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On the high glass-forming ability of Pt-Cu-Ni/Co-P-based liquids

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ABSTRACT

The continuous and isothermal crystallization diagrams of the $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ and the $Pt_{60}Cu_{16}Co_2P_{22}$ bulk glass forming compositions are determined using calorimetric experiments. In the case of the $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ bulk metallic glass, the formation of the primary crystalline phase can be prevented by rapid cooling in a conventional DSC. In contrast, for similar cooling conditions, the formation of the primary precipitating compound in $Pt_{60}Cu_{16}Co_2P_{22}$ cannot be prevented in a conventional DSC as also observed in in-situ synchrotron X-ray scattering experiments. This is attributed to a critical overheating, above which remaining structures dissolve, resulting in a drastic increase of the degree of undercooling, similar to what is observed in Zr-based BMGs. Using the classical nucleation theory, the combined thermodynamic and kinetic data are used to model the isothermal crystallization data for $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$, yielding an interfacial energy value of 0.11 J/m^2 between the primary nucleating crystal and the liquid. This value is three times higher than the value for good Zr-based glass-formers, suggesting that the interfacial energy plays a pivotal role in the exceptionally high glass-forming ability of Pt-P-based systems and compensates for the fragile liquid behavior and the large driving force for crystallization.

1. Introduction

Pt-based bulk metallic glasses (BMGs) have attracted considerable attention as potential alloys for jewelry applications due to their attractive color and high hardness in the as-cast state [1,2]. In contrast to conventional crystalline Pt alloys, their low liquidus temperature (T_l ~ 800–900 K [3–5]) and the absence of crystallization shrinkage is advantageous for the production of near net-shape parts by casting processes. Besides the processing from the equilibrium liquid, shaping can take place in the highly viscous, metastable supercooled liquid state by thermoplastic forming (TPF) through heating amorphous wrought material above the glass transition temperature, T_g. Pt-P-based BMGs exhibit an outstanding thermoplastic formability [6,7] due to their remarkable thermal stability ($\Delta T_x = T_x - T_g$) above the glass transition temperature [1,4] and their low melt viscosity in the supercooled liquid region that stems from their highly fragile liquid behavior [8], making them predestinated for shaping processes in the undercooled liquid state, like nanomoulding or blow molding [9,10].

The glass-forming ability (GFA) of a liquid, often evaluated as the critical casting thickness (d_c) of an amorphous alloy, is determined by how easily crystallization can be avoided. According to the classical nucleation theory, the rate at which crystals are formed is influenced by thermodynamic and dynamic factors i.e. the driving force for nucleation, the interfacial energy between liquid and nucleating solid phase, and the viscosity which is linked to the diffusivity in the liquid. Each factor fundamentally controls the crystallization kinetics and thus affects the GFA [11–14]. A systematic study on the parameters influencing the GFA of a liquid has recently been published by Johnson and co-workers [15]. In this study, the GFA of various glass-forming liquids is evaluated by correlating d_c with the reduced glass-transition temperature $T_{rg} = T_g/T_l$ and the kinetic fragility parameter m, defined as the slope of the $\log_{10}(\eta)$ vs. T_g/T curve at a viscosity of 10^{12} Pa s. In general, it can be stated, that a high T_{rg} value and a low m value correlate with a higher GFA. The high T_{rg} value can be considered as an indicator for a thermodynamic and kinetic stabilization of the liquid, and the low fragility (low m) value means that the liquids dynamics (e.g. viscosity, diffusivity, structural relaxation time) show a relatively low sensitivity against changes in temperature.

Investigations on the temperature dependence of viscosity and relaxation time revealed a kinetically fragile liquid behavior (high m values) for the $Pt_{60}Cu_{16}Co_2P_{22}$ and $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ bulk glass-

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forming liquids [8], suggesting that thermodynamic factors play a pivotal role for the high critical casting thicknesses of 16 and 20 mm, respectively [4]. Instead of relying on T_{rg} as the key indicator, in the present study, the origin of the high GFA of Pt-P-based BMGs is investigated on the basis of the driving-force for nucleation, the interfacial energy between the liquid and the primary nucleating crystal, and the kinetic fragility of the liquid. To this end, continuous and isothermal crystallization experiments are performed and used to validate available thermodynamic data. Employing thermodynamic and kinetic parameters, the classical nucleation theory is applied to the experimental crystallization data to derive a value for the interfacial energy.

2. Experimental

Master alloys with the Ni- and Co-containing composition $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ and $Pt_{60}Cu_{16}Co_2P_{22}$ were produced by alloying the raw elements (purity $\geq$ 99.5%) inductively in a fused silica tube under high purity argon. Subsequently, the samples were purified by melting the master alloys in dehydrated B_2O_3. Glassy specimens were produced by melting the purified master alloys in Al_2O_3 crucibles in a high purity argon atmosphere and casting them into a water-cooled copper mold using an Indutherm MC15 tilt-casting device. All samples were proven to be fully X-ray amorphous prior to further experiments.

Crystallization experiments were carried out in a power-compensated Perkin Elmer DSC8500 using Al and graphite pans for the low and high temperature regime, respectively. To prevent oxidation at high temperatures the samples were enclosed in a flux of B_2O_3 [16,17]. Samples were held at the maximum temperature of the DSC (973 K) for 120 s, which is 90–100 K above the liquidus temperature of the alloys {$T_l(Pt_{60}Cu_{16}Co_2P_{22})$ = 882 K, $T_l(Pt_{42.5}Cu_{27}Ni_{9.5}P_{21})$ = 874 K [8]}. Subsequently, the samples were cooled at various rates. In the isothermal experiments, samples were either heated from below T_g or cooled from 973 K (above T_l) to the desired temperature at a rate of 2 K/s.

The formation of the primary phase of $Pt_{60}Cu_{16}Co_2P_{22}$ upon cooling (q_c = 0.333 K/s) from 1048 K was observed in in-situ X-ray scattering experiments carried out at the *Deutsches Elektronen-Synchrotron* (DESY) in Hamburg/Germany. The structure of the sample was investigated in transmission at the high intensity beamline facility P02.1 at PETRAIII. The sample was placed in a silica tube with a diameter of 1 mm and a wall thickness of 0.01 mm under a constant flux of high purity argon and heated above the liquidus temperature using a lamp furnace. A wavelength of 0.20712 Å (59.86 keV) was used and the intensity was detected with a Perkin Elmer XRD1621 CsI bonded amorphous silicon detector (2048 pixels × 2048 pixels). The two dimensional X-ray diffraction patterns of the samples were integrated to obtain the intensity I(Q) using the Fit2D analysis software [18].

3. Results

Within the metastable supercooled liquid region, thermodynamic and dynamic factors promote in a combined way the effort of a liquid to access the energetically lowest state, i.e. the crystal. The energetic difference between the two states is released as heat during the transformation, reflected by an exothermic heat flow signal during a calorimetric measurement [19]. Fig. 1 shows a set of continuous cooling measurements performed on $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ in the DSC, starting from 973 K, i.e. above T_l, together with isothermal measurements starting from the glassy state. In Fig. 1(a) the liquid is cooled with the indicated cooling rates, q_c. The direction of the cooling process is indicated by an arrow, and the signals

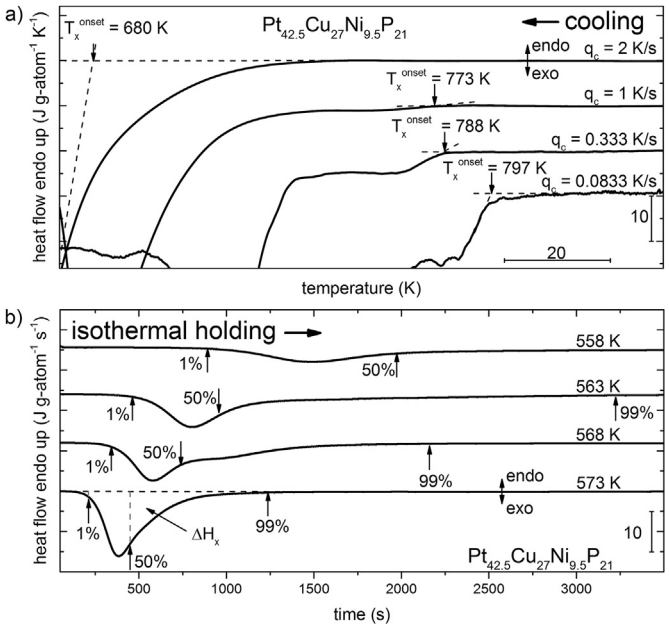

Fig. 1. (a) Heat flow signal of $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ (T_l = 874 K [8]) upon cooling at various rates form 973 K. The exothermic shoulder before the main crystallization peak gets less pronounced for higher cooling rates and vanishes at a rate of 2 K/s. Curves are shifted vertically for clarity. (b) Isothermal heat flow signal of $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ in vicinity of the glass transition. For higher temperatures, the crystallization event is more localized and shifted to shorter times.

are shifted along both axes for better comparison of the onset of crystallization, which is indicated with a downward arrow (T_x^{onset}). For relatively slow cooling rates ($q_c \leq$ 1 K/s) an exothermic shoulder is observed before the main exothermic event. This characteristic gets less pronounced as the cooling rate is increased and is not observed for a q_c of 2 K/s. For cooling rates $\geq$1.5 K/s an exothermic signal is observed upon reheating the sample at a rate of 0.333 K/s (Fig. 2), indicating that a non-equilibrium state is frozen in. At cooling rates of 2 and 3 K/s a glass transition (additional to that of B_2O_3) is observed in the heat flow signal (Fig. 2 (b), (c)). In first approximation, the released enthalpy upon heating in comparison to a fully amorphous sample is assumed to be proportional to the amount of glassy phase frozen in during quenching. In this case 20–30% of the samples cooled with q_c = 1.5 and 2 K/s are amorphous and 75% if the sample is cooled with 3 K/s. Fig. 1(b) shows the isothermal crystallization event for samples heated from the glassy into the supercooled liquid region and kept isothermally at the indicated temperatures. As expected, by increasing the annealing temperature, the onset of crystallization occurs at shorter times and the exothermic signal becomes sharper, indicating faster reaction kinetics. Analogous to $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$, the continuous cooling curve at 0.333 K/s of $Pt_{60}Cu_{16}Co_2P_{22}$ exhibits an exothermic pre-peak as depicted in Fig. 3(a). This pre-peak corresponds to the formation of the primary crystalline phase as shown by in-situ synchrotron X-ray experiments (Fig. 3(b)), revealing the development of Bragg-peaks slightly below the solidus temperature.

Fig. 4 shows the continuous cooling and heating transformation diagrams for the two investigated compositions, obtained by combining the onsets of crystallization upon continuous cooling with the values of the onset-temperature and the end-temperature of the glass-transition upon heating the glass (T_g^{onset} and T_g^{end}) as well as the onset of crystallization (T_x) as a function of the heating rate. The open circles represent the onset temperature of the