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Effect of Different Treatment on Corrosion Resistance of Sputtered Al Coating on Stainless Steel

Abstract: Aluminum coating on 1Cr18Ni9Ti stainless steel was prepared by magnetron sputtering method. The specimens were treated with pre-oxidation (PO) or vacuum diffusion annealing (VA). Hot corrosion resistance of the coatings beneath the deposits of Na_2SO_4 at 1050 °C was investigated. Corrosion products were analyzed by XRD and SEM. Results show that the presence of coating could improve the corrosion resistance of stainless steel. FeAl phase appeared after VA at 600 °C, which enhanced cohesive force between the coating and the substrate, and reduced the oxidation and sulfidation rate. PO treatment can protect the substrate more effectively than VA treatment for metastable Al_2O_3 formed during PO treatment can be translated to stable Al_2O_3 more quickly at high temperatures. The corrosion products of the two kinds of specimens with aluminum coating were both composed of Al_2O_3 , a little amount of FeS and Fe_2O_3 after 24 h corrosion. Al_2O_3 was formed mainly in the coatings, FeS was mainly distributed in the interface between coating and substrate of the specimens, and a small amount of FeS was distributed in the substrate. Al_2O_3 film remained intact after 24 h corrosion, and kept its protective effect on the substrate.

Keywords: magnetron sputtering, aluminum coating, heat treatment, pre-oxidation, hot corrosion

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1 Introduction

Austenitic stainless steel, the most widely used steel among stainless steel, has been increasingly used in coal-fired boilers, heat pipes, steam turbine and other fields, even in the supercritical and ultra-supercritical units [1–3]. Under the circumstance of high temperatures and S-

containing atmosphere, the remaining life of austenitic stainless steel with surface oxides is shorter than expected one, which is easy bring out potential safety hazard during service [4–7]. In order to enhance the corrosion resistance of stainless steel, one effective method is to apply protective coating on the surface of the material. The protective effect of high temperature coating depends primarily on whether the produced oxide film possesses excellent oxidation resistance. The aluminide coatings have become the most widely used high-temperature protective coatings for Al_2O_3 possesses excellent high-temperature corrosion resistance. Many researchers have studied various of aluminide coatings [8–11]. But the study on the pure aluminum coating being corroded in sulfate has been rarely reported. In this paper, pure Al coating was prepared on the surface of stainless steel 1Cr18Ni9Ti by magnetron sputtering method. And the hot corrosion resistance of the heat-treated specimens coated with molten salt Na_2SO_4 was tested in air at 1050 °C to study the influence of different treatment methods on the coating and the growth mechanism of Al_2O_3 .

2 Experimental

The experimental material is stainless steel 1Cr18Ni9Ti, with dimension of 12 mm × 8 mm × 1.5 mm, which was ground down to 1000-grit SiC paper, then cleaned ultrasonically in acetone and dried in air. The composition of 1Cr18Ni9Ti was listed as follows: C: ≤0.12, Si: ≤1.00, Mn: ≤2.00, P: ≤0.035, S: ≤0.030, Ni: 8.00~11.00, Cr: 17.00~19.00, Ti: 5(C-0.02) ~0.80 (numbers represent mass fraction, %). Al coating was prepared on the surface of specimens by HXTs-400II DC magnetron sputtering. Target material is pure Al (at.% ≥ 99.995%). Working gas was argon with the purity of 99.999%. Sputtering was carried out under the following conditions: experimental base pressure 5.0×10^{-3} Pa, argon working pressure 0.15 Pa, voltage 350V, electric current 1A. Argon gas flow was 15 sccm. Sputtering time was 3 h. After the coating was prepared, some of the specimens were treated with vacuum annealing at 600 °C for 2 h, which were denoted as VA alloys.

Some were treated with pre-oxidation at 600 °C for 2 h, denoted as PO alloys, and the others without vacuum annealing or pre-oxidation were denoted as BA alloys.

Afterwards, saturated Na_2SO_4 solution was brushed onto the specimens and dried. The above steps were repeatedly conducted until the total coating weight reaches 20~25 g/m² on every specimen, which is enough to maintain the consumption of salts throughout the hot-corrosion tests. Isothermal hot corrosion tests were performed in a box-type resistance furnace at 1050 °C in air for 24 h. The mass changes were measured and recorded discontinuously by Mettler-Toledo AG285 electronic balance with sensitive quantity of 1×10^{-5} g.

After hot corrosion, scanning electron microscopy (SEM) was used to observe the cross-sectional morphologies of the coating and the oxide scale, and x-ray diffraction (XRD) was conducted to identify the phase structure of the coatings and oxides.

3 Results and analysis

3.1 Compositions and cross section of the coatings

Figure 1 shows the XRD pattern and cross-sectional morphologies of the coating after VA treatment for 2 h at 600 °C. The XRD results indicates that FeAl phase was formed, indicating that interdiffusion occurred between the coating and the substrate after VA treatment. From SEM image, it can be seen that the combination between the coating and the substrate was close.

Figure 2 shows the XRD pattern and cross-sectional morphology of the coating after PO treatment for 2 h at 600 °C. It can be seen that Al_2O_3 was formed on the coatings after oxidation.

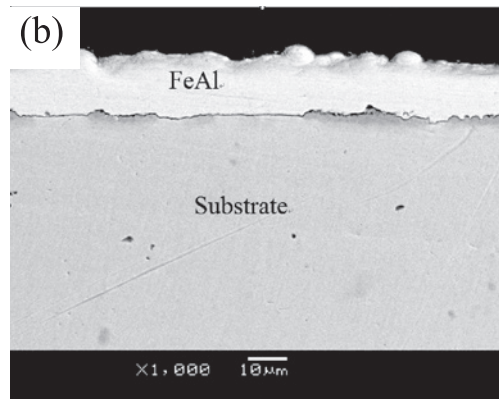
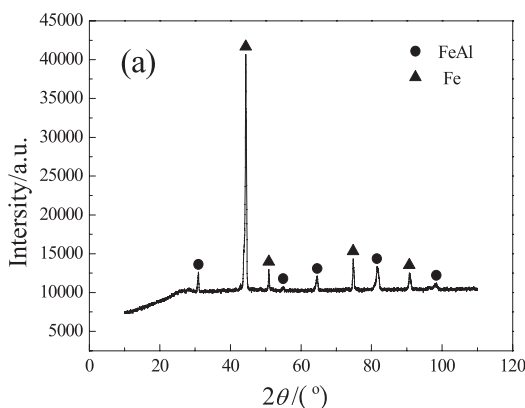


Fig. 1: XRD pattern (a) and cross-sectional morphology (b) of the VA sample

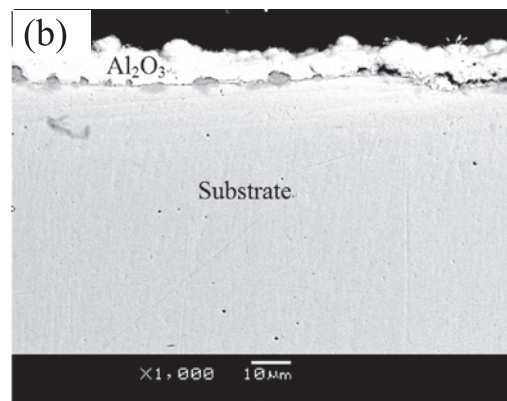
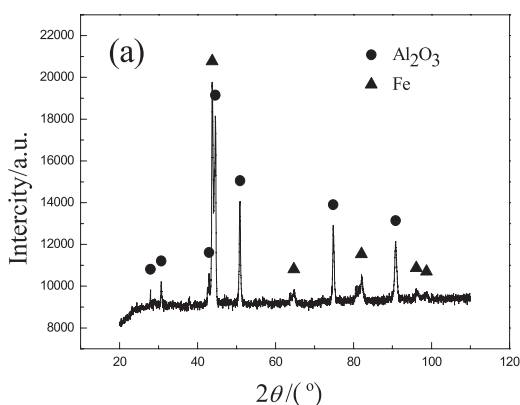


Fig. 2: XRD pattern (a) and cross-sectional morphology (b) of the PO sample

3.2 Corrosion kinetics

The corrosion kinetic curves of specimens corroded for 24 h in molten sulfate at 1050 °C are shown in Fig. 3. It can be

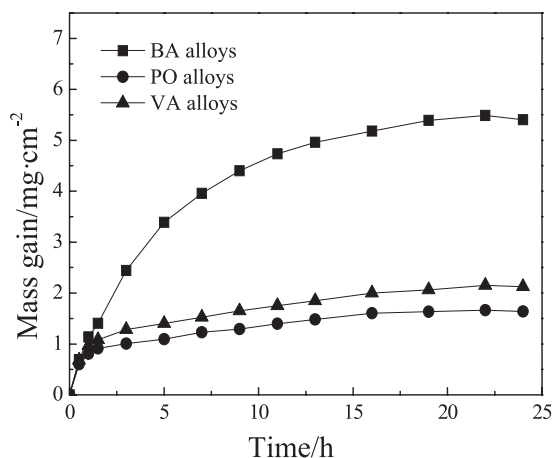


Fig. 3: Hot corrosion kinetic curves of the specimens after hot corroded for 24 h at 1050 °C

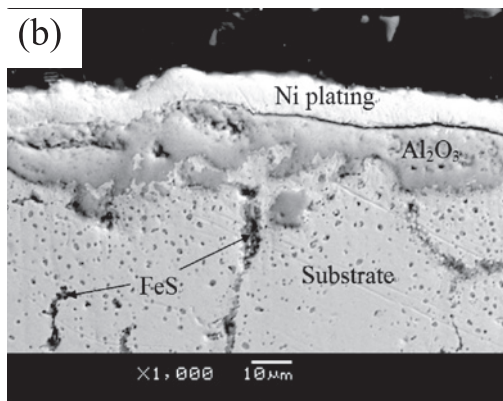
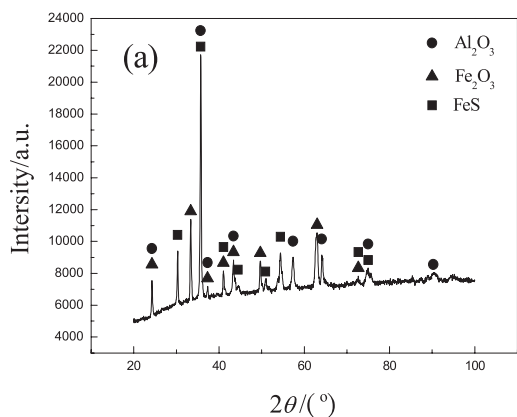


Fig. 4: XRD pattern (a) and cross-sectional morphology (b) of the VA alloy after hot corroded for 24 h

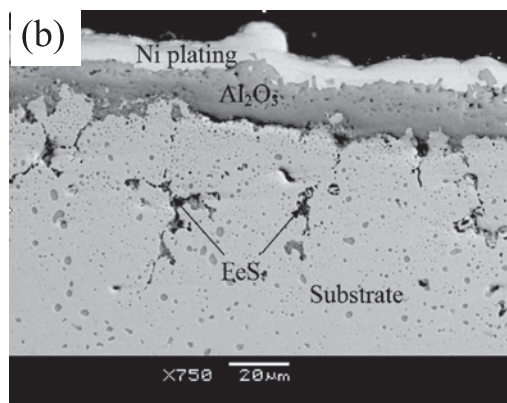
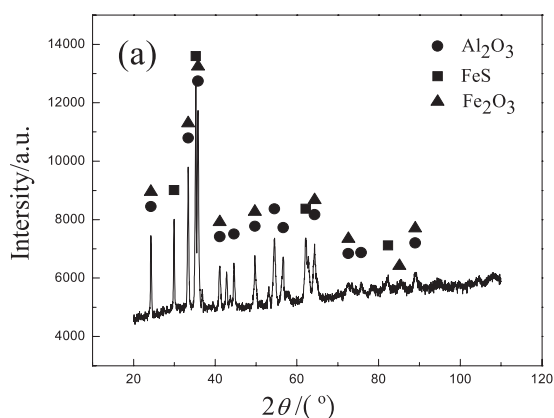


Fig. 5: XRD pattern (a) and cross-sectional morphology (b) of the PO alloy after hot corroded for 24 h

seen that the mass gain of the BA alloy was larger than those with coatings. This indicates that the presence of the coatings can enhance the corrosion resistance of specimens. Of the two alloys with Al coating, the PO alloy shows a lower mass gain as compared to the VA alloy, which suggests that PO treatment can protect the substrate better than VA treatment.

3.3 Phases analysis and microstructure of the corrosion products

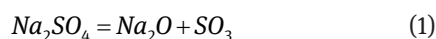
The XRD pattern for the VA alloy after 24 h corrosion at 1050 °C in air is shown in Fig. 4(a). It can be seen that both Al₂O₃ and FeS were formed. Figure 4(b) shows the cross-sectional image of the formed oxide scale. It can be seen that the Al₂O₃ in the surface layer remained dense.

The XRD pattern for PO specimens after 24 h corrosion at 1050 °C in air is shown in Fig. 5(a). X-ray diffraction on the oxide layer revealed the presence of Al₂O₃ and FeS. The cross section of the sample is shown in Fig. 5(b). It can

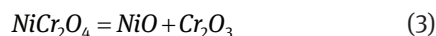
be seen that the coating can also protect the substrate. A small amount of FeS and Fe₂O₃ were formed in the substrate.

4 Discussion

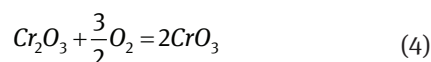
FeAl phase was formed between Al coating and the stainless steel substrate after VA treatment, which enhanced cohesive force between the coating and the substrate. When the specimen coated with the salt film of Na₂SO₄ is exposed to the oxidizing environment, it was first oxidized to form the oxide scale of Al₂O₃ and Fe₂O₃. In liquid deposit, the formula of the thermodynamic equilibrium is expressed as follows [12]:



In initial period, FeAl reacts easily with O₂ in molten Na₂SO₄ to form Al₂O₃ and Fe₂O₃ at 1050 °C. The oxide rate of Fe grows faster than that of Al [13]. With the formation of oxides, oxygen partial pressure decreases and sulfur partial pressure increases, which results in the formation of Fe and Al sulfides. Metal sulfides have large Pilling-Bedworth Ratio, which makes oxide film bear compressive stress, and thus the cracks are easy to initiate in the oxide layer, which allows oxygen to permeate the coating/matrix interface and accelerates the corrosion rate. When oxygen diffuses to the interface of coating/matrix, Cr is preferentially oxidized to form protective oxide Cr₂O₃. Subsequently Cr₂O₃ reacts with NiO to form NiCr₂O₄ spinel phase, which possesses a good protective effect on the matrix [14]. However, NiCr₂O₄ will decompose at high temperatures by the following reaction:

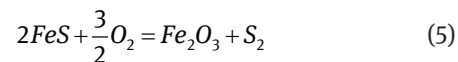


In this study, the experiment temperature is higher than 1000 °C, so the following reaction occurs:

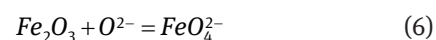


The thickness of Cr₂O₃ film decreases with the evaporation of CrO₃, which may in turn reduce the protection effect and promotes the dissolution of NiCr₂O₄. This process accelerates the oxidation rate.

On the other hand, as oxygen diffuses, the enhancement of oxygen concentration makes the sulfide oxidized to form loose oxides:



The formed sulfur further permeates to the metal and forms sulfide. Those reactions occur repeatedly, leading to the formation of oxides layer and sulfides layer. During the process, oxygen partial pressure increases with the consumption of the sulfur in Na₂SO₄, to maintain the oxidation process. The relatively enhancement of Na₂O makes the basicity increase locally, and basic fluxing occurs to the oxide scale as the following:



Thereafter, the FeO₄²⁻ diffuses outward and decomposes at the interface between the molten sulfate film and air to form porous Fe₂O₃ particles. Aluminum oxide is accumulated at the inner layer of oxides under the protection of iron oxide layer. As hot corrosion goes on, the sulfide and oxide in the scales increase the internal stress at the scale/matrix interfaces, which may damage the integrity of the scale. After the outside oxide being flaked, dense Al₂O₃ film would be exposed, which can slow down the hot-corrosion rate by rising critical concentration of the oxygen and sulfur necessary to diffuse to the matrix, and protect the matrix from further oxidation and sulfidation. From the above analysis, it can be concluded that the scale formed in the surface of the Al coating is Al₂O₃ and a little amount of FeS and Fe₂O₃ are formed at the scale/matrix interface. As shown in Fig. 4(b), the oxides on the surface is only a thin and dense layer of Al₂O₃ for the spalling of Fe oxides, and there are only few FeS, Fe₂O₃ and Al₂O₃ in the matrix. So FeAl compound enhances the hot-corrosion resistance of the alloy, which is in good agreement with the study of Lang Fengqun [15].

Different from the VA treatment, metastable γ-Al₂O₃ layer was formed on the coating after 2 h PO treatment at 600 °C. γ-Al₂O₃ can be translated to θ-Al₂O₃ at 1050 °C [16], and θ-Al₂O₃ may further be translated to α-Al₂O₃, which is accompanied with volume contraction and the formation of tensile stress in oxide film, and further leads to the cracking or even spalling of oxide scales. Thus, the mass gain of PO alloy is large at the primary stage of oxidation. The formation of α-Al₂O₃ enhances the critical concentration of O and S atoms necessary to diffuse through oxide film to the matrix, and hinders the diffusion of O and S to the matrix. As corrosion goes on, O and S atoms on the

surface of scale diffuse through oxide film to the matrix due to the increase of the partial pressures of O and S to bring out further corrosion. Similar to the VA alloy, when sulfur is consumed, the basicity increases locally, and the basic fluxing may dissolve Fe_2O_3 to FeO_4^{2-} , which then diffuse outward to the interface of molten salt and air to decompose. However, different from VA alloy, metastable Al_2O_3 after pre-oxidation can be translated to stable Al_2O_3 more quickly, which can protect the matrix more effectively. Compared Fig. 4(b) with Fig. 5(b), it can be seen that the Al_2O_3 layer on PO alloy is more dense and uniform than that on VA alloy. It is concluded from analysis that Al coating after PO treatment has better hot-corrosion resistance than that after VA treatment.

5 Conclusions

1. The specimens with Al coating on the surface possess better hot-corrosion resistant than those without Al coating. After 24 h corrosion, the oxide layer of the specimens with Al coating mainly consists of Al_2O_3 , FeS and Fe_2O_3 are distributed in the scale/matrix interface, and a little amount of which are distributed in the substrate.
2. FeAl phase appeared after VA treatment at 600 °C, which enhanced cohesive force between the coating and the substrate, and decreased the oxide rate and sulfide rate.
3. Metastable Al_2O_3 formed during PO treatment can be translated to stable Al_2O_3 more quickly at high temperatures. Compared to the specimens after VA treatment, the Al_2O_3 layer formed on the surface of PO alloy is more dense and uniform, and possesses better corrosion resistance.

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