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Citation: Journal of Applied Physics **116**, 103516 (2014); doi: 10.1063/1.4895586 View online: http://dx.doi.org/10.1063/1.4895586 View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/116/10?ver=pdfcov Published by the AIP Publishing

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Evaluation of flow units and free volumes in metallic glasses

L. Z. Zhao,¹ R. J. Xue,¹ Z. G. Zhu,¹ Z. Lu,¹ E. Axinte,² W. H. Wang,¹ and H. Y. Bai^{1,a)} ¹Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China ²Gheorghe Asachi Technical University of Iasi, Faculty of Machine Manufacturing & Industrial Management, 700500 Iasi, Romania

(Received 13 July 2014; accepted 2 September 2014; published online 11 September 2014)

We investigate the changes of the fractions of flow units and free volumes in two typical metallic glasses by variation of their preparation cooling rates. It is found that the fractions of the flow units and the free volumes show a similar dependence on the cooling rate, which is suggestive of the existence of a strong connection between them. The microstructural correlation between flow units and free volumes of the metallic glasses is discussed, which could be helpful for understanding the formation and structural features of the flow units as well as their effects on mechanical properties and relaxation behaviors in metallic glasses. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4895586]

I. INTRODUCTION

Upon cooling below the melting point T_m , the molecular or atomic motions in liquids rapidly slow down.¹ If a liquid is cooled fast enough, the crystallization process can be avoided, the glass transition from a liquid state to an amorphous solid state occurs, and the relaxation time of the system at the glass transition temperature T_g exceeds the time scale of the experiment. The glass transition is essentially the falling out of equilibrium of the system, and the resulting glass is thus not in thermal equilibrium² with flow units and free volumes, and the properties of the glass in general depend on the production history of the glass such as the cooling rate.^{3–7} The more slowly a liquid is cooled, the longer time available for structural relaxation,¹ and the more stable the glass is.

The free volume model, which was proposed by Cohen and Turnbull⁸ and developed by Spaepen,^{9,10} is visualized as the physical space for atomic movement, and the cooling rate can significantly change the content of free volume in a metallic glass (MG).^{2,11–17} Beukel *et al.* and Slipenyuk *et al.*^{18,19} used the recovery enthalpy to quantify the free volume in MGs and proposed a linear relationship between the recovery enthalpy and the fraction of the free volume. The free volume model has been widely used for the description of various features and properties of metallic glasses;²⁰ however, the model could not explain the microscopic mechanism of relaxation in the supercooled liquid as well as the inhomogeneous deformation with formation and evolution of shear bands.²¹

Recently, intensive studies have shown that there exists the nano-scale structural inhomogeneity in MGs. Computer simulations and experiments also show that liquid-like regions in MGs with viscoelasticity flow feature act as the flow units, accommodating the deformation and initiating the shear banding.^{22–29} The liquid-like regions in glass have even been directly imaged by aberration-corrected transmission electron

microscopy.²³ According to the perspective of the flow units model, the MGs can be regarded as elastic matrix combined with liquid like flow units.^{26,27} The liquid like flow units have low density and high mobility, and the fraction of free volumes in flow units may be much larger than that in the glassy matrix,³⁰ and there could be a connection between the flow units and free volumes. These flow units can be activated and percolated by applied stress or elevated temperature, inducing the global plasticity or relaxations of MGs. The concentration of flow units can be estimated by the fictive temperature T_{f_2} which is a useful parameter to describe the cooling rate induced thermal history, the defects of flow units, and microstructure evolution of a glass²² and is defined as the contribution of the structural relaxation process to the properties of a glass, such as enthalpy, refractive index, and specific volume.31-37

In this work, by systematic scrutiny of the changes of the concentrations of flow units and the free volumes in the $La_{60}Ni_{15}Al_{25}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MGs upon the change of the cooling rates in their preparation, we show a linear relationship between the concentrations of flow units and the free volumes. The implications of the results for understanding the structural heterogeneity in MGs are discussed.

II. EXPERIMENTS

We selected two MGs of $La_{60}Ni_{15}Al_{25}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ that have good glass forming ability and a wide and distinct supercooled liquid region. The $La_{60}Ni_{15}Al_{25}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MGs in bulk and ribbon forms were prepared by melt casting and melt spinning, respectively. To remove the different thermal history in each MG sample and make them in the same relaxation state, we heated each MG sample to their supercooled liquid region and hold for 3 min at the temperature of 493 K for $La_{60}Ni_{15}Al_{25}$ and 600 K for $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MGs. And the MG samples with different cooling rates were prepared by cooling to ambient temperature with different cooling rates. In the supercooled liquid region of the MGs, the enthalpy of all samples is the same, which confirms that the different

^{a)}Author to whom correspondence should be addressed. Electronic mail: hybai@iphy.ac.cn

thermal history in each sample is reset when reheating to the supercooled liquid region.³⁸ The structures of the as-cast MG and MGs prepared with different cooling rates were ascertained by X-ray diffraction (XRD) and different scanning calorimetry (DSC). Thermal analysis was carried out using DSC (Perkin-Elmer DSC8000) at the rate of 0.33 K/s under a constant flow of high purity argon gas. The DSC was calibrated according to the melting points of indium and zinc. The onset temperatures of the glass transition T_g and the crystallization event T_x of the La₆₀Ni₁₅Al₂₅ and Pb₄₀Ni₁₀Cu₃₀P₂₀ MGs are about 461 K, 560 K and 509 K, 647 K, respectively.

III. RESULTS AND DISCUSSIONS

Figure 1 shows a schematic plot of the flow unit and free volume change of a glass during quenching process with different cooling rates. In the high temperature region (AB), the kinetics of free volume annihilation is fast enough to keep equilibrium. At lower temperatures (BCD), an excess amount of free volume is frozen in glass. Comparing the two curves, one can infer that with the increase of cooling rates, the flow units and the free volumes will increase. We investigate the effects of cooling rates on the concentration of flow units and the free volumes in the La60Ni15Al25 and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs using DSC measurements. To get the MG samples with different cooling rates, we reheated the MGs to the supercooled liquid region and then cooled to ambient temperature at different cooling rates. Figure 2 presents the DSC curves of the as-cast MG and the glassy samples of La₆₀Ni₁₅Al₂₅ and Pb₄₀Ni₁₀Cu₃₀P₂₀ obtained with different cooling rates. The DSC curves show that there is a weak cooling rates dependence of the T_g , and the T_g keeps almost the same within the experimental error. Broad exothermic peaks can be seen from the as-cast MG samples, which are a part of the structural relaxation of the glass. However, all the samples with different cooling rates show endothermic peaks, and the samples with lower cooling rates absorbed more heat to reach the equilibrium supercooled liquid region, which infers that the samples are in a lower energy state and more stable. This is due to the free volumes frozen during cooling can be recovered in the subsequent DSC runs,



FIG. 1. Temperature dependence of the concentration of the flow units and the free volume during quenching with different cooling rates.



FIG. 2. DSC curves for the as-cast MGs and samples with different cooling rates in $La_{60}Ni_{15}Al_{25}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MGs, and the heat flow is normalized by the sample mass.

resulting in an overshoot in the DSC signals. From the free volume model, there exists a proportionality relationship between the enthalpy change and the free volume change (or the concentration of defect change) during the structural relaxation and glass transition processes,^{18,19} which suggests that the microstructural configuration of these MGs has been changed by the cooling rates.

The enthalpy change ΔH of the La₆₀Ni₁₅Al₂₅ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MGs was estimated by integrating the release heat flow in DSC traces,³⁶ which is illustrated in Fig. 3(a). In the DSC curves of all the MGs, the heat flow is almost zero indicating that structural relaxation does not take place before 373 K. At 493 K for $La_{60}Ni_{15}Al_{25}$ and 600 K for Pd₄₀Ni₁₀Cu₃₀P₂₀, the MG samples are in the supercooled liquid state and their enthalpy is almost same regardless of their different thermal history [see Figs. 2(a) and 2(b), the DSC curves collapse before 373 K or in the supercooled liquid state]. So, the enthalpy change ΔH of the MGs was calculated by integrating the heat flow from 373 to 493 K for La₆₀Ni₁₅Al₂₅ and 373 to 600 K for Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs, respectively. The definition of the fictive temperature T_f has been given by Moynihan *et al.*³² and Hodge,³⁹ and the T_f was estimated by the enthalpy change³⁶ as is illustrated in Fig. 1. The variation of the enthalpy and the T_f with different cooling rates was plotted in Fig. 3(b). It can be seen that with the increases of cooling rates, the enthalpy change decreases and the T_f increases. The MGs with smaller cooling rates



FIG. 3. (a) The illustration of the calculation of enthalpy change ΔH on DSC curve. (b) Cooling rates dependence of the fictive temperature and the enthalpy change in La₆₀Ni₁₅Al₂₅ and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs. (c) Cooling rates dependence of the effective concentration of flow units in La₆₀Ni₁₅Al₂₅ and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs.

have less frozen-in concentration of flow units, and the MGs approach a lower energy and stable state. As shown in Fig. 3(b), the relationship between the enthalpy and the effective concentration of the flow units *c* can be well fitted as

$$\Delta H(q) = \Delta H_{eq} / (1+c) = \Delta H_{eq} / \{1 + [a/(b+1/q)]^{p}\},$$
(1)

where ΔH_{eq} is the equilibrium enthalpy change at $q \rightarrow 0$, and $c = [a/(b + 1/q)]^{\beta}$ (where *a*, *b*, β are constants, and *q* is the cooling rate), which corresponds to the effective concentration of the flow units. In the extreme case, when $q \rightarrow 0$, $c \rightarrow 0$, one gets $\Delta H(q) = \Delta H_{eq}$, which means the enthalpy change approaches that of the equilibrium state. In Fig. 3(b), one can see that the relationship between the T_f and the concentration of the flow units *c* can be well fitted as

$$T_f(q) = T_{f0}/(1-c) = T_{f0}/\{1 - [a/(b+1/q)]^{\beta}\}, \quad (2)$$

where T_{f0} is the Kauzmann temperature, $c = [a/(b+1/q)]^p$. When $q \to 0$, $c \to 0$, $T_f(q) = T_{f0}$, which means the glass is in the ideal state in this extreme case. The relationship between T_f and the *c* agrees well with the recently found relationship between some properties and the concentration of the flow units.^{36,40,41}

According to the theory of Beukel, there is a linear relationship between the released enthalpy change (ΔH) and the free volume fraction change (Δx) during the structural relaxation and glass transition processes^{18,19}

$$\Delta H = A \Delta x, \tag{3}$$

where A is a constant. For the temperature range of the structural relaxation process is from T to T_{eq} , then during the structural relaxation process, the free volume change Δx between x(T) (the free volume at temperature T) and $x(T_{eq})$ (the free volume at temperature T_{eq}) corresponds to the enthalpy change $\Delta H(T, T_{eq})$ from T to T_{eq} . According to the theory of Beukel, in the equilibrium supercooled liquid temperature region, Eq. (3) can be presented as $(C_p)_{eq} = Adx_{eq}/$ dT = A/B (C_p represents the specific heat for a glassy system), and $x_{eq}(T_{eq}) = (T_{eq} - T_0)/B$,⁴² where T_0 is the Vogel-Fulcher temperature and B is a constant. Thus, from the C_p , B, T_0 and B, A, and $x_{eq}(T_{eq})$ can be estimated. The free volume at any temperature x(T) then can be deduced from the enthalpy change from T to T_{eq} and $x_{eq}(T_{eq})$ as

$$x(T) = x_{eq}(T_{eq}) + \Delta H(T, T_{eq})/A.$$
(4)

Based on the enthalpy change during glass transition measured by DSC and the theory of Beukel,^{18,19} the *B* and T_0 were determined to be 4874.5 and 316 K, 4062.5 and 442 K, respectively, for the La₆₀Ni₁₅Al₂₅ and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs.^{43,44} The free volumes are estimated to be 0.0363 and 0.0389 at 493 K and 600 K in La₆₀Ni₁₅Al₂₅ and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs, respectively. From the DSC result, the (C_p)_{eq} for the La₆₀Ni₁₅Al₂₅ and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs, respectively. From the DSC result, the constant *A* can be estimated to be A = 79.8 and 77.1 kJ mol⁻¹ for the La₆₀Ni₁₅Al₂₅ and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs, respectively.

Based on Eq. (4), the free volume frozen in MGs with different cooling rates was estimated and presented in Figs. 4(a) and 4(b). The free volume exhibits a linear increase with increasing temperature, indicating that the equilibrium state is achieved for the system in this temperature range. Figure 4(c) presents the free volume frozen in MGs with different cooling rates in the La₆₀Ni₁₅Al₂₅ and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs. The relationship between the free volume and the cooling rate can be fitted as follows:

$$x = [a/(b+1/q)]^{\beta}.$$
 (5)

Figure 5 shows the plot of flow units against free volumes for the two MGs at different cooling rates. The data reveal nearly a one-to-one correspondence between the concentration of flow units and free volumes in the two typical MGs upon cooling rate, indicating that there is an approximately linear relationship within the error bars between the concentration of flow units and the free volumes as

$$c = kx + b, \tag{6}$$



FIG. 4. (a) Temperature dependence of the free volumes in $La_{60}Ni_{15}Al_{25}$ MG; (b) in $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MG. (c) Cooling rates dependence of the free volume.



FIG. 5. The relationship between the free volume and the concentration of flow units in the $La_{60}Ni_{15}Al_{25}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MGs at different cooling rates.



FIG. 6. Schematic illustrations of the free volume and flow units in MGs. The red atom areas represent the flow unit, the blue atom areas represent the densely packed elastic matrix, and the green dotted circles represent the distribution of free volumes.

where *k* and *b* are constants. The found relationship provides information about the evolution of flow units and free volume as well as the structural features of a MG. According to the free volume model, the MGs are not in a fully closed packed state, and the free volume in MGs is uniformly distribution. However, in the perspective of flow unit model, the MGs can be regarded as elastic matrix combined with nano-scale liquid like flow units. The MG is structural inhomogeneous and the distribution of defects in MGs is random and heterogeneous.^{22–28,45–49}

Based on our above results and the results of Refs. 22, 23, 36, 40, and 41, we schematically illustrate the relationship of flow units and free volumes in MGs in Fig. 6. The red atom areas represent the defects of flow units with higher potential energies and the looser packing densities, the blue atom areas represent the densely packed elastic matrix with the relatively homogeneous structure, and the green dotted circles represent the free volumes. One can see that the glass consists of the elastic substrate and flow units where the most free volumes locate, and the free volumes do not like to distribute homogeneously in MGs but mainly locate in the areas of flow units, which accords with the recent report that the plastic flow is associated to the flow units or liquid-like sites in MGs.^{22,50} Our results might also suggest that the concentration of flow units is a key parameter for description the relaxation and mechanical properties of MGs.

IV. CONCLUSIONS

We show that there is a linear relationship between the concentrations of the free volume and the flow units in MGs. The MGs are inhomogeneous with highly localized flow units, and the free volumes mainly distribute in these flow units, where the atomic packing is relatively loose. The results could be helpful for understanding the microscopic origin of the dynamics of the glass, structural relaxation, and other properties in MGs.

ACKNOWLEDGMENTS

The financial support of the NSF of China (Grant Nos. 51271195) is appreciated. We thank Y. T. Sun, P. Wen, D.

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- ¹P. G. Debenedetti and F. H. Stillinger, Nature **410**, 259–267 (2001).
- ²K. Vollmayr, W. Kob, and K. Binder, J. Chem. Phys. **105**, 4714 (1996). ³H. N. Bisland, J. Am. Comm. Soc. **27**, 270 (1954).
- ³H. N. Ritland, J. Am. Ceram. Soc. **37**, 370 (1954).
- ⁴C. Y. Yang, D. E. Sayers, and M. A. Paesler, Phys. Rev. B **36**, _8122(1987).
- ⁵C. T. Limbach and U. Gonser, J. Non-Cryst. Solids **106**, 399(1988).
- ⁶G. P. Johari, A. Hallbrucker, and E. Mayer, J. Phys. Chem. **93**, 2648 (1989).
- ⁷R. Brunning and M. Sutton, Phys. Rev. B **49**, 3124 (1994).
- ⁸M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959).
- ⁹M. H. Cohen and G. S. Grest, Phys. Rev. B 20, 1077 (1979).
- ¹⁰F. Spaepen, Acta Metall. **25**, 407 (1977).
- ¹¹M. E. Launey, R. Busch, and J. J. Kruzic, Scr. Mater. 54, 483 (2006).
- ¹²Y. Z. Yue, R. Von der Ohe, and S. L. Jensen, J. Chem. Phys. **120**, 8053 (2004).
- ¹³J. R. Fox and H. C. Andersen, J. Phys. Chem. 88, 4019 (1984).
- ¹⁴J. Baschnagel, K. Binder, and H. P. Wittmann, J. Phys. 5, 1597 (1993).
- ¹⁵S. K. Lai and M. S. Lin, J. Non-Cryst. Solids 117–118, 907 (1990).
- ¹⁶H. Miyagawa and Y. Hiwatari, Phys. Rev. A **40**, 6007 (1989).
- ¹⁷R. Speedy, Mol. Phys. 83, 591 (1994).
- ¹⁸A. Van den Beukel and J. Sietsma, Acta Metall. Mater. **38**, 383 (1990).
- ¹⁹A. Slipenyuk and J. Eckert, Scr. Mater. **50**, 39 (2004).
- ²⁰P. S. Steif, F. Spaepen, and J. W. Hutchinson, Acta Metall. **30**, 447(1982).
- ²¹M. Bletry, P. Guyot, J. J. Blandin, and J. L. Soubeyroux, Acta Mater. 54, 1257–1263 (2006).
- ²²J. C. Ye, J. Lu, C. T. Liu, Q. Wang, and Y. Yang, Nature Mater. 9, 619 (2010).
- ²³P. Y. Huang, S. Kurasch, J. S. Alden, A. Shekhawat, A. A. Alemi, and D. A. Muller, Science **342**, 224 (2013).
- ²⁴H. B. Yu, X. Shen, Z. Wang, L. Gu, W. H. Wang, and H. Y. Bai, Phys. Rev. Lett. **108**, 015504 (2012).
- ²⁵H. Wagner, D. Bedorf, S. Kuchemann, M. Schwabe, B. Zhang, W. Arnold, and K. Samwer, Nature Mater. **10**, 439 (2011).
- ²⁶W. H. Wang, J. Appl. Phys. **110**, 053521 (2011).

- ²⁷Z. Wang, P. Wen, L. S. Huo, H. Y. Bai, and W. H. Wang, Appl. Phys. Lett. **101**, 121906 (2012).
- ²⁸A. V. Granato, Phys. Rev. Lett. 68, 974 (1992).
- ²⁹W. H. Wang, Prog. Mater. Sci. 57, 487 (2012).
- ³⁰M. H. Cohen and D. Turnbull, Nature **189**, 131 (1961).
- ³¹A. Q. Tool, J. Am. Ceram. Soc. 29, 240 (1946).
- ³²C. T. Moynihan, A. J. Easteal, M. A. Debolt, and J. Tucker, J. Am. Ceram. Soc. **59**, 12 (1976).
- ³³C. T. Moynihan, Rev. Mineral. **32**, 1 (1995).
- ³⁴C. T. Moynihan, S. K. Lee, M. Tatsumisago, and T. Minami, Thermochim. Acta 280, 153(1996).
- ³⁵D. J. Plazek and K. L. Ngai, *Physical Properties of Polymers Handbook* (AIP Press, Woodbury, NY, 1996).
- ³⁶Z. G. Zhu, P. Wen, D. P. Wang, R. J. Xue, D. Q. Zhao, and W. H. Wang, J. Appl. Phys. **114**, 083512 (2013).
- ³⁷V. H. Hammond, M. D. Houtz, and J. M. O' Reilly, J. Non-Cryst. Solids. **325**, 179 (2003).
- ³⁸Z. Evenson and R. Busch, Acta Mater. **59**, 4404 (2011).
- ³⁹I. M. Hodge, J. Non-Cryst. Solids **169**, 211 (1994).
- ⁴⁰D. P. Wang, Z. G. Zhu, R. J. Xue, D. W. Ding, H. Y. Bai, and W. H. Wang, J. Appl. Phys. **114**, 173505 (2013).
- ⁴¹R. J. Xue, D. P. Wang, Z. G. Zhu, D. W. Ding, B. Zhang, and W. H. Wang, J. Appl. Phys. **114**, 123514 (2013).
- ⁴²M. E. Launey, J. J. Kruzic, C. Li, and R. Busch, Appl. Phys. Lett. 91, 051913 (2007).
- ⁴³Z. F. Zhao, P. Wen, C. H. Shek, and W. H. Wang, Phys. Rev. B 75, 174201 (2007).
- ⁴⁴J. C. Qiao and J. M. Pelletier, J. Appl. Phys. **112**, 033518 (2012).
- ⁴⁵Y. F. Shi and M. L. Falk, Phys. Rev. Lett. **95**, 095502 (2005).
- ⁴⁶H. Tanaka, Nature Mater. 9, 324 (2010).
- ⁴⁷W. Dmowski, T. Iwashita, C.-P. Chuang, J. Almer, and T. Egami, Phys. Rev. Lett. **105**, 205502 (2010).
- ⁴⁸M. J. Demkowicz and A. S. Argon, Phys. Rev. B 72, 245206 (2005).
- ⁴⁹T. Fujita, K. Konno, W. Zhang, V. Kumar, M. Matsuura, A. Inoue, T. Sakurai, and M. W. Chen, Phys. Rev. Lett. **103**, 075502 (2009).
- ⁵⁰L. S. Huo, J. F. Zeng, W. H. Wang, C. T. Liu, and Y. Yang, Acta Mater. **61**, 4329 (2013).