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The role of surface oxide composition on the fatigue strength of metallic glass wire

A.O. Olofinjana [a],*, N.Y. Voo [b]

[a] Faculty of Science, Health, Education and Engineering, University of the Sunshine Coast, Maroochydore DC Qld 4558, Australia
[b] Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, BE1410 Brunei Darussalam

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ABSTRACT

The application of cyclic bending has been the most practical way in evaluating the fatigue behaviour of thin sub-millimetre wires. For metallic glass wires, the fatigue behaviour is typically expressed in the form of strain–cycle relationship because conversions of applied bend strain to stress require the accurate measure of the modulus of elasticity (E). Here, we have applied the use of ultra-nano indentation testing (UNHT) to determine modulus of elasticity of metallic glass wire of compositions $Fe_{77.5-x}$ $Cr_XSi_{7.5}B_{15}$ (x = 0, 4, 8). It is found that the modulus of elasticity averaged 187 ± 5 GPa and do not show any marked dependence on the Cr substitution for Fe. The value of E so measured was used to represent fatigue data in stress–cycle configuration. It is shown that fatigue limits were both composition and atmosphere dependent. The ternary $Fe_{77.5}$ $Si_{7.5}B_{15}$ alloy wire had fatigue limit dependent on humidity ranging from 1 GPa in ambient (60–70% RH) to 1.86 GPa at reduced humidity (10% RH) and no limit in aqueous environment. It is also evident that Cr substitution of Fe in the ternary alloy wire, improved the fatigue behaviour, reaching a fatigue strength of 2.32 GPa for alloy wire with 8 at.% Cr. The effects of composition and atmosphere on fatigue limits are related to the role played by the composition of oxide film on the wire surface. XPS studies indicated that Cr containing wires had established Cr/Si oxides that were responsible for protection against an environmentally induced fatigue failure. The drop in fatigue strength for Cr containing wire in the aqueous medium is due to the reduced protection as a result of the deterioration of the high temperature oxide that is not reformed at room temperature because of low Si chemical activity.

1. Introduction

Metallic glass wires produced through the rapid solidification of metallic melt stream can now be routinely produced by rotating water bath process [1] and a number of other related processes [2–6]. These wires are known for their high static tensile strengths, typically about 3–4 GPa depending on compositions [4,7,8]. Thermo-kinetic requirements for fully amorphous structure requires that the (Fe–Co)–Si–B family of alloys can only be produced in thin sections typically of the order of 20 μm for ribbons and 100 μm for wire shaped. These amorphous structured wires have been proposed [9,10] for advanced magnetic applications, especially because of their unique combinations magnetic properties that includes very low coercivity [10,11], large Bachhausen jumps [9,12], zero and negative magneto-striction [10] and giant magneto-impedance [9,11,13] that make them as useful candidate materials in magnetic field based sensor devices.

The fatigue behaviours of these glassy wires have variously been studied and are often presented as strain–cycle [1,7,8,14–16]. The use of cyclic bend–unbend to evaluate fatigue has come to be accepted for engineering materials of fibrous dimensions and has been used many times (see e.g. [1,7,17,18]). For conventional materials like steel, the primary strain–cycle fatigue data are easily converted to the familiar stress–cycle relationship because steel, has a well-known value of elastic modulus (E) determined, through the reliable uni-axial tensile tests. Such methods for steel or other conventional materials in wires form readily provide a reliable fatigue data with the fatigue limits recognised as the fatigue strengths. However, for metallic glass wires, E is not easily determined through a universal axial test, because of the small diameters imposed by process limitations. And since these family of metallic glass compositions are not available in bulk, it relies on unconventional methods such as acoustic and nano-indentation [1,16,19] to evaluate E. These have returned various values for E as 110–156 GPa for ribbons and wire samples. These results were obtained in the early stages of instrumented indentation and the indentation conditions were not even specified.

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* Corresponding author. Tel.: +61 466903778; fax: +61 754565453.
E-mail addresses: aolofinj@usc.edu.au, olofinjana@gmail.com (A.O. Olofinjana).

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With recent revisions of Oliver–Phar method [20] for evaluating *E* from indentation data, instrumented indentations has vastly improved in its accuracy. Refinements to the calibration procedure with careful identification of first point of contact are enabled by extremely slow surface approach velocity of the order of 10 nm/s and with a 3-nm oscillation in harmonic displacement at a frequency of 80 Hz.

Recent preparations [21,22] of bulk metallic glass in the composition $Fe_{72}Nb_4Si_{4.8}B_{19.2}$ (close to compositions of the Fe-based wire used in this study) made possible the evaluation of elastic properties through uniaxial compression of 25 mm diameter rods and these tests returned values of elastic modulus of 180–200 GPa for Fe-based with metal/metalloid atomic ratio of 75/25 that is similar compositions in the present study. This is the first indication that earlier returned values of *E* for Fe–Si–B metallic glass wires are possibly fraught with errors leading to underestimations that made comparison of fatigue strength with conventional materials like steel misleading.

Here, we present the result of ultra nano indentation on wire samples and applied the evaluated modulus to fatigue data. The environmental dependence of fatigue strength was investigated through the examination of the role of solid thin oxides on the surface of the wires.

2. Experimental

The metallic glass wires used in this study were obtained by multi-stream wire casting in a rotating water bath as described in [5,23]. The amorphous structure was confirmed by X-ray diffraction and differential scanning calorimetry. The fatigue tests were conducted in various atmosphere and the methods were described elsewhere [15] to give strain–cycle data. For ultra-nano indentation tests, wire samples were mounted in a slow setting resin and polished to 1 μm finish. A section of polished wire is shown in Fig. 1.

Nano indentation was carried out using CSM, ultra nano indenter with optical microscope and AFM on the same platform. The optical microscope and the AFM were used to navigate selected area of indentation to make sure all indents were close to the centre of wire. Data acquisition was set at 10 Hz, with maximum load of 5000 μN. Instrumented indentation using a Berkovich triangular pyramid indenter at reference contact force was set at 20 μN and the indenter approach distance at 2000 nm with approach and retract speed of 2000 nm/min.

X-ray photo electron spectroscopy (XPS) examination of surface of wire samples was done in a PHI spectrometer using non-monochromatic Mg K_α radiation (1253.6 eV). In all cases, a light 1 min Ar^+ etching was done for all samples in order to reduce the contribution of extraneous carbon C1s peak that characteristically accompany XPS surveys. Further studies of surface composition were followed by longer systematic Ar^+ sputtering. Higher resolution elemental analyses were done for Fe-2p, Cr-2p, and Si-2p at pass energy of 25 eV. These elements are the suspected oxide forming components of the alloy wires.

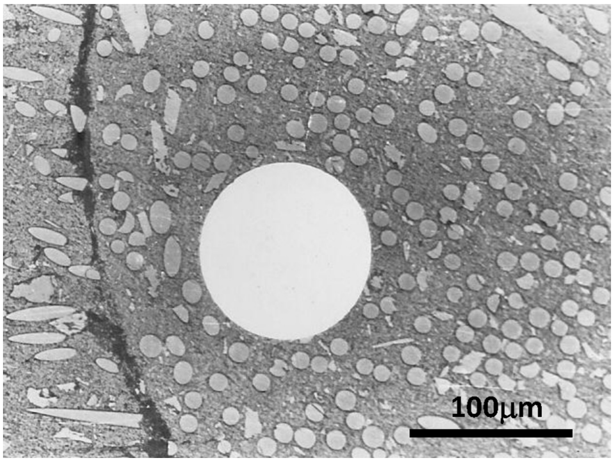

Fig. 1. Optical photograph of a typical Section of metallic glass wire section upon which UNHT was performed.

3. Results and discussion

3.1. Ultra-nanoindentation and determination of E

The typical load and unload curve for $Fe_{69.5}Cr_8Si_{7.5}B_{15}$ is shown in Fig. 2. The use of Oliver–Pharr method normally gives effective modulus through the analysis of the unloading curve that is generally assumed to be elastic. It is generally agreed that the material modulus (E_m) can be evaluated from [24]: $\frac{1}{E_{eff}} = \frac{1-\nu^2}{E_m} + \frac{1-\nu_i^2}{E_i}$ where, E_{eff} is the composite modulus of indenter and material directly measured from the slope of unload curve, and E_t is indenter modulus which in this case is diamond and ν and ν_t are respectively material and indenter modulus. For all measurements ν was assumed to be 0.3.

The hardness values were determined from the ratio of maximum load to projected areas. For the glassy wire composition, $Fe_{69.5}Cr_8Si_{7.5}B_{15}$, the average hardness was determined to be 14 ± 0.5 GPa while the indentation modulus was 187 ± 5 GPa. Though the value of elastic modulus determined here is much higher than that used earlier [16,19], it compares with the general expectation of the elastic behaviour of bulk metallic glass ($Fe_{72}Si_{4.8}B_{19.2}Nb_4$) of similar metal/metalloid ratio determined through the trusted uni-axial method [21,22]. The fracture stress (σ_f) of this family of metallic glass wires has been reported to be [1,8] about 3.5–4 GPa. The indicated E/σ_f ratio of ~0.02 in this work is therefore consistent with ratios long predicted [1] for metallic glasses, thus validating the result from this work. Since elastic modulus of metallic glasses are strongly dependent on metalloid content, there was no statistical variation of *E* with Cr content of the alloy wire and the same value of *E* was used for all the wire in evaluating the fatigue data.

Earlier use of nano indenting for evaluation of elastic modulus of metallic materials has always given values at variance with the known values. The inaccuracy for the attempts at using instrumented indentation for evaluating *E* for ductile metallic materials has been attributed to the large plastic deformation and the

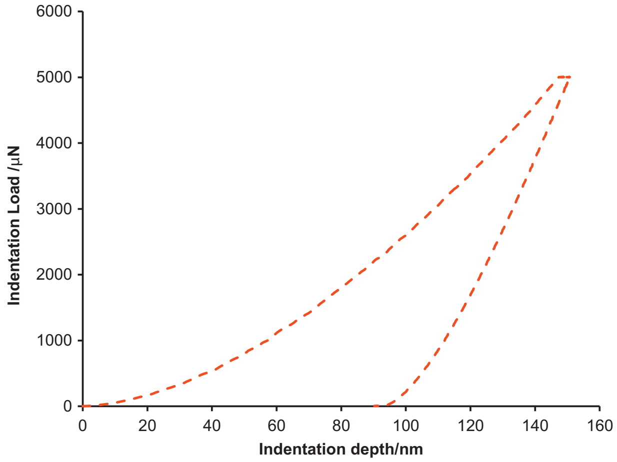

Fig. 2. Typical load-unload indentation depth data, obtained from UNHT test.