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*Short Communication*

# The Corrosion Behaviors of Amorphous, Nanocrystalline and Crystalline Ni-W Alloys Coating

*Xiangyong Liu*[2], *Zhen Xiang*[1], *Junchao Niu*[1], *Kada Xia*[1], *Ying Yang*[1], *Biao Yan*[1], *Wei Lu*[1,*]

[1] School of Materials Science and Engineering, Shanghai Key Lab. of D&A for Metal-Functional Materials, Tongji University, Shanghai 200092, China
[2] Ji'nan Rail Transit Group Co. Ltd., No.2000 Shunhua Rd., Jinan 250101, China
[*]E-mail: weilu@tongji.edu.cn

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The corrosion behaviors of amorphous, nanocrystalline and crystalline Ni-W alloys coating were systematically investigated by ultrasonic-assisted direct current electrodeposition. Through potentiodynamic polarization test and electrochemical impedance spectroscopy analysis, it was found the self-corrosion trend of nanocrystalline coating<crystalline coating<amorphous coating, whereas the anti-corrosion property trend of nanocrystalline coating>crystalline coating>amorphous coating in alkaline solution contrary to that in acid solution. The mechanism of corrosion resistance is amorphous homogenous structure and $WO_3$ films in acid solution and coating high electrical resistance in alkaline solution corresponding to different structure, respectively.

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**Keywords:** Ni-W alloy coating; ultrasonic-assisted direct current electrodepostion; nanocrystalline; amorphous; crystalline; corrosion behavior.

## 1. INTRODUCTION

Ni-W alloys coating, owing to their excellent properties including corrosion and wear resistance, good thermal stability and high mechanical strength, have been potentially widely application in corrosion protective projects.[1-3] Particularly, Ni-W alloys coating substituted for hard chrome plating is a promising environmental friendly alloys. The fabricating technique of Ni-W alloy coatings is mainly based on co-deposition. In such a technique, W is co-electrodeposited from aqueous solutions with iron group metal Ni forming Ni-W alloy [4, 5]. However, defects, especially cracks, are unavoidable to occur during the electrodeposition due to the side reaction of hydrogen evolution. Consequently, these defects lead to low corrosion resistance, which would result in destructive and unexpected failure. In addition, many new processing techniques, including complexing agents, heat treating, pulse current and other assist equipment, are employed in the fabricating of Ni-W alloy coatings and contribute to Ni-W alloys coating with less defects and excellent properties [5-8].

Furthermore, some investigators suggest that Ni-W alloy coatings with amorphous structure exhibits better corrosion resistance and chemical stability than other structure [4, 9]. However, to further illustrate a better insight into the function and clarify the mechanism in this alloy system, it's necessary to investigate the corrosion behavior and mechanism of amorphous, nanocrystalline and crystalline Ni-W alloys coating.

According to our previous work, the nanocrystalline, amorphous and crystalline Ni-W coatings with uniformed and compacted structure were successfully prepared by electrodeposited under ultrasonic-assisted direct current with different current density [10]. Therefore, in present work, it is necessary to further systematically investigate the corrosion behaviors of amorphous, nanocrystalline and crystalline Ni-W alloy coatings in NaCl solution at different pH values. It was found that the self-corrosion trend of nanocrystalline coating (NC) <crystalline coating (C)<amorphous coating (A), whereas the anti-corrosion property trend of nanocrystalline coating>crystalline coating>amorphous coating in alkaline solution (pH=10) contrary to that in acid solution (pH=3), which owing to the amorphous homogenous structure and $WO_3$ films in acid solution and coating high electrical resistance in alkaline solution.

## 2. EXPERIMENTAL

In the present study, amorphous, nanocrystalline and crystalline Ni-W coatings were obtained by ultrasonic-assisted direct current electrodeposition. An electrolytic solution was prepared by dissolving fixed amounts of high-grade chemical reagents and it was consisted of 0.06 M $NiSO_4\cdot 6H_2O$, 0.14 M $Na_2WO_4\cdot 2H_2O$, 0.3 M $Na_3C_6H_5O_7\cdot 2H_2O$, 0.5 M $NH_4Cl$, 0.7 M $H_3BO_3$ and 0.3 M complexing agent. The pH of electrolytic solution was adjusted to 7 using HCl acid solution. A standard three-electrode cell was employed. A saturated calomel electrode (SCE) and platinum were used as reference and counter electrodes, respectively. A cleaned copper plate with an area of 1 cm*1 cm was used as a substrate and the working electrode. During plating the electrolytic solution was stirred with both stirrer and ultrasonication at 70˚C [6]. Ni-W coatings were electrodeposited using ultrasonic direct current at current density from 0.01 to 0.50 A/cm$^2$.

All electrodeposited specimens were ultrasonically cleaned and degreased before electrochemical testing. The corrosion resistance of the Ni-W coatings was studied in 0.5 M NaCl solution open to air at 20˚C with pH values from 3 to 10. The Tafel curves were measured with a scan rate of 1 mV/s.

## 3. RESULTS AND DISCUSSION

### *3.1. Electrodeposited Ni-W alloys coating*

The amorphous, nanocrystalline and crystalline Ni-W coatings were successfully prepared by ultrasonic-assisted direct current electrodeposition. The amorphicity of the amorphous Ni-W alloy coating is identified by one broad peak around 2θ in the range of 40˚–50˚ in XRD patterns. By contrast, the nanocrystalline and crystalline Ni-W alloy coating appearing to crystallization is illustrated by obvious crystallization peak of (111), (200), (220) and (311), as shown in Fig. 1. By the Scherrer equation calculation, the average grain size of amorphous, nanocrystalline and crystalline is 2 nm, 5 nm and 13 nm, respectively, which was smaller than that of other reported amorphous structure [11].

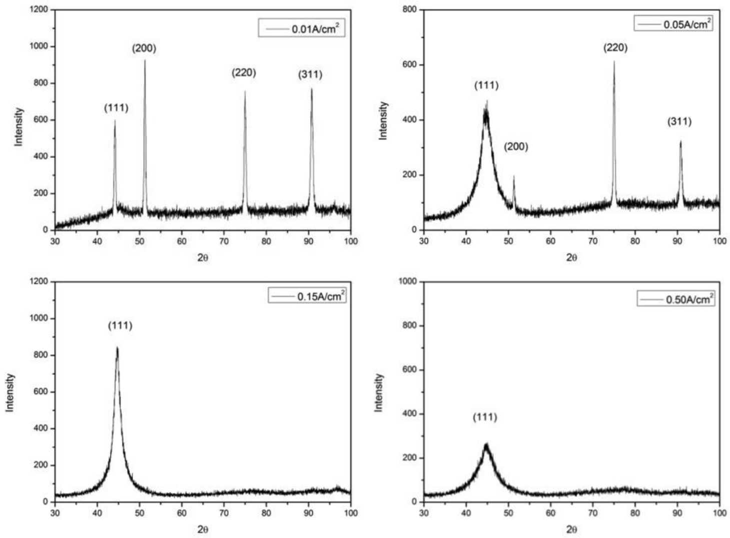


**Figure 1.** XRD patterns of electrodeposited Ni-W coating under ultrasonic-assisted direct current electrodeposition: amorphous, nanocrystalline and crystalline.

### *3.2. Corrosion Behavior*

#### *3.2.1. The effect of pH (3, 7, 10) on the self-corrosion of Ni-W alloys coating*

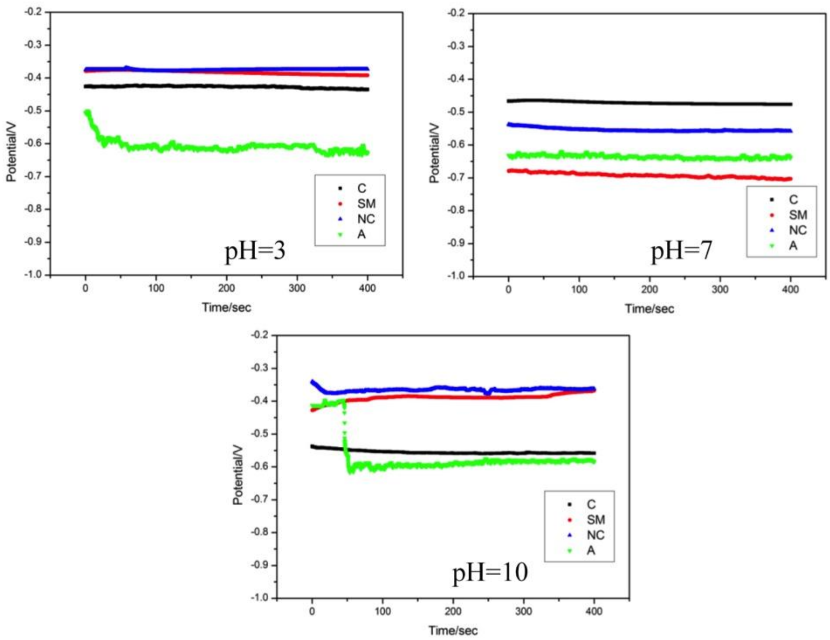


**Figure 2.** The OCP value of amorphous (A), nanocrystalline (NC) and crystalline (C) Ni-W alloys coating in pH=3, 7 and 10, 0.5M NaCl solution, respectively.

To investigate the effect of pH (3,7,10) on the self-corrosion of Ni-W alloys coating in NaCl solution, the open current potential (OCP) value of amorphous, nanocrystalline and crystalline Ni-W alloys coating in pH=3, 7, 10, 0.5M NaCl solution is shown in Fig.1. It was reported that the OCP value is related to the self-corrosion ability. It is clearly seen that there is no change of OCP value both in acid and alkaline solution, whereas the big change in neutral solution. Hence, it is concluded that the OCP value trend of A<C<NC represents the self-corrosion trend of NC<C<A both in acid and alkaline solution, and OCP value trend of A<NC<C for the self-corrosion trend of C<NC<A in neutral solution. Therefore, it can be safely draw conclusion that amorphous Ni-W alloy coating have a biggest self-corrosion resistance among these three Ni-W alloys coating, which may owe to the no structure defects including grain boundaries.

*3.2.2. The effect of pH (3, 7, 10) on the polarization character of Ni-W alloys coating*

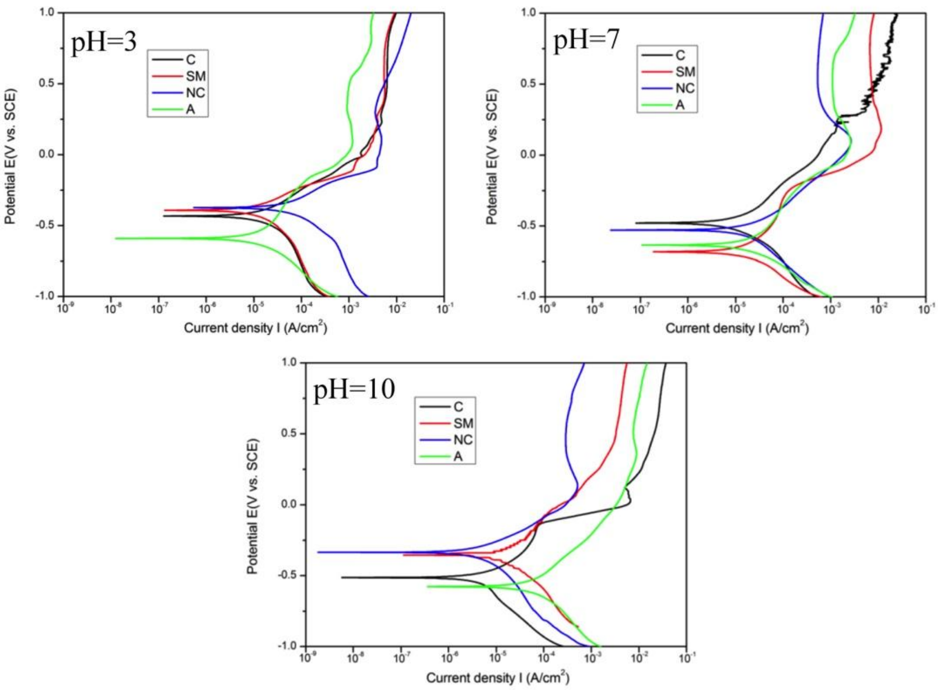


**Figure 3.** Polarization curves of Ni-W alloy coatings comprising of amorphous (A), nanocrystalline (NC) and crystalline (C) in pH=3, 7 and 10, 0.5 M NaCl solution, respectively.

It was clear that OCP cannot reflect the corrosion dynamics process. Hence, to further illustrate the corrosion property of Ni-W alloys coating, the polarization curves of Ni-W alloys coating are characterized and shown in Fig. 3. The Tafel parameters such as corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and Tafel slope are summarized in Table.1. It was reported corrosion potential and corrosion current density related to the resistance to corrosion, higher value of corrosion potential and corrosion current density corresponding to more difficult corrosion. Therefore, it was obviously seen that the trend of resistance to corrosion of A<C<NC in acid and alkaline solution, and that of A<NC<C in neutral solution.

**Table 1.** Corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and Tafel slope of Ni-W alloy coatings in 0.5 M NaCl solution with different pH values.

| Tafel parameters | pH | A | NC | C |
|---|---|---|---|---|
| $E_{corr}$ (mV) | 3 | -0.59 | -0.37 | -0.43 |
| | 7 | -0.63 | -0.53 | -0.48 |
| | 10 | -0.58 | -0.34 | -0.51 |
| $I_{corr}$ ($A/cm^2$) | 3 | 1.17E-05 | 2.21E-05 | 1.46E-05 |
| | 7 | 1.65E-05 | 6.24E-06 | 7.77E-06 |
| | 10 | 5.83E-05 | 6.33E-06 | 1.10E-05 |
| ba (mV) | 3 | 102 | 86 | 97 |
| | 7 | 108 | 112 | 120 |
| | 10 | 104 | 121 | 118 |
| bc (mV) | 3 | 99 | 108 | 110 |
| | 7 | 101 | 114 | 108 |
| | 10 | 117 | 107 | 112 |

### *3.2.3. The effect of pH (3, 7, 10) on the electrochemical impedance spectroscopy character of Ni-W alloys coating*

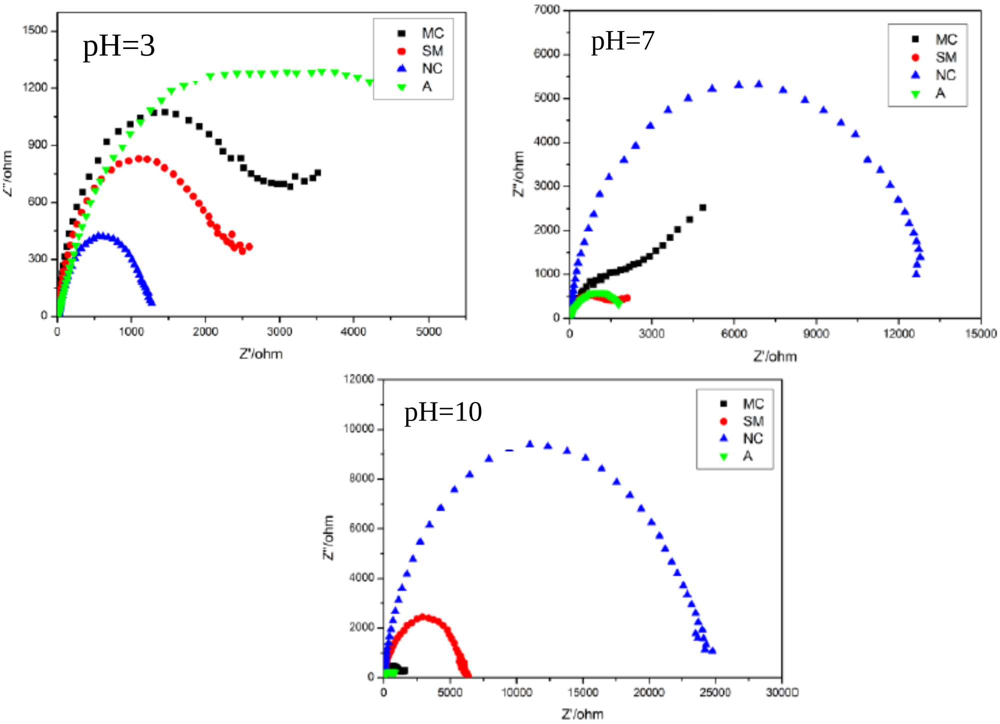


**Figure 4.** Electrochemical impedance spectroscopy character of Ni-W alloys coating composed of amorphous (A), nanocrystalline (NC) and crystalline (C) phases in pH=3, 7 and 10, 0.5 M NaCl solution, respectively.

However, the OPC value and polarization curve of Ni-W alloys coating just reflect the transient corrosion dynamics process. To get more information of corrosion characters of Ni-W alloys coating, the electrochemical impedance spectroscopy character was shown in Fig. 4. It was well documented that the size of capacitive loops corresponding to resistance value of surface charge transferring. Hence, the bigger diameter of capacitive loops related to more resistance value of surface charge transferring stands for lower corrosion rates. Consequently, it was clearly seen that the trend of corrosion resistance of NC<C<A in acid solution and that of A<C<NC in neutral and alkaline solution.

It was suggested that in acid and neutral alkaline solution, amorphous structure has homogenous structure without any structure defects, besides, the formation of stable $WO_3$ [12, 13] contribute to good corrosion resistance, whereas the nanocrystalline structure contributes to the corrosion process result from the more active sites and more grain boundary providing the atomic transferring tunnel [14]. Besides, in neutral solution, the nanocrystalline structure trended to form compact corrosion resistance coating contributes to good corrosion resistance. It was reported by Alimadadi [15] that there are two types of microstructure in Ni-W alloys: single phase nanostructure and two phase nanostructure including Ni-W amorphous phase, which would reduce corrosion resistance drastically. In addition, Sriraman [16] reported that finer crystallites of the coating leads to the increase of surficial area fraction of the intercrystalline region in the triple junction area. The high intercrystalline surficial area fraction will generate more diffusion paths for the transport of alloying elements, which accelerates the corrosion considerably. Therefore, in alkaline solution, the nanocrystalline structure with more grain boundary providing more corrosion active sites have homogeneous corrosion[14, 16~18], which decreases corrosion rate, whereas for amorphous structure the $WO_3$ coating is unstable [13] in alkaline solution and $NiWO_4$ film is not exist. Besides, the Ni-W coatings with crystalline structure show poor corrosion resistance that is resulted from the rough surface morphology with a lot of cracks and pores.

## 4. CONCLUSIONS

In this work, it was systematically investigated the corrosion behaviors of amorphous, nanocrystalline and crystalline Ni-W alloy coatings. It was found that the self-corrosion trend of NC<C<A, whereas the anti-corrosion property trend of A<C<NC in alkaline solution contrary to that in acid solution. The amorphous homogenous structure without any structure defects and containing stable $WO_3$ film in the acid solution exhibits excellent corrosion resistance. However, the passivation coating of $NiWO_4$ and stable $WO_3$ film of amorphous structure coating cannot exist in alkaline solution. Besides, nanocrystalline Ni-W coating show homogenous corrosion which contributes to the improved anti-corrosion performance in the alkaline solution and the crystalline Ni-W coatings show poor corrosion resistance that is resulted from the rough surface morphology with a lot of cracks and pores.

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