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An Electrodeposition Method of Nickel–Graphene Composite Coatings on Ti–6Al–4V alloy

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Abstract: The main objective of this work has been the deposition of Nickel (Ni)–Graphene nanoplatelets (GNPs) composites on a Ti-6Al-4V alloy substrate via a pulse current technique from a Watt's type bath. The characterization of the coatings was done by structural surveys, hardness measurements and wear tests. In this current work, XRD and SEM analysis demonstrated the better grained and compact property of the Ni-GNPs deposits. The surface roughness of the composite coatings was significantly decreased with the addition of GNPs. Furthermore, the addition of GNPs in the Ni matrix improved both hardness and wear behaviour of the composite coating compared to the pure Ni coating.

Keywords: Electrodeposition, Titanium, Surface modification, Wear.

1. Introduction

Titanium (Ti) and its alloys have been widely used in many sectors such as marine, medical, chemical, automotive, aircraft and aerospace components. Such a wide range of their applications is related to high tensile strength, low density and high resistance to corrosion (Roodposhti et al., 2018). However, their poor wear resistance due to the low resistance to plastic shearing and the relatively high friction coefficient is one of factors limiting their widespread usage in load bearing applications (Pohrelyuk et al., 2018). For this reason, some surface engineering methods can be applied to Ti and its alloys to enhance service life of many engineering components (Zhecheva et al., 2015).

Among the composite deposits, nickel (Ni) electrodeposition by the co-deposition with various particles in electrolytic bath seems to be promising due to their high hardness, high wear, lubricity and good corrosion resistance. Graphene nanoplatelets (GNPs) are one of the most promising carbon based materials due to its extremely high Young's modulus up to 1 TPa and fracture strength approaching 125 GPa (Rashad et al., 2015). According to the available literature, the electrodeposition of composites on difficult substrates such as Ti requires overcoming the major challenge of achieving high codeposition rates and a uniform distribution of particles in the Ni matrix (Baraka et al., 2002). Pulse electrodeposition is a well-known method in the field of composite coatings. If used instead of the direct current (DC), pulse current (PC) in the electrodeposition leads to several advantages including refinement of crystallites, reduction of porosity, enhanced adhesion to the substrate, more uniform distribution of the coating, and improvement of mechanical properties (Kumar et al., 2013).

In this paper, pulse electrodeposited Ni-GNPs composite coatings with different content of GNPs were obtained and the morphology and microstructure of Ni-GNPs composite coatings electroplated on Ti-6Al-4V alloy were investigated. In addition, wear resistance of resulted Ni-GNPs composite coatings were also studied.

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2. Material and Method

GNPs reinforced Ni composite coatings were prepared under PC method from Watt's-type bath. Chemical compositions and electrodeposition conditions are given in Table 1. GNPs supplied by GRAFEN-IGP2 (Grafen Chemical Industries, Turkey) with a lateral dimension of ~5 nm and a thickness of ~5–8 nm were added into a plating bath containing 50 ml of the solution. A nickel plate was used as the anode and Ti-6Al-4V alloy plate was used as the cathode. The bath was stirred by magnetic stirrer with a stirring rate of 300 rpm and heated to 50 °C. The electrodeposition was carried out using a PC power supplier. Before electrodeposition, the Ti-6Al-4V alloy substrates were polished mechanically with 1000 grit SiC paper. After polishing, the substrates were cleaned in distilled water, sonicated in acetone to remove the impurities, and subsequently dried in air. Immediately following further washing in 50 gL^{-1} NaOH solution at room temperature for 1 min and activation in a mixture of 20% HNO_3 and 20% HF for 1 min, the substrate was immersed into the bath for electrodeposition.

Table 1. Chemical compositions and electrodeposition conditions.

$NiSO_4.6H_2O$	300 gL^{-1}
$NiCl_2.6H_2O$	50 gL^{-1}
H_3BO_3	40 gL^{-1}
SDS (Sodium dodecyl sulfate)	0.2 gL^{-1}
GNPs	0-0.2 gL^{-1}
Temperature	50 ± 5 °C
Substrate	Ti-6Al-4V
pH	4 ± 2
Current density	4 A/dm^2
Anode	Ni plate
Type of current	Pulse current (PC)
Magnetic stirring	300 rpm

After electrodeposition, the surface morphology and cross-sectional microstructure of Ni composite coatings were characterized using a Scanning Electron Microscopy (SEM) coupled with an Energy Dispersed Spectrometer (EDS) and an Optical Microscopy (OM), respectively. The phase constituents of the coatings were determined by X-ray diffraction (XRD) using CuKα radiation with a Panalytical Empyrean diffractometer. The cross-sectional microhardness of the coatings was measured using a Vickers diamond indenter at an applied load of 50 g for 15 s.

Dry sliding wear tests were performed on a reciprocating wear tester at 25 °C and 40% relative humidity under normal load of 5 N. A ball made of Al_2O_3 with diameter of 10 mm was used to wear samples with a constant sliding speed of 1.7 cm s^{-1} for the total sliding distance of 50 m. During wear testing, friction coefficient data was continuously recorded. After the wear tests, wear tracks were analyzed by using a contact type profilometer and the worn surfaces were examined by a SEM.

3. Results and Discussion

The morphologies of Ni and Ni-GNPs composite coatings produced on the Ti-6Al-4V alloy substrate are illustrated in Figure 1. The pure nickel coating exhibited a dense structure with pyramidal Ni grains (Fig. 1 a). However, Ni-GNPs composite coatings with addition of the GNPs into the plating bath had finer and more regular grains than the GNPs-free ones. It may be concluded that introduction of GNPs leads to the refinement of the grains and improvement of the morphology uniformity in the composite coating surfaces. This claim was confirmed by roughness results that had been given in Table 2. By increasing embedded particles, the surface became smoother. Actually, the addition of GNPs increases the number of nucleation sites and prohibits matrix growth, which, in turn, facilitates the formation of fine grains (Algul et al., 2015). Figure 1 (b - c) clearly showed that the grain structure of the composite coating surfaces was uniaxial and uniform.

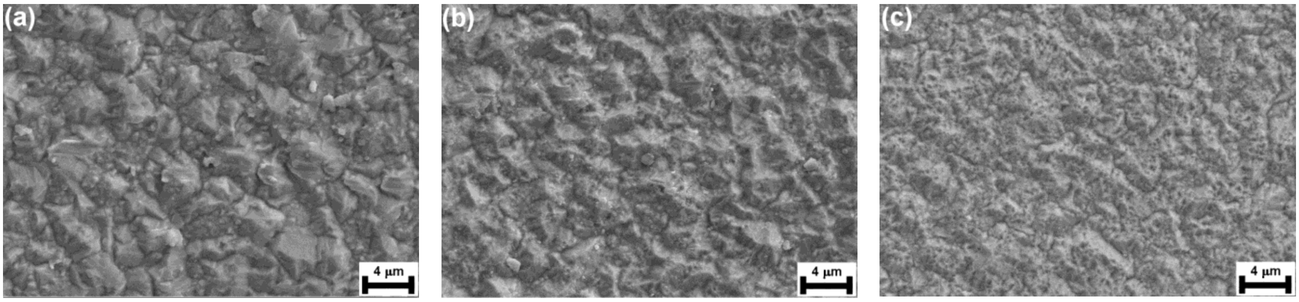


Figure 1. Surface morphologies of (a) pure Ni and Ni-GNPs composite coatings with (b) 0.1 gL^{-1} and (c) 0.2 gL^{-1} GNPs in the plating bath.

Table 2. Roughness results of pure Ni and GNPs reinforced Ni composite coatings.

GNPs Content (gL^{-1})	Roughness parameters		
	Ra	Rz	Rt
0	0.27	2.3	3
0.1	0.22	1.6	2.6
0.2	0.16	1.2	2.5

OM images of the cross-sections of Ni-GNPs composite coatings with 0.1 gL^{-1} and 0.2 gL^{-1} GNPs in the plating bath are shown in Figure 2. The obtained composite coatings were dense, homogenous, and uniform and no microcracks or pores were observed between the substrate/coating interfaces.

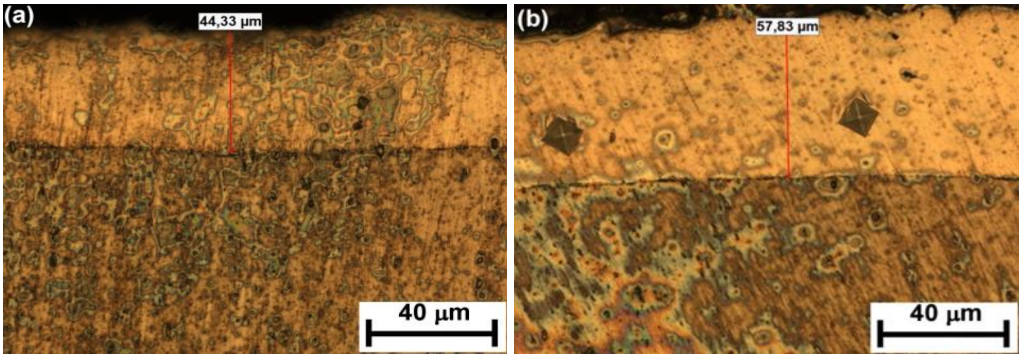


Figure 2. Cross-section OM micrographs of Ni-GNPs composite coatings with (a) 0.1 gL^{-1} and (b) 0.2 gL^{-1} GNPs in the plating bath.

XRD patterns for pure Ni as well as Ni-GNPs composite coatings are presented in Figure 3. According to the curves, with the incorporating of GNPs, the absorption intensity of the diffraction peak decreased. Also, the effect of grain refinement of the GNPs in the Ni matrix due to the peak broadening around 51–53° as shown in Fig. 3 b improved the structure of composite coating and made it uniform, compact and fine grained (Algul et al., 2015). No carbon peak belong to GNPs was detected from the XRD pattern in Fig. 3, probably due to the formation of low quantity and highly dispersive distribution of the fine GNPs (Uysal et al., 2016). To confirm the existence of GNPs in the composite, EDS was used to measure the GNPs content (marked by white circle) and the result is shown in Fig. 4, which clearly confirmed the presence of GNPs in the Ni matrix.

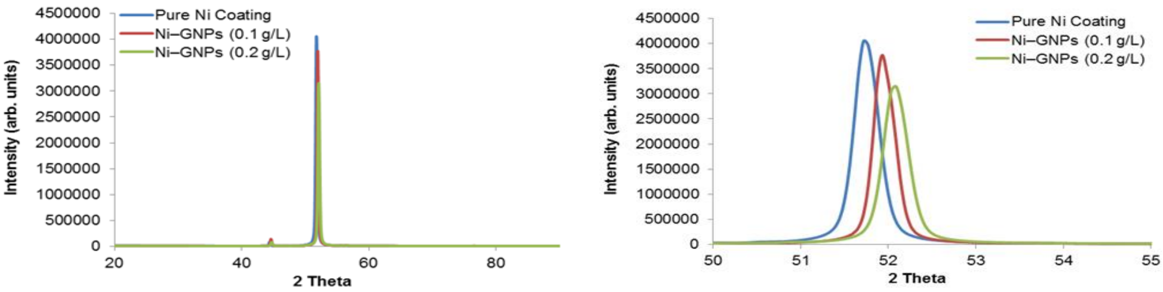
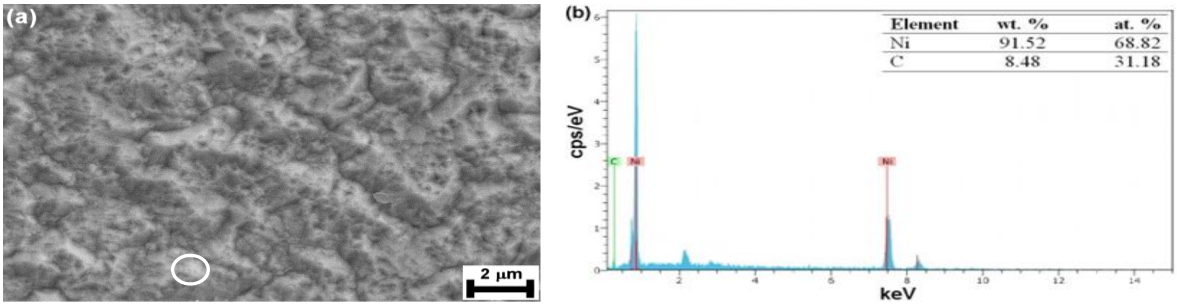


Figure 3. XRD patterns observed for (a) pure Ni and Ni-GNPs composites with different content of GNPs (b) detailed (1 1 1) diffraction of Ni.



Element	wt. %	at. %
Ni	91.52	68.82
C	8.48	31.18

Figure 4. (a) SEM image and (b) EDS analysis of Ni-GNPs composite coating electroplated with a 0.2 gL^{-1} GNPs in the plating bath.

Figure 5 shows difference in microhardness for pure Ni and Ni-GNPs composite coatings. The pure Ni coating exhibited the hardness of 320 HV$_{0.05}$, in agreement with the typical values of pure Ni. The coating electroplated with a 0.2 gL^{-1} GNPs in the plating bath had the maximum hardness of 395 HV$_{0.05}$, about 23 % larger than that of the pure Ni layer. It is clear that an increase in amount of particles' co-depositing caused the increase of hardness of the composite coatings. The mechanism of strengthening the matrix is mainly due to grain refinement, particle strengthening and dispersion hardening effects (Yu et al., 2018).

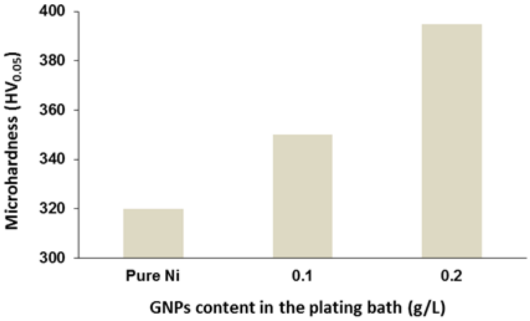


Figure 5. Microhardness variation of pure Ni and Ni-GNPs composite coatings.

The friction coefficient as a function of sliding distance for Ti-6Al-4V alloy, pure Ni coating and Ni-GNPs composites with different content of GNPs are presented in Fig. 6. According to the curves, the friction coefficients of Ni-GNPs composite coatings were significantly lower than those of pure Ni coating and Ti-6Al-4V alloy. Figure 6 also revealed that all the composite coatings exhibited a steady value with minor fluctuations, and the composite coating with 2 gL^{-1} GNPs had the lowest friction coefficient. On the other hand, the Ti-6Al-4V alloy showed friction coefficient values in the range of 0.6-0.9 with relatively heavy fluctuations. Mindivan (2017) who investigated tribological behavior of Polyamide 6–GNPs composites, reported that GNPs acting as a lubricant diminished the direct contact between the counter face and the matrix.

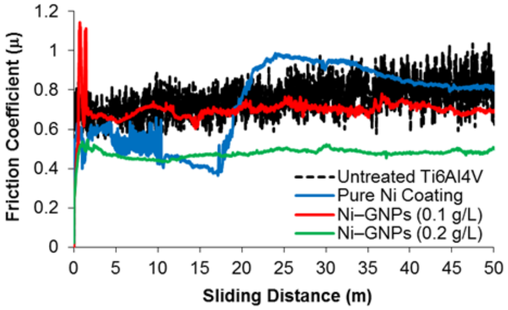


Figure 6. Friction coefficient vs sliding distance for Ti-6Al-4V alloy, pure Ni coating and Ni-GNPs composite coatings.

The common view of wear tracks of the Ti-6Al-4V alloy, pure Ni coating and Ni-GNPs composites with different content of GNPs is shown in Fig. 7. When the track width was examined, the wear resistance of Ti-6Al-4V alloy improved after PC electrodeposition. Clearly, the width of the wear track of the Ti-6Al-4V alloy (Fig. 7 a) was larger than those of the pure Ni and GNPs reinforced Ni composite coatings as shown in Fig. 7 b - d. Moreover, it can be found that the worn surface of the Ti-6Al-4V alloy exhibited a mixture of abrasion and extensive plastic deformation. A relatively smooth worn surface was detected for the pure Ni and Ni-GNPs composites. Especially, Al_2O_3 ball did not create any measurable wear loss on the worn surface of the Ni-GNPs composite coating with 0.2 gL^{-1} GNPs in the plating bath. Table 3 shows the wear rates of untreated and treated samples. Wear rate value of untreated Ti-6Al-4V alloy was found higher than pure Ni and Ni-GNPs composites. It is inferred that the GNPs in the coating bring about an improvement in wear resistance, which could be attributed to the GNPs slightly removed from the Ni matrix. Thus, the GNPs acting as a solid lubricant would take the loads transmitted from the Ni matrix and cause a shear force decrease between the contact face (Algul et al., 2015). It is worth mentioned that the dispersion strengthening by incorporating GNPs can't be ignored. Consequently, the wear resistance could be improved by including the well distributed GNPs in Ni matrix.

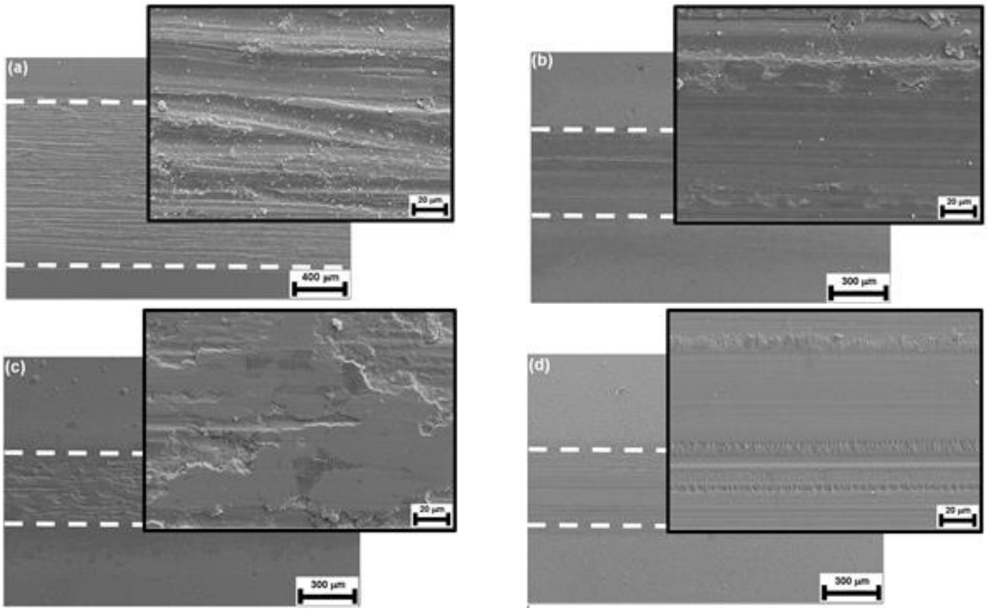


Figure 7. Low and high magnification SEM micrographs of wear tracks generated on the (a) Ti-6Al-4V alloy, (b) pure Ni coating and Ni-GNPs composite coatings with (c) 0.1 gL^{-1} and (d) 0.2 gL^{-1} GNPs in the plating bath.

Table 3. Wear rates of Ti-6Al-4V alloy, pure Ni and Ni-GNPs composite coatings.

Samples	**Wear Rate ($x10^{-4}$ mm^3/Nm)**
Untreated Ti-6Al-4V	5.64
Pure Ni	0.44
Ni-GNPs (0.1 gL^{-1})	0.24
Ni-GNPs (0.2 gL^{-1})	0

4. Conclusions

In this study, pure Ni and Ni-GNPs composite coatings were successfully prepared on the Ti6Al4V by pulse electrodeposition. The XRD and SEM analysis demonstrated the better grained and compact property of the Ni-GNPs deposits. The microhardness, wear resistance and friction coefficient of the pure Ni were greatly improved by loading GNPs from 0 to 0.2 gL^{-1} in the bath. In summary, the best behavior of friction behaviour was the coating that was treated with 0.2 gL^{-1} GNPs.

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