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Glass-liquid transition in a less-stable metallic glass

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A stable metallic glass, SMG, is often viewed as an amorphous alloy exhibiting a reversible glass↔liquid transition. Here we show experimentally that even in a less-stable metallic glass, LMG, which is prepared only by rapid melt quenching and promptly crystallized without glass transition at the ordinary heating rate, sufficiently rapid heating exposes the glass→liquid transition by suppressing crystallization. The experimental glass transition T_g and crystallization T_x temperatures were plotted as a function of heating rate β, for $\mathrm{Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}}$ of SMG and for $\mathrm{Zr_{70}Ni_{30}}$ of LMG. Two extrapolated curves, $T_g-\log\beta$ and $T_x-\log\beta$, intersect at a quite small β, e.g., $\sim 10^{-4}$ °C/min, for SMG, whereas their intersection occurs at a large β, e.g., ~ 10 °C/min, for LMG. Such a large β that is comparable to conventional heating rates makes it difficult to observe the reversible glass transition in LMG, and reflects low thermal stability of the glassy state.

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Since amorphous Au-Si was successfully prepared from its melt by rapid solidification in 1960,[1] a large variety of amorphous alloys have been produced. Unlike other glassy solids, most of amorphous alloys readily transform to a crystalline phase on heating without going through supercooled liquid. Around 1970, Chen and Turnbull[2–4] discovered relatively stable amorphous alloys in noble-metal-based systems which exhibit a distinct and reversible glass-liquid transition. In 1990s, highly stable amorphous alloys without necessarily containing noble metals and/or metalloids have been discovered in multicomponent systems.[5] These amorphous alloys exhibiting a distinct and reversible glass-liquid transition are called "metallic glasses," in conformity with the definition that "a glass is an amorphous solid which exhibits a glass transition,"[6] although all the rapidly quenched (RQ) amorphous alloys can be regarded as "glasses" in a sense that they have once undergone the glass transition during the melt quenching.

The presence of the glass→liquid transition on heating apparently evidences a high thermal stability of supercooled liquid and thereby amorphous states, and appears to be directly connected with the thermodynamic property of glass-forming liquid. In contrast, the crystallization of amorphous alloys is obviously kinetic behavior related with the diffusion of atoms. Thus, even in an amorphous alloy seemingly showing no glass transition (hereafter we refer to as a less-stable metallic glass "LMG," in contrast to a stable metallic glass "SMG"), the glass transition could be observed if the crystallization can be suppressed somehow. It is naturally expected that T_g of LMG is observable at extremely high heating rates, but this has not been demonstrated so far. Actual observation of T_g will remove any speculation associated with the glass transition of LMG. In this paper, we show the presence of the glass transition in LMG, and measured glass-liquid transition temperatures T_g as well as crystallization temperatures T_x by calorimetric measurements at various heating rates β. The aim of the present measurements is to clarify the difference in nature of the glass transition between SMG and LMG metallic glasses.

We have chosen $\mathrm{Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}}$ (of metal-metalloid alloy system) as SMG and $\mathrm{Zr_{70}Ni_{30}}$ (of purely metallic system) as LMG. Differential scanning calorimetry (DSC) measurements in $\mathrm{Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}}$ and $\mathrm{Zr_{70}Ni_{30}}$, prepared by the melt-spinning method, were made using a standard commercial instrument (Perkin Elmer Diamond DSC) with samples of about 5–10 mg. Heat flow was measured during heating at a constant rate up to 500 °C/min, being the highest rate attainable by this instrument. At usual heating rates of the order of 10 °C/min, $\mathrm{Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}}$ exhibits the glass →liquid transition at about 300 °C,[7] whereas $\mathrm{Zr_{70}Ni_{30}}$ does not.[8,9]

Figure 1 shows the DSC profiles of $\mathrm{Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}}$ (SMG) measured at various heating rates β. The solid curves are the profiles of the first heating run on as-prepared samples above melting temperatures, and the dashed curves are those for the second heating run on the crystallized samples. Note that the onset temperature of crystallization T_x is more largely shifted towards a high temperature with increasing β than T_g. Finally, melting takes place at about 525 °C under $\beta = 10$–40 °C/min, accompanied by a sharp endothermic peak. The melting behavior gets complicated at larger β, because metastable phases are formed on crystallization and melt at a lower temperature than the equilibrium phases do. Apart from this complexity, the areas of the characteristic peaks are almost proportional to β, which indicates that the actual sample temperature follows the nominal heating rate in the measurements. Here it is important to note that the melting temperature T_m is virtually invariant with a change in β.

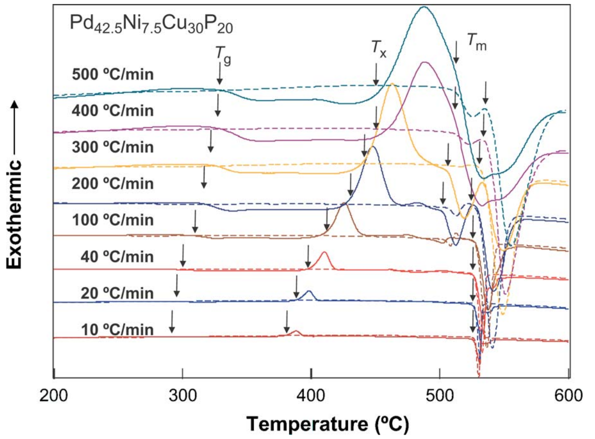


FIG. 1. (Color online) DSC profiles of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ of SMG measured in the first (solid curve: For the amorphous phase) and the second (dashed curve: For the crystalline phases) heating runs at various heating rates β. Mark- ers indicate the onset temperatures of the glass transition T_g, crystallization T_x, and melting T_m.

Figure 2(a) shows β dependence of the subtracted DSC profiles for $Zr_{70}Ni_{30}$ (LMG), and 2(b) the profiles (1st and 2nd runs) at β=500 °C/min and the heat-capacity difference, ΔC_p, between 1st and 2nd runs. As seen in Fig. 2(a) at 10 to 40 °C/min only the exothermic peak for the crystallization (into Zr_2Ni intermetallic compound) appears. However, with increasing β, T_x is markedly shifted toward a higher temperature, and the glass transition takes place at a temperature slightly below T_x. This verifies that the glass transition occurs even in LMG and is not usually detected only because the competing transformation to crystalline phases prevails under the standard heating condition. Figure 2(b) shows details of profiles obtained at β=500 °C/min. It is clearly seen that a distinct endothermic peak associated with the glass transition appears after a slight exothermic peak due to structural relaxation. Although the fact that T_g is located close to T_x apparently makes it difficult to separate the two reactions, the heat-capacity difference ΔC_p between the supercooled liquid and crystallized state which is estimated to be about 0.1 J/g °C (8.1 J/mol °C) at T_g is close to the value at T_m.[10]

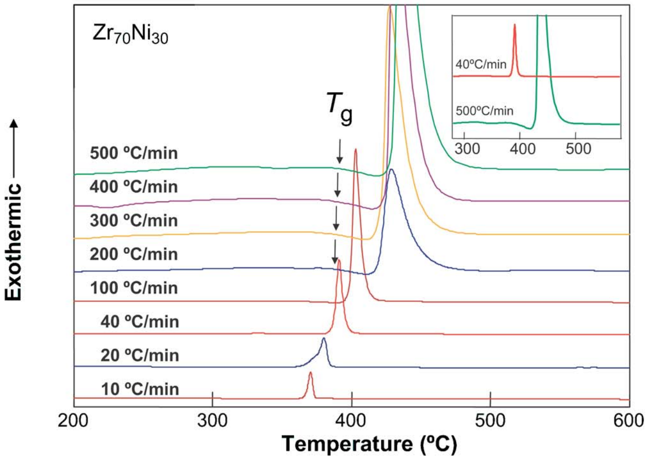
The T_g and T_x values for the two alloys are plotted against log β in Fig. 3. It is found that these characteristic temperatures can be expressed in Lasocka's empirical form:[11]

$$T_{x,g} = a_{x,g} + b_{x,g} \log \beta. \tag{1}$$

In both glassy alloys, T_x is significantly raised by increasing β, which is natural since crystallization is a kinetic process controlled by atomic diffusion. On the other hand, the variations of T_g with β are much smaller. The slight increase of T_g could be attributed to the structural relaxation that proceeds during heating. According to Chen,[12] the value of b_g ranges 4.6–23 for metallic glasses; the present values of b_g (about 6.9 for $Zr_{70}Ni_{30}$ and 19 for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$) are within this range.

Intersection of the two extrapolated curves, T_g-log β and T_x-log β, will provide useful information on the nature of the glass transition. We can see a large difference in the behavior between SMG and LMG. The intersection takes place at a quite small β for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ of SMG ($\beta_c \approx 7.2 \times 10^{-4}$ °C/min), whereas it occurs at a relatively large β for $Zr_{70}Ni_{30}$ of LMG ($\beta_c \approx 17$ °C/min). Since the former heating rate is far below conventional heating rates used for observation of T_g in a laboratory time scale, the reversible glass transition is always observable. Namely, SMG such as $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ shows a similar glass transition behavior to that of other (oxide, polymeric, ionic) stable glasses. SMG has a random network structure consisting of covalently bonded metal-metalloid clusters.[13] These strongly bonded clusters are considered to behave like molecules in the other types of glasses. Thus, their kinetics is mainly subject to the temperature dependence of viscosity. On the other hand, β_c for LMG is of the ordinary time scale. In the glassy alloys containing only metallic elements, the mobility of atoms is expected to be considerably higher than that in SMG because

(a) β dependence



(b) β = 500ºC/min

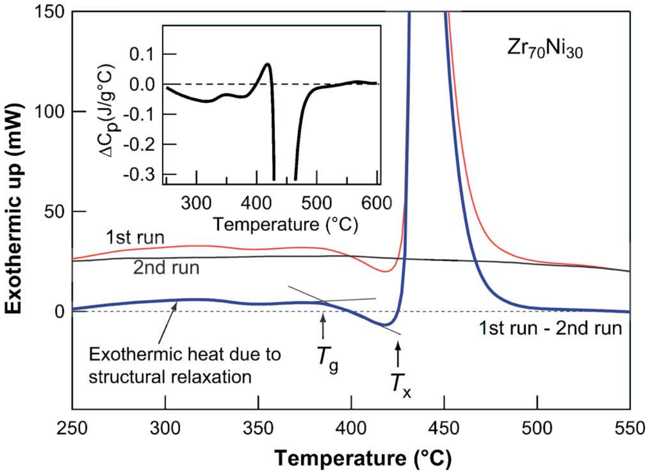


FIG. 2. (Color online) (a) DSC profiles of $Zr_{70}Ni_{30}$ at various β obtained after subtracting the profile of second run from that of first run. The glass transition is clearly recognized at about and above 200 °C/min. (b) DSC profiles of first run and second run at β =500 °C/min. For reference, the heat-capacity difference ΔC_p between first and second runs is also shown in the inset.

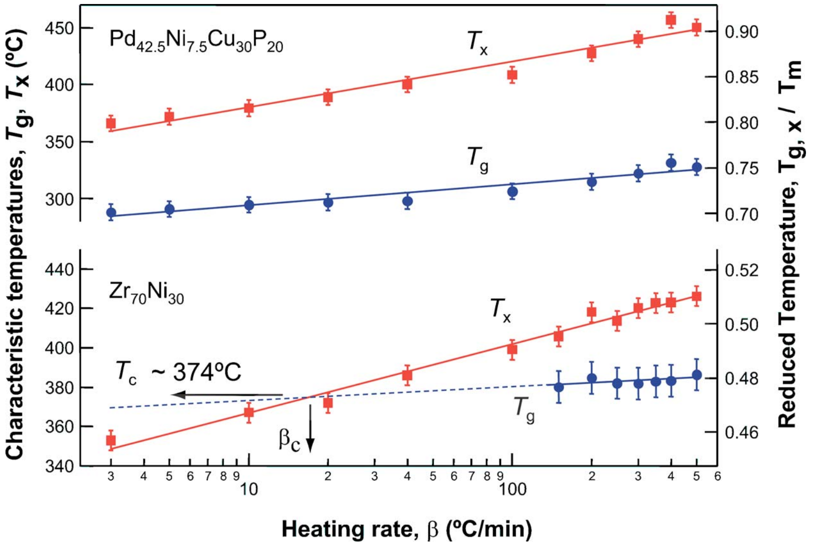


FIG. 3. (Color online) Dependence of the onset temperatures of the glass transition and crystallization, T_g and T_x, on the heating rate β for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Zr_{70}Ni_{30}$ metallic glasses.

metallic bonds are dominant in LMG. Thus, the kinetics of LMG is mainly subject to diffusion of each atom rather than the corporative motion in viscous behavior. Consequently, it makes hard to observe the reversible glass transition of LMG with the ordinary heating rate.

In addition, the intersection temperatures are $T_c \approx 216\ ^\circ\mathrm{C}$ $(0.61T_m)$ for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $T_c \approx 374\ ^\circ\mathrm{C}$ $(0.47T_\mathrm{m})$ for $Zr_{70}Ni_{30}$. Here, it is noted that, for $Zr_{70}Ni_{30}$, the glass transition is not observed at a small β. From the characteristic temperatures we obtain a following relation. For a SMG such as $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$,

$$T_c < T_g < T_x^* . \tag{2}$$

In contrast, for a LMG such as $Zr_{70}Ni_{30}$,

$$T_x^* < T_c . \tag{3}$$

T_x^* is the value of the crystallization temperature at small β within the laboratory time scale (e.g., the order of 1–10 °C/min) and corresponds to the temperature at which atoms start to lose/acquire mobilities on cooling/heating. Thus, the relative location of T_c against T_x^* gives a measure of the thermal stability of metallic glasses.

According to literature,[14,15] the temperature T_c given by the intersection of the two curves is close to the Kauzmann temperature T_K, which is thermodynamically defined as the temperature at which the entropy of liquid (disordered phase) becomes equal to that of crystal. Actually, according to a thermodynamic estimation by Wunderlich and Fecht,[10] T_K of binary Zr-Ni amorphous alloys is $T_K/T_m \approx 0.48$, surely being very close to T_c ($\approx$0.47) for $Zr_{70}Ni_{30}$ in Fig. 3. Since the crystallized sample was composed mainly of Zr_2Ni intermetallic (ordered) compound, the entropy of the crystal at 0 K is considered close to the zero-entropy ground state (but not an ideal ground state because of the off-stoichiometric composition). Hence, if $T_c \approx T_K$ holds also in this case, an intriguing feature can be drawn from the present experimental result. In the glass transition of LMG having the relation of Eq. (3), upon heating the ergodicity is sufficiently restored at around T_c, because atoms acquire appreciable mobilities above T_x^*. Therefore, if $T_c \approx T_K$, it is hardly imagined that the ideal glass transition at T_c (or actual glass transition occurring at T_g) is purely due to kinetic freezing. However, this expression is very controversial, because kinetic freezing inevitably occurs in the vicinity of T_K in terms of temperature dependence of equilibrium viscosity that follows Vogel-Fulcher-Tammann law. Hence, the physical meaning of the intersection temperature T_c in Fig. 3 needs to be reexamined; we are now considering this from the viewpoints of atomic mobility (diffusion) and inhomogeneous microstructure consisting of "mobile" and "less-mobile" regions.[16]

In conclusion, we have shown that the glass → liquid transition of LMG such as $Zr_{70}Ni_{30}$, in which it is not usually detected due to prior crystallization, is observable only at high rates, e.g., $\beta \sim 500\ ^\circ\mathrm{C/min}$. The two curves of T_g-log β and T_x-log β intersect at a quite small β (e.g., $\beta_c \sim 10^{-4}\ ^\circ\mathrm{C/min}$) for SMG. In contrast, for LMG the intersection occurs at a large β (e.g., $\beta_c \sim 10\ ^\circ\mathrm{C/min}$) that is comparable to conventional heating rates, which makes it difficult to observe the reversible glass transition in LMG. Thus, the magnitude of β_c may be a measure for the thermal stability of glassy solid.

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[1] W. Klement, R. H. Willens, and P. Duwez, Nature (London) **187**, 869 (1960).
[2] H. S. Chen and D. Turnbull, J. Chem. Phys. **48**, 2560 (1968).
[3] H. S. Chen and D. Turnbull, Acta Metall. **17**, 1021 (1969).
[4] H. S. Chen and D. Turnbull, Acta Metall. **22**, 1505 (1974).
[5] M. Telford, Mater. Today, **7** 36 (2004).
[6] S. R. Elliott, *Physics of Amorphous Materials* (Longman, London and New York, 1984).
[7] N. Nishiyama, A. Inoue, and J. Z. Jiang, Appl. Phys. Lett. **78**, 1985 (2001).
[8] J. Saida, M. Kasai, E. Matsubara, and A. Inoue, Ann. Chim. (Paris) **27**, 77 (2002).
[9] Z. Fu-Qian, Mater. Sci. Eng. **97**, 487 (1988).
[10] R. K. Wunderlich and H. J. Fecht, Z. Metallkd. **91**, 552 (2000).
[11] M. Lasocka, Mater. Sci. Eng. **23**, 173 (1976).
[12] H. S. Chen, Rep. Prog. Phys. **43**, 353 (1980).
[13] C. Park, M. Saito, Y. Waseda, N. Nishiyama, and A. Inoue, Mater. Sci. Technol. **40**, 491 (1999).
[14] R. Busch, Y. J. Kim, W. L. Johnson, J. Appl. Phys. **77**, 4039 (1995).
[15] P. R. Okamoto, N. Q. Lam, and L. E. Rehn, Solid State Phys. **52**, 1 (1999).
[16] T. Ichitsubo, E. Matsubara, T. Yamamoto, H. S. Chen, N. Nishiyama, J. Saida, and K. Anazawa (unpublished).