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Effect of shot-peening on the corrosion resistance of a Zr-based bulk metallic glass

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Surfaces of bulk glassy $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ samples were shot-peened for different times and their corrosion behaviour was tested in 0.01 M $Na_2SO_4 + x$M NaCl ($x = 0$; 0.01; 0.1) and 6 M HCl. Slight improvement of spontaneous passivity but a decrease of pitting resistance are detected with prolonged shot-peening duration. The corrosion damage evolution is governed by the nature of the mechanically generated defects and their surrounding stress fields.

Keywords: Amorphous alloy; Bulk metallic glass; Corrosion; Surface modification; Shot-peening

Work-softening of metallic glasses due to the localization of plastic deformation in shear bands leads to their early failure [1]. Shot-peening a Zr-based metallic glass induces a compressive surface stress and enhances the nucleation of shear bands near the surface, thus improving metallic-glass plasticity in compression, and in bending [2]. Peening induces heavy plastic deformation by repeated impacts on the surface and alters the structure of the metallic glasses, inducing structural atomic anisotropy and dilatation [3], but also relaxation of the glassy structure [4,5]. Synchrotron radiation and differential calorimetry studies have shown that the effects of shot-peening on the atomic structure of the metallic glass may be as deep as 150 μm from the surface.

An important criterion for the applicability of bulk metallic glasses is high long-term corrosion stability. Various corrosion studies on Zr-based glasses [6–10] demonstrated that samples in as-cast or mechanically ground states are spontaneously passive within a wide pH value range at room temperature. This is attributable to a rapid formation of thin barrier-type films composed of the oxides of the valve-metal components, i.e. mostly Zr and Al oxides. However, in chloride media pitting corrosion is commonly noticed. This is often initiated at structural defects in the glass and is related to the selective dissolution of valve-metal components while the rapidly growing pit becomes enriched in Cu. More recent studies [11] revealed that the particular surface state of a Zr-based bulk metallic glass which is obtained by different mechanical grinding and polishing techniques can significantly influence the corrosion behaviour, in particular the pitting initiation susceptibility.

The present paper reports the effects of shot-peening (causing severe mechanical disruption and enhanced oxidation of near-surface regions) of Zr-based bulk metallic glass samples on their anodic passivation and pitting behaviour in neutral and acidic solutions.

For sample preparation, ingots of the nominal composition $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ were prepared by arc-melting the pure elements in an Ar atmosphere. The ingots were re-melted several times for homogenization. By injection Cu mould casting plate samples of 10×70 mm and 2 mm thickness were prepared. By subsequent transversal cutting test samples of 10×10 mm size and 2 mm thickness were obtained. The bulk glassy microstructure of the samples was confirmed by X-ray diffraction, electron microscopy and thermal analysis. Details are described elsewhere [12].

Before shot-peening the sample surfaces were mechanically ground down to SiC grit 4000. A Guyson Euro 2SF system with 300–400 μm diameter glass beads accelerated by gas at 6.0 bar was used to peen two

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parallel sides of the samples. Shot-peening was carried out at 298 K (room temperature) in air for different times, i.e. 30 and 60 s; to reduce significant heating of the sample, peening for 15 s was followed by 40 s of thermal equilibration.

For corrosion studies alloy samples in as-cast, in mechanically ground (grit 4000) and in air aged (20 h) states and in shot-peened states were electrically connected and embedded in epoxy resin. Electrochemical measurements were conducted in a single compartment cell with SCE reference electrode (E(SHE) = 0.241 V) and Pt net counter electrode which was connected to a Solartron SI 1287 electrochemical interface. As base electrolyte a nitrogen-purged 0.01 M Na_2SO_4 electrolyte (pH 7) was used. For pitting tests 0.01 and 0.1 M NaCl were added. The open circuit potential (OCP) was monitored for 30 min before a polarization experiment was started. Cyclic potentiodynamic measurements were performed with a scan-rate sr = 10 mV s^{-1} and were started firstly in anodic direction. Linear anodic polarization curves were recorded with sr = 0.5 mV s^{-1} and started at (OCP–50 mV). All electrochemical tests were repeated at least two times to ensure high reliability of the data. Additionally, shot-peened samples were immersed for 2 min in 6 M HCl solution. The corrosion damage morphologies were examined with electron microscopy (JEOL JSM 6400).

In order to analyse the relation between the surface state of the glassy $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ samples and their corrosion behaviour, firstly the morphological characteristics of the sample surfaces were evaluated. Due to the shot-peening treatment in air, the glassy alloy samples changed their outer appearance from a mechanically polished mirror-like metallic lustrous state to a yellow–brown rough flat-lustrous state. The colour change indicates that the collisions of the beads with the sample surface led to local temperature rise and in consequence to surface oxidation. Indeed, during the shot-peening a heating of the samples and even spark formation was noticed. Figure 1 shows SEM images of glassy alloy sample surfaces which were shot-peened for different durations. After a treatment for 30 s a variety of single defects can be distinguished. Single deep spherical craters are visible where accelerated beads hit the surface. Those are surrounded by slip line patterns related to shear bands in the material or by even partly detached sample pieces. At sites where pieces were fully detached, traces of vein-like morphologies occur as they are typically observed on fracture surfaces of compressed samples. Moreover, cracks, scratches and features of detached pieces were found all over the sample surface. After prolonged shot-peening for 60 s all these features occur with a high density and are superimposed, leading to an extremely rough surface state.

For studying the effect of shot-peening treatments on the passivation behaviour of the bulk glassy $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ alloy, fast anodization experiments were performed in sodium sulphate solution after free exposure for 30 min. Figure 2 shows cyclic potentiodynamic polarization curves of samples shot-peened for 60 s in comparison to those of as-cast and ground states. For the original cast sample surface the open circuit potential is established after 30 min of free exposure at ∼−0.30 V vs. SCE. After mechanical grinding and air-ageing, the OCP shifts to more noble values, i.e. to ∼−0.20 V vs. SCE. This shift must be attributed not only to topographical changes of the sample surface but also to some chemical modifications. Surface analytical studies of as-quenched alloy surfaces revealed the presence of nanometre thin Zr-, Al- (and Ti-) oxide films and underlying metallic Cu [8,13]. Moreover, from early studies it is known that on as-quenched states of those glassy alloys a high-temperature tetragonal ZrO_2 forms, which only very slowly transforms into a low temperature monoclinic oxide in humid media [14]. By grinding,

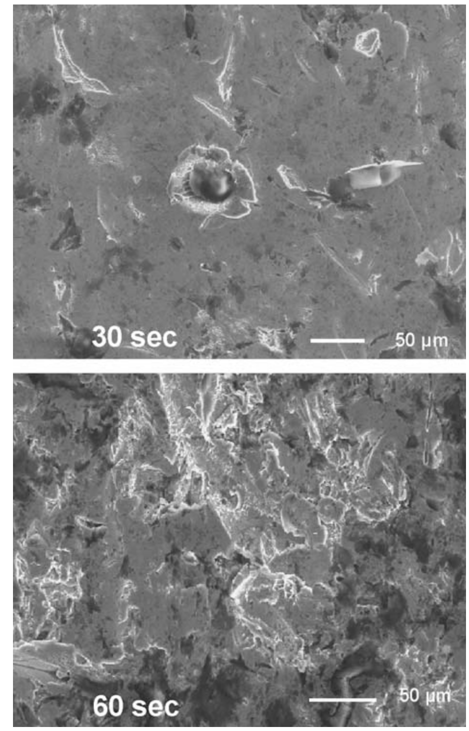

Figure 1. SEM images of the surface of bulk glassy $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ samples after shot-peening for 30 and 60 s.

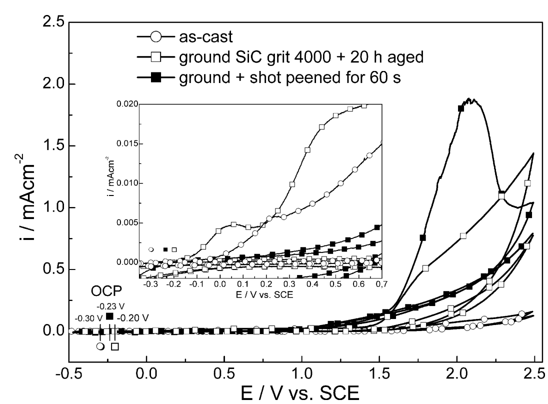

Figure 2. Cyclic potentiodynamic anodic polarization curves recorded for bulk glassy $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ samples with different surface states in 0.01 M Na_2SO_4, pH 7 (inset: magnification of the curves in the low anodic polarization regime).