Bull. Mater. Sci., Vol. 29, No. 5, October 2006, pp. 491–496. © Indian Academy of Sciences.

Characteristics of electrocodeposited Ni–Co–SiC composite coating

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MS received 6 June 2006; revised 3 August 2006

Abstract. Electrodeposited composites are gaining importance for their advantages including low cost, ease and simplicity of operation to tailor made coatings for tribological applications. Generally, composites containing carbides (like SiC) are preferred for high wear resistance along with increased hardness, improved corrosion resistance, and high temperature oxidation resistance as compared to alloy and pure metal electroplating. In the present work, electrolytic codeposition technique was adopted in the deposition of Ni–Co–SiC composite coating on mild steel substrate, using nickel alloyed with cobalt as the binder phase with SiC as dispersed particles. To improve the properties of coating further, Cr plating was also performed. Since the particle size and volume percent variation of dispersoid have great importance in codeposition, so the effect of these two variables on the process of codeposition and properties was observed. Morphological studies of Ni–Co–SiC coating were carried out with scanning electron microscopy and X-ray diffraction analysis to correlate the mechanical and corrosion behaviour of the coating.

Keywords. Metallic substrates; reinforcement; interfacial adhesion; abrasion resistance.

1. Introduction

Electrocodeposited composite coatings consist of a metal or alloy matrix containing dispersion of second phase particles. These particles can be hard oxides or carbide particles such as Al_2O_3, TiO_2, SiO_2, SiC, WC or diamond or a solid lubricant such as PTFE, graphite or even liquid containing microcapsules that improve wear resistance and reduce wear friction (Zahavi and Hazan 1983; Ghouse 1984; Greco 1989; Wang and Hutchings 1989; Roos *et al* 1990). Electroplated Ni coating is used for the purpose of wear resistance in car engine. With increasing availability of micron-sized particles, there is growing interest in the electrolytic and electroless codeposition of these particles. The major challenges of the codeposition of micron-sized particles seem to be the codeposition of a sufficient number of particles, and avoiding agglomeration of particles suspended in plating solution (Viderine and Podlaha 2001).

In this work, the electrolytic codeposition of micron and submicron SiC particles from Nickel Watt's solution has been carried out. Properties such as hardness, sliding wear test and corrosion testing of such nickel composite coatings were investigated. The effect of particle size and number of particles suspended in the plating solution on the concentration of codeposited particles is reported. Ni–Co alloy, which possesses good adhesion, low stress, corrosion resistance, and is thermally stable with excellent magnetic properties, is a particular choice as recording head materials for computer hard drive industries. However, a few researchers have reported on the incorporation of SiC particulates in electrodeposited Ni–Co alloy coating (Ferkel *et al* 1994; Hu and Chan 2004), though it has been known that the dispersion of SiC particulates significantly contribute to improve the friction-reducing antiwear abilities of metal–matrix composites.

2. Experimental

The plating bath used was a nickel sulphate bath. The composition and range of experimental operating parameters are given in table 1. The average particle sizes of SiC used in the experiment were about 6 and 10 microns. The crystal structure of SiC was identified by X-ray powder diffraction and it consisted of hexagonal α-phase. A nickel plate of $60 \times 70 \times 4$ mm was used as anode, and a mild steel plate of the same size of thickness, 1 mm, was used as the cathode. The bath was stirred by a magnetic stirrer and heated/maintained at the required temperature. Six Ni–Co–SiC and Ni composite coatings were produced under varying conditions of particulate size and their concentration in the electrolyte.

Each plating solution was thoroughly mixed by magnetic stirring for 10 h, and maintained at the operating parameters. Time taken for codeposition was 1 h. Complete ripple free rectifier was used for d.c. current of 2 amp. After codeposition, all the samples were cut. The mass increment of deposit was measured and estimated on the basis of the mass difference before and after electrocodeposition. The

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*Author for correspondence (rkyadava@rediffmail.com) layer thickness was estimated by using Leica Q 500 MC, a video image analyser and data processing software. The influence of metal quantity in both the particle sizes of SiC was investigated.

Surface microstructure was observed using a field emission scanning electron microscope. X-ray diffraction patterns of the composite coating were taken for structural investigation (Hitachi S-4200) provided with a digital system of image recording.

The microhardness of the codeposited coating was measured using Vickers diamond indenter at an applied load of 25 g for 10 s. The total thickness of the coating was around 110 μm. Further sliding wear test was performed on a machine consisting of sliding pins of test materials against hardened En 24 steel discs of 120 mm diameter and of hardness $57R_c$. The sliding speed, 0·5 ms^{-1}, and sliding distance, 400 m, were maintained constant. The wear was expressed as volumetric wear factor (cm^3/Nm). This wear factor was calculated by dividing the total volumetric wear loss by applied load and total sliding distance. SEM micrograph after wear test was taken. Corrosion testing was done by weight loss method in 3·5% NaCl water for 192 h. The samples were weighed after every 24 h and weight loss was calculated using Mettler electronic balance with an accuracy of 0·0001 g. Then corrosion rate was converted to MPy. The surface of the worn specimens was studied using an image analyser and a scanning electron microscope.

To observe the corrosion behaviour of the electrodeposited Ni–Co–SiC composite, a novel film of corrosion resistant metal chromium was prepared on composite substrate by its electrodeposition in a bath containing 150 gl^{-1} of $Cr_2(SO_4)_3 \cdot 6H_2O$ of pH 2·5, current density, 2 A/dm^2, temperature, 60°C of 2 h duration. Dilute sulphuric acid was used to adjust the electrolyte pH.

3. Results

The variables of the bath were determined as the optimum value after several hit and trial attempts. This ensured a smooth codeposition layer surface as well as more codeposition of SiC were achieved under the conditions of pH, 4·5, temperature, 55°C and current density, 2 A/dm^2 and sodium lauryl sulphate as surfactant (Ferkel *et al* 1994; Mockute *et al* 2002). The surface morphology of a typical Ni–Co–SiC codeposition layer is shown in figure 1. It is apparent that the composite layer obtained in this method is smooth and SiC particulates are uniformly distributed in the Ni–Co matrix. The cross-section of this layer also exhibits uniformly distributed SiC particles in the matrix. This also confirms that the chosen parameters for electrodeposition were suitable. The presence of surfactant sodium lauryl sulphate improved the deposition. The effect of varying the particle size and concentration was observed for further testing. It is apparent that improving the concentration of SiC in the electrolyte increases its incorporation in the layer. This greatly affects its properties such as hardness, wear behaviour and corrosion protection.

The SiC particle size distribution in the layer shows that particles ranging from 6–10 μm in size are dominant in the deposition layer. The lesser weight presence of larger particles suggests that it is difficult to embed them into the deposition layer. It is well known that when an inert particle is successfully embedded on the cathode, it should overcome the dislodging force acting on it. Basically, the smaller particles are easier to deposit since the dislodging forces acting on the particles become correspondingly smaller. The deposition greatly depends on the inert particle size. Data of variation in coating thickness with vol. % of SiC in electrolyte for different particle sizes is given in table 2. With regard to the surfactant, it has been reported that surfactant improves zeta potential of the particulates. This increased zeta potential offers an extra adhesion force between the inert particles and the cathode and results in increasing amount of the embedded SiC particles.

Table 1. Operational parameters of Ni–Co–SiC composite coating.

$NiSO_4 \cdot 6H_2O$	250 g/l
$NiCl_2$, $6H_2O$	30 g/l
H_3BO_3	40 g/l
$CoSO_4 \cdot 7H_2O$	40 g/l
SiC particles	25–75 g/l
Sodium lauryl sulphate	0·2 g
Parameter for equipment setup:	
Current density	2 A/dm^2
Temperature of bath	55°C
pH	4·5
Stirring rate	250 rpm
Plating time	60 Min
Density of nickel	8·902 g/cm^3
Density of SiC	3·217 g/cm^3

4. Discussion

The experimental results have revealed the influence of concentration and particle size of SiC in the electrolyte on

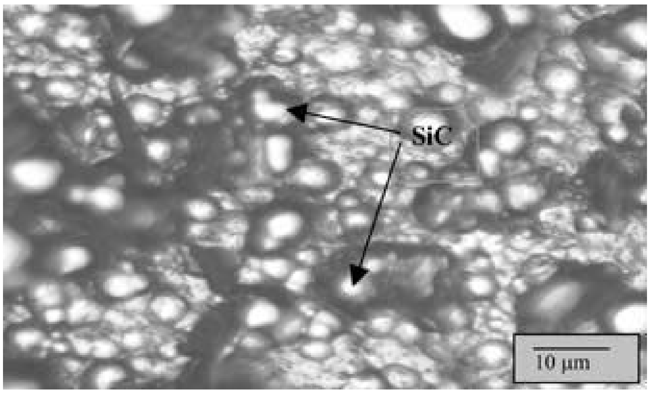

Figure 1. Image analyser micrograph of Ni–Co–SiC composite coating.

Table 2. Variation in hardness with volume fraction of SiC particles on the deposits as functions of particle size and concentration in the bath (hardness of Ni–Co coating, 240 VHN).

Size of SiC particle	Concentration of SiC particles suspended in electroplating bath (g/l)	Average value of coating thickness	SiC content in the deposit (Vol. %)	Average value of Vickers hardness $(\mathrm{kg/mm^2})$
6 µm	25	30·2	5·8	410
	50	50·5	11·0	456
	75	62·6	16·2	517
10 µm	25	36·4	6·4	477
	50	58·8	12·6	512
	75	75·7	17·8	573

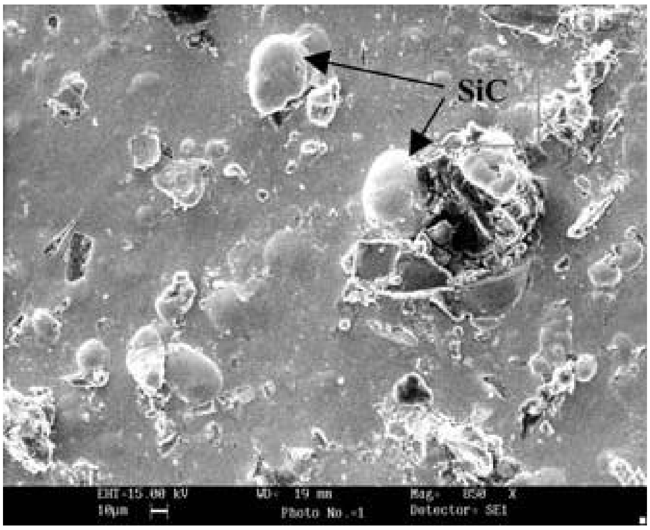

Figure 2. SEM micrograph of Ni–Co–SiC composite showing agglomeration of SiC particles (electrodeposition without surfactant sodium lauryl sulphate).

the incorporation of SiC in the composites. The mechanism of composite Ni–Co–SiC nano-coatings formation can be explained by a phenomenon of SiC adsorption by Ni–Co ions of the electrolyte. Together with an increase in the SiC amount in the bath, the Ni–Co ions adsorbed on the SiC particle rises and their discharge in this form on the cathode takes place. Addition of $CoSO_4$ in the electrolyte significantly enhances hardness of the Ni–SiC codeposition. The coating thickness shows a variation over varying size and concentration of SiC in the electrolyte. The higher the concentration of SiC, the higher is the vol. % of deposition and thickness of coatings as well (table 2). The lower SiC particle size gives the lesser vol. % of deposition. This is attributed to the fact that heavy particles are difficult to be carried by the Ni–Co ions due to lower effect of their throwing power. Higher concentration of SiC particles in electrolyte promotes agglomeration and increases the difficulty to keep particles uniformly mixed and suspended in the plating bath. Figure 2 shows a typical microstructure consisting of irregularly shaped electrodeposited particles of SiC embedded in Ni–Co matrix as revealed by the scanning electron microscope.

The agglomeration of SiC particles results in non-uniform distribution in the matrix, however, this problem was significantly overcome by the addition of surfactant like sodium lauryl sulphate in the electrolyte. It was confirmed that addition of suitable surfactant could not only improve the stability of the suspension by reducing the surface tension and the surface charge of suspended particles but also enhances the electrostatic adsorption of suspended particle on a cathode surface by increasing their positive charge. This addition indeed decreases the agglomeration of SiC particles. Therefore, a higher percentage of uniformly distributed submicron SiC particles were obtained. These SiC particles being spherical in shape got deposited along with Ni–Co during electrodeposition on the substrate. Well dispersed SiC particles appeared in white particle shape. But the increased amount of surfactants adsorbed on the surface of the inert particles would enhance the possibility of the weak and strong adsorption effect (Fransaer *et al* 1992). As mentioned above, dispersion of inert particles in the bath is important since it will affect the amount of the codeposited inert particle as well as homogeneity in the matrix.

The maximum vol. % of deposition in our procedure is obtained with 6 µm grit size having a concentration of 75 g/l in the electrolyte at pH 4·8. The effect of variables of bath concentration and particle size in the codeposited Ni–Co matrix is incorporated in table 2. It appears that the volume of deposition is very much affected by the particle size. The deposition in 6 µm size is more in comparison to that of 10 µm size. Uniform distribution of SiC particles in the deposit was observed in SEM micrograph. The SiC particle size distribution in the layer is elucidated by image analysis technique. It appears that the volume fraction of codeposited SiC particles increases with the SiC concentration in the electrolyte. It may be ascribed to the fact that sodium lauryl sulphate assists in the SiC codeposition (Benea *et al* 2001).

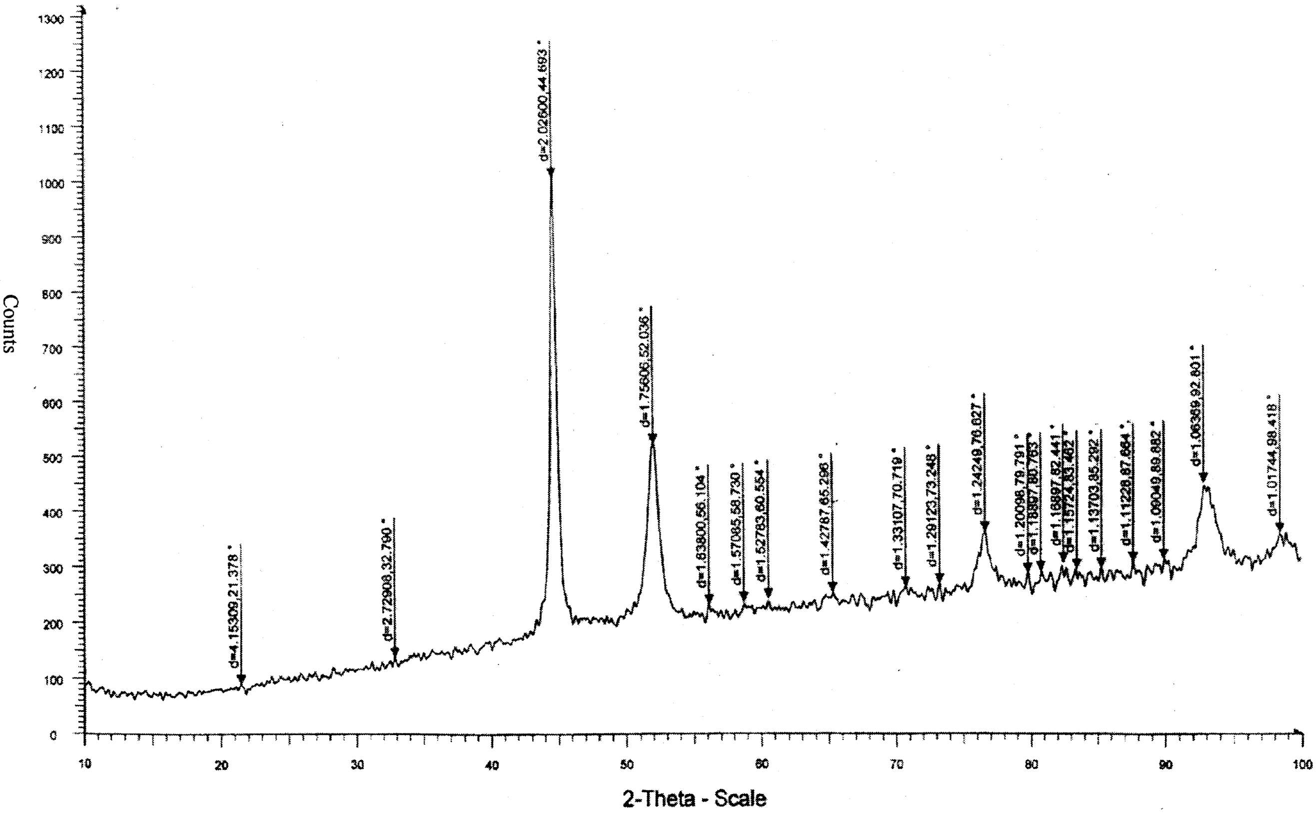

Figure 3. X-ray diffraction profiles of the electrodeposited Ni–Co–SiC composite coating.

The X-ray diffraction pattern revealed the presence of SiC in the Ni–Co crystalline matrix during electrodeposition (figure 3). The pure Ni peak is obtained at $2q = 45°$, 52°, 76°, 99°. The maximum intensity peak was obtained for (111) plane. The cobalt peak was obtained at $2q = 93°$ but only one characteristic peak is observed due to the lesser volume presence of Co content in the coating (i.e. $< 5\%$ by volume). The presence of SiC is also indicated by weak characteristics line in the range of $2q = 56–75°$ and $2q = 80–89°$. This pattern confirms that the Ni is present as main element in the matrix containing Co and SiC in the binder phase.

The microstructure also shows that the amount of SiC particles embedded in the matrix enables the codeposition layer to resist wear. Vickers hardness of composite coatings were measured. The Vickers hardness increases with increasing amount of SiC particles in Ni–Co coatings (table 2). Microhardness of Ni–Co matrix was observed to be 240 kg/mm^2. The hardness values of composite ranged from a minimum of 410 kg/mm^2 to a maximum of 573 kg/mm^2 of SiC particle content. The Vickers hardness of SiC is very high as compared to Ni–Co plating. The Vickers hardness of all Ni–Co–SiC coatings investigated is higher than the pure Ni–Co electroplating. Lower hardness value is obtained at a lower volume percentage of 10 μm size SiC particles. Indeed, it is known that the hardness and other mechanical properties of the metal matrix composites depend in general on the amount and size of the dispersed phase, apart from the mechanical characteristics of the matrix, particles and interfaces.

The amount and size define two kinds of mechanism in the metal matrix composites viz. dispersion strengthening and particle strengthening. A dispersion-strengthened composite is characterized by a dispersion of fine particles with 6 μm size. The optimum performance is also dependent on the interparticle spacing (i.e. the distance between the two SiC particles deposited), because in dispersed phase the matrix carries the load and the fine particles impede the motion of dislocations. The inter particle distribution is also a dominant consideration. If the inter particle spacing is larger than 5 μm the load is carried by both the matrix and the particles. This is proven by Garcia observation (Garcia *et al* 2001). So, in our experiment, 10 μm size reinforced strengthening is achieved because particles restrain matrix deformation by a mechanical constraint. Actual mechanism which is active in the Ni–Co–SiC composite coating of this work becomes evident by plotting of the Vickers hardness and wear behaviour of these coatings. The increase in hardness noted in these composite coatings containing 10 μm size as compared to 6 μm is linked to the particle strengthening effect. Higher volume percentage deposition is obtained with 6 μm size. Presence of fine SiC particles make the dispersion more uniform throughout the Ni–Co matrix but it also makes the structure brittle due to inherent brittle nature of the SiC particles. On the contrary, for the 10 μm size of SiC, the deposition of SiC is lesser so the interparticle spacing is more and these are rigidly held as reinforcements in the Ni–Co matrix (Saitou *et al* 2002; Kumar *et al* 2004). Due to bigger size of SiC in case of 10 μm size, the surface coating is coarser and the other contacting wear surface comes in contact with the SiC particles first and then the Ni–Co matrix. SiC ceramic having high hardness and wear resistance is accounted for the higher hardness and high wear resistance of 10 μm size deposition as compared to 6 μm. The highest hardness and wear resistance in this experiment is obtained with 10 μm size particle having 75 g/l concentration in the electrolyte. Figure 4 shows comparison of wear characteristics for different SiC particle sizes. The coating at different concentrations show that a low volume percent of submicron SiC particles in the coating results in nearly same wear resistance as a coating containing a higher volume percent of micron sized particles. The abrasive wear in the wear tracks after the sliding test suggests that the debris and pulled out SiC particles have an adverse effect when they remain in the sliding contact area (Hou *et al* 2002). A competition thus takes place between the beneficial increase in the hardness due to reinforcing SiC particles codeposited with the Ni–Co matrix and their adverse abrasive effects. The abrasive wear of the metal matrix composites increases with increasing amount and size of the abrasive particles, as does the hardness of the metal matrix composites. Therefore, in composite coating the increase in size of the particles codeposited in both the cases is positive. An increase in the number density of the codeposited particles produces higher hardness and the mechanical strength, also results in increase in the abrasion wear when reinforcing particles are pulled out of the composite coating during sliding wear (Wang *et al* 2004). This costrengthens the bonding between SiC particles and Ni matrix. The SEM micrograph (figure 5) shows that the wear in case of 10 μm takes place in steps due to elastic sliding of the SiC particles and they are pulled out of matrix making a pit on the surface. On the contrary 6 μm size being smaller do not occupy more surface area in the matrix. So their bonding with matrix is poorer as compared to the coating of SiC of 10 μm size.

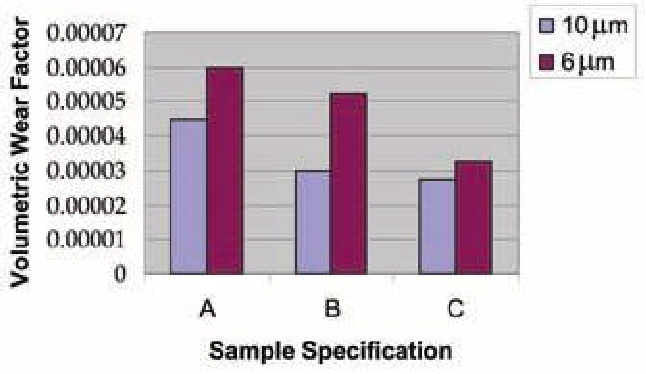

Figure 4. Variation in wear characteristics of Ni–Co–SiC composite coating with size and volume of SiC particles present in the electrolyte.

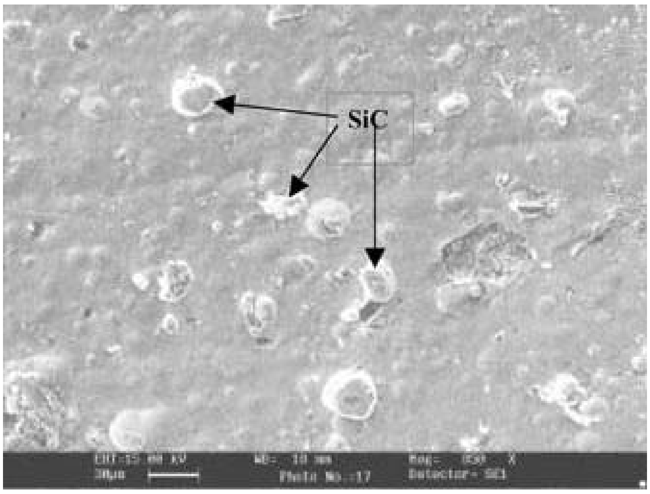

Figure 5. SEM micrograph of Ni–Co–SiC deposition composite coating after wear showing worn out SiC particles.

The corrosion study has shown that the corrosion rate improves significantly with Cr deposition. The corrosion rate is slower for high concentration of SiC particles due to excellent corrosion resistance of ceramic particles. However, the surface of the coating deteriorates more with the 10 μm size particles. It is due to the fact that near the surface the coarser sized SiC particles are easily attacked by the salt sodium chloride solution. In Ni–Co matrix the SiC embedded region is more prone to crevice type of corrosion. This looses the SiC and fresh nickel surface is exposed for reaction with sodium chloride. This leads to pitting corrosion. The lower effect of salt on the 6 μm size coating is due to uniformly distributed SiC particles in Ni–Co matrix.

5. Conclusions

Based on the above investigation, the following conclusions are drawn:

(^{2}) It is feasible to prepare Ni–Co–SiC composite with co-deposition of corrosion resistance chromium in the Ni–Co electroplating bath. It shows a size dependent co-deposition behaviour of SiC particles. Codeposition efficiency increases substantially with decreasing particle size.

Addition of surfactant compound like sodium lauryl sulphate in the electrolyte additionally results in better homogeneous dispersion of SiC. Particles in the electrolyte favour the positive contribution to enhance the embedded SiC volume percent in the deposition layer.

The volumetric wear increases with decreasing particle size of SiC. This is due to reduced interparticle spacing of SiC particle in nickel–cobalt matrix.

(V) The increased hardness observed in this composite is due to high particle volume percentage of SiC in the matrix.

(VI) The corrosion protection potential of Ni–Co matrix embedded with finer size of SiC particles increases due to presence of chromium. The finer size of SiC particles gives better corrosion resistance as compared to coarse one. This composite coating shows substantial improvement in corrosion resistance as compared to pure Ni plating.

Acknowledgement

The authors would like to express their thanks to Prof. A N Tiwari, Indian Institute of Technology, Mumbai, for his kind assistance in carrying out scanning electron microscopy.

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