Comparative studies on the corrosion behavior of some Zr-based amorphous alloys having different compositions in nitric acid medium

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Abstract—The corrosion studies were performed on different composition of Zr-based bulk amorphous ribbon alloys such as Zr₅₀Cu₃₀Ni₅Al₁₀, Zr₆₀Nb₂Cu₂₀Ni₈Al₁₀, Zr₅₀Nb₂Cu₂₀Ni₈Al₁₀, Zr₅₇Nb₃Cu₂₀Ni₈Al₁₀ and Zr₆₀Pd₃Cu₁₅Ni₁₀Al₁₀ alloys at room temperature. The amorphous nature of all the above mentioned alloys was confirmed by X-ray diffraction (XRD). The corrosion behavior was investigated using potentiodynamic polarization and weight loss analysis methods at room temperature. Surface morphology of these corroded samples were investigated by optical microscopy and scanning electron microscopy (SEM). The results of the investigations revealed the fact that Nb containing Zr-based bulk amorphous alloys shows better corrosion resistance among all the investigated alloys due to the presence of Nb₂O₅. The presence of Nb₂O₅ on the surface of Nb containing Zr-based bulk amorphous alloy after immersion in HNO₃ medium was confirmed by X-ray photoelectron spectroscopy (XPS) techniques.

Keywords—Amorphous alloys, Corrosion, SEM, XPS.

1. INTRODUCTION

BULK metallic glasses generally exhibit outstanding mechanical properties such as high mechanical strength, high fracture toughness and good corrosion resistance which cannot be obtained for conventional materials [1]. Among glass forming systems, Zr-based multi-component alloys have received more attention due to the easy castability and high thermal stability against crystallization together with interesting mechanical properties [2], [3]. Environmental degradation pertains to the study of oxidation and corrosion behavior of the amorphous alloy in terms of its utility and various engineering applications. In order to investigate the performance of highly corrosion resistant amorphous alloy, electrochemical investigations were carried out on Zr-based amorphous alloys by many researchers such as Dhawan et al. [4] in aqueous HNO₃ solutions, Raju et al. [5] in Na₂SO₄ and NaCl, S. Pang et al [6] in HCl, NaCl and H₂SO₄ solutions and Qin et al. [7] in NaCl medium. The interest for the present investigation resulted primarily from the lack of sufficient data in the literature on the corrosion behaviour of the Zr-based bulk amorphous alloys in different concentration of nitric acid.

The motivation for the present study was derived from the need of searching a high corrosion resistant glassy alloy in nitric acid environment for various engineering applications. Therefore the main motive of this work is to analyze the corrosion resistance of different Zr-based bulk amorphous alloys using weight loss analysis methods in 1 M HNO₃, 6 M HNO₃ and 11.5 M HNO₃ medium at room temperature. Detailed surface characterization has been carried out using XRD, SEM and XPS techniques.

I. Experimental Procedure

A. Materials and Micro-structural Characterization

As-received glassy ribbons of Zr₅₅Cu₃₀Ni₅Al₁₀, Zr₆₀Nb₂Cu₂₀Ni₈Al₁₀, Zr₅₀Nb₂Cu₂₀Ni₈Al₁₀, Zr₅₇Nb₃Cu₂₀Ni₈Al₁₀ and Zr₆₀Pd₃Cu₁₅Ni₁₀Al₁₀ of dimensions 3 mm x 30 μm were used for the investigation. Amorphous nature of the Zr-based amorphous alloy was characterized by XRD technique.
B. Weight Loss Analysis

As-spun ribbon specimens of Zr-based amorphous alloys were cut in same size and were cleaned with distilled water, acetone and dried in air. The surface area and initial mass of each sample were measured and the samples were then immersed in the aqueous medium at room temperature. Each sample was weighed after immersion in the solution for 480 h. The microgram balance (Mettler Toledo) used to measure the actual weight loss of the samples has an accuracy of ±10 µg. Equation (1) is used to determine the corrosion rates [8]:

\[
CR(mm/y) = 87.6 \frac{W}{DAT}
\]

Where, \( W \) is weight loss in mg, \( D \) is density of the material in g/cm\(^3\) and \( A \) is area of the sample exposed to the corrosive environment in inches.

C. Surface Morphology

The surface morphology of the virgin and treated samples was investigated using optical microscope (Radical Universal Trinocular Metallurgical – RMM-8TCE), scanning electron microscope (ZEISS EVO 18). The chemical composition of the treated samples was investigated by XPS using ESCA+ Omicron Nanotechnology (Oxford Instrument, Germany) at MRC MNIT, Jaipur.

1. Results and Discussion

Micro-structural Characterization

Fig. 1 (a) is XRD pattern of Zr-based ribbon alloys using Cu-K\(\alpha\) radiations whereas the XRD pattern of as-spun Zr-based bulk amorphous alloys is predominantly amorphous. Similarly Fig. 1 (b) also exhibits the broad maxima in the range from 35° to 50°. No significant peaks corresponding to crystalline phases were identified. These XRD patterns revealed the amorphous nature of the all samples.

Fig. 1 XRD pattern of (a) different composition of Zr-based ribbon alloys using Cu-K\(\alpha\) radiations; (b) Zr\(_{55}\)Cu\(_{30}\)Ni\(_8\)Al\(_{10}\) amorphous ribbon using Co-K\(\alpha\) radiations
Weight Loss Analysis

![Graph showing corrosion rate versus concentration of HNO₃ for different Zr-based amorphous ribbon alloys](image)

Fig. 2 Corrosion rate versus concentration of HNO₃ plot of different as-spun Zr-based bulk amorphous ribbon alloys exposed in different concentration of nitric acid medium at room temperature for 480 h duration. The corrosion rate of as-spun Zr₅₅Cu₃₀Ni₅Al₁₀, Zr₆₀Nb₂Cu₂₀Ni₈Al₁₀, Zr₅₉Nb₃Cu₂₀Ni₈Al₁₀, Zr₅₇Nb₅Cu₂₀Ni₈Al₁₀, and Zr₆₀Pd₅Cu₁₅Ni₁₀Al₁₀ amorphous ribbon alloys was calculated using weight loss method in various concentration of nitric acid. The plot of the corrosion rates versus concentration of nitric acid of these Zr-based amorphous ribbon alloys at room temperature is shown in fig. 2. The as-spun Zr₆₀Pd₅Cu₁₅Ni₁₀Al₁₀ amorphous alloy shows the highest corrosion rate in all concentrations of nitric acid among all the investigated Zr-based amorphous alloys. Fig. 2 revealed that the corrosion rate of all investigated Zr-based amorphous alloys increases with the increase in concentration of HNO₃. It is noticeable from fig. 2 that the Nb containing Zr-based amorphous alloy shows better corrosion resistance in all concentration of nitric acid than Zr₆₀Pd₅Cu₁₅Ni₁₀Al₁₀ and Zr₅₅Cu₃₀Ni₅Al₁₀ amorphous alloy. In 11.5 M HNO₃ solution Zr₅₉Nb₃Cu₂₀Ni₈Al₁₀ amorphous alloy shows least value of corrosion rate which is significantly less than other alloys. In fact Zr₅₉Nb₃Cu₂₀Ni₈Al₁₀ amorphous ribbon alloy exhibits better corrosion resistance in nitric acid environment among all investigated Zr-based amorphous alloys. In the present study, at higher concentration of HNO₃ medium, a significant decrease in corrosion rate has been observed due to the formation of passive layer of niobium oxide.
Surface Morphology

Fig. 3 Optical micrographs of Zr-based bulk amorphous alloys after immersion in different concentration of nitric acid medium for 480 hr at room temperature
Fig. 4 SEM micrographs of Zr-based bulk amorphous alloys after immersion in different concentration of nitric acid medium for 480 hr at room temperature

The surface morphology of the Zr-based amorphous ribbon alloys after immersion in nitric acid medium were examined by optical microscopy and scanning electron microscopy. Fig. 3 shows the optical micrographs of Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$, Zr$_{60}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$, Zr$_{59}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$, Zr$_{57}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$ and Zr$_{60}$Pd$_{5}$Cu$_{15}$Ni$_{10}$Al$_{10}$ amorphous ribbon alloys after immersion in 1 M and 11.5 M aqueous HNO$_3$ medium for 480 hr at room temperature. Fig. 3 revealed that Zr$_{59}$Nb$_{3}$Cu$_{20}$Ni$_{8}$Al$_{10}$ amorphous alloy possesses better corrosion resistance among all investigated Zr-based bulk amorphous alloys. The optical micrograph of Zr$_{60}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$ and Zr$_{59}$Nb$_{3}$Cu$_{20}$Ni$_{8}$Al$_{10}$ amorphous alloys exhibit the presence of passive layer on the surface of immersed sample in 1 M and 11.5 M HNO$_3$ solution. These results revealed that the surface of Zr$_{57}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$ amorphous alloy immersed in 1 M HNO$_3$ (fig. 3 (g)) and 11.5 M HNO$_3$ (fig. 3 (h)) was profoundly corroded than the surface of Zr$_{60}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$ and Zr$_{59}$Nb$_{3}$Cu$_{20}$Ni$_{8}$Al$_{10}$ amorphous alloys. On the other hand, Zr$_{60}$Pd$_{5}$Cu$_{15}$Ni$_{10}$Al$_{10}$ amorphous alloy was severely corroded among all investigated Zr-based bulk amorphous alloys as shown in optical micrographs (fig. 3 (i) and 3 (j)). Fig. 4 exhibits the SEM micrographs of Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$, Zr$_{60}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$, Zr$_{59}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$, Zr$_{57}$Nb$_{2}$Cu$_{20}$Ni$_{18}$Al$_{10}$ and Zr$_{60}$Pd$_{5}$Cu$_{15}$Ni$_{10}$Al$_{10}$ amorphous ribbon alloys after immersion in 1 M aqueous HNO$_3$ and 11.5 M aqueous HNO$_3$ medium for 480 hr. The SEM micrographs revealed that the Zr$_{59}$Nb$_{3}$Cu$_{20}$Ni$_{8}$Al$_{10}$ glassy alloy shows clean surface (fig. 4 (e) and (f)) as compared to all other investigated alloys in 1 M and 11.5 M HNO$_3$ medium. The formation
of oxide pockets were observed on the surface of Zr\textsubscript{59}Nb\textsubscript{3}Cu\textsubscript{20}Ni\textsubscript{8}Al\textsubscript{10} amorphous alloy after immersion in 11.5 M HNO\textsubscript{3} medium as shown in fig. 4(f). SEM results exhibit that the Zr\textsubscript{55}Cu\textsubscript{30}Ni\textsubscript{5}Al\textsubscript{10} (fig. 4 (a) and (b)) and Zr\textsubscript{60}Pd\textsubscript{5}Cu\textsubscript{15}Ni\textsubscript{10}Al\textsubscript{10} (fig. 4 (i) and (j)) amorphous alloys were severely corroded in nitric acid medium. SEM results indicate the possibility of pilling off of the passive film formed on the Zr\textsubscript{60}Nb\textsubscript{5}Cu\textsubscript{20}Ni\textsubscript{8}Al\textsubscript{10} alloy at 11.5 M HNO\textsubscript{3}, as shown in fig. 4 (d). These optical and SEM results were in good agreement with results of weight loss analysis.

**XPS Study**

Fig. 5 High resolution XPS spectra of Zr for as-spun and immersed Zr\textsubscript{59}Nb\textsubscript{3}Cu\textsubscript{20}Ni\textsubscript{8}Al\textsubscript{10} amorphous alloy in 11.5 M HNO\textsubscript{3} medium for 480 hours (a) before sputtering and (b) after 10 min sputtering

To understand the compositional changes on the surface of Zr\textsubscript{59}Nb\textsubscript{3}Cu\textsubscript{20}Ni\textsubscript{8}Al\textsubscript{10} amorphous alloy after immersion in 11.5 M HNO\textsubscript{3} medium, XPS studies were carried out on as-spun and immersed sample. The high resolution XPS spectra of Zr and Nb for as-spun and immersed Zr\textsubscript{59}Nb\textsubscript{3}Cu\textsubscript{20}Ni\textsubscript{8}Al\textsubscript{10} amorphous alloy in 11.5 M HNO\textsubscript{3} for 480 hours, before and after sputtering of 10 minutes, are shown in fig. 5 and 6, respectively. The fig. 5 (a) represents the Zr 3d spectra of as-spun and immersed Zr\textsubscript{59}Nb\textsubscript{3}Cu\textsubscript{20}Ni\textsubscript{8}Al\textsubscript{10} amorphous alloy before sputtering and fig. 5 (b) shows the Zr 3d spectra of as-spun and immersed Zr\textsubscript{59}Nb\textsubscript{3}Cu\textsubscript{20}Ni\textsubscript{8}Al\textsubscript{10} amorphous alloy after 10 minutes sputtering. The deconvolution of Zr 3d spectra was done in the terms of metal Zr\textsuperscript{0} and oxide ZrO\textsubscript{2} based on the literature values of their binding energies. The peaks of ZrO\textsubscript{2} were observed at the binding energies 183.3 eV and 185.7 eV corresponding to the peaks of Zr3d\textsubscript{5/2} and Zr 3d\textsubscript{3/2}, respectively [9], [10]. These peaks corresponding to ZrO\textsubscript{2} were observed before sputtering of the sample in both the conditions of sample i.e. surface of as-spun alloy and after immersion in nitric acid medium. The intensity of XPS peaks corresponding to ZrO\textsubscript{2} was high in the case of immersed sample. The peaks at 179.3 eV and 181.7 eV corresponding to metallic Zr [11] were observed after 10 min of sputtering along with peak corresponding to Zr\textsuperscript{4+} for as-spun alloy. However, the immersed sample has shown the presence of ZrO\textsubscript{2} along with metallic Zr after 10 min sputtering of the sample. The presence of ZrO\textsubscript{2} on the surface of as-cast sample was due to the formation of native oxide, which could not be observed after 10 min of sputtering.
The surface of as-spun sample exhibited the presence of Nb(peaks corresponding to metallic Nb at 203.6 eV and 206.4 eV binding energy, as shown in fig. 6 (a) [12], but the surface of immersed sample clearly exhibited the presence of XPS peaks corresponding to the Nb\(^{2+}\) state at 208.0 and 210.7 eV (fig. 6 (a)), respectively which are assigned to Nb\(_2\)O\(_5\) [12]. No peak corresponding to metallic Nb could be observed on the surface of Zr\(_{59}\)Nb\(_3\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) amorphous alloy after immersion in 11.5 M HNO\(_3\) medium. Fig. 6 (b) revealed that the as-spun alloy shows the presence of metallic Nb after 10 min of sputtering, whereas the immersed sample exhibits the XPS peaks corresponding to Nb\(^{5+}\) state indicating the presence of Nb\(_2\)O\(_5\) after 10 min of sputtering.

These XPS results revealed the fact that the formation of passive film of ZrO\(_2\), Al\(_2\)O\(_3\) and Nb\(_2\)O\(_5\) take place on the surface of Zr\(_{59}\)Nb\(_3\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) amorphous alloy after immersion in HNO\(_3\) medium. Since ZrO\(_2\) layer has a strong passivation ability and high corrosion resistance in H\(^+\)-containing solutions [13] thus, it protects the alloy from corrosion. Also, Nb\(_2\)O\(_5\) possesses corrosion resistant properties [14] hence it is useful in protecting the alloy from corrosion attack in aqueous solutions.

Conclusions

The corrosion behavior of Zr-based amorphous alloys such as Zr\(_{55}\)Cu\(_{30}\)Ni\(_5\)Al\(_{10}\), Zr\(_{60}\)Nb\(_2\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\), Zr\(_{59}\)Nb\(_3\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\), Zr\(_{57}\)Nb\(_3\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) and Zr\(_{60}\)Pd\(_2\)Cu\(_{15}\)Ni\(_{10}\)Al\(_{10}\) alloys in 1 M HNO\(_3\), 6 M HNO\(_3\) and 11.5 M HNO\(_3\) concentration of nitric acid medium has been investigated by weight loss analysis. It is concluded from above mentioned investigations that Nb-containing Zr-based amorphous alloys possesses better corrosion resistance among all investigated alloys. The better corrosion resistance of Nb-containing Zr-based bulk amorphous alloys was attributed to the formation of passive layer containing ZrO\(_2\) and Nb\(_2\)O\(_5\) which was confirmed by XPS study.

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