Surfactant-free commercial electroless bath with low concentration of SiC nanoparticles to prepare the NiP-SiC nanocomposite coatings

M Khodaei and A Mohammad Gholizadeh
Faculty of Materials Science and Engineering, K. N. Toosi University of Technology, Tehran, Iran
E-mail: khodaei@kntu.ac.ir

Abstract

Fabrication of NiP-SiC nanocomposite coatings through the electroless deposition in a commercial electrolyte containing the low concentrations of SiC nanoparticles on carbon steel substrate was studied in this work. The confirmation of co-deposition of Ni matrix and SiC nanoparticles was investigated by evaluating the effect on morphology, crystal structure, and corrosion behavior of the heat-treated coatings which were investigated by scanning electron microscope, x-ray diffraction (XRD), and electrochemical measurements, respectively. The XRD results revealed that the heat-treated NiP and NiP-SiC coatings consisted of Ni and Ni3P phases, which the calculated faction of Ni3P phase for NiP and NiP-SiC samples is 58.2 and 62.2%, respectively. The corrosion resistance of nanocomposite samples is higher than that of pure NiP sample (9 to 76% corrosion inhibition efficiency). The tribological behavior of the coatings was characterized by microhardness measurement and ‘pin on disk’ wear test. By co-deposition of SiC nanoparticles, the hardness of heat-treated NiP is significantly increased (near 25%) and the wear loss is reduced (near 48%), especially at high sliding distance during wear test. The sample prepared through the surfactant-free electroless bath containing the 1 g l\(^{-1}\) SiC nanoparticle showed the best corrosion as well as wear resistance.

1. Introduction

Electrolytic and electroless plating of the Ni-based coatings have been utilized for corrosion and oxidation as well as wear protection of plane steels used in different industries such as oil and gas industries. Among them, the autocatalytic Ni electroless method, in which the Ni atoms deposit on the surface by autocatalytic reduction of Ni\(^{2+}\) ions, possesses the advantages to the electrolytic Ni deposition [1]. These advantages are not only non-consuming the electrical current, but also the ability to the formation of uniform coatings on the parts with complex geometric (deep whole and sharp edges) because of the variation of current density along the surface during the electrolytic processes [1, 2]. Hence, the electroless deposition is interesting especially from an industrial point of view. In the last decades, the enhancement in performance of plated Ni coatings has been pursued by the development of advanced coatings such as composite Ni coatings by both electrolytic and electroless methods. Co-deposition of particles as a second-phase along with Ni leads to the formation of Ni composite coatings which have been reported superior properties in comparison to the pure Ni coatings [1, 3]. Earlier works in the composite Ni coatings have been fabricated by incorporating the micron size particles and the possibility of the incorporation of nanomaterials has introduced a new generation of composite coatings (nanocomposite coatings), which demonstrate enhanced physical, mechanical, and functional properties as a result of nanoscale effects [3]. Selection of second-phase has been performed according to expected improvement in the performance of the Ni layer such as providing the higher corrosion resistance and/or improving the tribological behavior (high hardness, low wear loss, and lower/higher friction coefficient). Hence, various nanostructured second-phase such as Al\(_2\)O\(_3\) [4], ZnO [5], TiO\(_2\) [6], SiO\(_2\) [7], Si\(_3\)N\(_4\) [8], ZrO\(_2\) [9], WC [10], TiC [11], Diamond [12], and SiC [13–16] have been used especially for electroless Ni coatings to deposit nanocomposite coatings. It is reported [17] that SiC codeposits well with many different metals.
A commercial nickel electroless solution
2. Materials
2. Experimental
(prepared using the lowest concentration SiC nanoparticles addition, surfactant-assisted electroless deposition through bathes containing the relatively low concentration of β-stabilizer was used for electroless Ni-P plating. Commercially available plane steel sulfate as nickel source, sodium hypophosphite as reducing agent, and suitable amounts of additive and electrolyte electroless bath such as delay in the starting of the electroless deposition due to the indirect contact of substrate hypophosphite ions by surfactant, or suppressing the reduction process of Ni ions due to the coverage of Ni and hypophosphite ions by surfactant, which leads to the reduction in the deposition rate of the coatings. Reducing the bonding strength of the interface of matrix and reinforced particles within the composite coatings can be another adverse effect of using the surfactant.

Hence, surfactant-free electroless nanocomposite depositions of the NiP electroless bath has been investigated, especially few reports for NiP-SiC nanocomposite coatings using the low mass concentration of SiC nanoparticles in the bath (0.25 and 1 g l⁻¹ [15], 1–3 g l⁻¹ [16]) or even high mass concentration of nanoparticles (3–9 g l⁻¹ [21]). Incorporation of the SiC nanoparticles within the Ni matrix has been proved by their effect on the hardness as well as corrosion resistance of the coatings. It was shown that the corrosion resistance of NiP-SiC nanocomposite coating deposited through the NiP electroless bath contains the 0.25 g l⁻¹ SiC nanoparticles is higher than that of pure NiP [15]. In addition, the NiP-SiC nanocomposite coatings prepared through the surfactant-free bath containing the 1–3 g l⁻¹ SiC nanoparticles showed improved corrosion resistance for the sample prepared through the bath containing the 2 1 g l⁻¹ SiC nanoparticles [16]. The advantage of low concentration of solid second-phase in the electroless bath is the ability to disperse by mechanical agitation, which can prepare a stable suspension while using the nanoparticles with continuous agitation.

Therefore, the study of electroless bath mixed with nanoparticles in low concentration can be a straightforward route to preparing the nanocomposite electroless coatings, which is interesting for industrial point of view. Up to now, only few reports [15, 16] have been published on NiP-SiC nanocomposite coatings prepared by electroless bath containing low concentration of nanoparticles, which their corrosion behavior were characterized. In this work, the tribological behavior of NiP-SiC nanocomposite coatings fabricated by a commercial electroless bath with low concentration of SiC nanoparticles (less than 3 g l⁻¹), without using the surfactant, and employing the simple agitation for uniform dispersion of nanoparticles has been investigated. The successful incorporation of SiC nanoparticles within the coatings has been confirmed by their effect on morphology, corrosion behavior, and hardness of the coatings. The effect of SiC nanoparticle concentration in the electroless bath was investigated on tribological behavior of the heat-treated coatings.

2. Experimental
2.1. Materials
A commercial nickel electroless solution (SLOTONIP 70A (9%–11%P), Schloter, Germany) containing nickel sulfate as nickel source, sodium hypophosphite as reducing agent, and suitable amounts of additive and stabilizer was used for electroless Ni-P plating. Commercially available plane steel (St37) rod was used as substrate, β-SiC nanoparticles (US Research Nanomaterials Inc.) with an average size of 45–60 nm were used as hard second-phase. Transmission electron microscopy image of SiC nanoparticles, which is provided by the manufacturer, are presented in figure 1. Reagent grade NaOH, H₂SO₄, HCl, ammonia 25% solution, acetone (Merck; Germany) were used as received.
2.2. Preparation of samples
St37 plane steel discs (5 cm diameter and 0.7 cm thickness) were used as the substrate. The substrates were polished with sandpapers of #400 to #1200 and sequentially cleaned by acetone using an ultrasonic bath (frequency of 50 kHz). Then the substrates were subjected to pickling treatments before the coating process as following steps; 20 min in 20 wt% NaOH aqueous solution at 70 °C, 3 min in 10 vol.% H2SO4 solution, and 1 min in 15 vol.% HCl solution. After each step, the substrates were washed with distilled water and after that the substrates were transferred to the plating solution (400 ml) which was in a 600 ml glass beaker on the magnetic stirrer hotplate. The temperature of the plating solution was kept at 90 ± 5 °C and it was stirred at 150 rpm to generate a consistent agitation for suspension of particles in the plating solution. Ammonia 25% solution was used to maintain the pH value of the plating solution around 4.7 during deposition. The similar procedures were performed to deposit the composite coating, except as various amounts of SiC nanoparticles as second phases are added to the plating bath. To ensure the complete de-agglomeration and dispersion of second phases, the plating solutions were subjected to the high-intensity probe ultrasonic (frequency of 120 kHz). All samples were deposited for a time of 90 min. After the deposition, the samples were washed by distilled water, dried and heat-treated under Ar atmosphere at temperature of 400 °C for 1 h using a quartz tube furnace (Azar Furnace, Iran). These heat treatment parameters are optimum conditions for NiP electroless coatings for both pure NiP [1] and NiP-SiC composite [23] coatings and all samples heat-treated in this condition for better comparison. The name of the samples and a short description of the preparation are presented in table 1.

### Table 1. The name of the samples and description of the fabrication routes of the samples in this work.

| Sample name | Electroless deposition of |
|-------------|--------------------------|
| NiP         | pure Ni-P solution       |
| NiP-0.5SiC  | Ni-P solution containing of SiC nanoparticles (0.5 g l⁻¹) |
| NiP-1SiC    | Ni-P solution containing of SiC nanoparticles (1 g l⁻¹) |
| NiP-2SiC    | Ni-P solution containing of SiC nanoparticles (2 g l⁻¹) |
| NiP-3SiC    | Ni-P solution containing of SiC nanoparticles (3 g l⁻¹) |

2.3. Characterization
Optical microscope (Leica, Germany) was used to observe the cross section of coatings. Surface morphology of samples as well as wear track of the samples was observed by scanning electron microscope (SEM; VEGAII TESCAN, Czech). The field emission scanning electron microscope (FESEM; TESCAN-MIRA3, Czech) equipped with an attachment for energy dispersive spectrometry (EDS) was used to determine the
microstructure as well as elemental analysis of the coatings. X-ray diffraction (XRD) by CuKα radiation with a scanning rate of 0.2°/min was performed using PHILIPS diffractometer (PW 1730, Netherlands) to identify the phases in the coatings. The existing phases were determined using the International Centre for Diffraction Data-Powder Diffraction Files (ICDD PDF) database.

The hardness of the samples was measured by a Vickers micro-hardness tester (Buehler Micromet II, Germany) according to the ASTM B578 with load of 100 g (HV100) for a dwell time of 10 s. The hardness value was reported as an average of five measurements after removing the highest and lowest values. Wear behavior of the coatings was determined by pin-on-disc test (using the Parsayesh System, Iran) based on ASTM G99. The wear tests were carried out at ambient condition (temperature of about 25°C and relative humidity of about 35%) by applying a load of 30 N against AISI-52100 steel pin with the hardness of 60 HRC under sliding speed of 1 m s⁻¹. The sliding distance was chosen 500 m and in order to determine the weight loss of sample during test, the samples were weighted preciously using a balance with accuracy of ±5 μg after each 100 m sliding distance. Corrosion behavior of the samples was studied by polarization tests using EG&G Model 273A, USA. The tests were performed after 30 min of immersion in 3.5 wt% NaCl solution with scan rate of 10 mV s⁻¹ within the potential range of −250 to +1000 mV with respect to the open circuit potential (OCP). The electrochemical setup consists of a saturated calomel electrode (SCE) reference electrode, a platinum counter electrode, and the samples as a working electrode. The Tafel extrapolation of polarization curves using Zview software was used to determine the corrosion potential (Ecorr), corrosion current density (Icorr), and polarization resistance (Rp) of the samples.

3. Results and discussion

Since a low concentration of SiC nanoparticles without using the surfactant has been tried in this work to prepare the nanocomposite coating, several characterizations including the morphological and structural as well as corrosion behavior investigations have been performed to reveal the successful incorporation of nanoparticles within the coatings. Finally, the effect of SiC nanoparticle concentration in electroless bath on tribological behavior of the heat-treated NiP nanocomposite coatings has been investigated. The heat treatment parameters (400°C for 1 h) are optimum conditions for NiP electroless coatings for both pure NiP [11] and NiP-SiC composite [23] coatings and all samples heat-treated in this condition for better comparison.

3.1. Morphological and structural characterizations

To investigate the effect of incorporation of SiC nanoparticles into the heat-treated electroless Ni-P coating, the surface morphology of the samples was observed by scanning electron microscope as shown in figure 2. As can be seen, the significant difference can be observed between the surface morphology of NiP and NiP-xSiC nanocomposite coatings. By incorporation of SiC nanoparticles, the NiP-1SiC showed significant nodular structure after heat treatment and by increasing the content of SiC nanoparticles into the plating bath, the nodular morphology of the surface after heat treatment will be refined (NiP-2SiC) and it was disappeared in NiP-3SiC sample. It is worth mentioning that the surface of the NiP coating is relatively smooth by incorporation of SiC nanoparticles and no micro-crack and porosity are detected on the surface of the samples.

The cross section of samples was observed by optical microscope and that of NiP and NiP-2SiC samples are shown in figure 3. As can be seen, the thickness of the NiP sample is about 11.2 micron and by incorporation of SiC nanoparticles in the plating bath the thickness of the NiP-2SiC sample is reduced to around 8.7 micron. Different thickness of NiP and NiP-nanocomposite samples prepared by same plating time can be due to the increasing the solid surfaces in the bath as a result of the presence of nanoparticles, which are the active place for reduction of Ni ions. Hence, the layers deposited through the baths containing the nanoparticles has a lower thickness.

To confirm the presence of the SiC nanoparticles in the NiP electroless coatings, the surface of etched samples using 30 vol.% HNO₃ aqueous solution for 5 min was investigated using the FESEM equipped with EDS analyzer. The EDS spectra of NiP and NiP-2SiC samples along with the FESEM images of corroded surface of NiP-2SiC sample at different magnification and the corresponding elemental EDS maps are shown in figure 4. Figures 4(a) and (b) compare the EDS spectrum of NiP and NiP-2SiC and the weight and atomic percentage of elements are tabulated (presented in the inset of figures 4(a) and (b)). The EDS spectra confirm the presence of Ni and P elements in NiP sample, whereas Si and C along with Ni and P elements are the main elements in the NiP-2SiC sample. It is worth mentioning that the presence of the peak of Fe is related to steel substrate and that of oxygen can be due to the oxidation during chemical etching of the coatings (sample preparation for this test). As can be seen in figures 4(c)–(e), the nanoparticles can be identified and further recognized at higher magnification. The elemental mapping images corresponding to figure 4(c), presented in figures 4(f)–(i), reveal that the Ni and P atoms are entirely distributed over the whole surface and the Si and C atoms are also presented.
in the surface of NiP-2SiC sample, indicating the relatively uniform distribution of the embedded SiC nanoparticles.

To investigate the effect of the presence of the SiC nanoparticles on the crystallite structure of the heat-treated Ni-P coatings, the x-ray diffraction (XRD) analysis has been performed on the NiP and NiP-2SiC samples, as shown in figure 5. The results revealed that the both pure (NiP sample) and composite (NiP-2SiC sample) composed of the Ni phase with face-centered cubic (FCC) crystal structure as well as precipitated nickel phosphide (Ni₃P) with body-centered tetragonal (BCT) crystal, which is precipitated during heat treatment of

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**Figure 2.** SEM micrograph of surface of the (a) NiP, (b) NiP-0.5SiC, (c) NiP-1SiC, (d) NiP-2SiC, (e) NiP-3SiC samples at two different magnifications.
the Ni coatings; i.e., Ni(P) solid solution. The Ni and Ni$_3$P phases were identified by ICDD PDF no. 00-004-0850 and 01-074-1384, respectively, which were reported as the main phases of a heat-treated electroless Ni-P coating [1, 13, 14]. The optimum heat treatment condition for the commercial electroless Ni-P has been reported to be 400 °C for 1 h [23] for complete crystallization of Ni matrix and precipitation of Ni$_3$P phases within the matrix. To have a better comparison, the heat treatment for the nanocomposite samples was also selected same as heat treatment condition of pure NiP samples, which is also reported previously as an optimum condition for NiP-SiC [13, 21, 23] composite electroless coatings. The formation of intermetallic phases between Ni and Si (Ni$_x$Si$_y$) by heat treatment at a higher temperature than 400 °C and longer time than 1 h has been reported in NiP-SiC [23]. As can be seen, the heat-treated NiP-2SiC sample has also consisted of Ni and Ni$_3$P phases, similar to the NiP sample, except as representing the higher intensity for the diffraction peaks of Ni$_3$P at the XRD pattern of NiP-2SiC sample in comparison to those at NiP sample. This indicates the higher precipitation of Ni$_3$P phase during heat treatment as a result of the presence of SiC nanoparticles which can promote the heterogeneous nucleation of Ni$_3$P.

To identify the content of phases in the samples by assuming the intensity of x-ray diffraction peaks, the Rietveld method was employed using the Maud program to refine the diffraction patterns. The modified Pseudo-Voigt profile function was used to model the peak profiles. The Pseudo-Voigt function is an approximation for the Voigt function, which is a convolution of Gaussian and Lorentzian function. It is often used as a peak profile in diffraction for cases where neither a pure Gaussian nor Lorentzian function appropriately describe a peak. Instead of convoluting those two functions, the Pseudo-Voigt function is defined as the sum of a Gaussian peak and a Lorentzian peak, weighted by a fourth parameter $\eta$ (values between 0 and 1) which shifts the profile more towards pure Gaussian or pure Lorentzian when approaching 1 or 0 respectively. Refinements were continued upon the achieving the convergence and reaching to the weighted profile R factor ($R_{wp}$ factor of about 20%). The refinement plots for the samples are presented in the figure 5. The calculated weight percent of Ni and Ni$_3$P phases using a MUAD program for NiP sample are 41.8 and 58.2% and those for the NiP-2SiC samples are

![Figure 3. Optical microscope images of the cross-section of the (a) NiP, (b) NiP-2SiC.](image-url)
37.8 and 62.2%, respectively. Using similar method, it was shown [24] that the nucleation of Ni₃P will start upon heat treatment above 300 °C and the content of Ni₃P reach to about 50 ∼ 60 wt% as calculated based of XRD analysis.

3.2. Corrosion behavior
Since the increase in the corrosion resistance of the Ni-P coatings by incorporation of ceramic nanoparticles has been numerously reported [1] especially for the NiP-SiC nanocomposite coatings [13, 15, 16], the corrosion resistance of the samples prepared by different baths (containing the different amount of SiC nanoparticles) after heat treatment at 400 °C for 1 h are measured by electrochemical method to confirm the incorporation of SiC nanoparticles within the coatings. The potentiodynamic polarization curves of the samples in the 3.5 wt.% NaCl are shown in figure 6.

The corrosion current density ($J_{corr}$) and corrosion potential ($E_{corr}$) of the samples were determined by extrapolating of the linear sections of the anodic and cathodic Tafel lines. These results along with the values of cathodic ($\beta_c$) and anodic ($\beta_a$) Tafel slopes are presented in table 2. In addition, the value of the polarization resistance ($R_p$) and the corrosion inhibition efficiency (IE%) of the presence of SiC nanoparticles within the coatings were calculated using the Stren-Geary equation (equations (1)) and (2), respectively, and summarized in table 2.

Figure 4. EDS spectrum of the HNO₃ etched surface of (a) NiP and (b) NiP-2SiC sample (the inset is element weight and atomic percentage); (c)–(e) FESEM images of NiP-2SiC sample at different magnification; (f)–(i) EDS elemental map corresponding to the FESEM image at (c).
where the $I_{\text{corr(x)}}$ and $I_{\text{corr(0)}}$ are the corrosion current densities for the NiP-xSiC samples (Ni-P coating with different amount of SiC nanoparticles) and the NiP sample (pure Ni-P coating), respectively.

It is worth mentioning that the best condition of heat treatment for NiP-SiC nanocomposite sample to achieve the highest corrosion resistance is the temperature of 400 °C for a time of 1 h [13, 21]. It is concluded that the increase in the heat treatment of NiP-SiC nanocomposite samples from 400 to 700 °C lead to the reduction of corrosion inhibition efficiency (IE%) of the presence of the SiC nanoparticle from 77.6 to 68.5% [13]. It is also reported that the heat treatment at 600 °C for even 10 min lead to the reduction in corrosion resistance [21]. These results are mainly related to the reaction of the SiC nanoparticles with the Ni matrix at higher temperature than 400 °C, which was detected by the formation of Si$_x$Ni$_y$ compounds.

According to table 2, all nanocomposite samples showed higher polarization resistance and lower corrosion current densities than NiP sample, which demonstrates the effective incorporation of SiC nanoparticles. Generally, the main reported mechanism of corrosion resistance of electroless Ni-P coatings is the formation of the enriched phosphorus layer as a result of preferential dissolution of nickel that can react by water to form an adsorbed hypophosphite anions (H$_2$PO$_2^-$) layer [25]. This layer can prevent the penetration of the water and corrosive ions into the metallic layer. In addition, the $E_{\text{corr}}$ of nanocomposite samples shifted to the positive direction. Incorporation of the SiC nanoparticles in the heat-treated Ni-P coating (containing the Ni matrix and

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R_p = \frac{\beta_n \beta_k}{2.303 I_{\text{corr}} (\beta_n + \beta_k)}
\]

(1)

\[
IE\% = \left(1 - \frac{I_{\text{corr(x)}}}{I_{\text{corr(0)}}}\right) \times 100
\]

(2)
Ni$_3$P dispersing phase can form the Ni$_3$P-SiC corrosion microcells, which the formation of such microcells has been also revealed elsewhere for other metallic composite coatings during corrosion \[12\]. In these galvanic microcells, nickel would act as an anode and consequently the dissolution of nickel is preferred leading to move the corrosion potential of nanocomposite coating toward the noble direction. Hence, in the nanocomposite samples, the accelerated formation of a nickel passive film at the surface of coating, i.e., the thicker phosphorus-rich film, could be a reason of their higher corrosion resistance in comparison to the NiP sample. Furthermore, incorporated reinforcements act as grain refiner during the plating of Ni matrix as well as during the subsequent heat treatment creating the more grain boundaries, which promote the formation of the passive layer. In addition, presence of reinforcements within the coating can act as physical barrier to the penetration of corrosive ions leading to retard the corrosion process. However, increasing the amount of SiC nanoparticles in plating solution results in increasing the interface between particles and nickel matrix within the deposited coatings. This is obvious from surface morphology of the samples (figure 2) that the size of cauliflower-like morphology of the coating reduces by incorporation of SiC nanoparticles. As can be seen in table 2, the corrosion inhibition efficiency (IE%) of the presence of SiC nanoparticles within the NiP coating is increased first by increasing the SiC concentration in electroless bath (reaching to the IE% of 76.1) and then decreased by a further increase in the concentration of nanoparticles reaching to the IE% of 9.4 for the NiP-3SiC sample. The IE% for the NiP-SiC nanocomposite fabricated through the bath contains the 2 g l$^{-1}$ SiC nanoparticles is calculated based on the other reported to be 77.6\% \[13\], or 96.3\% \[16\] and by increasing the concentration of SiC nanoparticles in the bath to 4 g l$^{-1}$ and 8 g l$^{-1}$, the IE% reduced to 62.9\% and 49.4\%, respectively. A similar result is also reported.

Table 2. Anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel slopes, corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) of the samples calculated by Tafel extrapolation of Potentiodynamic polarization curves along with polarization resistance ($R_p$) and corrosion inhibition efficiency (IE\%) of the samples.

| Sample   | $\beta_a$ (mV/decade) | $\beta_c$ (mV/decade) | $E_{corr}$ (mV versus SCE) | $I_{corr}$ ($\mu$Acm$^{-2}$) | $R_p$ (k$\Omega$.cm) | IE\% |
|----------|----------------------|----------------------|-----------------------------|-----------------------------|---------------------|-------|
| NiP      | 97.5                 | 87.3                 | $-389.6$                    | 2.97                        | 6.7                 | 0     |
| NiP-0.5SiC | 79.1                 | 95.7                 | $-159.2$                    | 1.88                        | 10                  | 36.7  |
| NiP-1SiC  | 99.1                 | 101.9                | $-250.9$                    | 0.71                        | 30.7                | 76.1  |
| NiP-2SiC  | 92.8                 | 90.5                 | $-371.6$                    | 2.14                        | 9.3                 | 27.9  |
| NiP-3SiC  | 91.7                 | 94.1                 | $-378.7$                    | 2.69                        | 7.5                 | 9.4   |

Figure 6. Potentiodynamic polarization curves of the heat-treated samples in 3.5 wt.% NaCl solution.
for NiP-SiC nanocomposite coatings elsewhere [16], which the calculated IE% based on their results revealed the significant reduction of IE% by increasing the amount of SiC nanoparticles from 96.3% (for the sample synthesized by bath 2 1 g l\(^{-1}\) SiC nanoparticles) to 3.8% (for the sample synthesized by bath 2 1 g l\(^{-1}\) SiC nanoparticles). For the NiP-3SiC sample of this work, the significant reduction in IE% to 9.4 can be due to the effect of high concentration of SiC nanoparticle within the coating. As can be seen in figure 2(e), the cauliflower-like morphology is disappeared which seems to be resulted from high amount of SiC nanoparticles compared to the Ni atoms and/or agglomeration of SiC nanoparticles. Such discontinuity of Ni matrix and incorporated nanoparticles by increasing the amount of nanoparticles in the coating can be the main reason for decreasing the corrosion resistance of NiP-2SiC and especially NiP-3SiC samples in comparison to the NiP-1SiC sample.

### 3.3. Tribological behavior

The tribological behavior of the heat-treated samples was investigated by measuring the hardness and performing the unlubricated ‘pin on disc’ wear test. The surface hardness of the heat-treated samples has been measured to confirm the incorporation of SiC nanoparticles within the coatings prepared by different baths and the microhardness values are compared in figure 7. It worth mentioning that the hardness of the NiP sample before heat treatment was 582 ± 10 HV\(_{100}\) whereas, the hardness reaches 1007 ± 12 HV\(_{100}\) after heat treating at 400 °C for 1 h. Generally, the hardness of heat-treated Ni-P electroless coatings is a result of crystallization of amorphous Ni-P metallic matrix as well as Ni\(_3\)P precipitation in the matrix, and the heat treatment at 400 °C for a time of 1 h is the optimum condition [1]. Furthermore, the heat treatment at 400 °C for 1 h in NiP-SiC nanocomposite coatings is also the optimum condition [13, 14]. The heat treatment for 1 h at a temperature lower than 400 °C resulted in lower hardness in comparison to that for the sample heat-treated at 400 °C [14]. In addition, the achieved hardness for the NiP-SiC nanocomposite heat-treated at 400 °C (~1300 HV) can be decreased to around 1200 HV by increasing the heat treatment temperature to 700 °C, which can be due to the degradation of SiC as detected by the formation of Si\(_x\)N\(_y\) compounds at high temperature [13]. The hardness of the samples prepared by different baths is increased by the increase in the content of SiC nanoparticles, which can reveal the incorporation of hard ceramic nanoparticles within the Ni matrix. On the other hand, it is reported [16] that the hardness of the heat-treated NiP-SiC nanocomposite samples fabricated by the baths containing the 0, 1, and 2 1 g l\(^{-1}\) SiC nanoparticles is 735 ± 27, 780 ± 32, and 1194 ± 35 HV\(_{100}\) respectively, whereas by further increasing the concentration of SiC nanoparticles in the bath to 3 g l\(^{-1}\), the hardness of the heat-treated sample was significantly decreased to 846 ± 24 HV\(_{100}\). In our work, such a continues significant increase in the hardness by increase in the concentration of SiC nanoparticles of electroless bath, and especially achieving the high hardness as 1257 ± 19 HV\(_{100}\) for the NiP-3SiC sample, can result from the retarding the plastic deformation of the Ni matrix, i.e. dispersion hardening mechanism [1, 3]. Furthermore, the grain refinement of the Ni matrix as a result of nucleation agents (SiC nanoparticles), which can be easily recognized by comparison of surface morphologies in figure 2, could be another reason for increasing the hardness. The reduction of grain size, i.e., higher grain boundaries, leads to the existence of higher barriers to the dislocation motion. Such increase in the microhardness of NiP nanocomposite coating by incorporation of ceramic nanoparticles has been numerously reported elsewhere [7, 14, 16].

The wear characteristics of the samples were investigated using an unlubricated ‘pin on disc’ wear test at room temperature using a hardened steel pin as a counter-face. The amount of applied load during the wear test...
was chosen as high as 20 N to achieve comparable weight loss during abrasion since the lower applied loads showed no significant effect on some samples. The variation of the average coefficient of friction and the weight loss (measured every 100 m sliding distance) during the sliding for all samples are demonstrated in figures 8(a) and (b), respectively. As can be seen in figure 8(a), the friction coefficient of the samples reaches their relatively stable values after initial sliding distance (less than the first 100 m sliding distance), which can be due to the relatively high applied load (20 N) in these investigations. The average friction coefficient of the NiP sample \( (\mu_{\text{NiP}} = 0.702) \) is relatively high, whereas the incorporation of SiC nanoparticles leads to the reduction in the friction coefficient to \( \mu_{\text{NiP-1SiC}} = 0.559 \) and \( \mu_{\text{NiP-2SiC}} = 0.611 \). Such reduction in friction coefficient can result from the increase in the hardness of coatings by the presence of SiC nanoparticles leading to the lowering the formation of wear asperities as well as the lowering the contact area between the surface of the sample and pin. The reducing of the friction coefficient of Ni based coatings by incorporation of ceramic nanoparticles such as TiO\(_2\) \([6]\), SiO\(_2\) \([7]\), and SiC \([14]\) has been previously reported. In addition, as can be seen in figure 8(b), the weight loss of the NiP-xSiC samples during sliding up to 100 m sliding distance is to some extent similar to that of the NiP sample and the weight loss is reduced significantly at higher sliding distance especially for the NiP-1SiC sample. After 500 m of sliding distance, the NiP-1SiC sample presents a reduction of about 48% in the weight loss during sliding in comparison to the NiP-sample, which similar result has been reported for NiP-SiC nanocomposite fabricated on AZ31 Mg alloy \([14]\).

In order to find more, SEM images of the worn surface of the samples after the first 100 m sliding distance are shown in figure 9. A relatively wide and deep wear track with an edge can be observed on the worn surface of the NiP sample (figures 9(a)-1), which can be the main reason for the high friction coefficient. Higher magnification image of the wear track (figures 9(a)-2) reveals the micro-cracks, irregular pits, and severe plastic deformed areas. As can be seen in the worn surface of the NiP-1SiC sample (figure 9(b)), the width of the wear track is more or less similar to that of NiP samples, but the wear track is shallow without edge that indicates the lower plastic deformation in the wear track of NiP-1SiC sample, which is the main reason of its low friction coefficient as well as low weight loss. Higher hardness of NiP-2SiC and NiP-3SiC samples in comparison to the other samples results in the wear track with lower width (figures 9(c) and (d)). On the other hand, the NiP-3SiC sample demonstrates the higher friction coefficient \( (\mu_{\text{NiP-3SiC}} = 0.749) \), which can be due to the change of wear

**Figure 8.** (a) Friction coefficient and (b) weight loss as function of the sliding distance for the samples.
mechanism from two-body to three-body abrasion as can be seen clearly in figure 9(d). This can be confirmed by the higher weight loss of NiP-3SiC samples during the wear test after the first 100 m sliding distance. In general, the NiP-3SiC sample shows the highest weight loss during the wear test, which exhibits the abrupt change in friction coefficient during the test after sliding distance of 400 m, indicating the weak mechanical properties of coatings with high embedded nanoparticles.

Figure 9. SEM micrograph of the worn surface of the (a) NiP, (b) NiP-1SiC, (c) NiP-2SiC, and (d) NiP-3SiC samples at two different magnifications.
4. Conclusions

Surfactant-free electroless baths containing the different content of SiC nanoparticles (0–3 g l⁻¹) were used to deposit NiP layers (NiP and NiP-xSiC samples) and the heat-treated samples (at 400 °C for 1 h) were investigated to confirm the incorporation of nanoparticles and demonstrate their effects. We investigated on the structure, morphology, hardness, tribological and corrosion behavior of the heat-treated coatings. The results revealed that the heat-treated NiP and NiP-SiC coatings consisted of Ni and Ni₃P phases, with high faction of Ni₃P phase for NiP-SiC samples as a result of the presence of SiC nanoparticles. By co-deposition of SiC nanoparticles, the hardness of NiP (1007 ± 10 HV₁₀₀) is significantly increased to 1257 ± 19 HV₁₀₀. The average friction coefficient of the NiP sample (μₜₙₐₚ = 0.702) is reduced by incorporation of SiC nanoparticles (μₜₙₐₚ,₃SiC = 0.559 and μₜₙₐₚ,₂₅SiC = 0.611), which can be attributed to the role of SiC nanoparticles as a load-bearing part in increasing the hardness. However, the friction coefficient is increased by a further increase in the SiC content (μₜₙₐₚ,₅SiC = 0.749), which can be due to the high content of hard second-phase leading to the change of wear mechanism from two-body to three-body abrasion as confirmed by electron microscopy investigations. In addition, the weight loss during the sliding for NiP-1SiC samples is lower than that for NiP sample and the weight loss is increased by further increase in the SiC content of the coatings.

Data availability statement

No new data were created or analysed in this study.

ORCID iDs

M Khodaei © https://orcid.org/0000-0003-0076-8872

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