

# Influence of structural relaxation on the fatigue behavior of a $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk amorphous alloy

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## Abstract

The cyclic fatigue behavior of two as-cast amorphous  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$  alloys was examined. Although both had identical compositions, the fatigue endurance strength ( $10^7$  cycles) was higher for the alloy with less free volume, as determined by differential scanning calorimetry experiments. Such differences are believed to result from the processing cooling rates.

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## 1. Introduction

Bulk metallic glasses have emerged over the past 15 years as materials with unique and attractive properties due to their near theoretical strengths combined with reasonably high fracture toughness, excellent corrosion resistance, high formability and low damping. A number of alloy systems have been developed which may be processed in bulk amorphous form (>1 mm section thickness), including those based on lanthanum [1], magnesium [2], zirconium [3,4], palladium [5,6], iron [7], platinum [8], copper [9] and nickel [10,11]. The first commercial metallic glass alloy with composition  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ , known as Vitreloy 1™, is used today in several commercial applications and has received considerable attention with regard to its fracture and fatigue properties [12–19]. An understanding of the mechanical properties of such alloys is paramount if these materials are to realize their potential as structural materials, with fatigue properties being of critical importance for applications involving cyclic load-

ing. Thus, the effort to understand the micromechanisms that control the fatigue properties of metallic glasses presents an ongoing area of research.

Although metallic glasses do not have a traditional microstructure like their crystalline counterparts, structural differences may exist which can affect their mechanical properties. The deformation of a metallic glass requires the existence of free volume, i.e., extra volume relative to a fully dense glass, that is frozen into the atomic structure and allows physical space for atomic movement under mechanical loading [20,21]. Accordingly, it is expected that changes in the free volume should affect the mechanical properties as well. For example, when Vitreloy 1™ is charged with hydrogen to fill up some of the free volume, significant increases in the hardness, fatigue threshold, and Paris fatigue exponent are observed along with decreases in the fracture toughness [22,23]. Similar embrittlement is also observed when Vitreloy 1™ is annealed without crystallization [24]. Here embrittlement occurs since the free volume is decreased by structural relaxation, a well known phenomenon also observed in traditional thin ribbon amorphous metals [25].

Structural differences may exist in as-processed glasses as well. Amorphous solidification of an alloy from the liquid state involves the kinetic suppression of nucleation

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and growth of crystallites. The kinetic glass transition involves sudden changes of the specific heat capacity [26] and the expansion coefficient [27], while free volume, enthalpy, and configurational entropy are frozen in. Noting that the Zr–Ti–Ni–Cu–Be glass-forming system has a very low critical cooling rate of about 1 K/s [3,28], differences in the cooling rate above this critical value may result in variations in the physical and thermodynamic properties, in particular the enthalpy and free volume of the system. Such variations should lead to differences in the mechanical properties as well, as outlined above. Accordingly, this study investigates the fatigue life behavior of a  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$  amorphous alloy processed by two different manufacturers which have different free volumes in the as-processed conditions.

## 2. Experimental procedures

### 2.1. Sample preparation

Experiments were performed on two fully amorphous as-cast plates with the same nominal composition,  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ , commercially known as Vitreloy 1™. One plate (2.6 mm thick, 56 × 85 mm) was produced and supplied in the year 2004 by Liquidmetal® Technologies (Lake Forest, CA, USA) while the second plate (4.8 mm thick, 64 × 40 mm) was produced in 1994 by Howmet Corporation (Whitehall, MI, USA). The latter was stored at ambient temperature and pressure until testing was conducted for this study. Both alloys were determined to be fully amorphous based on X-ray diffraction results. In addition, representative specimens of both sets of samples were polished and etched (45 ml H<sub>2</sub>O, 45 ml HNO<sub>3</sub>, and 10 ml HF) and examined using optical microscopy with differential image contrast to observe if any crystallites were present; however, no crystallites were found. Beam specimens, with nominal dimensions 2 × 2 × 60 mm, were cut from the as-received plates with a Buehler Isomet 1000 precision saw. Each beam was then visually inspected to ensure no defects or notches were present on the surface, which would create favorable sites for crack nucleation. Specimens were tested with the surfaces in the “as machined” condition; no subsequent grinding or polishing was performed. Profilometry scans, using a Veeco Dektak® 8 Advanced Development Profiler, were conducted on the outer surface of the beams in the direction of the bending stress to determine the surface roughness of the samples, as expressed by the arithmetic average roughness,  $R_a$ . Results were similar for both sets of samples with a mean value of  $R_a = 1.62 \mu\text{m} \pm 0.64 \mu\text{m}$ .

### 2.2. Fatigue testing

Fatigue tests were conducted in three-point bending using a BOSE ELeCTroForce ELF 3200 computer-controlled testing machine. Specimens were cycled (20 Hz, sinusoidal waveform) in load control until complete failure

at room temperature using a constant load ratio,  $R = \sigma_{\min}/\sigma_{\max}$ , of 0.1, where  $\sigma_{\max}$  and  $\sigma_{\min}$  are the maximum and minimum stresses experienced during the loading cycle. The three-point bending fixture had a center to end span of 24.2 mm.

### 2.3. Differential scanning calorimetry

Calorimetric measurements were performed on a Perkin Elmer Diamond differential scanning calorimeter (DSC) with heating rates of 0.25, 1, 2, and 3 K/s at ambient pressure. Analyses were carried out on small 50–90 mg pieces of the as-processed material.

## 3. Results and discussion

The normalized stress amplitude,  $\sigma_a/\sigma_{\text{uts}}$ , is plotted as a function of cycles to failure,  $N_f$ , for both  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$  alloys in Fig. 1, where the stress amplitude,  $\sigma_a$ , is  $1/2(\sigma_{\max} - \sigma_{\min})$ . Data is normalized by the ultimate tensile strength reported in the literature,  $\sigma_{\text{uts}} \approx 1900$  MPa, at which point catastrophic failure occurs [29]. Fig. 1 shows that the fatigue life behaviors of the two alloys are quite different. At a given value of  $\sigma_a/\sigma_{\text{uts}}$ , fatigue lifetimes are significantly shorter for the Liquidmetal produced alloy. The Howmet and Liquidmetal alloys were found to display  $10^7$  cycle fatigue strengths at  $\sigma_a/\sigma_{\text{uts}}$  values of 0.20 and 0.09, respectively.<sup>2</sup> Those values correspond to a stress range,  $\Delta\sigma = \sigma_{\max} - \sigma_{\min}$ , of 768 MPa and 359 MPa, respectively. Additionally, examinations of the fracture surfaces for each specimen were carried out using field-emission scanning electron microscopy (FESEM). Observations of fatigue fracture surfaces indicated that cracking originated from the beam corners and below the center loading pin where the stress was highest. Furthermore, no significant differences in the morphology of the crack initiation sites were observed between the alloys. Such results suggest that differences in crack forming inhomogeneities were not responsible for the differences in fatigue lifetime, i.e., cracks consistently formed at the highest stress concentration.

Although the Howmet alloy specimens had longer fatigue lives, calculations of the stress–intensity factors at final fracture suggest that its toughness was lower. Based on the corner-crack configuration observed on the fracture surfaces, the stress–intensity factor solutions for a quarter-elliptical corner crack in a finite plate subjected to bending loads were applied to estimate the fracture toughness [30]. Although all samples failed by corner cracks, only a few had well defined quarter-elliptical shapes suitable for stress–intensity analysis. For the Liquidmetal alloy, four different samples had such crack shapes with a mean

<sup>2</sup> Although these values are higher than reported in Ref. [14] for Vitreloy 1™, it is important to note that the different loading configuration and surface treatments affect the fatigue life, making direct comparisons of little utility.

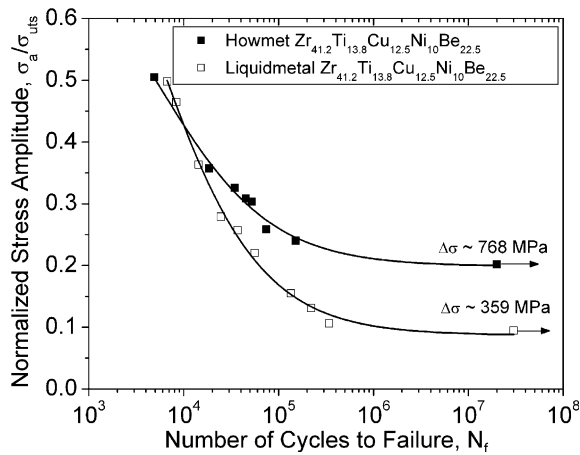


Fig. 1. Stress/life data for Vitreloy 1™ alloys presented in terms of the normalized stress amplitude,  $\sigma_a/\sigma_{uts}$ , plotted as a function of cycles to failure,  $N_f$ .

$K_c = 24.8 \pm 8.0 \text{ MPa}\sqrt{\text{m}}$ . Similarly, the mean fracture toughness of the Howmet alloy was calculated at  $18.8 \text{ MPa}\sqrt{\text{m}}$  based on two samples with well defined crack geometries, here the standard deviation is not relevant due to limited data. Since lower fracture toughness should shorten the fatigue life, this implies that the fatigue crack initiation and/or growth portions of the fatigue lifetimes must have been sufficiently longer to offset this effect. Thus, despite the fact that both alloys possess the same atomic composition, the different fracture and fatigue behavior suggest that structural differences exist within the materials.

Hydrogen embrittlement presents one possible source for the differences in properties, particularly for the Howmet material which was produced roughly 10 years prior to testing and may have absorbed hydrogen over that time. However, the onset glass transition temperature,  $T_g$ , and the onset crystallization temperature,  $T_x$ , were determined using the DSC to be essentially identical for both alloys at each heating rate (i.e., within  $\pm 1 \text{ K}$ ). Suh and Dauskardt [22,23] reported that  $T_g$  and  $T_x$  both increase with hydrogen charging, implying that a variation in the hydrogen levels between the alloys is not responsible for the observed differences in fatigue life behavior.

As for possible compositional differences, the glass transition temperature,  $T_g$ , as well as the undercooled liquid region,  $\Delta T$ , given by Waniuk et al. [31] for Vitreloy 1™ are identical to the experimentally determined  $T_g$  and  $\Delta T$  for the Liquidmetal and Howmet alloys. Such values are sensitive to small changes in composition [31], ruling out variations in the nominal versus actual compositions for these two materials. Finally, analysis of the crystallization peaks of the DSC scans suggest there are no differences in crystallinity between the alloys that may be present below the detectability limit of the X-ray diffraction analysis.

Fig. 2 shows heat flow data for specimens that are heated through the glass transition at ambient pressure and a constant heating rate of 1 K/s. Based on Fig. 2, the Howmet alloy shows a pronounced endothermic heat

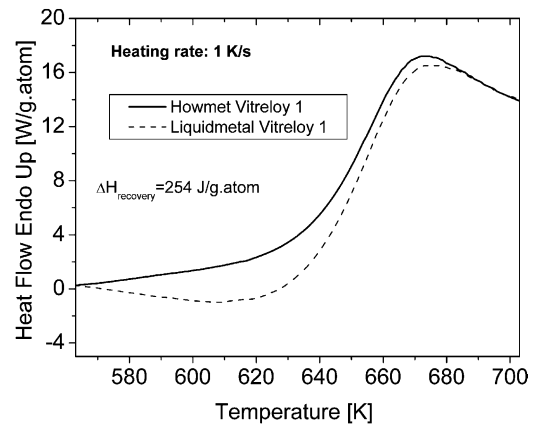


Fig. 2. Typical heat flow curves for  $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$  samples measured at ambient pressure and constant heating rate. These data are for 1 K/s, while similar results were observed for each other heating rate.

recovery in the glass transition region when compared to the Liquidmetal alloy. This behavior was typical for each heating rate used and can be attributed to an enthalpy difference between the Liquidmetal and Howmet samples. Quantification of the enthalpy difference between the two materials was achieved by taking the area between the two heat flow curves. Based on experiments at four different heating rates, the average and standard deviation of the enthalpy differences were found to be  $250 \pm 24 \text{ J/g atom}$ . Enthalpy recovery in this alloy [24] and a similar Zr-based amorphous alloy ( $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ ) [32] has been observed previously in experiments where annealing was performed to allow for structural relaxation, which reduces the free volume. Based on the deduced enthalpy differences it is determined that the Howmet alloy is in a more relaxed state than the Liquidmetal produced material.

This difference may not be attributed to the different ages of the alloys; however, since the relaxation time for amorphous  $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$  at ambient temperatures is many orders of magnitude longer than the 10 years experienced by the Howmet alloy [33]. The observed enthalpy difference is thus suspected to be due to variations in cooling rates during processing. It is likely that the Howmet alloy was quenched at a lower rate than the Liquidmetal alloy, which in turn brought it into a different enthalpy state. This situation is analogous to the annealing experiments in Refs. [24,25,32], which yielded different enthalpy states, since slower cooling gives longer time exposure at elevated temperatures.

Under the assumption that the enthalpy change is proportional to the volume change, the average free volume per atom,  $v_f/v_m$ , may be determined. Masuhr et al. [34] calculated the free volume per atom,  $v_f$ , for Vitreloy 1™ according to the Cohen and Grest model [35],

$$v_f = \frac{k}{2c_0} \left( T - T_0 + \sqrt{(T - T_0)^2 + \frac{4v_a c_0}{k} T} \right), \quad (1)$$

with the following fit parameters [34]:  $bv_m\zeta_0/k = 4933$  K with  $b = 0.105$ ,  $4v_a\zeta_0/k = 162$  K, and  $T_0 = 672$  K.<sup>3</sup> The atomic volume  $v_m$  of Vitreloy 1™ has been reported as  $1.67 \times 10^{-29}$  m<sup>3</sup> near the liquidus [27]. The Cohen and Grest model provides the values for the free volume of the supercooled liquid even below the calorimetric glass transition which can be obtained by long time relaxation experiments. To estimate the proportionality between the volume change and the enthalpy change, published data of enthalpy difference,  $\Delta H$ , with respect to the crystalline mixture for the supercooled liquid and the frozen-in amorphous state was used for an alloy with slightly different composition ( $Zr_{46.25}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$ ) [32] since data for Vitreloy 1™ was unavailable. Consequently, the proportionality relation between the average free volume per atom,  $v_f/v_m$ , and the enthalpy change,  $\Delta H$ , was determined to be

$$v_f/v_m = 0.080\Delta H, \quad (2)$$

where  $\Delta H$  is given in kJ/g atom. Therefore, knowing the average difference in the enthalpy change,  $\Delta H$ , between the Howmet and Liquidmetal alloys, Eq. (2) was used to estimate the free volume difference,  $\Delta v_f/v_m$ . This free volume difference was found to be  $\sim 0.02\%$ .

Existing models for the deformation of metallic glasses predict that a reduction in free volume will retard plastic deformation [20,21]. This reduced ductility results in longer fatigue lives (Fig. 1) and lower fracture toughness (here and in Refs. [22–24]). The present results, where a reduction in free volume was achieved by structural relaxation, are consistent with fatigue crack growth data for glasses with reduced free volume from hydrogen charging, which demonstrated slower crack growth rates and higher fatigue thresholds for hydrogen charged glasses [23]. While it is currently unclear what effect, if any, the free volume has on crack initiation, it is clear that the combined effects on crack initiation along with the lower fatigue crack growth rates more than offsets any reduction in fatigue life that would occur due to the lower toughness.

Finally, it is becoming apparent that simply knowing the composition of a metallic glass, even in its as-processed state, is not enough to determine the mechanical properties. Akin to knowing the microstructure in traditional alloys, a knowledge of the structural state (i.e., free volume) of metallic glasses is necessary to understand their mechanical properties, even in the absence of subsequent annealing or hydrogen embrittlement. This may account for some of the drastic reported variations in the fatigue life behavior between similar bulk metallic glasses, e.g., see Refs. [14,37], while also affecting the fatigue properties for in situ bulk metallic glass composites achieved by partial crystallization during processing [38].

<sup>3</sup> The  $T_0$  used in the Cohen and Grest model is different from the  $T_0$  used in the Vogel–Fulcher–Tamman (VFT) relation which has a value of 412.5 K for Vitreloy 1™ [36].

## 4. Conclusions

Based on an experimental study of the cyclic fatigue behavior of two as-cast plates of fully amorphous  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ , the following conclusions can be made:

1. Although both alloys were tested in the as-cast condition, significant differences were observed in the fatigue lives, which were attributed to differences in their free volumes.
2. The enthalpy difference between the two alloys was measured to be  $250 \pm 24$  J/g atom, with the corresponding free volume difference,  $\Delta v_f/v_m$ , estimated to be 0.02%. This difference resulted in a factor of two difference in the  $10^7$  cycle fatigue strength,  $\sigma_a/\sigma_{uts}$ , which was 0.09 for the unrelaxed and 0.20 for the relaxed alloy.
3. Even in the absence of subsequent annealing or hydrogen embrittlement, structural (i.e., free volume) differences may exist between metallic glasses of identical composition depending on the specific processing conditions. This can have a marked effect on the mechanical properties, specifically the fatigue life and fracture toughness.

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