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HIGH TEMPERATURE DEFORMATION OF A Mg-Cu-Gd BULK METALLIC GLASS: IMPACT OF PARTIAL CRYSTALLIZATION

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Abstract. A $Mg_{65}Cu_{25}Gd_{10}$ alloy is produced under the form of 6 mm diameter amorphous rod and its ability to be formed at high temperature is studied. In the supercooled liquid region, the usual transition between Newtonian and non-Newtonian behaviors is detected as a function of temperature and strain rate. A particular attention is also given to the effect of partial crystallization on the high temperature deformation of the alloy: large viscoplastic deformation ability is maintained up to relatively high crystal fraction. The main effect of crystallization on mechanical behavior is a reinforcement effect, which can vary with experimental conditions. Finally, crystal volume fractions are roughly estimated by a simple model used to predict reinforcement due to the dispersion of particles in a viscous matrix.

1. INTRODUCTION

Bulk metallic glasses (BMG) show interesting mechanical properties like high stresses to failure or large elastic strains and are then promising materials for structural applications. Magnesium-based BMG can be produced in bulk form and thus provide new interesting light alloys. The efforts to develop such Mg-based BMG first succeeded with Mg-Cu-Y compositions [1], but more recently the substitution of yttrium by gadolinium gave the opportunity to obtain glassy rods with larger diameters [2,3]. It is well-known that BMG exhibit a particularly large deformability when they are deformed in the supercooled liquid region (SLR), allowing the production of complex shapes by appropriate forming techniques. The high temperature deformation of BMG has received sustained attention in the past but essentially in the case of Zr-based BMG [4]. For Mg-based BMG, very few information is available, except the work of Wolff and co-authors [5]. Moreover, due to their way of elaboration, BMG are strongly out of equilibrium materials. This means that during high temperature deformation, crystallization can occur and result in a huge variation of the apparent viscosity. In consequence, it is of importance to get information about the effect of partial crystallization on the viscoplastic properties of the glass. The objectives of this work are to study the deformation of a Mg-Cu-Gd glass in the vicinity of T_g in both amorphous and partially crystallized states.

2. ELABORATION AND THERMAL STABILITY

Elements with purity greater than 99.9% were melted under argon. Copper and gadolinium were first melted together prior to homogenization with the magnesium. The $Mg_{65}Cu_{25}Gd_{10}$ bulk metallic

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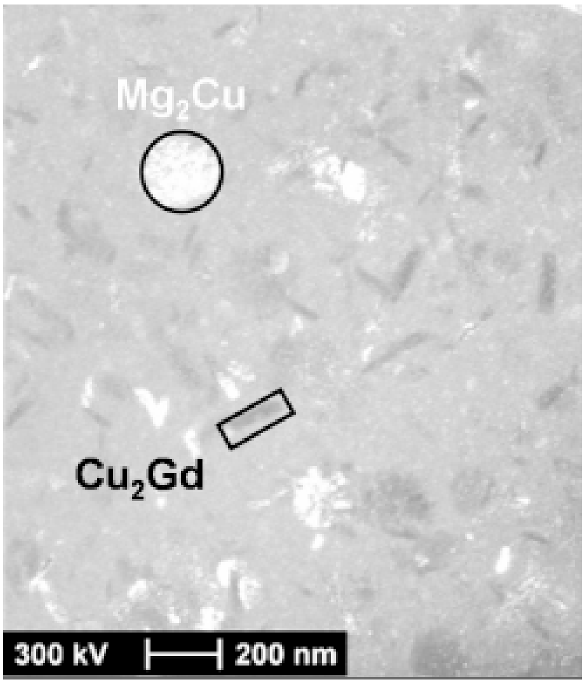

Fig. 1. TEM dark-field image of a heat treated $Mg_{65}Cu_{25}Gd_{10}$ glass.

alloy was obtain by copper mould casting in the form of 6 mm rods. X-Ray Diffraction (XRD) of the sections of the rods reveals the characteristic broad diffraction peak of metallic glasses and shows no crystalline peak confirming the amorphous state of the samples. Thermal stability was studied by Differential Scanning Calorimetry (DSC) at a heating rate of 10 K/min. The glass transition temperature T_g was found close to 418K and the onset of the main peak of crystallization T_x to 472K.

Partially crystallized samples were produced by heat treatments performed at 438K (i.e. = T_g + 20K) in oil bath. A transformed fraction F_T was calculated from an isothermal DSC curve according to $F_T(t_1) = \int_0^{t_1} H(t)\,\mathrm{d}t \,/\, \int_0^{\infty} H(t)\,\mathrm{d}t$ where $H(t)$ is the released heat flow. This procedure has been previously applied in the case of Mg-based BMG [5] or even in the case of Zr-Based BMG that leads to the crystallization of complex populations of crystals [4]. After complete transformation at this temperature, F_T = 1 and the sample is named “fully transformed”. For such a fully transformed sample, XRD measurement reveal the presence of crystalline peaks over a residual amorphous broad pattern and DSC measurements at a heating rate of 10 K/min reveal that the two small exothermic events at higher temperature still exist. The fully transformed sample is then only partially crystallized and not fully crystallized.

At 438K, the transformation is complete after about 1 hour and significant transformed fractions are obtained only after times longer than approximately 30 min. Fig. 1 displays a typical dark field TEM observation of a partially crystallized alloy at 438K for 30 minutes (corresponding to a transformed fraction F_T of 0.2). The crystallization process (reaction kinetics, nature of the crystals, sizes…) at this temperature has been previously studied [6]. Two different kinds of crystallites appear: sphere-shaped Mg_2Cu with diameters of about 200 nm and rod-shaped Cu_2Gd with dimensions typically of 100 nm long and 50 nm wide. Even if the crystallization of these two compounds in the $Mg_{65}Cu_{25}Gd_{10}$ glass is expected to lead to a modification of the composition of the residual matrix, in the investigated domain which corresponds to limited crystal extent, DSC measurements of the partially crystallized samples did not reveal a significant change in T_g.

3. HIGH TEMPERATURE DEFORMATION IN THE AMORPHOUS AND PARTIALLY CRYSTALLIZED STATES

To get information about the rheology of the glass in the SLR, strain rate jump tests were performed between 408K (T_g - 10K) and 438K (T_g + 20K) in air. The samples were 4 mm in diameter and 6 mm in height. The temperature was reached at 10 K/min and a minimum waiting time of 300 s was applied before compression. The strain rates varied from 10^{-4} s^{-1} to 8.10^{-3} s^{-1}. Some overshoots were detected at 418K and 408K but remained lower than 15% in amplitude. Fig. 2 displays the variation with strain rate and temperature of the apparent viscosity. The usual transition from Newtonian to Non-Newtonian behavior is observed when temperature decreases or when strain rate increases. One can note that the Newtonian behavior is preserved in a large part of the investigated experimental domain. The Newtonian viscosity η_N (i.e. when the viscosity does not vary with the strain rate) at T_g is close to 5.10^{10} Pa.s which is lower than the value of 10^{12} Pa.s frequently reported for BMGs [7,8]. Newtonian viscosities are strongly dependent on temperature since they vary by a 10^3 factor when temperature rises from 30K. Assuming an Arrhenius law for η_N, an activation energy of

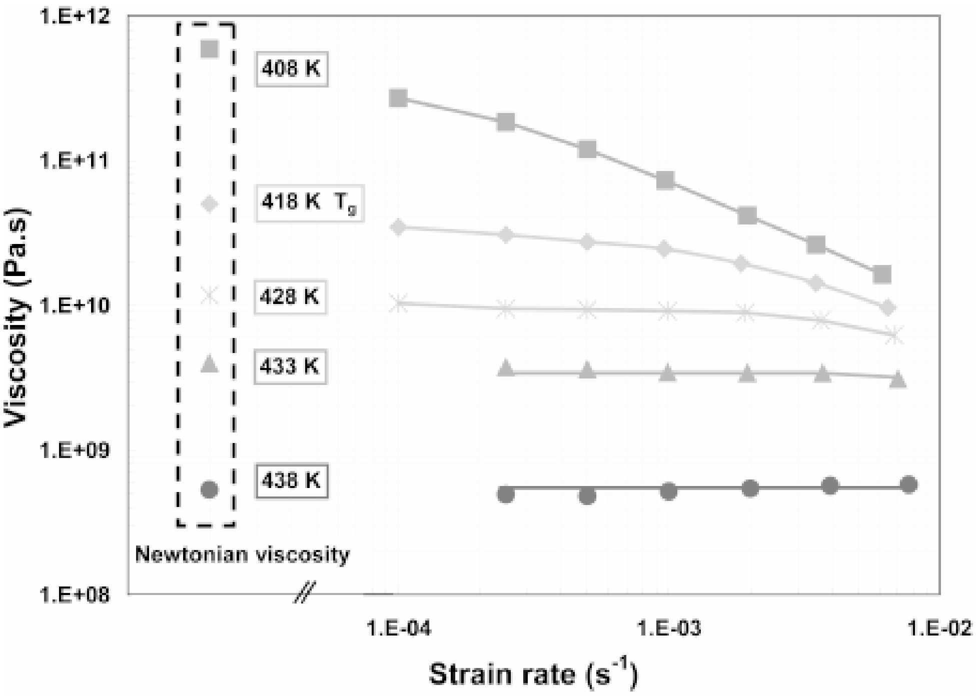

Fig. 2. Viscosity versus strain rate in the amorphous state.

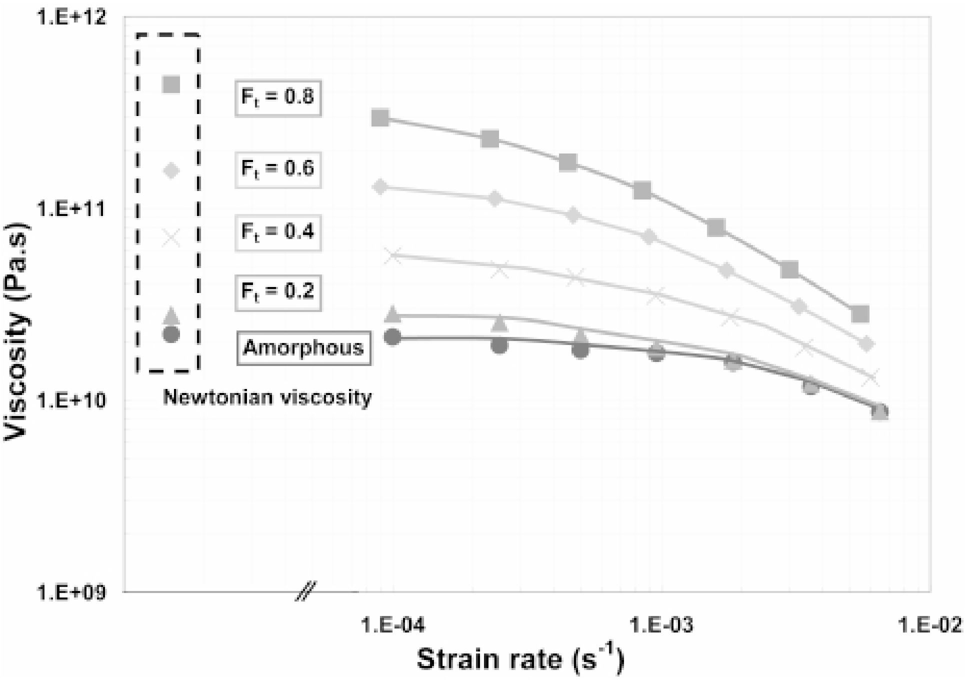

Fig. 3. Viscosity versus strain rate in the partially crystallized state.

3.5 eV is measured. This value is significantly lower than those reported for Zr [7] or Pd [8] based BMG for which values close to 5 eV were measured.

Alloys with various values of F_T were also tested at T_g with the same strain rate tests than the amorphous samples described previously. Up to F_T = 0.8, the samples could be deformed and no important cracks were detected on the outer part of the samples. The fully transformed specimen appeared brittle and could not be significantly deformed at

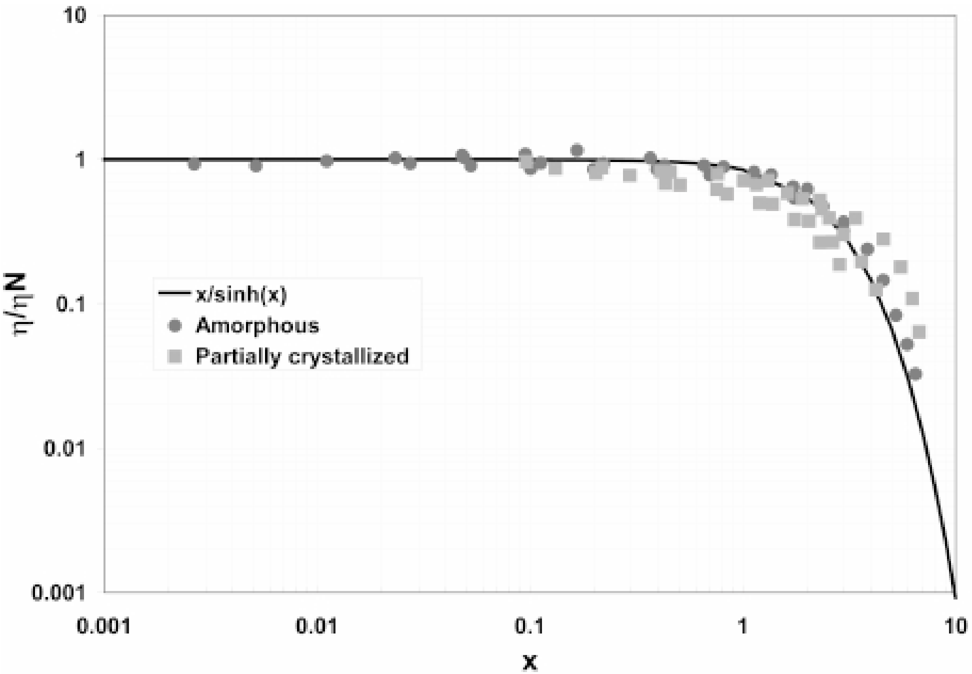

Fig. 4. Master curve for the normalized viscosity η/η_N following Eq. (2).

418K. Fig. 3 shows the associated variations with strain rate of the apparent viscosities. Viscosities increase monotonically with transformed fractions. The Newtonian to non-Newtonian transition is also affected by crystallization and is shifted to lower strain rates as far as crystallization occurs.

4. DISCUSSION

Master curves that gather results obtained at various temperatures have been frequently drawn in the case of zirconium based BMG [4,7]. For instance, in the framework of the free volume model, the strain rate in uniaxial loading can be related to the flow stress according to:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right) \quad (1)$$

with σ the flow stress, k the Boltzmann constant, T the temperature and V the activation volume. The values of V identified using Eq. (1) were found close to 320 Å^3 in both amorphous and partially crystallized state when measured at T_g. This value is in good agreement with previous studies performed on others Mg-based BMG [9]. When temperature increases, theses values decrease (e.g. at 423K, $V \approx 280$ Å^3) as also reported for other BMGs [4,9].

Knowing that for Newtonian behaviors, $\sigma V << kT$ a master curve can thus be derived to gather the variations of the viscosity with strain rate at various temperatures since:

$$\frac{\eta}{\eta_N} = \frac{\sigma V / 2\sqrt{3}kT}{\sinh\left(\sigma V / 2\sqrt{3}kT\right)} = \frac{x}{\sinh(x)} \quad (2)$$

with $x = \sigma V / 2\sqrt{3}kT$. Fig. 4 displays this variation of η/η_N with x for the amorphous alloy, confirming the ability to describe the mechanical response of the glass by the formalism of the free volume model. In Fig. 4, are also plotted the data of the partially crystallized alloys. The capacity to maintain the master curve whatever the investigated amount of crystals suggests a relative similarity in the mechanisms of high temperature deformation between the studied microstructures. In other words, the main consequence of partial crystallization is the important hardening effect.

In the case of a suspension of particles in a viscous matrix, the variation with particle amount of the Newtonian viscosity can be given by [10,11]:

$$\eta_N = \eta_{N0}\left[1 - \frac{\phi}{\phi_m}\right]^{-q\phi_m} \quad (3)$$

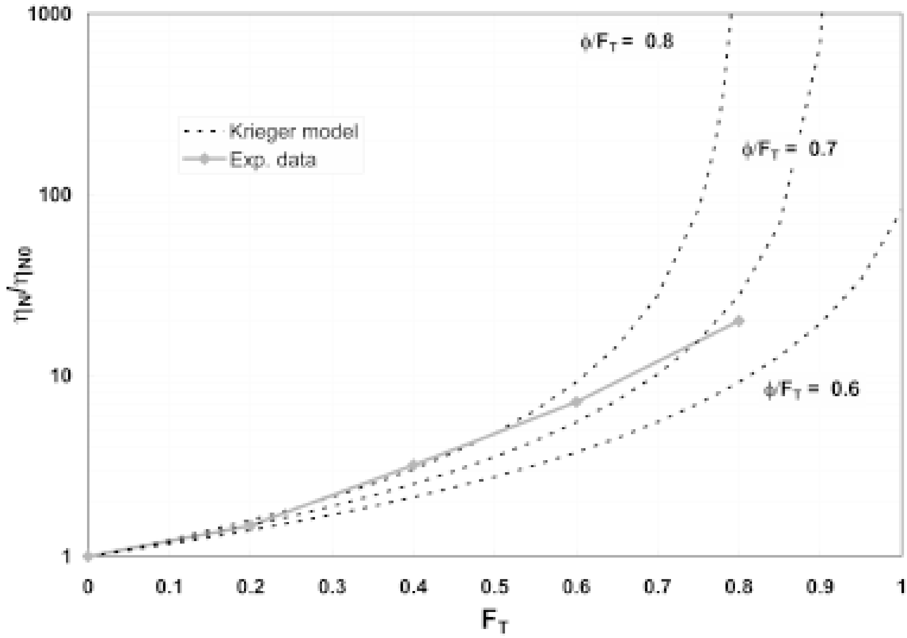

Fig. 5. Viscosity reinforcement for various ϕ/F_T compared to Krieger model.

with η_{N0} the Newtonian viscosity of the matrix without particles, q an exponent frequently equal to 2.5, ϕ the volume fraction of particles and ϕ_m the maximum volume fraction of particles ($\phi_m = 0.64$ in the case of a random close packing for a dispersion of spherical spheres with the same diameter). Relation (3) has been often used for a Newtonian matrix in the case of rigid, non-interactive, spherical particles admitting all the same size. In the present work, many of these conditions are more or less fulfilled. Newtonian behaviors can be observed whatever the crystal amount, the size of the crystals is roughly constant, they can be considered as rigid and due to their relatively large size, the mean distance between them remains quite high, suggesting that interactions between the particles are probably limited. Relation (3) assumes that the characteristics of the matrix do not change when the volume fraction of particles varies. In the case of the studied Mg-Cu-Gd glass, it was shown that the glass transition temperature of the residual glass remains roughly constant during crystallization, suggesting that the rheological characteristics of the glass do not change significantly with crystallization.

In the case of partially crystallized BMGs, it is always difficult to measure accurately the volume fraction ϕ of crystals. As already mentioned, in the present investigation, only a transformed fraction F_T was measured by DSC. In particular, the complete transformation is likely to correspond to a crystal volume fraction significantly lower than 1 since for the fully transformed sample, some amorphous phase was still clearly detected by XRD. In other words, $\phi \leq F_T$. Since Eq. (3) establishes a relation between the reinforcement factor η_N/η_{N0} and ϕ, from the knowledge of η_N/η_{N0} one can get a rough estimation of ϕ and consequently of the ratio ϕ/F_T which can be considered as constant in first approximation. In this framework, Fig. 5 compares the experimental reinforcement factors with predictions deduced from equation (3) with various values of ϕ/F_T. In the experimentally investigated domain, this comparison suggests a value of ϕ/F_T in the range 0.7 - 0.8. This means that, in the case of the sample for which a value of $F_T = 0.8$ is measured, the volume fraction of the crystals is about 0.6. One must remind that despite this relatively large amount of crystals, a good capacity of deformation was preserved. Additional work is however obviously required before any definite conclusion since strong hypotheses have been done in this preliminary work. For instance, as illustrated by the TEM observation shown in Fig. 1, rod-shaped crystals (Cu_2Gd) are produced during crystallization, which means that spherical and non-spherical particles coexist in the experimental dispersion, which probably leads to a more delicate use of Eq. (3).

5. CONCLUSION

The deformation of a Mg-Cu-Gd BMG in the SRL has been studied in both amorphous and partially crystallized state. In both cases, a large viscoplastic deformation ability was obtained except for the largest transformed fraction. Viscosities are strongly dependent on temperature and strain rate and show a transition from Newtonian to non-Newtonian behavior. In the investigated experimental domain, the presence of crystals results essentially in a reinforcement effect maintaining the capacity to describe the mechanical behavior by the formalism of the free volume model. Nevertheless, since crystallization promotes non-Newtonian behaviors, this reinforcement factor depends on temperature and strain rate. Finally, thanks to a simple model predicting the mechanical behavior of dispersed particles in a viscous matrix, crystal volume fractions were roughly estimated.

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REFERENCES

[1] A. Inoue, A. Kato, T. Zhang, S. G. Kim and T. Masumoto // *Mater.Trans., JIM* **32** (1991) 609.

[2] H. Men and D.H. Kim // *J. Mater. Res.* **18** (2003) 1502.

[3] H. Ma, L. L. Shi, J. Xu Y. Li and E. Ma // *Appl. Phys. Lett.* **87** (2005) 181915.

[4] M. Blétry, P. Guyot, Y. Brechet, J.J. Blandin and J.L. Soubeyroux // *Mater. Sc. Eng. A* **387-389** (2004) 1005.

[5] U. Wolff, N. Pryds, E. Johnson and J.A. Wert // *Acta Mater.* **52** (2004) 1989.

[6] J.L. Soubeyroux, S. Puech, P. Donnadieu and J.J. Blandin // *J. All. Comp.* **434-435** (2007) 84.

[7] Q. Wang, J.M. Pelletier, J.J. Blandin and M. Suery // *J. Non Cryst. Solids* **351** (2005) 2224.

[8] H. Kato, Y. Kawamura, A. Inoue and H.S. Chen // *Appl. Phys. Lett.* **73** (1998) 3665.

[9] B. Gun, K.J. Laws and M. Ferry // *Mater. Sci. Eng. A* (2007) **471** (2007) 130. j.msea.2007.02.121.

[10] I.M. Krieger // *Adv. Coll. Interf. Sc.* **3** (1972) 111.

[11] D. Quemada // *Eur. Phys. J. Appl. Phys.* **1** (1998) 119.