

SENSITIVITY OF VISCOPLASTIC AND VISCOELASTIC PROPERTIES TO NANOCRYSTALLIZATION IN A Zr BULK METALLIC GLASS

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Abstract. The effect of partial crystallization on the mechanical properties of a zirconium based bulk metallic glass is investigated in the glass transition interval. The viscoplastic and viscoelastic properties are studied using compression tests and mechanical spectroscopy. Partial crystallization results in an hardening effect in both viscoplasticity (i.e. increase of the viscosity for a given strain rate) and viscoelasticity (i.e. decrease of the loss modulus and increase of the storage modulus) indicating a decrease in atomic mobility. The shapes of both the viscosity / strain rate curves and of the DMA curves are merely the same whatever the investigated crystal amount. However, the apparent activation energy is decreasing as far as crystallisation occurs suggesting possible changes in the mechanisms of viscoelastic and/or viscoplastic deformation.

1. INTRODUCTION

Bulk metallic glasses (BMG) exhibit interesting mechanical properties since they combine a high fracture stress, a particularly large elastic domain (up to 2%) and significant fracture toughness. Moreover, their formability between the glass transition temperature T_g and the crystallization temperature T_x is particularly important and it is thus possible to produce complex-shaped components using appropriate forming processes. Thus, the effect of temperature on deformation has been increasingly studied in the recent past, particularly in the case of zirconium-based BMG [1,2]. Another interesting property of BMG is the ability to obtain nanocomposites after heat treatments nearby the glass transition temperature. One can note that such crystallization can also occur during high temperature forming of the glass. In this context, the

effect of partial crystallization on the mechanical properties of BMG at room temperature has been also investigated [3,4]. However, at high temperature, the effect of nanocrystallization on deformation remains quite poorly documented [5,6]. The presence of crystals generally increases significantly the flow stress but its impact on the mechanisms of deformation remains unclear. The aim of the present investigation is to study the effect of partial crystallization on the mechanical properties in the supercooled liquid region of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (so-called Vit1).

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The Vit1 alloy was supplied by Howmet Corp. (USA) as a 3.3 mm thick sheet. Differential scanning calorimetry (DSC) measurements were carried out in

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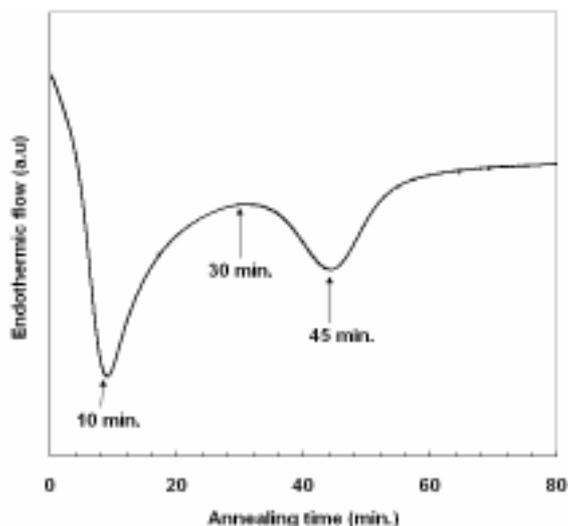


Fig. 1. DSC isothermal annealing curve at a temperature of 683K showing the two crystallization events and the selected annealing times.

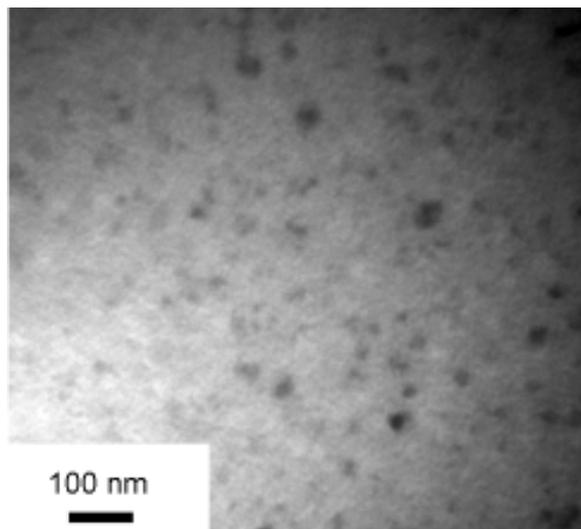


Fig. 2. TEM bright field observation of a sample annealed 10 min at 683K (the mean crystallite size was measured to be about 30 nm through multiple TEM observations).

a Perkin Elmer Diamond DSC. The produced crystals were characterised by transmission electron microscopy, the thin foils being prepared by ion beam milling (4 keV, 10°). The samples used for the high temperature compression tests were rods of 3 mm in diameter and 5 mm in height. Mechanical spectroscopy experiments measurements were performed in torsion mode using a spectrometer described elsewhere [7]. Frequency of 1 Hz and a constant heating rate of 10 K/min were selected and rectangular specimens with dimension 40x3x1 mm were used. In this device, a periodic shear stress is applied and the corresponding strain is measured. From the stress/strain ratio, the complex modulus $G = G' + iG''$ is measured where G' is the storage modulus (i.e. the elastic component) and G'' is the loss modulus (related to the viscoelastic and to the viscoplastic components). From such measurements, one can also deduce the complex compliance $J = 1/G = J' - iJ''$.

3. STUDIED MICROSTRUCTURES

DSC curves of the amorphous alloy at a heating rate of 10 K/min. were previously published [8] and showed the characteristic step changes arising from the glass transition (T_g defined as the inflexion point is equal to 637K), followed by a super-cooled liquid region and then three exothermic peaks re-

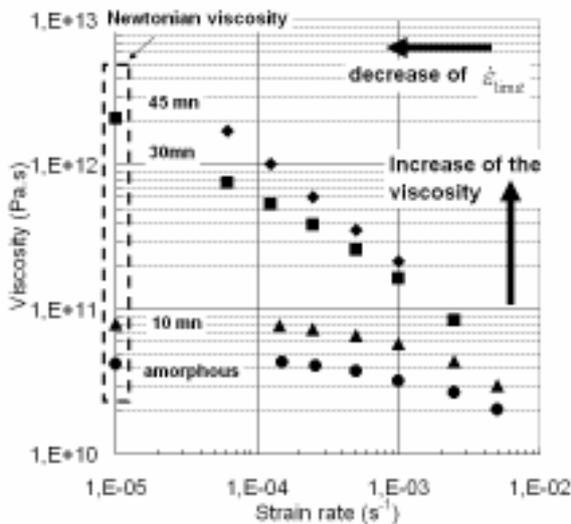
spectively at 705K, 727K, and 774 K, associated to three crystallisation events. To study the effect of such crystallization on the mechanical properties, an annealing temperature of 683K was chosen leading to the vanishing, after approximately 60 min of the two first crystallization events. Fig. 1 displays the DSC isothermal annealing curve at this temperature. Annealing times corresponding to the maximum of the first peak (10 min), the end of the first peak (30 min) and the maximum of the second peak (45 min) were selected. A typical bright field TEM observation of a sample annealed 10 min at 683K is shown in Fig. 2. Relatively equiaxed crystals with a typical size of about 30 nm are dispersed in the matrix, this size estimation being confirmed by measurements performed on several TEM observations. For longer annealing times, the mean size of the crystallites remains roughly constant but the quantity of crystals increases.

4. EFFECT OF CRYSTALLIZATION ON VISCOPLASTIC AND VISCOELASTIC PROPERTIES

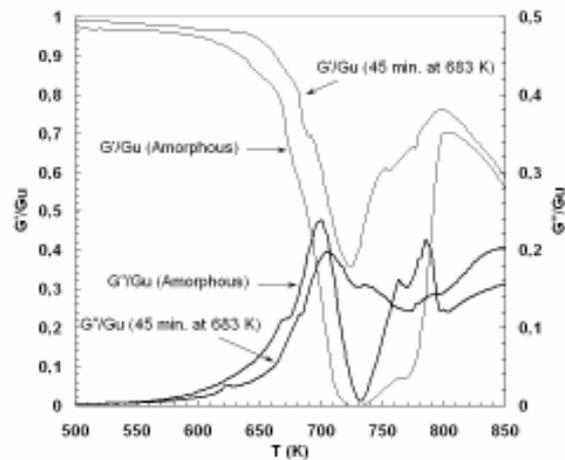
Strain rate jumps were performed in the case of the four studied microstructural states at three temperatures: 633K, 646K, and 663 K. In the studied temperature interval, no significant additional crys-

Table 1. Calculated values of the apparent activation energies (kJ/mol) deduced from Newtonian flow in compression tests and DMA analyses.

	amorphous	10 min.	30 min.	45 min.
Compression	440	360	230	-
DMA	390	380	270	190

**Fig. 3.** Viscosity versus strain rate for the various samples at a temperature of 646K.

tallization occurs during the strain rate jump tests. From these tests, viscosities were calculated and Fig. 3 displays the variation with the applied strain rate of these viscosities at 646K. For the amorphous alloy, the curve shows the typical shape of viscosity in amorphous materials with a merely constant viscosity for the low strain rates and a decrease when strain rate is higher than a limit strain rate ($\dot{\epsilon}_{\text{limit}}$). As far as crystallisation occurs, the viscosity is increased and the non Newtonian behaviour is promoted. One can note that due to this change in rheology, the reinforcement factor for a given transformed fraction will depend on the applied strain rate (e.g. it will be reduced for high strain rates). Despite these effects, the shape of the curves appears relatively similar whatever the degree of crystallisation. This is confirmed by the ability to get a master curve to describe the viscous flow as function of strain rate. In such a construction, the apparent viscosity is normalized by the Newtonian viscosity whereas the curves are

**Fig. 4.** Normalized elastic modulus (G'/G_u) and loss modulus (G''/G_u) as a function of temperature for the amorphous alloy and for the alloy heat treated 45 min at 683K (10 K/min, 1 Hz).

also shifted along the strain rate axis towards a reference curve, taken at a given temperature. Consequently, this curve suggests a similitude of mechanical responses of the alloy in the investigated temperature domain whatever the microstructural state.

Fig. 4 displays the normalized elastic modulus (G'/G_u) and the loss modulus (G''/G_u) deduced from the DMA experiments as a function of temperature for the amorphous alloy and for the alloy annealed 45 min at 683K, at a frequency of 1 Hz and a constant heating rate of 10 K/min. To facilitate the comparison, curves were normalized by G_u with G_u the unrelaxed modulus. G_u was taken equal to the value of the modulus at low temperature (25 °C), for which G'' can be neglected. As already reported in the case of amorphous alloys [9, 10], several domains can be detected as a function of temperature whatever the microstructural state. Up to about the glass transition temperature, only limited variations of G'/G_u and G''/G_u are measured.

Between approximately 650K and 720K, G'/G_u decreases sharply whereas G''/G_u reaches a maximum value close to 0.25. These phenomena, which are generally referred to the main relaxation (called also α relaxation in amorphous materials), are associated with the glass transition process. For higher temperatures, G'/G_u increases again, which is attributed to significant crystallization in the glass. The curves corresponding to the sample previously annealed 45 min at 683K display the same shape but the minimum value reached by the normalized elastic modulus is higher than the one of the amorphous sample while the maximum of the loss modulus is close to 0.2 which is lower than the value measured for the amorphous sample. This difference can be interpreted as a loss of atomic mobility in the partially crystallized sample. The curves corresponding to the other analyzed samples have not been drawn in Fig. 4 but they exhibit the same kind of behaviour.

Finally, all these data support the idea of a similarity in the deformation behaviour for the amorphous and the partially crystallised alloys, keeping in mind of course that large reinforcement effect can be obtained. However, thanks to the strain rate jump tests, Newtonian viscosities η_N can be extrapolated and assuming an Arrhenius law for the dependency of η_N on temperature, the effect of crystallization on the apparent activation energy can be calculated, except for the alloy treated during 45 min from which it was not possible to identify η_N for the experimental data. The associated values are given in Table 1. For the amorphous alloy, a value equal to 440 kJ/mol is measured, which is in agreement with previously reported values in the case of Zr based BMG [11, 12]. The interesting point is that the measured activation energy decreases as far as crystallization occurs. This conclusion was confirmed by the results obtained in DMA. Indeed, assuming a Maxwell model to describe the mechanical response in such conditions, one can establish a direct relation between the dissipating compliance J'' and the viscosity ($J'' = 1/\omega\eta_N$, with ω the oscillation pulsation) and consequently measure an apparent activation energy still assuming an Arrhenius law for η_N . The resulting values are also given in Table 1 and are in agreement with those deduced from compression tests. This decrease of the apparent activation energy as far as crystallization develops in the glass can be attributed to a progressive change with crystallization of the mechanical behavior of the residual glass. Such a change can result from a modification in the com-

position of the matrix. However, since one considers only Newtonian viscosities, one can expect high values of the activation energy as previously reported for various zirconium based BMGs [11, 12]. Another cause could be related to the possible deformation of the crystallites during the deformation of the composite. If such situation occurs, it would probably lead to a decrease of the apparent activation energy since values significantly lower than 400 kJ/mol are generally measured during deformation of metallic (or even intermetallic) crystals. However, observations of the materials after deformation do not support such a view since the equiaxed shapes of the particles are maintained. Finally, one can wonder about the possible effect due to the nanometric size of the crystallites. Indeed, a small crystallite size corresponds, for a given volume fraction of crystals, to a large interface area between the crystals and the amorphous matrix. In such a framework, some atoms could be "trapped" nearby the crystallites, leading to a decrease of the nucleation rate of flow defect and, consequently to a perturbation of the flow in the residual glass. Such small size also quickly results in small distances between crystallites, which could as well perturbate the flow in the matrix. It would be hence interesting to produce different crystal size corresponding to a fixed crystallite volume fraction in order to deal with this aspect. Additional work is however obviously needed before any conclusion about these aspects.

5. CONCLUSIONS

The effect of crystallization of Vit1 on the mechanical properties at high temperature was investigated thanks to compression and DMA tests. It was shown that partial crystallization decreases the atomic mobility. It also increases the Newtonian viscosity and promotes the non Newtonian regime in viscoplastic deformation. This influence is also visible in DMA analyses through the decrease of the loss modulus. Nevertheless, the results suggest a relative similarity between the mechanisms of deformation but the activation energy for the viscous flow is reduced as far as crystallization occurs.

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