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Characterization of Ni-based coatings on carbon steel by electron microscopy

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ABSTRACT

Coatings formed from NiCoCrAl were deposited by a combination of electroplating and pack cementation on a carbon steel substrate. The effect of Co concentration and temperature on the oxidation and hardness properties of the carbon steel was studied. The microstructure and morphology of the coatings were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The microhardness of the coated samples was evaluated by a Vickers microhardness tester. FeNi(5%)CoCrAl coated sample exhibited better oxidation and hardness properties than that of FeNi(1%)CoCrAl coated sample. The microstructure and phase constitution of these coatings developed at 800 °C were similar. Samples coated at 800 °C and 1000 °C consisted of three and two layers, respectively. The formation of an intermetallic layer in all the coatings was confirmed. The γ-(Ni,Fe), β-(Ni,Al) and ζ hexagonal structures were identified in the coated layers of all samples, while orthorhombic Al_3Ni was only identified in the samples coated at 800 °C. An analysis of the correlations between the structure, hardness properties, oxidation behaviors, and phase formation is also discussed.

1. Introduction

Oil and gas industries continue to depend on the use of carbon steels in pipes due to their availability and ability to fulfill many of the mechanical, structural, fabrication and cost requirements of the various applications. The use of carbon steels represents a choice based on economics, a key issue in the effective use is the poor general corrosion and oxidation performance [1–4]. To improve the surface properties, a number of surface modifications are performed with different techniques where coatings are deposited on the carbon steel surface. Recently, Ni-based coatings have come into a wide use because of their good wear resistance and durability at high temperatures [5]. Additions of cobalt, chromium, and aluminum to the coating materials promote the hardness, and formation of intermetallic phases, and increase the oxidation/corrosion properties [6–11].

Methods for depositing this type of coating include thermal spraying, CVD (chemical vapor deposition) and PVD (physical vapor deposition) methods [12,13]. In the present study NiCoCrAl is diffusion-coated onto low carbon steel by electrodeposition to create a NiCo coat followed by pack cementation with Cr and Al. Nickel–cobalt electroplating is utilized in a large number of applications due to its good strength, toughness, and resistance to corrosion/wear [14]. The pack or solid state chromizing and aluminizing processes are widely applied processes due to simplicity and cost-effectiveness [15].

At present the deposition of Ni-based coatings on carbon steel is still limited and there are no studies of NiCoCrAl coatings deposited by electroplating and pack cementation processes where the microstructure, oxidation resistance at high temperature, and hardness properties were systematically examined. The present work is undertaken to study the structural, hardness, and oxidation characteristics of the NiCoCrAl coatings using electroplating and pack cementation. Furthermore, a comparison is made to observe the structural differences and determine the resistance of coatings in high temperature, extreme environments by subjecting all the coatings to testing in similar environments.

In multi-layer coatings, such as those with NiCo–Cr–Al layers, it is not straightforward to determine the phase sequence from the substrate to the outermost layer due to the limitations of X-ray analysis. The characterization of the coated layers requires the use of advanced analytical techniques, and especially cross-section transmission electron microscopy (XTEM) is always mandatory. Further, selected area electron diffraction (SAED) and high-resolution image (HRTEM) obtained from areas of interest in the coated layer was used to provide a detailed identification of the phase distribution in the coating. The

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results of these methods correlate well with crystal structure analysis of the phases within the coating. A detailed description of the coated layer is important because we expected this layer to be the most important layer in protective coating applications.

Therefore, this paper focuses on detailed characterizations of the micro/nanostructure of the multilayers formed on carbon steel during electroplating and pack cementation processes. Other investigations such as the oxide scale characteristic and hot corrosion behavior of this coating will be reported separately.

2. Experimental procedure

2.1. Coating processes

Commercial carbon steel sheets of St-37 were cut in dimensions of approximately 15 × 10 × 1.5 mm and degreased and polished progressively by hand finishing before being placed in an electrolyte solution. NiCo electroplating of the substrate was performed at two concentrations of cobalt, Ni(1 wt.%)Co and Ni(5 w.%)Co. The compositions of the electrolyte solution baths containing nickel sulfate, cobalt sulfate, nickel chloride, and boric-acid as shown in Table 1. The reagents were dissolved in distilled water and the pH adjusted in the range of 3.6–3.8. Prior to the deposition of NiCo, the substrate was coated with a Ni-strike solution for 30 s containing nickel chloride and chloride acid as shown in Table 1. The electrolyte temperature was maintained at 50 °C with a thermostatic bath and the NiCo deposition time was 120 min with a constant current density of 20 mA/cm^2. After the electroplating process, the sample was rinsed in distilled water and dried in saw dust before final weighing. Afterward, chromizing continued by aluminizing was carried out. For the pack mixtures, Cr and/or Al powder, NH_4Cl halide salt, and alumina powder, were used as donor, activator, and filler of the pack, respectively. The substrates were covered with the pack powder in cylindrical alumina crucibles. The formulations of the powder mixtures and the pack condition are summarized in Table 2. To explore the effect of thermal treatment temperature on the coatings, several experiments were performed at temperatures of 800 °C and 1000 °C, resulting in the successful development of three coating samples, as detailed in Table 3.

2.2. Examination and characterization

The microhardness of the coatings was measured using a Shimatzu-HMV-2 microhardness tester by applying a 200 g load for 10 s. Five measurements were conducted on each sample and the results were averaged. Finally, a high temperature oxidation test was carried out at 800 °C for 100 h. Isothermal oxidation tests of the specimens were conducted in static air in a muffle furnace for several intervals of exposure times, such as 4 h, 10 h, 19 h, 31 h, 46 h, 66 h, 90 h, and 100 h. In each interval, the specimens were kept in the furnace as temperature cooled to room temperature. An electronic balance with the sensitivity of 10^{-5} g was used to measure the mass changes of the specimens.

An initial characterization was performed using a 20 kV SEM (JEOL, JSM6380LA) equipped with an energy dispersive X-ray spectroscope (EDS). This characterization detailed the microstructure, surface morphology, and a point/linear microanalysis of the surface. The coating thickness was also determined using this technique. After initial characterization, a cross-section TEM (XTEM) specimen was prepared by an argon ion slicer (IS, JEOL EIS 9100) to ensure minimum structural damage. To prepare the specimen for the slicer, a coated bulk specimen was cut to 2.8 × 0.1 × 0.45 mm. An angle of irradiation, between 2° and 5.5°, with an argon flow rate of 7.3 to 7.8 (arbitrary units) was selected to obtain a thin foil specimen with minimum damage. A 200 kV TEM (JEOL JEM 2010F) equipped with an energy dispersive X-ray spectroscope (EDS) was used to observe the microstructural characteristic of the coating structures. Two-dimensional (2D)-selected area electron diffraction (SAED) pattern was performed to identify the phases in the coated layer. In addition, a multi beam high voltage TEM (JEOL JEM ARM 1300) was also used for high resolution XTEM images and the nanostructure analysis.

Table 3
Designation of the three types of coating.

Sample no	Description
#1	Ni(1%)CoCrAl, Coated at 800 °C
#2	Ni(5%)CoCrAl, Coated at 800 °C
#3	Ni(5%)CoCrAl, Coated at 1000 °C

3. Results and discussion

3.1. Effect of Co content on the hardness and structural properties

It is understood that the hardness, surface morphology, and high temperature oxidation may be influenced by the Co content in the NiCo electrodeposited on the substrate [16]. In the present study, 1 wt.% Co (sample #1) and 5 wt.% Co (sample #2) were used for the

Table 1
Formulation of Ni electroplating.

Ni-*strike*			NiCo-*Watts*			
Chemical	Formula	Concentration	Chemical	Formula	Concentration (g/L)	
					1 wt.%Co	5 wt.%Co
Nickel chloride	$NiCl_2 \cdot 6H_2O$	250 g/L	Nickel sulfate	$NiSO_4 \cdot 7H_2O$	326.7	313.5
Chloride acid	HCl	125 mL	Cobalt sulfate	$COSO_4.6H_2O$	3.3 L	16.5
			Nickel chloride	$NiCl_2 \cdot 6H_2O$	45	45
			Boric acid	H_3BO_3	40	40

Table 2
Formulation of the pack mixture.

Chromizing Temp: 800 °C & 1000 °C Time: 10 h			Aluminizing Temp: 800 °C & 1000 °C Time: 20 min		
Chemical	Formula	Concentration (wt.%)	Chemical	Formula	Concentration (wt.%)
Chromium	Cr	30	Aluminum	Al	25
Alumina	Al_2O_3	60	Alumina	Al_2O_3	70
Ammonium chloride	NH_4Cl	10	Ammonium chloride	NH_4Cl	5