CYCLIC OXIDATION OF Ni-La₂O₃ COMPOSITE

COATINGS ELECTRODEPOSITED ON NICKEL

AND Fe26Cr STAINLESS STEEL ①

Peng Xiao[1, 2], Li Tiefan[1, 2], Wu Weitao

1   State Key Laboratory for Corrosion and Protection, Institute of Corrosion and
     Protection of Metals, Chinese Academy of Sciences, Shenyang 110015
2   Laboratory of Atomic Imaging of Solids,
     Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110015

ABSTRACT   A coating of nickel with La₂O₃ oxide particles has been codeposited onto the surface of nickel as well as Fe26Cr stainless steel for improving their high temperature oxidation resistance. Both specimens of nickel and Fe26Cr stainless steel deposited with Ni-La₂O₃ composite coatings exhibited a much better resistance to cyclic oxidation in air at 900 ℃ than those of the two bare materials. Electron probe microscope analyses revealed that, for both Ni-La₂O₃ coated nickel and Fe26Cr stainless steel, a La₂O₃-rich NiO layer close to the gas/scale interface was produced after the composite film had been thoroughly oxidized during the thermal cyclic processes. It is believed that the enhancement of cyclic oxidation resistance of nickel and Fe26Cr stainless steel deposited with the Ni-La₂O₃ codeposits coatings may be related to the incorporation of La₂O₃ particles (especially those with the size of several nanometers) into NiO scale. The mechanism of the effect of La₂O₃ dispersoids on the oxidation behavior of nickel and Fe26Cr stainless steel was also discussed in details.

Key words   nickel   Fe26Cr stainless steel   cyclic oxidation   electrodeposited Ni-La₂O₃ composite film

1 INTRODUCTION

It is well known that the addition of so-called reactive element (RE) and its oxide into alloy or coating may improve those oxidation resistance at high temperature. Recently, Li and co-workers[1] developed a β-NiAl type composite coated with dispersive RE_xO_y (RE = Y, La, Gd, etc) particles obtained by a technique of two sequential steps: electrodeposition of Ni-RE_xO_y composite film onto superalloy and thereafter aluminizing. The authors[2, 3] further revealed that the incorporation of La₂O₃ particles with diameter below 20 nm into α-Al₂O₃ scale is responsible for the slow growth of the scale on the La₂O₃-modified β-NiAl coating compared with β-NiAl coating. By considering the well understandable oxidation mechanism of nickel and

meanwhile the blades of air compressor of aeroplane engines made of the stainless steel at present, in this paper, the cyclic oxidation behavior of the electrodeposited Ni-La₂O₃ composite films on both nickel and Fe26Cr stainless steel has been investigated and discussed in details.

2 EXPERIMENTAL

Plates of both nickel with the purity over 99.9% and Fe26Cr stainless steel, whose chemical compositions are listed in Table 1, were cut into small specimens with dimensions of 10 mm × 10 mm × 1 mm and 10 mm × 10 mm × 2 mm separately. The specimens were abraded with silicon carbide paper to 800 grit and then electrolytically codeposited with a film of Ni-La₂O₃ from a nickel-electrolyte containing desired con-

centration of La_2O_3 particles (purity> 99.98%) with the parameters of 2.0 A/dm^2, 25~ 35 ℃ and pH = 6. The added La_2O_3 particles were kept suspended and dispersed in the baths through mechanical agitation during electrolysis. The contents of La_2O_3 codeposited into the composite film were mainly dependent on the concentration of the particles in the electrolyte as well as the agitation strength, and the codeposited thickness of the composite film was determined by the depositing time. For comparison, specimens of nickel and Fe26Cr stainless steel plates without and with a nickel-plating were also prepared, the latter was obtained using the same electrolytic bath and the same parameters as that for preparing the composite film but without adding La_2O_3 particles. All the specimens were, prior to oxidation, polished with 2.5 μm diamond paste.

Table 1   Chemical compositions of Fe26Cr stainless steel(%)

Cr	Mo	Si	Mn	S
26.5	1.1	0.12	0.02	0.01

P	C	N	Fe
0.012	50×10^{-4}	130×10^{-4}	bal.

The cyclic oxidation at 900 ℃ was carried out in a furnace where specimens could be kept at 900 ℃ for a 50 min exposure followed by a 10 min cooling to room temperature. The oxidized specimens were periodically weighed and inspected through SEM/EDX, OM and EPMA. In order to better understand the effects of La_2O_3 particles on the oxidation behavior of the codeposited film, both microstructures of the isothermally unoxidized and oxidized composite films on nickel were investigated at 200 kV in a JEM-2000EX high resolution electron microscope with a point resolution of 0.21 nm.

3   RESULTS

3.1   Morphology and microstructure of Ni-La₂O₃ codeposited film

The codeposited La_2O_3 particles from an electrolyte containing 30 g/L La_2O_3 particles are revealed to be in size of micrometers under OM observation as seen in Fig. 1(a). SEM revealed a view of the distribution of particles on the surface of the composite film (Fig. 1(b)). Fig. 1(c) is a TEM dark-field image, which shows that most of those above so-called micro-particles, in fact, are "agglomerated cluster" consisting of particles with size far less than micrometer-size in the composite film. Further magnifying the particle clustered zone in atomic level, dispersoids of La_2O_3 nanocrystallites with diameter below 5 nm were also usually found as shown in Fig. 1(d). It is presumed that such nano-particles originated from the added La_2O_3 powder or from those slight dissolution in the bath.

3.2   Cyclic oxidation of nickel coated with electrodeposited Ni-La₂O₃ composite

Fig. 2 shows the dependence of mass change on time of cyclic oxidation for nickel plate and the same plate coated with nickel film as well as with Ni-La₂O₃ film up to 200h. The result indicates that among the three kinds of specimens, nickel coated with Ni-La₂O₃ films has the slowest scaling rate, which is also discrepant if the specimens coated with the different La_2O_3-containing composite film in various thicknesses. A number of thermal cyclic tests showed that, in general, the scaling rate among the specimens coated with codeposited composite films with corresponding thickness was decreased with the increment of contents of La_2O_3 particles in the film. But in some occasions, the nickel coated with composite film only contained 1.8% La_2O_3 particles also exhibited a better oxidation resistance as that illustrated in Fig. 2. Therefore, the state of La_2O_3 dispersoids in the composite film may play the major role in modifying the cyclic oxidation behavior of the specimen.

According to Fig. 2, nickel with a composite film in 6.5~ 7.0 μm thickness also has a low scaling rate as those with relatively thicker film. From the above results, it may be concluded that the codeposited film may be applied as a kind of good protective coating on nickel.

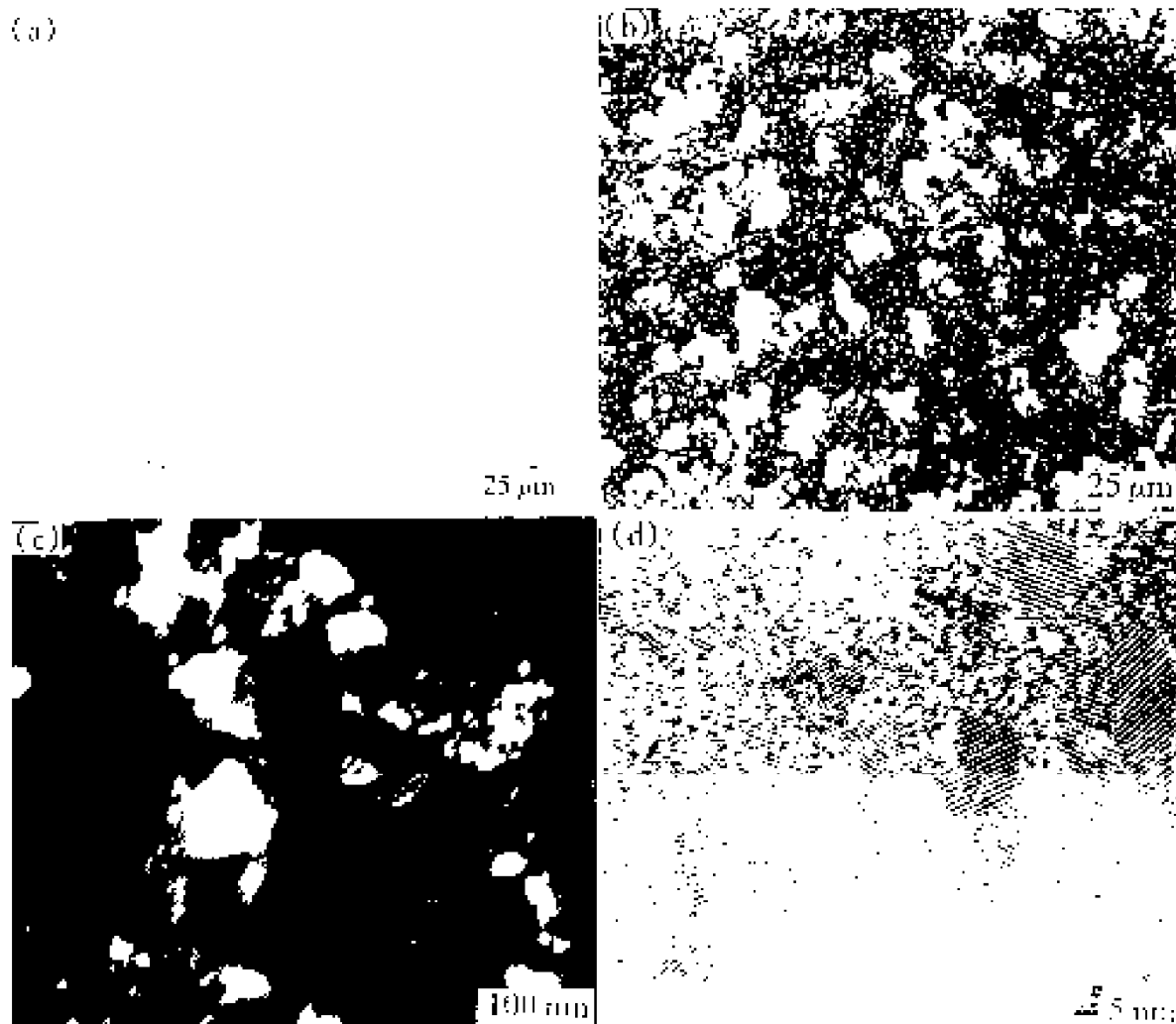The difference of surface morphology of

Fig. 1   Distribution of La₂O₃ dispersoids in composite film observed by
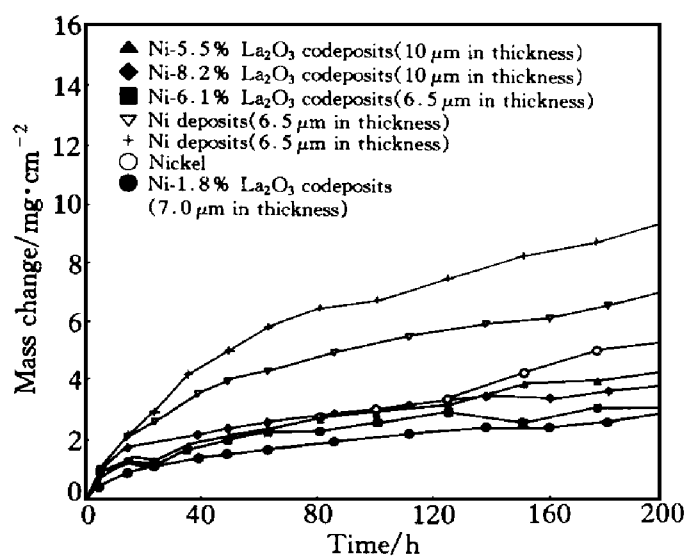OM (a), SEM (b), TEM (c) and HREM (d), respectively

Fig. 2   Mass change vs time curves of
various specimens cyclically
oxidized at 900 ℃ for 200 h

nickel plate with the composite film by comparison to those with and without nickel-plating is presented in Fig. 3, a finer-grained NiO scale was produced on the former specimens. Meanwhile, it is interesting to note that very fine pits can be clearly seen in NiO grains on the scale surface of the other two La₂O₃-free specimens.

After the specimens codeposited with the composite film having been isothermally oxidized at 900 ℃ for 24 h, the trace of La element through the whole thickness of the film oxidized was detected by EPMA[4]. La₂O₃ particles with size not below but over approximately 20 nm in NiO scale were also found by means of high resolution electron microscope[4]. Fig. 4 shows the electron-diffraction patterns of NiO oxide near the surface of the composite film after 1h oxida-

**Fig. 3   SEM morphologies of various specimens
cyclically oxidized at 900 ℃ for 200 h**

(a) —Nickel; (b) —Nickel coated with nickel deposits; (c) —Nickel coated with Ni-La₂O₃ codeposits

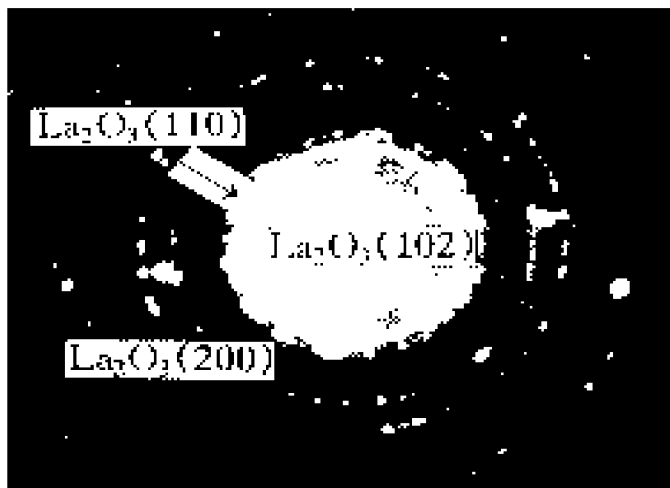**Fig. 4   Electron diffraction of NiO scale
near surface of composite film after
1 h cyclic oxidation, showing
La₂O₃ particles in scale**

**Fig. 5   TEM morphology of NiO scale
on composite film after 24 h
isothermal oxidation**

(La₂O₃ particles incorporated into
scale marked with " arrows")

tion, which indicates La₂O₃ particles existing in the scale. The TEM morphology after 24 hisothermal oxidation was presented as in Fig. 5, where part of La₂O₃ particles are marked with " arrows".

3. 3   Cyclic oxidation of Fe26Cr coated with electrodeposited Ni-La₂O₃ composite

The cyclic oxidation kinetics of bare Fe26Cr stainless steel plate and Fe26Cr steel plate with

nickel film as well as with Ni-La₂O₃ film are illustrated in Fig. 6, which indicates that the weight lose of oxide scale is inhibited after coating, and among the two films, the Ni-La₂O₃ composite one has a slower scaling rate. The phases existing in the oxide scales of different specimens after 50 h isothermal oxidation at 900 ℃ are given in Table 2.

The surface morphologies of the three cyclically oxidized specimens are shown in Fig. 7, which reveals that a significant amount of oxide
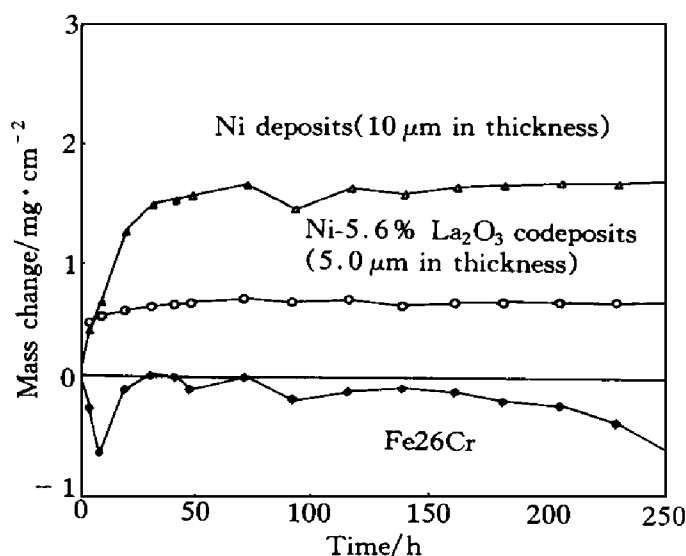
Fig. 6 Mass change vs time curves of various specimens cyclically oxidized at 900 ℃ for 250 h

**Table 2 Phases detected in oxide scale of three kinds of specimens**

Specimen	Composition
Fe26Cr	Cr_2O_3+ SiO_2+ Fe_xO_y
Fe26Cr+ Ni deposits	NiO+ Fe_xO_y (with slight dissolution of Cr)
Fe26Cr+ Ni·La$_2$O$_3$ deposits	NiO(with slight dissolution of Fe and incorporation of La$_2$O$_3$)

scale spallation, as seen in Fig. 7(a) , occurred on the bare stainless steel with lots of pores formed on the oxide-removed regions near the scale/ matrix interface as in Fig. 7(b) , and the scale spallation sometimes also took place on the nickel coated Fe26Cr, as in Fig. 7 (c) , here slight Si and Mo could be detected by EDX in "A"-marked area but not in "B" area. However, Fig. 7(d) indicates no oxide spallation on the Ni·La$_2$O$_3$ codeposited Fe26Cr. Therefore, the electrodeposited composite film is helpful to improve the oxidation resistance of stainless steel to high temperature.

4 DISCUSSION

The beneficial effects of RE or RE_xO_y on the oxidation of nickel have been studied by several authors[5- 10], but attention to the technique of incorporation of RE_xO_y particles into nickel by electrodeposition as well as oxidation behavior of nickel or other metal materials such as stainless steels coated with the electrodeposited Ni·La$_2$O$_3$ composite film has less been paid due to usually micrometer-size particles codeposited with nickel, which in common sense, will not have a positive role in improving the oxidation. Our present study indicates that both cyclic oxidation resistance of nickel as well as Fe26Cr stainless steel have been improved by codeposition of the Ni·La$_2$O$_3$ composite film onto those surface. The reason may be only related to the volume fraction of the particles with size of nanometers (Fig. 1(d)) among all the La$_2$O$_3$ particles deposited into the nickel film, since the further increment of the La$_2$O$_3$ contents would not cause the reduction of scaling rate of the films rigidly as seen in Fig. 2. From Fig. 4 and Fig. 5, it can be found that, during the oxidation of the composite film, deposited La$_2$O$_3$ particles were also incorporated into NiO grains as well as its grain boundaries. However, those nanoparticle below 5 nm (Fig. 1(d)) was difficult to be found in NiO scale in atomic level by high resolution electron microscopy. It is believed that the partial or complete dissolution of La$_2$O$_3$ nanoparticles with a size below 5 nm (or more or less than 5 nm) possibly occurred during oxidation at elevated temperatures. The presumption is reasonable if considering the dependence of dissolution of the second-phase dispersed particles on the surface free energy(surface tension) , the latter causes that La-O bonds at the surface of the La$_2$O$_3$ particle are not as strong as in its interior. The smaller the particle, the larger the surface energy, and the weaker the La-O bonds at particle surface. When the size of an added particle is so small that it is below the above-mentioned size-limit, the surface tension will reach a limit value driven by which La ions are injected from the weaker La-O bonds into adjacent NiO lattice. In view of high radius ratio of La^{3+} to Ni^{2+} ($\gamma_{La}{}^{3+}$ / $\gamma_{Ni}{}^{2+}$ = 1. 54) , high elastic energy will also be created in NiO lattice into which La$_2$O$_3$ particles have dissolved, thereafter, the decrement of elastic energy will drive
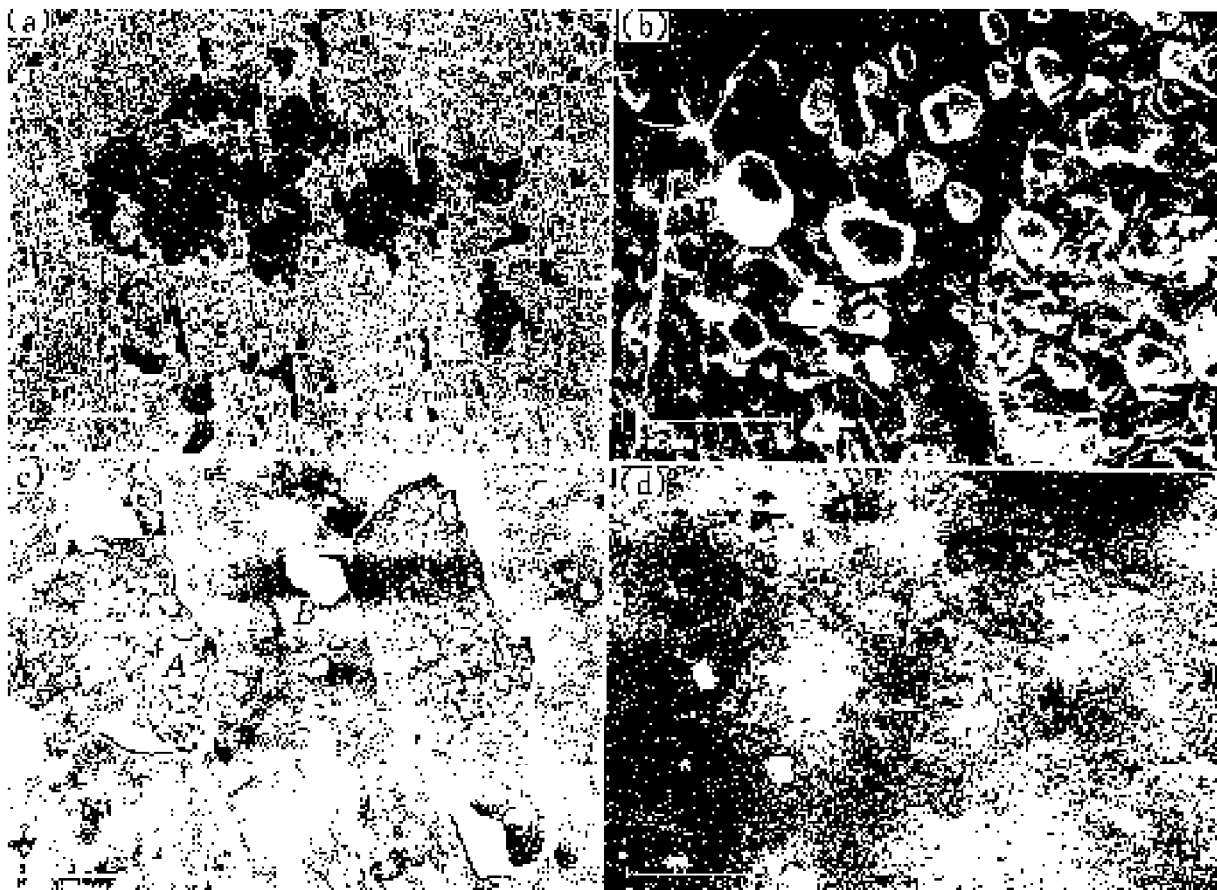
**Fig. 7   SEM morphologies of various specimens
cyclically oxidized at 900 ℃ for 200 h**

(a) —nickel; (b) —nickel coated with nickel deposits;
(c) —nickel coated with Ni-La₂O₃ codeposits; (d) —Fe26Cr coated with Ni-La₂O₃ codeposits

La^{3+} out of NiO lattice and segregate to its grain boundaries. The formation of finer NiO grains on the composite film may be just related to the segregation of La^{3+}, which plays a "solute drag effect" role in preventing NiO grains from further growing. Because pure NiO growth below 1 000 ℃ is mainly determined by outward diffusion of Ni^{2+} along the grain boundaries[11], the segregation of La^{3+} can reduce or inhibit the Ni^{2+} diffusion. According to the presumption, if the nano-meter size La_2O_3 in the composite film is all in homogeneous dispersion state, an induced consequence is that increasing the contents of La_2O_3 nanoparticles in the composite film to a certain level, will result in the effective inhibition of Ni^{2+} diffusion and the change of NiO growth mechanism from predominantly outward Ni^{2+} transport to predominantly inward O^{2-}

transport. The EPMA result[4] showed that La_2O_3 is doped in the outer part of NiO scale with thickness corresponding to those of the original codeposited film after the latter has been completely oxidized. It is a proof that, in some cases, that O^{2-} transport through the scale is a scaling-controlling process. In the meantime, the modification of oxidation mechanism of the composite film reduces the stresses produced in NiO scale and enhances the mechanical properties during thermal cycling. The opinion was also supported by the recent work of Cwzerwinski et al[8- 10]. who found that ceria sol-gel coating with the particles below 10 nm could modify the oxidation behaviors of nickel. Moreover, the improvement of Fe26Cr stainless steel in the presence of the Ni-La₂O₃ film is also contributed much to the La_2O_3-modified NiO scale creation.

But, it is interesting to note that the scaling rate of stainless steel with the nickel or Ni-La$_2$O$_3$ deposits is lower than that of nickel plate with the two kinds of deposits, this may be resulted from the doping effect of the elements from the steel matrix on NiO oxide during the cyclic oxidation process. The reason of the reduction of cyclic oxidation resistance of both the materials with Ni-plating is mainly that many defects, which are blocked by segregated La^{3+} as happened to the composite film, exhibits in the nickel deposits.

5 CONCLUSIONS

(1) The scaling rate of nickel during the cyclic oxidation at 900 ℃ through a coating of electrodeposited Ni-La$_2$O$_3$ composite film is reduced. Meanwhile, finer NiO grains were formed of the scale on the composite surface.

(2) The electrodeposited Ni-La$_2$O$_3$ composite film can be applied as a kind of protective coating, which may prevent the spallation of oxide scale on Fe26Cr stainless steel during the thermal cycling at 900 ℃.

(3) The incorporation of La$_2$O$_3$ particles into nickel through codeposition process shows great benefit to its oxidation performance, and La$_2$O$_3$ nanoparticles (below 5 nm) were clearly observed in the composite film. It is presumed that the modification of the growth mechanism for NiO scale is, to a great extent, contributed to the partial or complete inhibition of Ni^{2+} along grain boundaries through the segregation of La^{3+} which was originating from the dissolution of La$_2$O$_3$ nanoparticles at exposure temperature.

REFERENCES

1 Li T, Ma X. In: Guan H, Wu W, Shen J et al eds, Proc Inter Symp High Corrosion & Prot, Shenyang, June 1990, China. Shenyang: Liaoning Science and Technology Publ, 1991: 85.

2 Li T, Yu Y, Peng X, Xu S et al. J Corrosion & Prot, (in Chinese), 1992: 12: 284.

3 Peng X, Li T, Yu Y et al. J Rare Earth, 1994, 12: 149.

4 Peng X, PhD dissertation, (in Chinese). Institute of Corrosion & Protection of Metals, Chinese Academy of Sciences, 1995.

5 Moon D P. Oxid Met, 1989, 32: 47.

6 Moosa A A, Rothman S J. Oxid Met, 1985, 24: 133.

7 George P J. Mater Sci Eng, 1989, A116: 119.

8 Czerwinski F, Smeltzer W W. J Electrochem Soc, 1993, 140: 2606.

9 Czerwinski F, Smeltzer W W. Oxid Met, 1993, 40: 503.

10 Czerwinski F, Smeltzer W W. Oxid Met, 1995, 43: 25.

11 Atkinson A, Taylor R J, Hughes A E. Philos Mag, 1982, A45: 823.

(Edited by Peng Chaoqun)