Effect of Co Concentration on Hardness of NiCo Coating Layer Synthesized by Electroplating Method

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Abstract. Electroplating is one of coatings method to improve the surface properties of metal substrate against corrosion in industrial parts. Electro-deposition of NiCo coating depends strongly on Co content due to increasing hardness properties. Many parameters can be controlled by electroplating method to obtain optimum coating properties. In the present study, synthesis of NiCo coating layer has been successfully done on low carbon steel substrate with variation of 5, 15 and 20 wt% Co concentration and variation of pH 2 and 2.8 using electroplating method. Heat treatment (HT) was carried out at temperature of 800 °C for 5 h using horizontal heated furnace under argon gas inert. Hardness properties were tested by Vickers hardness before and after heat treated samples. Surface and cross-section morphology was characterized by field emission-scanning electron microscopy (FE-SEM), while chemical content was analyzed by energy dispersive spectroscopy (EDS). Crystal phase formed on coated sample was characterized by X-ray diffraction (XRD). The hardness testing result showed the optimum hardness value was obtained for the sample with Co composition of 15 wt% (499.04 HV) without heat treatment and with Co composition of 20 wt% (490.96 HV) for the heat-treated sample. According to FE-SEM results, it was revealed that the small particle size caused high hardness value on both samples, which heat treatment is one of the factors that affected the particle size. Moreover, XRD characterization identified crystal phase of NiCo formed on the coating layer.

1. Introduction

Piping system made by carbon steel is widely used in coal fired steam power plant. The pipe is utilized to distribute steam at relatively high temperature in the range of 500 – 700 °C. To meet the need, the pipe required superior properties, such as high corrosion resistance and high hardness. One of the solution to overcome the problem is the pipe’s surface coating using NiCo by electrodeposition technique. Nickel can improve the corrosion resistance by formation of nickel oxides as a protective layer [1]. Co plays an important role as coating material due to increasing hardness properties [2]. Therefore alloying of Ni and Co as coating material is required in order to obtain carbon steel with higher corrosion resistance and hardness properties [3-6].

In recent years, many studies have interested in Ni-Co electrodeposited on carbon steel substrate. Zamani, et.al [7] studied the effect of various Co content of electrodeposited Ni-Co layer on nickel substrate. In that research, Co concentration of 10 wt%, 17 wt% and 24 wt% in bath solution were...
investigated from the electrochemical aspect and its hardness properties. According to the results, it obviously understood that with an increase in the Co concentration in bath solution, Co content in the electrodeposited layer increases progressively from 25 at% and reached to 55 at%. Furthermore, it was known that the maximum hardness could be reached on 45 at% Co, while the hardness decreased with the increase in Co content up to 55 at%. These results were related to the fact that the decreasing grain size caused the hardness of Ni-Co coating increased. Not only Co concentration in bath solution, but also the electrolyte pH would affect the content of Co in Ni-Co coatings. The electrolyte was maintained in pH 5 for each Co concentration.

In addition, Tian Yang, et al [8] studied the effect of pH on Cr and Co contents in the Ni-Co-Cr coatings. Electroplating solution was prepared at pH 2.4 and 3.2. The results showed that Co content was approximately 15, 20 and 16 wt% for pH 2.4 and 3.2. The reduction of Co content in the coating layer might affect the hardness properties. Therefore, pH 2.4 - 2.8 was recommended based on this study.

In the present study, we investigated the effect of Co content in NiCo coating layer on the hardness properties. Electro-deposition technique was applied to deposit NiCo coating layer by adjusting the Co concentration in bath solution of 5, 15 and 20 wt% and controlling pH at 2.0 and 2.8. These two parameters are very important to obtain an appropriate Co content for hardness properties. Moreover, the correlation between hardness and micro structure as well as crystalline phase formed in NiCo coating layer will be discussed in this study.

2. Experimental Methods
Carbon steel plate was cut for 12 pieces with a $2 \times 15 \times 1.5$ mm$^3$ dimension. Carbon steel substrates were gradually grounded with 100, 300, 400, 800, 1000, and 1200 emery grade papers followed by washing with distilled water before coating process. In the beginning of coating process, carbon steel substrate was immersed in Ni strike solution with 3 A of DC current for 30 s. The Ni strike layer is useful to adhere a thin layer of nickel plating to the carbon steel substrate. For the second step, the substrate was electrodeposited in NiCo watt solution with 0.22 A of DC current for 120 minutes. Tabel 1 and table 2 show the composition of Ni strike and NiCo watt solution with various Co concentration, respectively. The NiCo watt solution was maintained at pH 2.0 and 2.8 and at temperature of 50°C.

Afterward, NiCo coating sample was heat treated at temperature of 800°C for 5 hours using horizontal heated furnace under Argon gas inert. The hardness of NiCo coating was measured using micro Vickers hardness (LECO Corp, FMX 2635) by applying a 300 gf for 13 s. Five measurements of hardness test were acquired on each coating sample to obtain an average hardness value (HN). A surface morphology, cross-sectional microstructure and elemental distribution of the samples before and after heat treatment were characterized by FE-SEM (JEOL, JIB4610F) and EDS (Oxford, X-MAX 50). Phase formed on the coating sample was identified by XRD (Smartlab, Rigaku) with Cu-Kα radiation operated at 40 kV and 30 mA for 20 started from 10° to 90°.

| Table 1. Composition of Ni strike                | Table 2. Composition of NiCo watt          |
|-----------------------------------------------|------------------------------------------|
| Component | Composition | Component | 5 wt% | 15 wt% | 20 wt% |
| CuSO$_4$.6H$_2$O | 50 (gram/L) | NiSO$_4$.6H$_2$O | 52.31 | 46.80 | 44.05 |
| O          | 50 ml      | Cr$_2$(SO$_4$)$_3$ | 21.69 | 19.40 | 18.26 |
| H$_2$SO$_4$ |            | CoSO$_4$ | 5 | 15 | 20 |
| Aquades    | balance    | H$_3$BO$_3$ | 10 | 8.95 | 8.42 |
|            |            | NiCl$_2$.6H$_2$O | 11 | 9.84 | 9.26 |
3. Results and Discussion
3.1 Effect of heat treatment and electrolyte's pH on hardness property of NiCo coatings with a various concentration of Co

Figure 1 shows the micro hardness of NiCo coating on carbon steel substrate before and after heat treatment at pH 2 and 2.8. The results show that the hardness of electrodeposited NiCo before heat treatment at pH 2 increased of about 46 VH from $\sim$407 VH to $\sim$453 VH with increasing of Co concentration from 5 wt% to 15 wt%, while the hardness decreased at 20 wt% of Co concentration with approximate value of 85 VH (figure 1 (a)). This trend was also occurred on NiCo coating on carbon steel substrate before heat treatment at pH 2.8 (figure 1 (c)). The highest hardness was achieved on 15 wt% of Co concentration with a value of $\sim$499 VH. The hardness enhancement related to the increase of Co content deposited on NiCo coating layer [7].

In contrast, figures 1 (b) and (c) show dissimilar trend in hardness after heat treatment. The hardness of electrodeposited sample at pH 2 in coorporation with pH 2.8 of 5 wt% and 15 wt% of Co concentration had the hardness bellow 200 VH, while the optimum hardness was about 490 VH measured on electrodeposited sample at pH 2.8 of 20 wt% of Co concentration as shown in figure 1 (d). According to these results, pH in electrolyte did not significantly affect the hardness properties [9]. Furthermore, the hardness of NiCo coating on carbon steel substrate decreased after heat treatment except for electrodeposited NiCo at pH 2.8 with 20 wt% of Co concentration. This is probably caused by a change in fine grained of coating surface which more ductile and as a consequence decreased the hardness.

3.2 Surface and cross-sectional morphology of NiCo coatings

Figure 2 shows the surface morphology of electrodeposited Ni-Co at pH 2.8 before and after heat treatment temperature of 800°C. The shape of particle on the surface of before heat treatment appeared irregular particles and after heat treatment looked like roundish particles. Before heat treatment, grain size of an electrodeposited NiCo layer with a 5 wt% Co was smaller than those with 20 wt% Co content. On the contrary, particle size of an NiCo layer with 5 wt% Co after heat treatment was bigger than an the layer with 20 wt% Co concentration. According to the hardness results shown in figure 1, an electrodeposited NiCo in 5 wt% Co had a higher hardness than an electrodeposited NiCo in 20 wt% of Co concentration before heat treatment (figure 1 (c)). Table 2 shows a measurement of particle size using free software of ImageJ. The smallest particle size was calculated of about 0.712 µm on electroplated NiCo at 20 wt% Co after heat treatment. Therefore, the hardness significantly increased up to $\sim$490 VH. The reason is due to a small particle size enable a large friction to insulate the indentation of Vickers hardness, thus the hardness increased [10]. In addition, a small particle size contributed to a high density of coating layer which was very beneficial to enhanced hardness. However, a high particle size related to the high porosity that caused hardness decreased [3].

Figure 3 shows a cross sectional microstructure and its elemental analysis of electroplated NiCo at pH 2.8 after heat treatment with various Co concentration. It showed a homogeneous coating layer was formed with low porosity. According to EDS line analysis, a deposition of Co content was detected in NiCo coating layer with concentration of about 20 at%, 42 at%, and 50 at% for 5 wt%, 15 wt% and 20 wt% of Co concentration in bath solution, respectively. A characterize of Co content was plotted and compared with previous results [7] as shown in figure 4. A blue graph is the present results and red graph is the previous results. This results corespond to the previous results that the highest of Co content reached to 55 at% from 24 wt% of Co concentration in bath solution [7]. The results concluded that Co content (at%) detected in NiCo coating layer increased gradually with increasing the Co concentration (wt%) in bath solution.
Figure 1. Micro hardness measurements of NiCo coating samples: (a, c) before and (b, d) after heat treatment at temperature of 800°C with pH 2 (upper) and pH 2.8 (bottom).

Figure 2. Surface morphology of electrodeposited Ni-Co at pH 2.8 and at various Co concentration: (a,c) 5 wt% and (b,d) 20 wt% before (upper) and after (bottom) heat treatment at temperature of 800°C.
Table 3. Particle size of NiCo coating layer

| Before heat treatment  | After heat treatment  | Before heat treatment  | After heat treatment  |
|-----------------------|-----------------------|-----------------------|-----------------------|
| 5 wt% Co              | 20 wt% Co             | 5 wt% Co              | 20 wt% Co             |
| 0.868 µm              | 3.494 µm              | 3.123 µm              | 0.712 µm              |

Figure 3. A cross sectional microstructure and its elemental analysis of electroplated NiCo at pH 2.8 after heat treatment at temperature of 800°C with various Co concentration: (a) 5 wt%, (b) 15 wt%, and (c) 20 wt%.

Figure 4. A relationship between Co concentration in bath solution and Co content in NiCo coating layer.

Figure 5. Phase identification using XRD analysis.

3.3 X-ray diffraction analysis

Figure 5 shows the phase identification of electrodeposited NiCo before and after heat treatment at pH 2.8 with 5 and 20 wt% of Co concentration. The result showed that the coating layer was identified to be mostly composed of α-NiCo. Heat treatment at 800°C promote the formation of stable α-NiCo with
face center cubic (fcc) structure which having a lattice parameter of 3.52 Å [11]. The dissimilar appearance on peak shape, peak width and peak height treatment indicated the differences in crystallite size and microstrain as well as defect structure that might attribute to the hardness properties of NiCo coating sample. It is known that the broader peaks indicated the smaller crystallites. According to the XRD (figure 5) and SEM results (figure 2), it was noticed that electrodeposited NiCo in 5 wt% of Co concentration before heat treatment and 20 wt% of Co concentration after heat treatment at temperature of 800 °C were having broad peaks, small crystallite size with considerably high hardness properties which were above 400 VH.

4. Conclusions
Electro-deposited NiCo layer was comprehensively evaluated in order to understand the effect of Co concentration on hardness properties. The results showed that NiCo coating layer developed by using electrolyte at pH 2.8 possessed Vickers hardness number (VH) higher than sample developed at pH 2. The optimum hardness with 499 VH obtained on NiCo coating on carbon steel substrate before heat treatment and prepared by using 15 wt% of Co concentration at pH 2.8. Moreover, the hardness was slightly decreased to about 490 VH on after heat treatment sample with the condition of 20 wt% of Co concentration at pH 2.8. According to the surface structure, heat treatment affected the changes in particle size of NiCo. The hardness has been found to increase with decreasing a particle size. It was also related to Co content deposited on NiCo coating layer which reaching 50at% with hardness above 450 VH.

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