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Oxidation behavior of electroless Ni–P, Ni–B and Ni–W–B coatings deposited on steel substrates

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ABSTRACT

High temperature oxidation behaviors of electroless Ni–P, Ni–B and Ni–W–B coatings that are deposited on mild steel substrates were investigated in a temperature range of 600–800 °C. Oxide films formed on the surfaces of the coated samples were characterized by X-ray diffraction analyses. Oxidation behaviors of the coatings were evaluated by monitoring the oxide character and iron diffusion through the structure by glow discharge optical emission spectroscopy (GDOES). The results indicated that oxidation properties of the coated steel depend not only on the coating itself, but also on the diffusion and interdiffusion processes, which take place between the substrate and the deposit. For Ni–P deposited steel, iron started to take part in the oxide structure during treatment at 700 °C, resulting in a loss of protective character of the oxide. Depletion of boron within the coating and formation of nickel borates were observed for B containing deposits. Diffusion of iron to the surface also took place at 700 °C for Ni–B coatings, but not as drastic as for Ni–P. Oxidation behavior of Ni–W–B coatings was similar to Ni–B coatings in general. However, the presence of W decreased the diffusion of iron to the surface and delayed the formation of iron oxides. At 800 °C, all three coatings started to degrade due to higher oxidation rate and iron diffusion to the surface. The results of this study showed that it is possible to increase the oxidation resistance of electroless nickel coatings by alloying them with W.

1. Introduction

Electroless nickel deposition is a well-known process that has found industrial applications both for corrosion protection and improvement of tribological properties of steel substrates. Ni–P and Ni–B are the most common types of electroless coatings. Electroless coatings have amorphous or nano-crystalline structure in their as plated forms and crystalline Ni and Ni_3P (Ni_3B) precipitates start to form after heat treatment in a temperature range of 300–400 °C. This treatment results in an increase of hardness via precipitation hardening and loss of electrochemical corrosion resistance to some extent [1–4]. For further improving the properties of these deposits, W has been started to be co-deposited along with nickel [5–9]. Electroless nickel coatings also have potential for use in a range of industries where high temperature oxidation can occur.

According to a previous study [10], oxidation of Ni–P deposits starts above 400 °C and above 800 °C, phosphide phases decompose resulting in a loss of P content with the evaporation of phosphorus that has migrated to surface. At 600 °C, formation of P_2O_5 along with a very thin film of NiO without phosphorus was observed. Another important aspect to be considered during oxidation of Ni–P coatings deposited on iron-based substrates is the incorporation of iron into the oxide structure. In a study conducted on oxidation behavior of Ni–P coated steels at 607, 695 and 765 °C, a pure thin NiO formation on the surface was observed for the experiment conducted at 607 °C. However, by the increase of oxidation temperature, iron penetrating through the Ni–P layer started to substitute nickel in the NiO lattice. By the increase of oxidation time and after reaching of the concentration of iron in NiO to a definite level, a different oxide, Fe_xNi_yO, with a variable but higher iron concentration began to grow on the surface. During further oxide growth, only a very small amount of nickel (if any) entered the oxide and the oxide formed almost totally converted into iron oxides [11].

Interdiffusion between Ni–P coating and steel substrate is another process that may take place during high temperature treatment of these structures. It was reported that an interdiffusion layer consisting of Ni and Fe was formed at the coating–substrate interface during annealing at 650 °C, which was accompanied by the outward diffusion of phosphorus away from the as-deposited Ni–P/steel interface [12]. Lack of phosphorus in the interdiffusion layer was also reported by Lin and Lai, who moreover claimed that the interdiffusion between carbon steel and electroless Ni–P deposit mainly takes place through grain boundaries below 690 °C and through the lattice at higher temperatures [13].

Studies conducted on high temperature oxidation behavior of electroless Ni–B deposits are limited [10,14,15]. In a study conducted on thermal oxidation behavior of electroless Ni–B coatings, an oxide film formation mainly composed of boron oxides and a concurrent partial

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sublimation of this oxide film were observed [14]. The kinetics and mechanism of thermal oxidation of electroless Ni–B and Ni–W–B coatings were also studied by the same group [15] and it was shown that the oxidation was mainly determined by properties of boron oxides. At temperatures over 300 °C, the oxidation was accompanied by the sublimation of boron oxides. Adding tungsten to the nickel coating insignificantly increased its oxidation rate but boron addition resulted in a considerable increase in the oxidation rate. It was suggested that glassy salts, highly penetrable to diffusion process, are formed as a result of the reaction between the low melting point boron oxides and metal oxides. Hence, the existence of boron in the structure directly affected the kinetics and mechanism of thermal oxidation [15].

Considerable findings are available in literature about the high temperature oxidation behavior of the Ni–P. However, similar studies for Ni–B and Ni–W–B coatings are limited and do not consider the role of interdiffusion processes that may take place between the substrate and the coating. Since the diffusion of iron during oxidation plays a key role on the overall oxidation behavior of the coated steel samples, the phenomenon needs to be further elaborated for Ni–B and also Ni–W–B coated steels. Therefore, this study aims to investigate the high temperature oxidation behavior of Ni–B and Ni–W–B electroless coatings deposited on steel substrates and compare their behavior with Ni–P coatings by taking into consideration both the oxidation and interdiffusion processes that take place concurrently during high temperature exposure. For this purpose, three different (Ni–P, Ni–B and Ni–W–B) electroless coatings were obtained on mild steel substrates and their time dependent oxidation behavior was investigated at 600, 700 and 800 °C. Temperature and time dependent oxide characters and interdiffusion layer formed between the substrate material and electroless deposit were investigated in detail by utilizing GDOES depth profiles, XRD and SEM/EDS analysis.

2. Experimental studies

Mild steel was used as the substrate material for deposition of the coatings. Commercial high P, Ni–P electroless bath with nickel sulfate and nickel hypophosphide and Ni–B electroless bath with nickel sulfamate and di methyl amino boran (DMAB) as main constituents were used in the studies. Deposition temperatures were 85 ± 5 °C and 65 ± 5 °C for P and B based coatings, respectively. Besides, Ni–W–B bath used was obtained by adding 5 g/L $Na_2WO_4.2H_2O$ into the DMAB based solution. Before pre-treatment, the specimens were mechanically ground with SiC paper up to 1200 grit and polished with 1 μm Al_2O_3 paste. Samples were degreased in hot alkaline solution for 5 min and deoxidized in dilute inhibited hydrochloric acid solution for 2 min. After each step, deionized water was used for rinsing and then the specimens were immediately immersed in the plating solutions for deposition. The duration of the coating processes was tuned to give an equivalent thickness of 11 ± 1 μm.

The prepared Ni–P, Ni–B and Ni–W–B coated steel specimens were oxidized in a temperature controlled tube furnace at 600, 700 and 800 ± 10 °C for different oxidation times. Oxide thicknesses and the composition of diffusion layer between the coating and the substrate were determined from GDOES depth profile measurements (Horiba JY, GD Profiler HR). Thicknesses of the sputtered layer were determined from the sputter crater by 3D optical profilometer (Veeco Wyko NT1100) and sputter depth vs. thickness values were calculated by assuming a homogenous sputter rate during GDOES measurements. Surface morphologies and compositions of the oxidized samples were observed using scanning electron microscopy with an energy dispersive X-ray spectroscopy (Jeol 5410/Noran). The phase structures of the oxide scales formed on the samples were identified with X-ray diffraction (Philips PW3710 attached with Xpert Pro) using Cu-Kα radiation generated at 40 kV and 40 mA, using glancing angle configuration. Angle of incidence was adjusted to 2° in order to get information from the near surface. Micro Raman spectroscopy measurements were conducted on oxidized Ni–B and Ni–W–B samples for further verifying of the structure of compounds that formed on the surface. For this purpose, micro-Raman spectrometer (Horiba JY HR 800) was used with 632 nm wavelength HeNe laser and 10 mW power.

3. Results and discussions

3.1. Characterization of as-plated coatings

Chemical compositions of the coatings used in oxidation experiments, as determined from GDOES and EDS measurements, are listed in Table 1. The Ni–P coating with its 12.6 wt.% phosphorus content falls into high P containing electroless nickel deposit group. The Ni–B coatings used in the study are in the low B containing electroless Ni–B group as indicated by their 0.5 wt.% B content. The introduction of 2 wt.% W into Ni–B deposits did not induce any change in the boron content of the coatings. All of the coatings, in their as deposited state, exhibited an XRD amorphous and/or nanocrystalline structure as expected.

3.2. Oxidation experiments

The oxidation experiments were carried out at 600, 700 and 800 °C for 1, 3, 5 and 10 h. XRD, GDOES and SEM analyses were conducted both for the investigation of the oxide and the interdiffusion layer.

3.2.1. XRD evaluation of oxidized surfaces

The phase structures of the oxide scales thermally developed on the coated steels that were subjected to oxidation tests for different temperatures and durations were identified using XRD measurements.

Nickel (Ni) and nickel phosphide (Ni_3P) phases were obtained for the Ni–P coatings treated at 600 °C. This is the typical behavior of electroless coatings, which are heat treated in this temperature range [1,4].

The oxide peaks started to become apparent above 600 °C (Fig. 1). $(Fe,Ni)_3O_4$ and Fe_2O_3 peaks started to become observable besides NiO, Ni and Ni_3P at 700 °C. At 800 °C, iron oxide peaks became sharper and seen as the major structure within the coating with the increase of oxidation duration. The intensities of mixed oxide peaks increased with the duration of oxidation for both temperatures as indicated in previous studies [11].

For Ni–B coatings oxidized at 600 °C, only nickel peaks were observable. No peaks of nickel borides were detected which are expected to be present in the structure as a result of the heat treatment. This can be an indication of loss of boron from the structure, by evaporation of them as boron oxides. The details of this observation will be discussed in the next section.

For samples oxidized at 700 °C for 1 h, nickel was the only phase detected by XRD (Fig. 2a). By the increase of oxidation duration to 3 h, very low intensity iron oxide peaks started to appear besides nickel. For samples oxidized for 5 hour intensities of nickel peaks decreased with an increase of the intensities of iron oxides. Interestingly for the sample treated for 10 h, no peaks other than very low intensity iron oxides were observable, highly probably indicating the formation of an X-ray amorphous glassy structure.

For Ni–B coatings oxidized at 800 °C, oxide film formation started to be observable after 1 hour treatment. In this case the major component of the oxide was detected to be a mixture of nickel borates ($Ni_2B_2O_5$ and $Ni_3B_2O_6$) and iron oxides along with nickel. By the increase of oxidation

Table 1
Chemical composition of the as-plated coatings.

Coating	Composition (wt.%)			
	Ni	P	B	W
Ni–P	87.4	12.6	–	–
Ni–B	99.5	–	0.5	–
Ni–W–B	97.5	–	0.5	2.0