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Highly dense diamond particle-reinforced Ni-P coatings fabricated by pulse-stirring co-electrodeposition

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Abstract

Highly durable nickel-phosphorus/diamond (Ni-P/diamond) composite coatings were developed and successfully fabricated *via* co-electrodeposition. Large diamond particles, 20−30 μm, were co-electrodeposited into a Ni-P matrix. This work investigates the influence of bath stirring and current density on the diamond particle content in their deposits and tribological properties. The resulting coatings had uniformly distributed diamond particles in their deposits. Unlike the samples prepared using continuous stirring, those prepared by pulse-stirring appeared to have a much higher diamond particle concentration in the coatings. Energy dispersive X-ray spectroscopy (EDS) shows that diamond contents of up to 25.98 wt% can be achieved by pulse-stirring at a current density of 0.1 A/cm^2. The friction coefficient was found to be relatively low and fluctuated in the range of 0.12 to 0.2. After subjecting specimens to a sliding wear test against a ZrO_2 counter surface, no worn area was observed in the samples prepared using pulse-stirring at current densities of 0.05 A/cm^2 and higher. This pulse-stirring fabrication technique allows the production of highly dense diamond particles incorporated into coatings with significantly enhanced wear resistance.

Keywords: Composite coating, Co-Electrodeposition, Friction coefficient, Wear resistance

1. Introduction

Electroplated hard coatings are widely used in many industries to provide corrosion and wear resistance for tools and mechanical components. The electrodeposition process is cost-effective and compatible with a vast variety of metals and alloys [1, 2]. Recently, co-electrodeposition of inert ceramic particles has been developed to further improve the hardness and tribological properties of coating materials [3-6]. This technique allows hard particles to be incorporated into a matrix of metals or alloys. During deposition, reinforced particles are first covered with metallic ions. Then, these particles, together with metallic ions, migrate to the cathode under an applied electric field, forming a composite deposit onto a substrate. Nickel-based alloys such as Ni-P, Ni-W and Ni-Co are normally used as matrix materials because of their excellent mechanical and tribological properties [7, 8]. To date, hard particles such as SiC, Al_2O_3, TiO_2, MoS_2, and diamond have been demonstrated to improve wear resistance and to reduce the coefficient of friction of Ni-based coatings [9-11].

Among a variety of coating materials, electrodeposited Ni-P coatings have been shown to have outstanding corrosion [7] and wear resistance [12, 13]. Electrodeposition of Ni-P is also considered eco-friendly, since no carcinogenic substances are involved in the process. Ni-P coatings have been used as decorative, anti-wear and anti-corrosion coatings in various applications. Unique applications such as those that required alloys with high electrical resistance at elevated temperature [14], or catalytic coating to improve hydrogen evolution have been demonstrated [8]. The hardness of pristine Ni-P coatings can reach up to approximately 520−540 Hv [14, 15] by controlling the grain size so that it is in the nanocrystalline regime. Recent work has shown that hardness of Ni-P can be enhanced by the formation of compositionally modulated multilayer structures [16].

Incorporation of diamond particles into Ni-P deposits has been demonstrated to greatly improve properties such as hardness, corrosion and wear resistance of the coatings [17, 18]. As it is one of the hardest known materials, micro/nanosized diamond particles are an ideal reinforcement phase to improve coating hardness and wear resistance. With diamond particle incorporation, the hardness of Ni-P/diamond composite coatings has been reported to be in the range of 580−620 Hv [15, 17] . Generally, the mechanical and tribological properties of composite coatings are affected by the level of the particle content in the deposit. However, traditional co-electrodeposition usually yields relatively low particle contents. This work demonstrates a facile fabrication technique using pulse-stirring that allows for production of highly-dense micron-sized diamond particles co-deposited into a Ni-P matrix. Comparison between the diamond contents of samples prepared by continuous stirring and those fabricated using a pulse-stirring technique is

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reported. The effect of various current densities on the morphology and tribological properties of the coatings are also investigated and discussed.

2. Materials and methods

2.1 Sample preparation

A low carbon steel (0.05 wt% C) was used as a substrate. It was cleaned with soap and treated with 10% NaOH for 20 min. The substrate was activated with 14% HCl before placing it in a plating bath. A Pt mesh and low carbon steel were used as an anode and a cathode, respectively. The coating area was 4 cm^2. The electrodeposition bath contained nickel sulphate ($NiSO_4 6H_2O$), nickel chloride ($NiCl_2 6H_2O$), boric acid (H_3BO_3), and phosphorous acid (H_3PO_3). The operating temperature was 60 °C and pH was set to 1.5 ± 0.5 with a stirring speed of 200 rpm and a 2 h deposition time. Large diamond particles, having sizes in the range of 20−30 μm, were used. The diamond concentration in the bath was fixed at 10 g/L. Current density was varied over the range of 0.01−0.1 A/cm^2. An alternating on-/off-stirring cycle was used in this work, in which the magnetic stirrer was switched between the ON and OFF settings. The on-stirring periods were set to 2 min, followed by off-stirring for 15 min. This was repeated for a total deposition time of 120 min. All chemicals were purchased from RCI Labscan, Ltd. and used without further purification. Figure 1 shows a summary of the Ni-P/diamond co-electrodeposition process.

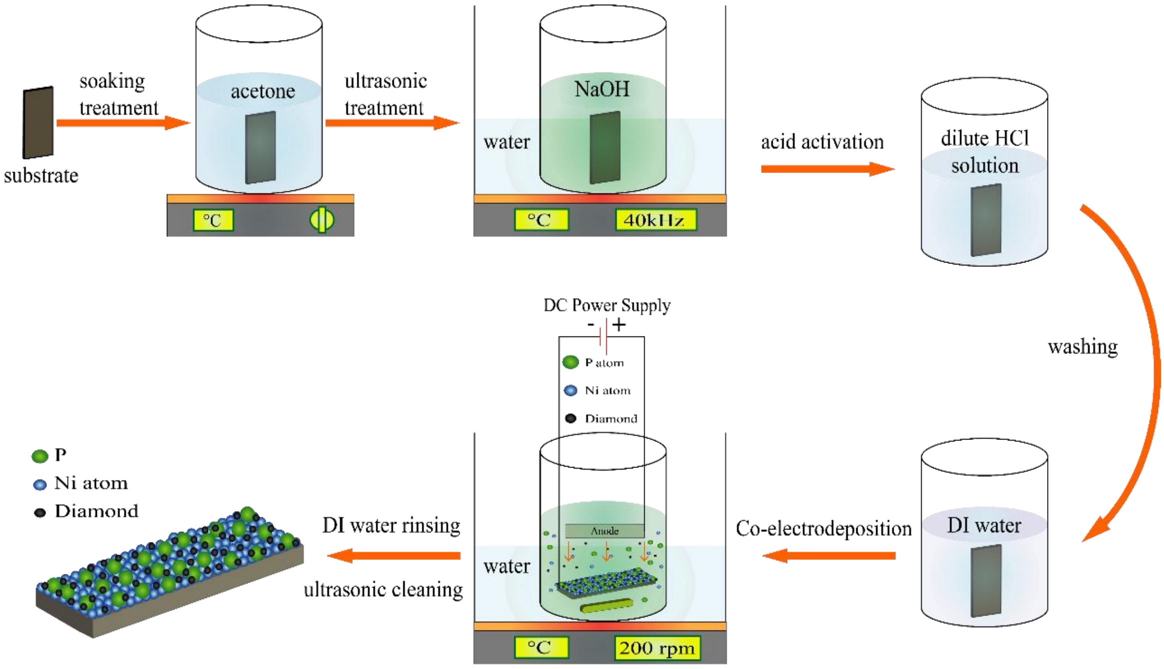

Figure 1 Co-electrodeposition process of Ni-P/diamond coating.

2.2 Characterization and tribological studies

Surface and cross-section were characterized using a Hitachi SU3500 scanning electron microscope (SEM). The thickness of the coatings was measured from the cross-sectional SEM images. The reported thickness value was an average of 5 measurements obtained from 5 different locations of the sample. The SEM was equipped for energy dispersive X-ray spectroscopy (EDS) and employed to determine the Ni, P, and diamond contents of the deposits. The profilometer was used to analyze the surface roughness, R_a, of the coatings. The reported surface roughness value was an average of 3 measurements obtained from 3 different samples.

The friction coefficient and wear properties of the Ni-P/diamond coatings were investigated using a ball-on-disk tribometer, with an external load of 10 N. A ZrO_2 ball was used as a counter surface material. The sliding velocity was set at 9.42 cm/s. Wear resistance was evaluated from the weight loss of the substrates after being subjecting to a test involving sliding for a distance of 500 m.

3. Results and discussion

3.1 Surface and cross-sectional morphologies

Nickel-phosphorus/diamond composite samples were successfully fabricated *via* a co-electrodeposition of relatively large diamond particles (20−30 μm). Figures 2a and 2b show the surface morphologies of resulting coatings prepared using continuous stirring and pulse-stirring cycles, respectively. Both samples were prepared in an electrodeposition bath containing the same diamond loadings, current densities, and deposition times. As shown in the SEM micrographs, both samples exhibited intact coating layers with uniformly distributed diamond particles. No cracking was observed on the surfaces of the deposits. It is notable that nodular or cauliflower structures [19, 20], usually found in co-electrodeposited coatings with finer particles, were not observed in our samples. Instead, the surfaces of the matrix materials appeared to be flat. Diamond particles were observed to protrude from the surface of the deposits. Unlike the formation of nodular structures, caused by ionic clouding found in samples incorporating smaller particles, a gravitational force-assisted sedimentation process is believed to be main deposition mechanism for our samples.

The density of incorporated diamond particles was found to be much higher in the samples prepared using the pulse-stirring technique (Figure 2b) than ones prepared using continuous stirring (Figure 2a). Repeated 2 min on- and 15 min off-stirring cycles allow diamond particles to become re-dispersed in the bath and deposited onto the growing Ni-P layers through sedimentation, respectively. This allowed diamond particles that failed to be deposited in earlier cycles to have renewed opportunities for incorporation into the coating. This simple fabrication technique resulted in Ni-P/diamond composite coatings with densely packed diamond particles.

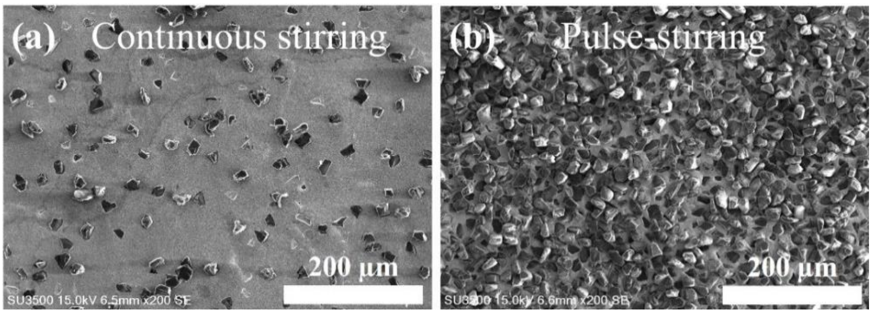

Figure 2 SEM micrographs showing surface morphologies of Ni-P/diamond composite coating prepared using (a) continuous stirring and (b) pulse-stirring. Both samples were prepared in an electrodeposition bath containing the same diamond concentration, 10 g/L, at a deposition time of 120 min. The current density was fixed at 0.03 A/cm^2.

Figure 3 shows SEM images of surface morphology of Ni-P/diamond composite deposits fabricated at various current densities. In all cases, large diamond particles, 20−30 µm, were observed to be uniformly co-deposited into the Ni-P matrix. This was associated with repeated on-/off-stirring cycles that helped diamond particles become redispersed in the bath before sedimenting and becoming embedded into a growing electro-deposited metal matrix. Unlike the deposition of nanosized diamond particles, which are strongly affected by current density [19], the surface morphology of coatings with larger diamond particles reported here was independent of the current density. For larger diamond particles, the particles were electrolytically deposited on the substrate along with metal ions due to the dominant gravitational force acting on the diamond particles.

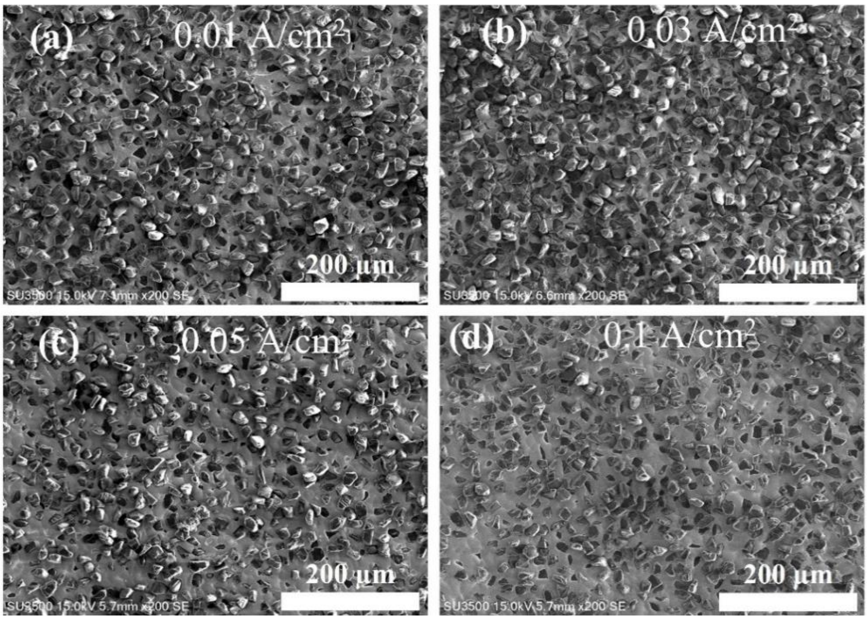

Figure 3 SEM micrographs showing surface morphologies of Ni-P/diamond composite coatings fabricated using various current densities (a) 0.01 A/cm^2, (b) 0.03 A/cm^2, (c) 0.05 A/cm^2 and (d) 0.1 A/cm^2.

Figure 4 shows SEM cross-sectional views of samples prepared using various current densities. Cross-sectional SEM images revealed a uniform distribution of diamond particles in the deposits. However, the sample prepared using a current density of 0.01 A/cm^2 had the thinnest deposited layer (Figure 4a). This was probably due to a lower deposition rate when a very low current density was applied. At higher current densities, 0.03, 0.05, and 0.1 A/cm^2, samples with similar cross-sections were observed as shown in Figures. 4b, 4c and 4d, respectively.

Energy dispersive X-ray spectroscopy was used to analyze the Ni, P, and diamond contents in the deposits. The EDS point analyses of Ni-P/diamond composite coatings, prepared at various current densities, are shown in Figure 5. Insets show the areas from where the EDS signals were acquired in each sample. The Ni, P, and diamond contents are summarized in Table 1. EDS spectra show that the phosphorus content in the sample produced at a low current density, 0.01 A/cm^2, was 9.90 wt%. The P content appeared to decrease with increasing current density. At a current density of 0.1 A/cm^2, the P content was reduced to 4.15 wt%. The tendency of decreasing P content at higher current densities for Ni-P/diamond coatings is in agreement with previous reports [21, 22]. In contrast, the diamond content was found to increase from 18.61 wt% to 25.98 wt% as the current density was increased from 0.01 A/cm^2 to 0.1 A/cm^2. This is consistent with the works of other researchers, who reported that the content of co-deposited diamond particles increased with current density [21, 23, 24].

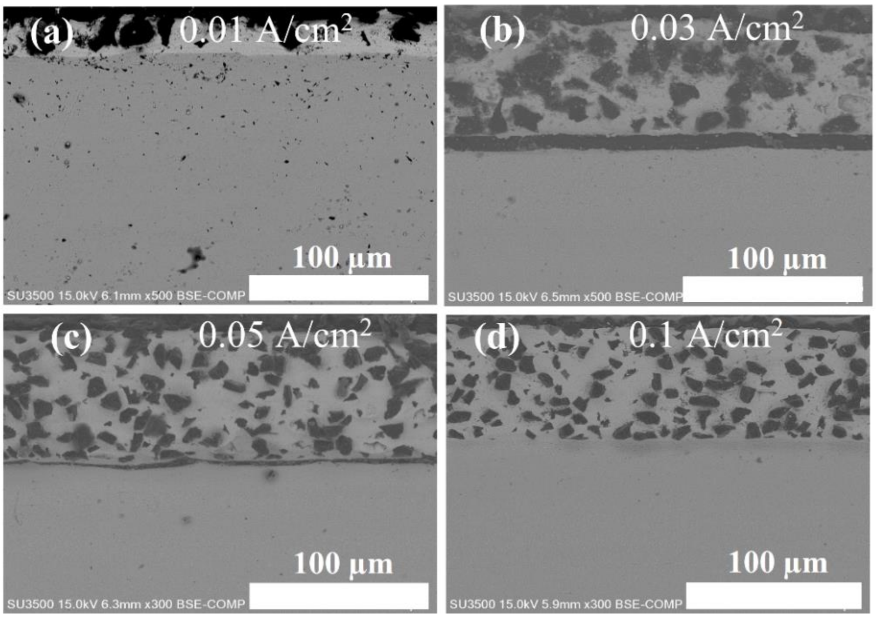

Figure 4 SEM micrographs showing cross-sectional views of Ni-P/diamond composite coatings prepared using various current densities, (a) 0.01 A/cm^2, (b) 0.03 A/cm^2, (c) 0.05 A/cm^2, and (d) 0.1 A/cm^2.

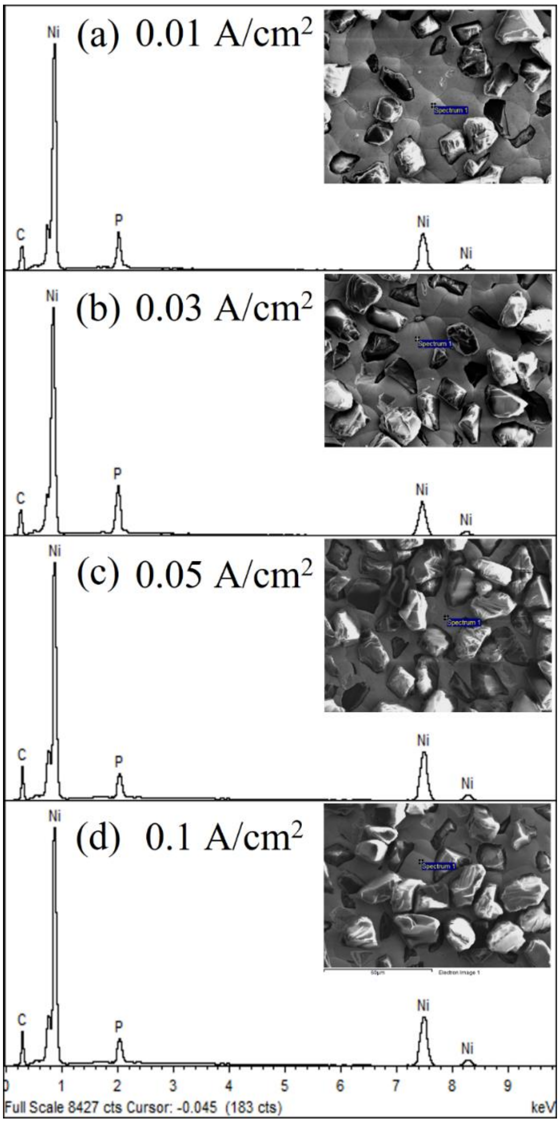

Figure 5 EDS spectra showing Ni/ P/ C contents in Ni-P/diamond composite coatings prepared at (a) 0.01 A/cm^2, (b) 0.03 A/cm^2, (c) 0.05 A/cm^2, and (d) 0.1 A/cm^2.

Table 1 Ni, P, C and diamond contents in Ni-P/diamond composite coatings deposited at various current densities.

Sample	**Ni (wt%)**	**P (wt%)**	**C (wt%)**	**Thickness (µm)**	**Surface roughness, Ra, (µm)**
Ni-P/D (0.01 A/cm^2)	71.49	9.90	18.61	20.8	3.132
Ni-P/D (0.03 A/cm^2)	67.76	7.68	24.56	70.3	3.148
Ni-P/D (0.05 A/cm^2)	68.43	6.85	24.72	143	2.649
Ni-P/D (0.1 A/cm^2)	69.87	4.15	25.98	115	2.564

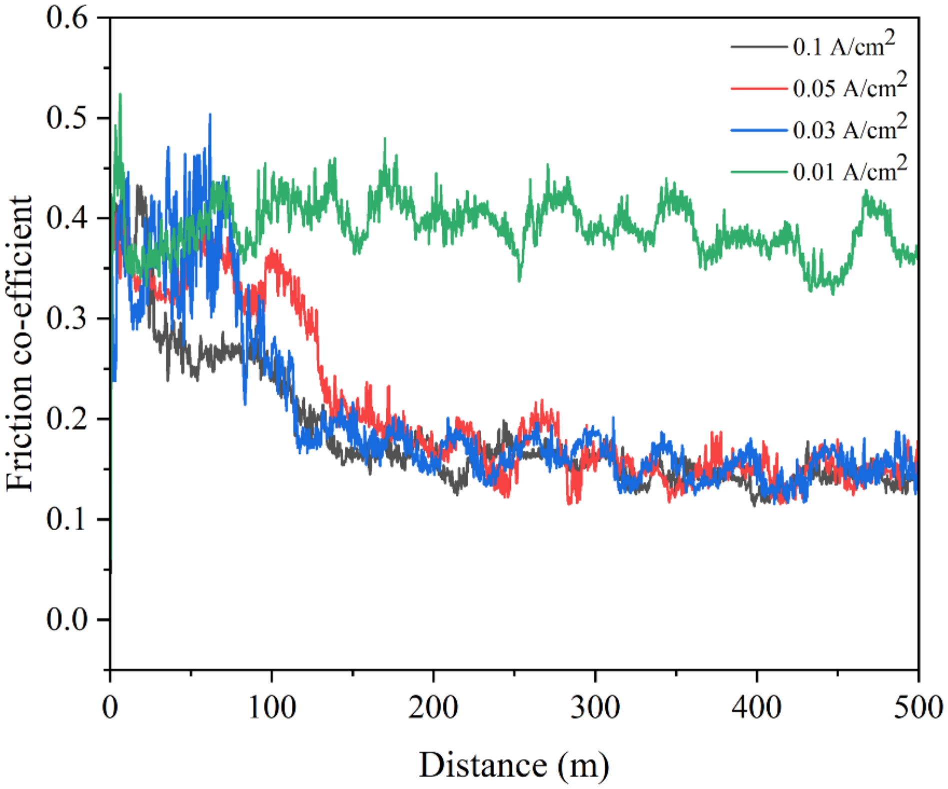

Figure 6 Friction properties of Ni-P/diamond deposits fabricated by the pulse-stirring method at various current densities.

3.2 Friction coefficient and wear

A ball-on-disc tribometer was used to determine the friction properties of the resulting Ni-P/diamond composite samples. Figure 6 shows the dynamic friction curves of Ni-P/diamond composited samples prepared at various current densities. The friction coefficient was found to vary between 0.12 to 0.53. The friction coefficient appeared to be highest for the sample fabricated using a current density of 0.01 A/cm^2. This might have been due to the thinner deposited layer and rougher surface of this sample. During the first 100 m sliding distance, the friction coefficient fluctuated greatly, probably due to redeposition of transferred materials during the initial wear process. After reaching stability, the friction coefficients of samples prepared using current densities of 0.03 A/cm^2 and higher were found to be relatively low, between 0.12 and 0.2. The friction coefficient values of these samples are much lower than those of pristine Ni-P coatings [16]. This is due to the significantly harder Ni-P coatings with densely packed diamond particles. It is notable that the hardness of these samples cannot be directly measured, since doing so would damage the indenter of the hardness testing instrument.

Wear performance of Ni-P/diamond composite coatings was evaluated from the weight loss of the samples during the ball-on-disc tests. Figure 7 shows the EDS spectra of the worn areas obtained after the wear test. The insets of this figure show SEM micrographs of the wear track. It was observed that the wear tracks were barely visible in all cases, since very little material was removed from the surfaces. The EDS spectra shown in Figures 7c and 7d reveal a small Zr peak (indicated as red arrow) in the worn area of the samples prepared at 0.05 and 0.1 A/cm^2. This indicates that some worn material from the ZrO_2 counter surface were deposited onto the samples. Although the hardness of the sample could not be measured directly, it is expected that the composite coatings developed in this work have a much higher hardness than that of ZrO_2 (1300 Hv). Table 2 summarizes the cumulative weight loss of Ni-P/diamond coatings prepared at various current densities. Weight loss was found to be very small for all samples, indicating their excellent wear resistance. The highest weight loss, 0.002 mg, was found in the sample prepared using a current density of 0.01 A/cm^2, which had the lowest diamond particle content. For samples prepared at current densities of 0.05 and 0.1 A/cm^2, no weight loss was observed. On the contrary, some samples showed weight gains (shown as negative values) resulting from redeposition of worn ZrO_2 counter surface materials. This suggests that the deposits have extremely high wear resistance. The results have shown that the pulse-stirring co-electrodeposition technique can be used to fabricate highly durable Ni-P coatings with significantly enhanced diamond particle incorporation.

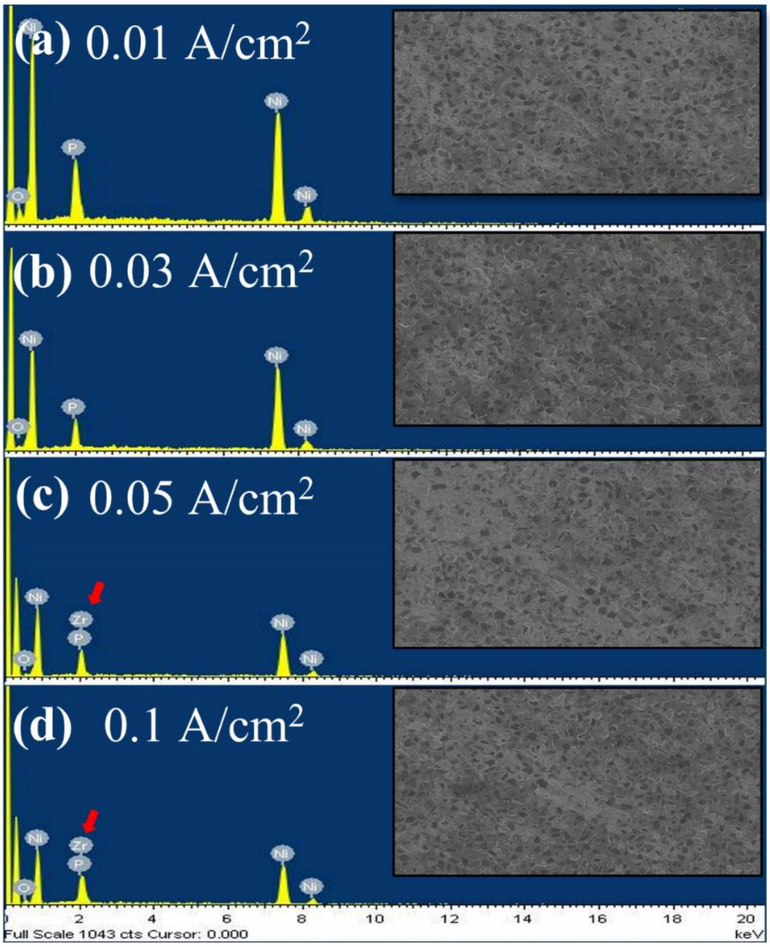

Figure 7 EDS spectra of worn areas of Ni-P/diamond coatings.

Table 2 Diamond content and weight loss of the Ni-P/diamond composite deposits.

Sample	**Diamond content (wt%)**	**Weight loss (mg)**
Ni-P/D (0.01 A/cm^2)	18.61	0.002
Ni-P/D (0.03 A/cm^2)	24.56	0.001
Ni-P/D (0.05 A/cm^2)	24.72	-0.006
Ni-P/D (0.1 A/cm^2)	25.98	-0.006

4. Conclusions

This work demonstrates successful fabrication of highly dense micron-sized diamond particle reinforced Ni-P coatings. Using a pulse-stirring method, a significantly higher number of diamond particles were found incorporated into the coatings. While the off-stirring periods allowed diamond particles to fall onto the growing Ni-P matrix through a gravitationally assisted sedimentation process, the short on-stirring periods cause diamond particles at the bottom of the plating bath to become redispersed and have renewed opportunities for incorporation into the coatings. For large diamond particles, current density was found to have less influence on the surface morphologies of the coatings. A maximal diamond content of 25.98 wt% was found in the samples prepared by pulse-stirring using a current density of 0.1 A/cm^2. These Ni-P coatings with highly dense diamond particles have low friction coefficients, as well as extremely high wear resistance. This study emphasizes the crucial process parameters that may be useful for future development of mechanical components with outstanding wear resistance.

5. Acknowledgements

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