Binary rare earth element-Ni/Co metallic glasses with distinct β-relaxation behaviors

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We report the formation of a series of rare earth element (RE)-Ni/Co binary metallic glasses (MGs) with unusual distinct β-relaxation peak compared with that of most of the reported MGs which usually exhibit as an excess wing or a shoulder. The β-relaxation behavior of RE-Ni/Co MGs is sensitive to the composition and the atomic radii of the RE and can be tuned through changing the fraction of RE-Ni (or Co) atomic pairs. The novel RE-Ni/Co MGs with distinct β-relaxation can serve as model system to investigate the nature of the β-relaxation as well as its relations with other physical and mechanical properties of MGs. © *2015 AIP Publishing LLC*.
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I. INTRODUCTION

It has become increasingly evident that metallic glasses (MGs) based on La as the major component together with Ni have exceptional mechanical and dynamic properties.[1–7] The isothermal and isochronal mechanical relaxation spectra of these La-based MGs such as $La_{60}Ni_{15}Al_{25}$ MG[1–4] have shown that the secondary or β-relaxation is prominent and well separated from the α-relaxation. The fast and distinct β-relaxation in these La-based MGs has significant impact on the mechanical properties such as macroscopic tensile plasticity demonstrated by the brittle to ductile transition in tension and follows the same temperature dependence of the β-relaxation time, τ_β.[5]

In a recent effort to understand why Ni containing La-based MGs are so special in β-relaxation properties,[6] we studied the compositional dependence of the dynamic properties by varying the constituents in the La-based MGs. The properties of the β-relaxation turn out to be very sensitive to the composition. It is found that the isochronal loss peak temperature of β-relaxation T_β is effectively determined by the total (La + Ni) content. When Cu is added into the alloy to replace either La or Ni, the T_β increases with decrease of the (La + Ni) content. An independent study of the effect on the loss of $La_{70}Ni_{15}Al_{15}$ by replacing Ni completely by Cu found the same effect,[7] where the pronounced β-relaxation peak transforms into a shoulder when Ni is completely replaced. Based on this result, binary La-Ni MGs with pronounced β-relaxation peak were found, while only excess wing exists in La-Al and La-Cu binary MGs. The observed effects on changing the composition of $La_{60}Ni_{15}Al_{25}$ indicate that the properties of the β-relaxation are mainly determined by the interaction between the largest solvent element La and the smallest element Ni. Recently, a prominent β-relaxation peak was also found in a similar yttrium-based MG.[8] Since both La and Y are rare earth elements (REs), naturally the question to ask is whether the unusual dynamics are general to similar MGs based on other RE. The answer in the positive was given by the isochronal loss modulus spectra of a series of RECoAl MGs where RE stands for Pr, La, Nd, and Sm. All these MGs have well resolved β-relaxation peak widely separated from the α-relaxation.[7] But the question still remains open whether the pronounced β-relaxation peak is general for RE-Ni/Co binary MGs.

To address the aforementioned questions, the purpose of the present study reported is to make a comprehensive study by mechanical spectroscopy of the dynamics of the binary MGs, $RE_{65}Ni_{35}$ and $RE_{69}Co_{31}$, where RE stands for lanthanum (La), praseodymium (Pr), neodymium (Nd), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), and erbium (Er). The β-relaxation of these binary MGs is characterized to confirm that the exceptional dynamics found in the La-based MGs containing Ni or Co is general for all other similar MGs based on any of the RE investigated. The finding of binary RE-Ni/Co MGs with pronounced β-relaxation peak with simple composition may offer wonderful opportunities for theorists to simulate as the development of binary Cu-Zr bulk MGs[9,10] which has stimulated much progress on the glass forming ability, structure, and mechanical properties of MGs.[11,12] The discovery of RE-Ni/Co binary MGs with pronounced β-relaxation peak may shed light on the investigation of β-relaxation in MGs, which still remains in controversy in spite of intensive experimental and theoretical investigations.[13–17] Besides, the β-relaxation behavior of the RE-Al and RE-Fe-Al MGs was also characterized which shows different behavior from RE-Ni/Co MGs. These interesting findings should spur others to search on the atomistic level for why the paring of RE with Ni or Co entails such special dynamics, and why replacement of Ni or Co by Al changes the dynamics so drastically.

II. EXPERIMENTAL

The ingots of the alloys studied in this work were prepared by arc melting the constituent elements in a Ti-gettered Argon atmosphere. Glassy ribbons were fabricated by the single-roll melt-spinning in an Argon atmosphere at

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the circumferential velocity of about 48 m/s. The thickness of the ribbons is about 10–20 μm. The amorphous nature of the samples was verified by the X-ray diffraction (XRD) using Cu K_α radiation and differential scanning calorimetry (DSC) with a heating rate $q_H = 20$ K/min. The dynamical mechanical properties of the MGs were measured on a TA Q800 dynamical mechanical analyzer, and tension mode was used in an isochronal mode with a heating rate of 3 K/min, strain amplitude of 10 μm, and single testing frequency of 1 Hz. The activation energy of β-relaxation was characterized by the dynamical mechanical properties of the MGs in tension mode with frequencies of 0.5, 1, 2, 4, 8, and 16 Hz.

III. RESULTS AND DISCUSSION

Figure 1(a) shows DSC pattern of a typical binary $Dy_{65}Ni_{35}$ MG. The glass transition temperature T_g and the crystallization temperature T_x of the MG can be observed and are indicated by the arrow. The T_g and T_x are 569 K and 591 K, respectively. However, not all the binary MGs display the glass transition signal due to instability of its supercooled liquid state, and the sample crystallizes almost simultaneously with the glass transition.[18] The T_g and T_x of the binary RE-Ni/Co MGs are listed in Table I. It can be seen that the T_x shifts to higher temperature with increase of the atomic mass of RE. The inset of Fig. 1(a) shows the XRD curve of the $Dy_{65}Ni_{35}$ MG, which displays the archetypal amorphous hump, indicating the amorphous nature. Figure 1(b) shows temperature dependence of the loss modulus G'' of $Dy_{65}Ni_{35}$ MG. A distinct β-relaxation peak could be observed in the lower temperature side and its peak locates about 421 ± 1 K. Followed the β-relaxation peak is the crystallization peak due to instability of the binary MG, which is in contrary to the $La_{60}Ni_{15}Al_{25}$ MG whose α-relaxation peak could be observed from the dynamical mechanical analysis.[1–4,6] Because our focus in the present investigation is on the β-relaxation of the RE-Ni/Co MGs, the intervening crystallization event does not affect the investigation of β-relaxation.

TABLE I. The T_g, T_x, T_β, and E_β of the RE-Ni/Co MGs.

Composition	T_g (K)	T_x (K)	T_β (K)	E_β (kJ/mol)
$La_{65}Ni_{35}$	...	442	315 ± 2	74 ± 3
$Pr_{65}Ni_{35}$	...	465	341 ± 2	69 ± 3
$Nd_{65}Ni_{35}$	...	480	349 ± 2	72 ± 3
$Gd_{65}Ni_{35}$	...	561	395 ± 2	118 ± 4
$Tb_{65}Ni_{35}$	559	576	404 ± 2	112 ± 4
$Dy_{65}Ni_{35}$	569	591	421 ± 2	105 ± 4
$Ho_{65}Ni_{35}$	598	616	428 ± 2	103 ± 4
$Er_{65}Ni_{35}$	...	643	446 ± 2	109 ± 4
$La_{69}Co_{31}$	...	427	296 ± 2	73 ± 3
$Pr_{69}Co_{31}$	...	451	310 ± 2	77 ± 3
$Nd_{69}Co_{31}$	...	469	323 ± 2	85 ± 3
$Gd_{69}Co_{31}$	...	554	378 ± 2	125 ± 4
$Tb_{69}Co_{31}$	...	569	391 ± 2	121 ± 4
$Dy_{69}Co_{31}$	...	584	406 ± 2	106 ± 4
$Ho_{69}Co_{31}$	...	625	420 ± 2	118 ± 4
$Er_{69}Co_{31}$	...	641	433 ± 2	116 ± 4

Figures 2(a) and 2(b) present the temperature dependence of loss modulus G'' of the $RE_{65}Ni_{35}$ MGs, where RE represents La, Pr, Nd, Gd, Tb, Dy, Ho, and Er, respectively. It can be clearly seen that the pronounced β-relaxation peak is universal for all the investigated RE-Ni MGs similar to that of the $Dy_{65}Ni_{35}$ MG, and the pronounced β-relaxation peak is also general for RE-Co ($RE_{69}Co_{31}$) MGs which is

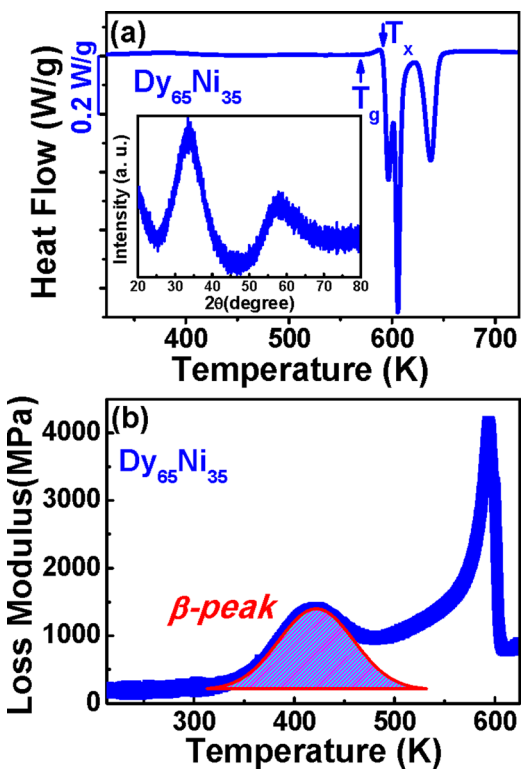

FIG. 1. (a) DSC traces of typical $Dy_{65}Ni_{35}$ MG ribbon. The arrows designate the T_g and T_x. The inset shows XRD pattern of the MG. (b) Temperature dependence of the loss modulus G'' for the $Dy_{65}Ni_{35}$ MG. The shaded area represents the β-relaxation.

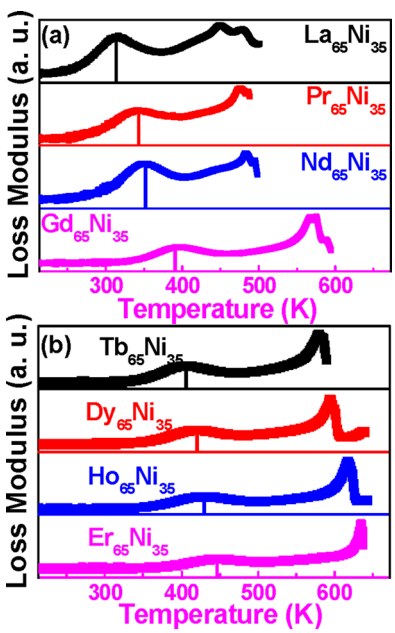

FIG. 2. Temperature dependence of the loss modulus G'' for the $RE_{65}Ni_{35}$ MGs, where RE represents (a) La, Pr, Nd, Gd and (b) Tb, Dy, Ho, Er. The line shows the position of the peak temperature of β-relaxation.

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not shown here. We note that $Ce_{65}Ni_{35}$ MG also exhibits pronounced β-relaxation peak (not shown), but we cannot get the $Ce_{69}Co_{31}$ amorphous phase. Such phenomenon is in stark contrast to most of the MGs showing only an excess wing or a shoulder.[19,20] The T_β of the MGs was determined by fitting with the procedure described in Ref. 2, and the lines in Fig. 2 show the position of T_β, which were listed in Table I. It can be seen that the T_β shifts to higher temperature side with increase of the atomic weight of the rare earth elements. The atomic weight of rare earth elements decreases with increase of the atomic radii.[21]

Figure 3(a) shows the T_β with the relative atomic ratio between RE and Ni/Co. The data of atomic radii of the elements were derived from Ref. 21. It could be seen that with the decrease of the atomic radii, the T_β shifts to higher temperature side, and an almost linear relationship exists between the relative atomic radii and the T_β. Figure 3(b) shows the temperature dependence of G'' at different frequencies of a typical $Dy_{65}Ni_{35}$ MG in the β-relaxation region. The T_β shifts to higher temperature side with the increase of frequency. The activation energy of β-relaxation E_β of MG can be determined from the Lnf vs. $1000/T_\beta$ plot.[1,13] The inset of Fig. 3(b) shows the Arrhenius fit of the measured data of $Dy_{65}Ni_{35}$ MG, and its E_β is determined to be 105 ± 4 kJ/mol, or $E_\beta \approx 22.2(\pm 0.8)RT_g$, which is roughly in agreement with the relationship found between the E_β and T_g in various MGs.[22] The activation energies of other RE-Ni/Co MGs are also listed in Table I.

Previous work shows that the β-relaxation is very sensitive to the composition,[1,6,8] and the value of enthalpy of mixing of the atomic pairs influences the β-relaxation behavior.[14] To characterize the compositional dependence of β-relaxation behavior of the RE-Ni/Co MG system, Ni/Co was replaced by Al, and the β-relaxation behavior of binary RE-Al MGs was studied. Figure 4(a) shows the temperature

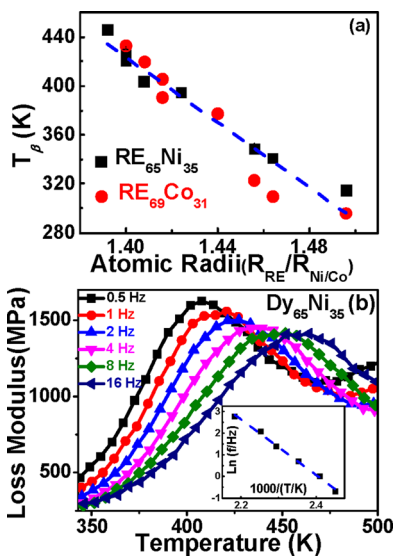

FIG. 3. (a) Relationship between the peak temperature of β-relaxation T_β and the relative atomic radii ratio between RE and Ni/Co. The error is of the order of the symbol size. (b) Temperature dependence of β-relaxation measured with frequencies of 0.5, 1, 2, 4, 8, and 16 Hz. The inset shows the plot of Lnf vs. $1000/T_{\beta,peak}$. The activation energy of β-relaxation E_β can be determined from the plot.

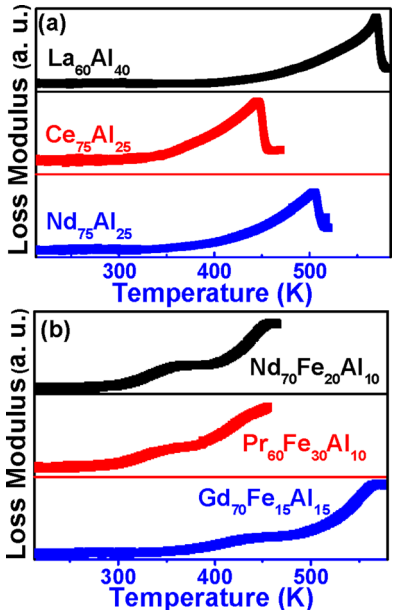

FIG. 4. (a) Temperature dependence of the loss modulus G'' for the (a) RE-Al MGs, where RE represents La, Ce, and Nd, and (b) RE-Fe-Al MGs, where RE represents Nd, Pr, and Gd.

dependence of loss modulus of RE-Al MGs, where RE stands for La, Ce, and Nd. In contrast with the RE-Ni/Co MGs, the binary RE-Al MGs exhibit an excess wing in the lower temperature side. This indicates that the Al plays a role in suppressing the β-relaxation in the RE-Al MGs. Because the Ni and Co are the magnetic elements, the question is then raised whether the pronounced β-relaxation is also general for RE-Fe binary MGs. Unfortunately, we cannot get amorphous phase of RE-Fe binary MGs. To get the amorphous phase, the Al was alloyed to prepare the RE-Fe-Al MGs. Figure 4(b) shows the temperature dependence of loss modulus of RE-Fe-Al MGs. In contrast with the RE-Ni/Co and RE-Al MGs, the β-relaxation of RE-Fe-Al MGs shows as a shoulder or hump. However, whether the "shoulder" behavior of β-relaxation of the RE-Fe-Al MGs arises from the effect of Al still remains unclear. It is found that the β-relaxation of GdCoAl and ErCoAl MGs also exhibits as a shoulder,[7] while when Al was removed from the GdCoAl and ErCoAl MGs, the binary Gd-Co and Er-Co MGs still exhibit a pronounced β-relaxation peak.

The β-relaxation is a universal feature of glassy dynamics which bears nontrivial connection to the α-relaxation.[16] However, the atomistic description of structural origin of the β-relaxation is still in debate.[17,23] The MGs combining metallic bonding and disordered atomic structures can serve as ideal systems for investigating the fundamental issues of glassy sciences.[24] Recently, computer simulations and experiments suggest that nano-scale liquid-like regions in MGs with viscoelasticity flow feature act as the flow units, accommodating the deformation and initiating the shear banding.[25–28] These flow units, which contain atoms with high mobility, low elastic modulus, and low packing density, can be activated and percolated by applied stress or elevated temperature, inducing the global plasticity or relaxations of MGs. On the other hand, many investigations indicate that

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the β-relaxation, which is the source of the localized atomic mobility in the glass state, is suggested to be closely related to the flow units, and obvious β relaxation is an indicator of the abundant flow units in a MG.[25–28] Our previous research shows that the La and Ni play a crucial role in influencing the β-relaxation behavior of the prototypical LaNiAl MGs. Based on our previous results, we deduce that the smallest element Ni has higher mobility in the La-based MGs.[6,29–31] As a result, the flow units in the La-based MG are mainly composed of La and Ni which make them jump faster. When Al was replaced by Ni/Co, the prominent β-relaxation peak transforms into an excess wing. Such effect is similar to the CuZr MG where the addition of Al could suppress the β-relaxation because the addition of Al tends to increase the atomic cluster with icosahedral symmetry,[14,32,33] and thus the concentration of flow units composed with atoms with higher mobility decreases. For the RE-Ni/Co MGs, the replacement of Ni/Co by Al decreases the concentration of flow units mainly composed by RE and Ni/Co, and the formation of icosahedral symmetry caused by the Al addition finally makes the diffusion of atoms sluggish.

IV. CONCLUSION

A series of RE-Ni/Co binary MGs with distinct β-relaxation peak were developed. The β-relaxation behavior of RE-based MGs is very sensitive to the composition and atomic radii of RE. When Ni/Co is replaced by Al, the pronounced β-relaxation peak transforms into an excess wing. The finding of binary RE-Ni/Co MGs may serve as model materials to investigate the β-relaxation in MGs due to its composition simplicity. However, the reason why pairing up RE and Ni/Co could facilitate flow units region with higher mobility still remains unanswered. Finally, the finding of RE-Ni/Co with pronounced β-relaxation peak may help to tune the mechanical properties of MGs due to the close relationship between the β-relaxation and mechanical properties.

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