High Temperature Corrosion Study of Zr-based Amorphous Alloys in Aqueous HNO₃ Media

Poonam Sharma, Anil Dhawan, S. K. Sharma

Abstract—The corrosion behavior of Zr-based amorphous alloys investigated at high temperature in aqueous nitric acid environment. Weight loss studies have been performed to determine the corrosion resistance of Zr₅₀Nb₃₅Al₁₀Ni₈Cu₂₀ and Zr₆₀Pd₁₀Al₁₀Ni₈Cu₂₀ amorphous alloys in aqueous HNO₃ media at boiling temperature. The SEM micrographs have been obtained to know the surface morphology of specimens after immersion in aqueous HNO₃ media. These results revealed the fact that Zr₆₀Pd₁₀Al₁₀Ni₈Cu₂₀ amorphous alloys showed poor corrosion resistance than Zr₅₀Nb₃₅Al₁₀Ni₈Cu₂₀ in aqueous HNO₃ media at boiling temperature.

Index Terms—Bulk amorphous alloys, Corrosion Rate, SEM, Weight loss.

I. INTRODUCTION

Reprocessing of spent nuclear fuel used in fast breeder reactors (FBRs) involves a series of complex processes in complicated equipment. Such systems incorporate as (1) dissolvers where hot or boiling nitric acid is used, (2) solvent extraction vessels for separation of uranium, plutonium and fission products using nitric acid at ambient temperatures, (3) evaporators to concentrate the products in the hot nitric acid and (4) storage tanks for keeping concentrated warm nitric acid containing radioactive wastes. So, during storage and operating condition of nuclear conditions of nuclear fuel reprocessing in highly oxidizing nitric acid media, a number of corrosion problems are brought in focus recently. The materials chosen for the fabrication of such reprocessing plant equipment should possess excellent corrosion resistance, ease of fabricability and reliability [1]-[3]. An excellent corrosion resistant material is required for the fabrication of dissolver components. It is well known that bulk metallic glass (BMG) materials possess remarkable physical, chemical and mechanical properties [4], [5]. Zirconium is known as a good corrosion resistant material in nitric acid environments [6]. Zircaloy-4 has been studied in nitric acid environment and it possess good corrosion resistance condition in comparison to CP-Ti, Ti–5%Ta, and Ti–5%Ta–1.8%Nb in 11.5 M HNO₃ [7]. The Ti-5%Ta1.8%Nb alloy was found more corrosion resistant than conventional stainless steel 304L and 304L (NAG) for fuel reprocessing applications [8]. Furthermore, Caltech group reported Nb containing Zr-based alloys, exhibiting outstanding GFA which allows relatively easy processing to obtain fully amorphous bulk material [9]-[10]. The corrosion resistance of Pd containing Zr based bulk amorphous alloys in NaCl solution has been studied [11]. Although Nb containing Ni-based bulk amorphous alloys [12], [13] and Nb containing Ti-based alloys [14] have been studied in nitric acid medium at boiling temperature but enough information is not available in the literature on corrosion behavior of Nb and Pd containing Zr based bulk amorphous alloy in nitric acid medium at boiling temperature.

So, the aim of the present work is to investigate the corrosion behavior of the Zr₅₀Nb₃₅Al₁₀Ni₈Cu₂₀ and Zr₆₀Pd₁₀Al₁₀Ni₈Cu₂₀ amorphous alloy using weight loss study in nitric acid environment at boiling temperature so as to compare the behavior of both amorphous alloys in boiling nitric acid at varying concentrations. The study will also be helpful in selecting the material for fuel reprocessing applications. The Scanning electron microscope is used to elucidate the origin of corrosion resistance by observing the surface morphology.

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II. EXPERIMENTAL

A. Weight loss analysis at boiling temperature

The as spun ribbon specimens of Zr₅₀Nb₃₅Al₁₀Ni₈Cu₂₀ and Zr₆₀Pd₁₀Al₁₀Ni₈Cu₂₀ amorphous alloys were cleaned with acetone and distilled water and dried in air. The specimens were weighed before immersing them into the test solution of concentrated nitric acid in boiling condition. The experimental setup used for the experiment is discussed in U. K. Mudali, R. K. Dayal, J. B. Gnanamoorthy [15]. In this setup a cold finger condenser was used to reflux the vapours of nitric acid into the solution. The specimen was suspended into boiling 1M, 6M and 11.5M HNO₃ through the Teflon thread for the period of 8 hour in each solution. The change in the weight of specimen was observed after the each test and corrosion rate of the Zr₅₀Nb₃₅Al₁₀Ni₈Cu₂₀ and Zr₆₀Pd₁₀Al₁₀Ni₈Cu₂₀ amorphous alloy was calculated for each concentration using the corrosion rate formula [16].

\[ \text{Corrosion Rate (mm/yr)} = \frac{87.6W}{DAT} \]

Where \( W \) = Weight loss in milligram; \( D \) = Density in gm cm\(^{-3}\); \( A \) = Surface area in cm\(^2\); \( T \) = Time in hours

B. Microscopic examination

Surface morphology of Zr₅₀Nb₃₅Al₁₀Ni₈Cu₂₀ and Zr₆₀Pd₁₀Al₁₀Ni₈Cu₂₀ amorphous alloys after immersion in
1M, 6M and 11.5 HNO₃ at boiling temperature was examined by scanning electron microscope ZEISS- EVO 18 SEM.

III. RESULTS AND DISCUSSION

A. Corrosion resistance of material in aqueous HNO₃ at boiling temperature

Fig.1 shows the corrosion rate values obtained for the Zr₅₉Nb₃Al₁₀Ni₈Cu₂₀ and Zr₆₀Pd₅Al₁₀Ni₁₀Cu₁₅ amorphous alloy in 1M, 6M and 11.5M HNO₃ at boiling temperature for 8 hours. Both alloys show least value of corrosion rate in 1M HNO₃ and the corrosion rate increases with increase in concentration. The alloy shows highest value of corrosion rate at 11.5M concentration of nitric acid. Both alloys follow the same trend of corrosion rate in different concentration of aqueous HNO₃ medium.

At boiling temperature the corrosion rate is low in 1M HNO₃ and 6M HNO₃ aqueous media in comparison to 11.5M HNO₃, due to severity of environment for both amorphous alloys. Although, Zr₆₀Pd₅Al₁₀Ni₁₀Cu₁₅ amorphous alloy is showing poor corrosion resistance than Zr₅₉Nb₃Al₁₀Ni₈Cu₂₀ amorphous alloy, possibly due to formation of strong protective passive layer of Nb₂O₅ in Zr₅₉Nb₃Al₁₀Ni₈Cu₂₀ alloy which is strong and corrosion resistant in nitric acid medium [14].

The Goldschmidt’s radii of Zr, Cu, Al, Ni, Nb and Pd are 0.160, 0.128, 0.143, 0.125, 0.147 and 0.146 nm, respectively, i.e. Cu and Ni are smaller atoms than others therefore mobility of these atoms is quite high. Though, an air-formed or native oxide film is present on the glassy alloys surface [17], the dissolution of these atoms underlying the native layer is possible by tunneling process during the applied potential of electrochemical corrosion [18]. Therefore in the present study the alloys possess two simultaneous reactions, (1) active dissolution of Cu and Ni (2) passivation of elements like Zr, Al, Nb and Pd.

B. Surface morphology

Fig. 2 and 3 shows surface morphology of Zr₅₉Nb₃Al₁₀Ni₈Cu₂₀ and Zr₆₀Pd₅Al₁₀Ni₁₀Cu₁₅ amorphous alloys immersed in 1M, 6M and 11.5M HNO₃ at boiling temperature respectively, examined by SEM. The corrosion rate increases with the increase in concentration of nitric acid at boiling temperature. The alloy was studied at boiling temperature for fix duration of 8 hours so as to see its behavior during this time. As no improvement in the corrosion resistance was observed during this duration, so the study was not extended for larger duration due to severity of the environment.
boiling temperature in comparison to Zr_{60}Pd_{10}Al_{10}Ni_{15}Cu_{15} amorphous alloy.

2. SEM micrograph results accounts the formation of better passive layer on the surface of Zr_{59}Nb_{5}Al_{10}Ni_{15}Cu_{20} amorphous alloy rather than Zr_{60}Pd_{10}Al_{10}Ni_{15}Cu_{15} in aqueous HNO_{3} media at boiling temperature.

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IV. CONCLUSION

1. The weight loss studies revealed that the Zr_{59}Nb_{5}Al_{10}Ni_{15}Cu_{20} amorphous alloys possess good corrosion resistance in aqueous HNO_{3} medium at boiling temperature.

FIGURE 3. SEM micrographs of Zr_{60}Pd_{10}Al_{10}Ni_{15}Cu_{15} amorphous alloy after immersion in (a) 1M HNO_{3} (b) 6M HNO_{3} (c) 11.5M HNO_{3} at boiling temperature.
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His research interest area is diffusion and oxidation study of amorphous alloys and surface study using XPS and AES. Many key invited lectures has been delivered by him in national and international conferences.

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