Surface & Coatings Technology 235 (2013) 155–164

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Refractory metal coatings on titanium to improve corrosion resistance in nitric acid medium

A. Ravi Shankar, U. Kamachi Mudali *

Corrosion Science and Technology Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, 603 102, India

ARTICLE INFO

Article history:
Received 9 March 2013
Accepted in revised form 8 July 2013
Available online 15 July 2013

Keywords:
Titanium
Refractory coating
Corrosion resistance
Nitric acid
XRD
SEM

ABSTRACT

Commercially pure titanium (Cp-Ti) is used as structural material in chemical processing industry where nitric acid is used as process medium. The corrosion resistance of titanium can be further improved by coating highly corrosion-resistant materials. Tantalum and niobium possess excellent corrosion resistance to nitric acid solutions of high concentrations and temperatures. In the present study refractory metal coatings of Ta, Nb and Ta + Nb were prepared by a simple thermo-chemical decomposition technique on titanium to improve corrosion resistance in nitric acid medium. The surface of titanium samples was applied with a solution containing oxides of Ta and/or Nb and treated at 1273 K for 5 h in vacuum. Characterization of the coated samples before and after corrosion test was carried out using Scanning Electron Microscopy (SEM), Energy Dispersive analysis of X-rays (EDX) and X-ray diffraction (XRD). SEM, EDX and XRD results confirmed the presence of refractory metal coatings on Ti. ASTM A262 practice-C test was conducted in boiling 65% nitric acid. Corrosion tests showed that Ta + Nb coated sample has four times better corrosion resistance than uncoated Ti and is only marginally higher than Ti–5Ta–1.8Nb alloy. The coating characteristics and corrosion resistance of Ta + Nb coated sample were found to be reproducible. XRD pattern of as-coated and corrosion tested surfaces is similar in Ta and Ta + Nb coated samples while α-Ti phase was observed in Nb-coated sample after corrosion. Three phase corrosion tests were also conducted on Cp-Ti, Ti–5Ta–1.8Nb alloy and Ta + Nb-coated Cp-Ti samples in boiling liquid, vapour and condensate phases of nitric acid. The corrosion rate of Ta + Nb coating was found to be higher in three phase corrosion test, however, a decreasing trend of corrosion rate was noticed with time. The paper highlights the results of the present investigation.

1. Introduction

Nitric acid is used as process medium in chemical processing industry and for spent nuclear fuel reprocessing application. Titanium (Ti) is widely used in the chemical processing and nuclear fuel reprocessing applications because of its good corrosion resistance in nitric acid medium [1,2]. However titanium exhibits high corrosion rate in vapour and condensate phases of nitric acid, due to less protective oxide film formation [3]. Ti–5Ta–1.8Nb is an indigenously developed alloy for improving corrosion resistance in nitric acid of high concentrations and temperatures [4]. However, due to high cost and limitations due to availability and fabricability of tantalum and niobium alternate methods were envisaged to improve corrosion resistance in nitric acid service.

Refractory metals like tantalum (Ta) and niobium (Nb) exhibit excellent corrosion resistance in nitric acid medium compared to titanium. Ta and Nb are the most corrosion-resistant metals to nitric acid at all concentrations and temperatures as high as 523 K because of the stable protective oxide passive films formed on their surface [5]. Niobium has excellent corrosion resistance to nitric acid (~0.25 mm/year in 70% HNO_3 at 523 K) [6]. Tantalum on the other hand is inert to nitric acid solutions of all concentrations and all temperatures, and the corrosion resistance is not reduced in the presence of chlorides in acid [7]. Therefore protective coatings of Ta and Nb can be effectively used for corrosion control and can provide long-term protection to Ti. Physical vapour deposition techniques such as sputtering, evaporation, and laser ablation deposition can be used but they have limitations in coating components of intricate geometries as they are line of sight processes. Niobium has been deposited on Ti by sputtering technique and plasma immersion ion implantation for improving corrosion resistance for biomedical and dental implant applications [8]. Among other techniques, Mehmood et al. [9] and Cardarelli et al. [10] deposited tantalum by molten salt electrodeposition, while Koivuluoto et al. [11] deposited by cold spraying technique. Chemical vapour deposition (CVD) technique is the most commonly used technique and Tantaline Inc, Massachusetts, USA has made corrosion-resistant Ta coating on 316 L SS by CVD technique [12,13]. Tantalum surface alloyed components developed by Gambale

* Corresponding author. Tel.: +91 44 27480121; fax: +91 44 27480301.
E-mail address: kamachi@igcar.gov.in (U. Kamachi Mudali).

0257-8972/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2013.07.028

et al. [14] are being used for corrosive hydrogen production process as well. However the organometallic precursors used in CVD such as tantalum dichloro-diethyoxy-acetylacetonate, penta-dimethyl-amino-tantalum, tantalum-chloro-tetradipivaloylmethane, tantalum penta-methoxide etc are scarcely available and expensive.

In the present study refractory metal coatings on commercially pure titanium (Cp-Ti) was attempted by a simple thermo-chemical diffusion method. The experiments were performed to obtain Ta, Nb and Ta + Nb coating on Cp-Ti using a solution containing oxide powders of Ta and Nb. The corrosion behavior of coatings was studied by ASTM A262 practice-C test and by three phase corrosion test and the results were compared with candidate materials like Cp-Ti and Ti–5Ta–1.8Nb alloy.

2. Experimental Details

Cp-Ti samples of size 20 × 12 × 3 mm were polished up to 80 grit emery paper. Three different solutions containing tantalum oxide, niobium oxide and tantalum oxide + niobium oxide were prepared. The solution used should be such that it can be applied over the entire surface with a paint brush and achieve uniform coating on the surface. The solution should have sufficient viscosity to hold the oxide particles on the entire surface, and solution should decompose or evaporate during heat treatment and allow the refractory particles to react/diffuse. The solution was prepared by mixing glycerol with sufficient amount of fine refractory oxide powder. The solution thus prepared in the form of paint was applied over the entire surface using paint brush. The coated samples were heat treated in a vacuum furnace at 1273 K for 5 h to form Ta, Nb and Ta + Nb coatings by metallothermic reduction.

In order to assess the corrosion performance, ASTM A262 Practice-C test [15] was carried out on Cp-Ti, Ti–5Ta–1.8Nb alloy and coated Cp-Ti samples in boiling 65% nitric acid. ASTM A262 Practice-C test simulate the conditions in liquid phase corrosion and does not consider the effects of vapour and condensate phase nitric acid corrosion and therefore the test represents for application below boiling point. Cp-Ti and Ti–5Ta–1.8Nb alloy samples were polished up to 600 grit emery paper while coated Cp-Ti samples were tested in the as-coated condition. The samples were immersed in boiling nitric acid using Teflon thread for a total period of 240 h. The test was carried out for 48 h and weight losses were recorded and the corrosion rates were calculated. Every 48 h fresh test solution was used and the test was repeated for five such 48 h periods and average corrosion rates were calculated. The details of corrosion test and experimental set up are described elsewhere [16,17]. To check the reproducibility of the coating process and corrosion resistance, the optimum coating process on Cp-Ti and subsequent characterization was repeated. In order to further understand the corrosion behaviour of optimum coating on Cp-Ti samples, three phase corrosion test was carried out. Titanium and its alloys can be used for nitric acid applications below boiling point of nitric acid and also above boiling point. However, when titanium and its alloys are exposed to nitric acid above boiling point, high corrosion rates were observed under nitric acid vapours and trickling condensates [3–5]. This is because the Ti ions released due to corrosion in vapour/condensate phase are collected in the boiling liquid solution and as a result the concentration of Ti ions in the boiling solution increases. The lack of Ti ions in the vapour/condensate region leads to accelerated corrosion due to the formation of non protective films while the excess Ti ions in the boiling liquid solution has an inhibiting effect. Therefore for application of titanium and its alloys in nitric acid medium above boiling point, three phase corrosion test was proposed which simulates the above conditions. The samples of desired size were prepared and tested by three phase corrosion test and the results were compared with other candidate materials like Cp-Ti and Ti–5Ta–1.8Nb alloy. The test was carried out in boiling 11.5 M nitric acid by suspending the samples in boiling liquid, vapour and condensate regions using Teflon thread for a total of 240 h. After every 48 h periods corrosion rate was calculated and the test was continued with fresh test solution. The average corrosion rate was calculated from the individual corrosion rates based on the samples weight losses after each 48 h test. The details of three phase corrosion test setup and experimental details are

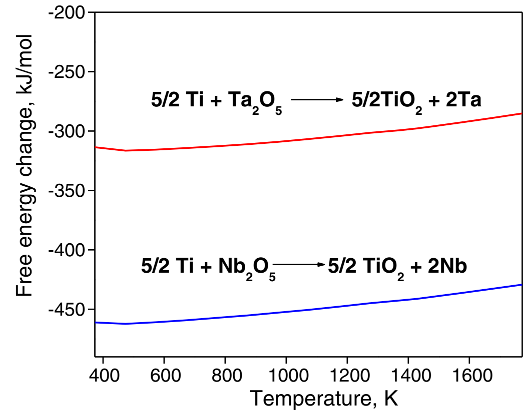

Fig. 1. Free energy change versus temperature graph for Ta and Nb reduction reaction.

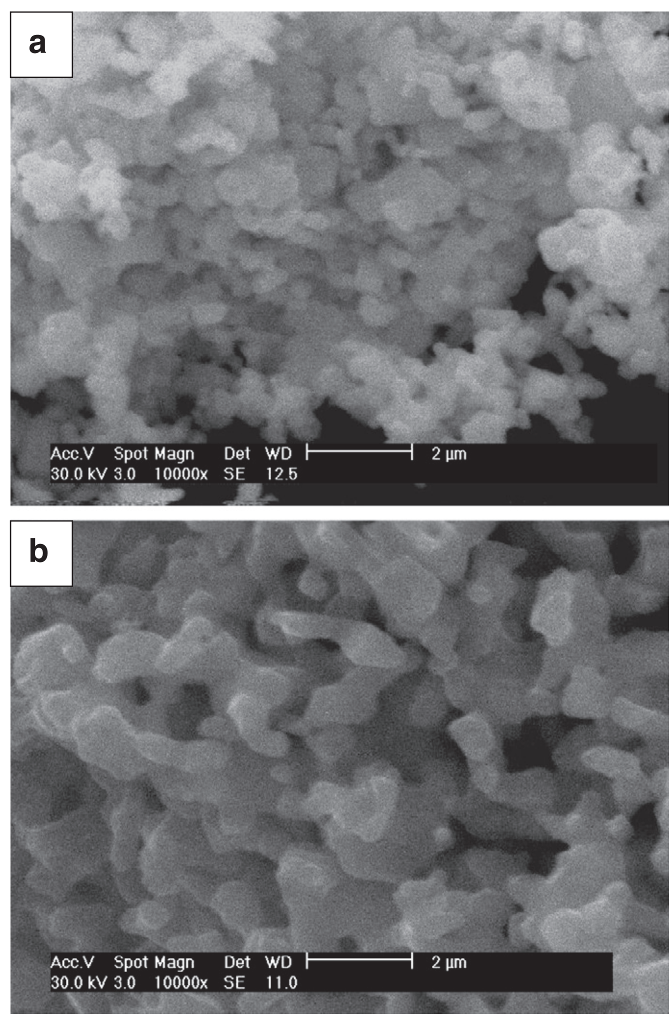

Fig. 2. SEM micrograph of (a) Ta_2O_5 and (b) Nb_2O_5 powder used for coating.