fermi level, E_F [30–33]. For the Al-transition metal (TM) - rare earth (RE) glass-forming systems, the diameter of the Fermi sphere ($2K_F$) is largely affected by the *sp-d* electron hybridization between Al atoms and TM atoms, whereas the diameter of the pseudo-Brillouin zone (K_P) is determined by the static atomic packing structure controlled primarily by the Al atoms and RE atoms. This line of reasoning suggests that it may be possible to improve GFA by adjusting the TM and RE contents to fine tune the K_F and K_P towards the optimal condition of $2K_F=K_P$.

The purpose of this paper is to test microalloying additions from this electronic structure perspective. The Al–Ni–Y ternary is selected as the base alloy, as most of the previously reported BMG-forming quinary alloys were derivatives from this systems [7,16]. We then consider micro-alloying using two types of minor additions, TM (using Co to substitute for Ni) and RE (La to substitute for Y): Co (one less 3*d* electron than Ni) to tune the degree of electron hybridization, and the larger-sized La to alter the static atomic structure and Brillouin zone size. We use X-ray photoelectron spectroscopy (XPS), electron energy-loss spectroscopy (EELS) and X-ray diffraction (XRD) spectrometry to monitor the effects of microalloying on K_F and K_P. The information obtained from experiments is then used as feedback to guide the direction of composition adjustment via further microalloying, moving towards $2K_F = K_P$. When this condition is satisfied as much as possible, one may elevate GFA and locate the best BMG composition in the Al-rich quinary system.

2. Background: model and projected trend

2.1. Fermi sphere–Brillouin zone interaction

For amorphous metallic alloys, their formation and stability were found to be influenced by a spherical-periodic resonance [34] between the electronic system and the static atomic structure. In the electronic system, the diameter of the Fermi sphere, $2K_F$, can be derived from a near-free-electron model [34]:

$$2K_F = 2\sqrt[3]{2\pi^2 n_0 Z} \tag{1}$$

where n_0 is the mean atomic number density and Z is the mean valence. For the Al-TM-RE glass-forming system, the electron hybridization effect between the Al-3p state and the TM-3d state is significant, leading to a much lower density of conduction electrons that affects the Fermi sphere-Brillouin zone interaction [35]. In such a case, the real electronic density of states deviates from the nearly-free electron behavior in Eq. (1), and comes instead from the composite contribution from both the nearly-free electrons (Z_{FEM}) and the hybridization electrons (Z_{hyb}) between Al-3p and TM-3d. The diameter of the Fermi sphere, $2K_F$, is then given by Ref. [36]:

$$2K_F = 2K_F^{FEM} - 2K_F^{hyb} = 2\sqrt[3]{2\pi^2 n_0 Z_{FEM}} - 2\sqrt[3]{2\pi^2 n_0 Z_{hyb}}. \tag{2}$$

Here, $2K_F^{FEM}$ and $2K_F^{hyb}$ are from the free electron model and the hybridization model, respectively. Z_{FEM} is the mean valence in the free electron model and Z_{hyb} is the hybridized valence. The atomic number density is $n_0 = \rho N_{Av}/M$, where ρ is the mass density of the MGs and M is the molar weight, and N_{Av} is the Avogadro's number.

The static atomic structure is represented by the diameter of the