Study of the Novel Ni/Co–SiC Coatings Deposited by Pulse Current Electrodeposition. Influence of the Pulse Frequency and the Duty Cycle

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Received: 20 November 2020 / Accepted: 10 January 2021 / Published: 31 January 2021

Ni/Co–SiC coatings were successfully deposited on mild steel via pulse current electrodeposition (PCE) technique. The impact of the frequency and duty cycle on the coating characteristics, such as surface morphology, the orientation of grains, crystal size, micro-hardness, the amount of deposited SiC CNPs, as well as corrosion resistance, were ascertained and discussed. The results indicate that the SiC particles tend to agglomerate, leading to the formation of particle clouds, having mean dimensions of approximately 116.1 nm, enveloped as second phases in the matrix of Ni/Co coating. The Ni/Co-SiC coating created at a duty cycle of 10% and 10 Hz pulse frequency was able to process the maximal SiC content equivalent to 11.5 v/v%. It also illustrates that, with the increment in pulse frequency or decrease in duty cycle, the coating grain assumes a smaller size. The Ni/Co-SiC coating synthesized at a duty cycle of 10% and 10 Hz pulse frequency manifest the maximum micro-hardness value of 672.5 kg/mm, and the Ni/Co-SiC coating deposited at 20 Hz and 30% has the maximum micro-hardness value of 642.2 kg/mm. In addition, the resistance of charge-transfer at the electrode/solution is known to affect the size of the semicircle, hence the size increases with the increment in pulse frequency and decrease in duty cycle.

Keywords: Ni/Co–SiC coating; pulse frequency; duty cycle; surface morphology; corrosion resistance

1. INTRODUCTION

Recently, deposition of ceramic nanoparticles (CNPs) within a single or multiple metallic matrix has attracted many researchers (domestically as well as abroad) owing to their outstanding chemical, physical and mechanical properties [1-6]. In general, CNPs function as reinforced phase particles. CNP’s such as SiC [7], Al2O3 [8], TiN [9, 10], and WC [11], are capable of remarkable enhancement in the surface hardness, anti-oxidation property, wear and corrosion resistance of the composite coatings.
Enhanced corrosion protection and tribological properties are the characteristics of Ni-based SiC composite coating on the metallic substrate [12, 13]. There have been several studies demonstrating that the key attributes of Ni-based SiC can be further enhanced by switching the matrix material to Ni-Co alloy instead of pure Ni [14-16]. Ni/Co-SiC nanocomposite coatings have been extensively investigated for their corrosion properties [17-20], but there are not many reports of Ni/Co-SiC coatings regarding their corrosion resistance properties.

As known, pulse current electrodeposition (PCE) is one of the most convenient, fast, and low-cost processing methods for depositing Ni/Co-SiC coating. Several factors are affecting the overall corrosion resistance of the coating, such as current density, duty cycle, frequency, the composition of the plating bath, etc. [21-23]. In our previous investigations [24-26], we have studied the effect of current density on nickel-based ceramic nanocoatings. The objective of the present investigation is to use PCE-deposited Ni/Co-SiC coating for enhancing the corrosion resistance of mild steel (MS). The impact of the frequency and duty cycle on the coating characteristics, such as surface morphology, the orientation of grains, crystal size, micro-hardness, the amount of deposited SiC CNPs, as well as corrosion resistance, were ascertained and discussed. Scanning electron microscopy (SEM) was employed to ascertain the surface morphological features of the coating. X-ray diffraction (XRD) was used to characterize the crystalline structural framework of the coating whereas the energy-dispersive X-ray spectrum (EDXS) was employed to determine the quantity of deposited SiC nano-particles. The corrosion resistance and micro-hardness of the coating were also estimated.

2. EXPERIMENTAL SECTION

A sheet of 65 steel was used to create an electrode for electrodeposition. An epoxy sealant was used to seal the specimen. An area of 2 cm² was left and designated as a working area. The steel electrode was polished with 200, 800, and 1000 grit emery papers sequentially before electrodeposition, and 20 g/L Na₂CO₃+5 g/L NaOH solution was subsequently used to wash it at room temperature, and a 1:1 HCl solution was used to activate it for 20 s. The solution in the plating bath employed for PCE-deposition comprised a mixture of CoSO₄⋅7H₂O 70 g/L, NiSO₄⋅7H₂O 250 g/L, NiCl₂⋅6H₂O 40 g/L, sodium citrate 25 g/L, SiC NPs (40 nm in diameter) 10 g/L, boric acid 20 g/L.

<table>
<thead>
<tr>
<th>Plating parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density (A/dm²)</td>
<td>4</td>
</tr>
<tr>
<td>Pulse frequency (Hz)</td>
<td>1, 10, 20</td>
</tr>
<tr>
<td>Duty cycle (%)</td>
<td>10, 30, 50, 70</td>
</tr>
<tr>
<td>pH</td>
<td>4.6</td>
</tr>
<tr>
<td>Bath temperature (°C)</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 1. The plating parameters for PCE-depositing the Ni/Co-SiC coatings.
Suspension of SiC NPs in electrolyte ultrasonic stirring for 20 min at 200 W prior to electrodeposition prevented the agglomeration of SiC NPs. The pulse frequencies altered between 1 and 20 Hz in PCE deposition, while the duty cycles varied between 10% and 70%. Table 1 lists parameters for plating for PCE-deposition of Ni/Co-SiC coatings.

S3400 SEM showed the elaborate morphology of the coating based on Ni/Co-SiC and EDXS in combination with SEM was used to estimate the total content of SiC NPs embedded within the coating. The coating was maintained at an average thickness of 70 μm. To ascertain the grain size and crystalline orientation, XRD measurements were performed with an X-ray Diffractometer (Philips D5000) with a source providing Cu Kα radiation. The specimen was scanned at a 20 value ranging from 10° to 80° and the scan rate was set at 0.03° per second.

Using a DT-950 Vickers Micro-hardness Tester, the Ni/Co-SiC coatings were tested for their micro-hardness, with 100 g applied load for a duration of 10s. The average value of five measurements conducted on each sample was obtained. Electrochemical impedance spectroscopy (EIS) measurements were employed to characterize the corrosion resistance of the Ni/Co-SiC coating in simulated seawater (NaCl 26.6 g/L, MgSO₄ 3.3 g/L, MgCl₂ 2.5 g/L, CaCl₂ 1.1 g/L). CS350 electrochemical workstation based on a three-electrode cell was utilized to measure the EIS, where the working electrode was a 65 steel, whereas the counter electrode was made out of a platinum sheet. The reference electrode is the standard saturated calomel electrode (SCE). The working electrode was submerged in the seawater for at least half an hour prior to the EIS measurement until a steady corrosion potential was attained. The EIS determination was carried out using a 10-mV disturbance, while a 10 mHz to 10,000 Hz measuring frequency was used.

3. RESULTS

3.1. Morphological analysis

The surface morphological characteristics of Ni/Co–SiC coatings synthesized at varying duty cycles and 10 Hz pulse frequency are depicted in Fig. 1.
Figure 1. SEM images of Ni–Co–SiC coatings deposited at different duty cycles: (a) 10%, (b) 30%, (c) 50%, and (d) 70%.

Figure 2. SEM images of Ni–Co–SiC coatings deposited at different duty cycles: (a) 50%, and (b) 70%.

The coatings exhibit an acicular and needle-like, branched structure. The acicular structural framework changes into a partially nodular morphology, as the duty cycle undergoes an increase, wherein the acicular and pointed trunks become shorter and close to the branches' length. Additionally, the coatings synthesized at 50% are compared in terms of their surface morphologies with those synthesized at 70% duty cycles as shown in Fig. 2, however, these coatings are characterized at a comparatively lower magnification compared to the ones in Fig. 1. It is evident that in terms of their structure, the coating synthesized at the low duty cycle, i.e., 50%, are rather firmer and finer compared to those synthesized at the 70% duty cycle.

For the Ni/Co-SiC coatings synthesized at the 30% duty cycle and different frequency pulses, the surface morphological characteristics are shown in Fig. 3. The coating is mostly nodular at 1 Hz, having only hardly any short fibers here and there. As the pulse frequency rises, the structure of the coating transforms to acicular. The increase in frequency from 1 Hz to 10 Hz, leads to a decrease in the number and length of trucked fibers, however, there is a simultaneous increase in the count of fibers that are branched. The surface characteristics of the SiC nanoparticles embodied in the coating are shown in Fig. 4. Seemingly, the SiC particles tend to agglomerate, leading to the formation of particle clouds,
having mean dimensions of approximately 116.1 nm, enveloped as second phases in the matrix of Ni/Co coating. This outcome is practically the same as the result reported by Yang et al. [27].

**Figure 3.** SEM images of Ni/Co-SiC coatings deposited at different pulse frequencies: (a) 1 Hz, (b) 10 Hz, and (c) 20 Hz.
3.2. SiC content embedded in the coating

Fig. 5 and 6, respectively depict the percent volume of the SiC nanoparticles embedded within the coating with respect to the frequency and the duty cycle. As evident, the SiC content in Ni/Co-SiC coatings tends to increase with the drop in duty cycle and the corresponding increment in pulse frequency. The Ni/Co-SiC coating created at a duty cycle of 10% and 10 Hz pulse frequency was able to process the maximal SiC content equivalent to 11.5 v/v%. In contrast, the coating deposited at 70% duty cycle and 10 Hz was found to have minimum SiC content equivalent to 6.7 v/v%. Moreover, the Ni/Co-SiC coating produced at a duty cycle of 30% and 1 Hz pulse frequency processed the minimum content of SiC content i.e 5.9 v/v%, while at 10 Hz and 30% the deposited Ni/Co-SiC coating had the maximum SiC content of 10.7 v/v%. The results are similar to the phenomena described by Liu et al. [28].
3.3. XRD characterization

The XRD spectrum of the synthesized Ni/Co-SiC coatings under the influence of different frequencies and duty cycles are depicted in Figs. 7 and 8, respectively. In the range of 2θ of 20~40° and 50~70°, the weak characteristic line arises due to SiC. Due to Ni and Co having a density roughly thrice as high as that of SiC, SiC has a very low weight percent. Therefore, SiC peaks showing up in the XRD data are rather weak. Besides, NiCo and other solid solutions with two phases are generated and identified because both Co- and Ni-salts are present within the bath.
Figure 7. XRD spectra of Ni/Co-SiC coatings obtained at various duty cycles: (a) 10% and (b) 50%.

Figure 8. XRD spectra of Ni/Co-SiC coatings obtained at various pulse frequencies: (a) 1 Hz and (b) 10 Hz.
Moreover, the inherent characteristic diffraction peaks corresponding to the Ni/Co-SiC coating become lesser in intensity with increasing frequency and dwindling duty cycle. The variation in pulse frequency and duty cycle, however, does not alter the XRD pattern of the coating. This experimental result is consistent with that investigated by Xu et al.[29].

Further, the measured XRD spectra are used to calculate the size of individual grains of the composite, and the results are depicted in Table 2. It illustrates that, with the increment in pulse frequency or decrease in duty cycle, the coating grain assumes a smaller size. Consequently, the coating is obtained with finer grains.

**Table 2.** The sizes of grains in Ni/Co-SiC composite deposited under different duty cycles and pulse frequencies.

<table>
<thead>
<tr>
<th>Plating parameters</th>
<th>Average size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duty cycle (%)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>30</td>
<td>53</td>
</tr>
<tr>
<td>50</td>
<td>57</td>
</tr>
<tr>
<td>70</td>
<td>62</td>
</tr>
<tr>
<td>Pulse frequency</td>
<td></td>
</tr>
<tr>
<td>(Hz)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>56</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>20</td>
<td>48</td>
</tr>
</tbody>
</table>

3.4. Micro-hardness test

Figs. 9 and 10 illustrate the values of the micro-hardness for the Ni/Co-SiC coating deposited with respect to different pulse frequencies and duty cycles. As demonstrated by the results, the coating varies in micro-hardness and the values lie in the 510 kg/m ~ 670 kg/mm range.

**Figure 9.** Effect of duty cycle on micro-hardness of Ni/Co-SiC coatings obtained at pulse frequency of 10 Hz.
Figure 10. Effect of pulse frequency on micro-hardness of Ni/Co-SiC coatings obtained at duty cycle of 30%.

With the increment in frequency and decrease in duty cycle, a rise in the micro-hardness is evident. The Ni/Co-SiC coating synthesized at a duty cycle of 10% and 10 Hz pulse frequency manifested the maximum micro-hardness value of 672.5 kg/mm, and the Ni/Co-SiC coating deposited at 20 Hz and 30% had the maximum micro-hardness value of 642.2 kg/mm. The phenomenon is consistent with the study stated by Xia et al. [30].

3.5. EIS measurement

The measured Nyquist and Bode diagrams at varying duty cycles and pulse frequencies on the prepared Ni/Co-SiC coatings are respectively shown in Figs. 11 and 12. The highlight of these curves is a single semicircular shape extended over the entire range of frequency.
Figure 11. Nyquist (a) and Bode (b) curves of Ni/Co-SiC coatings obtained at different duty cycles (pulse frequency 10 Hz).

Figure 12. Nyquist (a) and Bode (b) curves of Ni/Co-SiC coatings obtained at different pulse frequencies (duty cycle 30%).
Nonetheless, the resistance of charge-transfer at the electrode/solution is known to affect the size of the semicircle, hence the size increases with the increment in pulse frequency and decrease in duty cycle. The results are consistent with the investigation explicated by Xia et al. [31].

4. DISCUSSION

4.1. Influence of plating parameters on the deposition of SiC

It is evident from the present work that the low duty cycle allows the deposition of a higher content of SiC particles. According to the mechanistic details of adsorption proposed by Guglielmi's which comprise two steps [32], two consecutive adsorption steps result in complete co-deposition of the inert SiC nanoparticles. The first step involves rather loose adsorption of particles, arriving at the negative electrode, on the electrode itself with a simultaneous high extent of coverage of metal ions, thereby boosting the content of adsorbed particles to be deposited within the coating. Our work also reveals that with the increase in pulse frequency the SiC contents in Ni/Co-SiC coating first increases and then decreases slightly. A proper pulse frequency (such as 10 Hz) has the potential to generate a high overpotential during PCE deposition, thus generating energy in an increased amount for adsorbing inert particles of the likes of SiC.

4.2. Effects of plating parameters on the microstructures of the coatings

The prepared Ni/Co-SiC coatings predominantly possess a hexagonal close-packed (h c p) structure since the primary reflections of the solid solution based on Ni/Co in the XRD spectrum arise from (1 0 0) and (1 1 0) planes as shown in Figs. 7 and 8. Moreover, with the reduction in duty cycle and the increment in pulse frequency the size of the grain begins to dwindle, which in turn is linked to its impact on the quantity of SiC particles that are embedded in the coating. Since the SiC particles provide nucleation sites for electocrystallization, their presence is capable of affecting the grain size, thereby enhancing the nucleation process, whereas the growth of the crystal is effectively retarded by them. As previously analyzed, an impulse current with a low duty cycle and a high pulse frequency is able to increase the quantity of SiC grains deposited within the coating, thereby influencing the size of grains during electrodeposition.

Moreover, the over-potential is apparently the variable to ascertain the rate of nucleation [33]. A high instant over-potential could be generated by the high pulse frequencies in one pulse cycle thus enhancing the rate of nucleation. The growth of the grain is subsequently hindered. Additionally, the decrease of ON-time during one pulse cycle and a consequent decrease in the duty cycle can cause an increment in the charge-transfer current, which additionally decreases the grain growth and enhances the nucleation rate.
4.3. Influence of plating parameters on corrosion resistance and mechanical properties of coatings

In general, two factors influence the hardness of Ni-based SiC composite coating, namely the quantity of hard particles incorporated as well as the hardness of the metal matrix. Within a particular metal matrix, the micro-hardness of the composite is predominantly affected by the deposited nanoparticles. The mechanisms defined for hardening primarily fall into two categories and are ascertained by the size and amount of the nanoparticles. The mechanisms are referred to as particle strengthening and dispersion strengthening [34]. A material that is hardened as a consequence of dispersion strengthening is identified by fine particles dispersed within the matrix, the pinning of dislocations at particles that function as the dislocation pinning sites is primarily responsible for the strengthening effect and results in the flow stress being enhanced. The fine particles hamper the movement of dislocations whereas the matrix carries the load. A particle strengthened material, on the other hand, comprises particles having a large size (>1 μm) and a matrix. Although the matrix primarily carries the load, a part of the load is also carried by the particles and restricts any deformity in the matrix.

Due to the involvement of nanoparticles in electrode-deposition in this work, dispersion strengthening is the key channel for improving and enhancing the coating micro-hardness [35]. In the dispersion strengthening mechanism, there is a uniform contribution of the particles in the composite. The percent count of the particles in the composite becomes greater as the particle size becomes smaller, and the strengthening effect becomes better. Besides, the dimensions of the grain in the matrix also influence the hardness of the polycrystalline materials. Reduction in the grain size of the matrix generally leads to an increment in the hardness of the composite. In this investigation, the minuscule change in the grain size under the impact of different electrodeposition conditions is not adequate to cause a substantial disparity in micro-hardness. On the whole, it is generally assumed that the influence of duty cycle and pulse frequency on the micro-hardness characteristics of the coating relies on the quantity of deposited SiC nanoparticles.

Table 3. The charge-transfer resistance collected from EIS plots on Ni/Co-SiC coatings.

<table>
<thead>
<tr>
<th>Plating parameters</th>
<th>Charge-transfer resistance (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duty cycle (%)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4901.2</td>
</tr>
<tr>
<td>30</td>
<td>3654.1</td>
</tr>
<tr>
<td>50</td>
<td>2915.7</td>
</tr>
<tr>
<td>70</td>
<td>2797.6</td>
</tr>
<tr>
<td>1</td>
<td>2647.3</td>
</tr>
<tr>
<td>Pulse frequency (Hz)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3120.8</td>
</tr>
<tr>
<td>20</td>
<td>3479.4</td>
</tr>
</tbody>
</table>

An equivalent circuit model is employed to ascertain the corrosion resistance of the coatings synthesized in a variety of electrodepositing conditions, which comprises a parallel connection of a charge-transfer resistance with a solution resistance and a double-charge layer capacitance for analyzing the electrochemical parameters. The charge-transfer resistance is shown in Table 3, which, with respect
to the pulse frequency and duty cycle is irreversibly proportional to the rate of corrosion. Apparently, the charge-transfer resistance rises as the duty cycle decreases, suggesting an increased resistance to corrosion. Furthermore, the charge-transfer resistance increases, as the pulse frequency increases, thereby demonstrating an enhancement in the corrosion resistance of these composites.

The hardness, strength, chemical, and structural stability of the fabricated coatings is substantially enhanced by embodying the nanoparticles, for instance, SiC. The enhancement in these characteristics potentially increases the corrosion resistance of the coating. Moreover, the area effective for cathodic reduction is also reduced by the existence of inert SiC particles on the top-most layer. There is, thus, a resultant decline in anodic dissolution.

5. CONCLUSIONS

(1) The coatings exhibit an acicular and needle-like, branched structure. The acicular structural framework changes into a partially nodular morphology, as the duty cycle undergoes an increase, wherein the acicular and pointed trunks become shorter and close to the branches' length. The SiC particles tend to agglomerate, leading to the formation of particle clouds, having mean dimensions of approximately 116.1 nm, enveloped as second phases in the matrix of Ni/Co coating.

(2) The Ni/Co-SiC coating created at a duty cycle of 10% and 10 Hz pulse frequency was able to process the maximal SiC content equivalent to 11.5 v/v%. In contrast, the coating deposited at 70% duty cycle and 10 Hz was found to have minimum SiC content equivalent to 6.7 v/v%.

(3) In the range of 2θ of 20~40° and 50~70°, the weak characteristic line arises due to SiC. It also illustrates that, with the increment in pulse frequency or decrease in duty cycle, the coating grain assumes a smaller size.

(4) The Ni/Co-SiC coating synthesized at a duty cycle of 10% and 10 Hz pulse frequency manifested the maximum micro-hardness value of 672.5 kg/mm, and the Ni/Co-SiC coating deposited at 20 Hz and 30% had the maximum micro-hardness value of 642.2 kg/mm.

ACKNOWLEDGEMENT

This work has been supported by the National Natural Science Foundation of China (Granted no. 51974089), and Natural Science Foundation of Heilongjiang Province of China (Granted no. LC2018020).

References


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