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Effect of SiC and h/BN codeposition on microstructural and tribological properties of Ni-SiC-h/BN composite coatings

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Nanocrystalline Ni-SiC-h/BN composite coatings were fabricated by pulse current electrodeposition process from nickel sulfamate bath. Different contents of SiC nanoparticles and h/BN nanosheets (5-20 g/L each) were dispersed in the electrolyte to investigate the effects of dispersed particles on final properties of the composite coatings. Surface morphologies, microstructures, mechanical and tribological properties of the electrodeposited composite coatings were evaluated by using scanning electron microscopy (SEM), optical microscope, X-ray diffraction (XRD), Vickers microhardness, wear and coefficient of friction. Studies revealed that as compared to pure nickel coatings, electrodeposited Ni-SiC-h/BN composite coatings exhibited smooth and compact surface, increase in Vickers microhardness, grain refinements and enhanced tribological properties. In addition, as compared to either of Ni-SiC or Ni-h/BN composite coatings, presence of both types of particles together into nickel matrix revealed overall improved performance.

Key words: Ni-SiC-h/BN, Composite coating, Microhardness, Coefficient of friction.

Introduction

Codeposition of second phase ceramic particles into metal matrix either by electrodeposition or electroless deposition has been extensively studied in recent years due to their low cost and simple method of fabrication. It has been already revealed that these composite coatings possess excellent mechanical, anti-corrosion and improved tribological properties as compared to pure metal deposit [1-4]. Being an engineering material, nickel based composite coatings is demanded to be one of the promising candidate for several potential applications. The second phase particles are chosen in such a way to obtain the nature and properties of the composite according to need. For example, to increase mechanical properties of the deposit, hard ceramics particles like oxides, carbides, nitrides, diamond, etc. are preferred [1, 5-7]. Our previous study revealed that incorporation of hard ceramic particles, such as SiC nanoparticles, into nickel electrodeposits can effectively lower the grain size, increase Vickers microhardness, improve wear and corrosion properties as compared to pure nickel [8, 9]. Similarly, to improve wear and coefficient of friction, solid self-lubricating ceramics like graphite, sulphides, h-BN, etc. are chosen [10]. Although codeposition of solid lubricating ceramics significantly reduce the coefficient of friction, Vickers microhardness and other mechanical properties of composite coatings might be affected due to their layered structure, slip plane and soft nature.

Although many literatures report on the fabrication of electrodeposited nickel ceramics composite coatings containing only one kind of ceramic particles such as Ni-SiC, Ni-Al_2O_3, Ni-TiB_2, Ni-CeO_2, Ni-BN, Ni-diamond etc. however, only limited researches have been found on incorporation of two different kinds of ceramics (including one hard and another soft self-lubricating types) together into nickel deposit; such as SiC and hexagonal boron nitride (h/BN) [11]. Therefore, the present study is aimed to the fabrication of electrodeposited nickel matrix ternary composite coatings containing different contents of both hard SiC and soft hexagonal boron nitride (h/BN) ceramics by electrodeposition process and to investigate the effect of different contents of SiC and h/BN on surface morphology, microstructure, matrix crystallite orientation, and Vickers microhardness as the key properties of composite coatings. Similarly, a comparative study on wear and coefficient of friction were performed to illustrate the tribological properties.

Experimental

All electroplating experiments were conducted in a 250 ml glass beaker. The plating electrolyte was made using nickel sulfamate (purity $\geq$ 97%, Duksan pure chemical Co. Ltd) of which concentration and compositions are listed in Table 1. Sacrificial pure nickel balls inside a titanium basket were used as anode while 2 mm thick polished copper substrate with average surface roughness of 0.15 μm, Vickers microhardness of

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Table 1. Electrodeposition parameters and operating conditions.

Compositions	Parameters
$Ni(NH_2SO_3)_2$ (g/L)	300
$NiCl_2$ (g/L)	10
H_3BO_3 (g/L)	40
SiC (g/L)	5-20
h/BN (g/L)	5-20
CTAB (g/L)	0.2
SDS (g/L)	0.3
Saccharin (g/L)	2
Temperature (°C)	50
pH	4.0
Current density (mA/cm^2)	80
Stirring rate (rpm)	200
Plating time (min)	90

~ 140 HV, and exposed area 2.56 cm^2 was used as cathode. Electrolytic bath containing dispersed ceramics were mechanically stirred for 3 h followed ultrasonic dispersion for 30 minutes prior to electrodeposition. Electrolytic bath containing different contents of SiC and h/BN particles in the ratio 20 : 00, 15 : 05, 10 : 10, 05 : 15 and 00 : 20 g/L respectively prepared and represented by S-200, S-155, S-11, S-515 and S-020 respectively for convenience. Pulse current with average current density 80 mA/cm^2, pulse frequency 100 Hz, 50% pulse duty cycle (5 ms pulse ON and 5 ms pulse OFF time) were adjusted as pulse parameters during electrodeposition process. The electrodeposition time was set for 90 min. Sodium dodecyl sulphate (SDS) and Cetyltrimethyl ammonium bromide (CTAB) were used as anti-pitting agent and surfactants respectively.

After electrodeposition, the samples were cleaned in running distilled water followed by ultrasonic cleaning for 5 minutes in order to remove loosely adsorbed particles and then subjected for further analysis. Microstructures, phase compositions, and Vickers mi-crohardness of the samples were evaluated by SEM (JSM-6400, JEOL, Tokyo, Japan), XRD (Rigaku DMAX 2200, X-Ray Diffractometer, Japan), and Vickers microhardness (Buehler Ltd., USA), respectively. Wt.% of particles incorporated in the nickel matrix was evaluated by EDS analysis coupled with SEM. Vickers microhardness test was carried out by applying 0.98 N load for 10 seconds at 10 different places of sample, and the values were averaged.

Tribological properties of the electrodeposited Ni-SiC-h/BN composites were evaluated by wear test using tribometer (CSM instruments, TRN 01-04879) under ball on disk method. Steel ball (SAE52100) of measured hardness ~ 830 HV and diameter of 12.7 mm was used as counterpart ball and electrodeposited coatings as disk. A constant load of 5 N was set with the sliding frequency of 3 Hz for 10 minutes at the radius of 5 mm under dry condition. Coefficient of friction was recorded simultaneously during wear test and the worn surfaces were analysed by SEM.

Results and Discussion

Surface morphology and microstructural analysis

SEM micrographs of the surface morphologies of electrodeposited Ni-SiC-h/BN composite coatings are shown in Fig. 1. With the variation of different contents of SiC and h/BN, surface topographies of the samples exhibited some considerable variations. There appear to be considerable change in surface morphologies of sample S-200 (Fig. 1a) as compared to sample S-020 Ni-h/BN (Fig. 1e) composite coatings. Ni-h/BN composite coatings shows smoother surface with fine grains. On the other hand, pure nickel coating has shown relatively rough surface with larger polyhedral crystallites as shown in Fig. 1f. The refined surface morphologies of the composite coatings as compared to pure nickel coating might be resulted from the hindering of regular grain growth due to incorporation of second phase particles. Such obstruction of regular grain growth results to the formation of many alternative nucleation

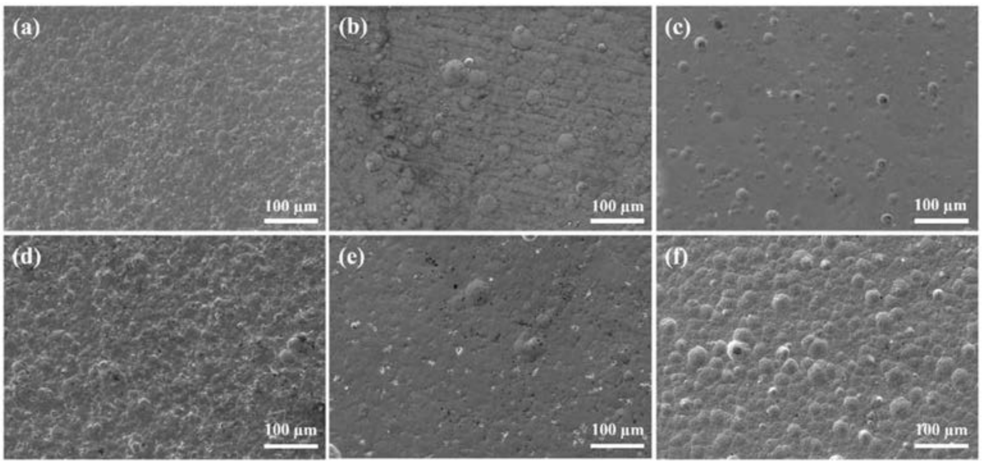

Fig. 1. SEM micrographs of the surface morphologies of different samples; a) S-200, b) S-155, c) S-11, d) S-515, and e) S-020 and f) pure Ni.

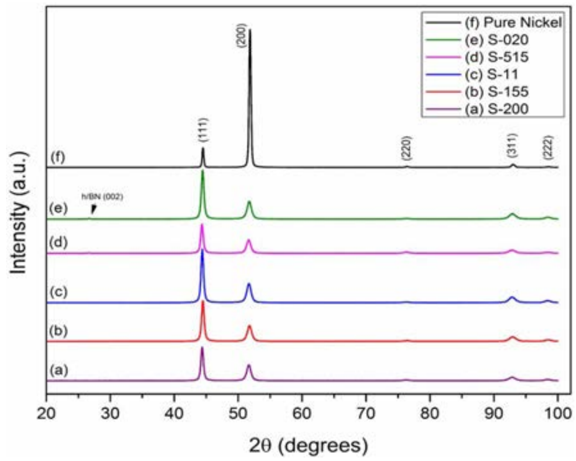

Fig. 2. XRD patterns of the Ni-SiC-h/BN composite coatings.

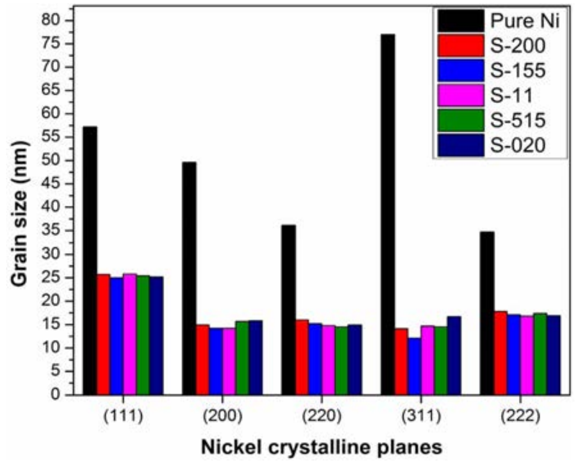

Fig. 3. Nickel crystalline grain size of different samples.

sites which gives rise to the fine nickel grains with different crystallite orientations. Compact and smooth surface with less porosity are usually desired for engineered coatings together with improved mechanical and anti-wear-friction properties.

XRD patterns of pure nickel and Ni-SiC-h/BN composite coatings with different contents of SiC and h/BN are shown in Fig. 2. It reveals that the typical nickel [100] crystallite plane is represented by intense (200) reflection peak in pure nickel coating. However, this preferred orientation of nickel crystalline plane has been modified in composite coatings in which attenuation of (200) peak and elevation of (111) peak. It suggests a change in nickel crystallite orientation pattern due to the incorporation of SiC and h/BN particles into the nickel matrix. This might be due to the incorporated particles that hindered the preferred grain growth and enhanced the alternative nucleation with different plane orientation. Similar results have been observed by different researchers [12]. Nickel crystalline grain size of different samples, based on broadening of XRD reflection peaks, have been calculated by using Scherrer's equation as shown in Fig. 3. Grain sizes of all the samples are significantly smaller as compared to pure nickel. Pure nickel coating has shown the largest grain size over 35 nm in all the planes. The effective reduction of nickel crystallite grain size of composite samples might be associated with higher incorporation of SiC and h/BN particles obstructing to regular grain growth. Therefore, a competition between incorporation rate of nanoparticles and nucleation rate of nickel has been established which resulted in the refining of nickel grains [11].

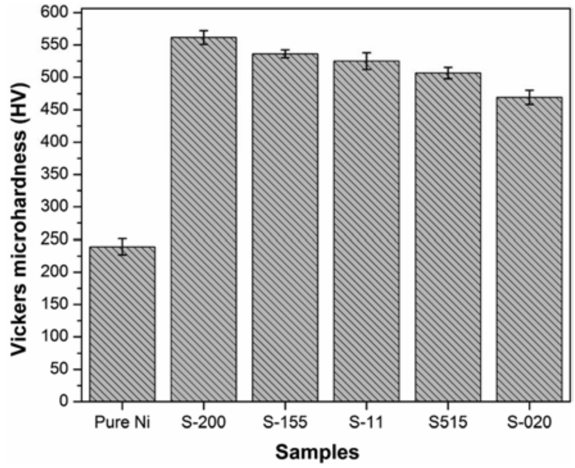

Fig. 4. Variation of Vickers microhardness of pure Ni and Ni-SiC-h/BN composite coatings with respect to the different contents of SiC and h/BN in the plating bath.

Vickers microhardness

Fig. 4 shows the variation of Vickers microhardness of pure nickel and composite coatings. It has been clearly observed that Ni-SiC composite coating (Sample S-200) has the highest value (~ 560 HV) of Vickers microhardness, and pure nickel has the least value (~ 240 HV). The trend also clearly shows decreasing the contents of SiC gradually decreased the Vickers microhardness. Incorporation of h/BN revealed relatively smaller increment in Vickers microhardness as compared to incorporation of SiC. However, it is significantly higher than that of pure nickel coating. The possible reasons for the increase in Vickers microhardness of the nickel composite coatings are as follows: (a) dispersion strengthening effect due to particles incorporation, (b) nickel matrix grain refining effects along with textural modifications due to both particles incorporation and (c) structure, size and hardness of second phase particles into the nickel matrix [13, 14]. When the reinforcements are in nanometric range, increase in Vickers microhardness is largely responsible due to dispersion strengthening, however, if the particles are submicron or micron size, then the particles act as load bearing agent and increases microhardness. Similarly, smaller grains are also responsible to increase microhardness that is connected to the Hall-Petch hardening effect induced by ultrafine grains [15]. The original dislocation model for this

Table 2. Wt.% of codeposited ceramic particles in nickel matrix.

	Electrodeposited composite samples				
	S-200	S-155	S-11	S-515	S-020
Wt.% of SiC/hBN (by EDX analysis)	3.92/ 0.0	3.61/ 6.50	3.32/ 9.21	1.27/ 10.04	0.0/ 8.5

relationship was based on the concept that grain boundaries act as barriers to the propagation of dislocations by forming dislocation pile-ups at grain boundaries, resulting into hard deposits. On the other hand, as compared to h/BN nanosheets, SiC nanoparticles are much harder. In addition, codeposited h/BN in this study has elongated nanosheet layered structure which are more prone to slippage of plane while β-SiC particles are hard and mostly spherical or oval shape. Table 2 shows the wt.% codeposition of SiC and h/BN nanoparticles into the deposit, obtained from EDS analysis. It seems that the codeposition of h/BN is much easier than that of SiC from analysis of EDS data of different samples. Also, it is interesting to note that less codeposition wt.% of the h/BN particle is found in its single phase dispersion (i.e. in S-020 sample) than that of mixed phase dispersions (i.e. S-11 and S-515 samples). This might be due to the influence in transport towards the electrode, facilitated by presence of SiC nanoparticles.

Tribological properties

Tribological properties of the electrodeposited nickel and nickel composite coatings were evaluated by ball on disk tribometer under dry condition at room temperature. Coefficient of friction, recorded simultaneously during wear test, is shown in Fig. 5. Pure Ni coating shows the highest coefficient of friction among all samples. From Fig. 5, it is revealed that the coefficient of friction has been found to be sharply

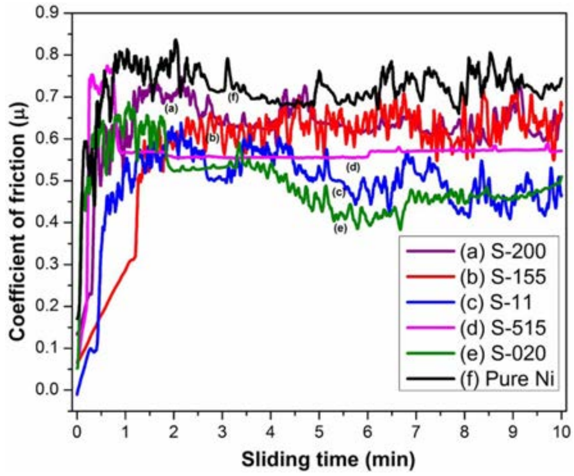

Fig. 5. Variation of coefficient of friction of different samples measured during wear test.

decreased from sample S-200 to S-11 and further gradually decreased from S-11 to S-020.There might be following two possible factors which influenced the change in coefficient of friction; (a) higher incorporation of h/BN (solid lubricant), and (b) reduction of nickel matrix grain size. It is to be noted that crystal structure of h/BN nanosheets is closely related to graphite or MoS_2, which are well-known materials for solid lubricant. Presence of h/BN facilitates lubricating action by slippage of planes. As a result, significant reduction in coefficient of friction can be observed. Increased content of such solid lubricant has a major role for decreasing coefficient of friction. Shahri *et al.* [16] also reported that incorporation of h/BN into the cobalt matrix considerably improved wear performance of Co-BN (h) composite coatings. Similarly, for a nanostructured composite coating, smaller grain is also one of the main factors for improving mechanical and tribological properties. Although Ni-h/BN has relatively smaller

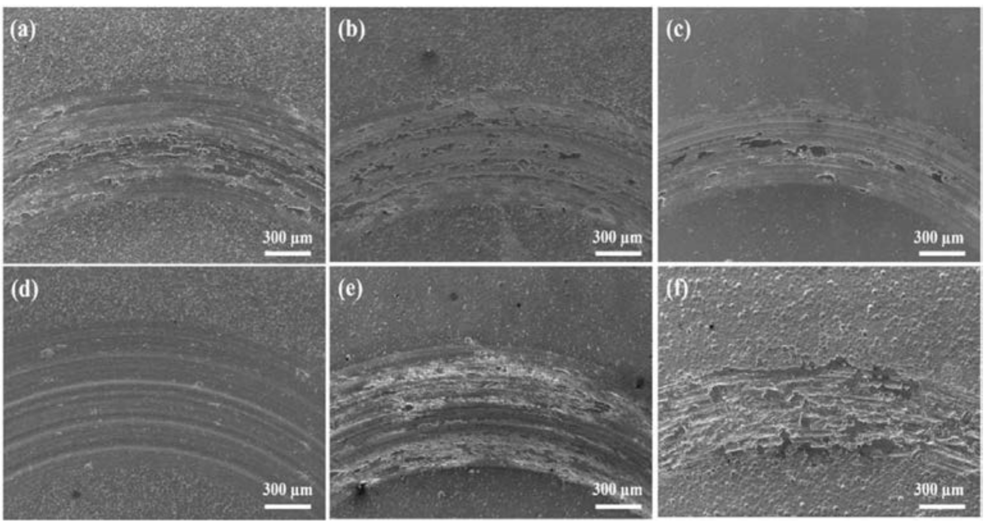

Fig. 6. SEM micrographs of the worn surfaces of different samples after wear test; a) S-200, b) S-155, c) S-11, d) S-515, and e) S-020, and f) pure Ni.

Vickers microhardness as compared to Ni-SiC, the proper combination of both reinforcements in S-11 sample has both the benefits of increase in Vickers microhardness, decrease in grain size and existence of h/BN as solid lubricant. Therefore, the coefficient of friction observed is closest to the one for Ni-h/BN (S-020) composite coating. Worn surfaces of pure nickel and Ni-SiC-h/BN composite coatings after wear test are shown in Fig. 6. Wear tracks have shown different nature of wear behaviors. The combination of different contents of incorporated hard and solid-lubricating nano-scale reinforcements (SiC, and h/BN) in electrodeposited composite coatings might have caused to decrease direct contact between nickel matrix and counter steel ball surface. In addition, the produced wear debris which contained a higher amount of reinforcements, also act as a secondary solid lubricant. As a result, improvement in coefficient of friction and wear behavior of composite coatings over pure nickel has been achieved.

Conclusions

Ni-SiC-h/BN composite coatings have been successfully prepared by pulse current electrodeposition process with different contents of SiC nanoparticles and h/BN nanosheets. Composite coatings exhibited smooth surface with refined grains, and increased Vickers microhardness as compared to pure nickel coating. Wear and coefficient of friction have been found to be dependent on nature and amount of codeposited particles. The lowest coefficient of friction was observed for Ni-h/BN composite coatings, however, Vickers microhardness was found to be little affected with only h/BN. On the other hand, improved matrix grain size, increased Vickers microhardness as well as improved wear and coefficient of friction was observed in the composite coatings prepared by addition equivalent amount of both SiC nanoparticles and h/BN nanosheets in the electrolyte.

Acknowledgments

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