



EFFECT OF AQUEOUS ENVIRONMENT ON FATIGUE-CRACK PROPAGATION BEHAVIOR IN A Zr-BASED BULK AMORPHOUS METAL*

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Introduction

Recently, a number of strongly glass forming metallic alloys have been found, most prominently the Zr-Ti-Cu-Ni-Be (1), Zr-Cu-Ni-Al (2), and Pd-Cu-Ni-P (3) systems, which may be produced in bulk form. In particular, the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%) alloy has already found commercial application for use in golf club heads, and currently is under consideration for use in other applications. Initial investigations of this alloy revealed that it has high tensile strength (~ 1.9 GPa) (4) and toughness properties ($K_{Ic} \sim 18\text{--}59$ MPa \sqrt{m}) (5–7). Moreover, in ambient temperature air, it exhibits fatigue-crack growth properties that are comparable to ductile crystalline metals, specifically showing a threshold stress-intensity range, ΔK_{TH} , below 3 MPa \sqrt{m} and a 2nd–5th order power-law dependence of growth rates on the stress-intensity range, ΔK (5,8).

Despite such promising mechanical properties, there is little information available on the performance of these glasses in electrochemically active environments. Consequently, in the present study, we examine the fatigue properties of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ amorphous metal in the presence of three environments, ambient air, de-ionized water, and sodium chloride solution, with the specific goal of identifying the role of environment in the fatigue-crack growth process.

Background

Variations in fatigue-crack growth rates with different local environments are generally associated with the synergism between chemistry and mechanical loading. Many ductile crystalline alloys display similar fatigue-crack growth behavior in ambient air and neutral aqueous solutions, with rates varying by less than half an order of magnitude. This relatively small effect of aqueous solution, termed true

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corrosion fatigue (9), is observed in crystalline metals, such as steels (10) and aluminum alloys (11). It has been proposed that the effect of a non-aggressive aqueous solution is minimal in these cases because an aqueous environment is present at the crack tip in both ambient air and aqueous solution (12). However, for specific combinations of alloy and solution composition, fatigue-crack growth rates are significantly higher than in relatively inert environments over a range in stress intensities that exceeds the onset of stress-corrosion cracking (K_{ISCC}). This fatigue behavior is marked by a plateau in fatigue-crack growth rate and is termed stress-corrosion fatigue (9). Indeed, such stress-corrosion fatigue is exhibited in solutions that contain chloride ions by many crystalline metallic alloys, such as maraging steel (13) and high strength titanium alloys (14). In this study, we will show that the fatigue behavior of amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ in de-ionized water resembles true corrosion fatigue, while its fatigue behavior in sodium chloride solution resembles stress-corrosion fatigue.

Experimental Procedures

As-received plates of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%) were processed by Hitchener Manufacturing Co. (Milford, NH) and provided by Amorphous Technologies International, Corp. (Laguna Niguel, CA). These plates were machined into compact-tension (C(T)) specimens with a thickness of 4.4 mm and a width of 20 mm. To insure that residual stresses present in the casting (8) did not affect behavior, ~ 1.5 mm of material was removed from all surfaces of the casting prior to machining. Fatigue tests were conducted at room temperature in air (relative humidity ~ 25 – 35%), in aerated de-ionized water, and in an aerated 0.5 M NaCl (98+%, Aldrich) aqueous solution prepared with de-ionized water. Samples were loaded at a constant load ratio ($R = K_{min}/K_{max}$) of 0.1 and a frequency, ν , of 25 Hz (sine wave) on an MTS model 831 servo-hydraulic test frame; testing procedures were in general accordance with ASTM standard E647. Both increasing and decreasing ΔK tests were performed using a K -gradient of $\pm 0.1 \text{ mm}^{-1}$. During cycling, crack lengths were monitored via unloading compliance, using a back-face strain gauge. Specimens tested in both air and aqueous solution were first pre-cracked in air. In cases where fatigue measurements were subsequently performed in an aqueous environment, solution was added while cycling the sample at ΔK of $1 \text{ MPa}\sqrt{\text{m}}$. Representative data for each environment are presented as fatigue-crack growth rates per cycle, da/dN , as a function of the applied stress-intensity range ($\Delta K = K_{max} - K_{min}$).

Using C(T) specimens that were initially fatigue pre-cracked in air and finally in the test solution, stress-corrosion cracking tests were conducted at constant load (increasing K). Because of the relatively low driving forces needed to drive the crack, a high precision load cell was used, which had a 200 N capacity. Stress-corrosion cracking results are presented as the crack velocity, da/dt , as a function of the applied K .

Results and Discussion

The variation in fatigue-crack propagation rates with applied ΔK for the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ amorphous metal tested in room air, deionized water and 0.5M NaCl solution is shown in Fig. 1. It is apparent that whereas growth rates in water are somewhat accelerated compared to air, growth rates in NaCl solution are dramatically higher. Indeed, growth rates in the NaCl solution are two to three orders of magnitude larger than those measured in air and de-ionized water, reaching about $4 \times 10^{-7} \text{ m/cycle}$ at ΔK values between 1 and 6 $\text{MPa}\sqrt{\text{m}}$. Moreover, fatigue threshold, ΔK_{TH} , values are reduced from $\sim 1.4 \text{ MPa}\sqrt{\text{m}}$ in air to 1.2 $\text{MPa}\sqrt{\text{m}}$ in water and to 0.8 $\text{MPa}\sqrt{\text{m}}$ in NaCl.

Incubation periods prior to the onset of cracking were observed in the NaCl solution. The length of these periods depended on the ΔK level and reached a few hours at a ΔK of 1 $\text{MPa}\sqrt{\text{m}}$. Once the crack

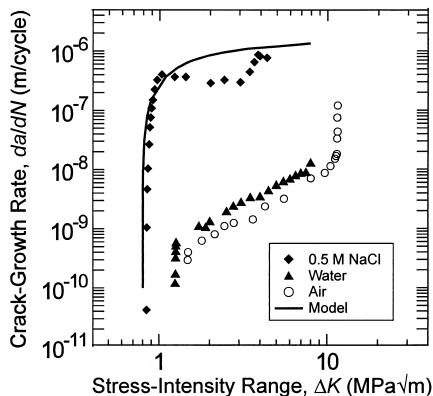


Figure 1. Fatigue-crack growth rates (under sinusoidal loading) in amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%) are plotted as a function of stress intensity range for three environments: 0.5 M NaCl, de-ionized water, and laboratory air (relative humidity $\sim 25\%$ - 35%). In addition, a comparison of experimentally measured fatigue-crack growth rates in NaCl to fatigue-crack growth rates calculated by the *superposition* or *process-competition* model. To plot the full stress intensity range for each condition, data points are acquired from at least two tests for each condition.

began to grow, however, growth rates near 10^{-6} m/cycle were reached in less than $500 \mu\text{m}$ of growth. After the incubation period, at a frequency of 25 Hz and a ΔK of $1 \text{ MPa}\sqrt{\text{m}}$, cracks typically propagated about 1 mm in about 1.7 minutes. These high growth rates were fully reproducible, and were observed in tests on seven separate specimens.

Since NaCl is clearly the most aggressive environment, it is surmised that the chloride ion, rather than hydrogen-assisted cracking or unassisted active-path corrosion at the crack tip, is primarily responsible for the marked environmental effect. Presumably the chloride ion alters the conditions at the crack tip, leading to an avalanche stress-corrosion effect. In fact, although the exponent m in the Paris power-law, $da/dN = C\Delta K^m$, ranges from 2 to 5 in air and water, it approaches zero in the plateau region of crack growth in NaCl. This plateau, which is characteristic of stress-corrosion fatigue, occurs at fatigue-crack growth rates, da/dN , of about 4×10^{-7} m/cycle (equivalent to a crack velocity of $\sim 10^{-5}$ m/s).

In order to examine the influence of stress-corrosion cracking (SCC) on fatigue, tests were performed in sodium chloride solution at constant (non-cyclic) load on three specimens to investigate the magnitude of the stress-corrosion effect. Results in the form of crack velocities as a function of the applied K are shown in Figure 2. It is clear that above a K_{ISCC} threshold, crack velocities increase suddenly by many orders of magnitude to reach a steady-state plateau between 10^{-5} and 10^{-4} m/s. This similarity in the magnitude of the crack-velocity plateaus under static and cyclic loading strongly suggests that a static load, stress-corrosion effect is responsible for highly elevated crack-growth rates during fatigue in the sodium chloride solution. In other words, the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ glass displays an extreme example of stress-corrosion fatigue, exhibiting remarkably high growth rates. Incubation times, dependent on K , were also observed during SCC; near K_{ISCC} , the incubation times were as long as three days.

It is likely that the high growth rates and crack velocities in the NaCl solution result from the slow and possibly incomplete repair of stress-induced damage to the oxide film at the crack tip. As a consequence of this slow repair, the oxide film at the crack tip does not adequately protect against stress corrosion in this amorphous alloy. In general, repair of an oxide film is slower at cell potentials near the active to passive transition or near the pitting potential, than at cell potentials in the middle of the passive regime. Under applied stress, this slow and possibly incomplete repair of the oxide allows time for stress corrosion to occur; however, the presence of the oxide on the flanks of the crack prevents

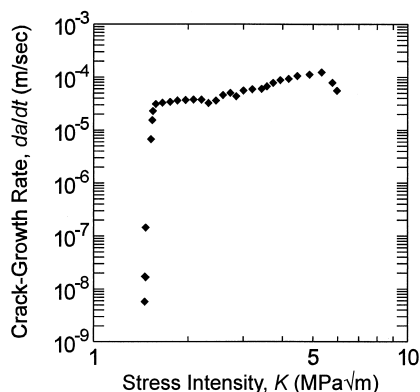


Figure 2. Stress-corrosion cracking velocities in the amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%) metal under sustained load are plotted as a function of the stress intensity, K , in aerated 0.5 M NaCl. Data shown have been acquired from one sample.

general corrosion that could stop crack growth by blunting the crack tip. In the case of amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ in 0.5 M NaCl, the oxide film presumably provides limited protection because the open circuit potential, at which all fatigue and SCC experiments were conducted, is quite close to the pitting potential (15). A means of protecting this amorphous metal from SCC is cathodic polarization, which would stabilize the oxide at the crack tip, possibly inactivating the chloride assisted mechanism of SCC. While cathodic polarization would likely inactivate chloride assisted SCC, it may cause hydrogen embrittlement by increasing the amount of hydrogen created during reduction reactions.

Finally, the current results may be compared to predictions from simple theoretical models for corrosion fatigue. Environmentally assisted fatigue-crack growth behavior has been described with *superposition* (16) and *process-competition* (17,18) models. In the superposition model, the mechanical (da/dN vs. ΔK , in a reference environment) and environmental (da/dt vs. K from stress-corrosion testing and da/dN vs. ΔK from true corrosion fatigue) contributions to cracking are linearly additive. In the process-competition model, on the other hand, the crack is assumed to grow at a given stress intensity by the faster of the mechanical or the environmentally assisted mechanism. For this amorphous alloy, both models predicted nearly identical values of fatigue-crack growth rates in sodium chloride solution, using an average value for K_{ISCC} of 0.8 MPa√m, as shown in Figure 1. In fact, a good fit between the calculated and experimentally measured values is reached using only the SCC data to calculate fatigue-crack growth rates. The contribution to the superposition model of fatigue in the reference environment was too small to contribute substantially to the overall fatigue-crack growth rates. In addition, the true corrosion fatigue term in the superposition model was not necessary to achieve a good fit to the data. Considering that the reference fatigue term and the true corrosion fatigue term are negligible in this case, fatigue-crack growth rates in NaCl can be estimated with the superposition model and the process-competition model as:

$$\left(\frac{da}{dN}\right)_{\text{eff}} = \int_0^{1/\nu} \left(\frac{da}{dt}(K(t))\right)_{\text{SCC}} dt, \quad (1)$$

where, $(da/dN)_{\text{eff}}$ is the fatigue-crack growth rate in NaCl, ν is the frequency, $(da/dt(K(t)))_{\text{SCC}}$ is the crack velocity in SCC, expressed as a function of stress intensity over the fatigue loading cycle, and t is time. Clearly, these predictions are fully consistent with experimentally measured corrosion fatigue

results in sodium chloride. This good fit suggests that stress-corrosion fatigue is the primary mechanism of fatigue of the Zr-based amorphous metal in NaCl solution.

Conclusions

Based on a study of the environmentally-assisted fatigue-crack growth properties of a bulk metallic glass, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%), in the presence of room air, deionized water, and 0.5 M sodium chloride solution, it is evident that although water causes a marginal increase in growth rates compared to behavior in air, NaCl solution causes a dramatic increase in growth rates by two or three orders of magnitude, accompanied by a marked decrease in ΔK_{TH} threshold. This is believed to be one of the largest effects of an aqueous environment on fatigue-crack growth in a metal reported to date. Values of crack-growth rates under sustained load (stress-corrosion) conditions in sodium chloride solution are comparable to crack-growth rates under cyclic loading in the same solution. The importance of stress-corrosion cracking on the crack growth in fatigue in NaCl is demonstrated using both superposition and process-competition models for corrosion fatigue. Although precise mechanisms are unclear, the chloride ions evidently have the ability to degrade the protection provided by the oxide film at the crack tip, permitting a large stress-corrosion effect to occur during SCC and fatigue.

Acknowledgments

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References

1. A. Peker and W. L. Johnson, *Appl. Phys. Lett.* 63, 2342 (1993).
2. A. Inoue, T. Zhang, N. Nishiyama, K. Ohba, and T. Masumoto, *Mater. Trans. JIM.* 34, 1234 (1993).
3. Y. He, R. B. Schwarz, and J. I. Archuleta, *Appl. Phys. Lett.* 69, 1861 (1996).
4. H. A. Bruck, T. Christman, A. J. Rosakis, and W. L. Johnson, *Scripta Metall. Mater.* 30, 429 (1994).
5. C. J. Gilbert, R. O. Ritchie, and W. L. Johnson, *Appl. Phys. Lett.* 71, 476 (1997).
6. R. D. Conner, A. J. Rosakis, W. L. Johnson, and D. M. Owen, *Scripta Mater.* 37, 1373 (1997).
7. P. Lowhaphandu and J. J. Lewandowski, *Scripta Mater.* 38, 1811 (1998).
8. C. J. Gilbert, V. Schroeder, and R. O. Ritchie, *Metall. Mater. Trans. A.* in press.
9. A. J. McEvily and R. P. Wei, in *National Association of Corrosion Engineers*, ed. O. F. Devereux, A. J. McEvily, and R. W. Staehle, NACE-2, p. 381, NACE, Houston (1972).
10. R. Hamano, *Metall. Trans. A.* 20A, 1055 (1989).
11. R. P. Wei, P. S. Pao, R. G. Hart, T. W. Weir, and G. W. Simmons, *Metall. Trans. A.* 11A, 151 (1980).
12. H. H. Johnson and A. M. Willner, *Appl. Mater. Res.* 34 (1965).
13. J. M. Barsom, *Eng. Fract. Mech.* 3, 15 (1971).
14. D. B. Dawson and R. M. Pelloux, *Metall. Trans.* 5, 723 (1974).
15. V. Schroeder, C. J. Gilbert, and R. O. Ritchie, *Scripta Mater.* 38, 1481 (1998).
16. R. P. Wei and J. D. Landes, *Mater. Res. Stand.* 9, 25 (1969).
17. I. M. Austen and E. F. Walker, in *International Conference on the Influence of Environment on Fatigue*, p. 1, IMechE, London (1977).
18. I. M. Austen and P. McIntyre, *Met. Sci.* 420 (1979).