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Effects of partial crystallization in Pt-Si-B-based bulk metallic glasses on glass transition and crystallization of the remaining amorphous matrix

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ABSTRACT

The influence of partial crystallization on the evolution of the characteristic temperatures, i.e. of the glass transition and the onset of crystallization, the density, and the mechanical properties of the bulk metallic glass $Pt_{49.95}Si_{6.4}B_{24}Ge_3Cu_{16.65}$ is investigated. Partial crystallization is introduced by annealing the alloy in a stabilized salt bath at 350 °C and for different times and quantified by the residual heat of crystallization as measured in differential scanning calorimetry. It is found that the crystalline regions are enriched in platinum and the remaining amorphous phase is enriched in copper. The evolution of T_g and T_x of the remaining amorphous phase can be quantitatively linked to the degree of copper enrichment of the amorphous phase as crystallization advances. Hardness increases steadily with the degree of crystallization from 570 HV in the as-cast state to 750 HV in the fully crystallized state. In contrast, compressive strength drops steadily with increasing crystallinity due to increasing brittleness.

1. Introduction

Bulk metallic glasses are complex alloys produced by rapid quenching of metallic melts. The potential for glass formation rather than crystallization upon cooling from the melt is limited to a restricted number of alloy compositions obeying in general certain criteria in terms of interactions of the alloying elements, atomic size relations and enhanced stability of the liquid phase compared to solid phases, as e.g. formulated by the "golden rules" of Inoue [1]. The glassy state is however kinetically stabilized and, hence, metastable and can be transformed in a more stable state by crystallization [1]. Besides annealing at temperatures above the glass transition temperature, T_g, other phenomena have been reported to lead to crystallization, namely irradiation [2–4], mechanical deformation [5–10] and dealloying [11].

Bulk metallic glasses exhibit interesting mechanical properties, i.e. high hardness, high yield strength and a large elastic strain range, making them particularly interesting as elastic energy storage materials as, e.g., in Golf clubs or springs of mechanical watches [12,13]. Their elastic deformation capacity is enhanced both by the increase in yield strength and the reduction in Young's modulus of the glassy state compared to its crystalline counterpart.

Partial crystallization can be used as a tool to introduce very small crystallites into otherwise homogenous glasses, producing a combination of amorphous matrix with uniformly distributed crystals [14]. By controlled partial crystallization it is possible to modify the mechanical and physical properties of BMGs. Often partial crystallization leads also to higher ductility since the crystals act as obstacles for the propagation of shear bands which leads to multiplication of the latter and more homogeneous deformation [15–17]. In some glass formers partial crystallization results in a significant increase in hardness, e.g. Al–Ni–Y and Al–Gd–Fe. This is attributed to the formation of finely distributed α-Al phase during crystallization [18,19]. The same improvement of hardness upon crystallization has also been observed in Fe-TM-Si-B systems (TM: Transition Metal) [14,20]. The mechanical properties of partially crystallized BMGs depend on the size, the composition, the volume fraction and the morphology of the crystalline phases that form from the glassy matrix.

The increase in hardness upon partial crystallization is governed by two phenomena; firstly, a phase mixture or composite effect and, in the event that the crystalline phase has not the same composition as the amorphous phase, secondly, a gradual compositional change of the remaining amorphous phase leading to changes in the matrix properties [21,22]. It has even been shown by Zhong et al. [23] for an $Al_{86}Ni_{11.67}Y_{2.23}$ alloy that the enrichment of nickel and yttrium in the remaining amorphous matrix upon primary crystallization of α-Al nanophase is the predominant contribution to increased hardness.

The influence of annealing and ensuing partial crystallization has been investigated in precious-metal based BMGs [24,25]. These precious-metal based BMGs (e.g. $Au_{50}Cu_{25.5}Ag_{7.5}Si_{17}$, $Pt_{60}Cu_{16}Co_2P_{22}$ and $Pd_{35}Pt_{15}Cu_{30}P_{20}$) unanimously showed an increase in hardness upon partial crystallization, with the Pt-P-based glassy alloy showing

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up to 54% of increase compared to the as-cast hardness of 420 HV [24]. Partial crystallization was also found to introduce fragility to $Pt_{60}Cu_{16}Co_2P_{22}$, observed by crack formation during indentation [25]. Recently, a new Pt-based BMG has been developed in the ternary Pt-Si-B system, namely $Pt_{49.95}Si_{6.4}B_{24}Ge_3Cu_{16.65}$. The detailed description of its development process is given elsewhere [26]. Compared to Pt-P-based glassy alloys, the Pt-Si-B based alloys are significantly harder, exhibiting 570 HV in the as-cast state. For this alloy the process of crystallization, the resulting crystalline phases, and the effect of partial crystallization have not been reported so far.

In the event that the remaining amorphous matrix is enriched in certain alloying elements, the characteristic temperatures of the amorphous phase should also evolve according to the new composition. While the phenomenon of partitioning of alloying elements in the crystallization of metallic glasses has been studied on various systems [27–31] the effect on the characteristic temperatures have received much less attention so far and, to our knowledge, no attempt has been made to describe this effect quantitatively.

In the present contribution we hence investigate the influence of partial crystallization on the partitioning of alloying elements between the crystalline and the amorphous phase in $Pt_{49.95}Si_{6.4}B_{24}Ge_3Cu_{16.65}$ and its effect on the evolution of the characteristic temperatures of glass transition, T_g, and onset of crystallization, T_x. We further report the evolution of density, hardness and compressive strength as a function of the degree of crystallization for this alloy.

2. Experimental methods

2.1. Materials

Ingots were prepared by mixing pure elements (Pt 99.9%, Si 99.99%, B 99.5%, Ni 99.5%, Cu 99.999%, Ge 98.5%) in a quartz tube under argon atmosphere (99.9999%) melted by induction heating. In order to investigate glass formation, glassy ribbons were produced by melt-spinning under argon atmosphere (99.9999%), with a linear speed of the copper disk of 26 m/s. Cast samples in the form of rods were produced in an arc-melter with oxygen-gettered argon atmosphere (99.9999%) by suction casting into copper moulds. Samples were (re-)melted and turned four times before casting. The mass of the ingot after melting was compared to the sum of the melted-in ingredients to verify that the nominal composition was actually obtained. Differences of less than 1 mg on a total charge of 5–7 g were accepted. The oxygen content in the alloys was measured by Inert gas fusion and was found to be consistently inferior to 20 ppm and typically around 8 ppm.

It should be noted that the arc-melter did not allow any direct measurement of the melt temperature before casting and any such measurement would have been affected by the strong temperature gradients present between the face exposed to the plasma and the face in contact with the copper chill. The temperature of the melt before casting might however influence the cooling rate and thus the time necessary to achieve a given degree of crystallization in each individual cast sample can slightly vary. Hence, series of crystallization treatments were conducted on discs coming from the same casting and having seen the same thermal history.

2.2. Annealing in stabilized salt bath

For controlled crystallization, a thermally stabilized salt bath was used; this was held at 350 ± 1 °C. All further analyses were carried out on a continuously treated set of samples i.e. pieces from as-cast rods were cut, then the whole rod was annealed for a given time, one or several samples were cut from the rod, and the remainder heat treated further, and so on. This made sure that the measured differences came essentially from the differences in heat treatment and not from casting-to-casting differences, cf. above. Indeed, it had been observed previously that the propensity to crystallization would vary slightly from one casting to the next by an amount that was non-negligible compared to the variations introduced by each step of the annealing treatment, cf. insert in Fig. 1. For each heat treatment condition at least three samples were prepared for the analyses. Different measures such as T_g, T_x, or density correspond to a mean between the samples for a given treatment time and the vertical error bars represent the standard deviation on those three values. The horizontal bars represent the range of the sample's possible crystallinity degree for a given annealing time measured based on three to five samples subjected to the same treatment.

2.3. Characterization techniques

2.3.1. General sample preparation

The suction-cast rods or parts thereof used in the characterization techniques described below were typically ground with SiC emery paper down to a grit size of F1200 and then polished on a deep cloth (Struers MD-NAP) with 1 μm diamond paste.

2.3.2. Structural analysis

The glassy structure of the samples was assessed by X-ray diffraction using an X'pert Philips machine equipped with a Cu K_α source. The working voltage was 40 kV and the current 45 mA. For melt spun ribbons XRD analysis was carried out on both the surface in contact with the copper wheel and the back. For the cast samples analysis was performed on polished cross-sections.

2.3.3. Thermal analysis

Thermo-physical properties were investigated by Differential Scanning Calorimetry (DSC Pegasus 404C Netzsch, Germany) under argon (99.9999%) flow, with a heating rate of 10 K/min in alumina crucibles. Glass transition temperatures were measured on the DSC curves as the inflection point of the step towards the endothermic values. The crystallization temperature was measured by the onset of the exothermic peak upon heating. Solidus and liquidus onset temperatures were both measured on the heating curve.

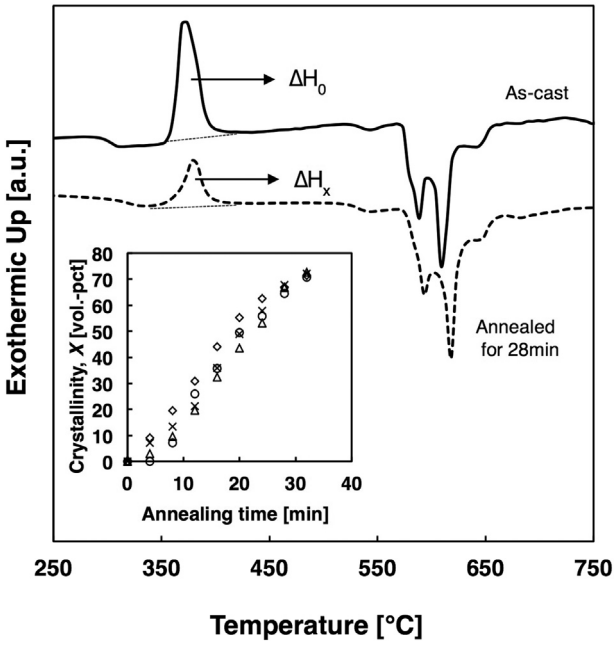

Fig. 1. The DSC pattern of the as-cast and partially crystallized 2 mm rods of alloy $Pt_{49.95}Si_{6.4}B_{24}Ge_3Cu_{16.65}$ produced by arc-melter. The variation of the crystallization time for different samples with the same composition is also shown in the insert.