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ScienceDirect

JOURNAL OF RARE EARTHS, Vol. 33, No. 2, Feb. 2015, P. 221

JOURNAL OF RARE EARTHS

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Study of yttrium and cerium on the oxidation resistance of silicide coatings prepared on Ti-6Al-4V alloy by pack-cementation process

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Received 17 April 2014; revised 8 August 2014

Abstract: Pure silicide coating and Y-Ce modified silicide coating were prepared on Ti-6Al-4V alloy by pack-cementation process. The structures as well as the isothermal oxidation behaviors of the coatings were comparatively studied. The results showed that both pure silicide coating and Y-Ce modified silicide coating prepared at 1080 ºC for 4 h were composed of a $TiSi_2$ outer layer, a TiSi middle layer and a Ti_5Si_4 inner layer. The oxidation tests showed that the Y-Ce modified silicide coating possessed much better oxidation resistance than the pure silicide coating at 1000 ºC, implying the beneficial effects of Y and Ce on the oxidation resistance of the coating.

Keywords: Ti-6Al-4V alloy; silicide coating; oxidation resistance; Y-Ce modification; rare earths

Titanium alloys are widely used in aerospace and power industries where high specific strength and stiffness are required[1,2]. With the use of titanium alloys, potential component weight savings of about 50% can be achieved compared to the conventional super alloys[3]. However, the oxidation resistance of titanium alloys is rather poor at temperatures above 550 ºC, as a result of the formation of a fast growing, non-protective TiO_2 scale, and this had seriously impeded their practical applications[4]. Two traditional approaches to protecting titanium alloys from oxidation at high temperature are alloying and/or applying protective coatings[5,6].

Intensive studies proved that alloying elements such as Al and Si can improve the high temperature oxidation resistance of titanium alloys effectively. However, addition of Si or Al requires either a silicon concentration more than 40 at.% or an aluminum concentration more than 50 at.% for a protective SiO_2 or Al_2O_3 scale formation[5]. The high concentration of Si or Al in the alloys would usually lead to deterioration of the mechanical properties of the alloys such as high temperature strength and room temperature ductility[7,8]. Therefore, the proper method of improving the high-temperature oxidation resistance of titanium alloys could be the protective coating method. Specially, silicide coatings can offer relative good oxidation resistance at high temperatures for titanium alloys due to the formation of amorphous SiO_2 scale, which may flow and heal cracks at high temperature[9].

However, the brittleness of pure silicide coatings hindered their long-term applications seriously[10]. Adding active elements such as Y or Ce to the coatings has proved to be available to refine the grain sizes and modify the brittleness of the coatings, and correspondingly reduces the oxidation rate and improves the adherence of the oxide layer[11–13]. However, few studies focused on the adding of Y and Ce into the coating simultaneously[14]. In this study, both pure silicide coating and Y-Ce modified silicide coating were prepared on Ti-6Al-4V alloy by pack-cementation process. The structures as well as the isothermal oxidation behaviors of the pure silicide coating and Y-Ce modified silicide coating at 1000 ºC were comparatively studied, in order to investigate the beneficial effects of Y and Ce on the oxidation resistance of silicide coatings.

1 Experimental

Commercially Ti-6Al-4V alloy substrates were cut into 10 mm×10 mm×5 mm coupons whose surfaces were polished up to $1000^{\#}$ SiC paper and ultrasonically cleaned in an ultrasonic acetone bath.

The pack mixtures used to prepare the pure silicide coatings and Y-Ce modified silicide coatings were respectively composed of $10Si\text{-}5AlCl_3\cdot 6H_2O\text{-}85Al_2O_3$ (wt.%) and $10Si\text{-}1.5Y_2O_3\text{-}1.5CeO_2\text{-}5AlCl_3\cdot 6H_2O\text{-}82Al_2O_3$ (wt.%). Si, Y_2O_3 and CeO_2 powders were used as the donor sources, $AlCl_3\cdot 6H_2O$ was used as the activator while Al_2O_3 was used as the filler. The powders were

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Foundation item: Project supported by the Shanxi Science and Technology Research and Development Program (2013KJXX-08)

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DOI: 10.1016/S1002-0721(14)60406-3

weighed according to the ratio and mixed appropriately. The particle sizes of each kind of the powders were less than 50 μm. The coatings were prepared by burying the substrates in the pack powders in an alumina crucible, which was sealed with Al_2O_3-based silica sol binder. An electric-tube furnace was employed for the preparation of the coatings. The deposition temperature was chosen as 1080 ºC and the holding time was chosen as 4 h. The furnace was heated to the desired deposition temperature at a rate of 15 ºC/min.

The oxidation behavior of the base alloy and coated samples were isothermally oxidized at 1000 °C in air in an electric furnace. The mass changes of each sample before and after oxidation tests were weighed using an electronic balance with an accuracy of 0.01 mg.

X-ray diffraction (XRD, Panalytical X'Pert PRO) was employed to identify the phases of the coatings and the oxide scales. A scanning electron microscope (SEM, JSM-6360LV) equipped with an energy dispersive spectroscopy (EDS) was employed to identified the microstructures and chemical compositions of the constituent phases of the coatings and the scales after oxidation.

2 Results and discussion

2.1 Coating structure

Fig. 1 shows the cross-sectional BSE images of the pure silicide coating and Y-Ce modified silicide coating prepared at 1080 ºC for 4 h, and the concentration profiles from the coating surfaces to the substrate are also given as illustration. The Y-Ce modified silicide coating was obviously denser and thicker than the pure silicide coating, which suggested that the addition of Y_2O_3 and CeO_2 in the pack mixtures had an obvious quickening effect on the coating growth rate. EDS analysis results shown in respectively Fig. 1(a') and (b') revealed that these two coatings essentially possessed similar coating structures. In detail, the concentrations of Si and Ti in the outer layers of both coatings were respectively about 63.4 at.% and 35.3 at.%, according to the binary phase diagram of Ti-Si[15], they were considered to be composed of $TiSi_2$ phase, and this was also confirmed by the XRD patterns conducted on the surfaces of these two coatings as shown in Fig. 2(a). The concentrations of Si and Ti in the middle layers of the two coatings were approximately equal to each other, implying that they were TiSi, evidenced by binary Ti-Si phase diagrams[15]. However, due to the considerably small thicknesses of the two middle layers, it is very hard to analyze them using XRD method. Compared to the middle layers, the inner layers of the two coatings were far thicker. EDS analysis results determined that the concentration of Si in these layers was about 43.1 at.%, suggesting that the inner layers were Ti_5Si_4. XRD patterns conducted on the new surfaces after striping the pure silicide coating and the Y-Ce modified silicide coating from their original surfaces by respectively about 25 μm and 30 μm also confirmed the formation of Ti_5Si_4 inner layers, as shown in Fig. 2(b).

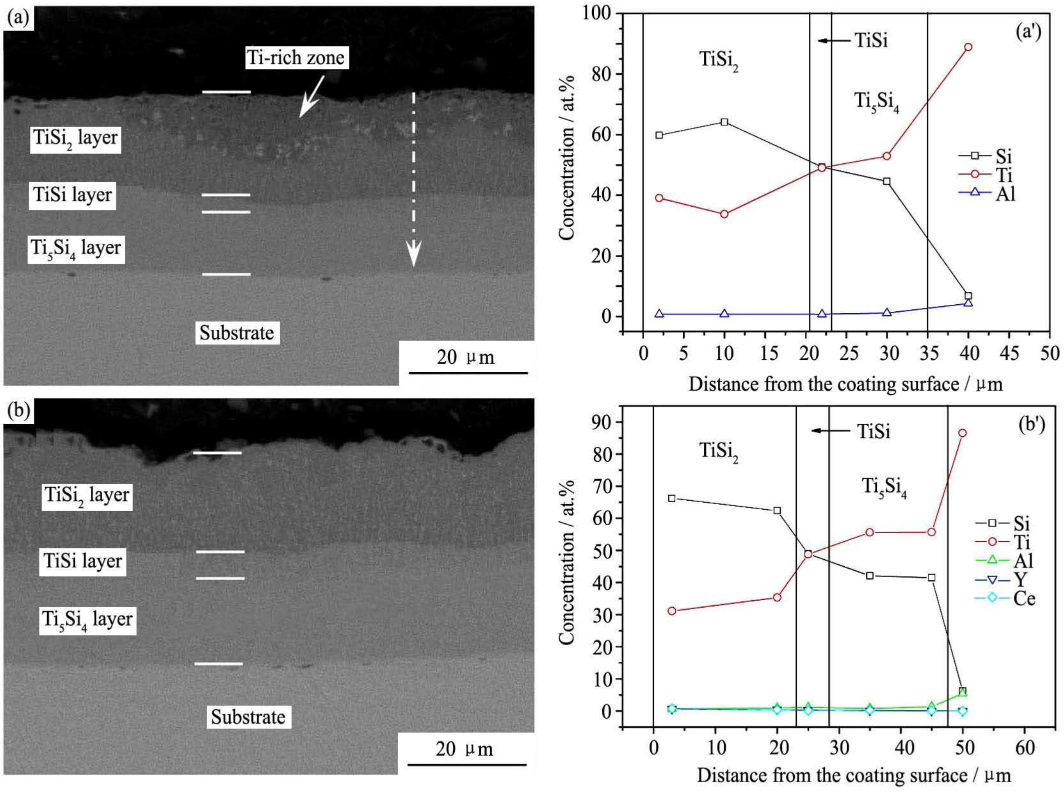

Fig. 1 Cross-sectional BSE images and concentration profiles of the pure silicide coating (a), (a') and the Y-Ce modified silicide coating (b), (b') prepared at 1080 ºC for 4 h