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Using thermoforming capacity of metallic glasses to produce multimaterials

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ABSTRACT

In addition to casting, thermoforming is a particularly interesting way to produce components in bulk metallic glasses since large strains can be achieved when the BMGs are deformed in their supercooled liquid region. The experimental window (temperature, time) in which high temperature forming can be carried out is directly related to the crystallization resistance of the glass. Such forming windows have been identified for zirconium based bulk metallic glasses thanks to thermal analysis and compression tests in the supercooled liquid region. Based on this identification, the thermoforming capacity of the studied glasses was used to produce multimaterials associating metallic glasses with conventional metallic alloys. Two processes have been preferentially investigated (co-extrusion and co-pressing) and the interface quality of the elaborated multi materials was studied.

1. Introduction

As for crystalline alloys, there are essentially two ways to produce BMG components: casting or thermo plastic forming. In the first case, the liquid alloy is directly cooled in a mould with the appropriate geometry. For metallic glasses, it requires controlling the cooling rate in order to avoid crystallization but it can also face difficulties in the case of complex geometries or thin section moulding. In the second case, owing to the usual macroscopic brittleness or the very high mechanical resistance when plasticity can be achieved, forming at room temperature is particularly difficult to perform. Increasing temperature is therefore required and metallic glasses can display a large forming capacity in their supercooled liquid region, typically for temperatures higher than their glass transition temperature in a similar way as silica based glasses or polymers. In such a region, the strain rate sensitivity parameter m can be equal to 1 with appropriated deformation conditions (assuming a viscoplastic law defined by $\sigma = K\dot{\varepsilon}^m$ with σ the flow stress and $\dot{\varepsilon}$ the strain rate). In this regime (so called Newtonian regime), the flow stress depends linearly on the applied strain rate or the viscosity (defined as $\eta = \sigma/3\dot{\varepsilon}$) is independent on the strain rate. It corresponds also to a particularly good plastic stability due to an optimum resistance to necking. Moreover, since the intrinsic "internal length" is particularly small (i.e. no grain size), well controlled surface geometries can also be achieved. It is the reason why BMGs also appear as particularly good candidates for microforming [1,2] or even for nanoforming [3].

The viscoplastic deformation of BMGs has received large attention in the past [4–9]. The Newtonian flow is typically obtained at high temperature and low strain rates whereas a transition from Newtonian to non-Newtonian flow behaviour is observed when the strain rate is increased or when the temperature is reduced. This transition has been attributed to stress-induced formation of defects in the glassy alloy [6]. If the strain rate is too high and/or if the temperature is not high enough, the homogeneous flow cannot be reached and the glass exhibits a brittle like behaviour. Obviously, such conditions must be avoided for thermo-processing. In the homogeneous flow domain, the best thermoforming ability is expected when the Newtonian rheology can be obtained (the later being easier when temperature is increased), but the amorphous structure of the glass must be retained during thermoforming. For temperatures higher than T_g, crystallization can occur after a given incubation time dependent on the temperature and modify drastically the viscosity [10]. In some cases, when crystallization becomes too important, the glass can no longer be deformed even at high temperature. In consequence, it is necessary for each metallic glass to be formed to get information about its thermal stability. Such information can be obtained by getting building transformation–temperature–time (TTT) curves giving for a selected temperature, the incubation time before crystallization starts and the time corresponding to the end of transformation. It must be also kept in mind that an additional difficulty is that

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Table 1
Glass transition temperature, crystallization temperature and ΔT interval for the two studied metallic glasses.

Studied glass	T_g (K)	T_x (K)	ΔT (K)
BMG1: $Zr_{52.5}Cu_{27}Al_{10}Ni_8Ti_{2.5}$	693	758	65
BMG2: $Zr_{44}Cu_{40}Al_8Ag_8$	706	784	78

deformation can affect the crystallization kinetics (in particular the incubation time), as previously reported for various BMGs [11,12] and has hence an effect on the incubation time.

A way to promote the use of metallic glasses is to investigate the possibilities to associate them with conventional metallic alloys in order to take advantage of the high strength of the glass and of the large ductility of the conventional crystalline alloy in a similar way as in the case of ceramic fibre reinforced alloys. In the past, ceramic fibre reinforced materials have been extensively studied thanks to the optimisation of various elaboration processes like liquid pressure infiltration [13] or diffusion bonding [14]. However, these processes require frequently high temperatures in order for the reinforcement to be well bonded with the matrix. In the case of two metallic alloys, co-extrusion is also a process which has been developed to manufacture bimetallic rods and tubes [15]. This technique is however difficult to perform when a brittle material (like a ceramic) is used for the core of the co-extruded rod. In this context, one advantage of a BMG is its ability to deform intensively under low stresses in the supercooled liquid region (SLR). Moreover, depending on the BMG, this SLR can correspond to temperatures close to the conventional temperatures of extrusion of light alloys. In the same way of thinking, the elaboration of multilayers involving metallic glasses and conventional crystalline alloys can be also considered since these laminates can be produced by high temperature co-pressing [16].

The aim of this paper is to demonstrate the feasibility of the elaboration of multi materials involving various bulk metallic glasses and conventional crystalline alloys by appropriate co-deformation processes carried out in the supercooled liquid region (SLR) of the selected BMG. In this study, two processes were investigated: co-extrusion and co-pressing.

2. Studied materials

Two zirconium based bulk metallic glasses have been preferentially used in this work: $Zr_{52.5}Cu_{27}Al_{10}Ni_8Ti_{2.5}$ (BMG1) and $Zr_{44}Cu_{40}Al_8Ag_8$ (BMG2) (at.%). Ingots were first prepared from elemental metals (purity of 99.99%) under argon atmosphere and the melting was repeated several times to get a homogenous alloy. The alloys were then cast in a copper mould to produce rods of 3 mm and 5 mm diameter. The amorphous state of the rods was confirmed by X-ray diffraction (XRD) with CuKα radiation. Thermal stability of the BMG was investigated by Differential Scanning Calorimetry (DSC) at 10 K/min, thanks to the measurement of the glass transition temperature T_g and the crystallization temperature T_x. Table 1 displays the values obtained for the two studied metallic glasses. For both glasses, it is interesting to note that the values of ΔT defined as the difference between the crystallization and the glass transition temperatures is quite large, typically larger than 50 °C. Such values of ΔT indicate that the thermal stability of these glasses is high and suggest that large enough thermoforming windows are expected to be found.

Three crystalline alloys were also selected for this work: an AZ31 (Mg–3Al–1Zn, wt.%) magnesium alloy in the form of 10 mm thick rolled plate, an Al-5056 (Al–5.0Mg–0.1Cu–0.1Mn, wt.%) aluminium alloy in the form of a 10 mm diameter extruded bar and an extruded pure copper rod.

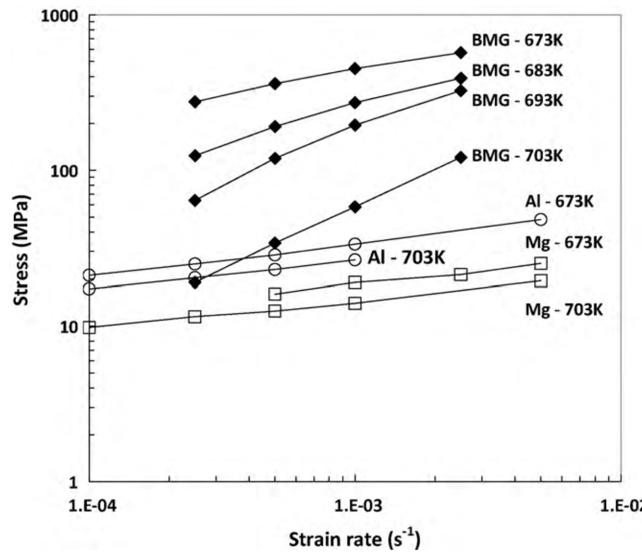

Fig. 1. Effect of temperature on the stress–strain rate curves for the BMG1, the aluminium and the magnesium alloys.

3. Identification of processing windows

The choice of the processing conditions requires getting data concerning the high temperature deformation of the selected materials. Such data were obtained thanks to compression tests in air. The samples were heated to a given testing temperature (heating rate of about 10 K/min.) and maintained for about 300 s to homogenize the temperature. Both strain rate jump tests and constant strain rate tests were carried out. The studied temperatures were typically around T_g with strain rates varying from 10^{-4} s^{-1} to 10^{-2} s^{-1}. Due to the difference between the glass transition temperatures of the two glasses, two temperature intervals were investigated, namely between 673 K and 703 K for BMG1 and between 703 K and 726 K for BMG2.

Fig. 1 displays the stress vs. strain rate curves obtained from the strain rate jump tests carried out in the case of the BMG1 and the aluminium and magnesium alloys. Regarding the glass, a Newtonian behaviour (i.e. $m = 1$) is obtained in a quite large strain rate interval when the deformation is carried out at 703 K (T_g + 10 K). It must be noted that for higher temperatures, the thermal stability of the glass is limited. For lower temperatures, the non-Newtonian behaviour is promoted in particular for high strain rates. For the aluminium alloy, a strain rate sensitivity parameter close to 0.2 is measured, suggesting that the alloy deforms by dislocation creep as expected for such experimental conditions [17]. A quite similar behaviour is observed for the Mg AZ31 alloy, also in agreement with previously reported behaviours for this alloy [18]. At 703 K and 2–3 × 10^{-4} s^{-1}, one can see that the glass and the Mg alloy display quite similar flow stresses whereas slightly higher flow stresses are expected for the Al alloy.

4. Elaboration of the multi materials

4.1. Co-extrusion

Details about the co-extrusion device and the first co-extrusion tests have been published elsewhere [19]. The diameter of the container of the extrusion device was equal to 7 mm and the conical die with an angle equal to 45° was 3 mm in diameter. The extrusion ratio was thus equal to 5.4. The specimen to be extruded consisted in a 7 mm diameter cylinder of the crystalline alloy in which a non emerging hole was machined. This hole was filled with a glass rod.

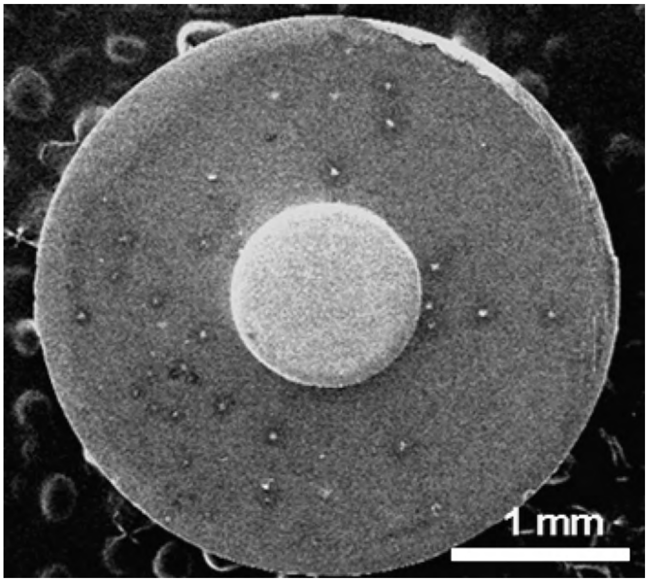

Fig. 2. SEM observation of the section of a co-extruded rod with a BMG core and a crystalline alloy sleeve.

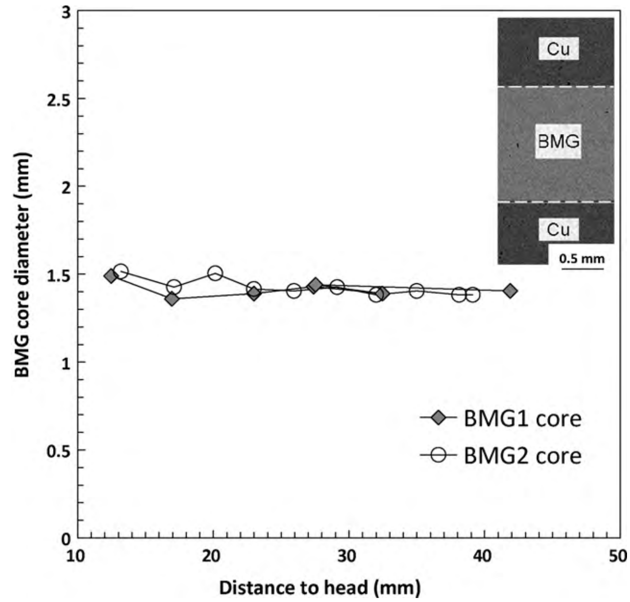

Fig. 3. Measurement of the BMG core diameter along the co-extruded rod for the two studied metallic glasses in the case of a sleeve in pure copper.

For each test, the specimen was introduced in the container when the extrusion temperature was reached and stabilized in the device. The ram speed was generally between 0.1 mm/min and 1 mm/min, corresponding to mean strain rates typically between 10^{-3} s^{-1} and 10^{-2} s^{-1} [19].

A typical SEM observation of the cross section of a co-extruded rod is shown in Fig. 2. In this figure, the core (white phase) is in metallic glass whereas the sleeve (grey phase) is in crystalline alloy. One can note that the glass core is well centered in the rod. Observations at higher magnifications showed that the interface quality was quite satisfactory, suggesting that a good bonding between the glass and the alloy has resulted from extrusion.

An important point in the control of the co-extrusion process is the capacity to produce rods displaying a core with constant dimensions along the rod since it has been demonstrated in the case of conventional bimetallic rods that significant variations in the core diameter could be obtained depending on the rheology differences between the two metals to be extruded [15]. In order to check this point, the diameters of the glass core in the rods were measured along the extruded rod and Fig. 3 displays these measurements for the two studied metallic glasses and a sleeve in pure copper. In this case, the two constituents displayed similar flow stresses for the selected conditions of co-extrusion. It can be seen from Fig. 3 that a relatively constant diameter is measured in the main part of the rod, knowing that the total length of the rod is about 50 mm. Moreover, this diameter (≈1.4 mm) is also close to the expected value deduced from its initial diameter and the extrusion ratio (≈1.3 mm).

Since the core diameter is constant along the rod, push-out tests could be carried out to get information about the quality of the interface. In such tests, a slice of the co-extruded rod was cut perpendicularly to the extrusion axis, a displacement rate was applied to the core and the resulting load was measured, as illustrated by the sketch shown in Fig. 4. The corresponding interface shear stress τ_i was calculated according to the equation $F = \pi d h \tau_i$ where F is the load, d is the core diameter and h is the initial height of the specimen. Values of the maximum interface shear stress of about 60 MPa were for instance measured for the Cu/BMG1 multi material. It can be noted that such values correspond roughly to the expected yield shear stress for the pure copper sleeve, typically close to 70 MPa assuming that it corresponds to half of the yield stress value measured in compression. Fig. 4 displays also a SEM observation of a co-extruded rod sample (in this case, the sleeve was in aluminium alloy) after a push-out test. Additional observations showed that a significant fraction of the core surface was covered by aluminium, confirming the idea that shear occurred preferentially in the crystalline alloy sleeve.

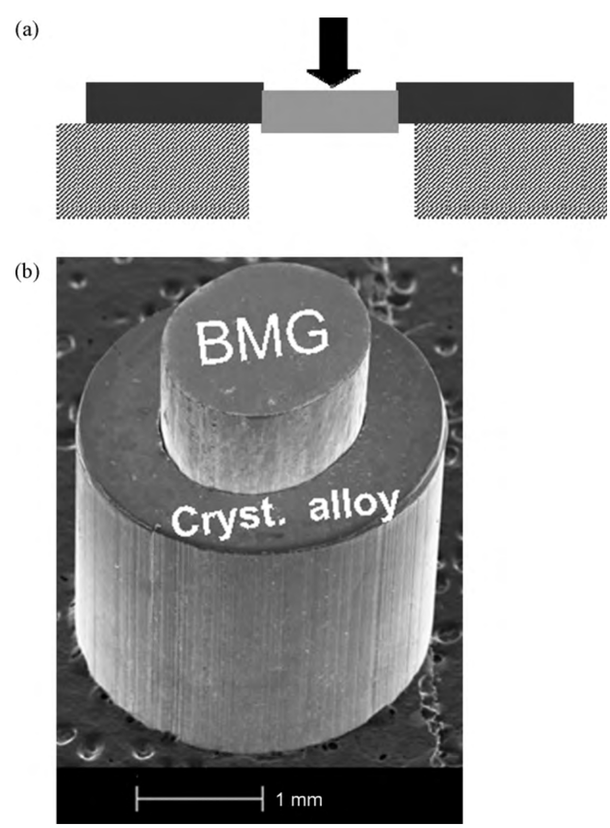

Fig. 4. (a) Scheme of the push-out test. (b) SEM observation of a co-extruded sample after a push-out test (sleeve in aluminium alloy).

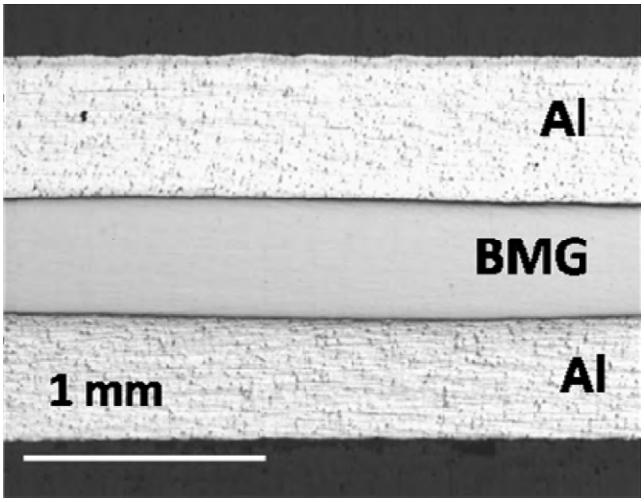

Fig. 5. Cross section of a three layers laminate obtained by co-pressing (skin in aluminium alloy, core in BMG1).

Table 2
Experimental values of the strain undergone by the glass for the Al/BMG1/Al and Mg/BMG1/Mg multilayers at the various temperatures of co-pressing.

Temperature (K)	673	683	693	703
ε_{exp} of the glass (Al/BMG1/Al)	0.04	0.1	0.34	0.90
ε_{exp} of the glass (Mg/BMG1/Mg)	0	0.02	0.16	0.51

4.2. Co-pressing

Two kinds of laminates, each one with three layers (one core in BMG1 and two skins either in aluminium or in magnesium alloys) were elaborated at various temperatures around the glass transition temperature of BMG1. A macroscopic strain of about 0.5 was applied at a strain rate equal to $2.5 \times 10^{-4}\,s^{-1}$. These conditions led to a co-pressing duration of 2000 s which allows keeping the amorphous structure of the glass whatever the selected temperature.

Fig. 5 displays a cross section of a produced three layer laminate with two skins in aluminium alloy and a core in BMG1. This laminate was co-pressed at 703 K for which the flow stress corresponding to a strain rate of $2.5 \times 10^{-4}\,s^{-1}$ is slightly higher in the aluminium alloy than in the glass (see Fig. 1). The stress ratio (or viscosity ratio) between the two constituents is a key parameter in the process and depending on temperature, the relative strains of the light alloy and the metallic glass can vary significantly. Table 2 summarizes the strain values undergone by the BMG1 glass for various temperatures of processing and for skins in aluminium or in magnesium alloys. For low temperatures, the mean strain in the metallic glass is very limited whereas it increases significantly with increasing co-pressing temperature. When co-pressing is performed at 703 K, the final local strain in the BMG1 core is larger than the imposed macroscopic strain whereas the final local strains in the aluminium skins are lower. In order to choose the co-pressing conditions, the strain distribution between the core and the skins can be estimated from the viscoplastic constitutive laws for the various materials (i.e. $\sigma = K\dot{\varepsilon}^m$) if iso-stress conditions of deformation (i.e. equal stresses in each constituent) are assumed and comparison between experimental strain values and predictions displayed a particularly good agreement since the difference was systematically less than 0.01.

SEM observations of the interfaces shows that, for optimised conditions of pressing (like those used to elaborate the multi material shown in Fig. 5), no cracks could be observed. Nevertheless, since pressing was carried out under argon atmosphere and not under vacuum in order to deal with a low cost process, some oxides could be detected along the interface. To evaluate the possible detrimental effect of such oxides, the estimation of the adhesion energy between the glass and the crystalline alloys is presently under progress thanks to 4-point bending tests.

5. Conclusion

Multi materials associating metallic glasses and conventional crystalline alloys were successfully elaborated by co-deformation performed at temperatures close to the glass transition temperature of the metallic glasses. Filamentary composites with a core in metallic glass were elaborated by co-extrusion whereas multilayered laminates were produced by co-pressing. For each case, optimum processing conditions were identified from the rheologies of the constituents deduced from compression tests at high temperature. After processing, it was shown that the strains undergone by the metallic glasses correspond roughly to what could be predicted from the constitutive laws of each constituent. In the case of co-extruded materials, push-out tests (interface shear stress measurements and SEM observations of the BMG core after testing) supported the idea that quite strong interfaces between the metallic glasses and the crystalline alloys could be obtained. In the case of co-pressed laminates, the measurement of the adhesion energy between the metallic glass and the crystalline alloys is presently under investigation thanks to 4-point bending tests.

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