Journal of Materials Science & Technology 35 (2019) 982–986

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

Main α relaxation and slow β relaxation processes in a $La_{30}Ce_{30}Al_{15}Co_{25}$ metallic glass

J.C. Qiao[a,*], Y.H. Chen[a], R. Casalini[b], J.M. Pelletier[c], Y. Yao[a,*]

[a] *School of Mechanics, Civil Engineering and Architecture, Northwestern Polytechnical University, Xi'an 710072, China*
[b] *Chemistry Division, Naval Research Laboratory, Code 6120, Washington DC 20375-5342, United States*
[c] *Université de Lyon, MATEIS, UMR CNRS5510, Bat. B. Pascal, INSA-Lyon, F-69621 Villeurbanne cedex, France*

ARTICLE INFO

Article history:
Received 25 July 2018
Received in revised form 14 August 2018
Accepted 15 August 2018
Available online 7 December 2018

Keywords:
Mechanical relaxation
Dynamic mechanical relaxation
α Relaxation
β relaxation
Physical aging

ABSTRACT

Dynamic relaxation processes are fundamental to understand the mechanical and physical properties of metallic glasses. In the current work, mechanical relaxations in a $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass were probed by dynamic mechanical analysis. In contrast to many metallic glasses, $La_{30}Ce_{30}Al_{15}Co_{25}$ metallic glass shows a pronounced slow β relaxation peak. Physical aging below the glass transition temperature T_g leads to an increase of the apparent activation energy and a decrease of the slow β relaxation magnitude. The correlation between the slow β relaxation and the main α relaxation is discussed.

1. Introduction

Dynamic kinetics is an important issue to better understand the glass transition, diffusion behavior, mechanical properties and physical properties in glass forming liquids (i.e., metallic glasses, amorphous polymers, oxide glasses and other non-crystalline solids) [1–4]. In general, there are two relaxation processes in glass forming materials: (i) the primary (also called α) relaxation that is evident around the glass transition temperature (T_g); and (ii) the secondary (β) process which is smaller in amplitude and is evident below T_g. The β relaxation and α relaxation modes for amorphous material has been observed based on the dielectric or mechanical spectroscopy. While the temperature dependence of the α process is complex, usually the secondary β relaxation obeys an Arrhenius temperature dependence. The β relaxation is connected to the localized atomic or molecular motion [3,5], while the α relaxation corresponds to more complex and correlated movements of atoms or molecules.

As a newcomer of glassy materials, bulk metallic glasses have aroused considerable interest in the past decades due to their special combination of structural and functional properties, such as higher strength, larger elasticity, lower elastic modulus and excellent corrosion resistance [6–11]. Specifically, compared with the amorphous polymers, metallic glasses exhibit relative dense atomic packing structure [12,13]. As a consequence, metallic glasses are excellent candidates to investigate the mechanical dynamics, especially to understand some of the important physical phenomena in metallic glasses such as: the origin of the plasticity, the correlation between mechanical relaxations and mechanical properties or the connection between α and β relaxations [14]. Recently, the relation between the β relaxations (fast and slow) and intrinsic plasticity in metallic glasses has been established [3,14]. In parallel, it has been reported that the activation energy of the slow β relaxation and shear transformation zones (STZs) are almost equal in metallic glasses [15]. In addition, the origin of slow β relaxation may be associated with diffusion of the smallest atoms in the metallic glasses [16]. It is believed that the slow β relaxation in metallic glasses is closely associated with the structural heterogeneity [17,18]. However, despite extensive experimental and theoretical efforts to clarify the physical properties of the β relaxation, up till now, the physical origin of slow β relaxation is still not clear and requires further study [19,20].

In previous investigations using mechanical spectroscopy, it was found that some La-based metallic glasses present an evident slow β relaxation peak [19,21], Pd-based metallic glasses show a "shoulder" [22,23], and many metallic glasses show only a submerged β peak or "excess wing" [24].

---

[*] Corresponding authors.
E-mail addresses: qjczy@hotmail.com (J.C. Qiao), yaoy@nwpu.edu.cn (Y. Yao).

https://doi.org/10.1016/j.jmst.2018.12.003

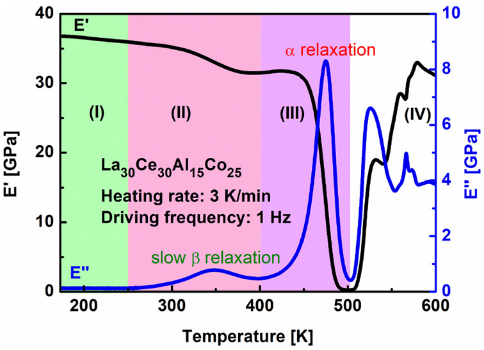

Fig. 1. Evolution of the storage modulus *E*' and loss modulus *E*" with temperature in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass.

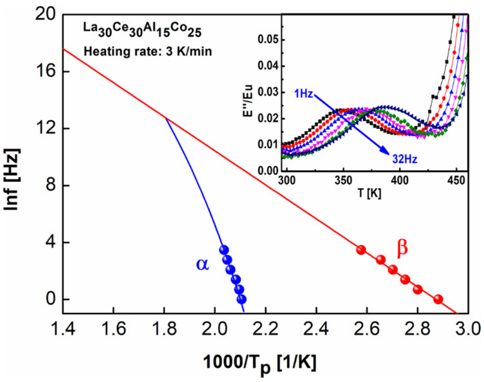

Fig. 2. Temperature dependence of peak values of main α relaxation and secondary β relaxation in a $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass. The α relaxation was fitted by VFT function and the slow β relaxation was fitted by Arrhenius equation. Inset figure is the normalized loss modulus as a function of the temperature with various driving frequencies (heating rate is 3 K/min). E_u is assumed equals to the storage modulus *E*' at room temperature.

For amorphous polymers, there are many studies in the literatures on the pressure effect and physical aging on the slow β relaxation [25–27]. Unfortunately, the information on the influence of physical aging on the slow β relaxation in metallic glasses is limited [28,29]. In the previous research [22], it was found that physical aging below the glass transition temperature T_g leads to a decrease of the magnitude of the slow β relaxation in Pd-based metallic glasses. Since $La_{30}Ce_{30}Al_{15}Co_{25}$ metallic glass presents a well-resolved slow β relaxation process, it provides an interesting case to investigate the effect of aging on the dynamics of glassy materials.

2. Experimental procedure

A $La_{30}Ce_{30}Al_{15}Co_{25}$ (at.%) bulk metallic glass was prepared by copper mold suction casting technique, as described in a previous work [30]. The glassy nature of the model alloy has been confirmed by X-ray diffraction (D8, Bruker AXS Gmbh, Germany). Dynamic mechanical tests of $La_{30}Ce_{30}Al_{15}Co_{25}$ metallic glass were performed using a commercial dynamic mechanical analysis apparatus (DMA, TA instruments Q800) with single-cantilever bending mode. Samples for DMA measurements with the dimensions of 30 mm (length) × 2 mm (width) × 1 mm (thickness) were carried out in a nitrogen-flushed atmosphere. In the framework of the DMA technique, the isothermal spectra, storage modulus *E*' and loss modulus *E*" E' of materials can be obtain both in isothermal or isochronal modes.

3. Results and discussion

The dynamic mechanical behavior of the glass-forming liquids or metallic glass matrix composite depends on both temperature and frequency [31]. Isochronal experiments were carried out at a given driving frequency (0.1 Hz) with a constant heating rate (3 K/min) during continuous heating from 173 K to 600 K. Fig. 1 presents the evolution of *E*' and *E*" E' with the temperature in this $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass. As described in other based bulk metallic glasses, there are four different temperature regions [4,32,33]: (i) at low temperature regime (from 173 K to 250 K), the $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass stays in amorphous state, the storage modulus *E*' remains nearly constant at a high value around 37 GPa, whereas the loss modulus *E*" is relatively low at about 200–300 MPa. Thus, the $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass in this temperature range behaves as an elastic solid with a high modulus. (ii) in the temperature range from 250 K to 400 K, *E*' drops slightly and *E*" E' shows a distinct peak around 350 K. This peak corresponds to the slow β relaxation process. Therefore, the presence of a well resolved β process in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass makes this system ideal for probing the glassy dynamic. (iii) the main α relaxation region (from 400 K to 510 K), which corresponds to the supercooled liquid region (SLR). Remarkably, we found that *E*' decreases drastically and loss *E*" E' reaches the maximum peak. This is associated to a drastic decrease in the viscosity. In the glass transition range, the α relaxation is present in all the bulk metallic glasses, which is associated with the dynamic glass transition phenomenon. For $La_{30}Ce_{30}Al_{15}Co_{25}$ the amplitude of the slow β relaxation is approximately 10% of that of the main α relaxation in metallic glasses, which is in good accordance with the other metallic glasses [21,34]. (iv) in the high temperature regime (temperature above 510 K), a dramatic increase of both *E*' and *E*" E' is observed, which is linked to the formation of crystalline phases (Fig. 2).

To determine the temperature effect to the α and slow β process, isochronal measurements of $La_{30}Ce_{30}Al_{15}Co_{25}$ were carried out at different driving frequencies (1, 2, 4, 8, 16 and 32 Hz), from which the dependence of the peak temperature of the two relaxations as a function of frequency was determined. The secondary β relaxation follows an Arrhenius behavior (activation energy of the secondary relaxation is 1.06 eV) while the temperature dependence of the main α relaxation can be described by the Vogel-Fulcher-Tamman (VFT) equation: $f=f_0\exp[-B/(T-T_0)]$. Here *f* represents the peak frequency, f_0 is a pre-factor expressing the high temperature limit, *B* and T_0 are the fitting parameters. In the current work, the values of these parameters are fitted as follows: $f_0 = 1.6 \times 10^{15}$ Hz, $B = 4748.8$ and $T_0 = 340.5$ K. Clearly, the crossover temperature T_c of the main α relaxation and slow β relaxation in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass is around 556 K. The results indicates that the slow β relaxation decouples from the main α relaxation at around 556 K.

During the rapid solidification process, energy (and free volume or enthalpy) are trapped in the metallic glass. Therefore, the glassy system stays in a non-equilibrium state. With the help of the physical aging below T_g, the glassy system equilibrates towards a more stable state or even equilibrium state if the aging time is long enough.

Fig. 3 illustrates the influence of annealing below the glass transition temperature T_g on the slow β relaxation and main α relaxation in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass (the aging temperature is 398 K and aging time is 24 h). The amorphous nature of the aged sample at 398 K with 24 h has been verified by XRD prior to DMA testing. As demonstrated in the figure, the amplitude of the slow β relaxation is reduced by aging below T_g. In addition, compared with the as-cast state, the peak position of the slow β relaxation moves to higher temperature. This phenomenon will lead to a change of the activation energy during the physi-

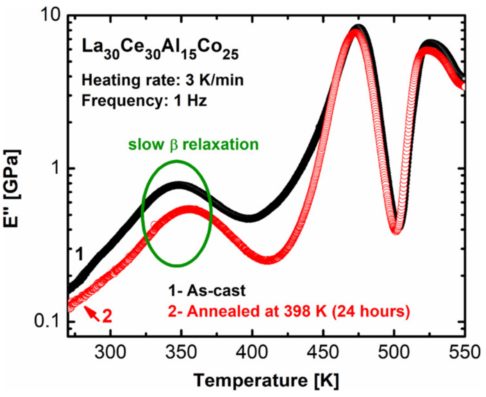

Fig. 3. Evolution of the loss modulus E'' with the temperature in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass. (1) As-cast state, (2) annealed sample (annealing temperature: 398 K with annealing time: 24 h).

cal aging. In contrast, the magnitude ant the temperature of the main α relaxation are almost independent of the physical aging. The current experimental results are in good agreement with the previous investigations. There are many models developed to describe the structural heterogeneity ("defects") based on the experimental, computational and theoretical analysis, such as liquid-like site [35], flow units [36], quasi-point defects [37] and interstitial defects [38] et al. According to the decrease of the loss modulus E'' in Fig. 3, physical aging below T_g leads to annihilation of "defects" in metallic glasses. Physical aging induces structural arrangements of atoms, as a result, the density and elastic modulus increase. Atomic mobility in metallic glasses is closely linked to the "defects". To some extent, the atomic mobility in metallic glasses corresponds to the concentration of the "defects". These results imply that the concentration of both local "defects" and the atomic mobility of metallic glass decrease during physical aging process. In contrast, the plastic deformation (i.e. cold-rolling [39]) and cryothermal cycling treatment [40–42] can rejuvenate the glassy materials. Rejuvenation of metallic glasses can improve the plasticity at ambient temperature.

The dynamic mechanical properties in glass-forming liquids are sensitive to the temperature as well as the driving frequency.. During the heating process, microstructure in amorphous materials evolves. Therefore, isothermal measurements were performed (isothermal temperature ranges from to 315 to 381 K, the interval temperature is 3 K) to probe the slow β relaxation in the $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass. Fig. 4 shows the loss modulus E'' of as-cast state and annealed glassy sample (the sample was annealed at 380 K with aging time 24 h). These measurements evidence that the peak maximum of the slow β relaxation moves to higher frequency by increasing the isothermal temperature. The activation energy of the slow β relaxation can be determined using an Arrhenius equation. As shown in Fig. 5, the apparent activation energy of the slow β relaxation in as-cast state is 0.86 eV, while the apparent activation energy of the annealed sample is 0.97 eV. The glass transition temperature T_g is 459 K [43]. Many investigations have documented that the activation energy of the slow β relaxation E_β in glass-forming liquids at as-cast or received state can be described as: $E_\beta \approx 24\,(\pm 2)\,RT_g$ [15,44]. The current work shows good agreement with the empirical relation of the glassy materials.

The kinetics of the physical aging for glass-forming liquids can be well described by the Kohlrausch-Williams-Watts (KWW) relaxation equation applied to the loss factor tan $\delta = E''/E'$:

$$\tan\delta\,(t_a) - \tan\delta\,(t_a = 0) = A\{1 - \exp[-(t_a/\tau)^{\beta_{\mathrm{aging}}}]\} \qquad (1)$$

where A is the maximum magnitude of the mechanical relaxation. τ is the characteristic relaxation time, τ_{aging} is the KWW exponent with values between 0 and 1. According to Eq. (1), the best fits of KWW equation to the time dependence of the loss factor at different aging temperatures are shown in Fig. 6. It is noted that the value $\beta_{\mathrm{aging}} = 0.561$ can well capture the experimental data. Based on the stress relaxation in metallic glasses, Wang et al. [45] reported that the β_{KWW} remains constant below T_g in $La_{60}Ni_{15}Al_{25}$bulk metallic glass. They found that when the temperature surpasses the slow β relaxation and below T_g, the parameter β_{KWW} keeps around 0.5. It suggests that many flow units start to move in a cooperative modes.

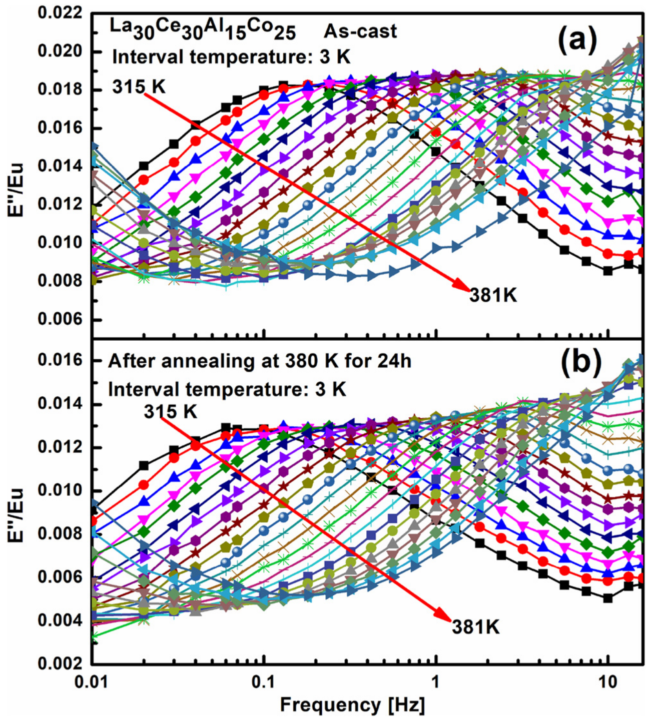

Fig. 4. Normalized loss modulus in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass as a function of frequency at different temperatures (315–318–321–324-327. . .381 K, the interval temperature is 3 K): (a) as-cast state and (b) annealed sample (the sample is annealed at 380 K with annealing time 24 h).

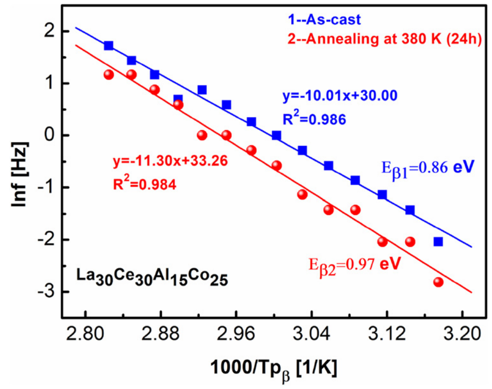

Fig. 5. Correlation between the frequency (f) and the peak value of the slow β relaxation in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass with different states (as-cast state and after annealed at 380 K with 24 h).

In order to understand the effect of physical aging on the slow β relaxation in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass, the annealed samples were also heated from room temperature to 623 K again (Fig. 7). It can be seen that by increasing the annealing temperature, the amplitude of the slow β relaxation decreases due to the glassy system shifts to more stable state.

In order to investigate the dynamic mechanical relaxation behaviors in the $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass, the loss

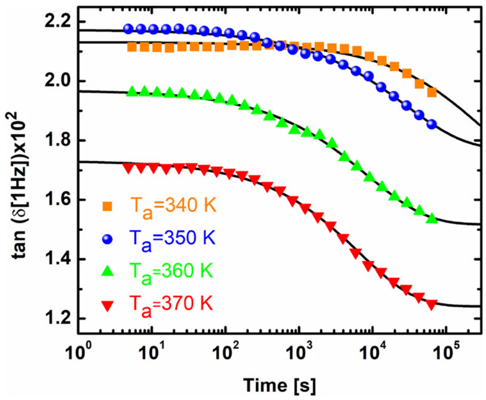

Fig. 6. Evolution of the loss factor tan δ with aging time of $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass at different temperatures, i.e., 340, 350, 360 and 370 K, respectively. Prior to the isothermal aging, the $La_{30}Ce_{30}Al_{15}Co_{25}$ metallic glass was heated to the aging temperature with 1 Hz at a heating rate of 3 K/min. The solid lines are the best fits by Eq. (1).

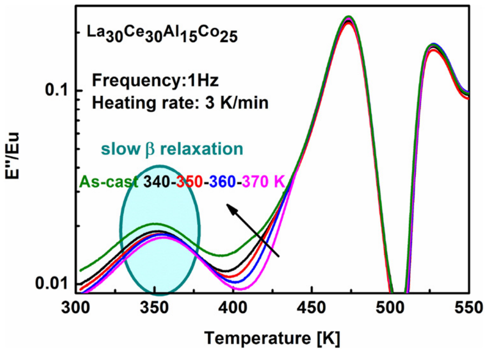

Fig. 7. The normalized loss modulus E''/E_u as a function of temperature in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass at different states. The arrow shows the direction of increased aging temperature going from as-cast state, and samples after annealing at 340, 350, 360 and 370 K for 24 h, respectively.

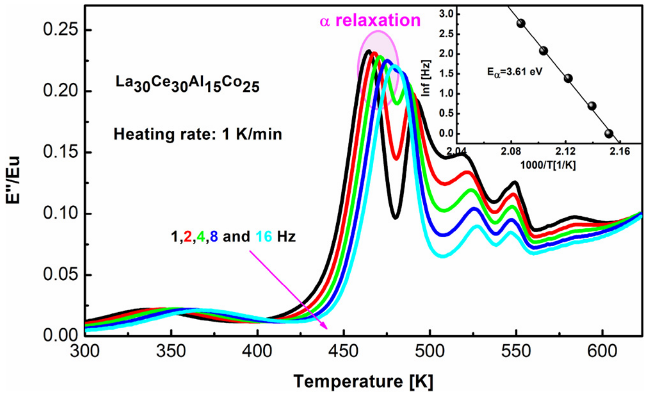

Fig. 8. Normalized loss modulus as a function of temperature with different frequencies at a given heating rate (1 K/min). Inset is the correlation between ln*f* and 1000/*T* for the main α relaxation, first and second crystallization processes. The linear plots are Arrhenius fittings. The activation energy of the main α relaxation is 3.61 eV.

modulus for the as cast sample as a function of temperature was measured with different driving frequencies (shown in Fig. 8). The inset of Fig. 8 shows the activation energy of the main α relaxation, first and second crystallization processes in the LaCe-based metallic glass. We found that the activation energy of the main α relaxation E_α is around 3.61 eV. It can be seen that the activation energy of the main α relaxation in $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass is about 4 times of the slow β relaxation. The current results are in good accordance with the previous investigations in other metallic glass system [46]. This suggests that the slow β relaxation is related to the movements of local atoms while the main α relaxation corresponds to cooperative motions of atoms. As reported in the previous literature, the slow β relaxation is closely associated with the diffusion behavior of the smallest constituent atom in metallic glasses [47]. However, compared with the slow β and main α relaxation processes, the crystallization behavior of metallic glass is linked to atomic arrangement to a great extent. As a consequence, the activation energy of crystallization behavior corresponds to a higher value.

4. Conclusion

Mechanical relaxation dynamical modes of $La_{30}Ce_{30}Al_{15}Co_{25}$ bulk metallic glass have been investigated by DMA. Compared with other metallic glasses, $La_{30}Ce_{30}Al_{15}Co_{25}$ metallic glass presents an evident slow β relaxation. Physical aging below the glass transition temperature T_g reduces the concentration of local "defects" in metallic glasses and causes a decrease of the intensity for the β process. The activation energy of slow β relaxation increases and amplitude of slow β relaxation decreases during physical aging below T_g. The well resolved β process in $La_{30}Ce_{30}Al_{15}Co_{25}$ makes it an ideal glass system to probe the mechanical relaxation behaviors in metallic glass.

Acknowledgements

The research was supported by the National Natural Science Foundation of China (Grant No. 51611130120, 11772257 and 11572249). JCQ is also supported by the Fundamental Research Funds for the Central Universities (No. 3102017HQZZ012 and 3102018ZY010) and the Astronautics Supporting Technology Foundation of China. R. Casalini acknowledges the support of the Office of Naval Research for the work at NRL.

References

[1] W.H. Wang, Prog. Mater. Sci. 57 (2012) 487–656.
[2] J.C. Qiao, J.M. Pelletier, J. Mater. Sci. Technol. 30 (2014) 523–545.
[3] H.-B. Yu, W.-H. Wang, K. Samwer, Mater. Today 16 (2013) 183–191.
[4] J.-M. Pelletier, D.V. Louzguine-Luzgin, S. Li, A. Inoue, Acta Mater. 59 (2011) 2797–2806.
[5] Q. Wang, S.T. Zhang, Y. Yang, Y.D. Dong, C.T. Liu, J. Lu, Nat. Commun. 6 (2015) 7876.
[6] B.A. Sun, W.H. Wang, Prog. Mater. Sci. 74 (2015) 211–307.
[7] C.A. Schuh, T.C. Hufnagel, U. Ramamurty, Acta Mater. 55 (2007) 4067–4109.
[8] A. Inoue, Acta Mater. 48 (2000) 279–306.
[9] H. Sun, K. Song, X. Han, H. Xing, X. Li, S. Wang, J. Kim, N. Chawake, T. Maity, L. Wang, J. Eckert, Metals 8 (2018) 196.
[10] Y. Huang, Z. Ning, Z. Shen, W. Liang, H. Sun, J. Sun, J. Mater. Sci. Technol. 33 (2017) 1153–1158.
[11] X. Wang, W. Dai, M. Zhang, P. Gong, N. Li, J. Mater. Sci. Technol. 34 (2018) 2006–2013.
[12] A. Inoue, A. Takeuchi, Acta Mater. 59 (2011) 2243–2267.
[13] T.C. Hufnagel, C.A. Schuh, M.L. Falk, Acta Mater. 109 (2016) 375–393.
[14] Q. Wang, J.J. Liu, Y.F. Ye, T.T. Liu, S. Wang, C.T. Liu, J. Lu, Y. Yang, Mater. Today 20 (2017) 293–300.
[15] H.B. Yu, W.H. Wang, H.Y. Bai, Y. Wu, M.W. Chen,Phys. Rev. B 81 (2010), 220201.
[16] H.B. Yu, W.H. Wang, H.Y. Bai, K. Samwer, National Sci. Rev. 1 (2014) 429–461.
[17] F. Zhu, H.K. Nguyen, S.X. Song, D.P.B. Aji, A. Hirata, H. Wang, K. Nakajima, M.W. Chen, Nat. Commun. 7 (2016) 11516.
[18] X.D. Wang, J. Zhang, T.D. Xu, Q. Yu, Q.P. Cao, D.X. Zhang, J.Z. Jiang, J. Phys. Chem. Lett. (2018) 4308–4313.
[19] C. Liu, E. Pineda, D. Crespo, Metals 5 (2015) 1073.
[20] H.-B. Yu, R. Richert, K. Samwer,Sci. Adv. 3 (2017), e1701577.
[21] Z. Wang, H.B. Yu, P. Wen, H.Y. Bai, W.H. Wang,J. Phys. Condens. Matter 23 (2011), 142202.
[22] J. Qiao, R. Casalini, J.M. Pelletier, H. Kato, J. Phys. Chem. B 118 (2014) 3720–3730.
[23] J.M. Pelletier, B. Van de Moortèle, I.R. Lu, Mater. Sci. Eng. A 336 (2002) 190–195.

[24] J.C. Qiao, Y.X. Chen, J.M. Pelletier, H. Kato, D. Crespo, Y. Yao, V.A. Khonik, Mater. Sci. Eng. A 719 (2018) 164–170.
[25] R. Casalini, C.M. Roland,J. Chem. Phys. 147 (2017), 091104.
[26] S.P. Andersson, O. Andersson, Macromolecules 31 (1998) 2999–3006.
[27] R. Casalini, C.M. Roland,Phys. Rev. Lett. 102 (2009), 035701.
[28] J. Qiao, R. Casalini, J.M. Pelletier,J. Chem. Phys. 141 (2014), 104510.
[29] Z. Wang, K.L. Ngai, W.H. Wang,J. Appl. Phys. 118 (2015), 034901.
[30] J.C. Qiao, Y. Yao, J.M. Pelletier, L.M. Keer, Int. J. Plasticity 82 (2016) 62–75.
[31] J.C. Qiao, B.A. Sun, J. Gu, M. Song, J.M. Pelletier, J.W. Qiao, Y. Yao, Y. Yang, J. Alloys. Compd. 724 (2017) 921–931.
[32] J. Qiao, J.M. Pelletier, R. Casalini, J. Phys. Chem. B 117 (2013) 13658–13666.
[33] X.F. Liu, B. Zhang, P. Wen, W.H. Wang, J. Non-Crystalline Solids 352 (2006) 4013–4016.
[34] L.Z. Zhao, R.J. Xue, Z.G. Zhu, K.L. Ngai, W.H. Wang, H.Y. Bai,J. Chem. Phys. 144 (2016), 204507.
[35] H.B. Ke, J.F. Zeng, C.T. Liu, Y. Yang, J. Mater. Sci. Technol. 30 (2014) 560–565.
[36] W.H. Wang, Y. Yang, T.G. Nieh, C.T. Liu, Intermetallics 67 (2015) 81–86.
[37] J. Perez, Acta Metall. 32 (1984) 2163–2173.
[38] V.A. Khonik,Chin. Phys. B 26 (2017), 016401.
[39] J.C. Qiao, J.M. Pelletier, H.C. Kou, X. Zhou, Intermetallics 28 (2012) 128–137.
[40] S.V. Ketov, A.S. Trifonov, Y.P. Ivanov, A.Y. Churyumov, A.V. Lubenchenko, A.A. Batrakov, J. Jiang, D.V. Louzguine-Luzgin, J. Eckert, J. Orava, A.L. Greer, NPG Asia Mater. 10 (2018) 137–145.
[41] Y. Sun, A. Concustell, A.L. Greer, Nat. Rev. Mater. 1 (2016) 16039.
[42] S.V. Ketov, Y.H. Sun, S. Nachum, Z. Lu, A. Checchi, A.R. Beraldin, H.Y. Bai, W.H. Wang, D.V. Louzguine-Luzgin, M.A. Carpenter, A.L. Greer, Nature 524 (2015) 200.
[43] R. Li, S. Pang, C. Ma, T. Zhang, Acta Mater. 55 (2007) 3719–3726.
[44] K.L. Ngai, S. Capaccioli,Phys. Rev. E 69 (2004), 031501.
[45] Z. Wang, B.A. Sun, H.Y. Bai, W.H. Wang, Nat. Commun. 5 (2014) 5823.
[46] Q. Sun, C. Zhou, Y. Yue, L. Hu, J. Phys. Chem. Lett. 5 (2014) 1170–1174.
[47] H.B. Yu, K. Samwer, Y. Wu, W.H. Wang,Phys. Rev. Lett. 109 (2012), 095508.