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Effect of element types on the glass forming ability of Al-TM-RE ternary metallic glasses using electron structure guiding

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ABSTRACT

The effect of TM (transition metal, Fe, Co, Ni) and RE (rare earth, La, Ce, Sm, Y, Gd, Er, Pr) element types on the glass forming ability (GFA) of $Al_{86}TM_9RE_5$ ternary alloy system has been studied based on the concept of Fermi sphere - Brillouin zone interaction. The effect of TM element is primarily on the electron hybridization between Al atoms and TM atoms, affecting the diameter of the Fermi sphere ($2K_F$). And the effect of RE element is mainly a change in the diameter of the pseudo-Brillouin zone (K_P). Their effects on the Fermi level and Brillouin zone size are monitored using spectroscopy experiments. The $|\delta| = |K_P\text{-}2K_F|$ criterion was proposed to evaluate the effect of GFA on the TM and RE elements. This criterion guided us to select an optimal GFA element ($Al_{86}Ni_9Y_5$) in the Al-TM-RE ternary alloy system and was confirmed by the experimental results.

1. Introduction

Al-based metallic glasses exhibit great potential in engineering materials [1–4] due to their ultra-high specific strength [5] and good corrosion resistance [6]. However, owing to its low glass forming ability (GFA), the largest size of Al-based bulk metallic glass (BMG) reported so far is only 1.5 mm [7–9]. The size limitation of Al-based metallic glasses has hindered its further applications.

Recently, plenty of thermodynamic criterions [10,11] and theoretical models have been proposed to aimed at overcoming this bottleneck problem of low GFA. It is generally accepted that an enhancement in GFA correlates well with the reduced glass transition temperature (T_{rg}). However, experimental observations of glass formation in the Al-TM-RE systems are often found to be in conflict with currently available rules or criteria [12]. GFA is in nature determined by the atomic structure. And chemical interaction and topological interaction between atoms determine the metallic glass stability. Miracle *et al.* has proposed the efficient cluster packing (ECP) model [13,14] and GFA is predicted from atomic structure [15]. However, ECP model is hardly applied in the Al-based MGs because it does not consider chemical contribution to glass stability. Bases on this model, an efficient atomic packing-chemistry coupled model has been used to describe the Al-TM-RE system [16,17]. In the *ab initio* molecular dynamics and reverse Monte Carlo simulation [18], Sheng and Shi have systematically studied the atomic packing in the Al-Ni-La, Al-Y-La and Al-Ni-Y-La MGs [19,20]. However, those atomic structure models and computational simulation can only reveal strong composition dependence for the GFA, and can not predict the influence of element types (RE and TM) on the GFA of Al-TM-RE ternary MGs [21] due to similar atomic sizes and valence electronic structures for the TM and RE elements. Therefore, the lack of quantitative guidelines prompted us to ponder from a different aspect: can the GFA sensitivity to the element types be further optimized from the perspective of the electronic structure changes?

It has been long recognized as the role of electronic structure to the stability of MGs. The *ab initio* pseudo potential method is used to calculate the interatomic forces for transition-metal-free glasses. Hafner established a close relation between glass formation and the formation of topologically close-packed intermetallic compounds [22,23]. For the transition-metal glass (Al-TM-RE alloys), it is invalid because of the hybridization between Al atoms and TM atoms. Furthermore, Nagel and Tauc [24] proposed a Hume-Rothery stabilization mechanism based upon the Fermi sphere - Brillouin zone interaction, in which the Fermi sphere with a diameter of $2K_F$ is in touch with the boundary of

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the pseudo-Brillouin zone with a diameter of K_P in reciprocal space. This means that the phase stability is enhanced when $2K_F = K_P$, which coincides with a minimum of the electronic density of states at the Fermi level, E_F [25–30]. For the Al-TM-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, which is similar to the compounds consisting of both transition metals and nontransition metals [31]. Moreover, the diameter of the pseudo-Brillouin zone (K_P) is determined by the static atomic structure which is controlled primarily by the Al atoms and RE atoms. It suggests that it may be possible to predict the GFA sensitivity to TM and RE element types in the Al-TM-RE ternary system by comparing the relationship between $2K_F$ and K_P.

The purpose of this paper is to investigate the influence of element types on the GFA of Al-TM-RE ternary MGs from the electronic structure perspective. The $Al_{86}TM_9RE_5$ ternary composition is selected as the base alloy composition, as it is the optimum glass forming composition for the Al-TM-RE ternary system [16,32]. TM (Fe, Co, Ni) element and RE (La, Ce, Sm, Y, Gd, Er, Pr) element are considered, in which TM element to tune the degree of electron hybridization and Fermi level and RE element to alter the static atomic structure and Brillouin zone size. X-ray photoelectron spectroscopy (XPS), electron energy-loss spectroscopy (EELS) and X-ray diffraction (XRD) spectrometry are used to monitor the effects of TM and RE element types on K_F and K_P. As $2K_F = K_P$ condition is satisfied as much as possible for different TM and RE elements, a high GFA could be expected.

2. Model and projected trend for the Al-TM-RE ternary system

2.1. Fermi sphere - Brillouin zone interaction

For amorphous alloys, their formation and stability were found to be influenced by a spherical-periodic resonance [31] 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 [31]:

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

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, which leads to a much lower density of conduction electrons that affects the Fermi sphere-Brillouin zone interaction [33]. In such a case, the real electronic density of states deviates from the nearly-free electron behavior in Eq. (1), and it is from the contribution of nearly-free electron (Z_{FEM}) and hybridization electron (Z_{hyb}) between Al-3P and TM-3d (Z_{hyb}). The diameter of the Fermi sphere, $2K_F$, is then given by Ref. [34]:

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

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 spherical pseudo-Brillouin zone, K_P, which can be obtained from the position of the pseudo-Bragg peak in the structure factor (X-ray scattering spectrum). Specifically,

$$K_P = \frac{4\pi sin\theta}{\lambda} \tag{3}$$

where X-ray wavelength is $\lambda = 0.1542$ nm and θ is the location of the main peak in the spectrum.

In the *K*-space, the ideal resonance state is satisfied at $K_P = 2K_F$, representing the equality of the two resonating subsystems [31]. As a result, the Fermi level lies at a minimum of the electron density of states [24,35].

2.2. Application to Al-TM-RE ternary system

Next, it is considered that the element types (TM and RE) effects on the Fermi sphere - Brillouin zone interaction upon the Al-TM-RE ternary system. $|\delta| = |K_P\text{-}2K_F|$ was proposed to identify the element types influence on GFA. There are two categories of element effect on the GFA for the Al-TM-RE alloys:

(i) The effect of TM element in the Al-TM-Y alloys. For the TM element of almost the same size (Fe, Co, Ni), only electron hybridization (between Al-3*p* and TM-3*d*) is affected due to the change in the availability of the 3*d* electrons. This moves K_F for the electron hybridization between Al and TM while K_P remains unchanged for the Al and Y. And the Fermi surface eventually touches the boundary of the quasi-Brillouin zone. It is concluded that the best GFA occurs near $|\delta|$ approach to 0. In other words, when $|\delta|$ becomes equal to 0, a minimum in the density of states results at the Fermi level. This is a scenario that reflects the GFA for the electron hybridization.

(ii) The effect of RE element in the Al-Ni-RE alloys. In this case, the hybridization between Al-3*p* and Ni-3*d* remains the same and K_F is unchanged, whereas K_P changes due to static atomic structure for the RE. When K_P is close to $2K_F$ ($|\delta| = 0$), the quasi-Brillouin zone becomes to touch the Fermi surface and the density of states is minimized at the Fermi level. This is another scenario that influents the GFA for the static atomic structure.

In the following, we will experimentally track the element types effects on K_P and $2K_F$. The K_F value is obtained using Eq. (2), which can be evaluated using X-ray photoelectron spectroscopy (XPS) and electron energy-loss spectroscopy (EELS). K_P is obtained from X-ray diffraction (XRD) spectrum using Eq. (3). Furthermore, to assess the influence on the density of electron energy states at the Fermi level, the electronic specific heat coefficient (γ) is measured for different element types. γ is known to directly scale with the density of states at the Fermi level [36].

3. Experimental procedures

3.1. Material and sample preparation

The $Al_{86}Ni_9RE_5$ (La, Ce, Sm, Y, Gd, Er, Pr) and $Al_{86}TM_9Y_5$ (Fe, Co, Ni) alloys were prepared by arc melting pure elements of nominal purities of above 99.9% under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The alloy ingots were melted six times to ensure compositional homogeneity. For rapidly solidified ribbons, samples were prepared with a cross-section of $0.03–0.05 \times 3$ mm^2 using a single roller melt-spinning technique in an argon atmosphere. Wedge-shaped samples were prepared by casting molten alloys into a wedge-shaped mold with an included angle of 5°.

3.2. Characterization of the alloys

The tip part of a wedge-shaped samples were investigated by XRD using a Rigaku D/max 2400 diffractometer (Tokyo, Japan) with