Hot Corrosion Behavior of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Glass}$ Composite Coating on Ti–47Al–2Cr–2Nb Alloy: Diffusion Barrier for S and Cl

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Received: 28 June 2018 / Revised: 19 September 2018 / Published online: 9 November 2018
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Abstract

Type I hot corrosion behavior of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--glass}$ composite coating based on Ti–47Al–2Cr–2Nb substrate was investigated in the mixture salt of 25 wt%NaCl + 75 wt%Na₂SO₄ at 850 °C. The results showed that there was a bidirectional ion exchange between composite coating and the film of mixed salts, and the sodium ion in the molten salts penetrated into the glass matrix of composite coating, while the potassium ion in the glass matrix dissolved into the molten salts. A decrease in hot corrosion rate was achieved for the coated alloy in comparison with the bared substrate due to the composite coating acting as a diffusion barrier to sulfur and chlorine and preventing the molten salts from diffusing to the coating/alloy interface during the hot corrosion exposure. Additionally, the composite coating decreased the oxygen partial pressure at the coating/alloy interface and promoted the selective oxidation of Al to form a protective Al₂O₃ layer.

Keywords Corrosion · Composite coating · Ti–47Al–2Cr–2Nb alloy · Diffusion

1 Introduction

As a satisfactory high-temperature structural material, TiAl intermetallic compounds have drawn considerable attentions due to their high specific strength in comparison with nickel-based superalloys. In order to further improve the performance of TiAl intermetallic compounds, modifications by adding multiple elements in TiAl-based alloys have been developed for applications at high temperatures ranging at 800–850 °C [1–4]. However, the practical applications are still hindered by the relatively poor high-temperature oxidation resistance and hot corrosion resistance, especially under circumstance containing NaCl [5–11]. As materials for aerospace applications, sulfate and

chloride salts may deposit on the surface and accelerate the degradation of the alloy. For instance, the sulfur contained in fuel oil and the chlorine in the saltwater (NaCl) in the air may be ingested and condensate on the surface of the alloy. Therefore, a good hot corrosion resistance coating against the salts is necessary for the TiAl-based alloys before their application.

Glass–ceramic coatings, recognized to possess good chemical stability and thermal durability at high temperature, are widely used as protective coatings to resist oxidative environment for titanium and nickel-based alloy [12–24]. Compared to coatings deposited by vacuum vapor, glass–ceramic coatings are lower cost, which made the glass–ceramic coatings more competitive in industry application. Works done by Xiong et al. [12, 13] reported the preparation and high-temperature behavior of enamel coating on titanium alloy, and the results showed the coating exhibits both good high-temperature oxidation resistance as well as saltwater synergic corrosion resistance. Similar conclusion were drawn by Sarkar et al. [14, 15], where an oxidation and hydrogen permeation-resistant glass–ceramic coating was achieved on γ -titanium aluminide alloy. Conventionally, the glass–ceramic coatings are usually prepared using a multi-step consisted with repeated melting and then quenching methods [12–15]. Aiming at obtaining good thermal and mechanical

Available online at <http://link.springer.com/journal/40195>

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properties, the glass composition should be well designed and then followed by specific heat treatments for nucleation and growth of crystalline phases in the glass [25]. In comparison, it will be theoretically more convenient and controllable to tailor the mechanical and thermal properties by adding ceramic inclusions directly into the glass matrix and controlling the amount as well as species of the inclusions.

It has been known for a long time that aqueous solution of binary alkali silicates possesses the property of high stability at high temperature, which entitled it to be widely used as lightweight refractory material and inorganic binder in high-temperature paint. When the water in the solution was evaporated gradually during the baking process, the small colloids aggregate, and gel and amorphous structure forms simultaneously [26]. The alkali silicate gel would form molten glass when heated to high temperatures. As a result, aqueous solution of binary alkali silicates could be a promising precursor for the glass matrix. In addition, the preparation procedures for the glass–ceramic composite coating can be simplified by using a slurry consisting of aqueous solution of binary alkali silicates and the ceramic powders.

Combining with aqueous solution of potassium silicate and inclusions of Al_2O_3 and SiO_2 , we have successfully obtained a novel SiO_2 – Al_2O_3 –glass composite coating. The high-temperature oxidation test magnified the composite coating functions as an effective oxygen diffusion barrier when coated on Ti–47Al–2Cr–2Nb alloy and significantly decreases the oxidation rate of the alloy [27]. In the current article, SiO_2 – Al_2O_3 –glass composite coating was prepared on Ti–47Al–2Cr–2Nb alloy, and the hot corrosion resistance was evaluated in the mixed salts (25 wt%NaCl + 75 wt% Na_2SO_4) in comparison with bare Ti–47Al–2Cr–2Nb alloy. The hot corrosion resistance mechanism of the composite coating is discussed.

2 Experimental Procedure

The Ti–47Al–2Cr–2Nb alloy (at%), with the main phase consisting with γ -TiAl phase and a small amount of α_2 -Ti₃Al was used as substrate. Rectangular specimens with nominal dimensions of 20 × 10 × 2.5 mm were cut from the alloy ingot by a spark-discharging machine. The raw specimens were firstly grounded with a final 600-grit SiC sand paper and then ultrasonically cleaned in ethanol for 15 min. For the specimens to be coated with glass composite coating, sand blast treatment was conducted before further ultrasonically cleaned in ethanol.

The concentration of potassium silicate in the aqueous solution in the current study was 40 wt%, and the ratio of SiO_2 to K_2O was control to be about 3:1 (Dayang Chemical

Plant). The particle sizes of the α - Al_2O_3 (Shenyang Laisheng plant) and SiO_2 (Sinopharm chemical reagent Co., Ltd) powders were ranged at 1–10 μm .

The preparation procedures of SiO_2 – Al_2O_3 –glass composite coating are described as follows: Firstly, the α - Al_2O_3 and SiO_2 particles were dispersed into aqueous solution of potassium silicate (ASPS) to form a slurry with the ratio of quartz: α - Al_2O_3 : ASPS is 3:1:10; secondly, the slurry was sprayed on the surface of Ti–47Al–2Cr–2Nb alloy using a manual painting gun in air to form a green coating about 30 μm in thickness and the estimated air pressure of spraying is about 0.4 MPa; finally, the sprayed coating was preliminary solidified at room temperature for 12 h and followed by a series of baking in the oven at 70 °C for 12 h, at 120 °C for 10 h, and then at 260 °C for 5 h, and finally firing at 900 °C for 60 min to obtain a dense SiO_2 – Al_2O_3 –glass composite coating.

The cyclic hot corrosion tests were conducted in static air at 850 °C in a muffle furnace for five cycles. For each cycle, the specimens were firstly deposited with 1.5–2.5 mg/cm² mixed salts by spraying a saturated solution of 75 wt% Na_2SO_4 + 25 wt% NaCl using a spray gun. Then the specimens were hanged using a nickel-based hook and exposed at 850 °C in the furnace to carry out the hot corrosion tests for a given duration, like 20 h. After one exposure cycle, the samples were taken out and then cooled down to the room temperature. The cooled specimens were washed at least two times in the boiled distilled water and dried in a hot flowing air. Before redeposition the new mixed salt to start the next cycle, the specimens were weighed using an electronic balance with sensitivity of 10^{−5} g. In consideration of experimental accuracy, three parallel samples of both bare alloy and alloy with coating were used in the hot corrosion test to obtain an average value of mass change.

The surface and cross-sectional morphologies of the specimens after hot corrosion were characterized by the field-emission scanning electron microscope (SEM, FEI INSPECT F 50, FEI, Hillsboro, OR) with an EDS (OXFORD X-Max, Oxford Instruments, Oxford, UK). The secondary electron mode was used to observe the surface morphology, and the back-scattered electron mode was adopted to observe cross-sectional microstructures of the specimens. Phase constitution of coating specimens after hot corrosion were determined by X-ray diffraction (XRD, X' Pert PRO, Cu K α radiation at 40 kV, PANalytical, Almelo, Holland). Electron probe microanalysis (EPMA-1610, Shimadzu, Kyoto, Japan) technique was employed to study the element distribution.

3 Results and Discussion

Optical images of the bare and coated Ti–47Al–2Cr–2Nb alloy after hot corrosion at 850 °C for 100 h are shown in Fig. 1. For the bare substrate, yellow and green oxide was formed. The obvious cracks on the oxide surface suggested the occurrence of the oxide spallation. Actually, spallation of the oxide could be observed by naked eye during the cooling and washing process. In comparison, the composite coating maintained intact after hot corrosion tests for the coated alloy.

The hot corrosion kinetics curves of the alloy with and without SiO₂–Al₂O₃–glass composite coating at 850 °C are shown in Fig. 2. The total mass gain for the substrate after 100 h hot corrosion at 850 °C was about 18 mg/cm² with mildly decreasing in the first 20 h and then monotonously increasing in the next 80 h. For the coated alloy, a mass decrease was observed in the first 40 h, followed by a mass increase in the next 60 h. Obviously, the SiO₂–Al₂O₃–glass composite coating decreased the hot corrosion rate of the Ti–47Al–2Cr–2Nb alloy remarkably in comparison with the bare substrate.

Figure 3 shows the XRD patterns of the bare Ti–47Al–2Cr–2Nb alloy and alloy with SiO₂–Al₂O₃–glass composite coating after 100 h hot corrosion at 850 °C. The main oxide formed on the bare alloy is TiO₂, a small amount of Al₂O₃, and Na₂Al₂Ti₆O₁₆. The formation of Na₂Al₂Ti₆O₁₆ is possibly due to the reactions between the molten salts and the oxides scale. Instead, phases reserved on surface of the alloy with SiO₂–Al₂O₃–glass composite coating are

Fig. 1 Optical images of the bare **a** and coated **b** Ti–47Al–2Cr–2Nb alloy after 100 h hot corrosion at 850 °C

Fig. 2 Hot corrosion kinetics of Ti–47Al–2Cr–2Nb alloy with and without the SiO₂–Al₂O₃–glass composite coating at 850 °C

quartz, cristobalite, Ti₅Si₃, Al₂O₃, Z-phase (Ti₅Al₃O₂), TiAl, and a minor NaAlSi₃O₈. TiAl was the phase of the substrate. Z-phase (Ti₅Al₃O₂), which is an Al-depleted phase usually formed beneath the oxides during the oxidation of the TiAl alloy, might be able to sustain the growth of alumina scale [27, 28]. According to our previous study, Z-phase (Ti₅Al₃O₂) is a new phase formed during preparation of the coating [27]. Cristobalite might be transformed from the quartz particles added in the composite coating due to the presence of mineralizer, such as Na₂O, K₂O [30]. As TiO₂, the commonest phase formed on Ti-based alloy, was not detected, it is reasonable to infer that the coating is still integral and could provide further protection for the coating in the following exposure.

The surface and cross-sectional microstructure of the bare alloy after hot corrosion at 850 °C for 100 h are shown in Fig. 4a, b. A rough surface with many protrusions was observed. The cross-sectional image shows that the oxide of the bare alloy had a multilayered structure. Large numbers of lateral cracks were observed in the oxide, which leads to the oxide spalled from the surface of the alloy easily during cooling, indicating the poor adherence of the oxide scale. Figure 4c shows the line scanning results of the oxide by EDS. From the surface of the oxides (left) to the oxides/alloy interface, one may see that a strong signal of Na and Ti appeared in the oxide scale near the surface, suggesting that the Na₂O in the mixed salts reacted with the oxide of the alloy and formed Na₂Al₂Ti₆O₁₆ at the surface of the oxides. Then it can be noted that Al₂O₃-rich layer and TiO₂-rich layer grew alternately in the oxides scale. The formation of TiO₂ layer results in a localized enrichment of Al beneath the TiO₂, which leads to selective oxidation of Al. However, the content of the Al could not sustain the exclusive growth of the Al₂O₃ layer,

Fig. 3 XRD patterns of the bare Ti-47Al-2Cr-2Nb alloy **a** and alloy with SiO₂-Al₂O₃-glass composite coating **b** after 100 h hot corrosion at 850 °C

Fig. 4 Surface morphology **a**, cross-sectional image **b** and line scanning results of the cross section **c** of the bare Ti-47Al-2Cr-2Nb alloy after 100 h hot corrosion at 850 °C

and therefore, alternant growth of TiO₂ and Al₂O₃ occurred. Finally, S aggregated at the oxides/alloy interface. Pits and voids were observed at the oxide/alloy interface, which

may be attributed to the formation and outward transportation of volatile chlorides (TiCl₂ and AlCl₃) at the oxide/alloy interface [9].

The surface and cross-sectional microstructure of the Ti–47Al–2Cr–2Nb substrate-coated alloy with glass composite coating after hot corrosion at 850 °C for 100 h are shown in Fig. 5a, b, where a flat surface was observed. The EDS analysis indicated that the glass composition is 62.9 at%O, 24.6 at%Si, 8.1 at%Na, 3.9 at%Al and trace amount of K (0.4 at%), while the amount of the potassium in glass matrix of as prepared coating is 13.6 at%, and no sodium was detected [30], indicating that the sodium ion in the salts have dissolved into the glass matrix of the composite coating while the potassium ion in the glass matrix have transported outwardly and dissolved into the mixed salts. Similarly, this ion exchange phenomenon was also observed between the silicate glass and KNO₃ [31–33]. As the mole mass of the sodium ion is smaller than that of the potassium ion, therefore, the ion exchange between the glass matrix of the composite coating and mixed salts could result in a decrease in the mass for the coated specimen, which lead to the mass loss in the first 40 h. An Al content of 3.9 at% was also detected in the glass phase, which is possible related to the dissolution of the alumina inclusions into the glass matrix at high temperature [34, 35]. The cross-sectional image in Fig. 5b shows that the coating

maintained intact after hot corrosion test. The inserted magnified image in Fig. 5b displayed that an interlayer formed at the coating/alloy interface. Two lines in Fig. 5c were drawn to show the interfacial reaction zone. From the left side of the interfacial reaction zone, one can see the first significant high peaks were Al and O, corresponding to an alumina-rich layer formed during hot corrosion tests. Then an Al-depleted zone was detected, corresponding to the Z-phase (Ti₅Al₃O₂) layer. The distribution of Ti is mainly limited beneath the Al₂O₃ scale, meaning no oxide of the titanium was formed at the surface of the coating or inside the composite coating during the hot corrosion exposure, which agrees with the XRD patterns.

It is worth noting that a discontinuous bright layer formed at the coating/alloy interface. According to EDS, it might be Ti₅Si₃. The interfacial reaction between coating and alloy during hot corrosion tests is similar to that during oxidation tests [27] as Z-phase (Ti₅Al₃O₂) layer, Ti₅Si₃, and Al₂O₃ layer were detected at the coating/alloy interface both during hot corrosion or oxidation exposure. This is because that inward diffusion of S and Cl were prevented by the composite coating (the diffusion barrier effect of the composite coating to S and Cl will be discussed in the

Fig. 5 Surface morphology **a**, cross-sectional image **b** and line scanning results of the cross section **c** of the Ti–47Al–2Cr–2Nb alloy with SiO₂–Al₂O₃–glass composite coating after 100 h hot corrosion at 850 °C

following section), and only O is able to diffuse to the coating/alloy interface.

The elemental mapping by EPMA was used to analyze the element distribution at the coating/alloy interface, as shown in Fig. 6. The elemental distribution conformed again that the sodium ion in the molten salts dissolved into the glass matrix, which is consistent to the analysis by EDS. An Al_2O_3 -rich layer was observed at the coating/alloy interface. The composite coating decreased the

oxygen partial pressure at the coating/alloy interface, as a result, promoting the selective oxidation of Al in alloy. S was not detected at the coating/alloy interface or in the composite coating, indicating that the composite coating has effectively prevented the inward diffusion of S from the molten salts to the coating/alloy interface.

For the four ions (Na^+ , O^{2-} , S^{6+} , Cl^-) in the molten salts (25 wt%NaCl + 75 wt% Na_2SO_4), the sodium ion dissolved and diffused into the glass matrix of the

Fig. 6 Element mapping (Al, O, Ti, Si, Na, K, S) for the Ti-47Al-2Cr-2Nb alloy with SiO_2 - Al_2O_3 -glass composite coating after 100 h hot corrosion at 850 °C

composite coating, while the potassium ion in the glass matrix dissolved and diffused into the mixed salts. Oxygen ion can diffuse from the air to the coating/alloy interface, probably through the glass phase in the composite coating. However, S and Cl were not detected in the alloy or at the coating/alloy interface, indicating that the composite coating effectively prevented the inward diffusion of S and Cl, as shown in Fig. 7a. S was reported to be able to diffuse in the silicate glass as SO₄²⁻ in the oxidized melts or as S²⁻ in the reduced melts, but the diffusion coefficient is very low [36, 37]. Therefore, it is probable that the diffusion coefficient of S in the composite coating at 850 °C is too low for the EDS or EPMA to detect its diffusion in the glass. Only a small amount of O is able to diffuse to the coating/alloy interface, and the low diffusion rate of oxygen in the composite coating resulted in the low-oxygen partial pressure at the coating/alloy interface, therefore, promoting the selective oxidation of Al and Al₂O₃ layer formed at the coating/alloy interface (Fig. 7b).

Fig. 7 Schematic diagram of the hot corrosion behavior of the SiO₂–Al₂O₃–glass composite coating on Ti–47Al–2Cr–2Nb alloy

4 Conclusions

1. The SiO₂–Al₂O₃–glass composite coating functioned as a diffusion barrier during hot corrosion exposure at the test temperature, which effectively prevented the sulfur and chlorine diffusing inwardly from the mixed salts to the coating/alloy interface. As a result, a remarkably improvement in the hot corrosion resistance was achieved on coated Ti–47Al–2Cr–2Nb alloy at 850 °C.
2. The low diffusion rate of oxygen in the composite coating resulted in the low-oxygen partial pressure at the coating/alloy interface, therefore, promoting the selective oxidation of Al. An Al₂O₃ layer was formed at the coating/alloy interface.

Acknowledgments This work was supported by the National Natural Science Foundation of China (Grant No. 51201171) and the National High Technology Research and Development Program of China (863 Program, Grant No. 2012AA03A512).

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