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Effect of Enamel Coating on Oxidation and Hot Corrosion Behaviors of Ti-24Al-14Nb-3V Alloy

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The effect of enamel coating on the isothermal and cyclic oxidation at 900 °C in air and on the hot corrosion resistance of Ti-24Al-14Nb-3V in both 85%Na_2SO_4 + 15%K_2SO_4 and 15%NaCl + 85%Na_2SO_4 molten mixed salts at 850 °C was investigated. The results indicated that Ti-24Al-14Nb-3V alloy exhibited poor oxidation resistance due to the formation of nonprotective Al_2O_3 + TiO_2 + $AlNbO_4$ scales and poor hot corrosion resistance due to the spallation of scales formed in molten Na_2SO_4 + K_2SO_4 and NaCl + Na_2SO_4. Enamel coating suppressed the migration of oxygen and corrosive ions into the substrate to improve the oxidation and hot corrosion resistance of Ti-24Al-14Nb-3V alloy. However, the dissolution of oxides components of the coating into the molten salts degraded enamel coating and the degradation of the coating involved a process by which Cl^- anion penetrated into the substrate through voids in the coating to accelerate corrosion of Ti-24Al-14Nb-3V alloy.

Keywords enamel coating, hot corrosion, oxidation, titanium aluminum intermetallics

1. Introduction

High temperature titanium alloys are considered as candidate materials for aerospace applications due to their high specific strengths (Ref 1). Ti-24Al-14Nb-3V alloys are promising high-temperature materials due to their high strengths and excellent superplasticity (Ref 2). However, the lack of oxidation resistance and oxygen contamination limit the technical application of titanium alloys to temperatures much lower than that allowed by their mechanical properties. When titanium alloys are exposed to oxygen-containing environments, the alloys may react with oxygen to form nonprotective oxides (generally the rutile TiO_2 and Al_2O_3 mixed scales rather than protective α-Al_2O_3 scales) in air. Meanwhile, oxygen dissolves into the substrate to form a hardened, oxygen-rich layer or so-called "oxygen embrittlement", which may in turn degrade the mechanical properties of the alloys (Refs 3, 4). To overcome these drawbacks of the titanium alloys, there is an ongoing interest in the development of oxidation-resistant alloys and oxygen barrier coatings. Various coatings have been developed with good protectiveness to the alloys, among which sputtered TiAl, TiAlCr, and Al_2O_3 coatings acted as effective oxygen-barrier, and enabled the coated alloys to maintain rather high tensile elongation after exposure at 600 °C for 100 h (Ref 5). On Ti alloys to coastal aerospace applications, sulfate and chloride salts may be deposited to accelerate the degradation of the alloys (hot corrosion). Thus, it is required that the coatings for Ti alloys should be resistant to both oxidation and hot corrosion. The authors (Ref 6) reported that both Ti-50Al-20Cr and Ti-50Al-10Cr coatings improved the oxidation and hot corrosion resistance of Ti-24Al-14Nb-3V in Na_2SO_4 + K_2SO_4 molten salts as a result of the formation of Al_2O_3 scales. However, Cl^- might be harmful for the protectiveness of Cr-containing coatings due to the formation of volatile $CrCl_3$ (Ref 7).

A recent study indicated that enamel is a good candidate of high temperature coatings for Ti-based alloys, due to its better compatibility with the substrate. Furthermore, it is economically more attractive than the coatings produced by means of the expensive PVD process (Ref 8). In the present work, the influence of an enamel coating for preventing Ti-24Al-14Nb-3V alloy from high-temperature isothermal and cyclic oxidation and hot corrosion in molten $(Na,K)_2SO_4$ and NaCl + Na_2SO_4 was evaluated.

2. Experimental Materials and Procedures

Ti-24Al-14Nb-3V was first homogenized at 1000 °C for 1 h and subsequently water quenched. The alloy ingot was cut into 15 × 10 × 2.5 mm specimens and ground down to 600#-SiC paper. The nominal enamel frit and the coating preparation method were given in Ref 9. The thickness of the enamel coating was about 30 μm.

The isothermal (discontinuous) oxidation was performed at 900 °C in air for times up to 100 h. The specimens were cooled for 30 min at room temperature and weighed using a balance with an accuracy of 10^{-4} g after oxidation for each 20 h. The cyclic oxidation tests were conducted at 900 °C with a cycle of 1 h and a total exposure time up to 100 h in static air. One cycle consisted of holding at 900 °C for 1 h and cooling for 15 min at room temperature. After each ten cycles, the specimens except the spalled oxides were weighted. Hot corrosion tests were carried out in molten 85%Na_2SO_4 + 15%K_2SO_4 and 15%NaCl + 85%Na_2SO_4 salts in air at 850 °C, respectively. After corrodeing for each 20 h, the specimens were taken out of the crucible and cooled in air to room temperature, and weighed after cleaning the specimens in boiling water and drying in air. The oxidized and corroded samples were examined by means

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of scanning electron microscopy equipped with energy dispersive x-ray spectroscopy (SEM/EDS), and x-ray diffraction (XRD) to characterize the microstructure and phases of the corrosion products.

3. Results

3.1 The Microstructure of Enamel Coating

The microstructure of enamel coating on Ti-25Al-14Nb-3V was shown in Fig. 1. The enamel coating appeared to consist of a gray matrix with fine particles. It was clearly seen that the enamel coating was very dense, uniform, and adhesive to the substrate alloy. But there were still voids in the coating due to volatility of gas as the coating was fired. The EDS analysis showed that the white particles were zirconia and alumina, which were added into the coating to improve its mechanical and oxidation performance.

3.2 Oxidation

Figure 2 shows the isothermal and cyclic oxidation kinetics of Ti-24Al-14Nb-3V alloy with and without enamel coating at 900 °C. The isothermal oxidation kinetics of the alloy followed a fast linear law, and the oxide scales broke off partly when the alloy was oxidized for 60 cycles. The mass gains of coated specimens are much lower than that of the uncoated.

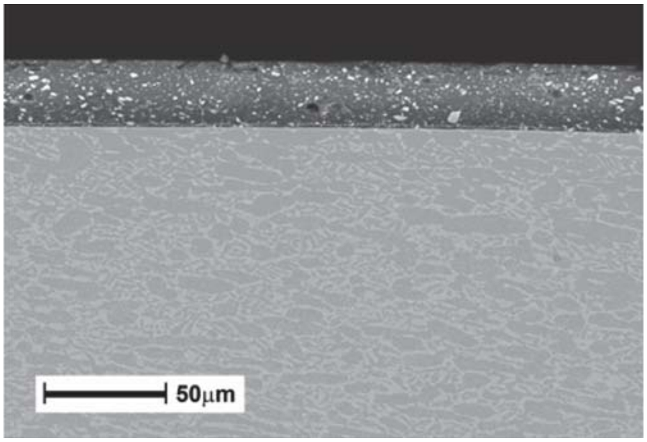

Fig. 1 Cross-sectional microstructure of Ti-24Al-14Nb-3V with enamel coating before oxidation and hot corrosion

Figure 3 shows the cross-sectional microstructures of Ti-24Al-14Nb-3V with and without enamel coating after isothermal oxidation for 100 h at 900 °C in air. Very thick and layered scales formed on the surface of the bare alloy. EDS and XRD analysis indicated that the scales were composed of TiO_2 + Al_2O_3 + $AlNbO_4$. However, the enamel coating kept intact after oxidation and no obvious interdiffusion of components could be detected at the interface of coating/substrate.

Figure 4 shows the cross-sectional microstructure of Ti-24Al-14Nb-3V with enamel coating after oxidation for 100 cycles at 900 °C in air. No oxidation products and interdiffusion were detected at the interface of coating/alloy after oxidation. It indicated that the enamel coating could protect the alloys from oxidation effectively.

3.3 Hot Corrosion

Figure 5 shows the corrosion kinetics of Ti-24Al-14Nb-3V in a mixture of 85%Na_2SO_4 + 15%K_2SO_4 and of 15%NaCl + 85%Na_2SO_4 in air at 850 °C, respectively. The spallation scales formed on the uncoated specimens and a light loss of weight was measured during corrosion of the coated specimens. Moreover, the weight loss of the coated specimen in NaCl + Na_2SO_4 melts was more than that in $(Na,K)_2SO_4$ melts.

Figure 6 shows the surface morphology and cross-sectional microstructure of enamel coating after corrosion for 100 h in melts $(Na,K)_2SO_4$ at 850 °C. The coated specimen kept uniform after corrosion. The EDS analysis indicated that the content of Ca^{2+} decreased companying with the increasing of Na^+ in the external surface of the enamel coating. But no S could be detected.

Figure 7 showed the cross-sectional microstructure of the bare alloy corroded for 1 h in molten Na_2SO_4 + K_2SO_4 at 850 °C. Thick layered corrosion products formed on the alloy. The outermost layer (A) was rather pure TiO_2 followed by a mixture of TiO_2 + Al_2O_3 oxides (B). Layer C was mixture oxides rich in oxygen (white layer). And beneath layer C, there was a Ti-rich layer D. Nb and V were also rich in this layer compared with the alloy before corrosion.

Figure 8 and 9 show the cross-sectional microstructures of

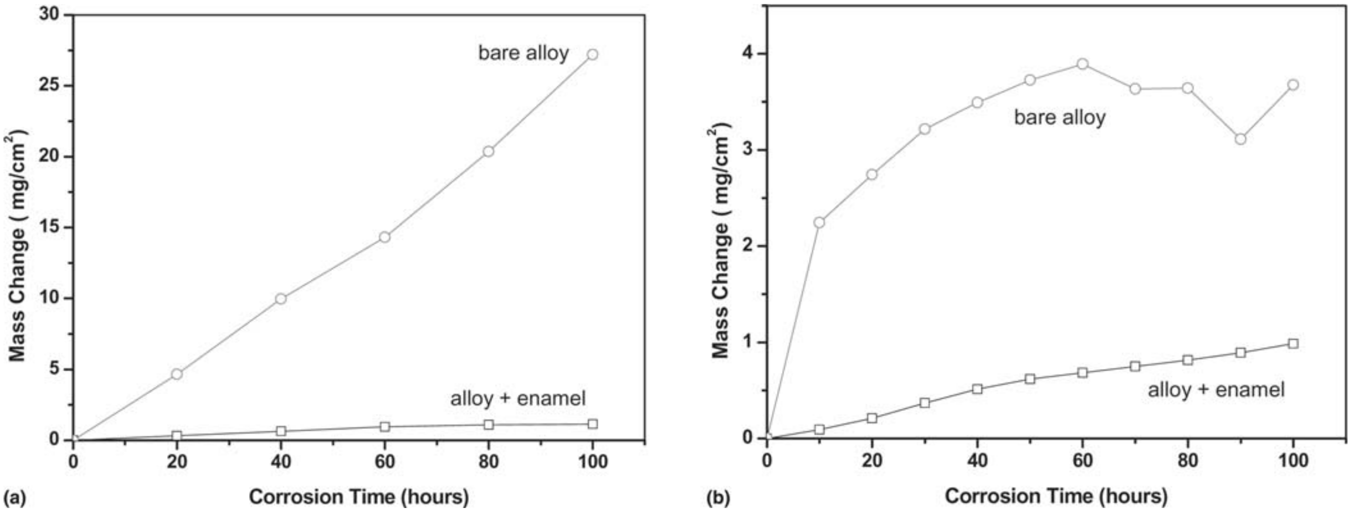

Fig. 2 (a) Isothermal and (b) cyclic oxidation kinetics of Ti-24Al-14Nb-3V at 900 °C in air

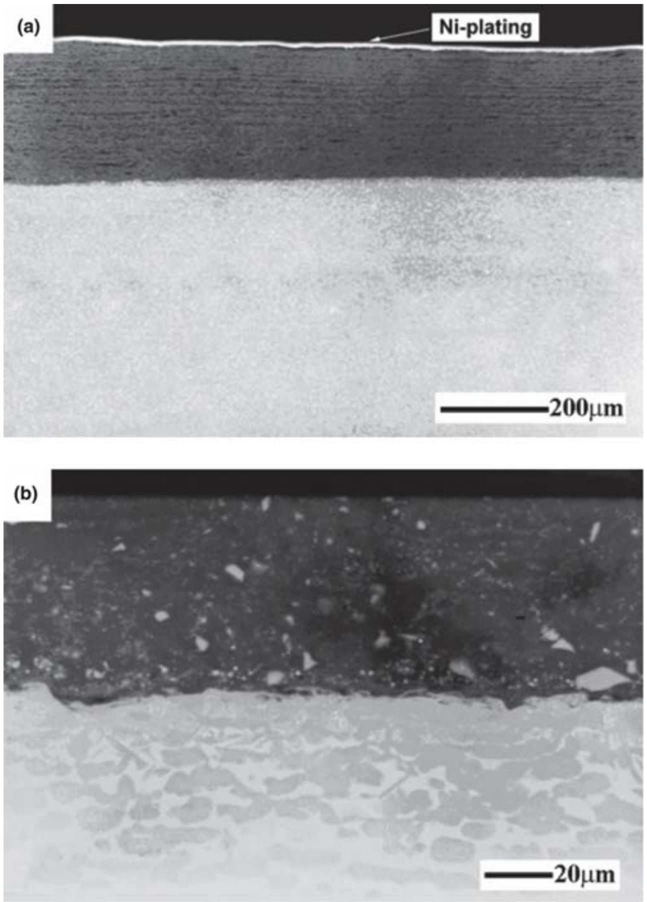

Fig. 3 Cross-sectional microstructure of Ti-24Al-14Nb-3V with enamel coating after isothermal oxidation for 100 h at 900 °C in air

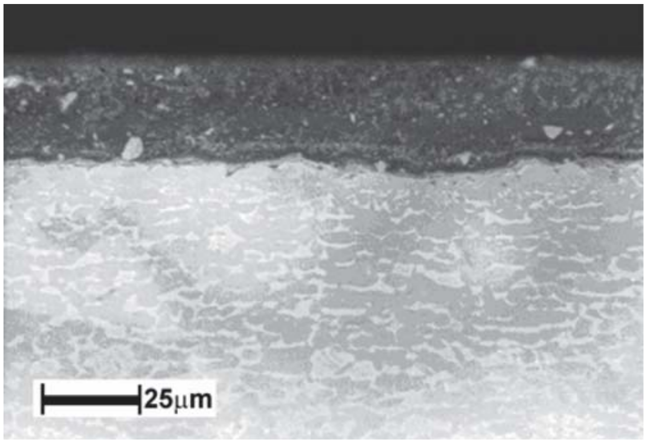

Fig. 4 Cross-sectional microstructure of Ti-24Al-14Nb-3V with enamel coating after 10 cycles oxidation at 900 °C in air

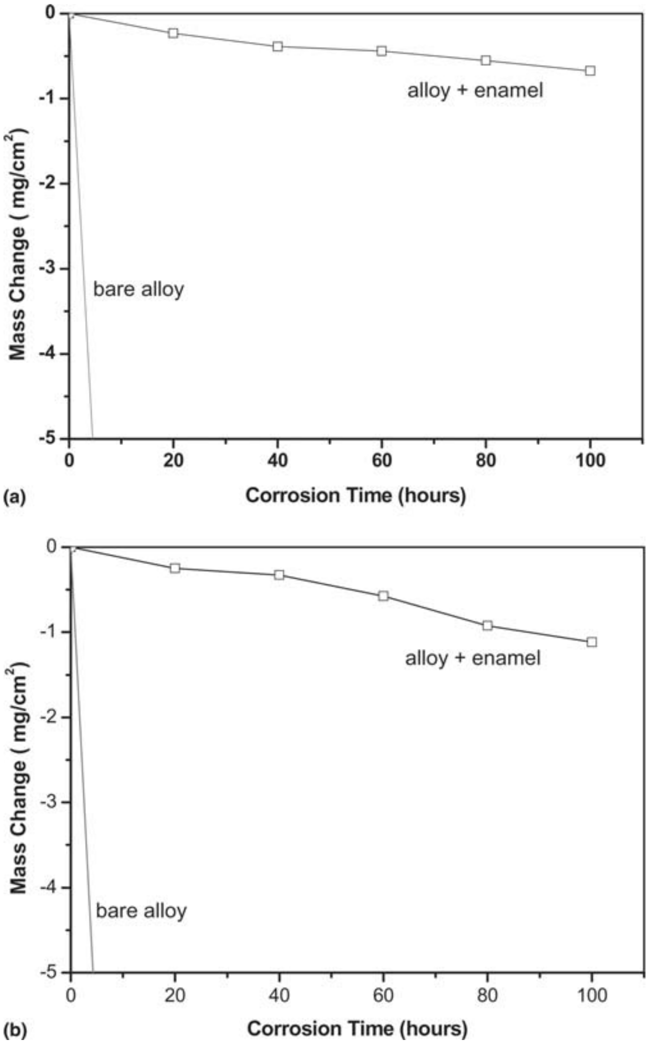

Fig. 5 Hot corrosion kinetics of Ti-24Al-14Nb-3V (a) in molten 85%Na_2SO_4 + 15%K_2SO_4 and (b) in 15%NaCl + 85%Na_2SO_4 melts at 850 °C, respectively

the specimens after corrosion for 5 h and 100 h in Na_2SO_4 + NaCl at 850 °C, respectively. After corrosion for 5 h in NaCl + Na_2SO_4, a thick five-layer corrosion scale formed on the alloy. EDS analysis indicated that the products were mainly composed of Al_2O_3 and TiO_2 mixture in regions of A, B, and D, and sulfides of Ti in area C and E. After corrosion for 100 h, the content of Ca decreased combining with the increasing of Na in the external surface of enamel coating. And Ti could be detected there (EDS analysis results). According to Fig. 9(b), there were a few cracks in the coating where the content of Cl^- anion was very high. At the interface of coating/substrate, there were some white corrosion products containing mainly Zn according to EDS. Moreover, many voids and pits in the substrate beneath the interface of coating/alloy indicated that obvious internal attack occurred.

4. Discussion

Oxidation and oxygen embrittlement degrade the mechanical performance of Ti alloys heavily. On one hand, a porous TiO_2 layer can hardly protect Ti alloys from oxidation. On the other hand, the solubility of oxygen in α-Ti is very high, up to 34 at.% (Ref 3), and led to the formation of the so-called "brittle α_2 phase", while oxygen contents higher than 1.5 at.% may reduce the ductility of the alloy (Ref 4). Ti-24Al-14Nb-3V alloy with very fine $\alpha_2 + \beta_0$ structure has excellent superplasticity. From the viewpoint of thermodynamics, however, the aluminum level of Ti-24Al-14Nb-3V is not sufficient to form continuous Al_2O_3 protective layers; instead complex nonprotective $TiO_2 + Al_2O_3 + AlNbO_4$ scales formed. Thus, the iso-

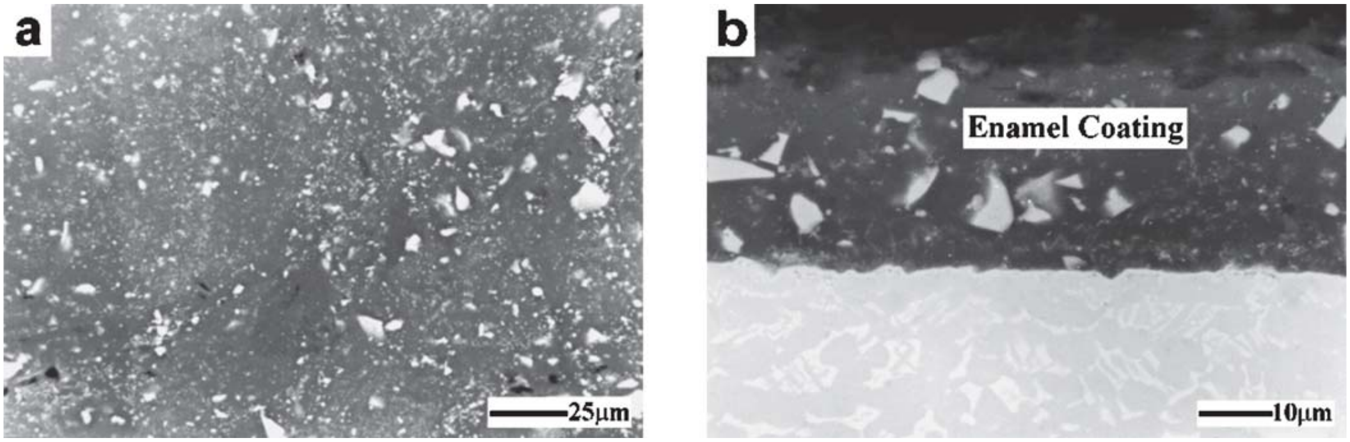

Fig. 6 (a) Surface morphology and (b) cross-sectional microstructure of Ti-24Al-14Nb-3V with enamel coating after 100 h hot corrosion in molten $(Na,K)_2SO_4$ at 850 °C

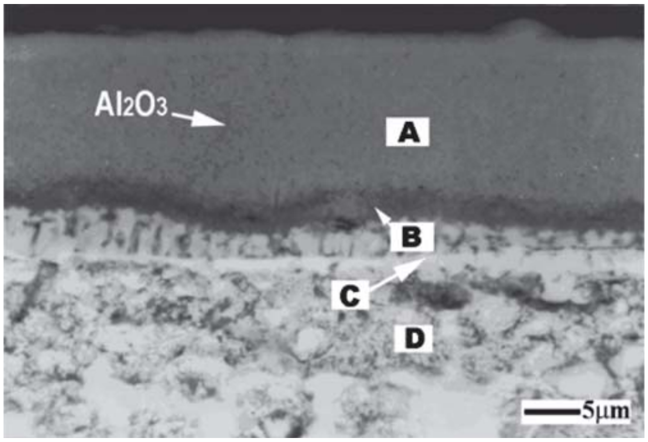

Fig. 7 Cross-sectional microstructure of Ti-24Al-14Nb-3V after corrosion for 1 h in molten $(Na,K)_2SO_4$ at 850 °C. (A: TiO_2 doped by Al_2O_3; B: Al_2O_3 doped by TiO_2; C: layer rich in oxygen; D: layer of internal corrosion and diffusion)

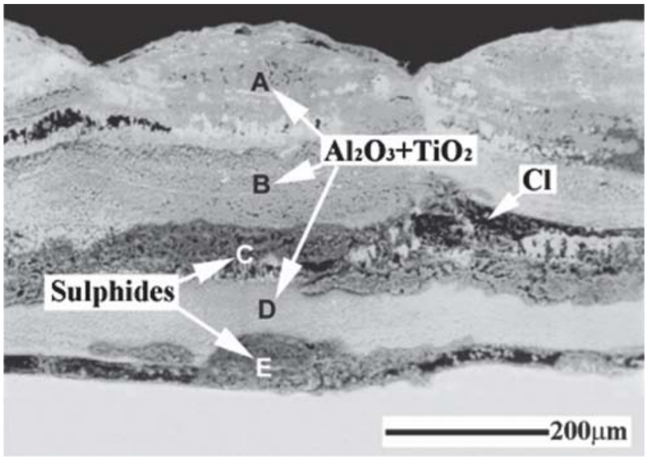

Fig. 8 Cross-sectional microstructure of Ti-24Al-14Nb-3V corroded for 5 h in $NaCl+Na_2SO_4$ melts at 850 °C

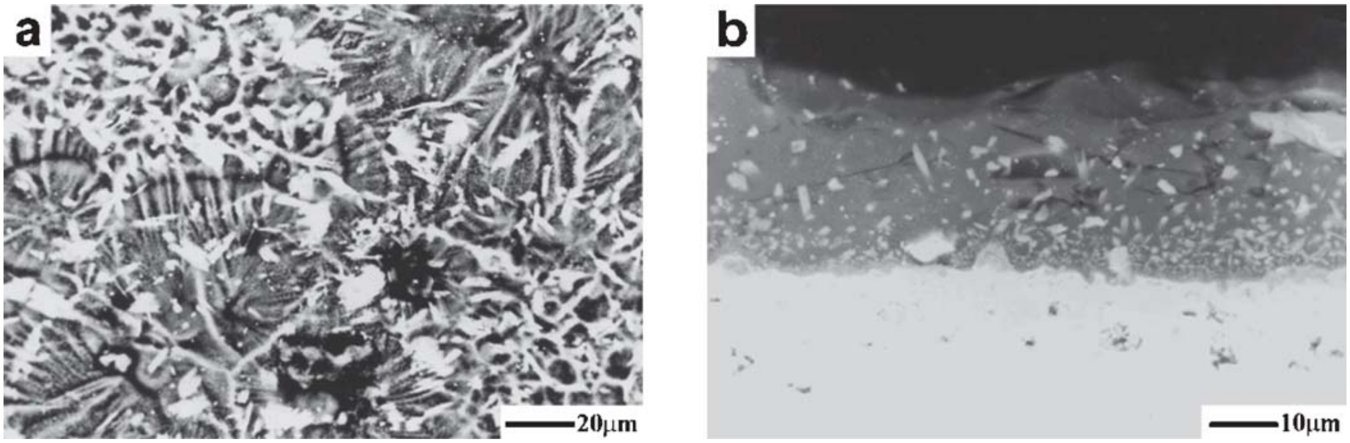

Fig. 9 (a) Surface morphology and (b) cross-sectional microstructure of Ti-24Al-14Nb-3V with enamel coating after corrosion for 100 h in molten $NaCl + Na_2SO_4$ at 850 °C

thermal oxidation kinetics of the uncoated alloys follow an approximate linear law at the temperatures range between 800 and 900 °C (Ref 6). During oxidation, Al and Ti diffuse outward to react with oxygen at the interface of oxide/substrate competitively, due to their similar affinity ability to oxygen. TiO_2 formed on Ti-24Al-14Nb-3V at the initial oxidation stage because the content of Al was lower than the criteria for the formation of protective alumina scales. With the depletion of

Ti, the Al_2O_3 and $AlNbO_4$ nodules began to form with the improvement of Nb. Then, layered mixture oxides formed on the alloy. From Fig. 3(b), it could be seen that diffusion voids formed in the layered scales. Moreover, severe spallation of oxide scales occurred during cyclic oxidation.

During corrosion in molten $(Na,K)_2SO_4$ salts at 850 °C, an initial TiO_2 scale formed on the alloy. The oxide scale was so porous that the succedent interstitial alumina nodules could form in the scale (Fig. 7). With the depletion of Ti, oxygen diffused inward through the external oxide scales (A) to react with Al and Ti at the interface of oxide/alloy to form alumina plus minor TiO_2 (layer B). A porous diffusion layer formed at the interface of oxide-scale/alloy due to the diffusion outward of metallic components of the substrate. The prior formation of the layered scales (A + B) could not obstruct the diffusion inward of oxygen and corrosives. Then, the layer rich in oxygen (C) and the layer of internal corrosion (D) formed. Furthermore, Cl^- anion could accelerate the corrosion of titanium alloys due to the cyclic formation of volatile $AlCl_3$. Then, Ti-24Al-14Nb-3V was subjected to severe corrosion in molten $NaCl + Na_2SO_4$ melts.

To improve the corrosion resistance of titanium alloys, the effects of alloying elements, surface treatment, and protective coatings on oxidation resistance of Ti alloys were widely investigated. Coatings may be the only direct way to protect the alloys from oxidation, corrosion, and oxygen embrittlement effectively to prolong the service lifetime of the alloys (Refs 6, 9–16).

MCrAlY coatings (Ref 17), ceramic coatings such as Si_3N_4 (Ref 18), SiO_2 (Ref 19), and Al_2O_3 (Refs 20, 21), glass-ceramic (Ref 22) coatings and TiAlCr (Refs 13–15) coatings were commonly applied to titanium alloys. However, there existed many inherent shortcomings in some aspects that limited their practical uses (Ref 9).

The enamel coatings (Refs 8, 9) may be a promising choice for Ti-24Al-14Nb-3V due to its good thermal and chemical stability, and its matched coefficient of thermal expansion (CTE) with the substrate. The CTE range of general enamels is $8.8 \sim 11.8 \times 10^{-6}$ °C $^{-1}$, and it can be adjusted by changing the enamel composition (Ref 23). An enamel coating with high CTE (about 10×10^{-6} °C $^{-1}$) was developed in the present work, to match that of Ti_3Al-Nb (10×10^{-6} °C $^{-1}$). Then, after 100 cycles of oxidation at 900 °C, the interface of coating/substrate Ti alloy kept intact.

Some special additives in enamel frit may improve the wetting ability of the molten enamel to the substrate during firing at an appropriate temperature. After firing, the enamel coating forms chemical bonds with the substrate (Fig. 1) instead of simple physical bonds as for the Al_2O_3 coatings. However, the volatilization of some additives may induce the dwelling of air bubbles and voids in the coatings after firing.

From the previously discussed analysis, it is evident that after firing the enamel coating will become compact with a good compatibility with the substrate because chemical bonding can be realized at the alloy/coating interface. Thus, it is not surprising that the enamel coating enables the Ti alloy to be protected from isothermal/cyclic oxidation and oxygen embrittlement, and even improves markedly the hot corrosion resistance of the Ti alloy in molten $(Na,K)_2SO_4$ or $NaCl + Na_2SO_4$.

However, EDS analysis of the enamel coating surface showed that the content of Ca^{2+} in the coating and the weight of the specimen decreased. It suggested that some oxides components of the coating were dissolved into the molten salts during corrosion. Furthermore, Cl^- anion may migrate into the coating through voids in the enamel coating and react with some oxides in the coating to replace the sites of oxygen in coating structure. Thus, the chlorides on the external surface of the coating may be dissolved into the molten salts. Moreover, others may diffuse into the coating and stay at the coating/alloy interface to react with the metallic components of the substrate. Then, the corrosion products containing Ti migrate outward to the surface of the coating along the inward diffusion passage of Cl^- anion.

In terms of the previous discussion, it seems insufficient for enamel coating to conduct corrosion test only for 100 h. From the results presented in this work, enamel should be improved to meet the demands of practical application for titanium alloys, because the coating was attacked during corrosion compared with the as-coated. The research on how to improve the performance of enamel coating is on the way.

5. Conclusions

The enamel coating showed rather good capacity to protect Ti-24Al-14Nb-3V alloy from isothermal and cyclic oxidation at 900 °C in air and from hot corrosion in molten both $(Na,K)_2SO_4$ and $NaCl + Na_2SO_4$ salts at 850 °C. Some oxides of enamel coating may be dissolved into salts during the coated alloy suffered from hot corrosion. Furthermore, the Cl^- anion may diffuse into enamel coating along voids in the coating to accelerate the corrosion of the substrate titanium alloys.

Acknowledgments

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