

Corrosion Behavior of Heat Treated Nanocrystalline Co-Ni-Fe Coating on Stainless Steel

*Koay Mei Hyie **

*Faculty of Mechanical Engineering, Universiti Teknologi MARA,
13500 Permatang Pauh, Pulau Pinang, Malaysia*

Zuraidah Salleh

C.M. Mardziah

Nik Rozlin Nik Mohd Masdek

Nor Azrina Resali

*Faculty of Mechanical Engineering, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia*

**hyie1105@yahoo.com*

ABSTRACT

Corrosion is an essential environmental phenomenon in industry that can deteriorate the performance of steel and shorten the lifetime of steel. The failure due to corrosion can cause leakage, fracture, contamination of corroded elements to the product or equipment having the corroded steel parts. To overcome the corrosion problem, nanocrystalline coating has been proposed to improve the corrosion resistance of steel. In this investigation, nanocrystalline Co-Ni-Fe was used to protect the stainless steel from sodium chloride environment. Co-Ni-Fe has been identified as a potential candidate in corrosion resistant coating. This material is recognized as a green material because it is not toxic and hazardous to environment. In this study, nanocrystalline Co-Ni-Fe having less than 30 nm crystallite size was developed by low cost electrodeposition method. The coating electrodeposition was carried out at pH 1 and current density of 0.143 A/cm². The synthesized Co-Ni-Fe coated stainless steel was heat treated at 700 °C in different types of gas conditions. This paper focused on comparison between the samples with and without heat treatment. Although there is no phase changed during the heat treatment as proven in XRD analysis, nanocrystalline Co-Ni-Fe heated using mixed gases showed the tendency to form the dendritic structure. In the presence of hydrogen and argon mixing gases in heating atmosphere, the sample revealed higher oxygen content of 5.34 wt% and exhibited the highest corrosion rate in sodium solution. Anyway, the coating still protected the stainless steel from

corrosion after exposed to 24 hours in salt fog test as compared to the pure stainless steel which was corroded at the same test. In conclusion, the heat treatment applied on the coating sample is believed to produce dense coating and thus enhance the corrosion resistance of the coated steel.

Keywords: *Co-Ni-Fe, Corrosion, Heat treatment, Sodium, Mixed gas.*

Introduction

In many engineering applications, surface coatings are used to increase the lifetime of component exposed to corrosion condition. High mechanical and corrosion protective properties of nanocrystalline alloy coatings are needed for the design and operation of devices, machine and structural systems in extreme environments [1].

Recently, many innovative methods have been developed to fabricate a protective coating on metal at nano-size particles [2]. Several processing techniques are currently available. They are electrodeposition, mechanical alloying, gas phase condensation of particulates and severe plastic deformation [2].

Among the groups, electrodeposition is an attractive approach for the preparation of nanocrystalline coating which provides a cost-effective and non-equipment intensive method [3]. The process of electrodeposition can be scaled and the deposition can be performed on a variety of substrates. This century-old process offers many advantages such as low-cost processing, rapidity, industrial applicability and higher deposition rate. Moreover, electrodeposition technique is potential to produce the structural features of materials at various size ranging from micrometer to nanometer. This technique also can be performed near room temperature using environmental friendly electrolytes and able to produce green product.

The urge to find the protective coating for hard chromium replacement has led to discovery of other materials which offer such capability but providing an environmentally friendly coating against toxic chromium. Nanocrystalline Cobalt-Nickel-Iron (Co-Ni-Fe) coatings have been appointed as the potential alternative for the hard chrome plating due to the good corrosion resistance. The nanocrystalline Co-Ni-Fe coatings have potential to be commercialized as the green protective coating materials [4]. These coatings can be applied in various applications required high demand on corrosion resistant properties.

The goal of the heat treatment process is to produce a coherent body with controlled microstructure, in some cases with controlled porosity [5]. It is an intention in this study to investigate the effect of the heat treatment on the corrosion properties of developed nanocrystalline Co-Ni-Fe coating. Although there are some researches done on the thin films of Cobalt alloys in terms of hardness and corrosion, nevertheless studies on the development of

heat treated Cobalt alloys is scarce. In this study, the heat treatment was conducted under two different inert gas atmospheres, which are 100% argon and mixing gases containing 95% argon + 5% hydrogen gas. In this paper, the nanocrystalline Co-Ni-Fe having particles size of less than 100 nm was heat treated to produce a great variety of microstructures and good corrosion resistance of the coating.

Marine salts adversely affect the durability of the infrastructure and reduce its service life [6]. Some particles naturally are generated by the action of wind on the seawater surface, thus form some ionic species such as chlorides and sulphates into the atmosphere [7]. The air containing sea spray causes accumulative deposition of ions on the external surface of structures that penetrate into the interior of the material through ionic diffusion causing its degeneration. Such environments are extremely risky to the materials as sodium can penetrate and crystallize inside the material. The chloride-rich seawater is a harsh environment that can attack the materials by causing pitting and crevice corrosion [8].

Hence, the objective of this study is to focus on the effect of sodium solution on the heat treated nanocrystalline Co-Ni-Fe coated stainless steels. Comparison was made between the corrosion behavior of nanocrystalline Co-Ni-Fe heat treated at different conditions.

Experimental Work

Electrodeposition process

An electrolyte solution was prepared prior to electrodeposition process. A mixture of solution contained CoSO_4 , NiSO_4 , FeSO_4 , H_3BO_3 , ascorbic acid and saccharin. Table 1 shows the molarity of precursors used in the stoichiometry preparation of Co-Ni-Fe electrolyte. The electrodeposition was set up using stainless steel as the cathode and graphite rod as the anode. Both graphite and stainless steel were parallel to each other in the electrolyte solution to ensure uniform coating. The DC power supply was used in this process and set at 0.143 A/cm² of current density. The solution was kept at pH of 1 throughout the electrodeposition process. The best coating without bubble formation was observed when the solution temperature was within 45°C to 50°C. A black Co-Ni-Fe coating was formed and covered fully on the stainless steel substrate after 30 minutes time of electrodeposition process.

Table 1: The molarity used in preparation of Co-Ni-Fe coating

Composition	Molarity (M)
CoSO ₄	0.075
NiSO ₄	0.200
FeSO ₄	0.030
H ₃ BO ₃	0.400
Ascorbic Acid	0.010
Saccharin	0.050

Heat treatment

The as-synthesized Co-Ni-Fe coated stainless steel was heated in a model HTF-15/300-50 of vacuum tube furnace. The temperature was chosen at 700°C based on previous finding [9]. The velocity of argon gas was 3 m/s². The soaking time and heating rate in this experiment were fixed at 45 minutes and 8°C/minute, respectively. After the heat treatment cycle, the samples were cooled in the furnace. In this paper, there were three different conditions to be compared. First sample was the as-synthesized Co-Ni-Fe coating without heat treatment. The other two samples were heated using two different types of gases; which were 100% argon and mixed gases containing 95% argon + 5% hydrogen gas.

Characterization

The phase formation and crystallite size of the as-synthesized and heat treated coating samples were investigated by X-ray diffractometer (XRD, Ultima IV, FD3668N). Coating morphology was performed by JEOL JSM-7600F, Field Emission Scanning Electron Microscope (FESEM). Elemental composition analysis was performed specially to observe the percentage of oxygen using OXFORD INSTRUMENTS EDX test, which was attached to FESEM equipment. Average surface roughness and microhardness of the electrodeposited coatings were determined by Optical 3D Surface Metrology and MITUTOYO MVK-H1, Vickers Microhardness instrument, respectively.

Corrosion test

The corrosion test in the artificial atmosphere which is termed as salt spray test was carried out in a salt spray chamber following ASTM B117-85. This testing enables to evaluate and compare basic corrosion performance of nanocrystalline Co-Ni-Fe with and without heat treatment process after exposure to sodium corrosive environment. The samples were exposed to a salt spray generated from a 5% sodium chloride solution. All the samples

were placed in the salt spray chamber for 24 hours. Surface micrographs of the corroded samples were taken using a camera.

Further corrosion testing was performed on nanocrystalline Co-Ni-Fe coated stainless steel using potentiodynamic polarisation. Sodium chloride solution was used in this test to compare the corrosion result obtained from salt spray test. A setting time of 15 min was assigned before experiment in order to stabilize the open circuit potential (OCP). The scan rate was 5.0mV/s from -500mV to 500mV vs. SCE.

Results and Discussion

Structural analysis

Figure 1 shows the XRD patterns of coating surfaces characterized by means of X-ray diffraction (XRD).

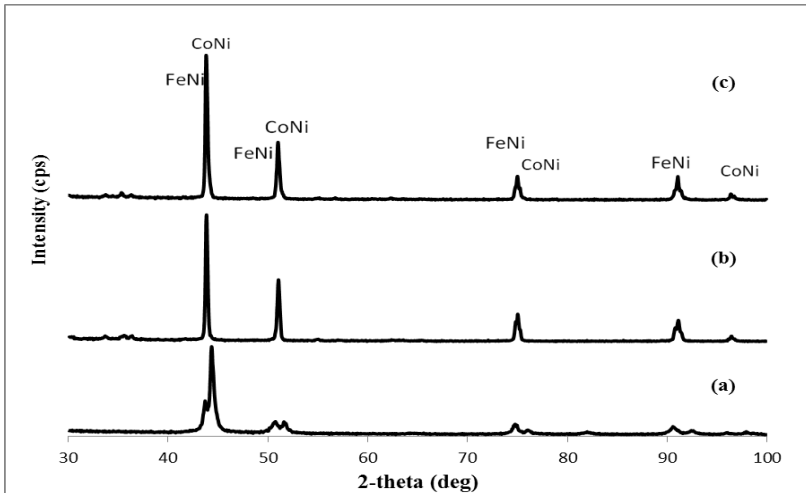


Figure 1: The XRD patterns of the nanocrystalline Co-Ni-Fe at different conditions (a) as-synthesized, (b) heated using argon gas and (c) heated using mixed gases

XRD patterns of all the samples were measured from 2θ angle of 30° to 100° with Cu $K\alpha$ radiation. The phases of FeNi and CoNi were detected in the entire XRD patterns. All the reflection patterns of these three nanocrystalline Co-Ni-Fe revealed the similar structure with as-synthesised nanocrystalline Co-Ni-Fe consisting mixture of FCC and BCC structures [10]-[11] at 2θ of 44° , 51° , 76° , 92.4° , and 96° , respectively. The peaks were identified with JCPDS No. 10745694 and JCPDS No. 31208. The peaks show that the coating is crystalline but not amorphous. No other contamination phase

appeared in the coating. The peak of 304-austenite stainless steel was not found in the entire XRD patterns. It showed that all samples were fully covered with Co-Ni-Fe coating. It can be summarised that no phase of coating was changed after the heat treatment process. It was also observed that the XRD patterns for the sample heat-treated in argon and mixed gases were slightly shifted to the left caused by the strain or changes in microstructure.

The crystallite size was calculated using the Debye Scherrer's equation [10]. From the XRD results, the crystallite size of the as-synthesised sample, heat treated sample using argon gas and heat-treated sample using mixed gases were 12, 23 and 28 nm, respectively. The crystallite size was increased after the heat treatment process due to grain growth. High temperature is possibly to reduce the voids due to the bridging of fine crystallites and resulted in formation of dense and closed pores structure.

Oxygen content

Five elements such as Co, Ni, Fe, O and C were detected in three samples. The EDX results of oxygen content are only shown in Table 2 as the difference was obvious compared to other elements. All the samples showed the existence of oxygen at low percentage value. This is confirmed with the XRD result where there was no oxide phase detected in the XRD patterns.

The presence of oxygen in the sample was due to the formation of oxide when the electrodeposited samples were exposed to the ambient temperature. The oxygen content in the sample after heat treatment exhibited lower value than the as-synthesised sample. Meanwhile, the sample carried out in an inert argon atmosphere produced less oxygen content compared to mixed gases.

It can be seen that the oxidation was less favourable at non-heat treated sample and heat treated sample using argon gas compared to the sample heat treated using mixed gases. Theoretically, the mixed gases composed of 5% hydrogen, which is a reducing gas and suppose to absorb the oxygen. However, the highest oxygen content was found unexpectedly in the sample heated using mixed gases. This might due to the oxygen content of the mixed gases atmosphere influences the dissolution rate. Moreover, the hydrogen content in the mixed gases could lead to a significant amount of hydrogen absorption. Hydrogen absorption occurs through diffusion and the presence of high oxides in the material. The highest oxide can lead to the corrosion due to the hydrogen has been absorbed relatively rapidly [12].

Table 2: The oxygen content and microhardness of the nanocrystalline Co-Ni-Fe coated stainless steel at different heating conditions

Condition	Oxygen (wt%)	Microhardness (HV)
As-synthesized	3.13	333
Heated in argon gas	2.01	449
Heated in mixed gases	5.34	289

Microhardness

Microhardness of nanocrystalline Co-Ni-Fe heated using mixed gases exhibited the lowest value compared to the other conditions as shown in Table 2. The microhardness of nanocrystalline Co-Ni-Fe heated using argon gas was found to be the highest due to the homogeneous particle distribution, compact and dense microstructure. These structures have resulted in the high volume fraction of the boundary atoms inside the particle boundaries. In these particle boundaries, the particles were preferred to be located compared to inside the particles. The existence of these particle boundaries also prevents the dislocation motion and formed the harder layer in the microstructure [13].

Particle morphology analysis

The morphology of nanocrystalline Co-Ni-Fe heat treated in different heat treatment conditions are shown in Figure 2. The microstructures in nanocrystalline Co-Ni-Fe without heat treatment and the nanocrystalline Co-Ni-Fe heated using argon gas produced the only irregular structure. Surprisingly, the irregular structure of nanocrystalline Co-Ni-Fe heated using mixed gases has the tendency to form the dendritic structure. The particle sizes for all nanocrystalline Co-Ni-Fe are increased when the sample is heat treated. The phenomenon is similar to the XRD finding.

The particle size of nanocrystalline Co-Ni-Fe heated using mixed gases was bigger compared to other samples. The particles were large, long and tend to agglomerate. The surface of nanocrystalline Co-Ni-Fe without heat treatment and with heat treatment using argon gas exhibited much denser structure and the number of pores was found to be reduced compared to the nanocrystalline Co-Ni-Fe heated using mixed gases. However, the existence of numerous dendritic structures in nanocrystalline Co-Ni-Fe heat treated in mixed gases condition promoted agglomeration and formation of inhomogeneous structure. The presence of dendrite particle on heat treated sample using mixed gases was due to the hydrogen evolution on microstructure. Hydrogen promotes dynamic recrystallization, which is mainly attributed to hydrogen promoted dendrite decomposition. Dendritic is

mainly associated with dislocation movement and the hydrogen can enhance the dislocation mobility and twinning [14].

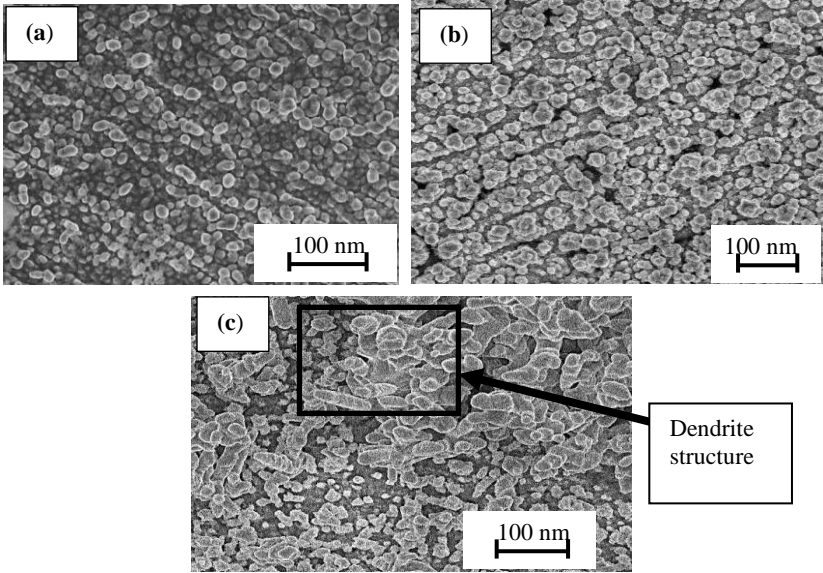


Figure 2: SEM images of electrodeposited samples heated in different conditions; (a) as-synthesized (b) argon gas and (c) mixed gases

The existence of the almost irregular particles and homogenous structure in nanocrystalline Co-Ni-Fe heated using argon gas has formed the interphases known as particle boundary. The number of boundary in the nanocrystalline structure was increased due to the disoriented arrangement and alignment of the particles. This mismatch orientation of the particles make the arrangement of atom boundary became more complicated and disordered. This phenomenon has led to the formation of high volume fraction of particle boundaries in the compacted nanocrystalline structure [15]. Furthermore, the growth rate of irregular particles is linearly proportional to the driving force; i.e. interface mobility is constant and subsequently tends to produce more homogeneous particle distribution [16].

Surface roughness

Figure 3 represents the surface roughness of nanocrystalline Co-Ni-Fe prepared in different conditions. It can be noted that smaller particle size leading to the formation of smoother surface. The lowest surface roughness value was obtained by the nanocrystalline Co-Ni-Fe heated using argon gas although the particle size of the as-synthesized sample was the smallest. It is believed that heat treatment improved the particles compactness and dense structure of nanocrystalline Co-Ni-Fe after heated using argon gas. High volume of disorderly arranged atoms in the particle boundaries for dense structure is the reason for smaller surface roughness.

Furthermore, it is noted that the inhomogeneous particles, dendrite structure and agglomeration are the reasons for rough surface of nanocrystalline Co-Ni-Fe sample after heat treated at mixed gas atmosphere. It is reported that the oxygen content in the coating surface may promote the voids formation [5]. As the oxygen content in this sample was higher, the voids on the surface morphology were formed due to the oxygen presence thus exhibited the roughest surface.

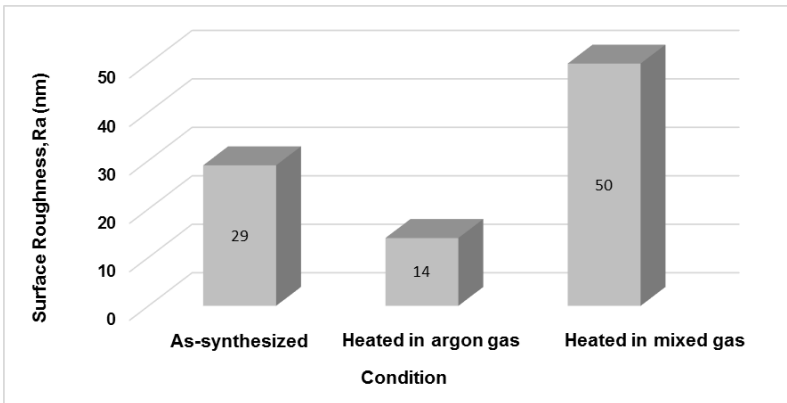


Figure 3: Surface roughness of the nanocrystalline Co-Ni-Fe coated stainless steel prepared at different conditions

Salt spray test result

Photographs of nanocrystalline Co-Ni-Fe coated stainless steel after salt spray test are presented in Figure 4. Surprisingly, it was observed that all samples exhibited no corrosion damage contrast to the corroded pure stainless steel.

With regard to corrosion, stainless steel is a very smart group of metals. The excellent corrosion resistance of stainless steel is caused by a

very thin layer of oxides in particular chromium and iron oxides. This oxide layer is so strong that it effectively isolates the steel from the environment despite a thickness of only a few nanometers. Unfortunately, the oxide layer may be damaged without repassivating when exposed to severe environment. Rapid penetration may occur causing the stainless steel to be a very short lifespan [17]. According to the reference [17], the pitting corrosion in stainless steel was affected by pH of the environment. With respect to pH, the pitting was observed with normal form of attack in 4 % sodium chloride at pH above 2.8. It can be seen that the fairly rapid general attack at lower pH values. Meanwhile the deepest pits occurred in the range pH 6 to 7, with less intense pitting in the more alkaline solutions, and with very little corrosion at pH 12. As the salt spray test was carried out at 5% sodium content and pH was around 6 to 7.5, the stainless steel was sacrificed after it was attacked by pitting corrosion. However, the Co-Ni-Fe coating protect the stainless steel from corrosion attack.

The XRD, EDX and FESEM analysis of the samples exposed to 24 hours salt spray test further evident where there is no corrosion products have been found on the coating surface. Hence, there is no chemical reaction happen during the immersion of coated sample in sodium chloride solution.

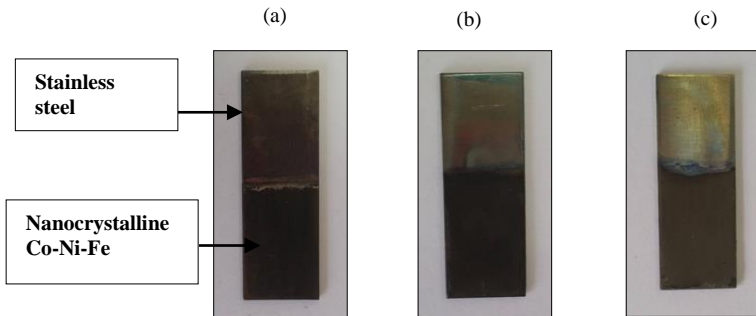


Figure 4: Physical observation of the nanocrystalline Co-Ni-Fe salt spray test; (a) as-synthesized, (b) heated using argon gas and (c) heated using mixed gases

Potentiodynamic Polarisation

The corrosion rate for the sample prepared at three conditions are listed in Table 4. During the process of corrosion, one or more redox (reduction and oxidation) reactions can take place. For instance, alloys of iron can produce a more cathodic reaction on the metal surface when the metal undergo oxidation. Thus, corrosion rate is affected by the amount of oxygen dissolved in the water [18]. The sample heated using argon gas showed the smallest corrosion rate due to less oxygen content found in EDX analysis. Anyway,

the corrosion rate for all samples exhibited lower values if compared to pure stainless steel which is about 0.3 mm per year [19].

The unusual properties associated with the ultrafine particle size, such as corrosion properties materials have been investigated by a lot of researchers. It is believed that the corrosion rate is reduced by the crystallite size reduction [20]. It is found in the Table 4 that the sample heated in mixed gas condition experienced the highest corrosion rate due to larger particles. Anyway, as for the comparison between the as-synthesized sample and the sample heated using argon gas, it seems that the oxygen factor is dominant than the size factor.

The corrosion properties of Co-Ni-Fe coating also depend on the crystal structure. The coating having BCC structure is less resistant to corrosion than the FCC and mixed FCC-BCC structure [21]. Thus, the Co-Ni-Fe coating having mixture of FCC-BCC crystal structures exhibited high corrosion resistance in this study.

Table 3: The corrosion rate of the nanocrystalline Co-Ni-Fe at different conditions

Condition	Corrosion rate (mmpy)
As-synthesized	0.0022
Heated in argon gas	0.0015
Heated in mixed gases	0.0049

Conclusion

In this work, it is concluded that the Co-Ni-Fe coated stainless steel exhibited better good corrosion resistance and hardness after the heat treatment process. It was expected that the material would achieve better densification with the expense of particle growth after heat treatment. The most favorable heating condition for nanocrystalline Co-Ni-Fe coatings is using argon gas. Although mixed gas is commonly known as the best condition for heat treatment in many materials, however, this condition is not favorable to Co-Ni-Fe coating. The hydrogen evolution may occur and thus deteriorate the performance of the coating.

Co-Ni-Fe coating has been proven in this study to protect stainless steel from corrosion in salt fog test. Corroion rate can be affected by particle size, oxygen content and crystal structure. The oxygen content factor is dominant in this study where the Co-Ni-Fe coated stainless steel heated in argon gas exhibited the best corrosion resistance performance due to lowest oxygen content found in the sample. Besides, the sample also performed the highest hardness and smoothest surface which is highly demanded in the coating performance to protect the substrate.

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