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A glance on the glass-transition phenomenon from the viewpoint of devitrification

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Abstract

The formation of a supercooled liquid region and devitrification behaviour of metallic glasses on heating are discussed in relation with the glass-transition phenomenon observed using differential scanning and isothermal calorimetries as well as X-ray diffraction and transmission electron microscopy (TEM). One of the most clear sequences of the glassy ↔ supercooled liquid phase transition is the change of the devitrification behaviour and the kinetics of the devitrification reaction in Al-based and some other alloys after the transition from the glassy to the supercooled liquid state. The significant variation in the devitrification behaviour and thermodynamic parameters indicate the difference between the glassy and the supercooled liquid phases.

Keywords: Glassy alloy; Glass-transition; Supercooled liquid; Devitrification

1. Introduction and target setting

The glass-transition phenomenon in metallic glasses has been studied extensively since they were first fabricated [1–3]. Structurally, glassy and liquid states are quite similar but as compared to a glassy solid state, liquid has zero value static shear modulus. Several theories of glass-transition have been put forward [4,5] and one of the most successful explanation is the mode-coupling theory [6]. A thermodynamic aspect of the glass-transition process has been pointed out by Kauzmann [7]. However, an important question which is still not completely answered is: Do glassy and liquid phases belong to the same phase, just observed at different temperatures, or the liquid–glassy phase transformation and vice versa (called glass-transition) indeed does take place? Three kinds of approaches have been formulated ([4,8–10], for example, among the other sources):

1. Glassy phase is just a frozen liquid, and thus, glass-transition is a kinetic phenomenon and no thermodynamic phase transformation takes place.
2. Glass-transition may be a second-order transformation as follows from the shape of the curves for the thermodynamic parameters, for example; specific volume or enthalpy, which exhibit a continuity at the glass-transition temperature while their derivatives like $\partial V/\partial T$ or $\partial H/\partial T$ exhibit a discontinuity (in a certain approximation) at the glass-transition temperature.
3. Glass-transition may be a first-order transformation as follows from the free-volume model.

At the same time, the abrupt change of the thermodynamic parameters during a first-order transformation is not obviously necessary. For example, it is not the case if the local chemical composition changes upon phase transformation, or in the case of displacive transformation.

A large number of the recently collected experimental data motivated us to have a closer look at the glass-transition phenomenon in metallic glasses from the viewpoint of devitrification of the glassy phase on heating.

2. Experimental details

The experimental procedure can be obtained from any of our previous works devoted to devitrification of metallic glasses [11], for example; in details the ingots of Al- and Cu-based alloys were prepared by arc-melting mixtures of pure elements in an argon atmosphere. Cu-based alloys are bulk glass formers while Al-based ones can be produced only as melt-spun ribbons. From these ingots, ribbon samples were prepared by a melt spinning technique. The structure of the samples was examined by X-ray diffractometry with monochromatic Cu Kα and synchrotron radiation as well as transmission electron microscopy (TEM). The phase transformations on heating were studied by differential scanning

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calorimetry (DSC) at a heating rate of 0.67 K/s and by differential isothermal calorimetry.

3. Glass-transition on cooling and heating in co-relation with devitrification behaviour

The slope of the enthalpy (H) of a liquid as a function of temperature curve, which is the specific heat capacity at constant pressure (C_p) per mol, changes in the certain temperature interval. The variation of the enthalpy on cooling is schematically shown in Fig. 1(a). The glass-transition on cooling takes place in the temperature range between the conditional beginning of glass-transition ($T_{\mathrm{bg}}^{\mathrm{C}}$) and the finish of glass-transition ($T_{\mathrm{fg}}^{\mathrm{C}}$) temperatures which can be treated as a glass-transition region. The intersection of the two slopes dH/dT gives an intermediate point which is called a glass-transition temperature $T_{\mathrm{g}}^{\mathrm{C}}$ attained at a certain cooling rate as glass-transition temperature is cooling rate dependent.

The glass-transition on heating (symbol (H)) takes place in the temperature range between the conditional beginning of glass → supercooled liquid transition ($T_{\mathrm{bg}}^{\mathrm{H}}$) and finish of glass-transition ($T_{\mathrm{fg}}^{\mathrm{H}}$) temperatures (area of change of slope) as monitored by the deflection of the DSC curve in Fig. 1(b) on heating. As it is difficult to detect the deflection point related to the beginning of change of slope this temperatures ($T_{\mathrm{bg}}^{\mathrm{H}}$) and ($T_{\mathrm{fg}}^{\mathrm{H}}$) are called conditional. As shown in the insert there is also a slight overshoot in C_p because the heating rate is much lower than the cooling rate upon the rapid solidification. The formation of a supercooled liquid is clearly observed in Fig. 1(b). On heating this state exists between $T_{\mathrm{fg}}^{\mathrm{H}}$ and devitrification temperature known as T_x. $T_{\mathrm{bg}}^{\mathrm{H}}$ is often treated as the glass-transition temperature in the literature. The $Cu_{55}Hf_{25}Ti_{15}Pd_5$ alloy (here and elsewhere throughout the paper all alloy compositions are given in nominal at.%) was taken for representation in Fig. 1(b) and (c) as it shows quite a large supercooled liquid region.

The glass-transition phenomenon was also monitored on heating by XRD measurements. Q is wave vector corresponding to the center of mass of the first diffraction maximum at room temperature (Q_0) and current temperature (Q_{T}) measured after completion of the structural relaxation process on heating (the sample was preliminary heated up to $T_{\mathrm{bg}}^{\mathrm{H}}$ to complete the structural relaxation) as is expressed in Fig. 1(c). It is postulated that $\Delta(Q_0/Q_{\mathrm{T}})$ scales with the linear size changes $\Delta(L_{\mathrm{T}}/L_0)$ provided that the interatomic interactions on thermal expansion are elastic [12]. The linear thermal expansion coefficient related to d(Q_0/Q_{T})/dT derivative changes within the glass-transition region from 1.4×10^{-5} to 4×10^{-5} K^{-1}. These values correspond to that of the solid [13] and liquid metals/alloys [14], respectively.

As it was shown in the previous works the supercooled liquid has the physical properties different from that of the glassy phase [15]. This results in a difference in the devitrification reaction proceeded from a glassy and a supercooled liquid phase in several glass-forming alloys provided that the nucleation and growth transformation mechanism is observed. One of the most clear consequences of the glassy ↔ supercooled liquid phase transition is the change of the devitrification behaviour and the kinetics of the devitrification reaction in Al–Y–Nd–Ni–Co and Al–Y–Ni–Co glassy alloys on crystallization from the glassy and the supercooled liquid state [16,17]. Table 1 shows the influence of the transformation temperature in the isothermal mode on the type of the devitrification (crystallization) reaction. The samples were annealed isothermally at the temperature around

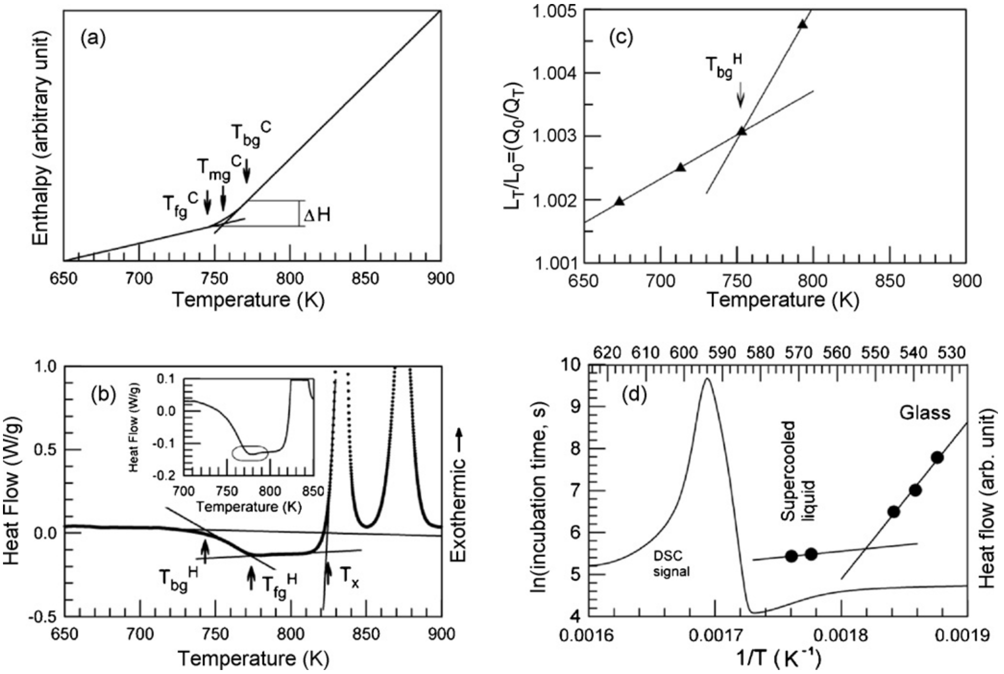

Fig. 1. (a) Specific heat H as a function of temperature (scheme). (b) DSC curve for $Cu_{55}Hf_{25}Ti_{15}Pd_5$ alloy and (c) the ration of X-ray diffraction peak positions Q_0/Q_{T} related to L_{T}/L_0 vs. temperature. (d) DSC trace and Arrhenius plot created using incubation time for phase transformation in $Al_{85}Ni_5Y_4Nd_4Co_2$ alloy.