

# Relaxation of metallic $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk glass-forming supercooled liquid

Ping Wen,<sup>a)</sup> De Qian Zhao, Ming Xiang Pan, and Wei Hua Wang

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

Ya Ping Huang and Mei Li Guo

*The Department of Material, Beihang University*

(Received 11 December 2003; accepted 13 February 2004)

The mechanical relaxation of metallic  $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$  supercooled liquid has been measured by dynamic mechanical analysis. The relaxation behaviors are found to fit well the Kohlrausch–Williams–Watts equation in time domain as well as the Havriliak–Negami equation in frequency domain. Characteristic quantities relaxation time and time–temperature superposition are among the properties also exhibited. The metallic supercooled liquid is found to have common relaxation characteristics of the nonmetallic glass-forming supercooled liquids, demonstrating a connection of the underlying physics for quite different classes of glass formers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1699467]

The dynamical characteristics in supercooled liquids (SLs) is the fascinating subject of many experimental and theoretical investigations.<sup>1–5</sup> Two significant common features in SLs are the non-Arrhenius temperature dependence of the average relaxation times and non-Debye linear response function. Most investigations of the dynamical characteristics in SLs have been processed in molecular organic SLs by dielectric relaxation and specific-heat spectroscopy.<sup>1,4–9</sup> Only a little work has been carried out in metallic SLs. Metallic SLs were a relatively strong liquid, while most molecular organic SLs are fragile.<sup>10–12</sup> So far, it is not known how metallic SLs accommodate the common relaxation features. Recently developed multicomponent bulk metallic glass (BMG)-forming alloys offer the possibility of performing day-long relaxation experiments in the metastable melt far above the  $T_g$ .<sup>13,14</sup> In this letter, we report the investigation of the mechanical relaxation of the representative  $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$  BMG-forming SL by dynamic mechanical analysis (DMA). The typical BMG-forming<sup>13</sup> SL has common relaxation characteristics of the glass-forming SLs.

The BMGs were prepared from a mixture of the elements of purity by arc melting, and were subsequently sucked into a copper mold with water cooling. The experimental apparatus used was a thermal mechanical analysis (DMTA IV). The specimens in the shape of rectangular sheets with dimensions of  $25 \times 5 \times 2$  mm<sup>3</sup> were used. Specimens were tested in a single-cantilever bending configuration. In the DMA experiments, the sample is protected in a nitrogen-flushed atmosphere. The experiment measures the mechanical response of a material subjected to forced oscillations as a function of the oscillation frequency. The storage modulus  $E'$  and loss modulus  $E''$  were measured in a frequency sweep mode under a sinusoidally applied strain of  $\pm 0.03\%$ . From the measurements of the in-phase and out-of-

phase response of the sample, the  $E'$  and  $E''$  can be determined.

Figure 1 exhibits the frequency dependence of  $E'$  and  $E''$  of the sample determined isothermally from 638 to 668 K. As can be seen from the data, the relaxing component of the elastic modulus is asymmetrical and slows down with decreasing temperature in the SL. These features are typical of susceptibility measurements in a SL exhibiting the typical primary ( $\alpha$ ) relaxation.<sup>1</sup> The curves drawn through  $E''$  data are optimized fits to match the observed values by use of the Kohlrausch–Williams–Watts (KWW) equation:<sup>15,16</sup> The Fourier transforms of  $d\{\Delta E \exp[-(t/\tau)^\beta]\}/dt$ , where  $\Delta E = E(f=\infty) - E(f=0)$ ,  $\beta$  a nonexponentiality parameter, and  $\tau$  average relaxation time. The fit yields a better representation in the peak region, but high-frequency data display lower values than the observed values. This is similar to the

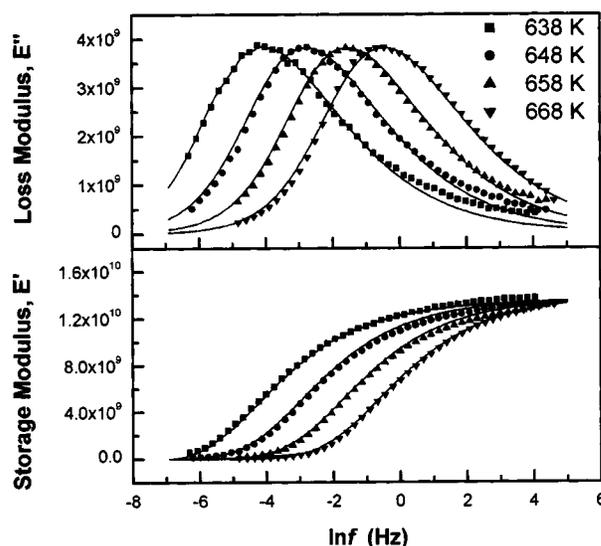


FIG. 1. The frequency dependence of the storage and loss modulus of metallic  $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$  SL determined isothermally by DMA at 638, 648, 658, and 668 K. The solid lines are the fits using the KWW equation.

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: pwen@aphy.iphy.ac.cn

TABLE I. The values of  $\beta$  and  $\tau$  in the KWW equation are listed for the primary relaxation in metallic  $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$  SL.

Temperature (K)	$\beta$	$\tau$ (s)
628	0.49	135
633	0.49	102
638	0.50	40
643	0.49	23
648	0.50	10
653	0.50	7.5
658	0.49	3.5
668	0.50	1.1
678	0.50	0.35

Nagel wing observed in dielectric relaxation.<sup>17</sup> Recently, it has been suggested the difference derives from a partly hidden  $\beta$  relaxation.<sup>17,18</sup> The curves drawn through the  $E'$  data were obtained by use of the parameter values obtained from the  $E''$  and by allowing  $E(f=0)$  to be additional fitting parameter. The quality of the  $E'$  fits confirms that our data obey the KWW relation. The fitted values of  $\beta$  and  $\tau$  are listed in Table I.  $\tau$  decreases rapidly from 135 s at 628 K to 0.35 s at 678 K, while  $\beta$  is about  $0.50 \pm 0.01$  within the temperature range from 628 to 678 K. These indicate that the KWW average relaxation time is dependent on temperature. On the contrary,  $\beta$  is almost independent of temperature.

The value of  $\beta$  is a characteristic parameter of relaxation of glass-forming liquids.<sup>1</sup> For most glass-forming liquids,  $\beta$  is close to 0.5 when temperature approaches  $T_g$ .<sup>4,6,9,14</sup> The departure of  $\beta$  from 1 indicates that an obvious heterogeneity exists in glass-forming SLs, even though the nature of the heterogeneity is not yet clear.<sup>2</sup> Thus, in a metallic SL, heterogeneity is exhibited with a low value of  $\beta$ . The dynamic heterogeneity is expected to result from the concentration fluctuations in the five-component system. On the other hand, the present experimental result supports that close to  $T_g$ ,  $\beta$  is independent of temperature, which is consistent with the results in most polymer SLs.<sup>4,6</sup> The temperature independence of  $\beta$  has been suggested to be a characteristic of primary relaxation.<sup>19</sup> Metallic SLs are relatively strong liquids<sup>11</sup> in which the second relaxation either hides below the high-frequency wing of the primary relaxation peak (consistent with Fig. 1) or lacks this feature altogether.<sup>20</sup> Therefore, the temperature independence of  $\beta$  is a characteristic of the primary relaxation in metallic SLs. However, the value of  $\beta$  is much smaller than that (0.8) determined by quasielastic neutron scattering at high temperature [above crossover temperature  $T_c$  (875 K)].<sup>21</sup> The difference indicates that a change of the relaxation behavior of the metallic undercooled liquid occurs at a constant temperature above  $T_g$ . This confirms that a decoupling occurs at  $T_c$  in the metallic SL, which is typical phenomenon for the glass-forming liquid.<sup>22</sup>

It should be addressed that the occurrence of time-temperature superposition (TTS) is correlated with the KWW-type relaxation pattern with  $\beta=0.5$ .<sup>6</sup> TTS refers to a situation in which the effect of changing temperature reduces to altering some characteristic relaxation time scale and perhaps the amplitude, while the shape of the loss profile (and  $\beta$ ) remains the same. As demonstrated by the master curve in Fig. 2, the metallic SL follows this rule within the temperature range from 628 to 678 K. This indicates that the relax-

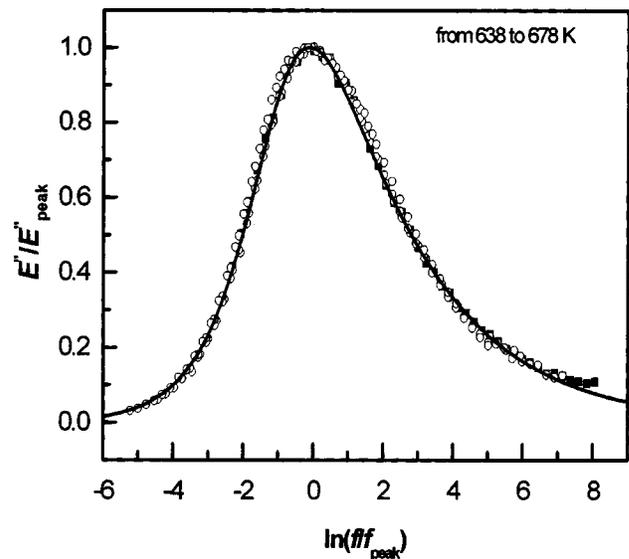


FIG. 2. The frequency dependence of loss modulus  $E''/E''_{\max}$  vs  $\ln(f/f_{\max})$ , obtained by normalizing the 638–678 K data in Fig. 1. The solid line is the fit using the HN equation.

ation of the metallic SL has the common relaxation characteristics in glass-forming SLs.

For susceptibility data determined in the frequency domain, it is more convenient for data reduction purposes to use the Havriliak–Negami function<sup>4,6,9,23</sup>

$$E^*(\omega) = E_{\infty} + \Delta E [1 - (i\omega T_{\text{HN}})^b]^{-g},$$

where  $b$  and  $g$  characterize the symmetric and asymmetric broadening, respectively,  $E_{\infty}$  is the modulus constant in the high-frequency limit and  $\Delta E$  the relaxation intensity. The representative example of how the loss data compares with the HN fits is shown in Fig. 2 with the solid line. The fits are optimized to match the master curve within the low- and high-frequency wings of the spectra; that is, away from the peak frequency, but still with the ranges of power behavior for the low ( $E'' \propto \omega^b$ )-frequency and high ( $E'' \propto \omega^{-bg}$ )-frequency side. The values of  $b$  and  $g$  deduced from the fit are 0.89 and 0.45, respectively. Lower exponential parameters of  $b$  and  $g$  yield a better representation in the peak region. As seen in Fig. 2, the higher frequency data displays higher values than the data of the HN curve. The better fits of the experimental data in Figs. 1 and 2 indicate that the KWW equation has some connection with the HN equation. Even though the HN equation is not a direct Fourier transform of the KWW equation, indicating no direct relationship between the KWW equation in the time domain and the HN equation in the frequency domain.

Thus, because TTS is obeyed in the metallic SL it is possible to measure the temperature dependence for the peak relaxation of  $\alpha$  process within an accessible, wide temperature scope. This is because the isothermal and isochronous curves formed by the loss susceptibility are similar in the SL obeyed TTS.<sup>1</sup> Figure 3 exhibits the typical storage and loss modulus of the BMG determined from 600 to 743 K at heating rate of 1 K/min at the frequencies of 0.02, 0.08, 0.3, 0.7, and 2.00 Hz, respectively. The measured temperature scope contains its SL region. Compared with the results in Fig. 1, the change of the storage and loss moduli in Fig. 3 has an

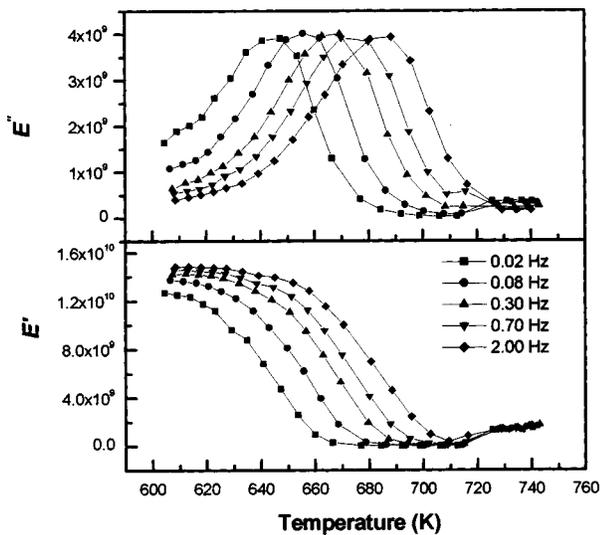


FIG. 3. The temperature dependence of storage and loss modulus of amorphous  $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$  determined by DMA at the heating rate of 1 K/min.

inverse tendency. During heating, the  $E'$  decreases rapidly to zero within a different temperature ranges at different loaded frequencies. The larger the frequency, the higher the temperature range is. The  $E''$  is characterized by an asymmetrical peak with a smaller slope at the low temperature side. Usually,  $f_{peak}$  is used as the average relaxation time. Figure 4 shows the temperature ( $T_{peak}$ ) dependence of the  $f_{peak}$  determined from the isothermal and continuous heating processes. A little difference between isothermal and continuous heating processes can be found. It is consistent with the fact that the isothermal process is the limit of the continuous heating process. The isothermal data are compatible with a Vogel-Fulcher-Tammann (VFT) function:  $f_{max} = f_0 \exp[-B/(T - T_0)]$ .<sup>4,23</sup> The values of  $f_0$ ,  $B$ , and  $T_0$  are  $1.2 \times 10^{13}$  Hz,

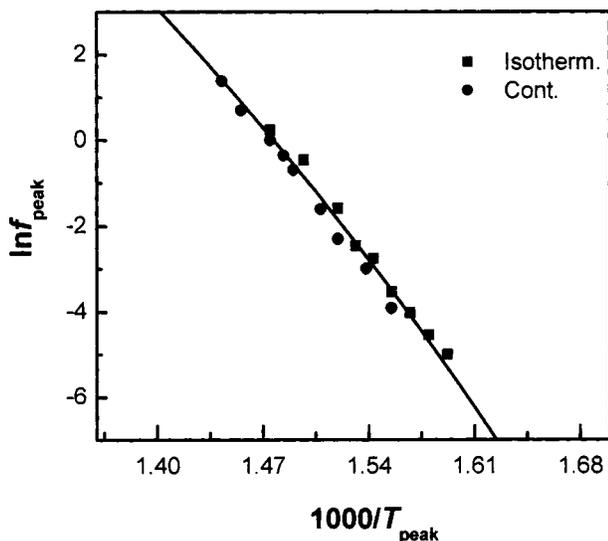


FIG. 4. The plots of  $\ln f_{max}$  against  $1000/T_{max}$  of the primary relaxation in  $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$  SL determined by continuous heating (●) and isothermal (■) conditions. The solid line is the fit for isothermal data by the VFT equation.

9749 K, and 352 K, respectively. The values of  $B$  and  $T_0$  are almost same as those determined from the temperature dependence of viscosity.<sup>11</sup> The dynamic mechanical technique provides information about the time scale of the molecular motion associated with sources of elastic dissipation mechanisms and therefore is related to bulk viscosity properties. At same time, the consistence implies that the bulk viscosity is related to the primary relaxation in the SL. With the VFT parameters, the fragility index  $m \{m = \log_{10} e \cdot [BT_g / (T_g - T_0)^2]\}$  is calculated to be 37, with the value of the glass transition temperature (620 K) determined by DSC at the heating rate of 10 K/min. The relationship between  $m$  and  $\beta$  departs obviously the correlation in most glass forming systems.<sup>10</sup> The departure is unexpected and will be a subject for further investigation.

In conclusion, the mechanical relaxation of the metallic  $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$  has been measured by dynamic mechanical analysis. As usual treatment in other SL, HN- and KWW-type relaxation patterns as well as VFT temperature dependence are good approximations for the present findings. It is interesting to note that TTS is obeyed in the metallic SL. The relaxation behavior indicates that the metallic SL has the common characteristics of the nonmetallic glass-forming liquids, demonstrating a connection of the underlying physics for quite different classes of glass formers.

The authors are grateful for the financial support of the National Science Foundation of China (Grant Nos. 10174088 and 50371097).

- <sup>1</sup>E. Donth, *The Glass Transition: Relaxation and Thermodynamics in Polymers*, Glass Transition (Springer, Berlin, 2001).
- <sup>2</sup>H. Sillescu, *J. Non-Cryst. Solids* **243**, 81 (1999).
- <sup>3</sup>C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, *J. Appl. Phys.* **88**, 3113 (2000).
- <sup>4</sup>R. Richert, K. Duvvuri, and L. T. Duong, *J. Chem. Phys.* **118**, 1828 (2003).
- <sup>5</sup>J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980).
- <sup>6</sup>N. B. Olsen, T. Christensen, and J. C. Dyre, *Phys. Rev. Lett.* **86**, 1271 (2001).
- <sup>7</sup>P. K. Dixon and S. R. Nagel, *Phys. Rev. Lett.* **61**, 341 (1988).
- <sup>8</sup>A. Schoenhals, F. Kremer, and E. Schlosser, *Phys. Rev. Lett.* **67**, 999 (1991).
- <sup>9</sup>O. E. Kalinovskaya and J. K. Vij, *J. Chem. Phys.* **114**, 2718 (2001).
- <sup>10</sup>R. Boehmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993).
- <sup>11</sup>E. Bakke, R. Busch, and W. L. Johnson, *Appl. Phys. Lett.* **67**, 3260 (1995).
- <sup>12</sup>G. Wilde, G. P. Goerler, R. Willnecher, and H. J. Fecht, *J. Appl. Phys.* **87**, 1141 (2000).
- <sup>13</sup>W. L. Johnson, *MRS Bull.* **24**, 42 (1999).
- <sup>14</sup>P. Wen, M. B. Tang, M. X. Pan, D. Q. Zhao, Z. Zhang, and W. H. Wang, *Phys. Rev. B* **67**, 212201 (2003); M. L. Lee, Y. Li, Y. P. Feng, and W. C. Carter, *ibid.* **67**, 132201 (2003).
- <sup>15</sup>R. Kohlrausch, *Ann. Phys. Chem.* **72**, 393 (1847).
- <sup>16</sup>G. Williams and D. C. Watts, *Trans. Faraday Soc.* **66**, 80 (1970).
- <sup>17</sup>N. B. Olsen, *J. Non-Cryst. Solids* **235-237**, 399 (1998).
- <sup>18</sup>H. Wagner and R. Richert, *J. Chem. Phys.* **110**, 11660 (1999).
- <sup>19</sup>I. Morfin, P. Lindner, and P. Boue, *Macromolecules* **32**, 7208 (1999).
- <sup>20</sup>A. Kudlik, C. Tschirwitz, S. Benkhof, T. Blochowicz, and E. Roesler, *Europhys. Lett.* **40**, 649 (1997).
- <sup>21</sup>A. Meyer, J. Wuttke, P. Petry, O. G. Randl, and H. Schober, *Phys. Rev. Lett.* **80**, 4454 (1998).
- <sup>22</sup>G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53**, 2372 (1970); **55**, 4245 (1971); **74**, 2034 (1970).
- <sup>23</sup>S. Havriliak and S. Negami, *Polymer* **8**, 101 (1967).