



Contents lists available at ScienceDirect

## Journal of Non-Crystalline Solids

journal homepage: [www.elsevier.com/locate/jnoncrysol](http://www.elsevier.com/locate/jnoncrysol)

Letter to the Editor

## Relaxation behavior on high frequency profile in strong/fragile metallic glass-forming systems

Z.F. Zhao<sup>a</sup>, P. Wen<sup>a</sup>, C.H. Shek<sup>b</sup>, W.H. Wang<sup>a,\*</sup><sup>a</sup> Institute of Physics, Chinese Academy of Sciences, Beijing 100080, PR China<sup>b</sup> Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, PR China

## ARTICLE INFO

## Article history:

Received 12 September 2009

Received in revised form 6 April 2010

Accepted 7 April 2010

Available online 3 May 2010

## Keywords:

Metallic glass;

Relaxation

## ABSTRACT

The coupling of the slow  $\beta$ -relaxation and the prominent  $\alpha$  relaxations in various metallic glass-forming systems with different fragilities is studied. The coupling of the  $\alpha$ - and slow  $\beta$ -relaxation depends on the fragility of the metallic liquids and causes an obvious violation of the time-temperature superposition principle in rather strong metallic glass-forming liquids. The results are qualitatively discussed based on the microstructural characteristic of the BMGs consisting of the dense-packing regions and loose-packing regions.

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The glasses relax into more stable states, and the inevitable relaxation accordingly makes it a powerful means for us to understand the nature of glass and glass transition. There are two relaxation modes [1–3]: one is the primary relaxation or  $\alpha$ -relaxation, which is closely related to the glass transition process; another is the secondary Johari–Goldstein relaxation or slow  $\beta$ -relaxation [4–11]. At the crossover temperature  $T_c$  above glass transition temperature  $T_g$ , the  $\alpha$ - and slow  $\beta$ -relaxations merge into one effective process. A change is generally found in a number of dynamic measurements around  $T_c$ , and it is believed that  $T_c$  signifies a qualitative change in the liquid behavior [12]. The slow  $\beta$ -relaxation, as a faster and more local relaxation mode, can be regarded as a precursor of  $\alpha$ -relaxation and it may probably relate to the superior mechanical performance of metallic glass [13–17].

Compared with other glass-forming liquids, the structure of metallic liquid is much simple and close to dense random packing of spheres without the complex intramolecular effect, rotational degree of freedom or angle jump. Therefore, it offers a good opportunity to understand the universal mechanism of complex relaxations in supercooled liquids as a whole. Recently the slow  $\beta$ -relaxation had also been found to be common in metallic glass-forming systems [18]. A connection between the dynamic behavior and the fragility of the metallic supercooled liquids has been found [18]. Nevertheless, how the  $\alpha$ - and slow  $\beta$ -relaxations interplay and the microstructural origin for this interplay remain elusive. It is thus of importance to systematically investigate the  $\alpha$ - and  $\beta$ -relaxations and

to find a link between the microstructural characteristic and the relaxation scenario.

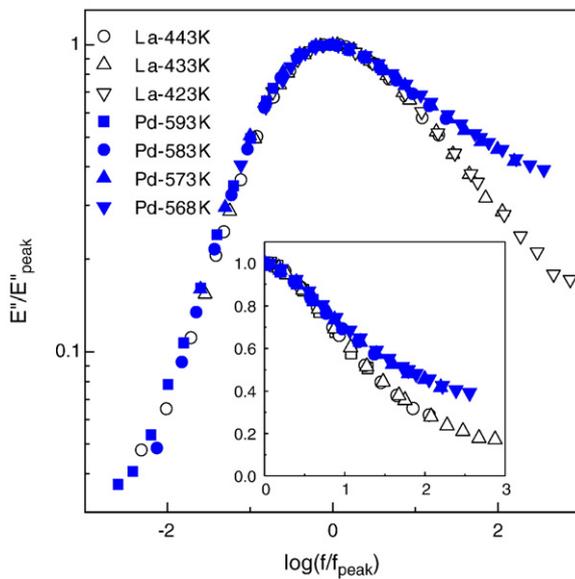
The validity of time-temperature superposition (TTS) TTS is another question in debate [17]. The violations were often explained as the interference from the slow  $\beta$  relaxation. More recently, a general opinion is that the  $\alpha$  process usually itself violates TTS as its widths of relaxation spectra measured at different temperatures change. So, it will be interesting to investigate the validity of TTS in some typical metallic glass-forming liquids.

In this letter, we report the study of the interplay of  $\alpha$ - and slow  $\beta$ -relaxations in strong and fragile BMGs [19] of  $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ ,  $\text{La}_{57.5}(\text{Cu}_{50}\text{Ni}_{50})_{25}\text{Al}_{17.5}$ ,  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  and  $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$  BMG-forming liquids using isothermal dynamic mechanical spectra. All dynamic mechanical measurements were performed on TA DMA-2980 dynamic mechanical analyzer (DMA) by single-cantilever bending method. A sinusoidal strain was applied during all dynamic mechanical measurements. The frequency dependence of young modulus ( $\pm 1\%$ ) can be determined by the frequency sweep measurements. The temperature error is controlled within  $\pm 0.1$  °C when isothermal measurements performed. Before DMA measurements, all samples had been heated into respective supercooled liquid region and cooled at constant rate ( $\leq 40$  K/min) to room temperature in order to erase the interfering of the formation of the as-cast samples.

Fig. 1 shows the respective master curves of isothermal dynamic mechanical measurements conducted on fragile  $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$  (568–593 K) and  $\text{La}_{57.5}(\text{Cu}_{50}\text{Ni}_{50})_{25}\text{Al}_{17.5}$  (423–443 K) BMGs. Both glasses show a prominent  $\alpha$ -relaxation peak in frequency ( $f$ ) domain. On the low frequency side of the loss peak, the BMGs show the same behavior while their performance on the high- $f$  profile is much different: the loss modulus of  $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$  is much larger than that of La-based BMG. After bifurcated at about 1 decade frequency,

\* Corresponding author.

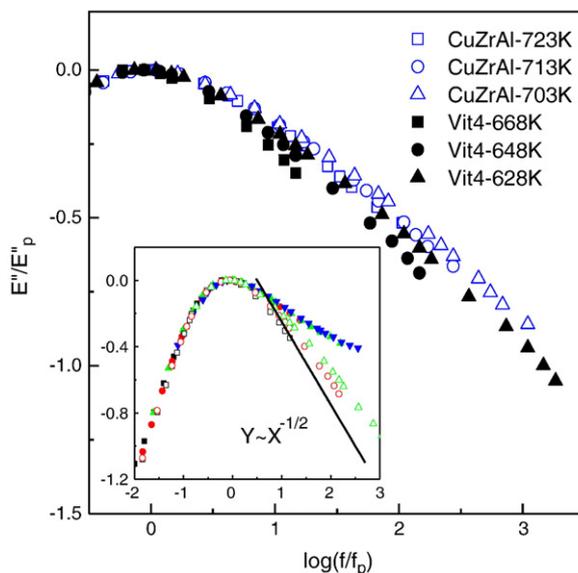
E-mail address: [whw@aphy.iphy.ac.cn](mailto:whw@aphy.iphy.ac.cn) (W.H. Wang).



**Fig. 1.** Master curves for Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> (568–593 K) and La<sub>57.5</sub>(Cu<sub>50</sub>Ni<sub>50</sub>)<sub>25</sub>Al<sub>17.5</sub> (423–443 K) BMGs of DMA measurements. The inset shows a magnified high-*f* part of their master curves.

the spectra of Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> possess larger value of normalized  $E''$  and the difference tends to increase with  $f$ . The inset in Fig. 1 shows a magnified high- $f$  part of their master curves. Despite of the difference on their intensity of normalized  $E''$ , both systems seem to conform to TTS. The DMA spectra in ramp mode show that both systems possess an obvious secondary relaxation mode below  $T_g$ . The intensity difference on the high- $f$  side of the isothermal DMA spectra comes from the intensity difference of the slow  $\beta$ -relaxation, which can also be obviously discerned in isochronal DMA spectra [18].

The isothermal DMA was also conducted on strong BMGs of (Cu<sub>50</sub>Zr<sub>50</sub>)<sub>92</sub>Al<sub>8</sub> (703–723 K) and Vit4 (628–668 K) and the high- $f$  part of their master curves are shown in Fig. 2. It is found that the data fall onto one curve for  $f < f_p$ , while the trends for  $f > f_p$  are  $T$ -dependent. This means that the dynamics of the two metallic liquids does not obey the TTS principle. The higher is the temperature, the narrower is

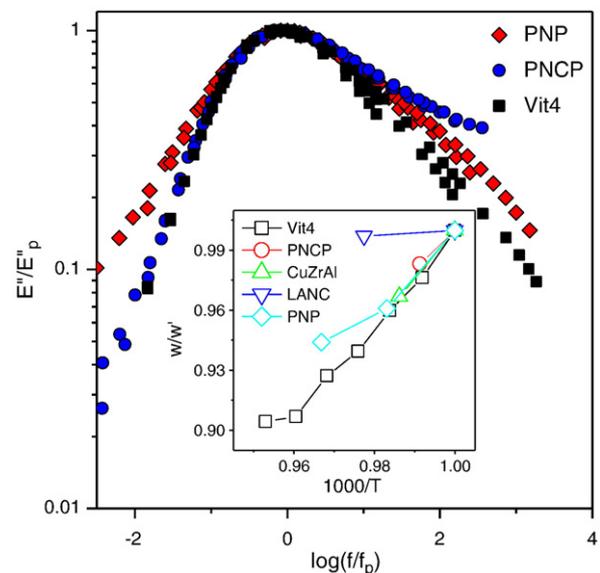


**Fig. 2.** The high-frequency part of the master curves for Vit4 (628–668 K) and (Cu<sub>50</sub>Zr<sub>50</sub>)<sub>92</sub>Al<sub>8</sub> (703–723 K) BMGs of DMA measurements. The inset shows a comparison of master curves for Vit4 (open) and Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> (solid), the solid line indicates a damp at  $f^{-1/2}$  on high frequency.

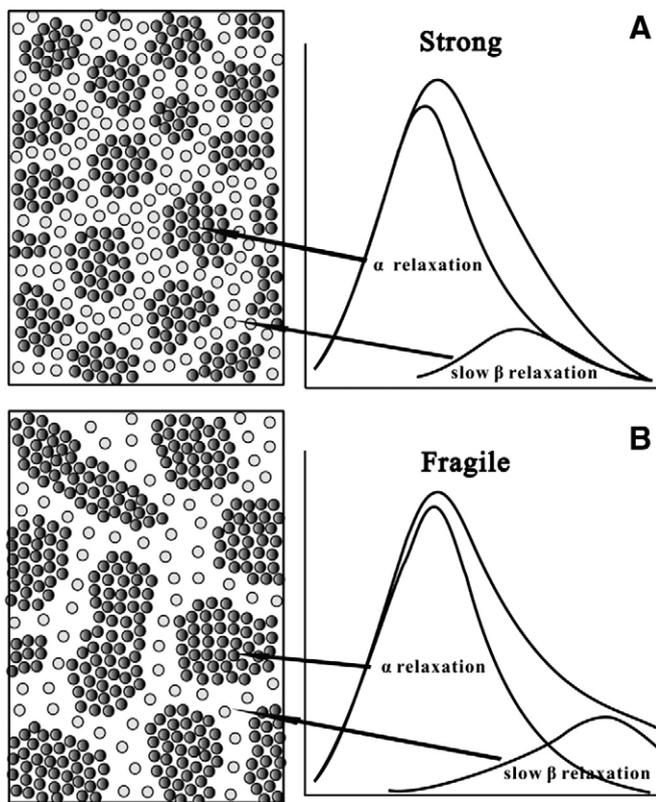
the distribution of the loss modulus. The inset in Fig. 2 shows a comparison of master curves for Vit4 and Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub>. The solid line indicates a damp at  $f^{-1/2}$  on high  $f$ . The two strong liquids behave in the same way on the low- $f$  side of the loss peak. An obvious difference can be found on high- $f$  profile of the fragile BMGs. This is in accord with the conclusions other researchers drawn [17]. It is noted that the damp on the high frequency of Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> deviated from the  $f^{-1/2}$  obviously.

The previous research affirmed that the  $\alpha$ - and the slow  $\beta$ -relaxations coexist in the bulk metallic glass-forming systems at temperature close to  $T_g$  [18]. No obvious peak representing the slow  $\beta$ -relaxation exhibits that the two processes are coupling. The coupling is related to the fragility of the SLs. In metallic supercooled liquids the low- $f$  part of slow  $\beta$ -process is fully obscured by the dominant  $\alpha$  peak. That means that the relationship between the  $T$ -dependent  $\alpha$ - and slow  $\beta$ -relaxation time  $\tau$  are different and dependent on the fragility. When approaching  $T_c$ , the average relaxation time for the two relaxation modes  $\tau_\alpha$  and  $\tau_\beta$  come progressively closer and the distributions of  $\tau_\beta$  may become narrower as  $T$  increases [20]. With respect to strong glass-forming systems, low- $f$  part of the slow  $\beta$ -relaxation is fully obscured by the dominant  $\alpha$  peak, thus both effects will make the  $E''$  on high  $f$  decrease as  $T$  increases. That is why the line shapes of strong BMGs become narrower with increasing temperature. However, for fragile systems, the low- $f$  part of the slow  $\beta$ -relaxation is only partly obscured by the  $\alpha$ -peak. The  $\tau_\alpha$  and  $\tau_\beta$  come progressively closer as  $T$  increases thus increase the  $E''$  between these two relaxation modes; meanwhile the distributions of  $\tau$  may become narrower which make the  $E''$  on the high- $f$  side of  $\alpha$ -peak decrease. The two inverse effects make the small deviation from TTS.

Fig. 3 shows master curves for Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>, Vit4 and Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> BMGs from DMA measurements. Compared with Vit4 and Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub>, Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> is of obviously different behavior at low frequencies, and its  $E''$  is distinctly higher than that of the other two systems. While its master curve is between Vit4 and Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> as the fragility indicated. Fig. 3 inset shows the temperature dependence of the normalized width  $w/w'$  of mechanical relaxation for these BMGs. The widths of mechanical relaxation  $w$  ( $w = W/W_D$ ) is normalized to the one measured at the lowest temperature  $w'$  to compare the trend of  $w$  changing with  $T$  for the different BMGs.



**Fig. 3.** Master curves for Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> (573–603 K), Vit4 (628–668 K) and Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> (568–593 K) BMGs from DMA measurements. The inset shows the  $T$  dependence of the normalized width  $w/w'$  of mechanical relaxation for the different BMGs.



**Fig. 4.** A schematic illustrations of the relation between the microstructural diagram and the relaxation modes of BMG. The black region is the dense-packing regions (DPRs) and the gray region is the loose-packing regions (LPRs). The  $\alpha$  relaxation originated from the DPRs while the slow  $\beta$  relaxation originated from the LPRs.

Actually all the BMG systems studied herein deviated from TTS to some extent since their  $w$  varies with  $T$ . With respect to the strong BMGs,  $w$  changes with  $T$  at high rates while for  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  this rate is smaller. On the other hand, the rate for fragile BMGs should be the smallest. The changing rate for  $\text{La}_{57.5}(\text{Cu}_{50}\text{Ni}_{50})_{25}\text{Al}_{17.5}$  is so small that the  $w$  almost remains unchanged, which may be due to the low intensity of the slow  $\beta$ -relaxation in this system. This indicates that the slow  $\beta$ -relaxation on high frequency profile of the dominant  $\alpha$  relaxation does have significant effects on the validity of TTS in BMGs as suggested before [17].

The microstructural origin for above observed phenomenon could be understood by a physical scenario of the microstructural characteristic of BMG, which assumed that the microstructure of BMGs may manifest as dense-packing regions (DPRs) and loose-packing regions (LPRs) [21–24]. In Fig. 4, the black regions represent the DPRs and the gray regions represent the LPRs. The  $\alpha$  relaxation is regarded

to origin from the DPRs while the slow  $\beta$ -relaxation originated from the LPRs [21]. The DPRs and LPRs are relative and the difference between these regions may be much different for glass-forming liquids with different fragilities. For a strong system, the difference between DPRs and LPRs may be minor and this may result in a minor difference between average relaxation time for  $\alpha$ - and slow  $\beta$ -relaxations. That is why only an excess wing can be discerned on the high- $f$  profile of  $\alpha$ -relaxation in strong liquids (Fig. 4A). While for a fragile system, this difference should be larger accordingly a more obvious manifestation of slow  $\beta$ -relaxation is reasonable (Fig. 4).

In summary, isothermal dynamic mechanical measurements have been performed on typical metallic BMGs with different fragilities. The slow  $\beta$  relaxation had significant effects not only on the high frequency behavior but also the validity of time-temperature superposition in strong/fragile metallic glass-forming liquids. The experimental results can be qualitatively explained by microstructural heterogeneity characteristic of BMGs.

### Acknowledgements

Financial support from the NSF of China (Nos. 50671118, 50621061 and 50731008) and MOST 973 (No. 2007CB613904) is acknowledged.

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