Applied Mechanics and Materials
ISSN: 1662-7482, Vols. 148-149, pp 534-537
doi:10.4028/www.scientific.net/AMM.148-149.534

Online: 2011-12-22

An Effective Approach to Improve the Oxidation Resistance of Ti-6Al-4V Alloy by Combination of Phosphorization and Silica Coating

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Keywords: Ti-6Al-4V; phosphorization; sol-gel derived silica coating; oxidation resistance

Abstract. A very effective approach to improve the oxidation resistance of Ti-6Al-4V alloy was proposed. The Ti-6Al-4V alloy was firstly phosphated and then coated by silica using sol-gel dip-coating technique. A duplex layer of TiP_2O_7 and amorphous silica was synthesized at the alloy surface. The isothermal and cyclic oxidation behavior of the treated alloy with silica coating and the corresponding bare alloy was investigated at 600 ^oC in static air to investigate the synergetic effect of phosphorization and amorphous SiO_2 coating on the oxidation resistance of the alloy. The isothermal and cyclic oxidation resistances of the alloy were greatly improved.

Introduction

Titanium and its alloys are widely used in the aerospace, automobile, biomedical, energy industry, and military applications due to their high strength, high-melting point, and good biocompatibility [1, 2]. The ductility of Ti-based alloy at room temperature has been improved greatly by alloying and microstructure controlling. However, the poor oxidation resistance is an obstacle to its practical applications due to the formation of less protective rutile TiO_2 on the surfaces during exposure to high temperature environments [3, 4].

Most of these methods need expensive apparatus, or time-consuming, or high-temperature treatment that limits their applications to thermally stable coatings. Sol-gel processes have been widely used to prepare various thin films for modifying the surface properties by low temperature treatment without altering the original properties of strength and toughness of the substrates [5, 6]. One of the most important advantages of the sol-gel technique is the ability to produce very small particles-usually in the nano-scale range. Coatings based on sol-gel technique have been applied to improve the oxidation resistance of intermetallic compounds α_2-Ti_3Al or γ-TiAl [7-11]. The surface treatment before the deposition of desired materials may play key role in the adhesion of the coating to the substrate. Herein, we used phosphorization technique to treat the surface of Ti-6Al-4V alloy, subsequently; the treated alloy was coated by silica coating derived from sol-gel dip-coating for the first time with the aim to investigate the synergetic effect on the oxidation resistance of the alloy.

Material and methods

Preparation of the phosphated specimens. The cut specimens with dimensions 10 x 12 x 2.0 mm using a spark wire machine from commercial Ti-6Al-4V alloy were polished on SiC paper up to the 1000 # polishing grade. The samples were degreased ultrasonically in acetone, cleaned by distilled water and dried in air before use. The degreased samples was put into the 85% phosphoric acid for 1 min, and then air dried for at least 12 h prior to further operations. The dried specimen was put into argon atmosphere, heated from ambient to 800 ^oC at 10 ^oC /min, maintained at this temperature for 5 min, then cooled down to ambient at 50 ^oC /min. Dip-coating.SiO_2 precursor solution was prepared as the method described in Ref. [11]. The specimens with chemical treatment were dipped into the SiO_2 sol and withdrawn at a rate of 1 cm/min using a dip-coating equipment, dried in air for 20 min at room temperature, and then dried at 75 °C in a vacuum dry oven stove for 40 min. Heat treatment in argon atmosphere was carried out after repeating five times dipping in argon atmosphere. The level furnace was then heated up to 150 °C at a rate of 5 °C /min, kept at the temperature for 1 h, and then heated up to 350 °C at the same heating rate and kept the temperature for 1 h, and finally it was heated up to 600 °C and kept the temperature for 3 h. The specimens were dipped for 15 times and sintered for three times.

Oxidation test and characterization. The specimens were oxidized discontinuously in air at 600 °C for times up to 100 h. A balance with an accuracy of 10^{-5} g was employed to characterize the oxidation kinetics. The specimens were kept in the furnace at the desired temperature for 1 h and then taken out to cool for 20 min in air at room temperature. This process was defined as one cycle, and the cycle was repeated 100 times. The surface morphologies and cross-sections of the oxidized samples were characterized by SEM/EDS, while the phase compositions of the oxide scales were analyzed using an XRD with Cu K_α radiation.

Results and discussion

Characteristics. The XRD patterns of the bare alloy and the phosphated alloy in the absent of SiO_2 coating are compared in Fig. 1, exhibiting peaks assessed to TiP_2O_7 as well as the substrate peaks. The three peaks characteristic of titanium pyrophosphate are observed which confirms that TiP_2O_7 is able to form during the heating ramp going to 800 °C. The TiP_2O_7 thin film on the surface of the alloy can act as an efficient diffusion barrier at high temperature [12], giving rise to a reduction in oxidation rate, as illustrated in the following oxidation kinetics behavior.

Very fine crystalline was observed on the surface of Ti-6Al-4V alloy after the chemical treatment. After chemical treatment, the specimens were coated by SiO_2. The deposited silica was amorphous, as reported in our previous paper [10, 11]. SEM revealed that the surface of the phosphated alloy with amorphous silica coating was homogeneous. Additionally, some pores and microcracks were observed on the surface of the thin film, attributing to the decomposition of organic component and the shrinkage of the thin film during heat treatment.

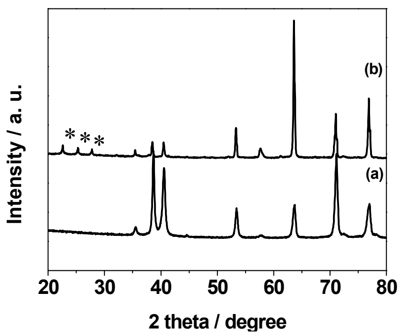

Fig. 1 XRD patterns of (a) the bare alloy and (b) the phosphated specimen without silica coating. The registered peaks are indexed to TiP_2O_7 and the other peaks are assigned to the substrate.

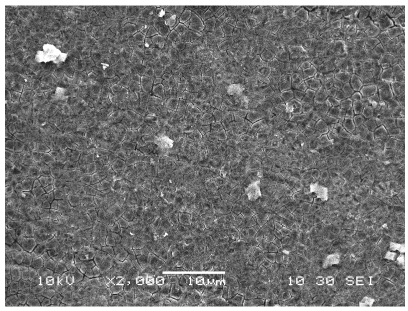

Fig. 2 Secondary electron images for the surface morphologies of the phosphated specimen with silica coating.

Oxidation kinetics. The mass gain of the phosphated specimens with silica coating was much lower than that of the bare alloy due to the co-existence of TiP_2O_7 and silica coating, indicating that the synergetic effect of surface treatment and silica coating greatly reduced the oxidation rate of Ti-6Al-4V alloy, as shown in Fig. 3. The average parabolic rate constants (k_p) of the treated alloy and the bare alloy were 3.26 x 10^{-13} and 3.25 x 10^{-11} g^2 cm^{-4} s^{-1}, respectively. The phosphated specimens with silica coatings exhibited much smaller parabolic rate constants than only silica coated one, suggesting that the chemical pretreatment benefited the oxidation resistance.

The cyclic oxidation kinetics curve for the bare alloy clearly demonstrated the characteristics of spallation, which occurred after 50 cycles. On the contrary, the coated specimens had the similar oxidation kinetics to the isothermal oxidation. The mass gain of the pretreated samples with silica coating kept increasing, as shown in Fig. 4, suggesting that the oxide scale formed on the coated specimen did not spall off during the whole cyclic oxidation test.

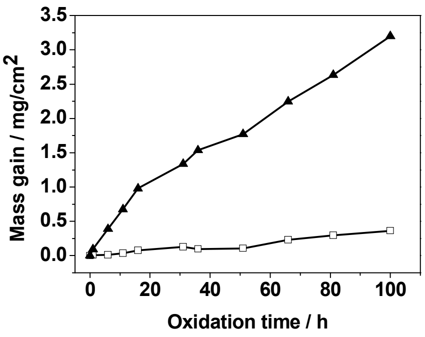

Fig. 3 Isothermal oxidation kinetics curves of the blank (filled triangle) and phosphated (open square) specimens with silica coating at 600 °C in air.

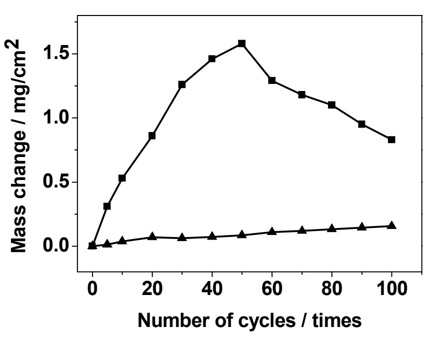

Fig. 4 Cyclic oxidation kinetics curves of the blank (filled square) and phosphated (filled triangle) specimens with silica coating at 600 °C in air.

Scale compositions. The phase compositions from XRD analysis of the oxide scales on the specimens oxidized for 100 h in air at 600 °C were shown in Fig. 5. For blank and coated specimens, the oxide scales formed on the surface were mainly rutile TiO_2. No diffraction signals assigned to α-Al_2O_3 phase were detected on two cases, possibly due to the lower content of alumina in the oxide scale than the detection limit. The peak registered to amorphous silica was detected. Furthermore, the peaks indexed to TiP_2P_7 were almost observed on the phosphated specimen since the shield effect of silica and titanium dioxide.

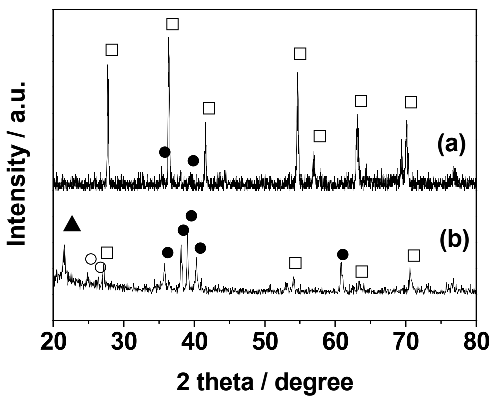

Fig. 5 XRD patterns of (a) bare alloy, and (b) phosphated alloy with silica coating. ●: alloy substrate, ○: TiP_2O_7, □: rutile titania, and ▲: SiO_2.

Scale morphologies. The loose and porous scales formed on the uncoated specimens were stratified, and much thicker than that on the coated ones, as shown in Fig. 6. The layer of TiO_2 and the mixture of minor amount Al_2O_3 and abundant TiO_2 was alternated after 100 h oxidation at 600 °C in air. The cross section of the phosphated specimen with silica coating was complex. The outmost layer was a discontinuous layer of TiO_2, which followed by complex intermediate layer (dark and white) plus an innermost continuous layer of TiP_2P_7 (gray). The intermediate layer was comprised of the deposited silica and newly formed rutile TiO_2.

The results obtained in the present examination showed that the combination of pretreatment and sol–gel SiO_2 films have beneficial effects on the oxidation resistance of Ti-6Al-4V in air. The present approach lead to drastic decrease in oxidation rates, elimination of spallation of the oxide scales during the cyclic oxidation.

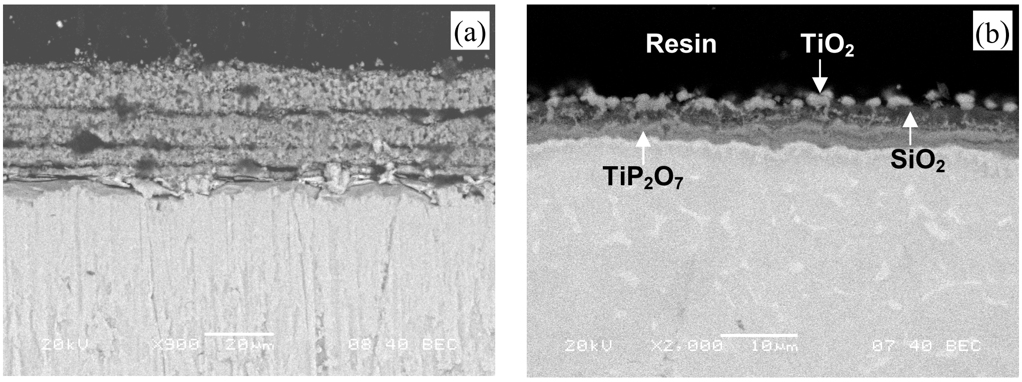

Fig. 6 Backscattered electron images for the cross-sectional morphologies of (a) blank and (b) phosphated one with silica coating after 100 h oxidation in air at 600 ^oC.

Summary

Phosphorization and subsequent deposition of silica film using sol-gel dip-coatings process were combined to improve the oxidation resistance of Ti-6Al-4V alloy. A layer constituted of TiP_2O_7 acting as a diffusion barrier was identified at the Ti-6Al-4V substrate surface after chemical treatment. The average parabolic rate constants of the treated specimens with silica coating was about two orders of magnitude smaller than those for the bare alloy. Spallation was greatly reduced on the pretreated alloy with silica coatings.

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