High Corrosion Resistant Ni-Based Glassy Alloys in Boiling Nitric Acid Solutions

C. L. Qin^{1,*}, K. Asami², H. Kimura², W. Zhang², D. V. Louzguine¹ and A. Inoue¹

¹WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

²Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloy possesses high corrosion resistance in severe environments, i.e. boiling 6N HNO₃ and 6N HNO₃ + 5 g/l Cr⁶⁺ solutions. In both solutions, the corrosion resistance of the Ni₅₇Nb₁₉Zr₁₉Ta₅ alloy is much better than that of NAR-310Nb stainless steel which is developed as nitric acid corrosion resistant stainless steel. XPS analysis reveals that the high corrosion resistance of the Ni-based glassy alloys is due to the formation of the highly protective passive film composed exclusively of Nb⁵⁺ and Ta⁵⁺ cations after immersion in the solution without Cr⁶⁺ ions, and Nb³⁺, Ta³⁺ and Cr³⁺ cations after immersion in the solution with Cr⁶⁺ ions.

[doi:10.2320/matertrans.ME200814]

(Received December 9, 2008; Accepted March 31, 2009; Published May 20, 2009)

Keywords: glassy alloys, corrosion resistance, nitric acid, polarization curves, X-ray photoelectron spectroscopy (XPS) analysis

1. Introduction

Since extremely corrosion resistant Fe-Cr-metalloid amorphous alloys were found in the middle of 1970s,¹⁾ one of the important features of amorphous alloys, i.e. high corrosion resistance, has been discovered. The absence of crystalline defects and the chemically homogeneous single-phase nature of amorphous alloys lead to the formation of a uniform passive film and hence are responsible for high corrosion resistance. Since then, various types of high corrosion resistant amorphous, glassy alloys and bulk metallic glasses have been developed by sputter deposition, melt spinning and copper-mold casting methods, as exemplified for Ni-Cr-metalloid,^{2,3)} Ni-valve metal,^{4,5)} (Cr,Mo,W)-valve metal,⁶⁻⁸⁾ Fe-Cr-Mo-P-C^{9,10)} alloy systems, which possess superior corrosion resistance in concentrated hydrochloric acid solutions. However, there have been no data about corrosion resistance of glassy alloys in boiling nitric acid solutions. For nuclear fuel reprocessing applications, reprocessing of spent nuclear fuel involves use of nitric acid of high concentrations and high temperatures. The boiling nitric acid also contains small amounts of other ions such as Cr⁶⁺, Ag²⁺, Ce⁴⁺, Cr₂O₇²⁻ etc. Therefore, the materials for fabrication of such reprocessing plant equipment should exhibit excellent corrosion resistance. Conventional materials do not have enough corrosion resistance such as AISI 304L stainless steel¹¹⁾ and even nitric acid grade stainless steel Uranus 65.¹²⁾

With the aim of searching for high corrosion resistant glassy alloys in severe environments, i.e. boiling 6N HNO₃ solutions with and without 5 g/l Cr⁶⁺, for nuclear fuel reprocessing applications, glass alloys selection is very important. Among various types of glassy alloys developed so far, the Ni₆₀Nb₂₀Zr₂₀ glassy alloys¹³⁾ chosen as a promising candidate for nuclear fuel reprocessing applications for three reasons: (1) The alloy possesses good mechanical properties and a large supercooled liquid region of 51 K. In supercooled liquid region, it can be fabricated into intricate shapes with a high level of dimensional accuracy. (2) The alloy can be formed in a wide ribbon size of a width of 50 mm and a thickness of 25 µm. (3) The 20 at% Nb content in alloy could

provide a strong passivating ability. Furthermore, due to higher corrosion resistance of Ta element than that of Nb element,^{14,15)} the addition of Ta to the Ni-Nb-Zr glassy alloy is expected to improve the corrosion resistance in such severe environments. So, the present work aims to investigate the corrosion behavior of the Ni-Nb-Zr-Ta glassy alloys in boiling HNO₃ solutions. X-ray photoelectron spectroscopy (XPS) and angle-resolved X-ray photoelectron spectroscopy (ARXPS) were performed to elucidate the origin of the high corrosion resistance by surface characterization.

2. Experimental

The alloy ingots of Ni-Nb-Zr-Ta were prepared by arc-melting mixtures of pure metals in an argon atmosphere. Ribbon samples were fabricated by melt spinning. The glassy single structure of the melt-spun ribbon samples was confirmed by X-ray diffraction using Cu Kα radiation.

Prior to immersion and electrochemical measurements, the specimens were polished mechanically with SiC paper up to grit 1500 in cyclohexane, degreased in acetone, washed in distilled water, dried in air, and further exposed to air for 24 h for good reproducibility. The corrosion rates were evaluated from the weight loss after immersion for 2 weeks in boiling 6N HNO₃ solutions with and without 5 g/l Cr⁶⁺. Three specimens for each alloy in the same solution were examined for the weight loss test. The average value was used for corrosion rate estimation. Electrochemical measurements were conducted in a three-electrode cell using a platinum counter electrode and an Ag/AgCl reference electrode. Potentiodynamic polarization curves were measured at a potential sweep rate of 50 mV·min⁻¹ after open-circuit immersion for about 20 min when the open-circuit potential became almost steady.

For surface characterization, X-ray photoelectron spectroscopy (XPS) and angle-resolved X-ray photoelectron spectroscopy (ARXPS) measurements were utilized by means of a SSI SSX-100 photoelectron spectrometer with monochromatized Al Kα excitation (hν = 1486.6 eV) for the melt-spun ribbon samples before and after immersion for 336 h in boiling 6N HNO₃ solutions with and without 5 g/l Cr⁶⁺. X-ray photoelectron spectra were measured at different

*Corresponding author, E-mail: clqin@wpi-aimr.tohoku.ac.jp

Fig. 1 Average corrosion rates of the Ni-based glassy alloys and NAR-310Nb stainless steel in boiling 6 N HNO₃ and boiling (6 N HNO₃ + 5 g/l Cr⁶⁺) solutions at 385 K open to air.

take-off angles (12, 35 and 90°) with respect to the plane of the sample, in order to observe the outer and inner layers of the passive film formed on the alloy. The composition of the surface film and the composition of the underlying alloy surface were quantitatively determined with a previously proposed method using the integrated intensities of photoelectrons under the assumption of a three-layer model of an outmost contaminant hydrocarbon layer of uniform thickness, a surface film of uniform thickness and an underlying alloy surface of infinite thickness as regards x-ray-photoelectrons.^{16,17)}

3. Results and Discussion

We firstly chose the Ni₆₀Nb₂₀Zr₂₀ and Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloys to measure the corrosion rates in boiling 6 N HNO₃ solutions with and without 5 g/l Cr⁶⁺ for 2 weeks. It was confirmed that all the melt-spun ribbon samples were completely a single phase glassy structure. Figure 1 shows the average corrosion rates of the Ni-based glassy alloys immersed in boiling 6 N HNO₃ and boiling (6 N HNO₃ + 5 g/l Cr⁶⁺) solutions, open to air for 2 weeks. The stainless steel NAR-310Nb which is known for high corrosion resistance in nitric acid is also examined in the same solutions for comparison. The temperature in both solutions is as high as about 385 K. The corrosion rates of the Ni₆₀Nb₂₀Zr₂₀ alloy are about 0.013 mm·year⁻¹ in 6 N HNO₃ and increases to 0.086 mm·year⁻¹ in Cr⁶⁺ ions containing solution. Meanwhile, after immersion in boiling 6 N HNO₃ solution for 2 weeks, the Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloy still maintains a metallic luster and displays a high corrosion resistance. Its corrosion rate is about 0.0048 mm·year⁻¹, which is about one order of magnitude lower than those of the Ni₆₀Nb₂₀Zr₂₀ alloy and NAR-310Nb stainless steel. In boiling Cr⁶⁺ containing solution, the corrosion rate is about 0.031 mm·year⁻¹ for the Ni₅₇Nb₁₉Zr₁₉Ta₅ alloy, whereas NAR-310Nb stainless steel dissolves completely within 44 hours, which corresponds to a very high corrosion rate of 23.74 mm·year⁻¹. These facts clearly indicate the superiority of the Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloy. Moreover, it is also found that the corrosion resistance of the Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloy is markedly enhanced in both solutions as

Fig. 2 Potentiodynamic polarization curves of the Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloy in boiling 6 N HNO₃ solutions with and without Cr⁶⁺ ions at 385 K open to air.

compared to that of the Ta-free Ni₆₀Nb₂₀Zr₂₀ glassy alloy, indicating the addition of 5 at% Ta is effective in improving the corrosion resistance in such severe environments. Therefore, it can be concluded that the Ta-containing Ni-based glassy alloy exhibits high corrosion resistance and its corrosion resistance is much higher than that of NAR-310Nb stainless steel in nitric acids of high concentration at high temperature. Next, we focus on the Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloy to further investigate the electrochemical properties and surface-related chemical characteristics of the alloy immersed in boiling nitric acid solutions.

Figure 2 shows the polarization curves of the Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloy in boiling 6 N HNO₃ solutions with and without Cr⁶⁺ ions, open to air. The alloy begins with a small active dissolution, followed by a passivation process with a low passive current density of the order of 10⁻² Am⁻² in boiling 6 N HNO₃ at a high temperature of around 385 K, indicating high corrosion resistance of this alloy. On the other hand, in boiling (6 N HNO₃ + 5 g/l Cr⁶⁺) solution, spontaneous passivation takes place for the alloy. However, its anodic passive current density of the alloy is higher than that in the solution without Cr⁶⁺ ions, which is in accord with the result of corrosion rates test. The alloy in Cr⁶⁺ containing solution shows a very noble open circuit potential. It can be simply explained by the reduction of Cr⁶⁺ ions. The higher cathodic reaction in the Cr⁶⁺ ions containing solution pushes up the immersion potential towards the positive direction, which is the reason why the presence of Cr⁶⁺ ions accelerates corrosion rates of the alloys.

In order to elucidate the origin of the high corrosion resistance of Ta-containing Ni-based glassy alloy, XPS measurements were performed to clarify the surface composition together with their chemical states of the Ni₅₇Nb₁₉Zr₁₉Ta₅ specimens as-polished mechanically or immersed for 2 weeks in boiling 6 N HNO₃ and boiling (6 N HNO₃ + 5 g/l Cr⁶⁺) solutions. The XPS spectra of the specimens over a wide binding energy region exhibited peaks of Ni 2p, Nb 3d, Zr 3d, Ta 4f, Cr 2p, O 1s, C 1s etc. The C 1s peaks arose from a contaminant hydrocarbon layer covering the top surface of the specimen. The O 1s spectrum

Fig. 3 The cationic fraction of elements in the surface film and the atomic fraction of elements in the underlying alloy just below the surface film for the $\text{Ni}_{57}\text{Nb}_{19}\text{Zr}_{19}\text{Ta}_5$ alloy (a) exposed to air and (b) immersed in boiling 6N HNO_3 and boiling (6N HNO_3 + 5g/l Cr^{6+}) solutions for 2 weeks after mechanical polishing.

consisted of peaks originating from oxygen in metal-O-metal bond, metal-OH bond and bound water. It is worth noting that the Cr 2p spectrum for the alloy immersed in Cr^{6+} containing solution for 2 weeks consists of two peaks at 577.8 and 587.5 eV, which are related to Cr 2p electrons of Cr^{3+} ions in the surface film.¹⁸⁾ No peak corresponding to Cr^{6+} ions was found. The spectrum peaks from alloy constituents were composed of peaks corresponding to their oxidized states in a surface film and the metallic states in an underlying alloy surface. However, on the other specimens after immersion in the both solutions, those peaks showed only oxidic peaks because of the surface films on the specimens were much thicker than the escape depths of photoelectrons.

Figure 3 shows the cationic fraction of element in the surface film ($[\text{M}^{\text{ox}}]/[\text{Ni}^{\text{ox}}] + [\text{Nb}^{\text{ox}}] + [\text{Zr}^{\text{ox}}] + [\text{Ta}^{\text{ox}}]$) and the atomic fraction of elements in the underlying alloy surface just below the surface film ($[\text{M}^{\text{m}}]/[\text{Ni}^{\text{m}}] + [\text{Nb}^{\text{m}}] + [\text{Zr}^{\text{m}}] + [\text{Ta}^{\text{m}}]$) for the $\text{Ni}_{57}\text{Nb}_{19}\text{Zr}_{19}\text{Ta}_5$ alloy (a) exposed to air and (b) immersed in boiling 6N HNO_3 and boiling (6N HNO_3 + 5g/l Cr^{6+}) solutions for 2 weeks after mechanical polishing. [M] denotes a molar concentration percent of the alloy constituent elements. In Fig. 3(a), when the alloy is exposed to air after mechanical polishing, Zr and Nb cations are largely enriched in the surface film, whereas Ni cations are deficient. In addition, the concentration of Ta cations slightly increases with respect to the alloy composition. This fact reveals that the preferential oxidation of Zr and Nb occurs during air exposure whereas Ni is scarcely oxidized. The major cation in the as-polished surface film is Zr^{4+} and followed by Nb^{5+} (Nb^{3+}), Ta^{5+} and Ni^{2+} . By contrast, metallic Ni is significantly concentrated in the underlying surface just below the surface film by air exposure, while the contents of Nb and Zr metal decrease. Meanwhile, we could

not detect Ta metal in the underlying surface. When the specimen was immersed in boiling 6N HNO_3 solution, it is interesting to find that the cations of the passive surface are composed exclusively of Nb^{5+} and Ta^{5+} . This result revealed that the air-formed film was not stable in boiling 6N HNO_3 and converted to the stable passive film that consisted only of Nb and Ta passivating elements, as a consequence of preferential dissolution of Ni and Zr elements during the immersion. In general, Ti, Zr, Nb and Ta alloying elements are all high corrosion resistant elements and show strong passivating ability. But in such severe environments, Ta and Nb elements demonstrate their strong passivating ability, whereas Zr and Ti elements show active dissolution behavior. After immersion in Cr^{6+} containing solution, we also found a certain amounts of Cr^{3+} ions in the surface which are from the solution, in addition to Nb and Ta cations. Consequently, the formation of the highly protective surface film composed exclusively of Nb^{5+} , Ta^{5+} or Cr^{3+} , is responsible for the high corrosion resistance for the present alloy in such severe environments. Combined the corrosion rates in two solutions presented in Fig. 1 and XPS results, it can be seen that the passive surface film consisting only of Nb and Ta cations after immersion in the solution without Cr^{6+} ions is more protective, stable and resistant to corrosion in comparison with that consisting of Nb, Ta and Cr cations after immersion in the solution with Cr^{6+} ions. Actually, the Cr^{3+} is also one of the corrosion resistance enhancing cations. For example, the sputter-deposited Ta-Cr alloys^{19,20)} which its surface film consists of Cr^{3+} and Ta^{5+} cations have extraordinarily high corrosion resistance; they have higher corrosion resistance than those of pure Ta and Cr metals. However, the Cr^{3+} cations in the surface film formed in the solution containing Cr^{6+} ions is just deposited from the solution and it might be not completely incorporated in the surface film. Thus, the passive surface film consisting only of Nb and Ta cations is more dense and stable to corrosion in comparison with that consisting of Nb, Ta and Cr cations.

On the other hand, XPS measurements were also carried out for Ta-free $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ glassy alloy. The passive films on the $\text{Ni}_{60}\text{Nb}_{20}\text{Zr}_{20}$ glassy alloy consisted only of Nb^{5+} cations after immersion in boiling 6N HNO_3 solution, and Nb^{5+} and Cr^{3+} cations after immersion in boiling (6N HNO_3 + 5g/l Cr^{6+}) solution. The big difference is the passive surface films for Ta-containing $\text{Ni}_{57}\text{Nb}_{19}\text{Zr}_{19}\text{Ta}_5$ alloy contains a certain amounts of Ta cations, in addition to Nb or Cr cations. From the corrosion point of view, it is well known that Ta element for enhancing the corrosion resistance is better than Nb element.^{14,15)} Therefore, it can be said that the protective quality of the surface films is improved by the addition of Ta element, and hence better corrosion resistance.

To determine the in-depth distribution of elements in the passive films on the $\text{Ni}_{57}\text{Nb}_{19}\text{Zr}_{19}\text{Ta}_5$ alloy, angle-resolved XPS measurements (ARXPS) were performed. The Al $K\alpha$ X-ray irradiation on specimen caused the excitation of the photoelectrons. The angle between the horizontal to the surface of the specimen and the direction of photoelectron to the detector was photoelectron take-off angle (θ). The change in the take-off angle, θ , of the photo-electrons from low angle to high angle gives information from the upper-most surface to the interior of the surface. In fact, the depth from the

Fig. 4 The change in cationic fraction of elements in the surface film for the Ni₅₇Nb₁₉Zr₁₉Ta₅ alloy after immersion for 2 weeks in (a) boiling 6 N HNO₃ and (b) boiling 6 N HNO₃ + 5 g/l Cr⁶⁺ as a function of take-off angle of photoelectrons.

surface is proportional to $\sin \theta$. Figure 4 shows the change in the cationic fraction of elements in the surface film for the Ni₅₇Nb₁₉Zr₁₉Ta₅ alloy after immersion for 2 weeks in (a) boiling 6 N HNO₃ and (b) boiling 6 N HNO₃ + 5 g/l Cr⁶⁺ as a function of take-off angle of photoelectrons. In Fig. 4(a), the contents of the Nb⁵⁺ and Ta⁵⁺ cations almost do not change with increasing take-off angle of photoelectrons. This fact indicates that the Nb⁵⁺ and Ta⁵⁺ cations are distributed homogeneously through the depth of the passive films for the Ni₅₇Nb₁₉Zr₁₉Ta₅ alloy immersed in boiling 6 N HNO₃ solution, which means the spontaneous passive film is compositionally homogeneous. On the contrary, in the passive film formed in 6 N HNO₃ + 5 g/l Cr⁶⁺ solution (Fig. 4(b)), there is a compositional gradient. The contents of Nb⁵⁺ and Ta⁵⁺ cations increase gradually with an increase in the photoelectron take-off angle, while that of Cr³⁺ cations decreases. The result reveals that the higher Cr³⁺ ions concentration in the outer part of the film compared with the inner part of the film. Reverse is seen for Nb⁵⁺ and Ta⁵⁺ contents. As Cr³⁺ ions result from the reduction of Cr⁶⁺ ions in the solutions, it is reasonable that the concentration of Cr³⁺ ions in the outer region of the passive film is higher than that in the inner region of the passive film.

4. Conclusions

The Ta-containing Ni₅₇Nb₁₉Zr₁₉Ta₅ glassy alloy exhibits high corrosion resistance in severe environments, i.e. boiling 6 N HNO₃ and 6 N HNO₃ + 5 g/l Cr⁶⁺ solutions. In both solutions, the corrosion resistance of the present glassy alloy is much better than that of NAR-310Nb stainless steel, which may be of great potential for nuclear fuel reprocessing applications. The high corrosion resistance of the Ta-containing Ni-based glassy alloy is attributable to the formation of the highly protective passive film composed exclusively of Nb⁵⁺ and Ta⁵⁺ cations after immersion in the solution without Cr⁶⁺ ions, and Nb⁵⁺, Ta⁵⁺ and Cr³⁺ cations after immersion in the solution with Cr⁶⁺ ions. According to ARXPS analysis, both Nb⁵⁺ and Ta⁵⁺ cations are distributed uniformly in depth of the passive film for alloy immersed in boiling 6 N HNO₃. On the contrary, the compositional

gradients are observed in the passive film formed in 6 N HNO₃ + 5 g/l Cr⁶⁺ solution; Cr³⁺ cations are concentrated in the exterior of the passive film while the contents of Nb⁵⁺ and Ta⁵⁺ cations increase in the interior of the film.

REFERENCES

- 1) M. Naka, K. Hashimoto and T. Masumoto: J. Jpn. Inst. Met. **38** (1974) 835–841.
- 2) H. Habazaki, T. Sato, A. Kawashima, K. Asami and K. Hashimoto: Mater. Sci. Eng. A **304–306** (2001) 696–700.
- 3) H. Katagiri, S. Meguro, M. Yamasaki, H. Habazaki, T. Sato, A. Kawashima, K. Asami and K. Hashimoto: Corros. Sci. **43** (2001) 171–182.
- 4) C. L. Qin, W. Zhang, H. Nakata, H. Kimura, K. Asami and A. Inoue: Mater. Trans. **46** (2005) 858–862.
- 5) A. Inoue, W. Zhang and T. Zhang: Mater. Trans. **43** (2002) 1952–1956.
- 6) X. Y. Li, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: Corros. Sci. **40** (1998) 1587–1604.
- 7) P. Y. Park, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: Corros. Sci. **38** (1996) 1649–1667.
- 8) J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: Corros. Sci. **40** (1998) 155–175.
- 9) S. J. Pang, T. Zhang, K. Asami and A. Inoue: Mater. Trans. **42** (2001) 376–379.
- 10) S. J. Pang, T. Zhang, K. Asami and A. Inoue: Mater. Trans. **43** (2002) 2137–2142.
- 11) K. Kiuchi, Yamanouchi, M. Kikuchi and Y. Kuriki: Proc. Third Int. Conf. on Nuclear Fuel Reprocessing and Waste Management **2** (1991) 1054.
- 12) A. Ravi Shankar, R. K. Dayal, R. Balasubramaniam, V. R. Raju, R. Mythili, S. Saroja, M. Vijayalakshmi and V. S. Raghunathan: J. Nuclear Mater. **372** (2008) 277–284.
- 13) H. Kimura, A. Inoue, S. Yamaura, K. Sasamori, M. Nishida, Y. Shinpo and H. Okouchi: Mater. Trans. **44** (2003) 1167–1171.
- 14) J. H. Kim, H. Yoshioka, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: Corros. Sci. **33** (1992) 1507–1518.
- 15) A. Kawashima, T. Sato, N. Ohtsu and K. Asami: Mater. Trans. **45** (2004) 131–136.
- 16) K. Asami and K. Hashimoto: Corros. Sci. **17** (1977) 559–570.
- 17) K. Asami, K. Hashimoto and S. Shimodaira: Corros. Sci. **17** (1977) 713–723.
- 18) K. Asami and K. Hashimoto: Corros. Sci. **24** (1984) 83–97.
- 19) J. H. Kim, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: Corros. Sci. **34** (1993) 1947–1955.
- 20) X. Y. Li, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: Corros. Sci. **40** (1998) 1587–1604.