Characterization of corrosion resistant on NiCoCr coating layer exposed to 5% NaCl

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Abstract. Highly corrosion resistant of carbon steel coated NiCoCr was applied in corrosive of marine environment. Carbon steel coated NiCoCr was prepared by a two step technique of NiCo electro-deposition and Cr pack cementation. The samples were exposed to 5 wt.% NaCl for 48 and 168 hours. The microstructure and corrosion product were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The corrosion resistance of carbon steel coated NiCoCr was found to be better than that of carbon steel substrate without coating. The results showed the microstructure of 48 h corroded sample has duplex layer composed of inner $\alpha$-(Ni,Co), $\alpha$-Cr and outer Cr$_2$O$_3$, while a quite thin and continues protective oxide of Cr$_2$O$_3$ was observed in outer layer of 168 h corroded sample. The formation of oxide scale rich in Cr$_2$O$_3$ has contributed for the better corrosion resistance of carbon steel coated NiCoCr, whereas the formation of non protective oxide of iron might caused low corrosion resistance of carbon steel substrate.

1. Introduction

Carbon steel is widely applied in the construction sector and is part of mechanical component in marine sector. Although carbon steel has excellent mechanical properties and low cost, ingress of aggressive environment in marine atmosphere can lead to the formation of unprotect surface due to the formation of hydrate iron oxide (rust, Fe$_2$O$_3$.H$_2$) [1]. Therefore, protection against extreme condition is required in order to maintain carbon steel performance. Carbon steel can be protected by applying metallic coating of resistant elements, such as nickel based coating. Nickel forms high melting and corrosion resistance phase [2-3]. Sharifi et al. investigated the corrosion resistance of Ni-Co coatings electrodeposited on steel substrate in sulphate bath [4]. The research revealed that the addition of cobalt with low content in nickel possesses good adhesion and increases the corrosion resistance of steel substrate due to the formation of a passive layer film of NiO or Ni(OH)$_2$ on the surface. The corrosion resistance of Ni-1%Co was measured 3.75 mpy after polarization test in 3.5%NaCl solution.

A 3.5%NaCl solution is used frequently as synthetic seawater to simulate the actual condition in marine atmosphere. However it is known that a 3.5%NaCl is more aggressive toward carbon steel than natural seawater [5]. In order to prolong the lifetime of Ni-Co coatings on carbon steel substrate, chromium is selected as alloying element or supplementary coating layer. Chromium shows good corrosion resistance in chlorine and in high temperature condition by forming Cr$_2$O$_3$ as a protective oxide scale [6]. Fernando et al examined the adhesive strength and corrosion resistance of Cr based coatings on carbon steel substrate. In that research, four types of samples was prepared, i.e, FeCr, FeCoCr, FeCoCrNi and FeCrNi alloys by arc sprayed coatings. In both cases, FeCoCr had the best...
corrosion resistance in 5%NaCl solution using salt spray method [7]. Further, NiCoCr coatings on carbon steel have exhibited good corrosion resistance after immersion test using 10%HCl as described in our previous study [8]. It revealed that the corrosion rate of uncoated carbon steel was 7.5 mm/y, which was almost 11 times greater than carbon steel coated NiCoCr with the corrosion rate of 0.67 mm/y.

According to the recent results, the present study investigated the corrosion resistance of duplex coating layer based on Ni-Co-Cr constituent using 5%NaCl. Electro-deposition and pack cementation techniques are applied to deposit NiCo as a first layer and chromium layer as a second layer, respectively. These two techniques are easiest and cheapest processes to deposit a coating layer and improve the corrosion resistance of carbon steel [9-10]. Thus, in this study, the micro-structural characterization and corrosion behavior of carbon steel coated NiCoCr is presented.

2. Experimental procedures
A rectangular shape with the dimension of 15×10×1.5 mm from a carbon steel plate was used as a substrate. A substrate was mechanically polished by using emery paper #100, #220, #400, #800, #1000, and #1200. After degreasing and washing with distilled water, the substrate was dried with hot air. Initially, Ni-5%Co was electro-deposited by using Ni-strike solution for 30 s followed by Ni-5%Co watt solution for 120 min with a constant current density of 20 mA/Cm². The composition of Ni-strike and Ni-5%Co watt solutions have been describe elsewhere [11]. After electroplating process, the sample was rinsed and dried before weighing. The second coating process is pack cementation of chromium or is well known as chromizing process. The pack powder was mixture of Cr, Al₂O₃ (inert filler) and NH₄Cl (activator) with the concentration (wt.%) of 30, 60, and 10, respectively. The pack was performed at temperature of 800 °C for 10 hours in Ar atmosphere.

The coating thickness was estimated by measuring the weight before and after the chromizing process. Corrosion test was carried out by an immersion test using 5%NaCl solution for 48 and 168 h. The mass loss was measured after exposure period using a balance with a sensitivity of 10⁻⁵ g. Corrosion rate in mills per year (mpy) was calculated from the weight loss formula by assuming that the substrate was uniformly corroded over the entire surface [11]. A surface morphology, cross-sectional microstructure and elemental distribution of the samples before and after corrosion test were characterized by FE-SEM (JEOL, JIB4610). Phase formed on the sample was identified by XRD (Smartlab, Rigaku) with Cu-Kα radiation operated at 40 kV and 30 mA. A nanostructural characteristic was observed by 200 kV TEM (JEOL, JEM 2010F) equipped with an energy dispersive X-ray spectroscope (EDS).

3. Results and discussions
3.1. Corrosion resistance
Figure 1 shows the mass loss of carbon steel with and without NiCoCr coating in 5%NaCl solution. The results indicated that the corrosion resistance of the coated sample is significantly higher than that of uncoated carbon steel not only for 48 hours but also 168 hours of exposure time. The corrosion rate of uncoated carbon steel was measured to be approximately 8.016 and 15.560 mpy for 48 and 168 hours immersion time, respectively. The corrosion rate increased more than two times with increasing immersion time. In addition, the corrosion rate of carbon steel coated NiCoCr was very low with a value of ~0.025 mpy and ~0.282 mpy for duration of 48 and 168 hours, respectively. The result showed the corrosion rate was 11 times lower than longer immersion time. It also revealed that the corrosion rate was significantly increased almost 55 times than uncoated carbon steel for duration of 168 hours. Thus, NiCoCr coating layer could act as a protective barrier against chloride ion attack into substrate which originated from 5%NaCl solution. The result was corresponded to sharifi.et.al results which showed that NiCo coating increased the corrosion resistance better than Ni pure coating [4]. Further, addition of chromium was increased corrosion resistance significantly in chlorine atmosphere [6].
Figure 1. Corrosion performance of carbon steel without and with NiCoCr coating immersed in 0.5% NaCl during (a) 48 h and (b) 168 h.

Figure 2. Phase identification using XRD analysis (a) carbon steel substrate, (b) NiCoCr coating, (c) 48 h, and (d) 168 h corroded samples.

3.2. X-ray diffraction analysis
Figure 2 shows the phase identification of carbon steel substrate, NiCoCr coating before and after corrosion for 48 h and 168 h exposure. The result indicated that the phases of as-coated sample mainly consist of γ-(Ni, Fe), α-(Ni, Co), and α-Cr with cubic structure. However, the oxide scale was identified to be mostly composed of α-Cr2O3 and a small amount of α-Cr. In addition, by exposing to longer corrosion time, the relative intensity of peaks for α-Cr decreased gradually, which means that more α-Cr2O3 was formed in 168 h corroded sample. It confirmed the previous result from corrosion performance that NiCoCr coating exhibited superior corrosion behavior due to the formation of protective oxide scale, α-Cr2O3, formed on the coating surface [6-8].

3.3. Surface morphology
Figure 3 shows surface morphology of NiCoCr coating sample before and after corrosion test for 48 and 168 h. It showed that the coated surface on carbon steel substrate was found to be irregular shape in nature. Moreover, figure 3b shows the irregular size fine grain with blocky structure was randomly separated on the entire surface of the scale. The continuous and very fine oxide particles were uniformly distributed on the surface of corroded sample after 168 h immersion time figure 3c. It confirmed that a well adherent and single protective oxide scale was homogenously distributed over the surface of 168 h corroded sample.
3.4. Cross-sectional morphology
The SEM method was employed to obtain the cross-sectional elemental mapping images of as-coated and corroded samples as shown in figure 4. The microstructural images show that typical two layers consisting NiCo layer and Cr layer were successfully formed on the samples. For as-coated sample, the homogenous layer was established with an approximate thickness of 32 µm and 5 µm for NiCo and Cr layer, respectively. The thickness of oxide scale was measured with an approximate of 5 µm and 1 µm for the corroded sample after 48 and 168 h exposure time, respectively.

Trace amounts of Ni and Cr are noticeably detected for as-coated samples figure 4 a-right. Different condition of coating can be distinguished in which strong intensity of Cr on the top layer of
the coated sample after corrosion test. The corrosion test promotes the formation of corundum structure of \( \text{Cr}_2\text{O}_3 \) that protect the substrate from harsh environment. In addition, a duplex scale consisting of Ni-Co-Cr with high content in inner scale and Cr-O in outer scale was examined in 48 hours corroded sample. On the contrary, only single oxide scale with high amount of Cr-O element was detected in 168 hours corroded sample. It revealed that longer immersion time produced stable, dense, slow growing \( \text{Cr}_2\text{O}_3 \) protective oxide as identified by XRD analysis in figure 2.

3.5. Nanostructure of protective scale

An XTEM analysis was performed to examine the detailed microstructure of the corroded layer. In addition, crystallographic technique is the main tool for phase identification in multiphase material. Thus, systematic phase identification by electron diffraction pattern indexation routines was performed. It has been clearly understood that the corroded sample has a thick oxide scale of about 2 \( \mu \text{m} \). The high magnification image observed by SEM in figure 4b and c was only focused on the top surface of the coated layer. Therefore, XTEM sample was prepared in the area adjacent the metal/oxide interface of the corroded sample as shown in figure 5. The results show that \( \text{Cr}_2\text{O}_3 \) grains were seen to nucleate at the scale/alloy interface on the corroded sample figure 5-top. It described the nucleation of \( \text{Cr}_2\text{O}_3 \) occurs at the scale/alloy interface during oxidation of NiCoCr coating system. Good adherence was observed on the metal/oxide interface. The presence of the \( \text{Cr}_2\text{O}_3 \) phase was also identified by electron diffraction figure 5-bottom. Point analysis in area 1, 2, and 3 and its selected area electron diffraction (SAED) patterns of 48 hours of corroded sample indicated the formation of \( \text{Cr}_2\text{O}_3 \), \( \alpha\)-Cr and \( \alpha\)-(Ni,Co). The oxide of \( \text{Cr}_2\text{O}_3 \) forms a corundum type lattice with hexagonal structure having lattice parameter of \( a = 0.4961 \text{ nm} \) and \( c = 1.360 \text{ nm} \) [13]. Further, \( \alpha\)-Cr and \( \alpha\)-(Ni,Co) identified in 48 hours of corroded sample possessed cubic structure with lattice parameter of \( a = 0.291 \text{ nm} \) and \( a = 0.352 \text{ nm} \), respectively [11]. In addition, only two phases of \( \text{Cr}_2\text{O}_3 \) and \( \alpha\)-(Ni,Co) was identified on the top of oxide layer in 168 hours of corroded sample.

Figure 5. Bright field XTEM images and SAED patterns of (a) 48 h and (b) 168 h corroded samples. 1-2-3 indicates the magnified images obtained from circled area in top figure and SAED pattern obtained from the point EDS analysis area.
4. Conclusions
NiCoCr coatings were successfully developed by electroplating and pack cementation techniques. The corrosion rate of uncoated and NiCoCr coating sample was very low with a value of ~0.025 mpy and ~0.282 mpy for duration of 48 and 168 hours, respectively. It showed that the corrosion resistance of carbon steel coated NiCoCr was 55 times higher than uncoated sample. The formation of Cr₂O₃ on the surface of coating layer could significantly protect the substrate in the corrosive environment. The results revealed that longer immersion time produced stable, dense, slow growing Cr₂O₃ protective oxide scale over the surface of corroded sample.

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