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Journal of Nuclear Materials 372 (2008) 277–284

journal of nuclear materials

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Effect of heat treatment on the corrosion behaviour of Ti–5Ta–1.8Nb alloy in boiling concentrated nitric acid

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Received 13 July 2006; accepted 8 March 2007

Abstract

The effect of heat treatment i.e., stress relieving (SR), mill annealing (MA), solution treatment (ST), aging (AG) and overaging (OA) on the corrosion behaviour of Ti–5%Ta–1.8%Nb alloy in nitric acid medium has been studied. The corrosion rates in liquid, vapour and condensate phases of boiling 11.5 M nitric acid determined by weight loss method for Ti–5Ta–1.8Nb was much lower compared to that of commercial purity titanium. The corrosion rate in condensate phase was higher than that in liquid and vapour phases. This has been explained by considering the formation of protective film on the sample exposed to the liquid and vapour phase and the inhibiting effect of titanium ions in the liquid phase. The microstructures after the various heat treatments consisted of different proportions of equiaxed and acicular α, martensite (α') and retained β phases. The homogeneous equiaxed α phase in OA and AG conditions provided good corrosion resistance compared to acicular α or α' phase in other heat treated conditions. Potentiodynamic anodic polarisation studies indicated spontaneous passivation in 11.5 M nitric acid.

1. Introduction

Titanium shows excellent corrosion resistance that results from the formation of very stable, continuous, highly adherent and protective oxide film [1]. The nature, composition, and thickness of the protective surface oxide that form on titanium alloys depends on environmental conditions. In most aqueous environments, the oxide is typically TiO_2, Ti_2O_3 or TiO [2]. The high oxidation potential of boiling HNO_3 aids formation of TiO_2 (rutile) and it is also possible to form chemically unstable TiO_3 [2]. Titanium possesses excellent corrosion resistance in nitric acid, but under relatively weak oxidizing conditions found in the vapour and condensate regions, titanium exhibits higher corrosion rates [3,4]. The corrosion resistance of titanium in condensed HNO_3 can be improved by alloying with refractory metals like tantalum and niobium which possess similar metallic ion sizes like titanium, low solubility in HNO_3 and form stable oxide film [5].

The reprocessing of spent mixed oxide or carbide nuclear fuel involves highly oxidizing boiling nitric acid, containing ions such as Cr^{6+}, Ag^{2+}, Ce^{4+}, $Cr_2O_7^{2-}$, Fe^{3+} etc. Commercial 304L stainless steel when used as structural material in the reprocessing plants, has shown severe intergranular and general attack in the above media [6]. Austenitic stainless steels have even undergone intergranular corrosion in the non-sensitized condition [6–8], which has been related to the presence of small amounts of phosphorous and sulphur at the grain boundaries [7–9]. The reduction in carbon, sulphur, phosphorus, silicon and boron levels and use of niobium and titanium as stabilisers decreased the intergranular corrosion of 304L stainless steel [10,11]. However, nitric acid grade stainless steels such as Uranus 65 showed unacceptable corrosion rates in the condensate phase (550 mpy) during three phase corrosion

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doi:10.1016/j.jnucmat.2007.03.216

test carried out for 100 h [12,13]. Therefore, highly corrosion resistant materials like titanium and zirconium alloys are considered for such corrosion conditions [6].

Ti–5%Ta–1.8%Nb alloy is a candidate material for vessels for dissolvers and evaporators for nuclear fuel reprocessing applications [5,14]. This alloy was classified as a two phase alloy containing α (hcp) and β (bcc) phases and the β transus of this alloy is about 867 °C [15]. The present communication addresses the corrosion resistance of this alloy in different heat treatment conditions, evaluated in liquid, vapour and condensate phases of concentrated nitric acid.

2. Experimental

The Ti–5Ta–1.8Nb alloy used in the present study was produced at the Nuclear Fuel Complex, Hyderabad, by vacuum arc re-melting. The chemical composition of the alloy used in the present study was 4.39 wt% Ta, 1.8 wt% Nb, 0.03 wt% Fe, 501 wppm O, 47 wppm N, 125 wppm C, 9 wppm H, and balance Ti. The composition of CP (commercial purity) Ti was 0.04 wt% Fe, 960 wppm O, 30 wppm N, 150 wppm C, 25 wppm H, and balance Ti. The Ti–5Ta–1.8Nb alloy was supplied in the hot extruded form. Hot extrusion was carried out from the ingots of size 192 mm diameter and 200 mm length to 30 mm dia rods. These rods were cold swaged to a size of 25 mm dia, followed by annealing at 650 °C for 1 h. The rods were subsequently cold rolled to sheet form (3 mm and 1.7 mm thick).

The samples for heat treatment were cut to the desired dimensions using a diamond cutter. The heat treatments provided to the samples are summarized in Table 1. Specimens of Ti–5Ta–1.8Nb in the above heat treated condition were wet polished up to 600 grit emery paper. Specimens were degreased in acetone and dried in hot air, and weighed up to an accuracy of 0.0001 g, before exposing them to the liquid, vapour and condensate phases of 11.5 M boiling nitric acid. Samples of CP titanium were also tested under similar conditions for comparison purpose.

Table 1
Heat treatments provided to the cold rolled sheets of Ti–5Ta–1.8Nb alloy

Heat treatment	Temperature, °C	Time, h	Cooling method
Stress relieving (SR)	640	2	Air cooling
Mill annealing (MA) (after SR)	700	4	Air cooling
Solution treatment (ST) (after SR)	840	2	Water quenching
Aging (AG) (after SR and ST)	550	4	Air cooling
Over aging (OA) (after SR and ST)	700	4	Air cooling

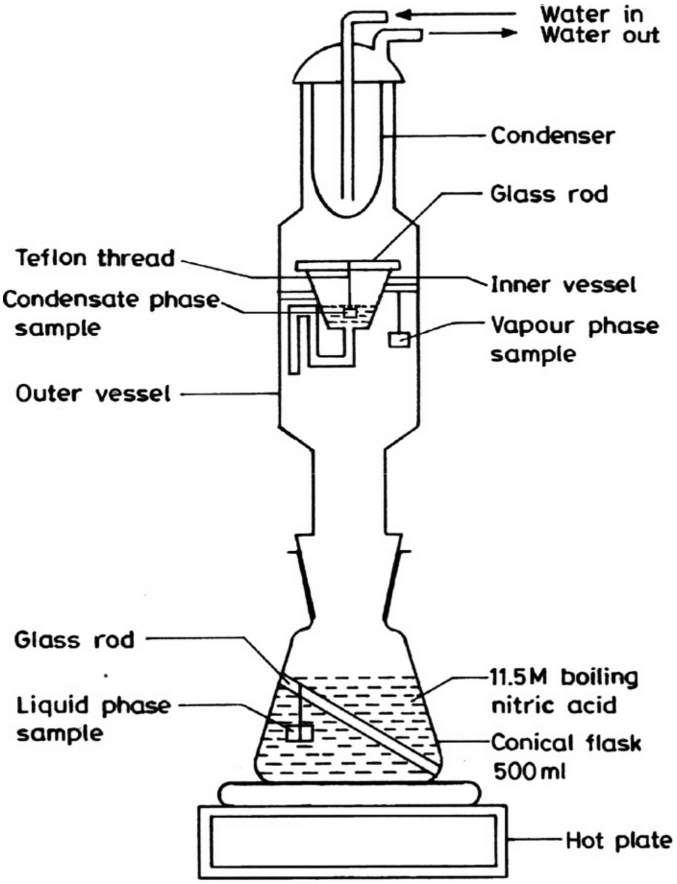

Fig. 1. Experimental arrangement for three phase corrosion study.

The experimental set up used in the present study is shown in Fig. 1, which is a modified version of the arrangement used by Furuya et al. [4]. In this testing apparatus, the corrosion rate in the condensate phase is not influenced by dissolved ions as the solution condensed in the inner vessel was automatically removed to the flask through siphon pipe and renewed at regular intervals. In the liquid zone, corrosion rate is influenced by dissolved ions and the concentrated soluble titanium ions in the solution act as corrosion inhibitor [4]. The ratio of volume of solution to the total specimen surface area in liquid, vapour and condensate phases together was about 75 ml/cm^2. The specimens were suspended in the liquid, vapour and condensate phases using Teflon thread and exposed for a total period of 240 h [16]. The specimens were removed after every 48 h, rinsed under distilled water, cleaned with acetone, dried in hot air and weight changes were recorded. The loose corrosion product present on the sample was removed during the cleaning process as it contributes to the weight loss. Fresh test solution was used for each period. Each test of 240 h duration was repeated three times to determine the variation in data. After completion of the test, the corrosion rates in individual periods and the average corrosion rate for the five individual periods were calculated.

Potentiodynamic polarisation experiments were performed using a Wenking potentiostat (Model Potentioscan POS 88). The scan rate used was 0.166 mV/s (10 mV/min). The reference electrode used was saturated calomel electrode (SCE) whose potential is +242 mV with respect to standard hydrogen electrode. The tests were carried out from 200 mV below the open circuit potential to a potential of +3500 mV vs SCE.

The effect of heat treatment on the microstructure was studied by optical microscopy. The surface microstructures of the corroded samples were studied in a ESEM Philips XL-30 scanning electron microscope. The nature of surfaces on some specific samples were also examined by Auger electron spectroscopy (AES) (OMICRON CMA 100), whereas sputtering was performed for 1 min with 3 KeV Ar ion gun and at a current density of 1 μA/cm^2.

3. Results

3.1. Microstructure

The microstructure of the as-received Ti–5Ta–1.8Nb alloy sample consisted of acicular $\alpha + \beta$ microstructure [15]. The microstructures of stress relieved, mill annealed, solution treated, and overaged samples as revealed from optical microscopy are shown in Fig. 2. The stress relieved (SR) microstructure indicated primary α and β phases (Fig. 2(a)). The mill annealed (MA) microstructure also revealed α and β phases (Fig. 2(b)), while the solution treated (ST) microstructure showed martensite (α′) and α phases (Fig. 2(c)). Over aging of the solution treated alloy resulted in coarse equiaxed α, and β along the grain boundaries (Fig. 2(d)). The microstructures of aged and over aged samples were similar.

3.2. Corrosion rate

The corrosion rates after five individual periods of Ti–5Ta–1.8Nb alloy in various heat treated conditions in liquid, vapour and condensate phases of 11.5 M boiling nitric acid are tabulated in Table 2. For conservative assessment, the maximum corrosion rate obtained out of the three sets are considered and tabulated in Table 2. The corrosion rates of CP titanium are also provided in the table. The average variation in corrosion rate data was determined to be ±0.35 mpy.

The corrosion rates for mill annealed, stress relieved, and solution treated conditions were nearly similar in each phase. The typical corrosion rate for these conditions, in

Table 2
Corrosion rate (in mpy) for three phase corrosion test in 11.5 M HNO_3

Material/condition	Liquid	Vapour	Condensate
CP–Ti	6.26	0.52	11.02
Ti–5Ta–1.8Nb–MA	0.31	0.91	2.64
Ti–5Ta–1.8Nb–SR	0.32	0.94	4.24
Ti–5Ta–1.8Nb–ST	0.12	1.47	3.26
Ti–5Ta–1.8Nb–OA	0	0.55	2.03
Ti–5Ta–1.8Nb–AG	0.1	0	1.54

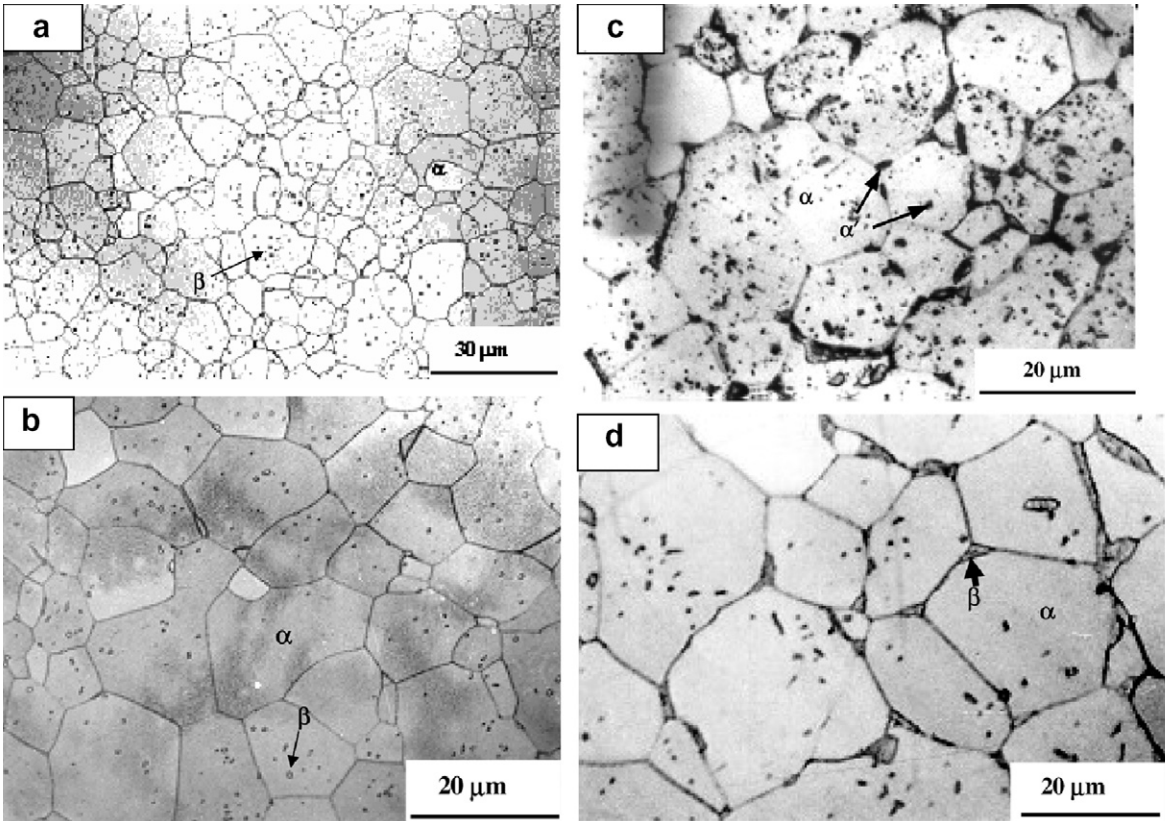

Fig. 2. Optical micrographs of microstructures of Ti–5Ta–1.8Nb alloy in (a) stress relieved, (b) mill annealed, (c) solution treated and (d) overaged conditions.

liquid phase was around 0.3 mpy, in vapour phase 0.9–1.4 mpy and in the condensate phase 2.6–4.2 mpy. The corrosion rate for the aged and over aged condition was lower compared to other heat treated conditions in all three phases. For all heat treated conditions the corrosion rate is higher in condensate phase compared to vapour and liquid phases.

3.3. Surface morphology

The surface morphologies of Ti–5Ta–1.8Nb alloy in the mill annealed condition after the three phase corrosion test in nitric acid for 240 h have been presented in Fig. 3. Uniform corrosion with microcracks and pores was observed on surface exposed to boiling liquid phase (Fig. 3(a)). In the sample exposed to vapour phase, (Fig. 3(b)) the microstructure indicated pit type of corrosion. In the condensate phase, accelerated attack was indicated (Fig. 3(c)), confirming the continuous dissolution and high corrosion rate in condensate phase.

Surface morphology of sample in overaged condition exposed to condensate phase is provided in Fig. 4(a) and

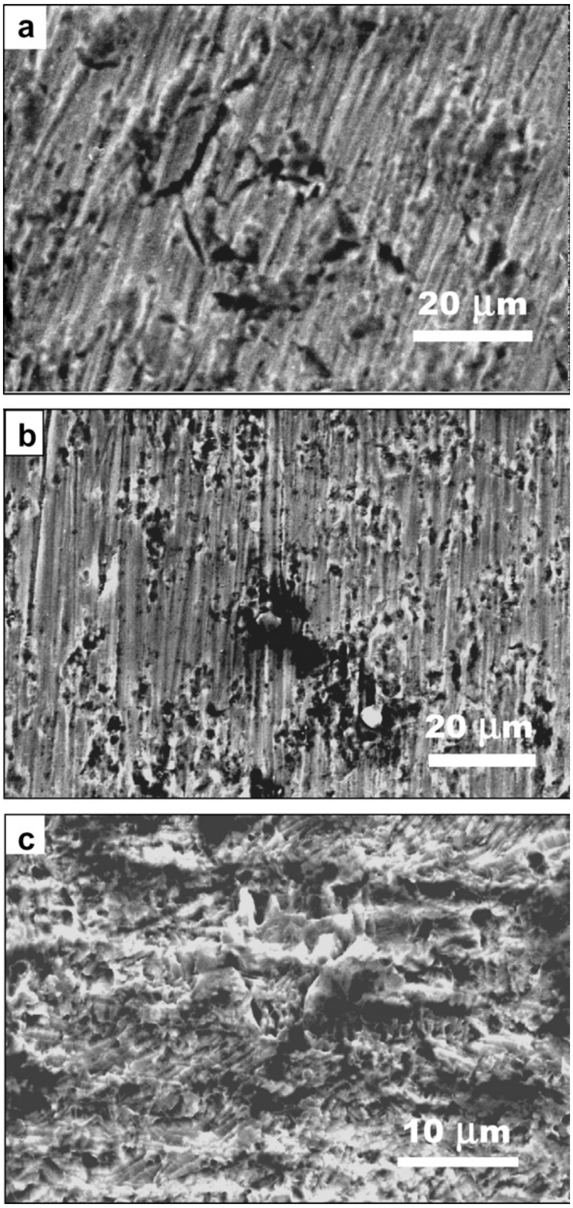

Fig. 3. Scanning electron micrographs of surface morphology of sample in mill annealed (MA) condition exposed to (a) boiling liquid phase, (b) vapour phase and (c) condensate phase of nitric acid for 240 h.

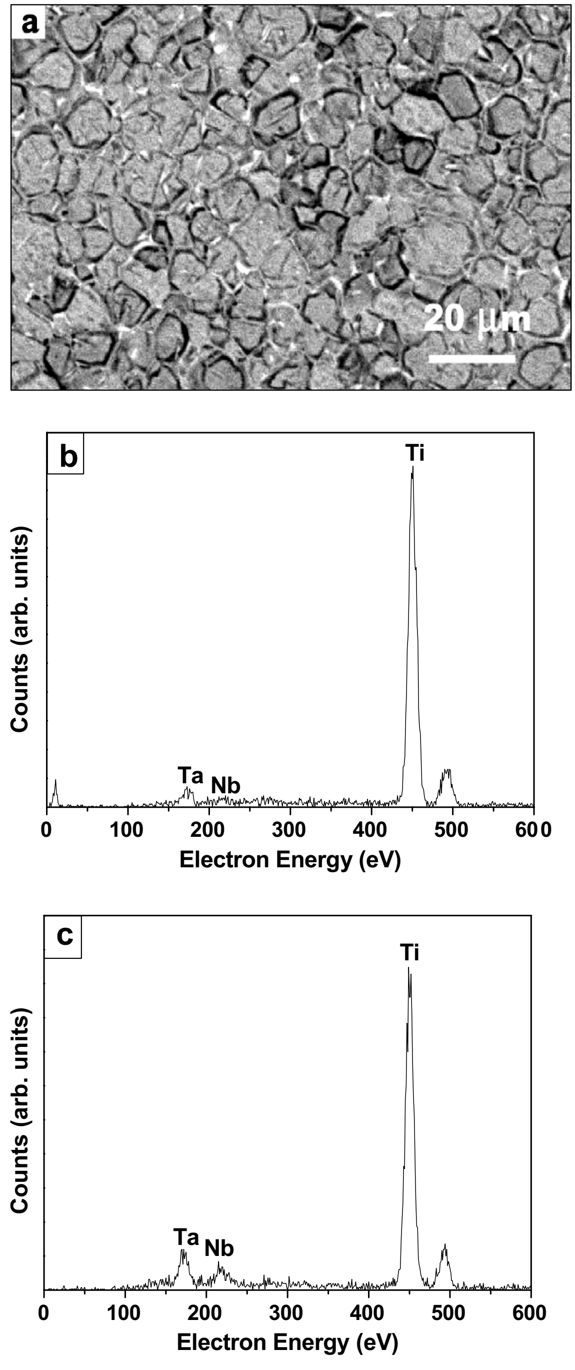

Fig. 4. (a) Scanning electron micrographs of surface morphology of sample in overaged (OA) condition exposed to condensate phase, (b) EDS spectra from the grain region and (c) EDS spectra from the grain boundary region.

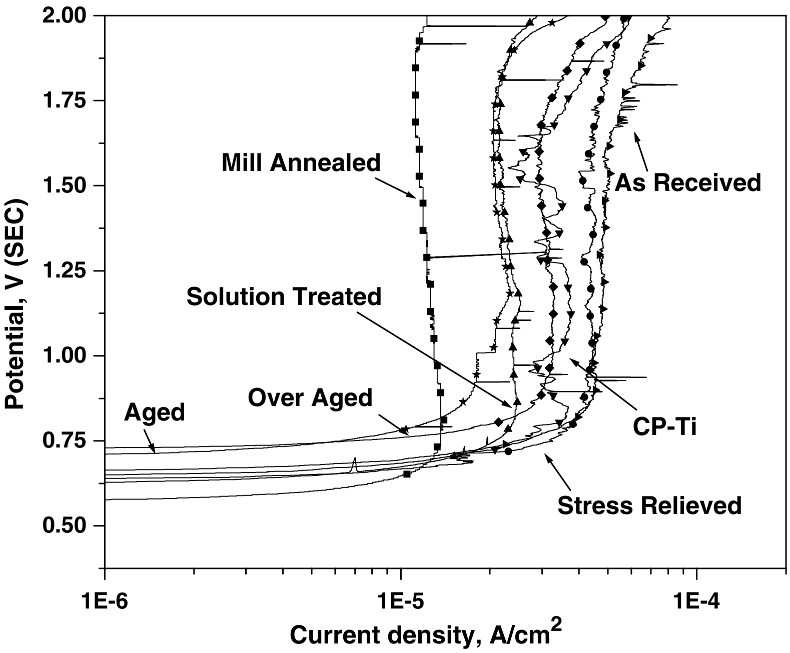

Fig. 5. Potentiodynamic anodic polarisation behaviour of Ti–5Ta–1.8Nb alloy in 11.5 M nitric acid solution at room temperature.

Table 3
Zero current potentials (ZCP) and passive current densities (i_{pass}) obtained from the potentiodynamic anodic polarisation tests

Material/condition	ZCP (mV vs SCE)	i_{pass} (A/cm^2)
CP–Ti	647	3.25×10^{-5}
Ti–5Ta–1.8Nb–As received	659	4.57×10^{-5}
Ti–5Ta–1.8Nb–MA	575	1.31×10^{-5}
Ti–5Ta–1.8Nb–SR	638	4.26×10^{-5}
Ti–5Ta–1.8Nb–ST	621	2.49×10^{-5}
Ti–5Ta–1.8Nb–OA	704	1.84×10^{-5}
Ti–5Ta–1.8Nb–AG	726	3.20×10^{-5}

the EDS spectra from the grain region and from the grain boundary region of Fig. 4(a) are provided in Fig. 4(b) and (c) respectively. This figure will be discussed in the next section.

3.4. Electrochemical behaviour

The potentiodynamic anodic polarisation behaviour of CP–Ti and Ti–5Ta–1.8Nb alloy has not been reported in highly concentrated (11.5 M) nitric acid. The potentiodynamic anodic polarisation curves for the Ti–5Ta–1.8Nb alloy in different heat treated condition and CP titanium in 11.5 M HNO_3 at room temperature have been compared in Fig. 5. The zero current potential and passivation current density values obtained from the polarisation curves of Fig. 5 are tabulated in Table 3.

4. Discussion

The oxidation potential of boiling HNO_3 is high enough to form protective (rutile) TiO_2 on the surface of titanium [2]. The decreasing corrosion rate in the liquid and vapour phases and continuous dissolution in the condensate phase for Ti–5Ta–1.8Nb alloy can be explained as follows. The presence of protective passive film on the samples tested in liquid and vapour phases was confirmed by color changes of the surface. The surface film on the alloy exhibited various colours from pale yellow to greenish colour after testing in liquid phase, and yellow colour after testing in vapour phase. In the sample tested in the condensate phase, the surface colour turned grey. The yellow colour film on titanium indicates an oxide film thickness of 100–250 Å, while a bluish green colour indicates film thickness from 700 to 1700 Å [6]. The oxide that formed on the sample tested in liquid phase was thicker compared to that on the sample tested in vapour phase. This may be related to the lower corrosion rate observed in the liquid phase compared to vapour phase.

The AES spectra from the unexposed and condensate phase exposed surfaces of CP titanium and Ti–5Ta–1.8Nb alloy in aged condition were presented in Figs. 6 and 7, respectively. Samples that were unexposed as well as exposed to condensate phase were compared for both CP titanium and Ti–5Ta–1.8Nb alloy. The AES spectra indicated that the surface chemical compositions were not much different for unexposed and condensate phase exposed samples of CP titanium and Ti–5Ta–1.8Nb alloy. This revealed that the nature of the surface film that formed on exposure to the condensate phase was similar to that in the unexposed state. The continuous dissolution of the Ti–5Ta–1.8Nb alloy in the condensate phase may also be due to the formation of unstable hydrated TiO_2 film, as reported by Steele [3]. In the case of the surfaces

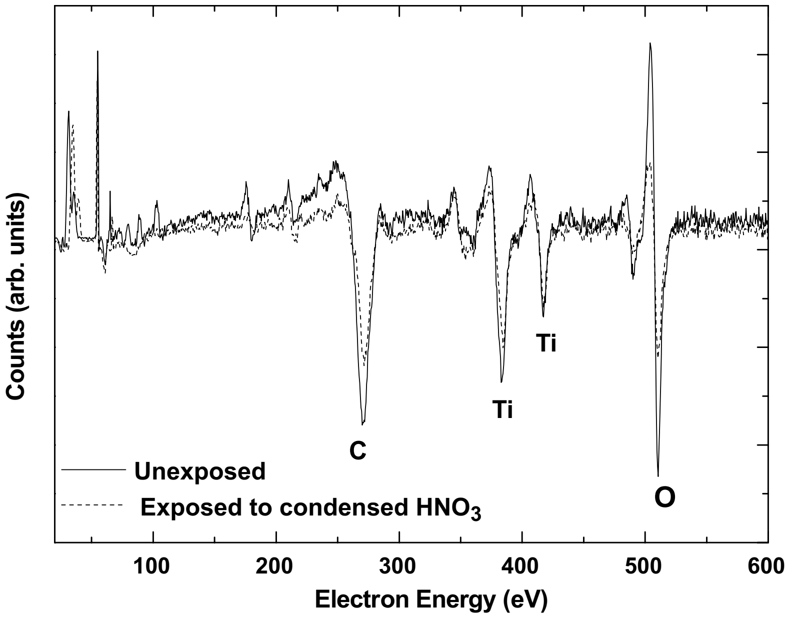

Fig. 6. AES spectra from the surface of unexposed CP–Ti and CP–Ti exposed to condensed HNO_3 for 240 h.

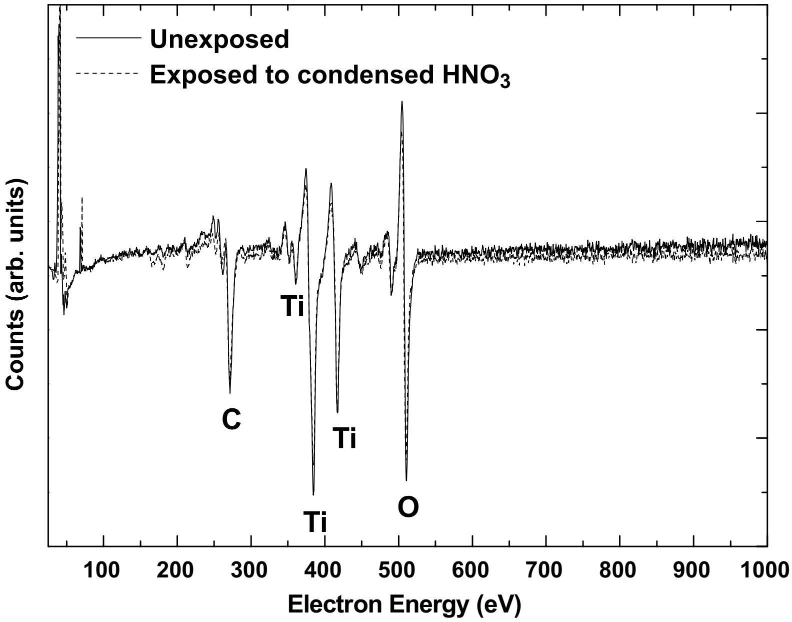

Fig. 7. AES spectra from the surface of unexposed Ti–5Ta–1.8Nb alloy and Ti–5Ta–1.8Nb alloy exposed to condensed HNO_3 for 240 h in AG condition.

of CP titanium and Ti–5Ta–1.8Nb exposed to liquid phase for 240 h, charging was observed during AES analysis and, therefore, AES spectra could not be obtained. This charging indicated that a stable, highly non-conducting surface film was formed on the surface after exposure in the liquid phase. Neville and Xu [17], reported that an enrichment of Mo was detected on Ti 5111 from the corrosion product at the pit site. It was also reported that the top passive film was enriched in titanium, due to preferential dissolution of Mo in Mo–Ti alloys in concentrated HCl. The lower corrosion rate and charging of the sample exposed to boiling nitric acid observed in our study is perhaps due to the enrichment of tantalum and niobium and preferential dissolution of titanium in top passive film.

The lower corrosion rate determined in the liquid phase can be explained by the self inhibiting effect of titanium ions in the liquid phase. This has been reported for the corrosion of CP titanium in 6 M HNO_3 [18]. In the condensate phase, there is solution renewal resulting in nitric acid with lack of titanium ions [4], which leads to higher corrosion rate, as observed in the study. The higher corrosion rate of CP titanium in liquid phase compared to Ti–5Ta–

1.8Nb may be due to lack of niobium and tantalum to enhance the protective properties of the surface film.

The corrosion rate for the aged and over aged condition was lower compared to other heat treated conditions. Mythili et al. [19] reported that aged microstructure is beneficial with respect to corrosion resistance since the microstructure consists of equiaxed α and the minimum amount of β distributed at the grain boundaries. In order to understand this further, local compositional analysis were obtained from the grain and grain boundary region of Ti–5Ta–1.8Nb alloy in OA condition exposed to condensate phase for 240 h (Fig. 4(a)). The compositions were determined using X-ray energy dispersive spectroscopy (EDS) available on the SEM. The analysis revealed tantalum and niobium were enriched along grain boundaries (9.21% Ta and 3.35% Nb) (Fig. 4(c)), while they were depleted inside the grain (4.4% Ta and 1.34% Nb) (Fig. 4(b)). A two phase structure is always detrimental from corrosion point of view. Therefore, alloying tantalum and niobium within a stable α phase region must be beneficial for long term corrosion resistance. As the ternary phase diagram for Ti–Ta–Nb system is not available, the maximum solubilities of tantalum and niobium in α titanium could not be found. From the EDS results, it appears that the maximum solubility of tantalum and niobium in α grain after aging was 4.4% and 1.34%, respectively. In view of this, an alloy of composition Ti–4.4%Ta–1.34%Nb should exhibit good corrosion resistance. This alloy might exhibit a single phase structure and, as the tantalum and niobium content, are lower, the alloy would be slightly more economical.

The higher corrosion rate for MA, SR and ST condition compared to the aged and over aged condition might be due to the presence of acicular α or α′ in the microstructure of MA, SR and ST condition. Fukuzuka et al. [20] reported that corrosion resistance is greatly deteriorated due to the acicular α phase present in CP titanium. It has been postulated that galvanic attack takes place between the alpha and beta interfaces when titanium is exposed to nitric acid, such that corrosion penetrates along the needles [21].

The zero current potentials was more noble for the OA and AG conditions compared to other heat treated conditions (Table 3). The corrosion rates determined in three phase corrosion tests were also lower for the OA and AG conditions. In these conditions, the microstructure was more homogeneous compared to other heat treated conditions. This homogeneity may be responsible for the shifting of potentials towards noble direction and subsequent lower corrosion rate. In concentrated nitric acid medium, 304L stainless steel and zirconium will undergo transpassive dissolution [3,22] while CP–Ti and Ti–5Ta–1.8Nb alloy does not undergo such transpassive dissolution as observed from the potentiodynamic polarisation curves. The potentiodynamic anodic polarisation of Ti–5Ta–1.8Nb alloy in all the heat treated conditions (Fig. 5) indicated good passivation properties, based on passive current density.

5. Conclusions

The corrosion behaviour of Ti–5Ta–1.8Nb alloy was evaluated in liquid, condensate and vapour phases of concentrated nitric acid. The effect of heat treatment on corrosion behaviour was addressed. The following were the salient conclusions of the study:

1. The corrosion rate in condensate phase was higher than in liquid and vapour phases in all heat treated conditions. The lower corrosion rate in the liquid and vapour phases has been related to the presence of protective rutile on the surface. The self inhibiting effect of titanium ions has been utilized to explain the lower corrosion rate measured in the liquid phase compared to the vapour phase.
2. The corrosion rate was similar in liquid, condensate and vapour phases for stress relieved, mill annealed and solution treated condition. The corrosion rate for aged and overaged condition were lower compared to other heat treated conditions. The reason for the improved corrosion resistance for aged and over aged condition has been attributed to homogeneous phase distribution. The higher corrosion rate observed for the SR, MA and ST conditions has been attributed to the acicular microstructure.
3. Potentiodynamic anodic polarisation studies indicated good passivation nature for all heat treated conditions.
4. The corrosion rate for Ti–5Ta–1.8Nb alloy in all the phases was lower compared to CP titanium.

Acknowledgements

The authors would like to acknowledge Mr R.V. Subba Rao, Dr G. Amarendra and Dr P. Shankar of Indira Gandhi Centre for Atomic Research, Kalpakkam, for AES and SEM analyses.

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