

# Understanding the Problem of Fatigue in Bulk Metallic Glasses

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Early studies suggested there was a severe problem with the fatigue resistance of some bulk metallic glasses (BMGs) and BMG matrix composites, while more recent studies begin to demonstrate a wide variety of fatigue behaviors may be possible for both fully amorphous BMGs and their composites. However, in order to truly understand and control the fatigue behavior of these materials, the role of such factors as thermomechanical processing, the corresponding glass structure, environment, and defects must be understood. Additionally, it is important to understand how these factors relate to the mechanisms of fatigue. This article reviews the current understanding in this regard, and identifies some of the challenges for the future development of fatigue-resistant BMG-based materials.

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## I. INTRODUCTION

**BULK** metallic glasses (BMGs) are a relatively new class of engineering materials with unique and unusual properties that make them potential candidates for many structural applications.<sup>[1]</sup> Favorable properties include near theoretical strengths combined with reasonable fracture toughness, low damping, large elastic strain limits, and the ability to be thermoplastically formed into precision-shaped parts with complex geometries,<sup>[2-4]</sup> all of which are generally distinct from, or superior to, corresponding crystalline metals and alloys. One property that has been perceived as a limitation for BMGs has been low fatigue resistance relative to crystalline metallic materials; indeed, the first study on  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ ,\* the most studied BMG,

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\*All compositions are given in terms of atomic percent.

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found the endurance limit to be only roughly 4 pct of the ultimate tensile strength ( $\sigma_{fat}/\sigma_{UTS} \approx 0.04$ ) for four-point bending with a load ratio of  $R = P_{min}/P_{max} = 0.1$ .<sup>[5]</sup> However, not all studies to date have been in agreement on this point. The reported  $10^7$  cycle fatigue strengths for  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$  vary by a factor of 7,<sup>[5-7]</sup> and fatigue thresholds,  $\Delta K_{TH}$ , vary by a factor of 3.<sup>[5]</sup> While some of the reported scatter may be explained by different testing configurations,<sup>[8]</sup> this does not account for all the observed variations, for example, those within single studies.<sup>[5,6]</sup> Furthermore, a recent review article has shown that when a broad array of Zr-based BMG chemistries are considered, a wide range of fatigue life behavior is observed and many Zr-based BMGs show behavior comparable to crystalline metals

(Figure 1),<sup>[9]</sup> suggesting initial concerns may have been specific to certain BMG compositions. Furthermore, while early attempts at making BMG matrix composites also resulted in low fatigue limits and fatigue thresholds,<sup>[10]</sup> the latter even worse than comparable fully amorphous BMGs, more recently developed BMG matrix composites demonstrate excellent fatigue resistance.<sup>[11,12]</sup>

While it is becoming apparent that it is likely possible to produce BMGs and BMG matrix composites with a rich variety of fatigue properties, the fatigue literature to date has been plagued by a high degree of scatter. Such scatter suggests that some important variables affecting the fatigue behavior of BMGs are not adequately understood or controlled in the experiments. Studies over the last few years have suggested that factors such as the thermal history,<sup>[6,13-15]</sup> mechanical history,<sup>[16-18]</sup> environment,<sup>[19-22]</sup> and defects<sup>[23-25]</sup> all may play a role in affecting the fatigue behavior of BMGs. However, most of those factors were rarely characterized, reported, or controlled in early fatigue studies on BMGs, which likely explains some of the reported scatter. Accordingly, the purpose of this article is to review how the preceding factors can affect the measured fatigue behavior of BMGs, identify gaps in the knowledge base, and suggest solutions for making BMG-based materials with both good and repeatable fatigue resistance.

## II. VARIABLES AFFECTING FATIGUE BEHAVIOR

### A. Thermal History

#### 1. Glass structure and free volume

The free volume is known to be an important factor in determining the mechanical properties of BMGs,<sup>[26-33]</sup> a point which has only recently been considered when comparing the fatigue behavior of as-cast amorphous alloys in the absence of hydrogen embrittlement or chemistry changes.<sup>[6]</sup> The generally accepted definition

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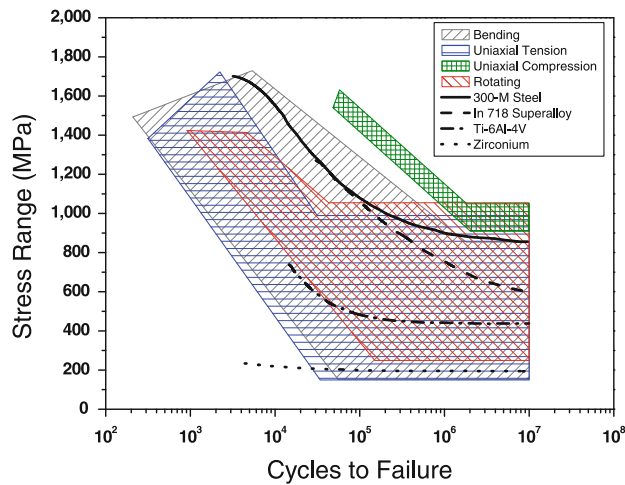


Fig. 1—Ranges of Zr-based BMG fatigue life behavior compared to several engineering alloys. Even in bending, where the worst fatigue performance was originally reported by Gilbert *et al.*,<sup>[5]</sup> ratios of fatigue life (stress amplitude) to ultimate tensile strength ( $\sigma_{fat}/\sigma_{UTS}$ ) range as high as 0.25 for certain compositions, which compares favorably with many crystalline alloys. Figure reproduced with permission from Ref. 9.

of free volume is the atomic volume in excess of a fully dense amorphous state, and thus, free volume is widely considered as the open volume sites that allow atoms to flow during deformation. When the free volume of a metallic glass is reduced (*e.g.*, by slow cooling or annealing), deformation and plastic flow is more difficult, the fracture toughness is reduced,<sup>[6,13,26–28,32]</sup> and the  $10^7$  cycle fatigue strength increases.<sup>[6,13]</sup> Indeed, the  $10^7$  cycle fatigue strength was found to vary by a factor of 2 for BMGs of identical composition ( $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ ) with different initial free volume states (Figure 2).<sup>[6]</sup> In that study, the free volume differences were quantified by thermal analysis using the enthalpy recovery method,<sup>[6,34]</sup> and only a marginal reduction in toughness was observed ( $\sim 26$  vs  $19$  MPa $\sqrt{m}$ ). Furthermore, for the similar  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  BMG composition, it has been shown that when the free volume is reduced by structural relaxation *via* sub- $T_g$  annealing, using appropriate times and temperatures to avoid crystallization,<sup>[34]</sup> the fatigue crack growth properties are unaffected. This is seen in Figure 3(a), where the fatigue crack growth behavior for samples annealed at 610 K (337 °C) for 1 and 10 times the relaxation time,  $\tau$ , essentially overlap the curve for samples that have simply been stress relieved. Note, at  $10\tau$ , the BMG is essentially fully relaxed and exhibits an order of magnitude drop in fracture toughness from 34 to 3 MPa $\sqrt{m}$ . Thus, it is surprising that there is negligible effect on the fatigue crack growth behavior. This insensitivity to initial-free volume state has been attributed to the fact that the free volume locally increases at the crack tip due to the intense deformation during fatigue cycling, as determined by depth profiled positron annihilation spectroscopy using the Doppler broadening technique.<sup>[14]</sup> Similar results were found for the various samples regardless of the initial free volume state, indicating that in the absence of hydrogen,

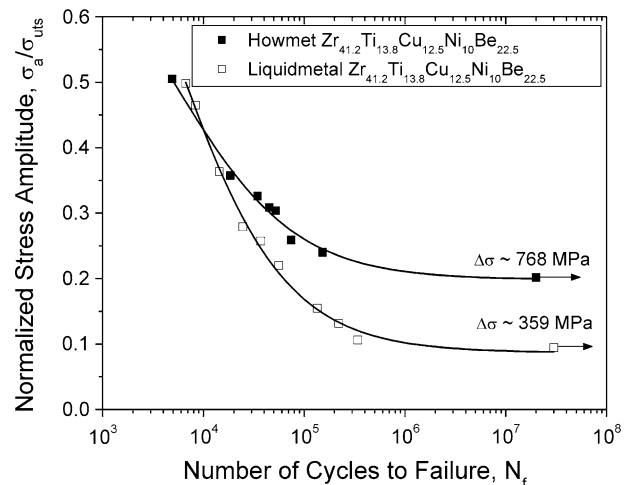
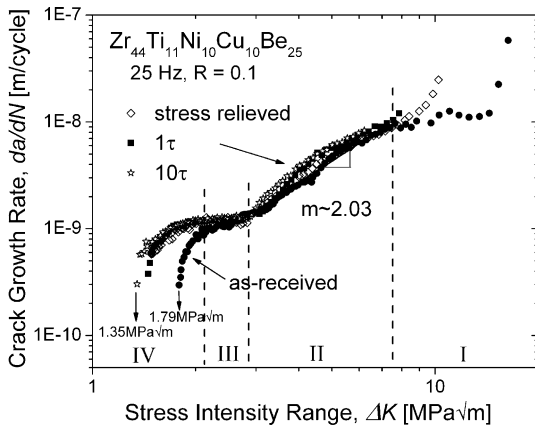


Fig. 2—Plot showing the difference in the 3-point bending fatigue life curves for  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$  BMGs produced by different manufacturers with different amounts of free volume. The Howmet produced material, with lower free volume, showed a higher fatigue limit. Figure reproduced with permission from Ref. 6.

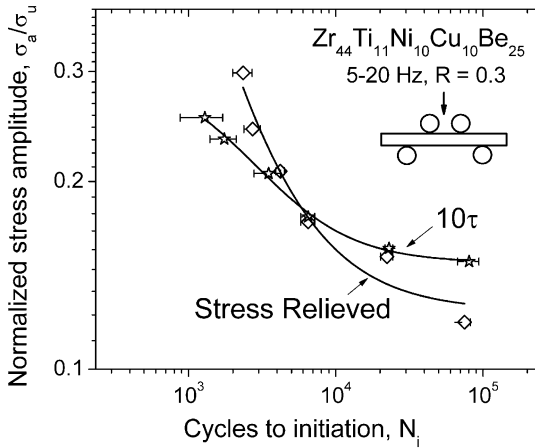
the free volume at the fatigue crack tip is determined by the local deformation and not the prior processing history. Finally, such results imply that differences in fatigue life behavior with free volume changes can be attributed to differences in the crack initiation behavior. Indeed, the number of cycles to initiate a crack shows a pronounced effect of free volume, as shown in Figure 3(b).<sup>[13]</sup>

In contrast to the preceding results, it has been observed that when free volume is filled with hydrogen, fatigue crack growth is slowed.<sup>[26,27]</sup> Such results are not inconsistent with the preceding concept of free volume creation at the crack tip. In the presence of hydrogen, the hydrogen atoms can easily move to fill any new free volume created. Thus, one may conclude that it is not only the amount of free volume, but also the local atomic environment, for example, the presence of hydrogen, that controls fatigue crack growth. Similarly, a study that attempted to affect the free volume of Zr-Cu-Al BMGs by adding 0 to 7 pct Pd found a linear increase in fatigue limit with increasing volume,<sup>[35]</sup> which again suggests the chemistry and local atomic environment play a significant role in addition to free volume. Also, it has been shown that not all free volume sites are equivalent and the distribution of different sized sites changes with deformation;<sup>[14,36]</sup> thus, different distributions of free volume sizes may influence the behavior as well.

Recent computational studies on model Cu-Zr and Cu-Zr-Al metallic glasses have found that the fraction of icosahedral sites is much more sensitive to changes in cooling rates and structural relaxation than free volume, and those authors suggest that the local (icosahedral) ordering may be a more significant factor for characterizing the structural state of metallic glasses and their mechanical behavior.<sup>[37,38]</sup> The role of such short-range ordering on fatigue behavior has yet to be explored; however, generalizing this concept to all metallic glasses may prove difficult. Indeed, it is suggested that



(a)



(b)

Fig. 3—(a) Plot showing there is no effect of the initial free volume state on the fatigue crack growth behavior for a  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  BMG annealed to three conditions: stress relieved (120 s at 573 K (300 °C)),  $1\tau$  (438 s at 610 K (337 °C)), and  $10\tau$  (4380 s at 610 K (337 °C)), where  $\tau$  is the structural relaxation time at 610 K (337 °C). There is, however, an effect of the residual tempering stresses in raising the threshold for the as-received BMG. (b) Plot showing that the number of cycles to crack initiation is affected by the free volume state, as illustrated by comparing the stress-relieved and  $10\tau$  conditions. Both figures reproduced with permission from Ref. 13.

icosahedral ordering should not play a role in Al-based glasses.<sup>[39]</sup> Overall, one may conclude that a simple model based on the amount of free volume controlling the fatigue properties is likely too simplistic, and various other aspects of the glass structure such as free volume site size and distribution, short and medium range order, as well as hydrogen all likely play a role in determining the fatigue properties.

## 2. Residual stresses

Residual compressive stresses up to several hundred megapascals may form on the surface of BMGs due to thermal tempering during the casting process.<sup>[40,41]</sup> In most literature studies, steps were typically not taken to relieve such stresses prior to fatigue testing. Thus, residual stresses were likely present during fatigue and fracture experiments, potentially affecting the results. Surface compressive stresses are well known to affect the

fracture properties of conventional oxide glasses (*i.e.*, tempered glass), and residual surface stresses caused by shot peening have recently been demonstrated to improve the uniaxial compressive and 3-point bending behavior of BMGs.<sup>[42]</sup> Furthermore, recent results show that the fracture and fatigue behavior can indeed be affected by thermal tempering stresses. The fracture toughness,  $K_{IC}$ , of a  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  BMG dropped by ~33 pct from 51 to 34  $MPa\sqrt{m}$  when the thermal tempering stresses were removed by annealing below the glass transition temperature,  $T_g$ .<sup>[13]</sup> Similarly, the fatigue threshold,  $\Delta K_{TH}$ , was found to decrease by ~25 pct from 1.79 to 1.35  $MPa\sqrt{m}$ , as shown in Figure 3(a).<sup>[13]</sup> In that figure, the as-cast samples contained thermal tempering stresses from the casting process, while the stress-relieved samples had the same free volume with no residual stresses. Thermal and structural characterization confirmed that the heat-treated BMG had neither structurally relaxed nor formed nanocrystals.<sup>[13,34]</sup> Thus, this provides clear evidence that some of the scatter in the reported fatigue thresholds (*e.g.*, in Reference 5) may be due to residual stresses. This effect is attributed to the compressive residual stresses near the sample surfaces that superimpose on the crack tip stress state, suppressing crack propagation. Fully amorphous BMGs produced with different cooling rates or section thicknesses, or machined from different regions of larger cast plates, may have different residual stresses at the crack tip, affecting the fracture and fatigue properties.

## B. Mechanical History

As described in Section II-A-2, surface residual stresses from thermal tempering can have a benefit for both the fracture and fatigue properties of BMGs. Alternatively, a mechanical way to induce surface residual stresses in a material is by shot peening. Shot peening has been demonstrated to be successful in providing compressive residual surface stresses in BMGs and improving the bending and compressive ductility.<sup>[42]</sup> However, an initial study on the fatigue behavior of a shot-peened  $Zr_{21.5}Ti_{42}Cu_{15.5}Ni_{14.5}Be_{3.5}Al_3$  BMG showed no benefit of shot peening on rotating bend fatigue life.<sup>[17]</sup> Instead, crack initiation was found to be shifted ~100  $\mu m$  below the sample surface, *i.e.*, under the compressive stress layer. It is currently unclear as to the exact reasons why shot peening-induced residual stresses were not beneficial for fatigue of this BMG, while thermally induced residual stresses do appear beneficial for a  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  BMG in improving both the fatigue threshold and fracture toughness.<sup>[13]</sup> However, it is important to note that the shot peening process, in addition to producing residual stresses, concurrently induces large amounts of inhomogeneous deformation into the sample surface region. Inhomogeneous deformation is known to occur by the production of free volume in the metallic glass.<sup>[43]</sup> Thus, while the shot-peened layer is under compressive stress, it is also expected to be in a state of higher free volume, which has been found by Launey *et al.* to make crack initiation easier.<sup>[13]</sup> Thus, with shot peening, there may

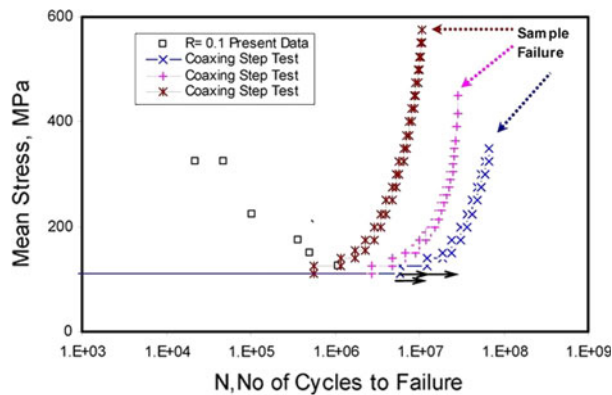


Fig. 4—Plot showing how the mean stress at failure can be coaxed as high as 575 MPa for a  $Zr_{41.8}Ti_{12.9}Ni_{9.5}Cu_{12}Be_{23.8}$  BMG by cycling below the fatigue limit. Figure reproduced with permission from Ref. 16.

be competing effects of mechanically altering both the surface stress state and the surface glass structure.

While shot peening has not been demonstrated to improve the fatigue properties to date, conversely, cyclic loading below the fatigue limit has been shown to be beneficial to the fatigue life for a  $Zr_{41.8}Ti_{12.9}Ni_{9.5}Cu_{12}Be_{23.8}$  BMG.<sup>[16]</sup> Using a fatigue coaxing step test, where the mean stress was increased after each prescribed number of cycles, it was found that the mean stress at failure, which would normally be below 200 MPa, could be increased substantially up to 575 MPa (Figure 4). Thus, even below the fatigue limit, where one might guess little change is occurring in the glass, in fact, significant mechanical changes are induced in the BMG that affect the fatigue behavior. Such results are similar to the findings of Packard *et al.*,<sup>[18]</sup> who found a hardening of a  $Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$  BMG after cyclically loading with a nanoindenter below the yield point even after a few ( $\leq 10$ ) cycles. While in both cases the mechanisms are still unclear, these results suggest that the mechanical behavior of BMGs are sensitive to loading history even at very low loading levels. Thus, there are likely potential possibilities for mechanically treating BMGs to tailor fatigue properties that have yet to be explored.

### C. Environment

Early studies on  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  BMGs in aqueous environments found a severe degradation in the fatigue crack growth properties in the presence of NaCl as well as a pronounced stress corrosion cracking effect under static loading.<sup>[20,21]</sup> Indeed, the threshold stress intensity range for fatigue crack growth,  $\Delta K_{TH}$ , was lowered below  $1 \text{ MPa}\sqrt{\text{m}}$ , and the growth rates at specific  $\Delta K$  values were found to increase by more than three orders of magnitude. More recent work has shown this corrosion fatigue effect to depend on the NaCl concentration, and also a similar, but less severe, effect was found for aqueous solutions containing  $NaClO_4$  or  $NaSO_4$ .<sup>[22]</sup> Those authors attributed the poor environmental cracking resistance of that BMG primarily to its

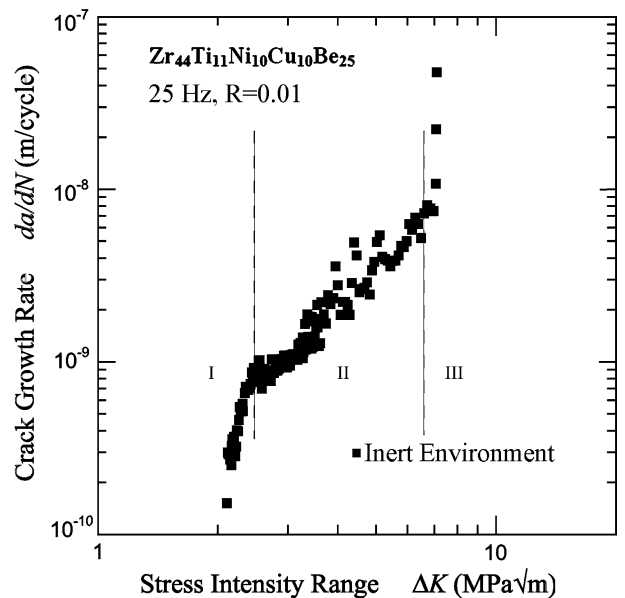


Fig. 5—Plot showing the fatigue crack growth curve of a  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  BMG tested in dry flowing  $N_2$  gas. When compared to Fig. 3(a), the fatigue threshold is higher and the plateau region at  $10^{-9}$  m/cycle is gone when testing is conducted in an inert environment. Figure reproduced with permission from Ref. 19.

chemical composition, which does not give a strongly protective oxide at the crack tip.

Fatigue crack growth data collected in ambient room air for  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  and  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  bulk metallic glasses (BMGs) found in the literature often display a plateau in the crack growth curve at around  $10^{-9}$  m/cycle, where the growth rate is relatively insensitive to the applied stress intensity range<sup>[13,44]</sup> (Figure 3(a)). In the fatigue of materials, such behavior generally indicates that something other than mechanical loading acts as the rate limiting step in the crack growth process, and that commonly is an interaction with the environment.<sup>[45–47]</sup> A  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  BMG, when tested in dry inert atmosphere, exhibits a significantly higher fatigue threshold,  $\Delta K_{TH}$ , and a characteristic three-region fatigue curve, as seen in Figure 5.<sup>[19]</sup> The plateau in the crack growth curve near  $\sim 10^{-9}$  m/cycle, seen in Figure 3(a), is not present in the fatigue curve measured in purified dry  $N_2$ , indicating that the fatigue behavior is degraded by the ambient air environment. Furthermore, changing the alloy chemistry can profoundly influence this effect. Recent studies on a  $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$  BMG showed that the plateau crack growth rates shift to a  $\sim 25$  times higher growth rate.<sup>[48]</sup> Furthermore, fatigue life experiments on Zr-Al-Cu and Zr-Al-Cu-Ni BMGs have shown no discernable difference in the  $S/N$  curves and fatigue limits for samples tested in air and vacuum.<sup>[49]</sup> While it is difficult to make direct links between the fatigue limit and fatigue threshold since the former is affected by both crack initiation and growth, such observations indicate that not all BMGs should be expected to have a similar degrading environmental effect on the fatigue behavior in ambient air.



Furthermore, it is interesting to note that not all studies on  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  BMGs have observed such a plateau for tests conducted in air or even deionized water, *e.g.*, References 5, 20–22, and 50. This suggests that the extreme environmental sensitivity of this composition in air may not be a simple matter of the presence of water vapor or oxygen. There is clearly much to be understood about the environmental effects on the fatigue behavior of Zr-based BMGs, including the specific role of various environmental species, the mechanisms of attack at the crack tip, and the role of specific elements in the various BMG compositions.

Environmental interactions such as oxidation and hydrogen embrittlement for metallic glasses have been documented in the literature,<sup>[26,27,51–61]</sup> and either could provide possible mechanisms that could affect fatigue crack growth rates in ambient air.<sup>[19]</sup> Interestingly, studies on hydrogen-charged  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  have actually shown a decrease in fatigue crack growth rates and an increase in the fatigue threshold with increasing hydrogen charging (Figure 6).<sup>[26]</sup> This suggests that hydrogen may retard fatigue crack growth, which was attributed to a combination of (1) roughness-induced crack closure and (2) the filling of free volume causing a change in the plastic flow behavior. Extensive hydrogen charging caused a very tortuous crack path, causing significant crack closure. However, uncharged samples tested in air show a straight crack path in both References 13 and 44 similar to the samples tested in inert atmosphere.<sup>[19]</sup> Thus, roughness-induced crack closure does not seem to be an important mechanism without hydrogen charging. Suh and Dauskardt pointed out that the overall fatigue crack behavior of hydrogen-charged  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  results from a

mutual competition of intrinsic embrittling mechanisms and extrinsic shielding mechanisms.<sup>[26]</sup> Thus, without hydrogen charging, small amounts of hydrogen entering the crack tip, perhaps from oxidation reactions with water vapor, may cause the material to behave drastically different than a BMG that was heavily hydrogen charged. In other words, the balance of this competition may be shifted under different conditions of hydrogen exposure.

#### D. Defects

Defects are invariably present in all materials, and BMGs are no exceptions. Defects that may aid in initiating fatigue cracks include voids, inclusions, surface scratches, quasi-crystals, as well as metastable and stable crystallites. Although defects in BMGs are usually quite small, BMG processing is not as well developed as traditional metal processing, and occasionally large defects are found even in commercial materials (Figure 7). In experimentally produced alloys, the possibility for unwanted defects is present as well, *e.g.*, as in Reference 48.

With regard to fatigue behavior, studies on crack initiation in  $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$  BMGs have often reported that (1) cracks initiate at defects and (2) crack initiation is almost instantaneous upon fatigue cycling.<sup>[23–25]</sup> In those articles, it is argued that if defects can be reduced or eliminated, there should be a positive benefit for the fatigue life. Indeed, a study on a  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  BMG found crack initiation to only occur after  $10^3$  to  $10^5$  cycles and that the amount of cycles needed to initiate cracks could be affected by sub- $T_g$  annealing,<sup>[13]</sup> as discussed in Section II-A-1. Also, a different study on a  $Zr_{41.8}Ti_{12.9}Ni_{9.5}Cu_{12}Be_{23.8}$  BMG suggests that the crack initiation process was not instantaneous for their material and may be affected by precycling below the fatigue limit, as discussed in Section II-B.<sup>[16]</sup> Such results suggest that instantaneous crack initiation is not an inherent trait of BMGs and may only occur in materials with a large defect

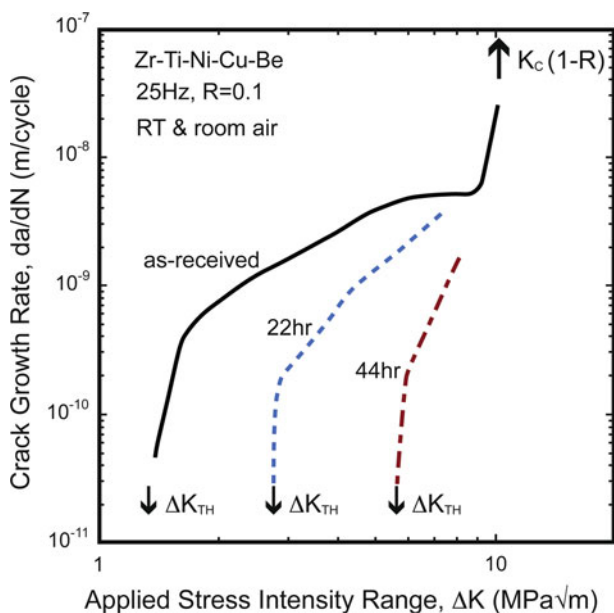


Fig. 6—Plot showing the effect of decreased fatigue crack growth rates and increased fatigue thresholds,  $\Delta K_{TH}$ , with hydrogen charging. The solid curve represents no charging, the dotted curve 22 h of hydrogen charging, and the dash-dotted curve 44 h of hydrogen charging. Figure reproduced based on data from Ref. 26.

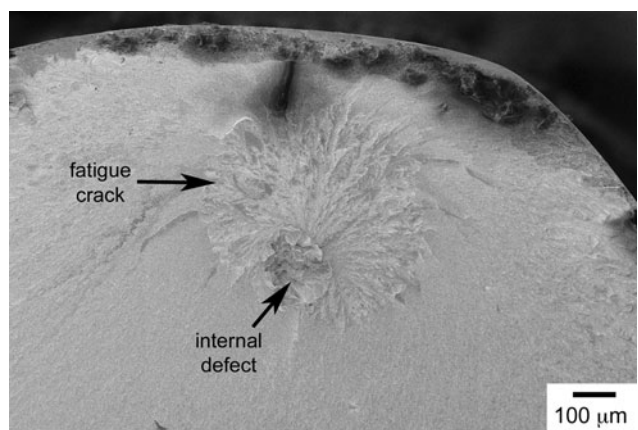


Fig. 7—Example of a fatigue failure that originated at a large internal defect in a commercially produced BMG. Photo courtesy of Dr. Maximilien Launey.

population, unfavorable residual stresses, or unfavorable glass structure or chemistry.

### III. STRATEGIES FOR IMPROVING FATIGUE BEHAVIOR

One recent proposed strategy to produce fatigue-resistant materials with tensile strengths similar to BMGs is to create semicrystalline BMG matrix composite materials based on the Zr-Ti-Nb-Cu-Be system.<sup>[11,12]</sup> Compared to the best fully amorphous Zr-based BMG tested in four-point bending where the ratio of fatigue life (stress amplitude) to ultimate tensile strength is  $\sigma_{fat}/\sigma_{UTS} = 0.25$ ,<sup>[62]</sup> these composites have an even higher ratio of 0.3, also measured in four-point bending.<sup>[11]</sup> While this composite approach has produced some materials with fantastic strength, toughness, tensile ductility, and fatigue properties, one should be careful before assuming it is a universal solution to fatigue problems. Indeed, early Zr-Ti-Nb-Cu-Ni-Be BMG matrix composites actually showed worse fatigue crack growth properties compared to many fully amorphous BMGs and fairly poor fatigue life properties.<sup>[10]</sup> The recent studies argue that the improvement in fatigue properties is the result of a refinement of the size scale of the crystalline phase spacing; however, to date, it is unclear if this is the main or only cause for the difference in behavior. Indeed, composites with a BMG matrix phase are likely to have at least some susceptibility to the variables discussed previously, including free volume and structure of the glass matrix phase, residual stresses, environmental attack, and defects. Furthermore, it is not clear if such composites will be able to take advantage of all of the recent advances in BMG processing,<sup>[63–67]</sup> and while fully amorphous BMGs might never achieve the fatigue resistance of BMG matrix composites, it has been shown that some compositions can have fatigue resistance comparable to many fully crystalline alloys (Figure 1).<sup>[9]</sup> Thus, fatigue studies need to continue for fully amorphous BMGs both as materials of interest for many applications and as a phase which will in part control the fatigue properties of BMG matrix composite materials.

More general solutions to the problems of fatigue in BMGs and BMG matrix composites will require a fundamental understanding of the variables and mechanisms that control the fatigue behavior of BMGs. Some potential strategies include the following.

(1) *Develop compositions resistant to environmental attack.* It is known that the Zr-Ti-Ni-Cu-Be BMG compositions are particularly bad in this regard,<sup>[19–22]</sup> which likely contributed to the very low fatigue limit observed by Gilbert *et al.*<sup>[5]</sup> and the overall bad reputation of BMGs for poor fatigue resistance. While there is in fact a large range of fatigue life behavior seen for different Zr-based BMG compositions<sup>[9]</sup> and some results suggest that not all Zr-based compositions exhibit an environmental effect in air,<sup>[49]</sup> the mechanisms for the environmental attack are poorly understood, and

thus science-driven strategies for designing BMGs to resist it are unknown at this point. Furthermore, very little is known about non-Zr-based compositions. Clearly, there are many potential BMG compositions to be examined that may not exhibit such detrimental environmental effects, but a fundamental understanding of the mechanisms involved will be needed to drive this pursuit.

(2) *Better control of thermomechanical processing.* As with crystalline metals, it is clear that the thermomechanical processing can vastly alter the mechanical behavior of BMGs by changing the amount of free volume, the glass structure, the residual stresses, *etc.* However, controlling these factors is challenging, because there are few techniques available for taking a snapshot of the free volume, glass structure, or residual stresses as can be done with crystalline materials using traditional microscopy and diffraction methods. For example, quantifying free volume generally involves relative measurements where the initial reference state is poorly characterized in an absolute sense,<sup>[14,34,36,68]</sup> while methods for investigating medium range order are in their early development stages.<sup>[69]</sup> Further development of characterization techniques will certainly help in this area, especially when there is much still to be understood about the mechanisms of many observed thermomechanical phenomena affecting fatigue behavior.<sup>[6,13–18]</sup>

(3) *Better control of defects.* It has been well documented that fatigue cracks can initiate at defects in BMGs even after only a few fatigue cycles,<sup>[23–25]</sup> although not all studies have observed such rapid crack initiation.<sup>[13,16]</sup> Several strategies might be employed to mitigate such effects. Eliminating defects is likely one effective strategy; for example, an arc furnace with tilt casting has been used to make crystalline inclusion-free BMGs for fatigue studies.<sup>[35]</sup> However, eliminating defects is likely not always practical for scaling up in an industrial setting. Alternatively, there may be strategies available for suppressing crack initiation and the role of defects, including thermomechanical treatments.<sup>[6,13,16]</sup> Again, further understanding of the mechanisms of fatigue and the interactions between defects, thermomechanical treatments, and environment will be needed to allow the development of strategies for preventing premature fatigue crack initiation.

### IV. SUMMARY

Similar to crystalline metals, the mechanical properties of BMGs are sensitive to many factors, including thermomechanical processing, the corresponding glass structure, environment, and defects. In order to truly understand and control the fatigue behavior of BMGs and BMG matrix composites, the role of such factors, and the mechanisms involved, must be understood. Unfortunately, there are many challenges in this regard. Unlike crystalline materials, which are easily characterized

by microscopy and diffraction methods, characterization of BMGs is quite challenging, especially with regard to glass structure, free volume, residual stresses, *etc.* Thus, solving problems of fatigue behavior in BMGs will require both further studies on fatigue mechanisms as well as further developments in characterization tools for BMGs.

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