Co-deposition and microstructure of Ni-nano SiC coating on metal

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Abstract. The study on co-deposition of Ni-nano SiC in sulphamate bath was conducted with different nano SiC concentrations from 1 to 20 g/l. The deposition of light inert SiC nanoparticles in Ni plating was investigated by scanning electron microscopy SEM and X-ray dispersive spectrometer EDX measurements. The microhardness and corrosion resistance were also measured to evaluate mechanical and corrosion properties of Ni-nano SiC coating on metal.

Keywords: Co-deposition, SiC nanoparticles, composite coating, microstructure.

1. Introduction
The co–deposition of particles, such as oxides, carbides with metals has been a goal of composite development to achieve a combination of properties that is not achievable by any of the materials acting alone. Several studies have showed that electrochemically embedded particles bring special properties to produced composite coatings, which can meet industrial requests. For example, diesel and gas turbine engines are subjected to high temperature corrosion and there is a great need to develop beneficial coatings for them. Recently, the ability to produce new composite materials based on reinforcing powders of decreasing particle sizes is very promising. It is proved that uniform dispersion of the co-deposited particles leads to the improvement of the mechanical, tribiological, anti-corrosive and antioxidized properties of the coatings [1, 2].

At present, the electrochemical deposition of nano-size particles in a metallic matrix has led to a new generation of composites due to the advantages of this technique. Ni–nano SiC composite, in particular, has been investigated for its high wear resistance. This property has led to commercial use in protection of friction parts, combustion engines and casting moulds [3, 4]. The main challenges in the co–deposition of nano–size SiC inert particles seem to be the co–deposition of a sufficient number of particles and avoiding the agglomeration of particles suspended in the plating solution. Our work aims to compare the mechanical properties and wear corrosion of pure Ni and Ni–SiC nano-composite coatings.

2. Experimental
Nickel coating was electroplated on brass plates from a 55°C Ni sulphamate bath at current density of
Prior to electroplating, the brass plates were polished with emery paper up to grade 2000 and rinsed in distilled water. The Ni sulphamate solution contained 90 g l\(^{-1}\) Ni ions as Ni sulphamate, 3 g l\(^{-1}\) NiCl\(_2\), 40 g l\(^{-1}\) H\(_3\)BO\(_4\) and 2 ml l\(^{-1}\) wetting agent (1% sodium dodecyl sulfate). Solution pH was adjusted to 4.5–4.7. To make Ni–SiC composite coatings, SiC powders with different concentrations of 1, 5, 10, 15, and 20 gl\(^{-1}\) were gradually added to the Ni sulphamate solution. The selected commercial SiC powder with an average diameter of 45-55 nm (Nanostructured & Amorphous Materials Inc., USA, β-SiC of 98% purity) was used as received without any treatment. The agglomeration was prevented by suspending the SiC particles in electrolyte and subjecting to magnetic stirring for a period of 15 hours. Electroplating was carried out for 60 mins with two stirring speeds (speed 5 and 8), and the thickness of the resulting deposits was in the range of 25-30 μm. Ultrasonic cleaning of composite surface was then executed after the electrolytic deposition to ensure that SiC particles were not only absorbed on the surface but embedded in the Ni matrix.

The microstructure of various deposits was observed using SEM spectrometer (SEM HITACHI 4800). The mass percentage of co-deposited SiC was measured via EDX system. The microhardness of the distinct deposits was measured by indenting across the polished cross sections and reported as an average of three values (Microhardness Tester MHT-10, Anton Paar). The corrosion potential of Ni-nano SiC coating was estimated by porosity and polarisation resistance measurements. An electrolyte was used as 3.5% NaCl solution open cell. Electrochemical experiments were performed using a potentiostat connected with a frequency response analyser AUTOLAB PGS30. A platinum counter electrode and a Calomen SCE reference electrode were also used.

3. Results and discussion

Figure 1 shows the cross-sections of the various deposits observed under an optical microscope (x500). The SiC particles are not clearly visible on the surface because of their small dimensions. It is only noted that the surface of Ni-SiC coating with low SiC concentration 1-5 gl\(^{-1}\) is not flat (figures 1a, 1b). As the inert particles' concentration in the solution increases, the flatness of coating surface increases as well (figures 1c, 1d; 15-20 gl\(^{-1}\)).

Micrographies presented by SEM measurements allow comparison between a pure Ni coating (figure 2) and Ni with nano-silicone carbide coating (figure 3). From the scanning electron microscope
images we can see the differences on surface morphology of pure Ni and composite coatings. The pure Ni deposit has a rather regular surface, whereas the composite coating develops in lumpy (nodular) disturbed surface structure. Smaller grain sizes could be observed in the composite coating (figure 3b) than in pure nickel coating. The surface structures of the two types of coating are different and they are expected to have behavior different with respect to corrosion property.

![Figure 2. SEM images of pure Ni plating.](image)

![Figure 3. SEM images of Ni-nano SiC plating with 5 g/l of SiC in the plating bath.](image)

The presence of silicone carbide is determined by EDX spectrum (figure 4). From the general EDX analysis, the total amount of nano SiC particles inside the deposit with concentration of SiC 5 g/l in the plating bath was calculated at 5.40 wt.% (figure 4a). Figure 4b displays the position of the calculated sample. It is certain to conclude that as we increase the inert particles concentration in the solution, the particles amount in the deposit increases too. It can be proved by the microhardness measurement of Ni-nano SiC coatings.

The relationship between inert SiC particles concentration and hardness of coatings is showed in table 1. The microhardness of the plated layers was determined through optic microscopy on cross-sections of the coatings (figure 1). The obtained results indicate the hardness of the various deposits was in the range of 319 to 466 HV, which was higher than that of pure Ni coating (<300 HV). It means that the strength of the coatings was evidently enhanced with deposits of small dimensional SiC particles.
Figure 4. (a) EDX spectrum of Ni-SiC nano coating, (b) Position image of the calculated sample.

Table 1. The relationship between SiC concentrations, hardness and corrosion porosity of Ni-nano SiC coatings.

| SiC concentration in solution, gl\(^{-1}\) | Hardness HV, kg/mm\(^2\) | Corrosion porosity density, cm\(^{-2}\) |
|------------------------------------------|---------------------------|----------------------------------------|
|                                          | Speed 5 | Speed 8 | Speed 5 | Speed 8 |
| 0                                        | < 300   | 7       |         |         |
| 1                                        | 319     | 339     | 14      | 10      |
| 5                                        | 328     | 328     | 11      | 8       |
| 10                                       | 364     | 382     | 7       | 8       |
| 15                                       | 378     | 393     | 6       | 7       |
| 20                                       | 387     | 466     | 4       | 5       |

Concerned with the different surface morphology of pure nickel and composite coatings, corrosion properties of coatings were tested. By porosity testing method, corrosion pore density was measured. The solution was a mixture of K\(_3\)[Fe(CN)\(_6\)] \(20 \text{ gl}^{-1}\) and NaCl \(10 \text{ gl}^{-1}\). The results shown in table 1 reveal that at low SiC nanoparticles concentration porosity density of the deposit is higher than pure nickel deposits, but it has decreased when the SiC concentration in deposits has increased. All the measurements in table 1 were carried out on coatings of two stirring speeds 5 and 8. It can be seen that at higher stirring speed, the hardness of the coating is higher but the porosity performs higher also when SiC concentration increases.

Figure 5. Impedance diagrams performed in NaCl 3.5% at different SiC concentrations of Ni-SiC coatings.
To verify corrosion property of Ni-SiC coatings polarisation resistance was measured also. It is evident that corrosion speed is low when resistance is high. Figure 5 shows the impedance diagram performed in 3.5% NaCl solution. The polarisation resistance of nano-composite coating is lower than that of pure nickel coating (12 kΩ cm$^{-2}$) when SiC concentration is low (7 kΩ cm$^{-2}$ at 1 gl$^{-1}$ SiC concentration and 9 kΩ cm$^{-2}$ at 10 gl$^{-1}$ SiC concentration), but it is higher when SiC concentration increases (13 kΩ cm$^{-2}$ at 20 gl$^{-1}$ SiC concentration). This result coincides with the measurement of porosity density of coatings, where increasing SiC deposit the porosity of coating decreases and hence corrosion resistance improves.

Gyftou et al. [5] in tribiological study of Ni matrix composite coatings containing nano and micro SiC particles considers that there are two factors correlated to improving wear resistance in Ni/SiC deposits: a variation of incorporation percentage of the SiC particles and the modification of crystallographic orientation. In the case of nano-size particles the influence on the adsorption-desorption phenomena during electrocrystallization is mild and all the deposits conserve the preferred orientation, but the observed changes of its quality are sufficient to alter the wear resistance. It is confirmed with our study on microstructure of Ni-nano SiC coatings on metal, where different deposits of SiC nanoparticles in plating clearly affect its corrosion properties.

4. Conclusion
In this work, the co-deposition and microstructure behaviour of a pure Ni and Ni with nano-structured SiC composite coatings were studied.

- An increase of coating hardness was observed with an increase of inert SiC particles amount in the deposit.
- At SiC concentration of 15-20 gl$^{-1}$ with particles size 45-55 nm and magnetic stirring, the hardness of the deposit is between 400 and 450 HV.
- The porosity of coatings decreases with increasing SiC concentration above 15 gl$^{-1}$, and corrosion resistance of nano-structured SiC-nickel composite coatings performs better compared to Ni coating.
- A proper choice of concentration and plating condition can lead to production of composite deposits that enhances both hardness and wear resistance.

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Acknowledgments
The authors wish to thank Dr. Ph. T. San, Dr. P. D. Long and Mr. D. H. Manh in the Institute of Materials science, VAST for their help in structure measurements. This research is supported by the Vietnamese National Fundamental Research program 2006-2008.