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Preparation and characterization of sol–gel Al_2O_3/Ni–P composite coatings on carbon steel

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Abstract

Ceramic films have been applied to improve the resistance against high temperature oxidation of carbon steels. Alumina film was prepared on carbon steel surface by a dip coating technique. Electroless Ni–P plating film has been pre-deposited as an intermediate layer to improve the adherence of the film to carbon steel substrate. The oxidation kinetics of coated sample was investigated by measuring weight gain at 800 °C for 100 h. The surface and cross-section morphology of samples before and after oxidation were characterized by scanning electron microscopy (SEM). The composition and element distribution at the interface of the coated samples were analyzed by energy dispersive spectroscopy (EDS) and EMAX.

The results show that the composite coating is uniform. The alumina coating adhesion strength to the substrate is up to 20 ± 2 N in scratch test because the alumina film presents interdiffusion of nickel and aluminum during heat treatment. The oxidation resistance test indicates higher oxidation resistance of as-coated carbon steel comparing to uncoated ones.

Keywords: Sol–gel processes; Alumina coating; Electroless plating Ni–P film; Adhesion strength; Oxidation resistance

1. Introduction

Carbon steels are widely used as a structural material in various engineering applications. However, failure of carbon steels because of the very high corrosion and oxidation rate in aggressive solutions and atmospheres has always been a concern. The use of coatings is specially recommended to protect these alloys at moderate temperatures. Oxidation resistance may be improved by using various surface coatings. A number of coatings have been adopted to improve its corrosion and oxidation resistance properties.

Ceramic coatings are known to be a promising surface technology because of their advanced oxidation, corrosion, and wear resistance. There are many technologies to get ceramic coatings on metallic substrates. Among these techniques, sol–gel technique is considered to be one of the most promising techniques, because it is simple, easy to implement, relatively inexpensive and allows coating of complex shaped geometry. At the same time sol–gel technique provides a precise composition control and easy-to-control dopants at a desired level. Extensive researches have been carried out on applying coatings of SiO_2, Al_2O_3, CeO_2, nano-TiO_2, ZrO_2–SiO_2, Al_2O_3–SiO_2, SiO_2–TiO_2–ZrO_2 etc. by the sol–gel technique to protect various metallic materials like mild steel, stainless steel, magnesium, aluminum and their alloys from chemical corrosion and oxidation [1–7]. Among these coatings, alumina is one of the most important protective coatings. But alumina shows non-wettable behavior and thermal expansion coefficients mismatch with carbon steel. To improve the adherence of the coating by sol–gel technology to its substrate, various pretreatments have been adopted, such as sand-blasting, phosphate treatment, chromating, hot dipping, combined laser/sol–gel processing and alloy intermediate precoating [8–10]. However, the modes of bonding are mainly mechanical and the bonding strength of films with steels is only several MPa.

The aim of this work has been to improve alumina layer bonding with carbon steel by electroless plating Ni–P alloy intermediate layer. The layer provides an excellent bond for the ceramic coating and substrate under high temperature and improves the oxidation resistance of the carbon steel.

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2. Experimental

2.1. Composite coatings preparation

45#carbon steel (carbon content: 0.42–0.50 wt.%) in annealed state was used as substrate. The sample was cut to 30 mm × 30 mm ×5 mm. The specimens were polished using abrasive papers progressively from 120 to 800 grit, degreased, cleaned and dried at 90 °C. The electroless nickel plating was processed under conditions listed in Table 1. The as-plated specimens were cured in a vacuum furnace at 180 °C for 1 h to improve coating adherence.

A boehmite sol was prepared by aluminum isopropoxide [$Al(OC_3H_7)_3$] and distilled water in molar ratio of 1:85. The mixture was intensively stirred at 85 °C for 1 h to extract the isopropanol, the nitric acid was added as catalyst (molar ratio of Al:HNO_3 = 1:0.2), cured for 24 h at 95 °C to get clear boehmite sol.

The nickel-plated specimens were dipped into the boehmite sol and withdrawn at 2 cm/min rate, then dried at 80 °C for 1 h in a vacuum furnace to get a thin gel film. The above processes were repeated times to get a sufficient thickness. The coated specimens were then treated at 600 °C for 1 h in an electric oven in air with heating rate under 3 °C/min.

2.2. Characterization of the composite coatings and adhesion test

The surface and cross-section morphology, chemical composition, and element distribution of the coated specimens were examined by SEM (*SIRION JY/T010-1996 FESEM*), EDS, and EMAX. Adhesion test was performed using a scratch tester (*WS-2002 auto-scratcher, China*) with a 120° cone diamond indenter (*rad.* 200 μm). A scratch was made on the surface of the coating by progressively loading from 0 to 100 N. A crack was initiated along the scratch groove accompanying a sound emission. A computer collected and recorded the sound emission signals and transferred the adherence curve of coating according to the sound emission intensity to evaluate the bond strength of the coatings.

2.3. Oxidation test

Oxidation tests of both as-coated and uncoated samples were performed at 800 °C for 100 h in air, the weight gain measured at regular intervals of 20 h. Afterwards, the microstructure of samples was analyzed by XRD (*Rigaku D/Max 2550PC X*) with diffraction angle range (2θ) 4–80°. Both surface and cross-section morphology of samples after oxidation were characterized by SEM, and the element distribution was analyzed by EMAX.

Table 1
The conditions of the electroless nickel plating.

Components	Parameters	Process parameters	
$NiSO_4$	25 g/L	Temperature	85–90 °C
NaH_2PO_2	23 g/L	pH value	4.5–5
$NaC_2H_3O_2$	15 g/L	Coating time	1 h
$C_6H_5Na_3O_7$	10 g/L	Film thickness	15–20 μm

3. Results and discussion

3.1. Characterization of the composite coatings

When the alumina sol had been coated on carbon steel sample surface by dipping in the boehmite sol bath directly, the alumina film scaled away from substrate after heating at 600 °C for 1 h. It indicates that the ceramic coating shows a non-wettable property, obstructing film nucleation, and a thermal expansion coefficient mismatch with carbon steel.

Fig. 1 shows the surface morphology of carbon steel with composite coatings. It can be observed that the surface is uniform without porosity and cracks. The EDS results as shown in Table 2 show that the elements of the composite coatings mainly contain Al and O. Fig. 2 presents the SEM micrograph the cross-section of sample with composite coating layer. There are two layers, the intermediate nickel layer is about 15 μm and the outer layer is alumina coating of about 7 μm. The line elements distribution was shown in Fig. 3, indicating that interdiffusion of nickel and aluminum is taking place along the

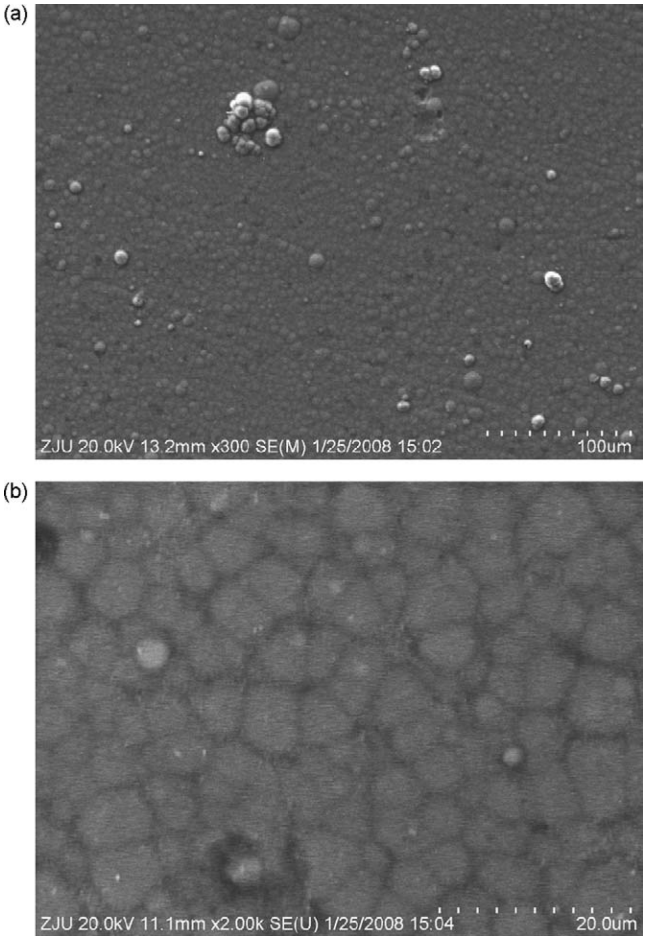

Fig. 1. (a) SEM surface morphology of the composite coatings and (b) higher magnification of (a).

Table 2
EDS analysis of sample with composite coatings.

Elements	Mass fraction (%)	Molar fraction (%)
C K	3.09	5.81
Al K	35.93	30.08
O K	39.58	55.88
Ni K	20.12	6.13
Total amount	100.00	100.00

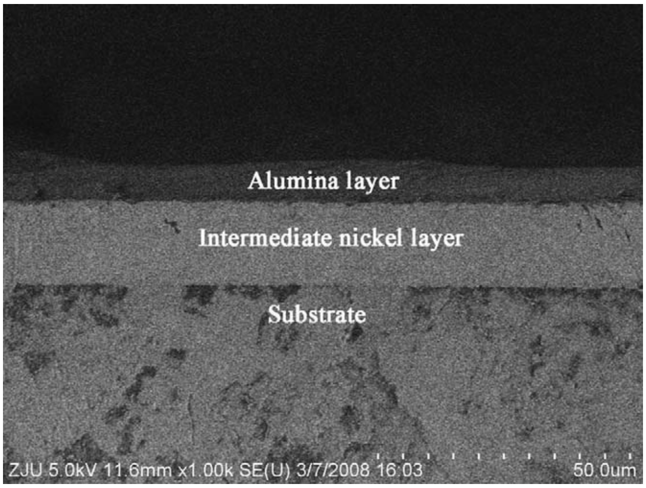

Fig. 2. SEM cross-section micrograph of the composite coatings.

interface, expected to be responsible for enhancing the interfacial bonding strength. It may also reduce the tension in the film shrinkage and expansion during heat treatment.

The results of adhesion of the composite coatings to the substrate, assessed by scratch tests are shown in Fig. 4. The critical load on coated samples is 20 ± 2 N. A few area of the coating was spalled around the indentation made with increasing load as seen in the micrograph of the scratch track. It indicates the adherence of the alumina coating to substrate is improved greatly by the intermediate nickel layer. Good adherence of the film to substrate is also a prerequisite to good oxidation resistance of carbon steel.

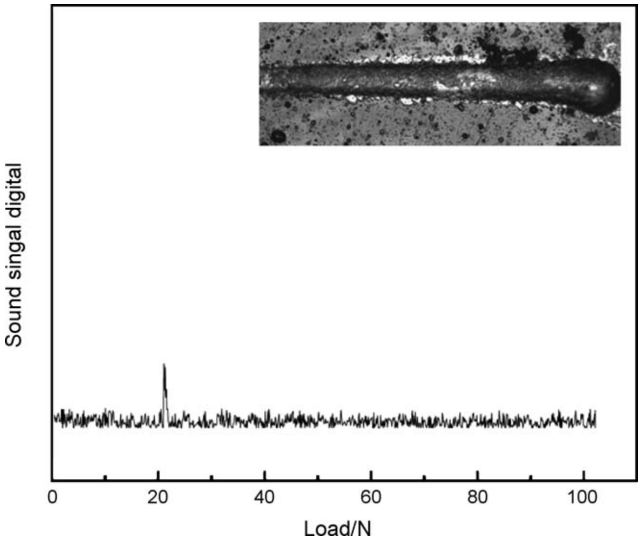

Fig. 4. Scratch test results on the composite coatings to the substrate.

3.2. Oxidation behavior

The oxidation kinetic curves for both as-coated and uncoated samples at 800 °C are shown in Fig. 5. The samples weight gain increase linearly with test time. Compared with that of an uncoated sample, the oxidation rate of the as-coated sample is reduced significantly. Massive oxide spalling of the uncoated sample occurred, and the fresh surfaces were exposed and the subsequent oxidation continued. As seen from Fig. 5 the uncoated sample had huge mass gains, its kinetics curve was plotted only within 40 h. In contrast, the mass gains of the composite coatings was far lower than that of uncoated sample. After being oxidized for 100 h the composite coating shows uniform and free of spalling, except for a few bulges indicated

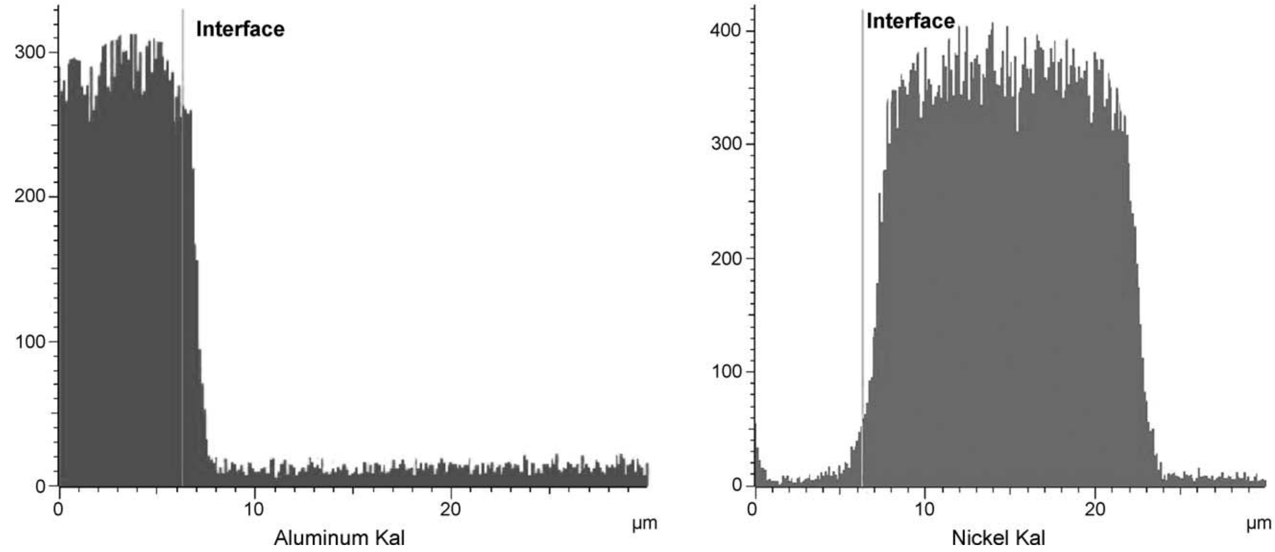

Fig. 3. Elemental line profile of cross-section of the composite coatings by EMAX.

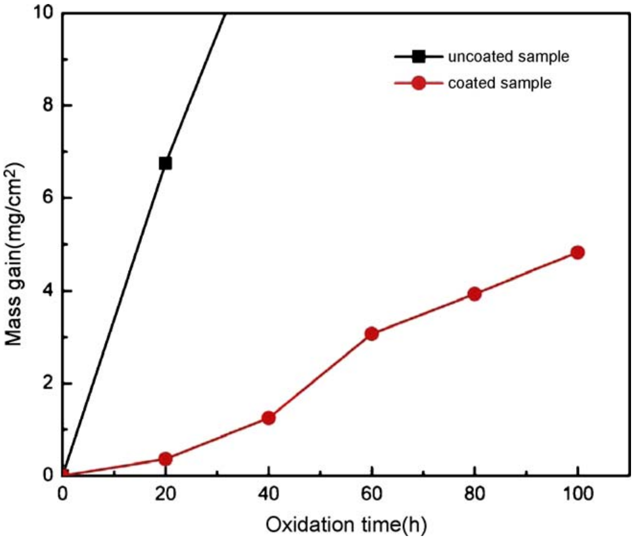

Fig. 5. Isothermal oxidation kinetics curves of uncoated and coated carbon steel at 800 °C.

Table 3
EDS analysis on the surfaces of arrow diagramming A in Fig. 6(b).

Elements	Mass fraction (%)	Molar fraction (%)
O K	21.54	49.49
Al K	01.44	01.97
Fe K	03.31	02.18
Ni K	73.71	46.25
Total amount	100.00	100.00

by arrow A in Fig. 6. Table 3 presents EDS analysis on the bulge area and the molar rate of aluminum and iron are 1.97% and 2.18% respectively. It indicates the outer alumina coating was spalled partly, and Ni intermediate layer exposed and NiO formed. It demonstrates that the composite coating retarded the inward-diffusion of oxygen and outward-diffusion of iron. Therefore, the alumina coating improved the oxidation resistance of carbon steel.

The XRD patterns of coated sample after 100 h of oxidation at 800 °C are presented in Fig. 7. The diffraction peaks corresponding to the iron oxide phase are very weak and the diffraction peaks corresponding to Al_2O_3 phase—intensive. Meanwhile, peaks of Ni and Ni_3P phases also appear on the XRD pattern. This shows that the carbon steel substrate was protected by the composite coatings.

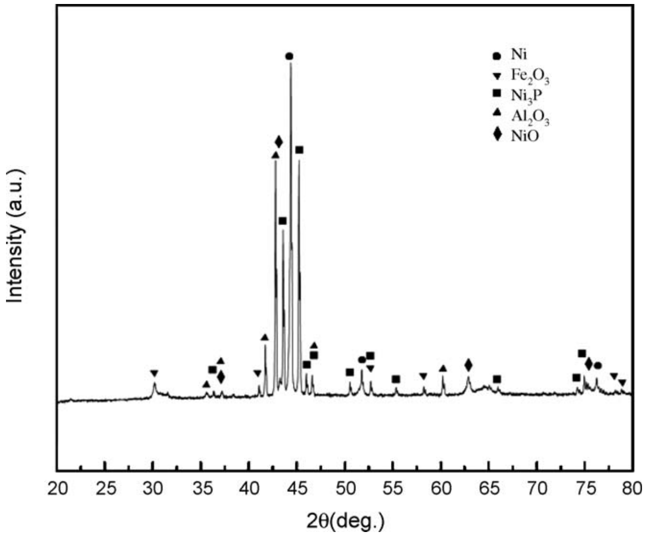

Fig. 7. XRD pattern of the coated carbon steel oxidized at 800 °C for 100 h in air.

4. Conclusions

Alumina film has been prepared on carbon steel surface with an electroless Ni intermediate layer and possessed an improved adherence to carbon steel substrate. The oxidation behavior of the composite coatings may be summarized as follows:

(1) The critical adhesion strength of the alumina coating is $\sim 20 \pm 2$ N to the sample substrate by scratch test. The strong adhesion is due to the interdiffusion of nickel and aluminum along the interface of the Ni intermediate layer and alumina coating.
(2) The oxidation resistance of carbon steel with composite coatings is significantly improved. Cracking and spalling of the oxide were not detected on the as-coated specimens.

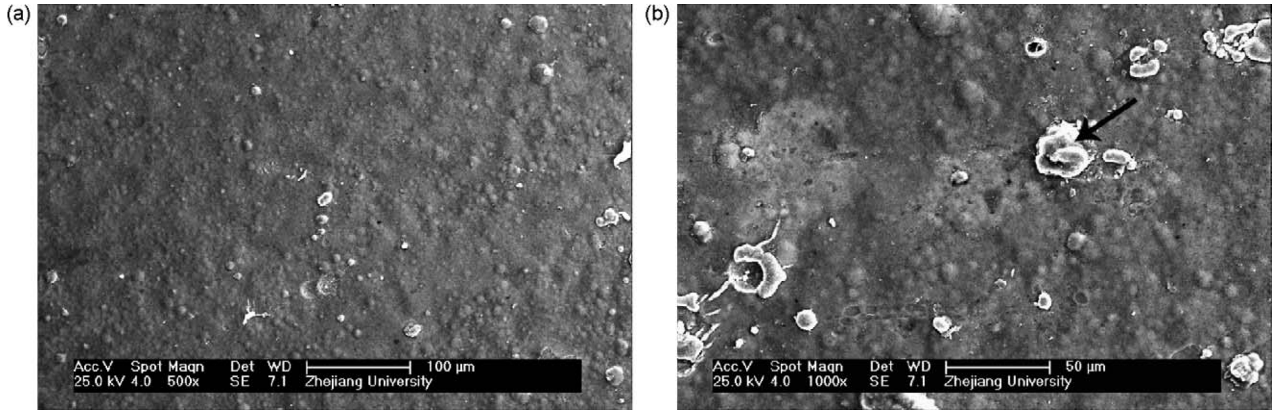

Fig. 6. (a) SEM surface morphology of coated carbon steel after oxidized for 100 h at 800 °C and (b) higher magnification of (a).

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