

**Corrosion and Surface Film Characterization of
TaNbHfZrTi High Entropy Alloy**

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ABSTRACT

TaNbHfZrTi high-entropy alloy (HEA) was prepared by arc melting alloying elements, and the formation of single phase bcc structure was confirmed. The developed HEA alloy exhibited low current density values during potentiodynamic polarization in 11.5 M HNO₃ at room temperature. The corrosion rate was negligible (0.002 mm/y) in boiling 11.5 M HNO₃ and the X-ray photoelectron spectroscopic (XPS) analyses confirmed that the passive film was predominantly composed of Ta₂O₅. In contrast, the air formed native film consisted of ZrO₂ and HfO₂. On the other hand, the potentiodynamic polarization studies indicated high corrosion current values for the HEA in 11.5 M HNO₃ + 0.05 M NaF at ambient condition. In boiling fluorinated nitric acid, the corrosion rate is high about 2.2 mm/y, and a severely corroded morphology was obtained. XPS investigations confirmed the presence of ZrF₄, ZrOF₂, and HfF₄ along with un-protective oxides of Ta, Nb, and Ti on the film.

Keywords: high-entropy alloy; casting; corrosion; passivation; XPS

INTRODUCTION

High Entropy Alloys (HEAs) are usually composed of four or five elements with equimolar or near equimolar elemental fractions, which form predominantly single solid solution phase [1, 2]. The HEAs exhibit four core effects such as high entropy effect, distorted lattice, sluggish diffusion, and cocktail effect [1, 2]. Owing to these effects, HEAs exhibit better mechanical, wear, corrosion resistance properties, and they also possess microstructural stability at high temperatures [1, 2]. Materials exhibiting excellent corrosion resistance, high strength and formability are desirable for the fabrication of dissolver components of reprocessing plant for the processing of spent nuclear fuels by aqueous route. Owing to the single phase structure as well as excellent mechanical and formability properties of TaNbHfZrTi HEA [3, 4], it can be considered as a candidate material for the fabrication of critical components in reprocessing plants. Thus, in the present study, the corrosion resistance performance of TaNbHfZrTi HEA was investigated in the processing media of boiling 11.5 M HNO₃, and 11.5 M HNO₃ + 0.05 M NaF encountered in the reprocessing plant.

EXPERIMENTAL PROCEDURE

The TaNbHfZrTi HEA was prepared using a vacuum arc melting of the high purity (99.99%) Ta, Nb, Hf, Zr, and Ti elements on the water-cooled copper hearth of the arc melting system. The ingot was melted at least five times and was flipped between each melting, for homogeneity. The arc melted TaNbHfZrTi ingot was characterized for phase analysis by X-ray Diffraction technique (XRD). The potentiodynamic polarization behavior of TaNbHfZrTi HEA in both 11.5 M HNO₃ and 11.5 M HNO₃ + 0.05 M NaF at room temperature, experiments were carried out using the electrochemical system with platinum and Ag/AgCl (3 M KCl) was used as counter and reference electrode, respectively, and at the scan rate of 0.00017 V/s. The corrosion rate of the TaNbHfZrTi HEA in 11.5 M HNO₃ and 11.5 M HNO₃ + 0.05 M NaF at boiling conditions (120 °C) was obtained using the test procedure described in ASTM A262 Practice C method [5]. The experiments were performed for five periods of 48 h (i.e. total exposure period of 240 h) with fresh solutions being used in each time. The surface morphology of the TaNbHfZrTi HEA samples subjected to weight loss studies was investigated using scanning electron microscopy (SEM). The X-ray photoelectron spectroscopic (XPS) was employed to analyze the surface chemistry of TaNbHfZrTi HEA before and after the corrosion studies.

RESULTS

The XRD pattern of the as-cast, TaNbHfZrTi sample is shown in Fig. 1 matched with body centered cubic (bcc) phase with the corresponding planes of (110), (200) and (211). The SEM micrograph inset of Fig. 1 revealed a typical dendrite microstructure for the as-cast TaNbHfZrTi HEA. Figure 2 shows the potentiodynamic polarization behavior of TaNbHfZrTi HEA in 11.5 M HNO₃, and 11.5 M HNO₃ + 0.05 M NaF and using Tafel extrapolation method the corrosion potential, E_{corr} and corrosion current density I_{corr} were obtained. The E_{corr} values were about 0.68 and 0.12 V, and the I_{corr} values were 0.2 and 2.1 $\mu\text{A}/\text{cm}^2$, respectively in nitric and fluorinated nitric acid. The low I_{corr} value indicated the high corrosion resistance of the TaNbHfZrTi HEA in nitric acid. The shift in the E_{corr} value to the active region, resulting in higher I_{corr} value is due to the high electronegativity and aggressive nature of fluoride ions. In a recent study, when the TaNbHfZrTi HEA was polarized until 2 V in nitric acid medium exhibited an un-attacked surface whereas in fluorinated nitric acid a slightly attacked with flaky morphology was observed [6]. Thus, it was inferred that the TaNbHfZrTi

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HEA exhibited a passive and pseudo-passive behavior, respectively in 11.5 M HNO_3 and 11.5 M $\text{HNO}_3 + 0.05 \text{ M NaF}$ medium at room temperature [6]. An insignificant corrosion rate of 0.002 mm/y and an un-attacked surface morphology (Fig. 3a) was obtained for TaNbHfZrTi HEA in 11.5 M HNO_3 at boiling condition (120 °C) for 240 h.

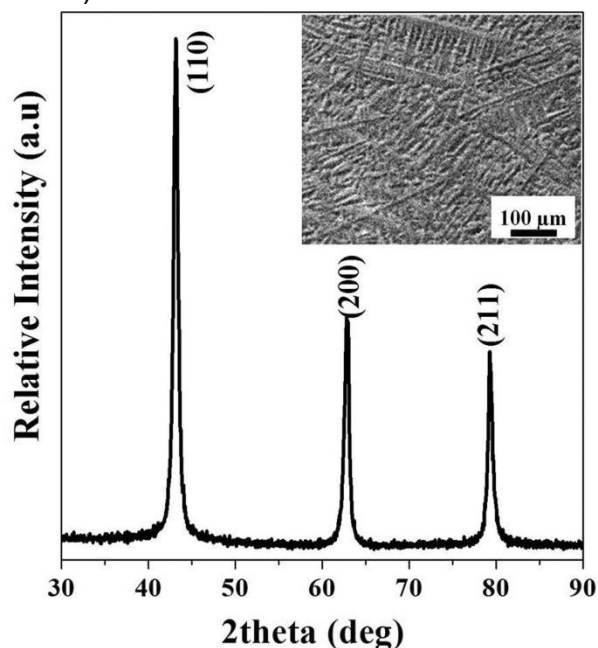


Figure 1: XRD and SEM microstructure of the TaNbHfZrTi HEA

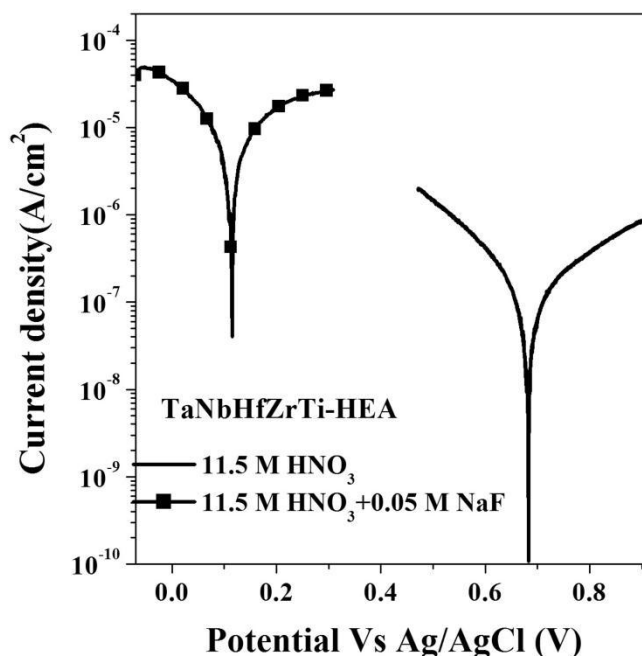


Figure 2: Potentiodynamic polarization behavior of TaNbHfZrTi HEA in 11.5 M HNO_3 and 11.5 M $\text{HNO}_3 + 0.05 \text{ M NaF}$ at room temperature

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On the other hand in boiling fluorinated nitric acid, the corrosion rate is high about 2.2 mm/y for an exposure period of 48 h. The sample surface appeared to be loosely packed like powder resembling a “dry land of drought conditions” as shown in Fig. 3b. After removing the loosely bound powder using an adhesive tape, the underneath surface was predominantly smooth surface, as shown in Fig.3c. Thus the film formed in boiling fluorinated nitric acid was unstable and unprotective.

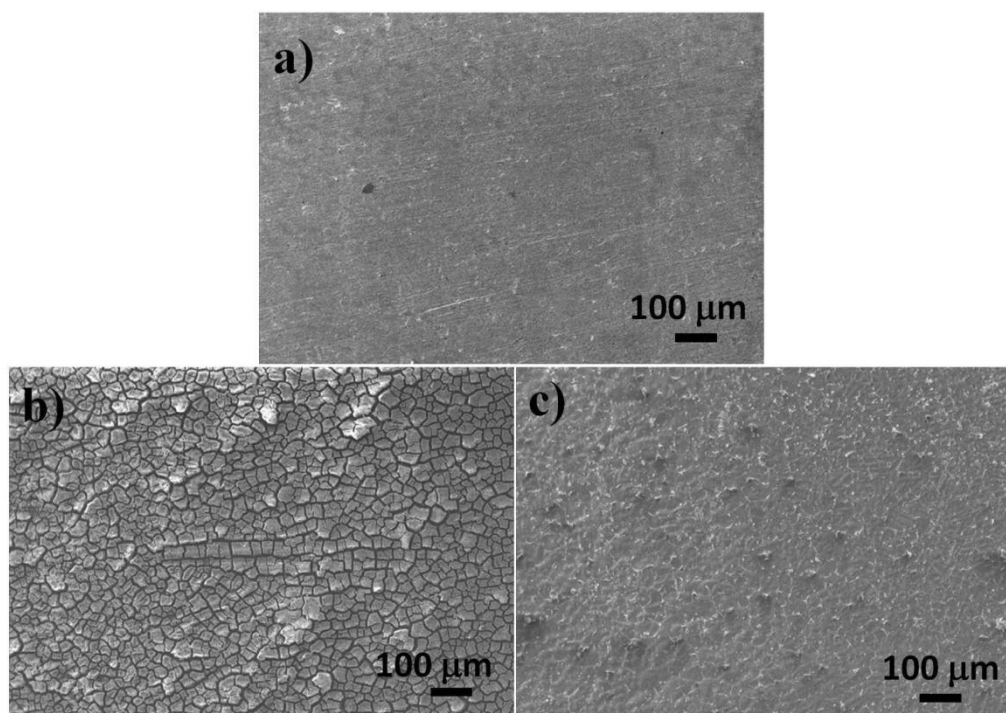


Figure 3: SEM images of the TaNbHfZrTi HEA exposed to (a) boiling 11.5 M HNO₃ for 240 h (b-c) boiling 11.5 M HNO₃ + 0.05 M NaF for 48 h (b) top-surface; (c) underneath surface, obtained after removing the loosely adhered particles of the top-surface shown in (a)

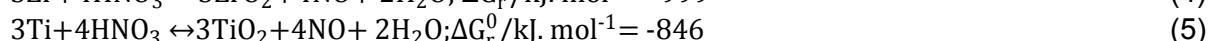
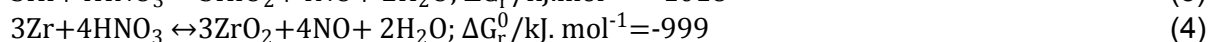
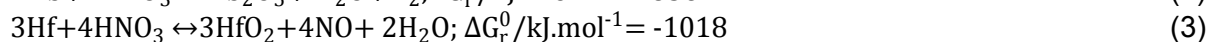
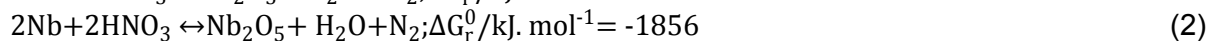
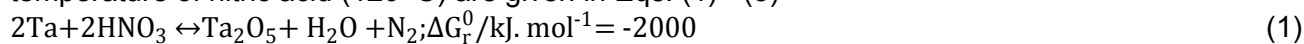
Table 1: Oxide and metallic concentrations of native and passive film of TaNbHfZrTi HEA

Photo electron lines	Oxidation/ Chemical state	Binding Energy (eV)		Atomic Concentration (%)	
		Native film	Passive film	Native Film	Passive film
Ta 4f _{7/2} ; 4f _{5/2}	Ta ⁵⁺ (Ta ₂ O ₅)	27.2; 29	26.3; 28.2	7.3	74
	Ta	22.1; 24	-	8.7	-
Nb 3d _{5/2} ; 3d _{3/2}	Nb ⁵⁺ (Nb ₂ O ₅)	208.2; 210.9	207.3; 210.1	5.5	12.8
	Nb	202.5; 205.3	-	14.1	-
Hf 4f _{7/2} ; 4f _{5/2}	Hf ⁴⁺ (HfO ₂)	17.9; 19.6	16.6; 18.2	13.1	4.1
	Hf	14.4; 16.1	-	8.9	-
Zr 3d _{5/2} ; 3d _{3/2}	Zr ⁴⁺ (ZrO ₂)	183.4; 185.7	182; 184.4	17.8	4.9
	Zr	178.9; 181.3	-	10.7	-
Ti 2p _{3/2} ; 2p _{1/2}	Ti ⁴⁺ (TiO ₂)	459.6; 465.3	458.5; 464.6	5.1	4.1
	Ti ³⁺ (Ti ₂ O ₃)	457.7; 463.5	-	3.5	-
	Ti	454.1; 459.5	-	5.3	-

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Detailed XPS spectra of TaNbHfZrTi HEA exposed to nitric and fluorinated nitric acid was reported elsewhere [6]. As shown in Table 1, the XPS analysis of the air-formed native film of TaNbHfZrTi HEA predominantly composed of ZrO₂ and HfO₂. Apart from oxide states, a total metallic concentration of about 47.7% was present. Further, it could be confirmed from Table 1 that the passive film formed in boiling nitric acid for 240 h was significantly enriched with Ta₂O₅, followed by Nb₂O₅. Unlike the native film, the surface of the passive film was completely in oxide state, and metallic states were not observed. The formation of the most stable oxides of the alloying elements of the TaNbHfZrTi HEA, with the calculated standard Gibbs energies of reaction at the boiling temperature of nitric acid (120 °C) are given in Eqs. (1) - (5)



From Eqs. (1) to (5) that the most negative value for ΔG_r^0 is for Ta₂O₅ which implies that formation of Ta₂O₅ is highly favorable and followed by Nb₂O₅, HfO₂, ZrO₂ and TiO₂, which is consistent with the XPS results. For the sample exposed to boiling fluorinated nitric acid for 48 h, the XPS analysis (Table 2) of the surface corresponding to Fig. 3b was predominantly composed of Ta₂O₅, Nb₂O₅, and TiO₂, whereas the underneath surface (Fig.3c) consisted of the stable and lower oxidation states of Ta, Nb, Ti, Zr, and Hf. The absence of HfO₂ and ZrO₂ and the presence of HfF₄, ZrOF₂, and ZrF₄ in the underneath surface was confirmed by XPS analysis.

Table 2: Concentrations of the oxide, fluoride and metallic states of TaNbHfZrTi HEA when exposed to boiling fluorinated nitric acid for 48 h

Photo electron lines	Oxidation/ Chemical state	Binding Energy (eV)		Atomic Concentration (%)	
		Top Surface	Underneath Surface	Top Surface	Underneath Surface
Ta 4f _{7/2} ; 4f _{5/2}	Ta ⁵⁺ (Ta ₂ O ₅)	26.3; 28.2	26.7; 28.6	51.6	22.2
	Ta ⁴⁺ (TaO ₂)	-	25.1; 27	-	5
	Ta ²⁺ (TaO)	-	23.6; 25.6	-	3.8
	Ta	-	22.4; 24.4	-	1.1
Nb 3d _{5/2} ; 3d _{3/2}	Nb ⁵⁺ (Nb ₂ O ₅)	207.4; 210.1	207.9; 210.6	34.7	11.3
	Nb ⁴⁺ (NbO ₂)	-	205.9; 208.7	-	9
	Nb ²⁺ (NbO)	-	204.4; 207	-	11.2
Hf 4f _{7/2} ; 4f _{5/2}	Hf ⁴⁺ (HfF ₄)	-	18.1; 19.7	-	9
Zr 3d _{5/2} ; 3d _{3/2}	Zr ⁴⁺ (ZrO ₂)	-	183.2; 185.6	-	6.3
	Zr ⁴⁺ (ZrOF ₂)	-	184; 186.4	-	4.6
	Zr ⁴⁺ (ZrF ₄)	-	185.7; 188.2	-	1.2
Ti 2p _{3/2} ; 2p _{1/2}	Ti ⁴⁺ (TiO ₂)	459; 464.8	459.3; 465	13.7	7.5
	Ti ³⁺ (Ti ₂ O ₃)	-	457.7; 463.3	-	5.6
	Ti ²⁺ (TiO)	-	456; 461.7	-	2.2

The formation of Ti-F, Ta-F and Nb-F states were not observed indicating that they were not formed at all. The formation of un-protective lower oxidation states such as Ta⁴⁺ (TaO₂), Ta²⁺ (TaO), Nb⁴⁺ (NbO₂), Nb²⁺ (NbO), Ti³⁺ (Ti₂O₃) and Ti²⁺ (TiO) and the HfF₄, ZrOF₂ and ZrF₄ were responsible for the high corrosion rate of TaNbHfZrTi HEA in fluorinated nitric acid. In the fluorinated nitric acid medium, two major competing reactions that can occur are the formation of respective metal oxides and metal fluorides of the alloying elements present in the TaNbHfZrTi alloy. The reactions for the formation of the corresponding metal oxides and their standard Gibbs energy values were described elsewhere [6] and found to be consistent with the XPS analysis of TaNbHfZrTi alloy when exposed to fluorinated nitric acid.

CONCLUSIONS

The TaNbHfZrTi HEA exhibited high corrosion resistance in boiling 11.5 M HNO₃, due to the formation of single bcc phase and protective Ta₂O₅ passive film and thus this alloy has a high potential for service in nitric acid. However, in boiling 11.5 M HNO₃ + 0.05 M NaF, the corrosion rate was found to be 3 orders of magnitude higher than that in nitric acid. XPS investigations confirmed the presence of ZrF₄, ZrOF₂, and HfF₄ along with the formation of un-protective oxides of Ta, Nb, and Ti. Thus, for service in fluorinated nitric acid, a high corrosion resistant HEA against fluoride ions have to be developed

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