Intermetallics 89 (2017) 123–132

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

# Corrosion behavior and surface film characterization of TaNbHfZrTi high entropy alloy in aggressive nitric acid medium

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## ARTICLE INFO

*Keywords:*
A. High-entropy alloys
B. Corrosion
C. Casting
D. Microstructure
F. Scanning electron microscopy
Spectroscopic methods

## ABSTRACT

Corrosion behavior of TaNbHfZrTi high-entropy alloy (HEA) was investigated in nitric and fluorinated nitric acid at ambient (27 °C) and boiling (120 °C) conditions. The alloy passivated spontaneously during potentiodynamic polarization in 11.5 M $HNO_3$ at ambient condition. The corrosion rate was negligible in boiling 11.5 M $HNO_3$, exposed for 240 h. Scanning electron microscopic (SEM) studies did not show any significant corrosion attack. The high corrosion resistance of TaNbHfZrTi HEA was attributed to its single phase bcc structure. X-ray photoelectron spectroscopic (XPS) analysis revealed that the protective passive film formed in boiling nitric acid was predominantly composed of $Ta_2O_5$, in contrast to the presence of $ZrO_2$ and $HfO_2$ in air-formed native film. Potentiodynamic polarization studies indicated a pseudo-passivation behavior of the HEA in 11.5 M $HNO_3$ + 0.05 M NaF at ambient condition. In boiling fluorinated nitric acid, SEM images of TaNbHfZrTi HEA displayed a severely corroded morphology indicating the instability of the metal-oxides of the alloying elements. XPS investigations confirmed the presence of $ZrF_4$, $ZrOF_2$ and $HfF_4$ along with un-protective oxides of Ta, Nb and Ti on the film, resulting in decreased corrosion resistance of TaNbHfZrTi HEA in fluorinated nitric acid.

## 1. Introduction

Recently, a novel class of advanced structural materials, called High-Entropy Alloys (HEAs) is gaining significant importance in the field of Materials Science [1,2]. Compared to conventional alloys containing one principal element, HEAs are usually composed of multiple elements with equimolar or near equimolar elemental fractions, which form predominantly single solid solution phase [1,2]. The four core effects of HEAs are high entropy effect, distorted lattice, sluggish diffusion, and cocktail effect [1,2]. Owing to these effects, HEAs exhibit solid solution strengthening with better mechanical, wear, corrosion resistance properties and they also possess excellent microstructural stability at high temperatures [1,2]. Initially, the development of HEAs was focused mainly on alloying elements containing Fe, Ni, Co, Cr, Mn, Cu, Ti, V and Al [3–6]. Senkov and co-workers [7,8] developed refractory WTaNbMo and WTaNbMoV HEAs that exhibited high yield strength even at an elevated temperature of 1600 °C. Subsequently, Senkov et al. [9] decreased the density of the HEA by replacing W and Mo with Ti, Hf and Zr and developed TaNbHfZrTi HEA with improved specific strength. This TaNbHfZrTi HEA exhibited homogeneous plastic flow and up to 40% compression strain with marked strain hardening at room temperature. The excellent ductility of TaNbHfZrTi alloy in compression allowed the material to be produced in thin sheet by cold rolling process [10]. The as-cast microstructure of TaNbHfZrTi HEA consisted of dendritic colonies whereas the cold rolled and annealed sample consisted of an equiaxed structure [9,10]. Both the as-cast and cold-rolled TaNbHfZrTi HEA exhibited a single-phase with bcc structure [9,10]. Consequently, researchers concentrated on developing several refractory elements based high-entropy alloys such as $NbCrMo_{0.5}Ta_{0.5}TiZr$ [11], TiZrNbMoV [12], Al(V)NbTaTiZr [13], CrNbTiVZr [14], AlHfNbTaTiZr [15], HfMoNbTaTiZr [16] and MoWAlCrTi [17]. Most of the studies on these HEAs were focused on the phase formation, microstructure and mechanical properties [11–16] and oxidation behavior [17,18]. The advantage of the mechanical properties of the HEAs could not be fully exploited since their corrosion resistance was not understood properly. Exhaustive reviews on the corrosion resistant HEAs based on non-refractory elements are available in literature, where the effect of alloying elements, processing methods, heat-treatment and corrosion behavior, mainly in $H_2SO_4$ and NaCl environments were discussed and compared with the conventional engineering alloys [19–21]. Only limited studies have been reported for the corrosion behavior of refractory HEAs such as $TiZr_{0.5}NbCr_{0.5}$,

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http://dx.doi.org/10.1016/j.intermet.2017.06.002
Received 24 March 2017; Received in revised form 23 May 2017; Accepted 6 June 2017

$TiZr_{0.5}NbCr_{0.5}V$ and $TiZr_{0.5}NbCr_{0.5}Mo$ in $H_2SO_4$ and NaCl solutions [22].

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. The search for advanced alloys with properties better than the existing conventional materials is a motivating factor among the researchers. The corrosion behavior of the HEAs in boiling 11.5 M nitric acid, which is the dissolution medium for the spent nuclear fuels from fast breeder reactors [23] is not reported in the literature. In addition, the effect of fluoride ions in boiling nitric acid on the corrosion behavior of the dissolver vessels handling Pu-rich mixed oxide fuels [24] need proper investigation. Owing to the single phase structure as well as good mechanical and formability properties of TaNbHfZrTi HEA [9,10], it can be considered as a candidate material for the fabrication of critical components in reprocessing plants. Apart from the application point of view, the role of alloying elements in the TaNbHfZrTi multi-component HEA contributing to its passivation behavior is less understood.

In the present study, the performance of TaNbHfZrTi HEA was investigated in boiling nitric acid with and without fluoride ions. Potentiodynamic polarization test was used to characterize the passivation behavior of TaNbHfZrTi alloy in 11.5 M $HNO_3$ as well as 11.5 M $HNO_3$ + 0.05 M NaF at room temperature. The corrosion rate of TaNbHfZrTi was determined by weight loss method in 11.5 M $HNO_3$ as well as fluorinated nitric acid media under boiling conditions. Scanning electron microscopic (SEM) and X-ray photoelectron spectroscopic (XPS) analyses were performed to corroborate the results of the studies pertaining to passivation and corrosion behavior of this alloy.

## 2. Experimental procedure

### 2.1. Alloy preparation

The TaNbHfZrTi equimolar alloy was prepared using a vacuum arc melting system (M/s. Edmund Buhler GmbH, Germany). A total weight of 5 g of the high purity (99.99%) Ta, Nb, Hf, Zr, and Ti elements were melted together on the water-cooled copper hearth of the arc melting system. Prior to melting, the arc melting chamber was evacuated to a vacuum level 0.035 Pa and back-filled with high purity argon. To promote homogeneity, the ingot was melted at least five times and was flipped between each melting.

### 2.2. Phase analysis and microstructural characterization

The arc melted TaNbHfZrTi ingot was characterized for phase analysis by X-ray Diffraction technique (XRD; INEL, France) using monochromatic Cu Kα radiation. For metallographic observation, the TaNbHfZrTi sample was wet ground in SiC emery paper up to 1200 grit and followed by final polishing in colloidal silica suspension to obtain a smooth mirror-like surface finish. To reveal the microstructure, the polished sample was chemical etched with the Kroll-reagent (2 ml HF, 3 ml $HNO_3$ and 100 ml distilled $H_2O$) for 10 s. The etched sample's surface was analyzed using scanning electron microscopy (SEM; SNE-3000M, Korea).

### 2.3. Potentiodynamic polarization studies

To understand the passivation behavior of TaNbHfZrTi HEA in both 11.5 M $HNO_3$ and 11.5 M $HNO_3$ + 0.05 M NaF at room temperature, potentiodynamic polarization experiments were carried out using the electrochemical system (Autolab, The Netherlands). For polarization measurements, a standard three electrode cell with the test sample as working electrode with an exposed area of 1 $cm^2$ was employed. The working electrode's surface was prepared by wet ground using SiC paper up to 1200 grit and cleaned in distilled water and acetone to have a reproducible surface. Platinum and Ag/AgCl (3 M KCl) were used as counter and reference electrode, respectively. The open circuit potential (OCP) of the sample was monitored for 1 h. After measuring the OCP, potentiodynamic polarization tests were carried out at the scan rate of 0.00017 V/s from 0.2 V below OCP to 2.0 V. Both the OCP and potentiodynamic polarization experiments were performed at least twice, for checking the reproducibility of the results.

### 2.4. Measurement of corrosion rate

The experimental set-up used for corrosion test in 11.5 M $HNO_3$ and 11.5 M $HNO_3$ + 0.05 M NaF at boiling conditions (120 °C) is described elsewhere [25]. A cold finger condenser was used to reflux the acid vapors into the test solution. In the same set-up, the corrosion experiments at room temperature were also conducted. The TaNbHfZrTi HEA sample surface was wet ground in SiC emery paper up to 1200 grit. The polished samples were degreased with acetone, dried and weighed before immersing them into the test solutions. The samples were suspended into the solution through a Teflon thread for a minimum exposure period of 48 h. Based on the extent of corrosion, 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 period as described in ASTM A262 Practice C method [26]. The immersion tests were carried out at least twice for all the conditions studied. After corrosion testing, the samples were removed, cleaned carefully and the change in weight was measured in a micro balance with resolution of 0.0001 g. From the weight loss experiments, the corrosion rates were calculated using Eq. (1).

$$Corrosion\ rate = \frac{8.76 \times 10^4 \times W}{dAt} \tag{1}$$

where, corrosion rate is expressed in mm/yr, W is weight loss in g, d is the theoretical density of the alloy (11.82 g/$cm^3$), A is the exposed surface area in $cm^2$ and t is the exposed time in h.

### 2.5. Surface characterisation

The surface morphology of the TaNbHfZrTi HEA samples subjected to potentiodynamic polarization and weight loss studies was investigated using SEM, in secondary electron mode at an accelerating voltage of 30 kV. To analyze the surface chemistry of TaNbHfZrTi HEA before and after exposure to 11.5 M $HNO_3$ and 11.5 M $HNO_3$ + 0.05 M NaF at boiling conditions, XPS was employed. For recording the spectra, SPECS Surface Nano Analysis GmbH, Germany, XPS was used with Al-Kα excitation. The data were processed by SpecsLab2 software and analyzed by CasaXPS software.

## 3. Results and discussion

### 3.1. Phase analysis and microstructure

The XRD pattern of the as-cast, TaNbHfZrTi sample is shown in Fig. 1a and the diffraction peaks matched with body centered cubic (bcc) phase with the corresponding planes of (110), (200) and (211). Since no additional peaks were present, it could be concluded that the TaNbHfZrTi alloy ingot was of single bcc phase and the calculated lattice parameter was about 3.404 Å, which is in good agreement with that of the reported value [9]. The SEM micrograph (Fig. 1b) revealed a typical dendrite microstructure for the as-cast TaNbHfZrTi HEA [9].

### 3.2. Potentiodynamic polarization behavior of TaNbHfZrTi HEA

Fig. 2 shows the potentiodynamic polarization behavior of TaNbHfZrTi in 11.5 M $HNO_3$, and 11.5 M $HNO_3$ + 0.05 M NaF. From Fig. 2, the corrosion potential, $E_{corr}$ and corrosion current density $I_{corr}$ were obtained using Tafel analysis [27]. The $E_{corr}$ values were found to