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Glass-transition process in an Au-based metallic glass

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ABSTRACT

In the present paper, the glass-transition phenomenon in an Au-based metallic glass has been studied using a step-scan calorimetry measurement. The existence of two distinct slopes within the glass-transition region one starting at low temperature (about 340 K) and the other at higher temperature (about 380 K) likely indicates two glass-transition processes. This phenomenon is rather related to different diffusion coefficients of the alloying elements in this complex alloy in solid state. Structural relaxation of the glassy phase before reaching the glass-transition region also shows a complex behavior.

1. Introduction

Apart from the amorphous materials obtained by thin film deposition [1] the first metallic glassy alloy (or metallic glass) [2], namely Au–Si, was produced by rapid solidification of the melt in 1960 [3]. Ternary Au–Si–Ge [4] and Au–Pb–Sb [5] alloys developed later demonstrated a better glass-forming ability (GFA). Later other noble metal-based metallic glasses were also produced including bulk metallic glasses [6]. Bulk metallic glasses (BMGs) also called bulk metallic glassy alloys defined as 3-dimensional massive glassy objects with a size of not less than 1 mm in every spatial dimension have been produced during the last 20 years in the thickness range of 10^0–10^2 mm by using various casting processes [7–11]. These materials having a non-crystalline structure [12] exhibit high strength [13], good wear and corrosion resistance [11,14].

The transition from liquid to glassy state taking place at the glass transition temperature (T_g) [15,16] is observed universally in various types of liquids at sufficiently fast cooling when crystallization is suppressed [17,18]. The process of vitrification in Pd-based BMGs was recently studied in-situ and intensification of covalent bonding with P atoms was found close to the glass-transition [19]. Glass formation is a complex phenomenon. Although, the glass-transition phenomenon in metallic glasses has been studied extensively [20–22] there are still considerable uncertainties in this field of materials science [23,24]. There are several gaps in obtaining a clear picture of glass transition, especially in metallic liquids. For example, a thermodynamic treatment of glass transition has been suggested by Kauzmann [25]. Several theories are used to describe glass transition [26–28] though none is really comprehensive so far.

In order to further study the phenomenon of glass transition, i.e. the transformation of a liquid into the glassy state and vise versa, in the present work we investigated the glass transition phenomenon in a $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy alloy developed earlier [29]. In order to minimize the kinetic effects associated with structural relaxation upon continuous heating, we measured the specific heat capacity as a material property, on annealing the glassy alloy in a step scan mode. Step scan measurements allow equilibrating the glassy phase before each subsequent measurement [30]. The studied alloy has a sufficiently high glass-forming ability and has good stability of a supercooled liquid for such an investigation.

2. Experimental procedure

The ingot of a $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ alloy (the composition is given in nominal at.%) was prepared by arc-melting mixtures of high purity elemental metals having more than 99.9 mass% purity in an argon atmosphere. From this ingot, glassy ribbon samples of about 20 μm in thickness and 1 mm in width were prepared by rapid

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solidification of the melt on a single copper roller at a tangential wheel velocity of 40 m/s. Bulk glassy samples contain a surface layer of crystalline phases [31] which colored their surface in gold, and were not used in the present work. No visible presence of such a surface layer (unless it is extremely thin) was observed in ribbon samples.

Then the glass-transition phenomenon was studied on continuous heating in a Seiko DSC and Perkin-Elmer Diamond DSC in a step scan mode. The glassy samples were heated and cooled at a rate of 83 mK/s (5 K/min), while the annealing (waiting) time between the steps was maintained at 60 s (1 min). The specific heat capacity at constant pressure (C_p) was measured by using heat release (ΔH) at each heating/cooling step.

3. Results

Fig. 1 shows the heat flow variation of the studied alloy on continuous heating as a function of temperature at a heating rate of 0.67 K/s. An enlarged plot up to 424 K indicates a possible double-stage structural relaxation shielding the glass-transition region visible at the first DSC run and when compared to the second run.

In order to rule out possible crystallization the $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy sample was annealed at 400 K close to the glass-transition region and no clear changes in the X-ray diffraction pattern were found. There is a slight decrease in the half width of the first diffraction maximum as a result of structural relaxation below T_g (Fig. 2).

Specific heat capacity (C_p) was measured in a step-scan mode on heating of an initial glassy phase up to above T_g and subsequent cooling to room temperature at 5 K/min (83 mK/s) with an annealing time of 60 s before the subsequent heating or cooling cycle (Fig. 3). The step-scan measurement allowed to get rid of the effect of structural relaxation (Fig. 1) as much as possible and to study the behavior of the glassy phase itself. The C_p of the glass increases gradually with increasing temperature from about 24 J/mol·K at room temperature. In the glass-transition region the slope of the plot changes twice: the first time at about 340 K and the second time at about 380 K. It may indicate two distinctly different glass-transition processes.

On further heating the specific heat reaches a maximum of 40.5 J/mol·K in the supercooled liquid state and remains nearly constant in this region before the sample starts to crystallize. This value is close to that obtained for liquid copper near its melting temperature [32] and Zr-based bulk glass-forming alloys [33] in the supercooled liquid state but lower than those reported for Au–Pb–Sb [34]. The excess heat capacity of the supercooled liquid of about 15 J/mol·K (as a difference between the values of C_p at 410 and 340 K) is close to that of the $Au_{81.4}Si_{18.6}$ alloy [35] and higher than that of some other glasses [36]. At step scan mode crystallization starts above 430 K. On crystallization C_p decreases to a reduced value close to that of the initial glassy state being extrapolated to a higher temperature (see triangle symbols in Fig. 3).

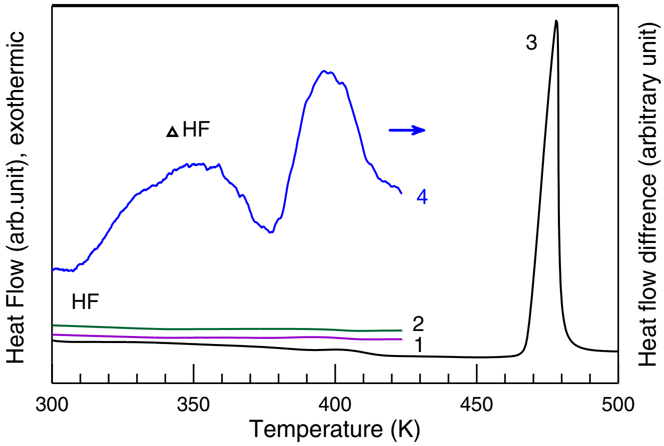

Fig. 1. DSC trace scanned at 0.67 K/s (heat flow — HF) and a magnified 10× difference in heat flow signals (ΔHF) between the 1st and 2nd DSC heating experiments to the glass-transition region up to 424 K. 1st measurement — initial sample, 2nd measurement — the sample pre-heated to 424 K and cooled down within the DSC furnace at the cooling rate in the order of 1 K/s. 3rd measurement is continuous DSC scan up to crystallization. The onset crystallization temperature is 467 K.

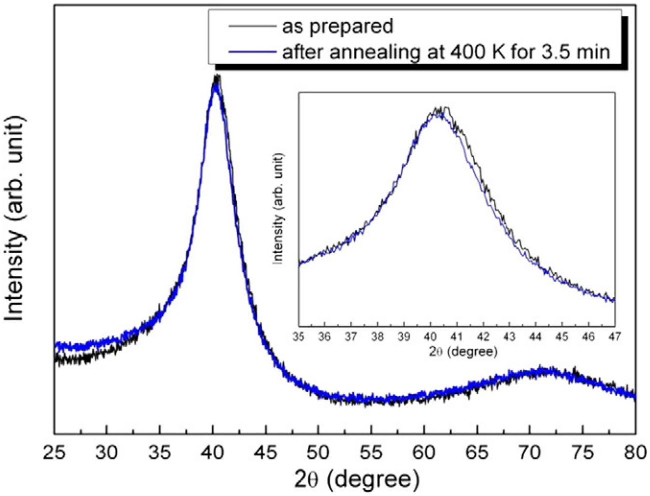

Fig. 2. XRD patterns of the as-solidified and annealed samples. The inset is a close up of the first diffraction maximum.

On cooling there is a weak hysteresis in the supercooled liquid state (the cooling curve is located somewhat lower in C_p values than the heating one), but in general, both heating and cooling cycles follow nearly the same trend showing a double-stage glass-transition. After that the sample was heated once again in the step scan mode, this time above the crystallization temperature (the sample crystallized above 430 K) and C_p was measured once again in a crystalline state (Fig. 3). After that the sample was melted in the DSC cell by heating up to 773 K, and then the C_p of a liquid was measured once again in the step scan mode on cooling at 83 mK/s to room temperature (Fig. 4). These experiments produced C_p values of the $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ alloy in glassy, crystalline, liquid and supercooled liquid states.

In order to calculate the difference in entropy (ΔS^{l-c}) between liquid and crystalline phases the temperature dependence of the

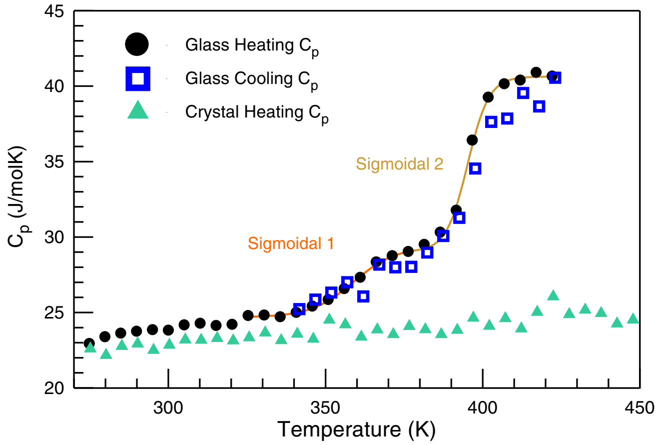

Fig. 3. C_p of glassy and crystalline phases measured on heating and on cooling (crystalline only on heating) as indicated. The heating and cooling rates were 83 mK/s. The annealing time between each heating and cooling step was 60 s.