

Observation of secondary relaxation in a fragile $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ bulk metallic glass

Zuo Feng Zhao, Ping Wen, and Wei Hua Wang^{a)}

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

C. H. Shek

Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, People's Republic of China

(Received 14 May 2006; accepted 29 June 2006; published online 18 August 2006)

The dynamic elastic moduli in the temperature domain of a $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ bulk metallic glass were measured with dynamic mechanical spectroscopy at frequencies less than 100 Hz. The primary relaxation is characterized by a single loss modulus peak and a rapid drop of storage modulus in the metallic supercooled liquid region. Below the conventional glass transition temperature, a pronounced shoulder in the loss modulus curves appears and the corresponding storage modulus decreases with increasing temperature. The phenomenon is common to glass formers of all types. The observations present the evidence of the existence of the slow β relaxation and affirm the universality of the separation of the primary and secondary relaxations in the supercooled liquid. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337876]

An important issue of the glass transition is whether the separation of the primary relaxation (α) and the slow β (Johari-Goldstein) relaxation is a universal in the glass-forming supercooled liquids (SLs) or not.¹⁻⁴ As a process that precedes primary relaxation in time, the slow β relaxation plays an important role in pursuing the origin of universal relaxations in glass-forming liquids and the dynamical glass transition.^{2,3} However, in many glass-forming liquids, particularly in rather strong glass-forming liquids,⁵ only an excess wing can be found on the high tail of the dielectric loss spectrum.⁶⁻⁹ Recently, more and more researches have affirmed that the excess wing has the same nature as the slow β relaxation.⁸⁻¹¹ The dielectric spectroscopy is a standard method in the investigation of the dynamics of the glass-forming liquids.⁷⁻⁹ Dynamical elastic modulus measurement is a supplement to understand the mechanics of the slow β relaxation of glass-forming liquids, especially metallic glass-forming liquids, the structure of which is very close to dense random packing of spheres. Nevertheless, little work on the slow β relaxation in metallic glasses has been reported.¹²

The excess wing has been found in the elastic modulus spectrum of the Zr-based SLs.¹³ The work indicates that the evidence of the slow β relaxation could be observed in the glassy region. In this letter, we present the moduli of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ metallic glass in the temperature domain measured at a continuous heating process and at low frequency (below 100 Hz). The $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ supercooled liquid is a rather fragile liquid among the available metallic glass-forming liquids (the fragility or steepness index m is 59).¹⁴ The fragile properties of the glass is helpful for observing the slow β relaxation in the glassy region during continuous heating at low frequency.⁷ It is found that below the conventional glass transition temperature a pronounced shoulder in E'' curves exists in the temperature domain, while E' decreases with increasing temperature. The results indicate the existence of the slow β relaxation in the bulk

metallic system and affirm that the slow β relaxation is not decoupled completely from the α relaxation in the metallic SL. The origin for the slow β relaxation in the metallic glass is discussed.

The $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ bulk metallic glass was prepared from a mixture of the pure elements by induction melting in a high-vacuum quartz tube. Its melted ingot was subjected to a B_2O_3 flux treatment at several times to remove the impurities. Metallic glassy sheet with dimensions of $100 \times 10 \times 1.2 \text{ mm}^3$ was formed by suction casting in a water-cooled copper mold. The amorphous nature of the specimen was confirmed by x-ray diffraction and differential scanning calorimetry. Rectangular samples with dimensions of about $30 \times 3 \times 1.2 \text{ mm}^3$ were used for the dynamic mechanical measurement carried out in a TA DMA2970 thermal mechanical analyzer. The complex elastic moduli were measured by the single-cantilever bending method in a nitrogen-flushed atmosphere. The storage modulus E' and loss modulus E'' were measured in a frequency sweep mode under a sinusoidal applied strain of $\pm 0.03\%$.

Figure 1 shows the temperature dependence of the storage modulus E' and the loss modulus E'' of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$

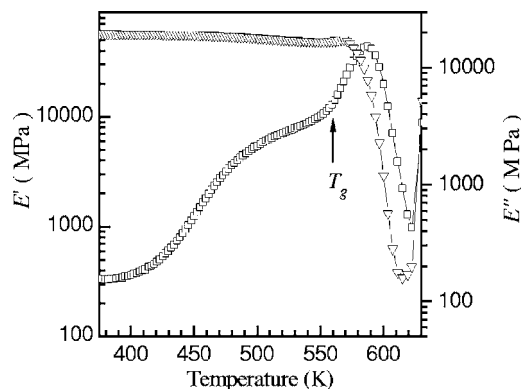


FIG. 1. Temperature dependence of the storage elastic modulus E' and the loss elastic modulus E'' of the as-cast $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ measured at 4 Hz at a heating rate of 3 K/min.

^{a)} Author to whom correspondence should be addressed; electronic mail: whw@aphy.iphy.ac.cn

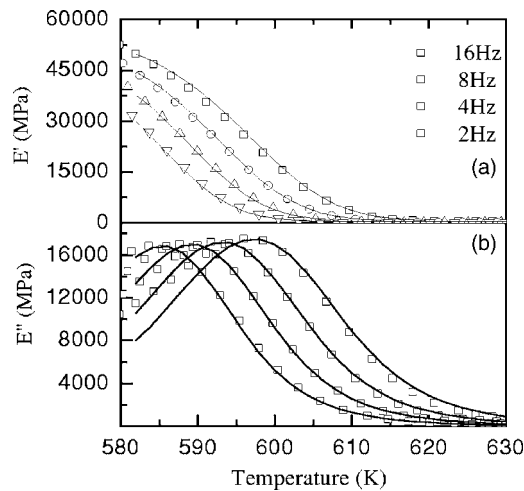


FIG. 2. Temperature dependence of the (a) E'' and (b) E' of the metallic glass measured at frequencies of 2, 4, 8, and 16 Hz in the supercooled liquid region. The solid lines are simulation results (see details in the letter).

at 4 Hz with a heating rate of 3 K/min. In order to avoid the effect of physical aging in the glassy region, the samples were cooled from the SL region with the cooling rate of 5 K/min prior to the dynamic mechanical analysis (DMA). The temperature dependence of E'' of the glass can be divided into four regions. Above 620 K, the onset of crystallization induces the increase of E'' and E' with the temperature. Below 620 K, an obvious peak can be found in the E'' curve. The temperature corresponding to the peak is 588 K, which is higher than the T_g (560 K) measured by differential scanning calorimetry (DSC) at the heating rate of 3 K/min. The peak is therefore related to the dynamics of the metallic SL. Below T_g , a pronounced shoulder appears in the high temperature region, and the E'' is independent of temperature at lower temperature. Compared with the temperature dependence of E'' , E' shows almost no change below T_g . Above T_g , E' decreases with increasing temperature.

The dominant peak of loss susceptibility d in the SL is usually related to the primary relaxation in SL. Figure 2 exhibits the typical characteristics of E'' and E' in SL. The peak E'' shifts to higher temperature with increasing loading frequency. With the frequency increasing from 2 to 8 Hz, the peak temperature increases from 583 to 591 K. The peak frequency can be considered as the mobility of atoms/molecules in the SL.² In other words, the average relaxation time decreases with increasing temperature. The frequency and the temperature of the peak are fitted well to the Vogel-Fulcher-Tammann function: $f_p = f_0 \exp[-B/(T-T_0)]$.² The values of f_0 , B , and T_0 of the metallic glass are 3.5×10^{13} Hz, 4084 ± 20 K, and 440 ± 3 K, respectively.

The primary relaxation in SLs usually obeys the *time-temperature superposition* (TTS) principle.² Given that the α relaxation in the metallic SL obeys the TTS principle and its averaged relaxation time has the form of the inverse f_p , the E' and E'' curves in the temperature region can be simulated with the Fourier transform form: $d\{\Delta E \exp[-(t/\tau)^\beta]\}/dt$, where $\Delta E = E(f=\infty) - E(f=0)$, β is a nonexponentiality parameter, and τ is the average relaxation time. ΔE and β are constant during the simulation. The constant value of the ΔE is consistent with the experimental data in Fig. 2, where the height of the E'' peaks is independent of temperature. The solid lines in Fig. 2 are the best fits for E' and E'' with τ

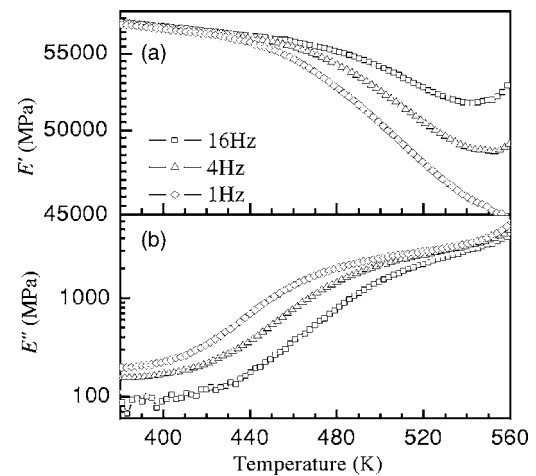


FIG. 3. Temperature dependence of the (a) E'' and (b) E' of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ metallic glass measured at frequencies of 2, 4, and 8 Hz in the glassy region and at a heating rate of 3 K/min.

$= 9 \times 10^{-14} \exp[4084 \pm 20/(T - 440 \pm 5)]$ and $\beta = 0.57$. The solid lines fit the high temperature side, i.e., above T_p , of the peak better, but the low-temperature data display higher value than the fitted line. Since the lower temperature limit of the fit is 580 K, which is 20 K above the T_g found from DSC, the departure implies the existence of another intrinsic relaxation in the metallic glass.

To highlight the shoulder, Fig. 3 plots the temperature dependence of the E' and E'' just below T_g for the metallic glass formed with a cooling rate of 3 K/min from SL. At lower temperatures, E' decreases linearly and slowly with increasing temperature, and E'' is almost independent of temperature. As temperature increases, E'' begins to increase faster, while E' decreases rapidly in the same temperature range. With the interference of the structural relaxation at temperatures close to T_g , a shoulder is found in the E'' curves. The decrease of E' corresponding to the shoulder is not so strong and is less than 20% for 4 Hz. The phenomenon is not only dependent on temperature, but also on the loading frequency. With increasing frequency the shoulder shifts to higher temperature region. Comparing with Fig. 1, it can be found that the relaxation process related to the shoulder will affect the primary relaxation at low temperature in deep supercooled region.

The shoulder cannot be attributed to physical aging of the metallic glass because it appears at temperature well below T_g , and the glass is formed with a slow cooling rate of 5 K/min. Moreover, the shoulder is accompanied with decreasing E' . On the other hand, the phenomenon is found at frequencies much less than 100 Hz, and therefore atomic vibration should not contribute to the shoulder. A reasonable explanation of the shoulder is due to the existence of some intrinsic motion in the metallic glass. From a dynamic point of view, the glass is formed from the SL falling out of the equilibrium, and the primary relaxation of the SL is truncated by the glass transition.² However, the slow β relaxation, the activation energy of which is less than the primary relaxation, can exist in the glass region.⁴ Therefore, the most convincing explanation is that a slow β relaxation exists in the metallic glass and that the shoulder in the E'' curves is related to the slow β relaxation. Figure 3 exhibits that the primary relaxation and the slow β relaxation are not separated completely in the temperature domain.

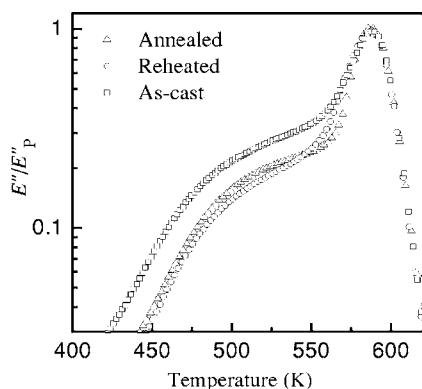


FIG. 4. Temperature dependence of the loss modulus of the as-cast $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass, the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glassy sample annealed at 538 K (below T_g) for four weeks, and the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glassy sample formed with a cooling rate of 5 K/min.

Figure 4 shows the temperature dependence of the reduced elastic modulus E''/E''_p , where E''_p is the elastic modulus at the peak, for three samples at different states tested at 2 Hz. Comparing with the sample annealed at 538 K (below T_g) for four weeks and the sample cooled from SL with a cooling rate of 3 K/min, the as-cast sample formed with a fast cooling rate has higher E''/E''_p . This is due to the effect of the physical aging occurring during heating. However, the temperature ranges of the shoulders of the three samples are the same. The slow β relaxation is independent of the original state of the samples.

The microstructure of the metallic liquid is close to a system consisting of an assembly spheres of different sizes.¹⁴ The slow β relaxation in the metallic system observed by the dynamic mechanical measurement must be related only to the translational motion of atoms because the reorientations of the spheres about their axis do not attribute to the elastic dipole.¹⁰ Moreover, since macroscopic liquidlike flow of the metallic glass was not observed in the time scale of the slow β -relaxation process in our experiment, the translational motion must be localized and involved only a few atoms. If the occurrence of such short-range translational motions involves essentially all atoms during the slow β relaxation, then the application of an external mechanical stress would permanently deform the glass in the β -relaxation time scale. Such permanent deformation is not observed and therefore the translational motions of atoms contributing to the slow β relaxation are small scale and involve only a special part of atoms in the metallic glass.

Our experimental results support the fact that the relaxation in the typical metallic SL is separated. However, due to the dynamic characteristic of the metallic SL, its slow β relaxation cannot be fully decoupled from the α relaxation even in deep SL.³ We confirmed experimentally that an excess wing can be found in the elastic spectrum of the SLs. The excess wing is related to the slow β relaxation overlapping with the primary relaxation in the metallic supercooled liquid. The observation of the excess wing as well as the relationship of the α relaxation and the slow β relaxation in various metallic glasses will be a subject for further investigation.

In conclusion, we present the evidence of the existence of the slow β relaxation through dynamic mechanical measurement during continuous heating process at frequencies lower than 100 Hz in the fragile $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ bulk metallic glass. The slow β relaxation arises from the translational motions of a special portion of atoms in the metallic glass.

The authors are indebted to G. Johari, K. Samwer, and K. L. Ngai for valuable discussions and support. They thank M. B. Tang, D. Q. Zhao, and M. X. Pan for experimental assistance. Financial support from the NSFC (No. 50321101) is acknowledged.

¹G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53**, 2372 (1970).

²E. Donth, *The Glass Transition* (Springer, Berlin, 2001), p. 2.

³K. L. Ngai, *J. Phys.: Condens. Matter* **15**, S1107 (2003); *J. Non-Cryst. Solids* **351**, 2635 (2005).

⁴K. L. Ngai and M. Paluch, *J. Chem. Phys.* **120**, 857 (2004).

⁵C. A. Angell, in *Relaxation in Complex System*, edited by K. L. Ngai and G. B. Wright (National Technical Information Service, Springfield, 1985), p. 3.

⁶P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, *Phys. Rev. Lett.* **65**, 1108 (1990).

⁷K. L. Ngai, *J. Chem. Phys.* **109**, 6982 (1998).

⁸U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, *Phys. Rev. Lett.* **84**, 5560 (2000).

⁹K. L. Ngai, P. Lunkenheimer, C. León, U. Schneider, R. Brand, and A. Loidl, *J. Chem. Phys.* **115**, 1405 (2001).

¹⁰A. Döb, M. Paluch, H. Sillescu, and G. Hinze, *Phys. Rev. Lett.* **88**, 095701 (2002).

¹¹G. P. Johari, *J. Non-Cryst. Solids* **307-310**, 317 (2002).

¹²J. M. Pelletier, B. Van de Moorte, and I. R. Lu, *Mater. Sci. Eng., A* **336**, 190 (2002).

¹³P. Wen, D. Q. Zhao, M. X. Pan, W. H. Wang, Y. P. Huang, and M. L. Guo, *Appl. Phys. Lett.* **84**, 2790 (2004); P. Rösner and K. Samwer, *Europhys. Lett.* **68**, 226 (2004); K. L. Ngai, *J. Non-Cryst. Solids* **352**, 404 (2006).

¹⁴D. N. Perera, *J. Phys.: Condens. Matter* **11**, 3807 (1990).