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Sub-T_g relaxation and multi-stage glass transition behavior for bulk glassy alloys

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ABSTRACT

We have found for the first time the following three important relaxation phenomena for amorphous and bulk glassy alloys (BGAs), namely, (1) sub-T_g reversible enthalpy relaxation for multi-component amorphous alloys, (2) sub-T_g dynamic storage modulus transition and loss modulus peak for BGAs, and (3) two-stage storage modulus transitions and loss modulus peaks in the T_g and supercooled liquid (SL) region for BGAs. Although these phenomena were discovered around 1984 for the sub-T_g enthalpy relaxation and around 1991 for the sub-T_g dynamic modulus peak and the two-stage glass transitions, these results and concepts are important even at present as fundamental properties for deep understanding of BGAs. This review is expected to provide an opportunity to develop much useful BGAs with high glass-forming ability (GFA), wide SL region and high ductility.

1. Introduction

Considering the development history of amorphous and BGAs, one can recognize two epoch making events of finding Au-Si amorphous alloy in 1960 [1] and La–Al–Ni BGA in 1989 [2]. The amorphous alloys which can be defined as a disordered alloy without detectable T_g have been developed since the first synthesis in 1960 by rapid quenching technique [1]. The alloy systems have been extended to wide alloy compositions, but their formations need very high cooling rates above approximately 10^5 K/s and the resulting maximum thickness of amorphous alloys has been usually limited to less than 100 μm for ribbon, 150 μm for wire and 40 μm for spherical powder [3,4]. On the other hand, BGAs have been synthesized in a variety of multi-component systems in conjunction with the developments of novel casting techniques since 1990 [5,6]. The maximum thickness of BGAs reaches 80 mm for Pd–Cu–Ni–P system [7] and its critical cooling rate is of the order 0.1 K/s [8,9]. The maximum thickness is significantly different between amorphous and glassy alloys. The difference is due to the difference in the stability of SL, but little is known about the reason for the difference in stability between BGAs and amorphous alloys. It is expected that the reason for the difference in atomic configurations between BGAs and amorphous alloys can be interpreted through structural relaxation studies. This research seems to contribute to the clarification of the origin for high GFA for multi-component BGAs.

We have performed a series of studies on enthalpy relaxation [10–14], dynamic relaxation and glass transition behavior [15–21] for amorphous and BGAs with different compositions and preparation processes, with the aim of getting the information on the relation between relaxed structure and properties as well as on the origin for the difference in the stability between amorphous and BGAs. In these studies, we have found that only the multi-component amorphous alloys containing two metallic elements or more show the sub-T_g enthalpy relaxation [10–12], while no sub-T_g enthalpy relaxation is detected for BGAs [16]. In addition, we have also found that BGAs show dynamic sub-T_g peak as well as multistage glass transitions [11], while neither dynamic sub-T_g peak nor two-stage T_g loss peak is detected for amorphous alloys.

This paper aims to review the two-stage enthalpy relaxation behavior of multi-component amorphous alloys and sub-T_g relaxation and multi-stage T_g behavior for BGAs and to investigate structural features and the origin of high stability for BGAs.

2. Enthalpy relaxation of Fe-based amorphous alloys

Fig. 1(a) shows the temperature dependence of apparent specific heat $C_p(T)$ of $(Fe_{0.5}Ni_{0.5})_{83}P_{17}$ amorphous alloy in as-quenched and

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annealed states for 13 h at 375–575 K [12]. The $C_{p,q}$, $C_{p,s}$ and $C_{p,a}$ present apparent specific heats of as-quenched, heated to the temperature above T_g and annealed states, respectively. The $C_{p,q}$ shows an irreversible exothermic reaction which starts at about 370 K, while the $C_{p,a}$ shows an excess endothermic peak which deviates at each annealing temperature (T_a) from $C_{p,s}$. The $C_{p,a}$ increases with increasing temperature, shows a maximum, then decreases and merges with $C_{p,q}$. The excess endothermic reaction occurs reversibly and is due to annealing-induced relaxed atomic configurations to unrelaxed atomic configurations which are in an equilibrium state at the measuring temperatures. By examining the excess endothermic peak behavior, one can get the information on the change in atomic configurations upon annealing. Furthermore, as shown in Fig. 1(b) [12], the temperature dependence of configuration enthalpy at each T_a can be evaluated from the data shown in Fig. 1(a). One can understand that the enthalpy of the as-quenched sample is higher by about 1200 J/mol than that for the relaxed amorphous phase after heating to above T_g.

Fig. 2 shows the temperature dependence of the differential specific heat $\Delta C_p(T)$ between the reference and annealed samples for $(Fe_{0.5}Ni_{0.5})_{83}P_{17}$ amorphous alloy [12]. The endothermic peak shows a maximum at T_a = 450 K, a minimum at T_a = 525 K and then increases approaching T_g, indicating that the endothermic reaction occurs through two stages. Fig. 3 shows the maximum differential specific heat ($\Delta C_{p,max}$), (a) and the enthalpy relaxation ($\Delta H_{\sigma,endo}$), (b) as a function of T_a for the Fe–Ni–P amorphous alloy subjected to annealing for 1–48 h. The $\Delta C_{p,max}$ and $\Delta H_{\sigma,endo}$ show distinguished two peaks with peak temperatures of 450 K for the first stage and near T_g for the second stage, indicating that the enthalpy relaxation takes place through two stages.

Similar two-stage enthalpy relaxation behavior was observed for $(Fe–Ni)_{75}Si_{10}B_{15}$ [10], $(Fe–Co)_{75}Si_{10}B_{15}$ [10], $(Co–Ni)_{75}Si_{10}B_{15}$ [10], $(Fe–Ni)_{75–85}B_{15–25}$ [12], $(Fe_{0.75}M_{0.25})_{83}P_{17}$ (M = Ni, Co, Mn, Cr) and $(Fe_{0.85}M_{0.15})_{83}P_{17}$ (M = Ni, Cr, V, Mo) [22] amorphous alloys. The endothermic peak shows a maximum around equi-atomic compositions of two metallic components and the peak temperature shifts to a high temperature side in the order of Ni, Co, Mn, Cr, V and Mo, in agreement with the melting temperature of M

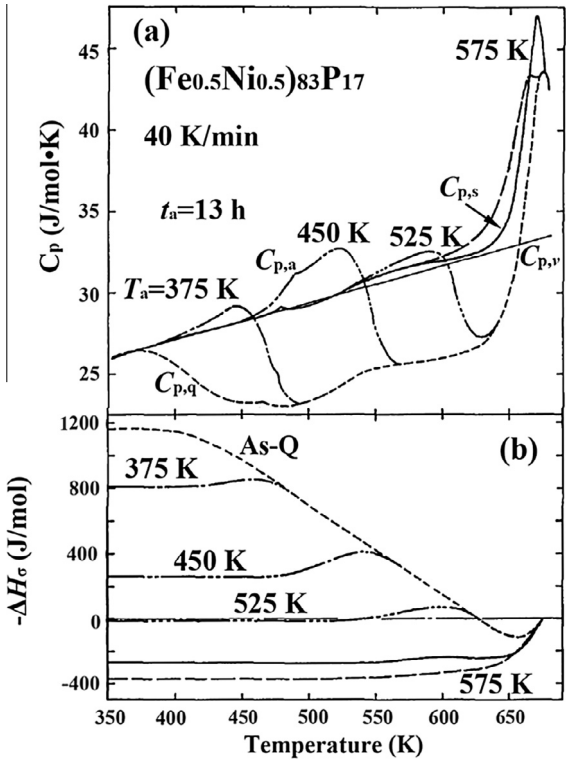

Fig. 1. (a) The endothermic peak of an amorphous $(Fe_{0.5}Ni_{0.5})_{83}P_{17}$ alloy subjected to anneals for 13 h at various temperatures from 375 to 575 K. (b) The change in the configuration enthalpy $-\Delta H_\sigma(T)$ corresponding to the appearance of the endothermic peak, where ΔH_σ(675 K) is set to zero.

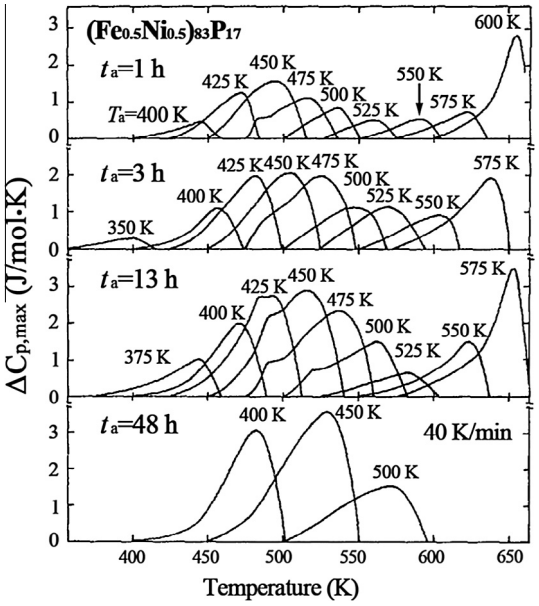

Fig. 2. The differential specific heat $\Delta C_p(T)$, between the reference and annealed samples for an amorphous $(Fe_{0.5}Ni_{0.5})_{83}P_{17}$ alloy subjected to anneals at various temperatures ranging from 400 to 600 K for different periods from 1 to 48 h.

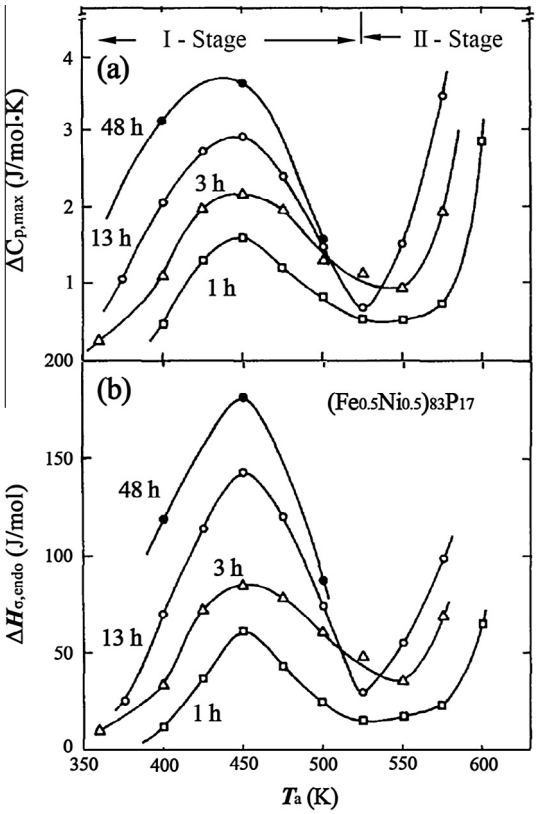

Fig. 3. The variations of the maximum differential specific heat $\Delta C_{p,max}$ (a) and the enthalpy relaxation, $\Delta H_{\sigma,endo}$ (b) as a function of annealing temperature for amorphous $(Fe_{0.5}Ni_{0.5})_{83}P_{17}$ alloy subjected to anneals for different periods from 1 to 48 h.