OXIDATION BEHAVIOR AND ELECTROCHEMICAL CORROSION PERFORMANCE OF Ti₃Al ALLOY WITH TiAl COATING

YANJUN XI, YONGJUN LIU, ZHIXIN WANG, JINBIN LU

Zhongyuan University of Technology, Zhengzhou, China

Magnetron-sputter deposition was used to produce Ti–48Al–8Cr–2Ag (at.%) coating on a Ti–24Al–17Nb–0.5Mo (at.%) alloy substrate. Oxidation behavior was studied in air at 900...1000°C. The results indicated that the oxidation rate of sputtered Ti–48Al–8Cr–2Ag nanocrystalline coating was lower than that of the Ti₃Al alloy at 900°C. The former formed a scale of merely Al_2O_3 and the latter formed a scale of TiO_2. However, the Ti–48Al–8Cr–2Ag nanocrystalline coating showed a little bit higher oxidation rate than Ti₃Al alloy at 1000°C, because outer TiO_2 scale formed and columnar boundaries of the coating gave a larger actual oxidation area than the original alloy. The electrochemical corrosion behavior was investigated in 3.5% NaCl solution at room temperature. The coating showed the excellent electrochemical corrosion resistance in 3.5% NaCl solution, because it exhibited stable passive polarization behavior without any overpassivation phenomena.

Key words: *Ti₃Al, TiAlCrAg nanocrystalline coating, high temperature oxidation, electrochemical corrosion.*

Titanium alunminides are promising intermetallic compounds for high temperature applications especially because of the possible weight reduction of structural components. Experimental evidence [1–3] has shown that titanium aluminides with aluminum content of about 50 at.% form nonprotective $TiO_2 + Al_2O_3$ scales rather than dense protective alumina scale. Therefore an attempt was made to protect them against oxidation by coating [4–6]. Recently, several investigations were focused on the oxidation of the Ti–Al alloy by the diffusion coatings formed by pack-codeposition of Al and Si [7–8] and Al Electrodeposition on the surface of Ti–Al [9].

Since a new class of TiAlCr coatings was proposed and they provided excellent oxidation protection for TiAl intermetallics [10–12], they received a considerable interest. The Ag-containing alloys possess relatively high ductility. TiAlCrAg alloys were investigated to exhibit excellent oxidation resistance [13]. Therefore, TiAlCrAg coatings may become a promising protective coating for Ti₃Al-base intermetallics, and few studies have been focused on it, especially on the electrochemical corrosion. This paper reports on the effect of the TiAlCrAg coating on the high temperature and electrochemical corrosion performance on the Ti₃Al alloy.

Experimental procedures. The Ti–48Al–8Cr–2Ag coating was prepared on the Ti₃Al alloy by magnetron sputtering technique. The target of 380×126×7 (mm) and the specimens of 10×10×2.5 (mm) were cut from an alloy ingot. The Ti₃Al alloy specimens were ground down to No.800 emery paper, peened and ultrasonically cleaned in ethanol. The sputtering parameters were as follows: the reaction chamber – $0.5×10^{-2}$ Pa; Argon pressure – 0.2...0.3 Pa; substrate temperature – 200°C; power – 1800 W; sputtering time – 8 h.

The coating possesses a columnar structure with a spherical surface. All sides of the specimens were coated with a thickness of about 20 μm. The deposition procedure, the morphology and microstructure of the coating were narrated in detail elsewhere [14].

Corresponding author: YANJUN XI, e-mail: yjxi@sina.com

Isothermal oxidation test was carried out at 900...1000°C in air. Thermogravimetric Analysis (TGA) was conducted for the characterization of the oxidation kinetics. The oxidized samples were analyzed by scanning electron microscopy (SEM) with energy dispersive X-ray diffraction (EDX).

Electrochemical polarization was carried out in a round bottom polarization cell. The potential of the working electrode was measured against saturated calomel electrode (SCE). A Pt plate was used as a counter electrode. The electrochemical corrosion was investigated using a CS300 potentiostat, interfaced to a computer.
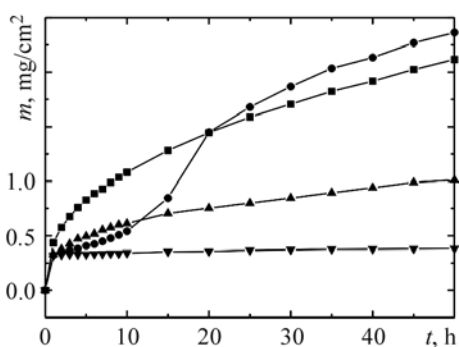

Fig. 1. Isothermal oxidation kinetics of specimens; ● – as-coated, 1000°C; ▼ – as-coated, 900°C; ■ – cast, 1000°C ▲ – cast, 900°C.

Results and discussion. Fig. 1 shows the results of the thermogravimetric analysis for different samples. The sample with Ti–48Al–8Cr–2Ag coating exhibits a lower oxidation rate than the cast Ti_3Al alloy at 900°C. In the initial stage, Ti–48Al–8Cr–2Ag coating exhibits a lower mass gain than the cast Ti_3Al based alloy at 1000°C, but with increasing time the weight gain of the coating exceeds the cast Ti_3Al based alloy after 20 h.

After oxidation in air, the specimens had a greyish colour. Fig. 2a, b shows the surface morphology and cross-sectional microstructure of cast Ti_3Al alloy after 50 h at 900°C. A continuous TiO_2 scale was formed on the alloy. The thickness of the scale was about 5 μm.
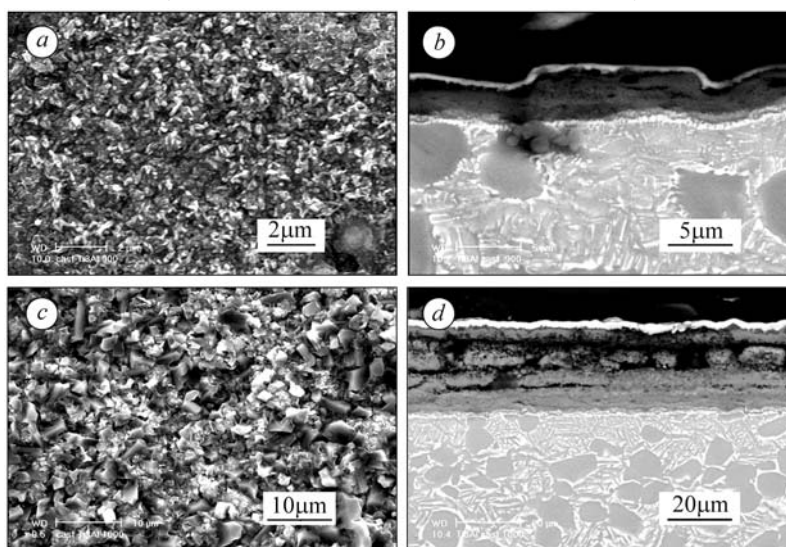

Fig. 2. Cast Ti_3Al alloy after 50 h oxidation at 900°C (*a, b*) and 1000°C (*c, d*): *a, c* – surface morphology; *b, d* – cross-sectional microstructure.

Fig. 3*a, b* shows the surface morphology and cross–sectional microstructure of Ti–48Al–8Cr–2Ag coating after 50 h at 900°C. A needle-shaped Al_2O_3 scale was formed on the surface continuously, so it provided excellent protection for the alloy at 900°C. Grain size reduction enhanced the formation of a continuous Al_2O_3 scale and improved oxidation resistance, observed here at 900°C. Due to Al diffusion from the coating to the substrate, a diffusion layer was formed near the substrate at the substrate/coating interface, and diffusion depth was about 5 μm.
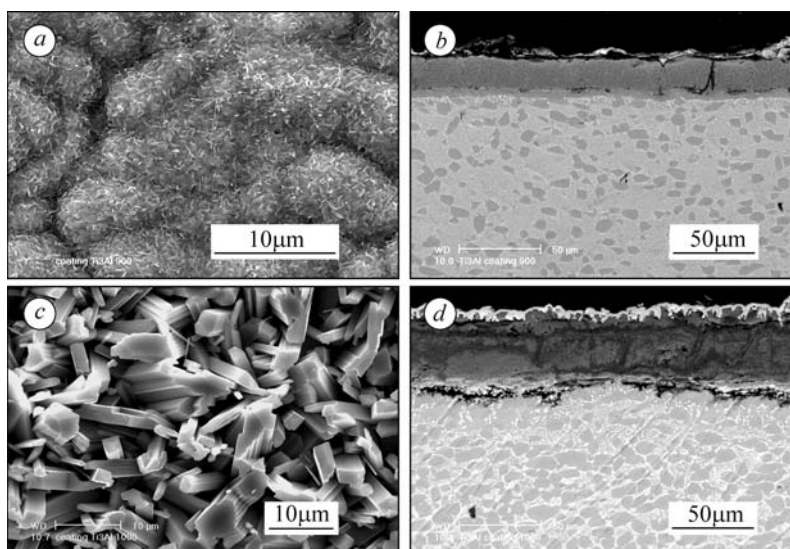
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Fig. 3. Cast alloy with Ti–48Al–8Cr–2Ag coating after 50 h oxidation at 900°C (*a*, *b*) and 1000°C (*c*, *d*): *a*, *c* – surface morphology; *b*, *d* – cross-sectional microstructure.

Fig. 2*c*, *d* shows the surface morphology and cross-sectional microstructure of cast Ti_3Al alloy after 50 h at 1000°C. This scale exhibits typical structure of Ti_3Al alloy oxidized in air. The scale consists mainly of titanium with some incorporated alumina grains. The thickness of Al_2O_3 + TiO_2 mixture scale was about 35 μm. Some cracks parallel to the sample surface occurred in the scale. The oxide scale detached easily during preparation of the metallographic cross-section. The alloy exhibited higher oxidation rate at 1000°C than at 900°C. EDX analysis revealed that the light zone beneath the scale was Nb rich.

Fig. 3*c*, *d* shows the surface morphology and cross-sectional microstructure of Ti–48Al–8Cr–2Ag coating after 50 h at 1000°C. A continuous TiO_2 scale was formed on the coating. A band of alumina crystals was present, especially beneath the outer zone of the coarse-grained rutile. In the case of the cross-sectional structure, we can also see that some Al_2O_3 was formed along the columnar grain boundaries. This partially explained the higher oxidation rate of the coating than that of the substrate under the same conditions. At the same time the outer thin Al_2O_3 scale indicated Al outward diffusion. Kirkendall voids were present at the coating/substrate interface as shown in Fig. 3*d*, which was the same as the results of the MCrAlY coating on the TiAl alloys [15]. They were mainly caused the different contents of the elements in the coating and the substrate. Although voids have no influence on the oxidation resistance in the present study, they will have a detrimental effect on the coating adherent to substrate, the fatigue properties of the substrate, and the long-term oxidation resistance of the coating. Therefore, diffusion and voids must be considered before it may be used in practice.

The coating oxidized more rapidly than the Ti_3Al substrate at 1000°C. SEM analysis indicated that the TiO_2 was the outer layer on the coating, and a nearly continuous Al_2O_3 scale under TiO_2 layer at 1000°C, and the scale on the coating was thinner than that on the substrate, which was different from the result of kinetics curves. There existed the boundaries or free surfaces between columnar, which might induce extra surface area for the coating. Yang [16] studied the influence of columnar microstructure of NiAl coating on its oxidation behavior at 1000°C. The results have revealed the columnar microstructure during oxidation which was the main reason of the high oxidation rate. The influence of columnar microstructure on oxidation behavior in the present study should be similar to that for NiAl coating.

In the present study, a different phenomenon from the traditional research was found. In the past, we also studied oxidation behavior of the TiAl coating on the TiAl alloy. The result showed that predominate Al_2O_3 scale was formed on the coating at 1000°C, and beneath Al_2O_3 scale the almost continuous layer of Al-depletion was present [14]. In the present study, the outer layer was not Al_2O_3 but TiO_2 on the coating after oxidation at 1000°C, partly because of different Al content in the coating and the substrate. After oxidation at 1000°C, some Al outward diffusion caused the Al_2O_3 formation under the TiO_2 layer. At the same time, due to much higher Al content in the coating than that in the substrate, some Al inward diffusion occurred. Thereby, the initial Al_2O_3 scale was formed due to the grain size reduction, and then the Al inward diffusion resulted in the Al activity decrease and Ti activity increased. Therefore, TiO_2 was formed on the surface due to outward diffusion of Ti along the columnar grain boundary.

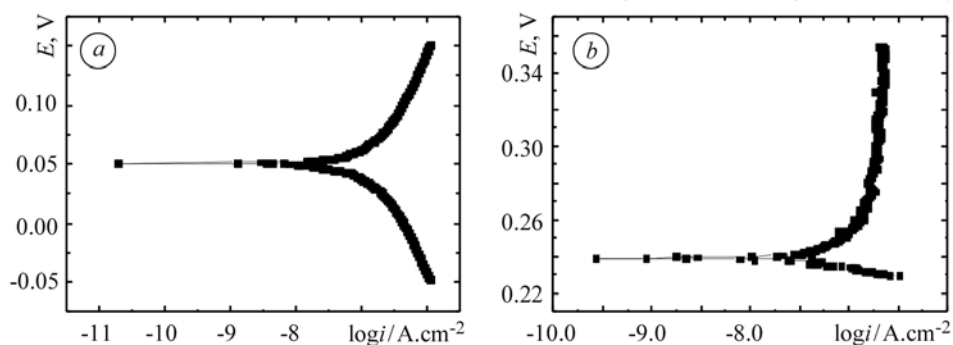Fig. 4. Potentiodynamic polarization curve of Ti_3Al alloy without (*a*) and with coating (*b*) in 3.5% NaCl solution at room temperature.

Potentiodynamic polarization curves for the Ti_3Al alloy and the Ti_3Al alloy with coating are shown in Fig. 4. The nature of polarization curves indicated that the corrosion potential of the alloy was much more negative than of the alloy with coating. The corrosion potential of the alloy is 0.05 V approximately, while the coating 0.24V. In addition, the coating exhibited the passivation phenomena obviously. The passive current density was maintained at about $10^{-6.7}A/cm^2$ without any overpassivation. The passive range in the coating exhibits the stable passive behavior. Therefore, the coating showed the excellent protection of the Ti_3Al alloy in the 3.5% NaCl solution at room temperature.

The experimental Tafel plots and polarization resistance (R_p) were analyzed. The zero current potential (E_{corr}), the cathodic (β_c) and anodic (β_a) Tafel slops, the estimated corrosion current densities (i_{corr}) and polarization resistance (R_p) are tabulated in the Table.

Tafel plots determined by Tafel extrapolation method and R_p by R_p fitting

	R_p, Ohm·cm^{-2}	β_a, mV	β_c, mV	i_{corr}, A·cm^{-2}	E_{corr}, V
Alloy	$7.11 \cdot 10^4$	129.6	128.8	$2.0 \cdot 10^{-7}$	−0.43
Alloy with coating	$3.19 \cdot 10^5$	$1.28 \cdot 10^6$	22.8	$2.77 \cdot 10^{-7}$	−0.26

CONCLUSIONS

The sputtered TiAlCrAg nanocrystalline coating showed a lower oxidation rate than the cast TiAlNb alloy at 900°C, because the former formed the pure Al_2O_3 scale and the latter formed the TiO_2 scale. The Ti–48Al–8Cr–2Ag nanocrystalline coating showed a little bit higher oxidation rate than the Ti_3Al alloy at 1000°C. The electrochemical corrosion behavior was investigated in 3.5% NaCl solution at room temperature. The alloy sputtered TiAl coating exhibited the stable passive polarization behavior without any overpassivation phenomena. The coating showed the excellent electrochemical corrosion resistance in 3.5% NaCl solution at room temperature.

РЕЗЮМЕ. Для виготовлення покривів на основі системи Ti–48Al–8Cr–2Ag (at.%), сформованих на підкладці Ti–24Al–17Nb–0,5Mo (at.%), використовували метод магнетронного розпилення. Характер оксидування досліджували в повітрі при 900...1000°C. Встановлено, що швидкість оксидування напиленого на Ti–48Al–8Cr–2Ag нанокристалічного покриву нижча, ніж на сплаві Ti_3Al. В результаті окиснення Ti–48Al–8Cr–2Ag утворюється плівка TiO_2, а після оксиснення сплаву Ti_3Al – плівка Al_2O_3. Нанокристалічний покрив, на якому сформували плівку TiO_2, продемонстрував дещо вищу швидкість оксидування, ніж сплав Ti_3Al, що пов'язано з тим, що плівка TiO_2 та межі стовпчастих кристалів покриву утворюють значно більшу ділянку реального оксидування, ніж вихідний сплав. Електрохімічну корозію вивчали у 3,5%-му розчині NaCl за кімнатної температури. Покрив був електрохімічно тривкий у ньому через стабільність пасивної поляризації за відсутності перепасивації.

РЕЗЮМЕ. Для изготовления покрытий на основе системы Ti–48Al–8Cr–2Ag (at.%), сформированных на подкладке Ti–24Al–17Nb–0,5Mo (at.%), использовали метод магнетронного распыления. Характер оксидирования исследовали в воздухе при 900...1000°C. Выявлено, что скорость оксидирования напыленного на Ti–48Al–8Cr–2Ag нанокристаллического покрытия меньше, чем на сплаве Ti_3Al. В результате окисления Ti–48Al–8Cr–2Ag образуется пленка TiO_2, а после окисления сплава Ti_3Al – пленка Al_2O_3. Нанокристаллическое покрытие, на котором сформировали пленку TiO_2, продемонстрировало несколько повышенную скорость оксидирования, нежели сплав Ti_3Al, что связано с тем, что пленка TiO_2 и границы столбовых кристаллов покрытия образуют значительно больший участок реального оксидирования, чем исходный сплав. Электрохимическую коррозию изучали в 3,5%-ом растворе NaCl при комнатной температуре. Покрытие оказалось электрохимически стойким в нем благодаря стабильности пассивной поляризации при отсутствии перепассивации.

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