

INFLUENCE OF RE OXIDE ADDITIONS ON HOT CORROSION BEHAVIORS OF NiAl COATINGS^①

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ABSTRACT

The influence of rare-earth (RE) oxide additions, e. g. Y_2O_3 and Gd_2O_3 on the hot corrosion behaviors of the NiAl coatings exposed to the $Na_2SO_4 + 25 \text{ wt. } -\% K_2SO_4$ fused salt at $850^\circ C$ was studied. The experimental results show that the RE oxide additions can not only reduce the corrosion rates of the coatings, but also lighten the corrosion degree of the sulfides on the coatings through the formation of stable RE-oxygen-sulfides which are aggregated in the surface corrosion areas of the coatings. With increasing additions, the effect of the RE oxides against hot corrosion will improve. Furthermore, the corrosion form of the sulfides will change from inhomogeneous corrosion, in which case the intracrystalline local corrosion is predominant, to mixed type corrosion, in which case the transgranular corrosion is predominant.

Key words: rare earth oxides NiAl based coatings hot corrosion

1 INTRODUCTION

Many investigations indicated that RE elements can remarkably improve the ability of alloys or coatings against high temperature corrosion^[1, 2]. Further studies showed that adding RE oxides into alloys or depositing them on alloy surfaces can obtain same effects^[3, 4]. Thus, the influence of various RE oxides, e. g. ThO_2 , CeO_2 , Y_2O_3 and La_2O_3 , on high temperature corrosion behaviors was studied. However, the above investigations were focused on the oxidation behaviors of the alloys with Cr_2O_3 films formed, and little attention has been paid to the alloys with Al_2O_3 films formed, especially their influence on the hot corrosion behaviors of the coatings. In the previous study, the authors found that the RE oxides added into typical NiAl coatings can considerably improve the ability of the alloys against high temperature oxidation behaviors^[5]. Based on this study, we select Y_2O_3 and Gd_2O_3 of better effects to further study the law of their influence on the hot corrosion be-

haviors.

2 EXPERIMENTAL

The Ni-based high temperature alloy M38G was used as substrate whose chemical composition (wt.-%) is 0.17C15.94Cr8.51Co4.04Al3.71Ti2.66W1.86Mo1.77Ta0.67Nb0.013BNi. The alloy was cut into samples with dimensions $10 \text{ mm} \times 20 \text{ mm} \times 3 \text{ mm}$, and a $\phi 2.5 \text{ mm}$ hole was drilled at one end of each sample, then the surfaces of the samples were abraded to 400 grit emery paper, and ultrasonic cleaning was conducted on the samples with acetone and ethanol etc. The processes to add RE oxides and prepare coatings were as follows: added pre-treated RE oxides into the solution of the electroformed nickel; under the condition of adequate stirring, co-deposition of nickel and oxides were carried out on the sample surfaces using the composite electroforming method; consequently the composite $Ni + RE_2O_3$ (Y_2O_3 , Gd_2O_3) coatings with dis-

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persive oxides particles were prepared, and the size of RE_2O_3 particles was smaller than $3\mu\text{m}$, the purities of the Y_2O_3 and Gd_2O_3 were 99.99% and 99% respectively. Through the control of the amount of RE_2O_3 addition into the solution and the electroforming conditions, the concentration of the RE_2O_3 in the coatings can be changed. Then at 900°C , the $\text{Ni}+\text{RE}_2\text{O}_3$ coatings were pack modified by aluminizing in $\text{FeAl} + \text{NH}_4\text{Cl}$ blended powder. Thereby, the composite $\text{NiAl} + \text{RE}_2\text{O}_3$ coatings with RE_2O_3 particles were prepared. For comparison, simple NiAl type coating without RE_2O_3 particles was prepared using electroforming and identical aluminizing process. The concentrations of the RE_2O_3 in the coatings were determined by chemical analysis.

The hot corrosion tests were conducted in the $\text{Na}_2\text{SO}_4 + 25\text{ wt. }-\% \text{ K}_2\text{SO}_4$ fused salt at 850°C . First, the fused salt was stirred adequately, and put into several ceramic crucibles with same volumes. After three identical samples had been embedded in each crucible, the crucibles were placed in the 850°C furnace to measure the hot corrosion behaviors of the alloys. After an interval of 10 h each time, the crucibles were taken out from the furnace, and when cooled the samples were taken out from the crucibles. After having been cleaned with boiling water, the samples were dried and weighed.

When there occurred severe local corrosion, the occurrence time was recorded. If the times for local corrosion to occur were different for identical samples, the mean value of the corrosion times was taken as the corrosion life. Likely, when there occurred corrosion damage in large areas, the corresponding times were recorded, and the shortest time for the corrosion to occur in the coatings was taken as the corrosion life. After an interval of about 25~30 h, the fused salt was changed.

The cross-section microstructures of the coatings after corrosion were examined. Light microscopic observations were used to determine the corrosion degrees and corrosion forms. EPMA analysis was used to determine the distribution law of elements on the cross-sections. X-ray technology was used to study the phase structures of the corrosion products on the surfaces.

3 EXPERIMENTAL RESULTS

Fig. 1 shows the corrosion kinetic curves of the coatings containing different amounts of Y_2O_3 or Gd_2O_3 in the $\text{Na}_2\text{SO}_4 + 25\text{ wt. }-\% \text{ K}_2\text{SO}_4$ fused salt at 850°C . In Fig. 1 the hollow points represent the occurrence times of local corrosion, and the dashed lines represent the changing curves after obvious corrosion damage. The kinetic curves in Fig. 1 indicate that there occurred local corrosion damage in the simple NiAl type coatings after about 40 h corrosion, and the corrosion damage became more obvious when the corrosion time reached 80 h. Consequently, there occurred weight loss. At this moment, severe macro-damage and local damage and stripping in the coatings could be observed. Generally speaking, the weight gain of the composite coatings containing Y_2O_3 and Gd_2O_3 is smaller than that of the simple NiAl type coatings, and the composite coatings have the characteristics of gentle weight gain at the initial corrosion stage, corrosion incubation and good integrity and no corrosion occurring on large areas. The concentrations of RE oxides have great influence on the corrosion kinetics. With increasing RE oxides additions, the ability of the coatings against hot corrosion improves. In the composite $\text{NiAl} + \text{Y}_2\text{O}_3$ coatings, except there occurred local corrosion damage in the coating with small Y_2O_3 addition (0.25 vol.-%), the other two coatings with high RE oxides additions kept good integrity, and the weight gain was small. In the three composite $\text{NiAl} + \text{Gd}_2\text{O}_3$ coatings, there occurred local corrosion at 90 h in the coatings with 0.59% or 2.45% Gd_2O_3 , while the coating with 2.45% Gd_2O_3 kept good integrity and had lowest corrosion rate. Fig. 2 shows the cross-section microstructures of the coatings after hot corrosion. The occurred severest damage in the simple NiAl coating, and in this case, the corrosion depth of the sulfides almost penetrated the whole coating. The distribution of the sulfides indicates that the corrosion of the NiAl coating is uniform, and there occurs no preferred corrosion, but the corrosion depth and area are large. The corrosion degrees of all the composite coatings are lighter than that of the simple NiAl coating; and the corrosion depends on the RE oxides addition amounts. When the RE

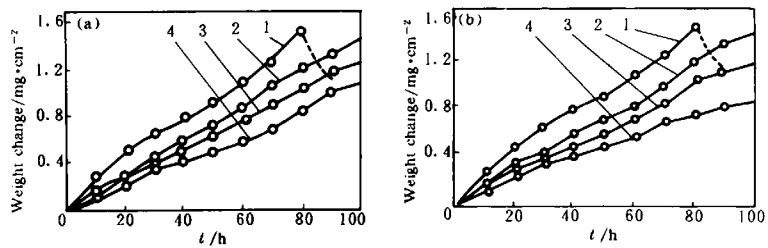


Fig. 1 Hot corrosion kinetic curves of composite NiAl+RE₂O₃ coatings in Na₂SO₄+25 wt.-% K₂SO₄ fused salt at 850 °C

- (a)—NiAl+Y₂O₃ coating: 1—NiAl; 2—NiAl+0.25 vol.-% Y₂O₃;
 3—NiAl+1.04 vol.-% Y₂O₃; 4—NiAl+2.84 vol.-% Y₂O₃
 (b)—NiAl+Gd₂O₃ coating: 1—NiAl; 2—NiAl+0.95 vol.-% Gd₂O₃;
 3—NiAl+2.45 vol.-% Gd₂O₃; 4—NiAl+3.5 vol.-% Gd₂O₃

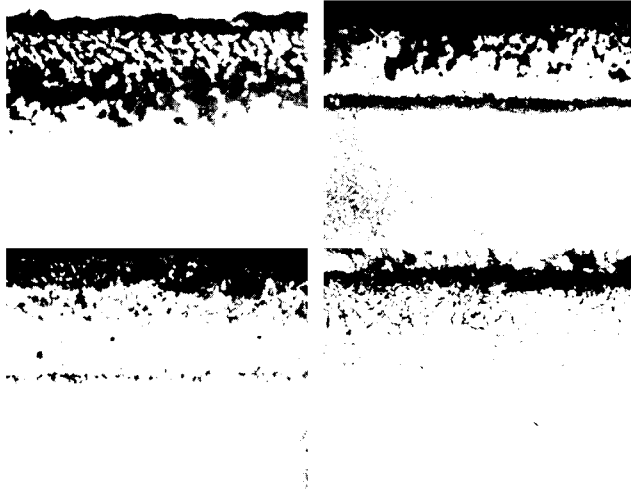


Fig. 2 Microstructures of coatings exposed to mixed fused salt at 850 °C for 100 h, $\times 400$

- (a) NiAl coating; (b) NiAl+0.25 vol.-% Y₂O₃;
 (c) NiAl+2.8 vol.-% Y₂O₃; (d) NiAl+2.45 vol.-% Gd₂O₃

oxide additions are small, e. g. 0.25% Y₂O₃, the corrosion presents mixed type of local intracrystalline corrosion and transgranular corrosion, name-

ly the NiAl phases suffered severe corrosion in the coating, and at other locations, the corrosion mainly occurred at the boundaries of the NiAl phase.

The locations on the coating surface where local macro-corrosion occurred correspond to the severe local corrosion areas on the cross-sections of the NiAl phase, and not to the transgranular corrosion areas. With further increasing RE oxides additions, the occurrence of local corrosion of the coatings weakened and the corrosion form changed into the combination of uniform corrosion on the surface and preferred corrosion on the inner side of the surface. Moreover, with increasing RE oxides additions, the depth of the whole corrosion area reduced.

Elemental maps on the cross-section of the coatings after corrosion indicate that the distribution of the corresponding products has a direct relationship with that of the RE oxides (Fig. 3). Take the EPMA analysis results of NiAl + 2.84 Y₂O₃ coating as an example. The elemental map of aluminium on the cross-section shows that under the condition of hot-corrosion, complete and continu-

ous Al₂O₃ films can form on the surfaces of the composite coating. Elemental sulfur mainly enriches in the surface layer of the coating, and the concentration of the sulfur in the inner layer is very low. Besides it distributes in the whole coating, the elemental yttrium from the Y₂O₃ mainly enriches at the coating/substrate interfaces and in the surface layer of the coating. The locations of the latter corresponds to those of the elemental sulfur. Further analysis shows that the elements in the substrate, e.g. Cr, Mo, V, enrich at the coating/substrate interfaces and dissolve very little in the coatings.

Fig. 4 presents the surface corrosion products determined by XRD of the NiAl + 2.84 vol.-% Y₂O₃ coating after hot corrosion at 850 °C for 100 h. It can be seen that the surface layer is mainly composed of β-NiAl, α-Al₂O₃, Ni₃S₂ and a little amount of complex phase containing RE. The surface of the coating with small Y₂O₃ addition has little enrichment of Y₂O₃ and no RE oxygen-

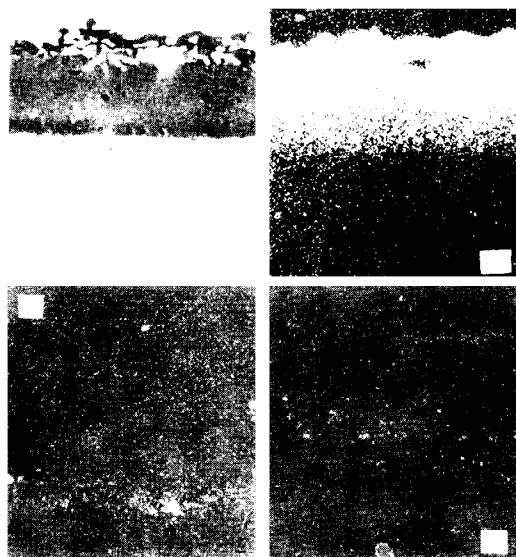


Fig. 3 Element maps on the cross section of NiAl + 2.84 vol.-% Y₂O₃ coating after hot corrosion at 850 °C for 100 h

sulfide, e. g. Y_2O_2S is found. The measurement results of the NiAl + Gd_2O_3 coatings are similar to those of the NiAl + Y_2O_3 coatings, but the kinds of their RE-oxygen-sulfides are difficult to determine.

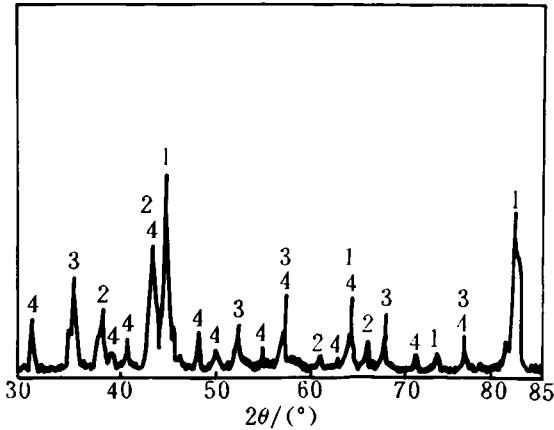


Fig. 4 X-ray diffraction analysis on the surface of NiAl + 2.84 vol.-% Y_2O_3 coating after hot corrosion at 850 °C for 100 h

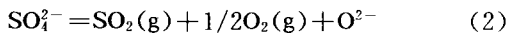
1—NiAl; 2— Al_2O_3 ; 3— Ni_3S_2 ; 4— Y_2O_2S

4 DISCUSSION

The ability of alloys or coatings against hot corrosion is determined by the protective behaviors of the oxide films formed on the surface. Many people researched the mutual reaction mechanism between the fused salt and the oxide film, and the acid base fluxing model has been widely accepted^[6, 7]. The corrosion behavior of the Al_2O_3 films in the high temperature hot corrosion range (800~950 °C) can be described using the base melting model; at the initial corrosion stage, the fused salt is neutral, and there may form corresponding oxide films on the alloy surfaces. For the Al_2O_3 films, there occurs;

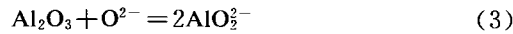


The formation of the Al_2O_3 films consumed a certain amount of O_2 , which led to the decrease of the oxygen potential at the film/fused salt surfaces, and brought about the following reaction;



The forward reaction results in the increase of the sulfur activity and the formation of inner sulfides related with the substrate, then makes the ac-

tivity of O^{2-} or Na_2O at the oxide film/fused salt interfaces further increase and makes the basicity of the fused salt increase, consequently the oxide films dissolve;



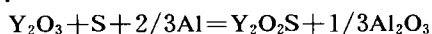
The AlO_2^- ions move through the fused salt toward the positions of high oxygen activity and separate out again, form porous Al_2O_3 films. The reciprocation of the above process will lead to the damage of the protective oxide films and the inner sulfide corrosion in the substrate. The above process mainly consists of the dissolution of oxide films and the formation of sulfides whose occurrence and development are influenced by RE additions.

First, the RE can promote the formation of the oxide films and improve their compactness^[8]. Further more, when there occur cracks in them, the oxide films have good self-remedy ability, then can more effectively prevent or impede the sulfur from penetrating the oxide films to form sulfides in the metallic substrate. At the initial corrosion stage, the long incubation of the composite coatings and small weight gain all proved that the rate by which the sulfur penetrates the oxide films reduces, and it is difficult for the inner sulfides to form. There will occur alkline dissolution in the Al_2O_3 films formed on the surfaces, and the RE will directly influence the dissolution rate of the oxide films. Under the condition of alkline fused salt, their dissolvability reduces and their chemical stability increases^[9]. The authors once found that there distributed nm-grade RE oxides particles in the Al_2O_3 films formed on the composite coatings^[10]. According to equation (3), due to the existence of RE oxides in them, the oxide films will only dissolve under stronger alkline conditions (O^{2-}). Consequently the corrosion process is slowed down and the protection of the oxide films improves.

Second, the RE oxides directly influence the formation of the sulfides and their properties. In general, sulfur is prone to combine with Al, Cr etc to form sulfides, for example, the main sulfides found in the experiment is Ni_3S_2 phase, which is prone to form low melting-point eutectic sulfides, and penetrates the substrate in autocatalysis. In the research of oxidation behaviors of alloys, it was found that sulfur has entrapment and it can improve the adhesive ability of the oxide film through

the reduction of its segregation^[11].

In the research of the sulfidation behaviors concerning Ni and Fe-Cr-Al alloys, Douglass *et al.*^[12, 13] found that the yttrium can promote the formation of Cr or Al sulfides and dissolve in corresponding sulfides. Y^+ can possess the substitutional locations of Cr in the N^- type Cr_2S_3 layer, then reduces the diffusion rate of the sulfur, and correspondingly reduces the corrosion rate. RE-bearing sulfides have the advantages of high melting points, high stability and low sulfur diffusion coefficient etc, e. g. The melting points of Y_2O_2S etc are higher than 1 000 °C, which is much higher than those of the common metallic sulfides. The Y_2O_2S found in the experiment may form as follows:



Through the above reaction, the sulfur can be stabilized in the form of stable sulfides and the formation ability of Ni, Cr, Al metallic sulfides is correspondingly weakened.

The amount and distribution of the RE oxides have a direct relationship with the corrosion behaviors of the composite coatings. With regard to the distribution of RE oxides in the coatings, after aluminization, part of the oxides dispersively distribute in the whole coatings, and the rest enriches at the coating/substrate interfaces^[14]. When their additions in the coatings are small, the RE oxides can only form a little amount RE-oxygen-sulfides by combining with part of the sulfur. Consequently there may occur severe local corrosion in the composite coatings like that in the simple NiAl coating. When their additions are higher, there will be enough RE oxides on the surface to take part in the formation of sulfides. Thereby, the sulfidation corrosion is uniform and limited in the surface layer. Meanwhile, the coating boundaries may act as short-cut tunnels, and there will form part of sulfides due to the rapid transgranular diffusion of the sulfur.

The discontinuous distribution and light corrosion degree of sulfides at the boundaries also provide an evidence that the existence of oxides at the boundaries can limit the corrosion to some degree.

5 CONCLUSIONS

The results of hot corrosion test in the $Na_2SO_4 + 25 \text{ wt. } -\% K_2SO_4$ fused salt at 850 °C show that the RE oxide additions, e. g. Y_2O_3 and Gd_2O_3 can effectively reduce the corrosion rate of the NiAl substrate. Through the formation of RE-oxygen-sulfides, e. g. Y_2O_2S and their enrichment on the surface corrosion areas, the RE oxides can effectively impede the corrosion of the sulfides on the coatings. With increasing additions, the effect of their improvement of ability against hot corrosion becomes more obvious. Furthermore, the corrosion form of the sulfides on the coatings' microstructures changes from predominant local intracrystalline corrosion with low additions to predominant transgranular mixed type corrosion with high additions.

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