ON THE BRITTLENESS OF BULK METALLIC GLASSES

V. KERYVIN[1] , C. BERNARD[1], J.-C. SANGLEBOEUF[1], Y. YOKOYAMA[2] and T. ROUXEL[1]
[1]LARMAUR, FRE-CNRS 2717, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes cedex, France
[2] Materials Science and Engineering, Faculty of Engineering, Himeji Institute of Technology,
2167 Shosha, Himeji City, Hyogo 671-2201, Japan

ABSTRACT

Fracture toughness studies are conducted on a Zr-based bulk metallic glass at room and low (77 K) temperatures. Samples, cast by different processing techniques, contain either crystalline defects or not. For SENB specimens containing 30 µm root radius notches, results indicate that a perfect glass without quenched-in defects is ductile at room temperature and brittle at low temperature (toughness of 72 $MPa.m^{0.5}$). On the contrary, imperfect glasses are brittle at room temperatures (toughness of 50 $MPa.m^{0.5}$) and brittler at low temperature (27 $MPa.m^{0.5}$). Fractographic observations clearly show the embrittlement caused by the dendrites at these two temperatures. These results are discussed on the basis of previous fracture studies with respect to the oxygen content in the samples.

1. INTRODUCTION

Bulk metallic glasses (BMGs) are known since the early 1990's (Inoue et al. [1]) to exhibit striking mechanical properties including large elastic strains (≈ 2 %) and high tensile strengths (more than 5 GPa for some of them) providing tremendous stored elastic energies. However, structural applications are limited by the lack of significant permanent deformation prior to failure.
Indeed, from a macroscopical point of view, submitted to tensile loadings BMGs fail in an elastic-brittle way and in compression BMGs also break in an elastic-perfectly plastic (few tenths of %) brittle way (Zhang et al. [2]). From a microscopic point of view, plastic deformation is highly localised in very thin shear bands which propagate rapidly. When these bands of intense straining reach the free surfaces of the sample, fracture occurs.
Moreover, the quite few studies concerning the toughness of BMGs, published since 1997, evidenced the embrittlement effects of annealing (Ramamurty et al. [3]), hydrogen (Suh and Dauskardt [4]) or crystallisation (Nagendra et al. [5]).
A major parameter which seems to have been neglected so far is the presence of dendrites in the as-cast BMGs. Indeed, even if new chemical compositions and high-cost advanced processing techniques have led to amorphous alloys with excellent glass forming ability (GFA), Zr-based BMGs (*e.g.*) lose their excellent GFA when oxygen impurity level is high leading to the formation of crystalline dendrites (Vaillant et al. [6]). Therefore, the present work aims to demonstrate the embrittlement of a BMG when such dendrites are present after quenching. To do so, toughness tests are conducted on a BMG either containing as-cast defects or not at room temperature and low temperature (77 K).

2. BODY OF PAPER

2.1 Experimental procedures

A $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at. %) bulk metallic glass is studied in this paper. Two different techniques were used to cast this glass. The first technique (further referred as A) of copper-mould casting

Fig. 1 – Typical dendritic structure in sample A (width of field 30 µm).

produced a composite (further referred as sample A) since a glassy matrix and micrometric dendrites are observed (see Figure 1 for an example of optical observation after chemical etching). The second technique (further referred as B) of tilt-casting (with ladle hearth type furnaces) developed by Y. Yokoyama et al. [7] produced specimens with no crystalline impurities (further referred as sample B): no detection by Scanning Electron Microscopy (SEM) or X-Ray Diffraction was evidenced. Great care is taken with respect to oxygen: very pure Zr is used (less than 40 ppm of oxygen) and the technique ends with samples containing less than 300 ppm of oxygen.
Changes in the mechanical behaviour with the casting technique were investigated by cutting specimens for three-points bending configuration. Using a 0.2 mm thick disk and finally a razor-blade covered with diamond paste, a sharp notch is created (root radius of 30 µm) to provide Single Edge Notch Beam (SENB) specimens. The load was applied with a mechanical test system operating under displacement control with a displacement rate of 10 mm/mn. Five samples corresponding to each technique A and B were tested and load-displacement data were recorded. The opening mode stress intensity factor K_I was determined following the SENB calibration described by Wakai et al. [8] which takes into account the span length-to-width ratio of the specimen.
Two testing temperatures were also used: a room temperature of 18°C (RT) and a low temperature of –196°C in liquid nitrogen (LT). After each test, fracture surfaces were observed by SEM (JEOL JSM 6301 F).

22 Results

Typical load-displacement curves are shown in Figure 2. The two first ones (a) and (b) concern sample B while the two last ones (c) and (d) deal with sample A. At room temperature sample A (curve (c)) exhibits a classical brittle behaviour. In that case the Linear Elastic Fracture Mechanics (LEFM) modelling allows to calculate a notch toughness value of 50 $MPa.m^{0.5}$. (The toughness values are only notch toughness values as no pre-cracking was made.) What is more striking is that sample B (curve (a)) is not at all brittle but completely ductile (actually on five specimens, only one really broke!). In that case it is of course not possible to determine a toughness value for sample B by LEFM; let us note however that the stress intensity factor reaches 73.4 $MPa.m^{0.5}$.In contrast, at very low temperature, both samples A and B (curves (b) and (d)) are brittle and their notch toughness values, calculated by LEFM, are respectively 27 $MPa.m^{0.5}$ and 72 $MPa.m^{0.5}$.

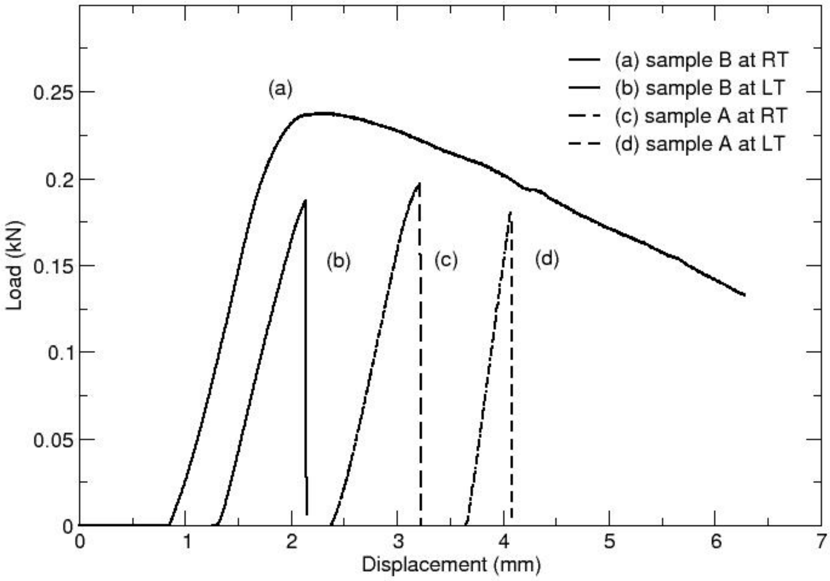
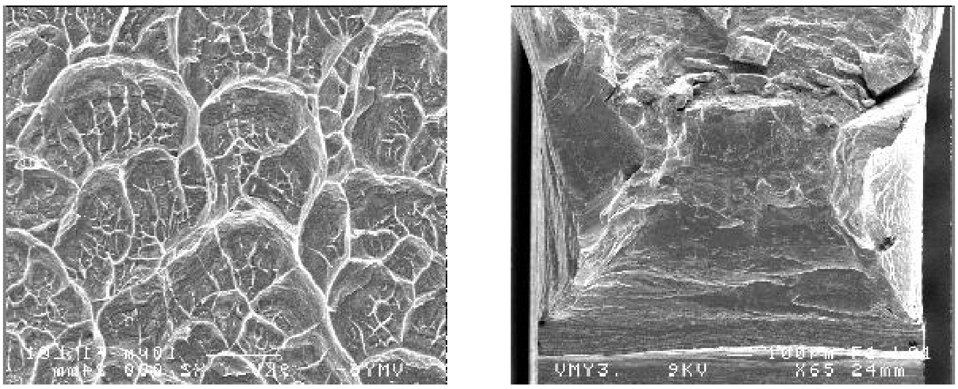


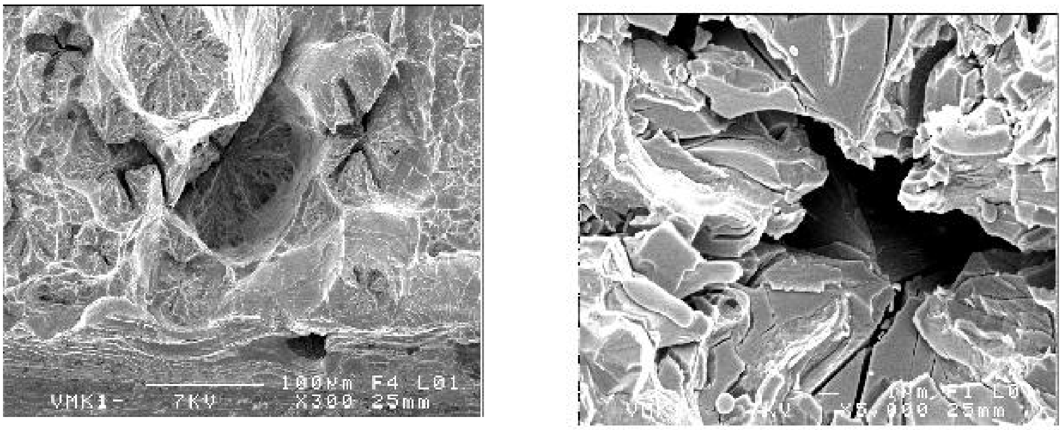
Fig. 2 – Typical load-displacement curves of samples A and B at room and low temperature.

To investigate the mechanisms of fracture and find out what differs in the two alloys, SEM is employed. When the behaviour is macroscopically brittle, the cross sections of the fracture surfaces are flat indicating plane strain testing conditions: there is no thickness effect on toughness.



. a b

Fig. 3 – SEM fracture surfaces of sample B broken at low temperature (a) a,d room temperature (b).



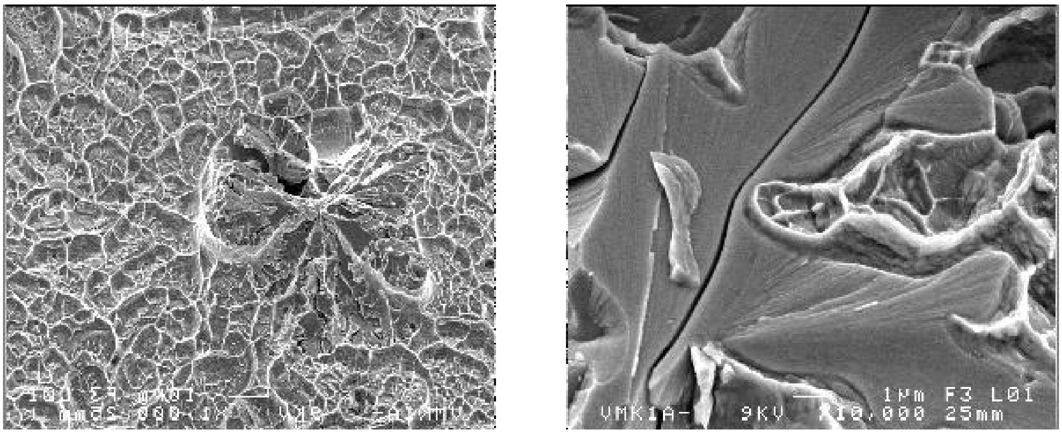
a b

Fig. 4 – SEM fracture surfaces of sample A borken at room temperature: global view (a) and detail (b).

For sample B, at low temperature, typical fracture surfaces are obtained, consisting in vein-like patterns (Figure 3 (a)). These patterns are similar to those obtained by shearing two plates in between which exists a thin viscous fluid layer. This dimpled region is often compared to the Taylor meniscus instability (Flores and Dauskardt [9]).
As far as the behaviour of sample B at RT is concerned, the specimens show an intense necking and the fracture surface is far from being flat illustrating a ductile behaviour (Figure 3 (b)).
Fracture surfaces of sample A at room and low temperature are then presented respectively in Figures 4 and 5.
At room temperature, Figure 4 (a) highlights the fact that some cells (of around 100 µm in diameter) are teared off from the other side of the fracture surface. The surface of these cells show vein-like patterns while their insides present cross-like patterns. These events are present all along the fracture surface. So, inside these cells are cross-like patterns whose dimensions and shapes agree strikingly with the dendritic structures present in sample A (see Figure 1). Taking closer looks inside by Figure 4 (b), it seems that dendrites were teared off from the glassy matrix leaving deep holes corresponding to the branches of the dendrites either by matrix/dendrite debonding or even maybe fracture of these dendrites (some debris are noticeable).
At low temperature, the fracture surface is flat and presents typical vein-like sometimes spotted by broken dendrites (see Figure 5 (a)). But this time fracture of these crystalline structures is obviously observed in Figure 5 (b). Indeed river patterns corresponding to fracture along specific crystallographic planes deviated by grain boundaries typical of a cleavage-like fracture are observed.

2.3 Discussion

Not so many studies have been conducted on the toughness of BMGs so far. Nearly all of these (Flores and Dauskardt [9], Conner et al. [10], Gilbert et al. [11], Lowhaphandu and Lewandowski [12]) concern the Vit1 glass (at % $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$). One of the conclusions of these successive works is the dependence of toughness on the root radius of the crack. In [12], for root radii of 65, 110 and 250 µm, a toughness between 100 and 130 $MPa.m^{0.5}$ is found while for a fatigue pre-cracked specimen a toughness of 18.4 $MPa.m^{0.5}$ is obtained. This is the reason why our



a b

Fig.5 SEM fracture surfaces of sample A broken at low temperature: global view (a) and detail (b).

present results should not be considered as intrinsic toughness values but rather as notch toughness ones (even if the notch is very sharp). A key point is the oxygen content of the samples. The first study on the Vit1 toughness [10] was made with raw materials containing 800 ppm of oxygen. No values of the oxygen content after quenching are given but 10-20 µm long dendrites are observed. In another study [11], the oxygen content is 1600 ppm after quenching. The other studies do not mention any of these features but their BMGs come from the same providers; therefore it is believed that their BMGs have dendritic structures because of oxygen contamination. Yokoyama et al. [7] show that above 1500 ppm, oxygen containing dendrites are present.

Sample A is a BMG where dendrites are observed (Figure 1) and sample B does not contain any dendrites because of the purity of the starting Zr and of the technique. For sample B at RT, a notch toughness value of 50 $MPa.m^{0.5}$ is obtained which is very consistent with the above mentioned studies (Flores and Dauskardt [9], Conner et al. [10], Gilbert et al. [11], Lowhaphandu and Lewandowski [12]). Particularly, Lowhaphandu and Lewandowski [12] have notch toughness values between 100 and 130 $MPa.m^{0.5}$ for notches between 65 and 250 µm and a toughness value of 18.4 $MPa.m^{0.5}$ for fatigue pre-cracked specimens.

Concerning the room-temperature ductility of sample B, a previous study (Yokoyama et al. [7]) showed on a very similar sample on bending tests that a conventional casting method makes the BMG brittle whereas ductility is observed when much care is taken regarding the oxygen content at the processing stage (as for sample B). It seems that efficient casting techniques can create BMGs with a ductile behaviour at room-temperature even in a SENB configuration (sharply notched specimens).

Fractography pictures on sample A clearly indicate that brittleness at RT comes from the presence of the dendritic structures. Their debonding from the glassy is the failure mechanism. The origin of the dendrites comes from oxygen contamination during processing of the Zr-based alloy (Vaillant et al. [7]). The polycrystalline structures are a $Zr_7Cu_4Al_3O$ compound with fcc structure. Being oxides (cermets) by nature their toughness values should be lower than the BMG one.

At LT the propagation path is no longer slant even at microscopic scale and the cleavage features indicate that fracture occurs through the dendrites and therefore is faster than at RT. The lower value of the toughness (27 compared with 50 $MPa.m^{0.5}$) is consistent with these fractographic assumptions. Another proof of the embrittlement by the dendrites is finally given by comparing toughness values of samples A and B at LT (72 and 27 $MPa.m^{0.5}$ respectively).

4. CONCLUSIONS

Some toughness experiments on a Zr-based bulk metallic glass gave us some hints on its fracture mechanisms. For 30 µm root radius notch cracked specimens, bulk metallic glasses are ductile at room temperature and the maximum stress intensity factor is more than 70 $MPa.m^{0.5}$. Subsequent studies with pre-cracked specimens are required to conclude whether BMGs are really ductile or blunting occurs at the crack tip because of the (even sharp) notch.

Moreover, BMGs containing crystalline defects originating from imperfect casting techniques (oxygen contamination, dendrites more than 10 µm long) are brittle at RT. Fractographic studies clearly incriminate the dendrites for this brittleness and values for samples containing dendrites have a toughness of 50 $MPa.m^{0.5}$ which is similar to previous studies.

At low temperature, perfect or imperfect BMGs are brittle but BMGs containing dendrites are brittler (27 $MPa.m^{0.5}$) than BMGs without dendrites (72 $MPa.m^{0.5}$). For samples containing these defects, fractography studies clearly indicate that the fracture path is flat at low temperature (cleaving the crystalline imperfections) while it is slant at RT (reaching the nearest dendrite by dendrite-glassy matrix debonding) and explaining a lower value of toughness at LT than at RT.

5. REFERENCES

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