Fabrication and Characterization of Electrodeposited Ni−SiC−h/BN Composite Coatings

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Ni−SiC−h/BN composite materials were prepared by electrodeposition technique with the dispersion of SiC (10 g/L) and h/BN nanosheets (10 g/L) in a nickel sulfamate electrolytic bath. Different ratio of sodium dodecyl sulfate (SDS) and cetyltrymethyl ammonium bromide (CTAB) surfactants were used to evaluate the effect of surfactants on the properties of the electrodeposited composite coatings. The coating samples were characterized by scanning electron microscopy, X-ray diffraction, Vickers microhardness test, scratch and tribology tests. The results revealed that the co-deposition of nanoparticles was significantly influenced by surfactants during electrodeposition process. Pyramidal or polyhedral nickel crystallites were observed at higher ratio of SDS/CTAB while smaller oval grains with refined surface morphologies were obtained at lower ratio of SDS/CTAB surfactants. In addition, wt% of particles co-deposition was increased, and Vickers microhardness, wear and coefficient of friction of the electrodeposited composite coatings were improved at increased CTAB and decreased SDS contents in the electrolyte during electrodeposition process.

KEY WORDS: Ni−SiC−h/BN; Composite coating; Surfactant; Microstructure; Scratch; Wear

1. Introduction

Composite electrodeposition is a method of co-depositing second phase fine particles with a growing metal or alloy matrix during electroplating process. Metal matrix composite (MMC) coating is extensively studied in recent years due to its enhanced mechanical, tribological, and electrochemical corrosion resistance properties as compared to pure metal[1,2]. Second phase reinforcements can be fine particles of metallic or non-metallic compounds and polymers. Nickel is a widely used metal matrix for such a reinforcement of ceramic particles since it can be a potential candidate for an alternative to hard chrome plating. Electrodeposited nickel coating, which possesses high tensile strength and good toughness, can be widely used in engineering parts. Recent researches on nickel matrix composite electrodeposition are mainly focused on fabrication of dispersion strengthening, wear and corrosion resistant coatings[3,4].

Ceramics particles are often chosen according to the need of desired properties of the composites. To increase hardness and other mechanical properties, co-deposition of hard ceramics particles such as SiC, Al_2O_3, Si_3N_4, and TiB_2 are preferred during electrodeposition[5−7]. Similarly, to increase material performance via reducing coefficient of friction and wear, solid lubricants such as h-BN, MoS_2, and PTFE are chosen for co-deposition, which intrinsically possesses such properties in the coatings[8−10]. Previous studies have reported that the co-deposition of second phase ceramic particles into nickel matrix by electrodeposition is influenced by operational parameters like current types, current density, temperature, pH, hydrodynamic motion of electrolyte, as well as presence of additives[1,11]. Pulse current electrodeposited composite coatings have shown the improvement in particles co-deposition, mechanical and tribological properties as compared to direct current electrodeposited composite coatings[1,12]. Generally, surfactants are used during composite electrodeposition process, which plays a vital role in improving suspension stability, reducing particles agglomeration, enhancing particles co-deposition, and minimizing hydrogen embrittlement in the coatings. Proper choose of surfactants is essential for the effective enhancement of deposit properties. Sodium dodecyl sulfate (SDS) and cetyltrymethyl ammonium bromide (CTAB) are the most commonly used surfactants in these processes[13,14]. Several investigations have been made on nickel matrix binary composite coatings such as

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Table 1 Electrolytic bath composition and operating parameters

Compositions	Parameters
$Ni(NH_2SO_3)_2$ (g/L)	300
$NiCl_2$ (g/L)	10
H_3BO_3 (g/L)	40
SiC (g/L)	10
h/BN (g/L)	10
CTAB (g/L)	0.1−0.6
SDS (g/L)	0.1−0.6
Temperature (°C)	50
pH	4
Current density (mA/cm^2)	60
Stirring rate (r/min)	200
Plating time (min)	60

Fig. 1 XRD patterns of the Ni−SiC−h/BN composite coatings.

Ni−SiC, Ni−Al$_2$O$_3$, Ni−Si$_3$N$_4$, Ni−h/BN, Ni−MoS$_2$, Ni−PTFE, Ni−diamond, and Ni−CNT, which showed enhancement of mechanical, tribological and corrosion resistant properties as compared to pure nickel[5,6,9,10,15,16]. However, very few studies have been made on the fabrication of nickel matrix ternary composite coatings, containing two different types of ceramics into a nickel matrix, which could enhance both mechanical and self-lubricating properties. Therefore, in the present research, we have extended our knowledge to fabricate and characterize the Ni−SiC−h/BN ternary composite coatings by electrodeposition process.

2. Experimental

2.1. Preparation of Ni−SiC−h/BN composite coating

All electroplating experiments were conducted in a 250 ml glass beaker. The plating electrolyte was made using nickel sulfamate (purity ≥ 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 0.15 μm, Vickers microhardness ∼140 HV, and exposed area 2.56 cm^2 was used as cathode. Cathode was ultrasonically cleaned in distilled water for 5 min before plating. Electrolytic bath containing both SiC, and h/BN particles (10 g/L, each) was ultrasonically dispersed for 30 min prior to electrodeposition. Pulse current with average current density 60 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 60 min with the average coating thickness of 80 μm. Different contents of SDS (0.1−0.6 g/L) and CTAB (0.1−0.6 g/L) were used together in order to investigate the effect of surfactants on properties of electrodeposited composite coatings. Thus, the prepared seven different samples with SDS/CTAB ratios of 0.6/0.0, 0.5/0.1, 0.4/0.2, 0.3/0.3, 0.2/0.4, 0.1/0.5, and 0.0/0.6 g/L have been assigned as SC-0, SC-1, SC-2, SC-3, SC-4, SC-5, and SC-6, respectively for convenience.

After electrodeposition, the samples were cleaned in running distilled water followed by ultrasonic cleaning for 5 min in order to remove loosely adsorbed particles and then subjected for further analysis. Microstructures, phase compositions, and Vickers microhardness of the samples were evaluated by
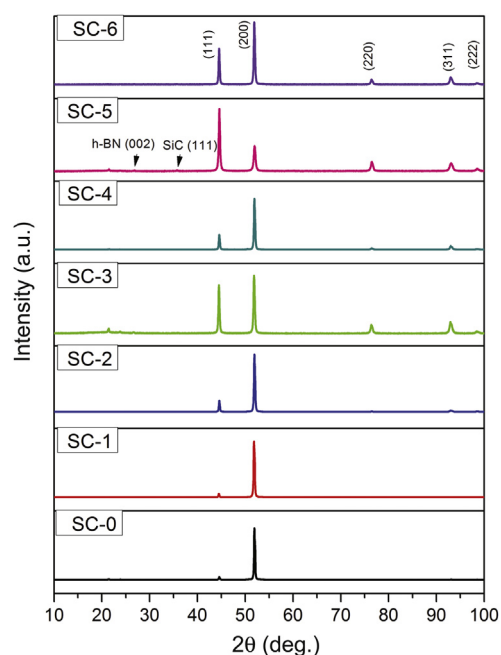
scanning electron microscopy (SEM, JSM-6400, JEOL, Tokyo, Japan), X-ray diffraction (XRD, Rigaku DMAX 2200, X-Ray Diffractometer, Japan), and Vickers microhardness (Buehler Ltd., USA), respectively. Weight percentage (wt%) of particles incorporated in the nickel matrix was evaluated by energy dispersive spectroscopy (EDS) analysis coupled with SEM. Vickers microhardness test was carried out by applying 0.98 N load for 10 s at 10 different places of the cross-sections of a sample and the values were averaged.

2.2. Scratch testing

Scratch testing was carried out on the surface of coated sample by using CSEM Revetest, scratch tester with diamond stylus of 200 μm in diameter at an angle of 120° under progressive load condition. Average surface roughness of the coated samples ranged from 0.5 to 0.9 μm. The initial load was set to 0 N with a progressive loading rate of 197.15 N/min until 100 N final loads. Coefficient of friction was also recorded simultaneously during scratch test. Scratched surface was analyzed by SEM.

2.3. Tribology test

Tribological properties of the electrodeposited Ni−SiC−h/BN composites were evaluated by using a 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 10 N was set with the sliding frequency of 3 Hz for 10 min at the radius of 5 mm under saline water as lubricating condition. The coefficient of friction was recorded simultaneously during wear test and the worn surfaces were analyzed by SEM.
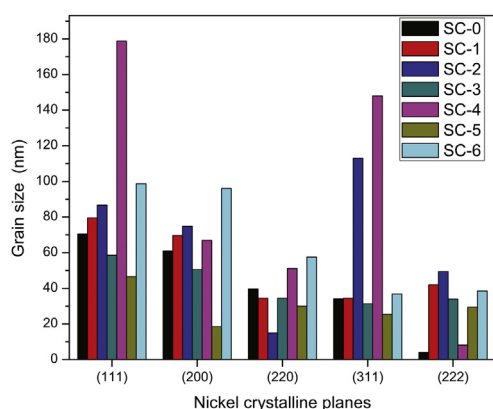
Fig. 2 Nickel crystalline grain size of different samples at different planes.

3. Results and Discussion

3.1. Microstructural analysis

XRD patterns of electrodeposited Ni−SiC−h/BN composite coatings with different contents of SDS and CTAB are shown in Fig. 1. It is interesting to note that the differential peak intensities have drastically changed depending upon the surfactants ratio variation under similar conditions. Relative intensity of (111) reflection peak of nickel matrix has been found to be gradually increased by increasing CTAB concentration and decreasing SDS concentration until SC-3 sample and then dropped in SC-4. In addition, the highest relative intensity of (111) peak is observed in SC-5 sample along with enhancement of (311) and attenuation of (200) reflection peak. In addition, a very small peak for SiC at 35.7 deg. (2θ) and for h/BN at 26.5 deg. (2θ) have also been detected in XRD of SC-5 sample. Absence of such peaks in other samples might be due to low content of particles beyond the detection limit by XRD. It has been reported that (200) reflection peak for Ni represents to the preferred (100) texture, which is associated with deposits that possess maximum ductility and minimum hardness and internal stress[17]. The enhancement of (311) and (111) nickel peaks is attributed to the dispersion of [211] orientation. Therefore, by evaluating main peaks intensity ratios, it can also be estimated that the change in mechanical properties by textural modifications of the electrodeposited nickel composite coatings. This result suggests that the proper ratio of surfactants is also an essential part to obtain the mixed orientations of the nickel crystallite planes for increasing harder and compact deposit.

Nickel crystalline grain size was also calculated by using Scherrer equation, based on the broadening of XRD reflection peaks, which is shown in Fig. 2. The nickel crystallite grain size for SC-5 sample is significantly smaller as compared to other samples. The effective reduction of nickel crystallite grain size of SC-5 sample might be associated with higher incorporation of SiC and h/BN particles, which obstruct the regular grain growth as well as reduce the ionic density near the cathode-electrolyte interface due to the presence of surfactants. Therefore, a competition between incorporation rate of nanoparticles and nucleation rate of nickel has been established which resulted in the refining of nickel grains.

SEM micrographs of the surface morphologies of electrodeposited Ni−SiC−h/BN composite coatings are shown in

Fig. 3. Depending upon surfactants variation, surface topographies of samples exhibited only little considerable variations. Pyramidal nickel crystallites were observed at higher ratio of SDS/CTAB while smaller oval grains with refined surface morphologies were obtained at lower ratio of SDS/CTAB surfactant. SC-4 sample shows agglomerated rough surface with polyhedral dissimilar grains. On the other hand, SC-5 and SC-6 samples show fine surfaces with similar topographies to each other. Compact and smooth electrodeposited composite coatings with less porosity are always desirable for improving wear-friction and corrosion resistance properties of the materials. Similarly, SEM micrographs of the cross-section of SC-5 sample with EDS mapping is shown in Fig. 4. It can be clearly observed that SiC and h/BN particles have been successfully co-deposited and well distributed into the coatings as shown by EDS mapping. Homogeneous distribution of both hard and soft reinforcements into the matrix is a popular choice because it can improve both mechanical and tribological properties. Hence, reinforcement of SiC nanoparticles increases microhardness and other mechanical properties whereas presence of h/BN improves the coefficient of friction and wear characteristics of the composite coatings.

3.2. Vickers microhardness

Vickers microhardness of composite coatings is shown in Fig. 5. It is interesting to note that the microhardness of composite coatings is increased by increasing CTAB and decreasing SDS contents. There are two possible reasons for the increase in Vickers microhardness of the nickel composite coatings in our study; namely dispersion strengthening effect due to particles incorporation and nickel matrix grain refining effects along with textural modifications due to both particles incorporation and use of surfactants. As it is well known, cationic surfactant, such as CTAB, plays an important role in particles co-deposition, since, it can modify the state of particle charge (zeta potential) into positive value by particles-surfactant adsorption phenomenon. Thus, it would increase the adhesion force towards cathode, resulting in higher rate of particles incorporation into the growing nickel matrix[18]. Similarly, Benea et al.[19] also found the improvement of uniformity and the amount of SiC dispersed particles in the composite coatings in presence of SDS surfactant. Therefore, the mutual effects of use of appropriate amount two different surfactants can significantly increase Vickers microhardness. On the other hand, smaller grains are also responsible for the increase in microhardness, which is connected to the Hall−Petch hardening effect[20,21] induced by ultrafine grains. The original dislocation model for this 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 in hard deposits. In this study, SC-5 sample, which also has the lowest nickel crystalline grain size, possessed the higher value of Vickers microhardness. Table 2 shows the weight percentage of co-deposited SiC and h/BN nanoparticles into the deposit, obtained from EDS analysis. It shows that SiC content is almost constant until SC-3 sample, however, it suddenly increased in SC-4 and reached maximum in SC-5 and then decreased in SC-6 sample. Therefore, the increase in Vickers microhardness of the composites at higher content of CTAB and lower content of SDS is thus due to the higher incorporation of SiC nanoparticles, which are hard in nature as well as refined grains of nickel matrix.
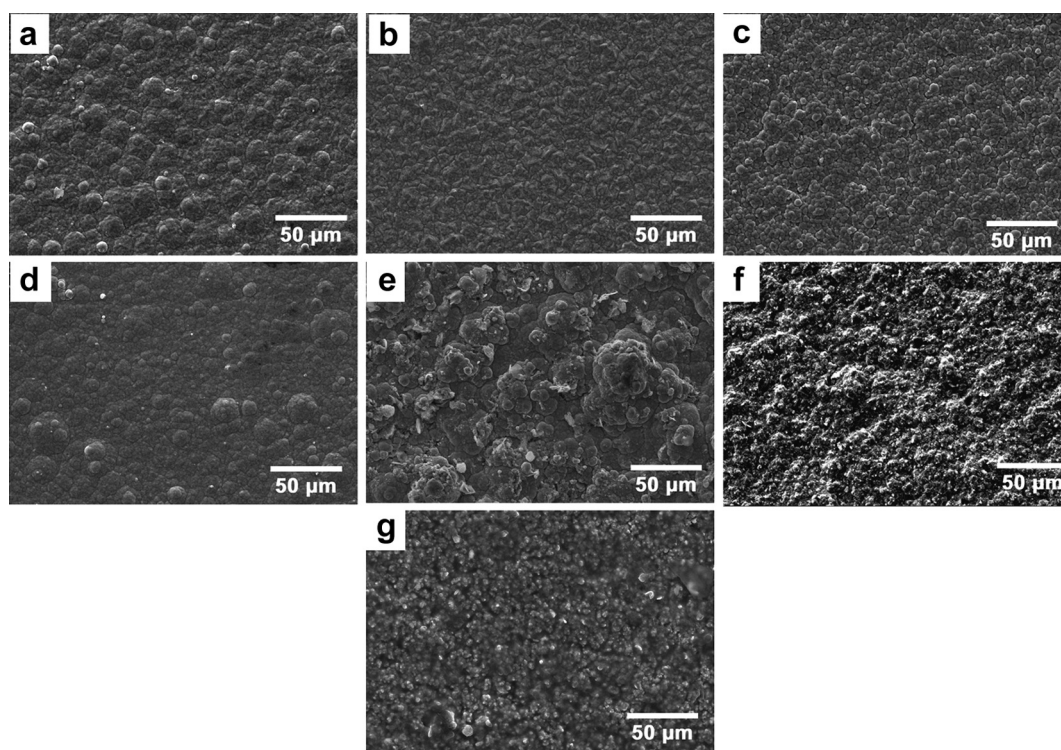
Fig. 3 SEM micrographs of the surface morphologies of different samples: (a) SC-0, (b) SC-1, (c) SC-2, (d) SC-3, (e) SC-4, (f) SC-5, (g) SC-6.
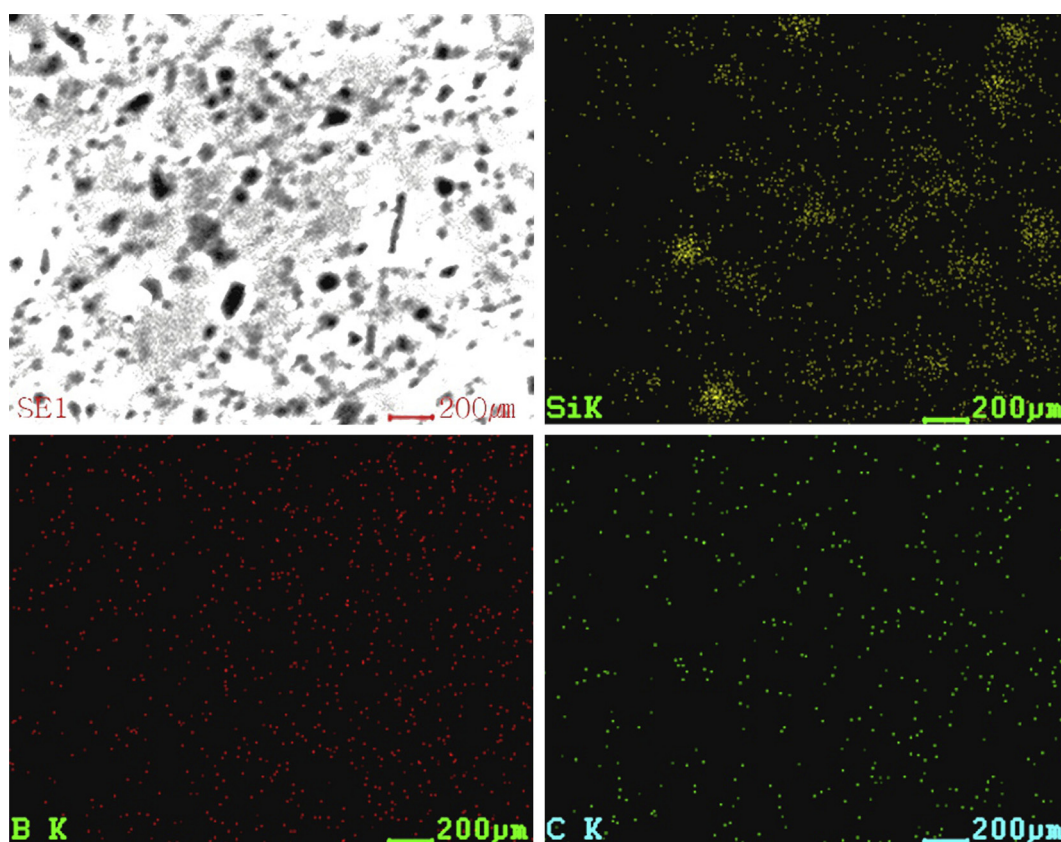

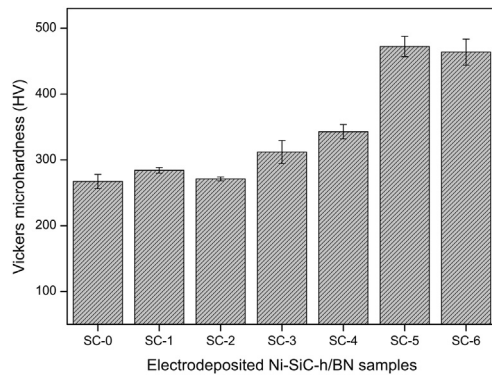**Fig. 4** SEM micrograph of the cross-section of SC-5 sample with EDS mapping.

Fig. 5 Variation of Vickers microhardness with respect to the different contents of surfactants.

3.3. Scratch test analysis

Fig. 6 shows the SEM micrographs of worn surfaces after scratch test. At higher concentration of SDS, the worn surface shows adhesive nature of scratch as shown in Fig. 6(a−c). In addition, a clearly visible adhesive crack is also present in

Fig. 6(a), which indicates the typical ductile nature of the composite prepared in presence of SDS, which is also supported from XRD (revealed by the enhanced intensity of (200) reflection peak). Fig. 6(d and e) shows both the adhesive and abrasive nature of worn surfaces, however, at higher content of CTAB, abrasive type of worn surfaces are more prominent. This observation might be related to the higher content of incorporated SiC nanoparticles into the matrix. Fig. 6(g) shows more brittleness as compared to other samples, in which several micro-cracks have been originated outside the scratched track. Addition of higher content of organic additives (such as CTAB) into the electrolytic bath may also lead to the detrimental effect on properties of electrodeposited coatings, since there is also a possibility that these additives can be co-deposited into the metal matrix, which originates more brittleness of the final product. Therefore, addition of higher amount of additives is also not good for electrodeposited engineering coatings. The width of the scratched track of SC-5 and SC-6 samples are significantly smaller as compared to other samples, which indicates the good scratch resistance of electrodeposited Ni−SiC−h/BN composite coatings prepared at higher ratio of CTAB/SDS. The coefficient of friction measured during the scratch test, as shown in Fig. 7(a), reveals that the sample prepared by using SDS only has the highest value among other samples. This might be caused by

Table 2 Weight percentage of co-deposited nanoparticles in Ni matrix and ball wear rate during tribology test

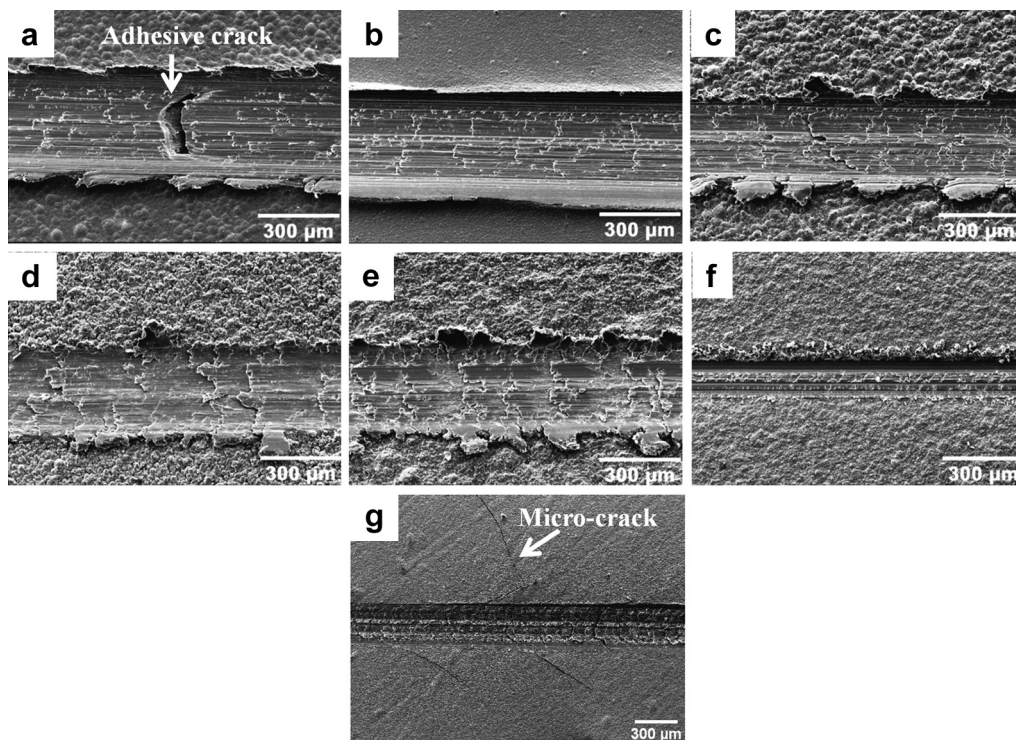|	Electrodeposited composite samples						
	SC-0	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6
wt% of SiC/hBN (by EDS analysis)	1.64/6.77	1.71/8.59	1.84/7.72	1.27/7.06	6.24/11.76	15.75/27.9	7.11/9.34
Ball wear rate ($\times 10^{-4}$ mm^3/Nm)	3.26	3.38	9.57	12.52	4.29	1.98	2.44

Fig. 6 SEM micrographs of the worn surfaces of different samples after scratch test: (a) SC-0, (b) SC-1, (c) SC-2, (d) SC-3, (e) SC-4, (f) SC-5, (g) SC-6.
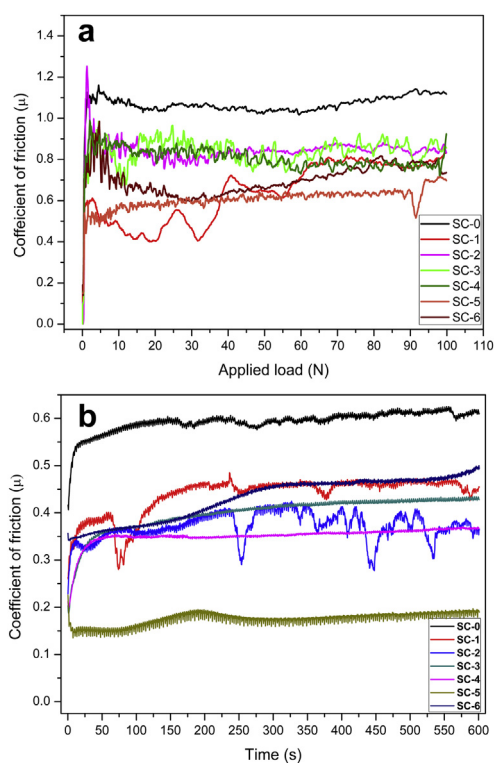
Fig. 7 Variation of coefficient of friction of different samples: (a) measured during scratch test, (b) measured during wear test.

the increased friction developed due to the adhesive nature of the coating. In contrast, SC-5 sample has almost uniform and the lowest coefficient of friction. Also, it shows the scratch failure around 90 N load during progressive scratch testing. Non uniform coefficients of friction obtained in some samples indicate the plowing of composite matrix and subsequent scratch failure at different loads.

3.4. Tribological properties

In order to investigate the tribological properties of the composite coatings, ball on disc type wear test has also been carried out. Fig. 7(b) shows the coefficient of friction recorded during the wear test. The trend of coefficient of friction during wear test is almost similar to that of coefficient of friction obtained by scratch testing. Ni−SiC−h/BN composite coating prepared in presence of SDS only shows the highest coefficient of friction, however, a significant reduction of coefficient of friction has been observed in SC-5 sample. There might be synergistic effect of higher incorporation of h/BN (solid lubricant) and also successive reduction of matrix grain size under appropriate amount of surfactants for decreasing the value of coefficient of friction. For a nanostructured composite coating, smaller grain is also one of the factors for improving mechanical and tribological properties. It can be seen in the worn surfaces of Ni−SiC−h/BN composite coatings after wear test (Fig. 8) that different nature of wear behaviors are observed. The combination of different contents of incorporated hard and self-lubricating nano-scale reinforcements (SiC and h/BN) in electrodeposited composite
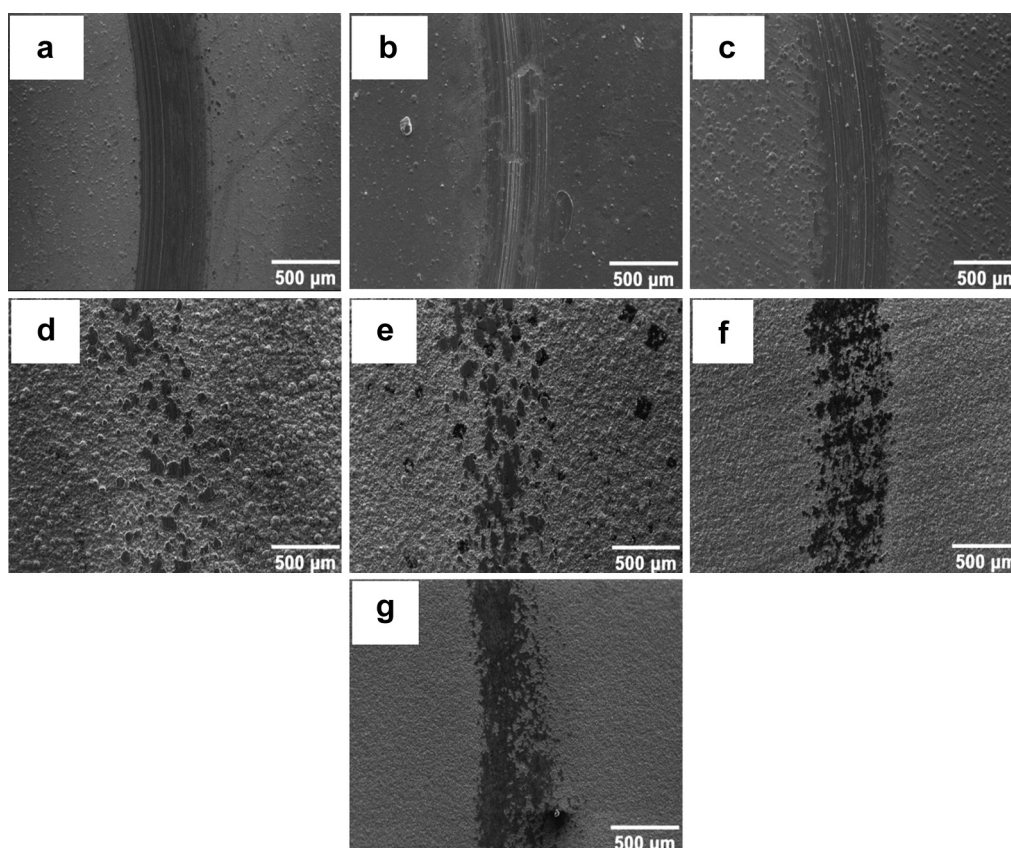

Fig. 8 SEM micrographs of the worn surfaces of different samples after wear test: (a) SC-0, (b) SC-1, (c) SC-2, (d) SC-3, (e) SC-4, (f) SC-5, (g) SC-6.

coatings might have caused the decrease of direct contact between metal matrix and counter ball surface. Consequently, there might have formed interface lubrication in a different way. In addition, the produced wear debris, which contained a higher amount of reinforcements, such as in SC-5 sample, also act as a secondary solid lubricant. As a result, improvement in coefficient of friction and wear rate is achieved. h/BN with self-lubricating nature has the same crystal structure as that of graphite, which makes it easy for producing slippage of layers. Shahri et al.[22] also reported that incorporation of h/BN into the cobalt matrix considerably reduced the coefficient of friction. The wear rate of counter ball is shown in Table 2. It shows that wear rate of counter ball is the lowest for SC-5 sample as compared to others.

4. Conclusion

Ni−SiC−h/BN composite coatings have been successfully prepared by electrodeposition techniques and the effect of surfactants (SDS and CTAB) on mechanical and tribological properties of electrodeposited coatings was evaluated. It has been found that ductile nature of the nickel matrix is retained in the sample prepared by addition of SDS, whereas harder deposit is obtained at higher content of CTAB. Weight percentage (wt%) of particles co-deposition was increased, and grains were refined with enhanced microhardness, scratch and tribological properties in the sample with the combination of surfactants as 0.1 g/L SDS and 0.5 g/L CTAB under similar conditions. Incorporation of solid lubricating h/BN nanosheets along with hard SiC nanoparticles can be a potential candidate to achieve both harder and self-lubricating materials.

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