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, $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$, 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.

Keywords: Al alloys; bulk metallic glasses; electronic structure; glass-forming ability; microalloying.

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 $\text{Al}_{86}\text{Ni}_8\text{Y}_6$ 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

Al₈₈Y₇Fe₅ 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 Al₈₆Ni₈Y₆ 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 Al₈₈Y₇Fe₅ metallic 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 *3d* 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]:

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

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 [36]:

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

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,

$$K_P = \frac{4\pi \sin \theta}{\lambda} \quad (3)$$

where the X-ray wavelength is $\lambda=0.1542$ nm (for Cu) 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 [34]. A consequence is that the Fermi level lies at a minimum of the electron density of states [29,37].

2.2 Application to Al-based multi-component MGs

We next consider the microalloying effects on the Fermi sphere - Brillouin zone interaction, upon the minor addition of TM or/and RE elements to the base Al-TM-RE ternary system. Figure 1 dissects the consequences by examining three separate scenarios: adding TM alone, or RE alone, and their composite effect. Prior to minor alloying in the Al-TM-RE base alloy, it is possible that either $2K_F < K_P$, or $2K_F > K_P$. Here we select the case of $2K_F < K_P$ as the example for illustration.

(i) The effect of sole TM addition. Upon substitution using another TM element of almost the same size (Co for Ni), only electron hybridization (between Al-3p and TM-3d) is affected due to the change in the availability of the 3d electrons. This moves K_F , while K_P remains unchanged, as schematically shown in Figure 1a~d. In an amorphous phase, it is reasonable to assume the quasi-Brillouin zone is spherical in shape [29], and the expanding Fermi surface eventually touches the boundary of the quasi-Brillouin zone. In other words, $2K_F$ is initially smaller than K_P in Fig. 1(a) but increases to $2K'_F$, and when it becomes equal to K_P , a minimum in the density of

states, $N(E_F')$, results at the Fermi level, see Fig. 1(b). This is a scenario that elevates the GFA.

(ii) The effect of sole RE addition. Figure 1e~h illustrates the effect on static atomic structure, when an RE element is substituted into the Al-TM-RE base alloy (such as La for Y). In this case, the hybridization between Al-3p and TM-3d remains the same and K_F is unchanged, whereas K_P changes due to the addition of the larger La. In Fig. 1(e), starting from K_P being larger than $2K_F$, the addition of RE decreases K_P towards K_P' . At the point when K_P' is equal to $2K_F$, the density of states is minimized at the Fermi level, see $N(E_F')$ in Fig. 1(f). Fig. 1(g) and (h) schematically depict this process of the quasi-Brillouin zone becoming smaller to eventually touch the Fermi surface. This is another scenario that enhances the GFA.

(iii) The composite effect of simultaneous TM and RE additions. The synergistic effect of electron hybridization and static structure changes is expected to provide a better chance to close in towards $2K_F = K_P$, more so than separately fine-tuning TM or RE alone. In other words, both K_F and K_P can be adjusted simultaneously by the addition of minor alloying elements (RE and TM species together) to best satisfy the condition $K_P = 2K_F$. As shown in Fig. 1(i) and (j), starting from K_P being larger than $2K_F$, the two can become equal by $2K_F$ increasing towards $2K_F'$ and at the same time K_P decreasing to approach K_P' . Eventually, when $2K_F' = K_P'$ is arrived, a minimum of density of states appears at the Fermi level. Figure 1(k) and (l) are the corresponding schematic diagrams to demonstrate this scenario.

In the following, we will experimentally track the microalloying effects on K_P

and $2K_F$. We obtain the K_F value using Eq. (2), where the key information is the hybridization electron between Al-3P and TM-3d, Z_{hyb} , 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, we will conduct measurement of the electronic specific heat coefficient, γ , along with micro-alloying. γ is known to directly scale with $N(E_F)$ [38].

3. Experimental procedures

3.1 Material and sample preparation

The $\text{Al}_{86}\text{Ni}_9\text{Y}_{5-x}\text{La}_x$ ($x=0\sim 4$ at.%) and $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0\sim 6$ at.%) 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 $0.03\text{--}0.05\times 3\text{ mm}^2$ using a single roller melt-spinning technique in an argon atmosphere. To evaluate the difference in the GFA for different compositions, wedge-shaped samples were prepared by casting molten alloys into a wedge-shaped mold with an included angle of 5° . Rod shaped samples were cast by the injection of the molten alloy into the cavity of a copper mold with a diameter of 1 mm and 1.5 mm.

3.2 Characterization of the alloys

The ribbons and the axial cross-section surfaces of the as-cast rods were

investigated by XRD using a Rigaku D/max 2400 diffractometer (Tokyo, Japan) with monochromated Cu K_α radiation ($\lambda=0.1542$ nm). Crystallization of the alloys was analyzed using differential scanning calorimetry (DSC) in a Perkin-Elmer DSC7 calorimeter under flowing purified argon at a heating rate of 20 K min⁻¹. To investigate the influence of the density of electron energy states at the Fermi level on the GFA, the low temperature specific heat C_p was measured on the Physical Property Measurement System (PPMS9000). The density of states at the Fermi level, $N(E_F)$, scales with the electronic specific heat coefficient, γ . The latter was obtained from linear least square fit of the data of C_p/T vs T^2 according to the equation: $C_p=\gamma T+\beta T^3$ [39]. XPS was performed using an ESCALAB250 photoelectron spectrometer and a monochromatic Al K_α radiation ($h\nu=1486.6$ eV). The surface of the sample was analyzed after short periods of Ar ion etching (4 keV) until the C 1s and O 1s signals were minimized. Binding energies were calibrated using the carbon contamination with C 1s peak value of 284.6 eV. The density of the melt-spun MGs was measured using the Archimedes method. The atomic number density ($=\rho N_A/M$) was calculated based on the density (ρ) of the MGs and their molecular weight (M), where N_A is Avogadro's number.

TEM samples were thinned by electropolishing in an electrolyte of 20 vol.% nitric acid and 80 vol.% methanol at -35 °C. High-resolution TEM imaging was obtained at 200 kV in a FEI Tecnai F30 electron microscope. EELS were acquired using a field emission analytical TEM equipped with a Gatan Model 678 Imaging Filter (GIF) in the mode of a camera length of 80 mm and a spectrometer collection

aperture of 3 mm. All spectra were examined for oxygen edges, and were ion milled to remove any surface oxides. These spectra were then de-convoluted by the Fourier-log method to remove multiple-scattering components from the spectra and background-subtracted by fitting the pre-edge background with a power-law function. Low loss and core edge EELS spectra were taken on different areas of the samples using either image mode or diffraction mode at various magnifications. The same background-subtracted window was applied to all spectra corresponding to the same edge. A large illumination area was used during acquisition so radiation damage on the samples could be minimized. Finally, normalized 3d white line intensities calculations were obtained from more than ten spectra for increased accuracy.

4. Results and discussion

4.1. Electron hybridization effect on GFA in the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ alloy system

We begin our discussion of the results by first examining the Al-Ni-Co-Y quaternary system, where Co is micro-alloyed into the base alloy to partially substitute for Ni. Figure 2 (a) shows x-ray diffraction scans for the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0\sim6$ at.%) amorphous ribbons. For these samples the main features are a prepeak and a main peak with a shoulder. It has been recognized that there is an obvious prepeak at scattering angles around $2\theta=20^\circ$ for Al-rich MGs in the measured XRD or neutron diffraction spectra [40-43]. And such a prepeak in the reciprocal space corresponds to certain medium-range correlations in real space [44]. With increasing Co substitution, the positions of the prepeak and the main peak, as well as the

intensity of the shoulder on the right-hand side of the main peak, are almost unchanged. However, the ratio of the area of the prepeak to that of the main peak, $S_{\text{prepeak}}/S_{\text{total}}$, changes significantly (see Fig. 2b). The prepeak in the XRD curves reflects the medium range correlation [9], which appears to vary with the Co addition. Specifically, an increased intensity of the prepeak is indicative of increased medium-range correlation of solutes, which are centers of solute-centered clusters. Interestingly, the critical thickness for glass formation also shows a similar dependence on the Co content, Fig. 2b. The larger the $S_{\text{prepeak}}/S_{\text{total}}$ value is, the higher the GFA. At $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_5$, $S_{\text{prepeak}}/S_{\text{total}}$ reaches its maximum at 5.6%, and the maximum thickness of fully amorphous sample reaches 1 mm (this is the highest GFA in the present Al-rich quaternary system, see Fig. 2c for characterization of this BMG). However, while local short-to-medium range order helps to rationalize the GFA peak among the selected $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0, 1, 1.5, 2.25, 3, 4.5, 6$ at.%) compositions, it does not guarantee that the optimized GFA has been found from the perspective of the $K_p=2K_F$ criterion.

We now proceed to check the GFA trend against this electronic structure criterion. To this end, we first correlate it with what would be expected from the effect on electron hybridization with increasing Co substitution. To monitor the latter, we measured the chemical shifts of solute constituents in these alloys using XPS. As shown in Table 1 for $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$, the Al $2p_{1/2}$ binding energies in the alloys shift to lower values by ~ 0.3 eV, in comparison with pure Al, whereas the Ni $2p_{3/2}$ and Co $2p_{3/2}$ binding energies in the alloys moved to higher values by ~ 0.3 eV compared to

those of pure Ni and Co. These shifts are unlikely to result from a real charge transfer, due to the high electrostatic energy, but instead can be interpreted as due to “filling” of empty TM-3d-states by Al-3p-electrons [45]. In addition, we found no shift in the binding energy of Y 3d, indicating no charge transfer between Al and Y. Figure 3 shows the Ni 2p_{3/2} core level peak and the associated satellite of the Al₈₆Ni_{9-x}Co_xY₅ alloys. With increasing Co content, the satellite peak decreases in its intensity, accompanying its shift away from the Ni 2p_{3/2} main peak: the distance between the satellite and the main line increases. As listed in Table 1, the Ni 2p_{3/2} satellite intensity and asymmetry index present a marked variation. Here, the Ni 2p satellite intensity is determined by the weight of unoccupied states of 3d character and by its position above the Fermi level E_F [46]. It is known that the change in asymmetry index of the core lines of Ni is closely associated with the variation of d states [47-49]. Thus the increase for Ni 2p_{3/2} asymmetry index in Table 1 caused by adding Co element is closely related to the increasing charge transfer from the Al atom to the Ni atom.

To further monitor the above Co-enhanced hybridization effect, we measured low-loss EELS spectra for the Al₈₆Ni_{9-x}Co_xY₅ ($x=0, 2.25, 3, 4.5$ at.%) MGs, as shown in Fig. 4. A slight increase of the plasmon peak energy is observed when Co atoms are added into the alloys, as summarized in Table 2. The plasmon energy can be evaluated using $E_p = \hbar\omega_p = \hbar\sqrt{e^2n_e / \epsilon_0m_e}$, where n_e is the electron density. Note that the plasmon energy increases gradually compared to Al (15 eV) with the addition of Co. With the addition of Co, an increased E_p implies a higher valence-electron density, which could lead to a stronger interatomic bonding and an increasing charge transfer

from the Al atom to the Ni atom. This agrees well with the trend revealed by the XPS results of the satellite and asymmetry index for the Ni $2p_{3/2}$ peak.

To provide quantitative information about the charge transfer associated with hybridization, we further measured the white line for L_2 and L_3 edges of the Ni and Co elements in the Co-free and Co-containing alloys. For transition metals with unoccupied 3d states, the transition of an electron from a 2p state to 3d levels leads to the formation of white lines. The atomic state changes from $2p^6 3d^{(m)}$ to $2p^5 3d^{(m+1)}$ after the excitation of a 2p electron, where m stands for the number of occupied 3d states. The L_3 and L_2 lines correspond to the transition of $2p_{3/2}$ to $3d_{3/2} 3d_{5/2}$, and $2p_{1/2}$ to $3d_{3/2}$, respectively, and their intensities are related to the unoccupied states in the 3d bands [50]. So one piece of information that can be obtained from examining the white lines is the electron transfer that occurs between the outer d states of transition metal atoms upon alloying. Pearson *et al.* [46] have concluded that the integrated intensities of white lines (or the sum of L_2 and L_3 edge intensities), normalized to the trailing background, decrease nearly linearly with increasing atomic number, reflecting the filling of the d states. Therefore, changes in the integrated white line intensity (relative to the trailing background) can be correlated directly with the changes in the number of d electron holes, i.e., charge transfer. The integrated white line intensities for L_2 and L_3 edges were calculated using the normalized method suggested by Pearson *et al* [51]. The white lines were isolated by modeling the background with a double step function. Firstly, a straight line was fitted to the background immediately following the L_2 white line over a region of approximately

50 eV, and was then extrapolated into the threshold region. This line was further modified into a double step of the same slope with onsets occurring at the white-line maxima. The ratio of the step heights was chosen as 2:1 in accordance with the multiplicity of the initial states (four $2p_{3/2}$ electrons and two $2p_{1/2}$ electrons). Secondly, the white-line area above this step function was then divided by the area in a normalization window 50 eV in width, beginning 50 eV past the onset of the L_3 white line. All the results presented are the average obtained from more than ten spectra. Finally, the 3d electron occupancy of Ni and Co in each alloy can be calculated by applying a linear correlation of the normalized white line intensity versus 3d occupancy [51], in the form

$$I=1.06(1-0.094n) \quad (4)$$

where I is the normalized white line intensity and n is the 3d occupancy electrons per atom (e.g., Ni). This equation allows the calculation of n from the measured normalized white line intensity. The 3d electron occupancy results are also listed in Table 2. The measured number of 3d electrons in Ni atoms increases slightly with the increase of Co content. This confirms that charge transfer indeed occurred from Al atoms to some outer 3d electrons of Ni atoms, in good agreement with the indications from the satellite and asymmetry index for the Ni $2p_{3/2}$ peak and the low-loss EELS spectra.

After confirming that Co has indeed changed the hybridization, we can now calculate the K_F of $Al_{86}Ni_{9-x}Co_xY_5$ ($x=0, 2.25, 3, 4.5$ at.%) amorphous alloys. Taking $Z(Ni,Co)=2$, $Z(Al)=3$, $Z(Y,La)=3$, we obtained K_F^{FEM} and K_F^{hyb} according to Eq. (2).

In using Eq. (2), the Z_{FEM} value of an alloy is calculated by the contributions of all the constituent elements, *i.e.* $Z_{FEM} = \sum_i C_i Z_i$, where C_i and Z_i are the atomic fraction and the electron concentration of element i , respectively, and Z_{hyb} is obtained from $Z_{hyb} = C_{Ni}(n_{Ni}-8) + C_{Co}(n_{Co}-7)$, in which the n_{Ni} and n_{Co} represent the 3d occupancy electrons per Ni and Co atom, respectively, and the values of n_{Ni} and n_{Co} are calculated from Eq. (4). The results are listed in Table 2. The variation of the K_F value with the Co content is presented in Fig. 6 (a). For our series of $Al_{86}Ni_{9-x}Co_xY_5$ amorphous alloys, K_P is constant (black line at 2.671), while $2K_F$ decreases with increasing Co content. To compare with the critical condition $2K_F=K_P$, we define a parameter $\delta=K_P-2K_F$. The best GFA composition ($Al_{86}Ni_{6.75}Co_{2.25}Y_5$) is seen to have the smallest δ value (circled in Fig. 6a) for all the $Al_{86}Ni_{9-x}Co_xY_5$ quaternary alloys studied. As mentioned earlier, this composition is indeed where the BMG reached the 1 mm size. At this point, $\delta=0.009$. Reducing the magnitude of δ further by fine-tuning the Co concentration (between 2.25% and 3% in Fig. 6a) is challenging, because K_F is not directly proportional to (such as linearly scaling with) the Co content: in $K_F = K_F^{FEM} - K_F^{hyb} = \sqrt[3]{2\pi^2 n_0 \sum_i C_i Z_i} - \sqrt[3]{2\pi^2 n_0 [C_{Ni}(n_{Ni}-8) + C_{Co}(n_{Co}-7)]}$, the n_{Ni} and n_{Co} (3d occupancy electrons per Ni or Co atom) are dependent on the Co content added, making the prediction non-trivial.

4.2. Effect of static structure on GFA in the $Al_{86}Ni_9Y_{5-x}La_x$ alloy system

We now switch to discuss La substitution for Y. Figure 7 (a) shows x-ray diffraction scans for the $Al_{86}Ni_9Y_{5-x}La_x$ ($x=0, 1, 1.5, 1.75, 2, 3, 4$ at.%) amorphous ribbons. With the increase of La content in the glassy samples, there is no detectable

variation in the intensity of the shoulder on the high-angle side of the main peak and the position of the prepeak, but the $S_{\text{prepeak}}/S_{\text{total}}$ changes with the La content. As shown in the Fig. 7 (b) and (c), $S_{\text{prepeak}}/S_{\text{total}}$ correlates with the GFA: the highest GFA with the critical size of 1 mm at $\text{Al}_{86}\text{Ni}_9\text{Y}_{3.25}\text{La}_{1.75}$ corresponds to the largest $S_{\text{prepeak}}/S_{\text{total}}$ value [9]. This is very similar to the observation in the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ alloy systems.

From X-ray scattering experiments we could evaluate the composition dependence of the K_P value to assess the effect of the static structure. Using Eq. 3, the K_P values for the $\text{Al}_{86}\text{Ni}_9\text{Y}_{5-x}\text{La}_x$ amorphous alloys were calculated, as shown in Fig. 6(b). The K_P decreases with increasing La content, with the $2K_F$ constant at 2.652 (blue line). From Figure 6(b), $\text{Al}_{86}\text{Ni}_9\text{Y}_{3.25}\text{La}_{1.75}$ is expected to be the best GFA composition among the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ alloys studied, as it displays the smallest δ ($\delta=0.009$). Indeed, BMG with 1 mm size was obtained at $\text{Al}_{86}\text{Ni}_9\text{Y}_{3.25}\text{La}_{1.75}$. From Fig. 6b, the value of K_P appears to be proportional to the La content added. In principle, it is then possible to get to $K_P=2K_F$ through fine-tuning La content between 1.75% and 2%. However, the chemical composition difference is only 0.25%, which is difficult to control/pinpoint in wedge-shaped mold casting and hard to distinguish in EELS.

4.3. Combined effects in the Al-Ni-Co-Y-La quinary system

From Fig. 2(b) and 7(b), we found that the minor addition of either Co or La to the Al-Ni-Y base alloy could lead to 1 mm-sized quaternary BMGs (at $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_5$ and $\text{Al}_{86}\text{Ni}_9\text{Y}_{3.25}\text{La}_{1.75}$, respectively). In the discussion above, this is ascribed to the hybridization effect of Co and the static structure effect of La, respectively. But these

two best compositions have not yet reached the lowest electronic density of states, since their $2K_F$ values are still slightly away from the corresponding K_P values. It would be interesting to strive to meet the condition of $2K_F=K_P$ as close as possible. This is more easily accomplished by multi-component alloying. In other words, we expand to the Al-Ni-Co-Y-La quinary system, by combining the effect of the Co addition with that of the La addition. As seen in Fig. 6(c) and (d), the closet match between $2K_F$ and K_P in this quinary system was arrived at the composition of $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$, where δ becomes as small as 0.001. Indeed, the GFA is elevated further with respect to the quaternary cases: at this composition a BMG 1.5 mm in diameter has been successfully obtained via copper mold casting. Figure 8(a) shows the outer appearance of the $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$ BMG sample and the amorphous features in the XRD spectra. The high-resolution TEM image and the selected-area electron diffraction (SAED) pattern of this alloy are presented in Fig. 8(b). The sample was taken from the center of the 1.5 mm as-cast rod. No crystals are visible in the high-resolution TEM image, which exhibits uniform amorphous structure. The broad halo in the SAED pattern confirms the presence of a single amorphous phase, which agrees well with the fully amorphous feature from the XRD result.

The best quinary Al-rich BMG composition reported above indeed holds the lowest electronic density of states at E_F . This conclusion is reached because we were able to assess the density of states at the Fermi level, $N(E_F)$, by measuring the electronic specific heat coefficient, γ . These two parameters directly scale with each

other, following [38]

$$\gamma = \left(\frac{\pi^2}{3}\right) k_B^2 N(E_F), \quad (5)$$

where k_B is Boltzmann constant. The minimum value of γ (*i.e.* the minimum $N(E_F)$) corresponds to a pseudo gap in the structure of energy band [52]. For comparison, we show in Fig. 9 the γ values for the best glass formers obtained in the ternary, quaternary and quinary Al-rich systems (*e.g.*, $\text{Al}_{86}\text{Ni}_9\text{Y}_5$, $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_5$ and $\text{Al}_{86}\text{Ni}_9\text{Y}_{3.25}\text{La}_{1.75}$, $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$). Remarkably, the $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$ BMG with the best GFA is found to present the minimum γ of all the alloys studied. This correlation between the γ and the GFA indicates that the electronic structural criterion, *i.e.* Fermi surfaces touching the quasi-Brillouin boundary, is useful in improving the stability of amorphous structure and for developing high-GFA Al-rich BMGs. This effect supplements the increase in driving force due to minor substitutional alloying, *i.e.*, the free energy of mixing (ΔG) of the alloys, which can be calculated [26, 53, 54] to be -18.85, -19.10, -19.15 and -19.36 kJ/mol, for $\text{Al}_{86}\text{Ni}_9\text{Y}_5$, $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_5$, $\text{Al}_{86}\text{Ni}_9\text{Y}_{3.25}\text{La}_{1.75}$, $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$, respectively.

5. Conclusions

This study reveals the beneficial microalloying effect of La and Co on the GFA in the Al-Ni-Y metallic glasses, consistent with the concept of Fermi sphere - Brillouin zone interaction. That is, the composition design can follow a route towards $2K_F = K_P$, when the electronic density of states at the Fermi level is minimized such

that the stability of the metallic glass is enhanced. The effect of Co is primarily on the electron hybridization between Al atoms and TM atoms, affecting the diameter of the Fermi sphere ($2K_F$), and that of La is mainly a change in the diameter of the pseudo-Brillouin zone (K_P). The best GFA can be obtained when the condition $2K_F=K_P$ is reached, which is more readily realized via simultaneous adjustment of Co and La additions. The optimization at $2K_F=K_P$ was confirmed by experimental evidence from XPS, EELS, XRD, and the electronic specific heat coefficient. As a result, a new composition, $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$, has been discovered, which produces fully glassy rods with a record size of 1.5 mm in diameter for Al-rich BMGs. Such electronic-structure-informed microalloying may also be a viable approach for the search of BMGs in other alloys based on Al or systems based on other engineering metals. It appears that at least in some alloy systems, $2K_F=K_P$ can be used on top of other guidelines to help locate the compositions with better GFA.

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References

1. H. Chen, Y. He, G.J. Shiflet, S.J. Poon, Mechanical properties of partially crystallized aluminum based metallic glasses, *Scripta Metall. Mater.* 25 (6) (1991) 1421-1424.
2. Y.H. Kim, A. Inoue, T. Masumoto, Increase in mechanical strength of Al-Y-Ni amorphous alloys by dispersion of nanoscale fcc-Al particles, *Mater. Trans. JIM* 32 (4) (1991) 331-338.
3. K. Ohtera, A. Inoue, T. Terabayashi, H. Nagahama, T. Masumoto, Mechanical properties of an $\text{Al}_{88.5}\text{Ni}_8\text{Mm}_{3.5}$ (Mm: misch metal) alloy produced by extrusion of atomized amorphous plus fcc-Al phase powders, *Mater. Trans. JIM* 33 (8) (1992) 775-781.
4. Y. He, S.J. Poon, G.J. Shiflet, Synthesis and properties of metallic glasses that contain aluminum, *Science* 241 (4873) (1988) 1640-1642.
5. A. Inoue, Amorphous, amorphous, nanoquasicrystalline and nanocrystalline alloys in Al-based systems, *Prog. Mater. Sci.* 43 (1998) 365-520.
6. A.P. Tsai, A. Inoue, T. Masumoto, Formation of metal-metal type aluminum-based amorphous alloys, *Metall. Trans. A* 19 (5) (1988) 1369-1371.
7. B.J. Yang, J.H. Yao, J. Zhang, H.W. Yang, J.Q. Wang, E. Ma, Al-rich bulk metallic glasses with plasticity and ultrahigh specific strength, *Scripta Mater.* 61 (2009) 423-426.
8. N.C. Wu, D. Kan, L. Zuo, J.Q. Wang, Efficient atomic packing-chemistry coupled model and glass formation in ternary Al-based metallic glasses, *Intermetallics* 39

(2013) 1-4.

9. N.C. Wu, M. Yan, L. Zuo, J.Q. Wang, Correlation between medium-range order structure and glass-forming ability for Al-based metallic glasses, *J. Appl. Phys.* 115 (4) (2014) 043523-043530.

10. G.Q. Li, K.B. Borisenko, Y.X. Chen, D.N. Manh, E. Ma, D.J.H. Cockayne, Local structure variations in $\text{Al}_{89}\text{La}_6\text{Ni}_5$ metallic glass, *Acta Mater.* 57 (3) (2009) 804-811.

11. H.W. Sheng, Y.Q. Cheng, P.L. Lee, S.D. Shastri, E. Ma, Atomic packing in multicomponent aluminum-based metallic glasses, *Acta Mater.* 56 (20) (2008) 6264-6272.

12. A. Inoue, Stabilization of metallic supercooled liquid and bulk amorphous alloys, *Acta Mater.* 48 (1) (2000) 279-306.

13. F.Q. Guo, S.J. Poon, G.J. Shiflet, Glass formability in Al-based multinary alloys, *Mater. Sci. Forum* 31 (2000) 331-337.

14. A. Inoue, K. Ohtera, T. Zhang, T. Masumoto, New amorphous alloys with good ductility in Al-Ce-M (M=Nb, Fe, Co, Ni or Cu) systems, *Jpn J. Appl. Phys.* 27(10) (1988) L1796-L1799.

15. W.H. Wang, Roles of minor additions in formation and properties of bulk metallic glasses, *Prog. Mater. Sci.* 52 (4) (2007) 540-596.

16. B.J. Yang, J.H. Yao, Y.S. Chao, J.Q. Wang, E. Ma, Developing aluminum-based bulk metallic glasses, *Philos. Mag.* 90 (23) (2010) 3215-3231.

17. J.Q. Wang, Y.H. Liu, S. Imhoff, N. Chen, D.V. Louzguine-Luzgin, A. Takeuchi, M.W. Chen, H. Kato, J.H. Perepezko, A. Inoue, Enhance the thermal stability and

glass forming ability of Al-based metallic glass by Ca minor-alloying, *Intermetallics* 29 (2012) 35-40.

18. C. Zhang, X.F. Bian, J. Guo, S.H. Wang, K.K. Song, C.D. Wang, B. Zhang, Effect of Pr addition on glass-forming ability of Al-Ni-Zr metallic glass alloy, *J. Alloys Compd.* 436 (1-2) (2007) 95-98.

19. K. Song, X.F. Bian, J. Guo, S.H. Wang, B.A. Sun, X.L. Li, C.D. Wang, Effects of Ce and Mm additions on the glass forming ability of Al-Ni-Si metallic glass alloys, *J. Alloys Compd.* 440 (1-2) (2007) L8-L12.

20. Z. Zhang, X.Z. Xiong, J.J. Yi, J.F. Li, Effects of substitution of La by other rare-earth elements on the glass forming ability of $\text{Al}_{86}\text{Ni}_9\text{La}_5$ alloy, *J. Non-Cryst. Solids* 369 (2013) 1-4.

21. Z. Zhang, X.Z. Xiong, W. Zhou, J.F. Li, Influence of substitution of La by Ce on the glass forming ability and crystallization behavior of Al-Ni-La alloys, *J. Alloys Compd.* 576 (2013) 181-186.

22. A. Sadoca, M. Sabra, O. Proux, J.L. Hazemann, K.S. Bondi, K.F. Kelton, Zr and Hf microalloying in an Al-Y-Fe amorphous alloy. relation between local structure and glass-forming ability, *Phil. Mag.* 88 (17) (2008) 2569-2582.

23. K.S. Bondi, A.K. Gangopadhyay, Z. Marine, T.H. Kim, A. Mukhopadhyay, A.I. Goldman, W.E. Buhro, K.F. Kelton, Effects of microalloying with 3d transition metals on glass formation in AlYFe alloys, *J. Non-Cryst. Solids* 353(52-54) (2007) 4723-4731.

24. A. Mukhopadhyay, K.E. Spence, L.Q. Xing, W.E. Buhro, K.F. Kelton, An Al-rich

- metallic glass with a large supercooled liquid region, *Phil. Mag.* 87 (2) (2007) 281-290.
25. C.T. Liu, Z.P. Lu, Effect of minor alloying additions on glass formation in bulk metallic glasses, *Intermetallics* 13(3-4) (2005) 415-418.
26. R. Li, S. Pang, C. Ma, T. Zhang, Influence of similar atom substitution on glass formation in (La-Ce)-Al-Co bulk metallic glasses, *Acta Mater.* 55 (11) (2007) 3719-3726.
27. D.B. Miracle, The efficient cluster packing model - an atomic structural model for metallic glasses, *Acta Mater.* 54 (16) (2006) 4317-4136.
28. Y. Liu, Local structure of Al-based amorphous alloys after microalloying by element substitution and after ball milling, Helmholtz-Zentrum Berlin, 2011.
29. S.R. Nagel, J. Tauc, Nearly-free-electron approach to the theory of metallic glass alloys, *Phys. Rev. Lett.* 35 (6) (1975) 380-383.
30. S. Hosokawa, H. Sato, N. Happo, K. Mimura, Y. Tezuka, T. Ichitsubo, E. Matsubara, N. Nishiyama, Electronic structure of $\text{Pd}_{42.5}\text{Ni}_{7.5}\text{Cu}_{30}\text{P}_{20}$, an excellent bulk metallic glass former: comparison to the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ reference glass, *Acta Mater.* 55 (10) (2007) 3413-3419.
31. P.F. Guan, T. Fujita, A. Hirata, Y.H. Liu, M.W. Chen, Structural origins of the excellent glass forming ability of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, *Phys. Rev. Lett.* 108 (2012) 175501-175505.
32. F.M. Alamgir, H. Jain, A.C. Miller, D.B. Williams, X-ray photoelectron spectroscopy analysis of bulk Pd-Ni-P metallic glasses, R.B. Schwarz, *Phil. Mag.* 79

(2) (1999) 239-247.

33. F.M. Alamgir, H. Jain, R.B. Schwarz, O. Jin, D.B. Williams. Electronic structure of Pd-based bulk metallic glasses, *J. Non-Cryst. Solids* 274 (1-3) (2000) 289-293.

34. P. Haussler, Interrelations between atomic and electronic structures-liquid and amorphous metals as model systems, *Phys. Rep.* 222 (2) (1992) 65-143.

35. U. Mizutani, T. Takeuchi, H. Sato, Interpretation of the Hume-Rothery rule in complex electron compounds: g-phase Cu_5Zn_8 Alloy, FK-type $\text{Al}_{30}\text{Mg}_{40}\text{Zn}_{30}$ and MI-type $\text{Al}_{68}\text{Cu}_7\text{Ru}_{17}\text{Si}_8$ 1/1-1/1-1/1 approximants, *Prog. Mater. Sci.* 49 (2004) 227-261.

36. M. Stiehler, J. Giegengack, J. Barzola-Quiquia, J. Rauchhaupt, S. Schulze, P. Haussler, Peculiarities in the plasma resonance of binary amorphous Al-TM alloys, *J. Phys. Chem. Solids* 68 (5-6) (2007) 1244-1248.

37. G. Hang, J.B. Qiang, F.W. Li, L. Yuan, H. Quan, Q. Wang, Y.M. Wang, C. Dong, P. Haussler, The e/a values of ideal metallic glasses in relation to cluster formulae, *Acta Mater.* 59 (15) (2011) 5917-5923.

38. N.W. Ashcroft, N.D. Mermin, *Solid State Physics*. Thomson Learning, 1976, p. 36-49.

39. U. Mizutani, K.T. Hartwig, T.B. Massalski, R.W. Hopper, Low-temperature specific heats of glassy $\text{Pd}_{1-x-y}\text{Si}_x\text{Cu}_y$ alloys, *Phys. Rev. Lett.* 41 (9) (1978) 661-664.

40. H.Y. Hsieh, T. Egami, Y. He, S.J. Poon, G.J. Shiflet, Short-range ordering in amorphous $\text{Al}_{90}\text{Fe}_x\text{Ce}_{10-x}$, *J. Non-Cryst. Solids* 135 (2-3) (1991) 248-54.

41. K. Ahn, D. Louca, S.J. Poon, G.J. Shiflet, Topological and chemical ordering

induced by Ni and Nd in $\text{Al}_{87}\text{Ni}_7\text{Nd}_6$ metallic glass, Phys. Rev. B 70 (22) (2004) 224103.

42. K. Saksl, P. Jovan, H. Franz, J.Z. Jiang, Atomic structure of $\text{Al}_{88}\text{Y}_7\text{Fe}_5$ metallic glass, J. Appl. Phys. 97 (11) (2005) 113507.

43. K. Saksl, P. Jovari, H. Franz, Q.S. Zeng, J.F. Liu, J.Z. Jiang, Atomic structure of $\text{Al}_{89}\text{La}_6\text{Ni}_5$ metallic glass, J. Phys-Condens. Mat. 18 (32) (2006) 7579-7592.

44 Y.Q. Cheng, E. Ma, Atomic-level structure and structure-property relationship in metallic glasses, Prog. Mater. Sci. 56(4) (2011) 379-473.

45. G. Trambly de Laissardière, D. Nguyen Manh, L. Magaud, J.P. Julien, F. Cyrot-Lackmann, D. Mayou, Electronic structure and hybridization effects in Hume-Rothery alloys containing transition elements, Phys. Rev. B. 52 (11) (1995) 7920-7933.

46. F.U. Hillebrecht, J.C. Fuggle, P. Bennett, Z. Zolnierrek, C. Freiburg, Electronic structure of Ni and Pd alloys. III. correlation effects in the Auger spectra of Ni alloys, Phys. Rev. B. 27 (4) (1983) 2179-2209.

47. N.J. Shevchik, Local density of states and core-hole conduction-electron interactions in the X-ray photoemission spectra of Pt and Ni, Phy. Rev. Lett. 34 (22) (1975) 1336-1339.

48. N.J. Shevchik, D. Bloch, XPS d bands and core levels of Pt-Ni alloys, J. Phys. F. 71 (3) (1977) 543-550.

49. J.C.W. Folmer, D.K.G. de Boer, XPS core level line shapes in metallic compounds: a probe for the nature of the electrons at the Fermi level, Solid State

Commun. 38 (12) (1981) 1135-1138.

50. O.L. Krivanek, J.H. Paterson, Elms of 3d transition-metal oxides: I. variations across the periodic table, *Ultramicroscopy* 32 (4) (1990) 313-318.

51. D.H. Pearson, C.C. Ahn, B. Fultz, *Phys. Rev. B*. White lines and d-electron occupancies for the 3d and 4d transition metals, 47 (14) (1993) 8471-8478.

52. H.B. Yu, W.H. Wang, H.Y. Bai, An electronic structure perspective on glass-forming ability in metallic glasses, *Appl. Phys. Lett.* 96 (2010) 0819021-0819023.

53. A. Takeuchi, A. Inoue, Quantitative evaluation of critical cooling rate for metallic glasses, *Mater. Sci. Eng. A* 304 (2001) 446-451.

54. A. Takeuchi, A. Inoue, Calculations of mixing enthalpy and mismatch entropy for ternary amorphous alloy, *Mater. Trans. JIM* 41(11) (2000) 1372-1378.

Figure captions:

Fig. 1 (Color online) 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_F remains constant, K_P 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.

Fig. 2 Metallic glass formation in the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0$ to 6 at.%) alloys. (a) XRD spectra. (b) The ratio of the area of the prepeak to that of the main peak, $S_{\text{prepeak}}/S_{\text{total}}$, correlated with the critical thickness of glass formation. (c) XRD pattern and DSC curve of the $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_5$ BMG rod with 1 mm diameter.

Fig. 3 Ni $2p_{3/2}$ and $2p_{1/2}$ XPS spectra for the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0$ to 6 at.%) alloys, normalized by the constant height of the main peak.

Fig. 4 (Color online) (a) Low-loss EELS spectra for $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0, 2.25, 3, 4.5$ at.%) metallic glasses. (b) Enlarged view of the plasmon peak around 15 eV.

Fig. 5 The Ni- $L_{2,3}$ edge and Co- $L_{2,3}$ edge EELS spectra for $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0, 2.25, 3, 4.5$ at.%) amorphous alloys.

Fig. 6 (Color online) (a) The dependence of $2K_F$ on Co concentration for the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0, 2.25, 3, 4.5$ at.%) alloys. (b) The dependence of K_P on La

concentration for the $\text{Al}_{86}\text{Ni}_9\text{Y}_{5-x}\text{La}_x$ ($x=0, 1, 1.5, 1.75, 2, 3, 4$ at.%) alloys. (c) The dependence of K_p on Co and La content for the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0, 2.25, 3, 4.5$ at.%) and $\text{Al}_{86}\text{Ni}_9\text{Y}_{5-x}\text{La}_x$ ($x=0, 1, 1.5, 1.75, 2, 3, 4$ at.%) alloys. (d) The relationship between $\delta=K_p-2K_F$ and critical thickness for glass formation, D_c , in the Al-Ni-Co-Y-La quinary system.

Fig. 7 Metallic glass formation in the $\text{Al}_{86}\text{Ni}_9\text{Y}_{5-x}\text{La}_x$ ($x=0, 1, 1.5, 1.75, 2, 3, 4$ at.%) alloys. (a) XRD spectra. (b) The ratio of the area of the prepeak to that of the main peak, $S_{\text{prepeak}}/S_{\text{total}}$, correlated with the critical thickness of glass formation. (c) XRD pattern and DSC curve of the $\text{Al}_{86}\text{Ni}_9\text{Y}_{3.25}\text{La}_{1.75}$ alloy BMG rod with 1mm diameter.

Fig. 8 (Color online) (a) DSC curve of the $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$ BMG. The insets show the rod sample with a diameter of 1.5 mm and its XRD pattern. (b) High-resolution TEM image and the corresponding SAED pattern (inset). The sample was taken from the center of the 1.5 mm as-cast rod.

Fig. 9 The γ value plotted in correlation with the critical diameter for glass formation, for the highest GFA compositions in the base ternary, the quaternary systems, and the quinary system in this study: $\text{Al}_{86}\text{Ni}_9\text{Y}_5$, $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_5$, $\text{Al}_{86}\text{Ni}_9\text{Y}_{3.25}\text{La}_{1.75}$ and $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{La}_{3.25}\text{Y}_{1.75}$.

Wu et al./Fig. 1

Wu *et al.*/Fig. 2

Wu *et al.*/ Fig.3

Wu *et al.*/Fig. 4

Wu *et al.*/Fig.5

Wu et al. / Fig. 6

Wu et al./Fig.7

Wu *et al.*/Fig.8

Wu *et al.*/ Fig.9

Table 1 Binding energy difference, for Y 3d, Al 2p_{1/2}, Ni 2p_{3/2}, and Co 2p_{3/2}, between pure element and the Al₈₆Ni_{9-x}Co_xY₅ ($x=0, 1, 1.5, 2.25, 3, 4.5, 6$ at.%) alloys, referred to as ΔBE_{Y3d} , $\Delta BE_{Al2p1/2}$, $\Delta BE_{Ni2p3/2}$ and $\Delta BE_{Co2p3/2}$, respectively. Also included are the change in binding energy, intensity and asymmetry index of the Ni 2p_{3/2} core level obtained from Fig. 3. ΔE_{sat} represents the binding energy difference between the main line and the satellite, I_{sat} gives the ratio of the satellite intensity to the total intensity of the main line and satellite.

Sample	ΔBE_{Y3d} (eV)	$\Delta BE_{Al2p1/2}$ (eV)	$\Delta BE_{Ni2p3/2}$ (eV)	$\Delta BE_{Co2p3/2}$ (eV)	ΔE_{sat} (eV)	I_{sat}	Asymmetry Index
Ni	—	—	0	—	5.8	29	1
Al ₈₆ Ni ₉ Y ₅	0	-0.28	0.29	0.30	8.16	8.75	1.32
Al ₈₆ Ni ₈ Co ₁ Y ₅	0	-0.30	0.30	0.28	8.31	8.69	1.34
Al ₈₆ Ni _{7.5} Co _{1.5} Y ₅	0	-0.30	0.30	0.31	8.46	8.65	1.37
Al ₈₆ Ni _{6.75} Co _{2.25} Y ₅	0	-0.29	0.31	0.30	8.63	8.59	1.40
Al ₈₆ Ni ₆ Co ₃ Y ₅	0	-0.30	0.30	0.28	8.70	8.55	1.42
Al ₈₆ Ni _{4.5} Co _{4.5} Y ₅	0	-0.29	0.29	0.29	8.77	8.47	1.46
Al ₈₆ Ni ₃ Co ₆ Y ₅	0	-0.29	0.30	0.29	8.85	8.33	1.48

Table 2 The electronic hybridization information obtained from the low-lose EELS peaks for the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Y}_5$ ($x=0, 2.25, 3, 4.5$ at.%) alloys. I_{Ni} and I_{Co} stand for the L_3/L_2 ratio of Ni and Co atoms, respectively. n_{Ni} and n_{Co} are the 3d occupancy electrons per Ni and Co atom, respectively. n_0 is the mean atomic number density, ρ is the mass density of the alloy, and E_p is the plasmon peak energy. $2K_F^{\text{FEM}}$ and $2K_F^{\text{hyb}}$ are calculated assuming the hybridization model and the free electron model, respectively [35].

Sample	I_{Ni}	n_{Ni}	I_{Co}	n_{Co}	ρ (g/cm ³)	n_0 ($\times 10^{20}$)	$2K_F^{\text{hyb}}$ (1/Å)	$2K_F^{\text{FEM}}$ (1/Å)	$2K_F$ (1/Å)	E_p (eV)
$\text{Al}_{86}\text{Ni}_9\text{Y}_5$	0.225	8.38	—	—	3.21	5.868	0.7800	3.4320	2.652	15.08
$\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_5$	0.224	8.39	0.3318	7.3080	3.22	5.885	0.7780	3.4360	2.662	15.38
$\text{Al}_{86}\text{Ni}_6\text{Co}_3\text{Y}_5$	0.223	8.40	0.3416	7.2097	3.23	5.903	0.7510	3.4360	2.685	15.44
$\text{Al}_{86}\text{Ni}_{4.5}\text{Co}_{4.5}\text{Y}_5$	0.222	8.41	0.3374	7.2520	3.24	5.921	0.7480	3.4430	2.695	15.50

Fermi sphere - Brillouin zone interaction ($K_p = 2K_F$)

Electron hybridization effect

Static structure effect

Density of states at the Fermi level

Combined effects

$\delta = K_p - 2K_F$ and critical thickness