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COMPARATIVE PERFORMANCES OF NI-SIC COMPOSITE COATINGS DEPOSITED BY CONVENTIONAL AND BRUSH ELECTROPLATING

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ABSTRACT

SiC particles are known as reinforced materials used to improve the coating's properties and performances. In this paper, Ni - SiC composite coatings were deposited by conventional electroplating from sulfate-chloride bath, and brush electroplating methods from modified chloride bath with different dispersed SiC contents. The plating conditions were investigated and the process' parameters were defined through electrochemical technique. Scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and micro-hardness test were used to clarify the effect of SiC content on coating's properties and performances. The hardness of brush electrodeposit reached the highest value of 525 HV when the concentration of SiC in the plating solution was 4 g/L, while the hardness of conventional electrodeposit was only 389.3 HV when the plating bath contained 20 g/L SiC. The characterized results show clear advantages of brush electroplating compared to the conventional method to form the coating with high micro-hardness.

Keywords: brush electroplating, sulfate-chloride bath, Ni - SiC composite coating, inert particle.

TÓM TẮT

So sánh tính chất của màng composite Ni-Sic được mạ bằng phương pháp mạ bể dung dịch và phương pháp mạ xoa

Hạt SiC được xem là vật liệu gia cường nhằm cải thiện tính chất và ngoại quan của các lớp màng composite. Vì vậy, trong bài báo này, lớp màng composite Ni - SiC được chế tạo bằng phương pháp mạ bể sulfate-chloride và phương pháp mạ xoa có gia cường bằng hạt SiC với các hàm lượng khác nhau. Các thông số của quy trình mạ được xác định bằng các kĩ thuật điện hóa. Các phương pháp phân tích và đánh giá tính chất vật liệu như kính hiển vi điện tử quét (SEM), phổ tán sắc năng lượng tia X (EDS), phương pháp đo độ cứng tế vi được sử dụng để khảo sát sự ảnh hưởng của nồng độ hạt SiC trong dung dịch mạ lên tính chất của lớp mạ. Độ cứng của lớp mạ xoa đạt giá trị cao nhất là 525 HV khi nồng độ của SiC trong dung dịch mạ là 4 g/L, trong khi đó độ cứng của lớp mạ bể chỉ đạt 389.3 HV khi sử dụng SiC ở nồng độ 20 g/L. Các kết quả nghiên cứu cho thấy rằng so với mạ bể, mạ xoa có nhiều ưu điểm hơn, đồng thời tạo ra lớp mạ có độ cứng tế vi cao hơn.

Từ khóa: mạ xoa, bể sulfate-chloride, màng composite Ni - SiC, hạt trơ.

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1. Introduction

Metal composite coatings containing inert particles such as silicon carbides, silicon nitrides, etc. have long been used in industrial applications. Among various investigated and applied metal composites, the nickel-silicon carbide coating (Ni-SiC) has attracted great attention from research and industry [1-4]. This type of composite coatings can be prepared via different methods, amongst which electrochemical deposition is considered most popular due to the simplicity of equipment used and convenient process control. Traditionally, the deposition is conducted via electroplating in conventional bath method with defined SiC particle content under stirring condition [2, 3]. Recently, the brush electroplating method using a modified chloride solution was proposed and applied in practice [5].

For decades, composite coatings with embedded SiC particles have been investigated intensively. These composite coatings express superior properties, including higher hardness, better erosion and corrosion resistance when the embedded particles sizes are reduced from micro- to nanoscale. However, with the reduction of particle size, the co-deposition content of the particles is also decreased, which substantially influences the coatings properties and performances [4-9]. Using the bath electroplating with sulphate-chloride solution, according to Calderon J. A. et al., the incorporation of SiC particles (average particle size of 25 nm) in nickel deposit produces refined grain and modifies the crystal structures, which enhances the Ni-SiC composite coatings' performance [4]. With similar bath composition, Giftou P. et al. reached 10% (vol.) of SiC incorporation percentage under direct current plating and even more under pulse plating conditions [8]. With brush plating, Nguyen D. H. et al showed a significant particle incorporation percentage in composite with 6.7% SiC (average particle size of 20 nm) at 120 A/dm^2 cathodic current density and an increase of microhardness to 450 HV for Ni-SiC layer, compared to the coating deposited from single nickel bath plating [5]. Hence, co-deposition technique can impact the particle incorporation into metal matrix, resulting in change of the coating's properties and its performance.

In this paper, to better understand the process and improve the coating's properties, Ni-SiC composites were prepared by the conventional and brush electroplating methods with different SiC content in solution. In conventional electroplating method, SiC particle suspended in the plating solution, while SiC particle clung to anode wrapped by absorbing foam material in brush electroplating method. Therefore, the SiC concentration in plating solution were 0÷25 g/L [10] and 1÷5 g/L [5], in conventional and brush electroplating methods respectively. Moreover, the SiC particle incorporation into deposit was investigated, and comparative performance characterization was conducted for both types of electroplated coatings.

2. Materials and methods

2.1. Samples preparation and co-deposition procedure

The Ni-SiC composite coatings were electrodeposited from aqueous nickel sulfate – chloride electrolytes with SiC nanoparticles suspension (average particle sizes of 200 nm). In the conventional electroplating method, the sulfate-chloride bath was used with following composition: 1.0 M $NiSO_4.7H_2O$, 0.15 M $NiCl_2.6H_2O$, 0.5 M H_3BO_3, 0.2 M $Na_3C_6H_5O_7$, 0.007 M $NaC_{12}H_{25}SO_4$, and SiC content in a range of 0÷25 g/L. For brush electroplating, the modified chloride complex solution was applied with following chemicals: 2.1 M $NiCl_2.6H_2O$, 2.2 M NH_4Cl, 0.25 M $(NH_4)_3C_6H_5O_7$, 0.35 10^{-3} M $NaC_{12}H_{25}SO_4$, and SiC content in a range of 1÷5 g/L [5]. The preferentially high chloride bath was used for enhancing conductivity and current distribution in solution-limited brush plating method. The pH values of both solutions were stabilized at 4.0 – 4.5 and temperature range was maintained from 40 to 50 ^oC.

The conventional electroplating process was performed in the sulfate-chloride solution, using nickel anode foil and CT3 mild steel (according to GOST 3SP/PS 380-94 standard) cathode substrate with 3x1.5x1.0 cm dimensions. The cathode substrate was pre-treated by mechanical polishing using emery paper down to 1200 grade, followed by degreasing in acetone/ethanol mixture, acid pickling, washing and drying in desiccator.

In the case of brush electroplating, a similar pre-treated mild steel substrate was connected to the negative output of a DC power supply, acting as a cathode. A MMO coated titanium anode described in [6] was wrapped with an absorbing foam material and connected to the positive anode of DC power supply. As above prepared plating solution was absorbed in foam and applied to the cathode substrate to close the electrolytic circuit. With the anode moving over the cathode surface, the electrodeposition process was continuously supported.

2.2. Characterization of coatings

Electrodeposition of composite coatings on steel cathode was investigated by the Autolab PGSTAT 30 potentiostat (Ecochemie B. V., The Netherlands) of the Institute for Tropicalization & Environment (ITE). Polarization curves were measured to define the dependence between electrochemical parameters and SiC contents in plating solutions. In the electrochemical cell arrangement, a steel cylinder with area of 0,785 cm^2 was used as working electrode for cathodic polarization measurement, the Ag/AgCl was served as reference electrode, and platinum rod was selected as counter electrode.

The morphology of the coatings was examined by scanning electron microscopy JSM 6480LV (Jeol, Japan) of the Institute for Nanotechnology (INT). The composition of the composite coating was tested by the energy dispersive analyzer system (EDS) of Laboratory for Nanotechnology (LNT).

The coating microhardness was measured by HWMMT-Xeries Microhardness Tester

of the Material Technology Key Lab. (MTLab, HCMUT) and the test forces were 100 gf and 200 gf.

3. Results and discussion

3.1. Electrochemical behavior of Ni-SiC composite co-deposition

Dependence between electrochemical parameters derived from the polarization curves and SiC contents in the plating solutions for bath and brush plating processes was described in Fig. 1 and Fig. 2 respectively. The similarity of the polarization behavior was revealed for both conditions.

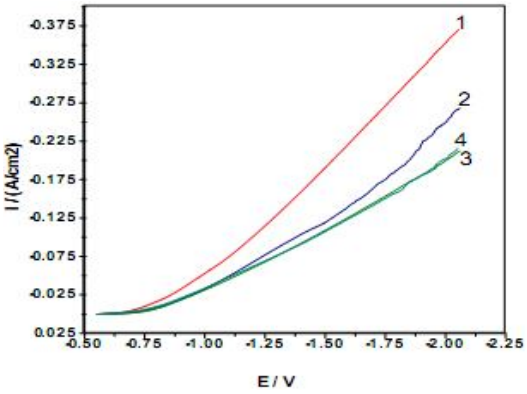


Figure 1. *Polarization curves at different SiC contents in bath plating solution.*
(1: 0 g/L SiC; 2: 15 g/L SiC; 3: 20 g/L SiC; and 4: 25 g/L SiC)

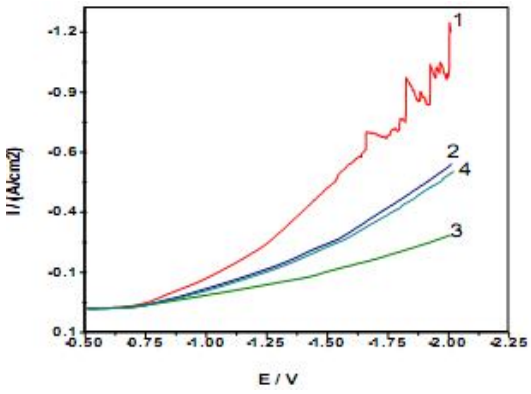


Figure 2. *Polarization curves at different SiC contents in brush plating solution.*
(1: 0 g/L SiC; 2: 3 g/L SiC; 3: 4 g/L SiC; and 4: 5 g/L SiC)

Cathodic polarization in bath conditions (Fig. 1) showed more negative discharge potential in the electrolyte with SiC inert particle suspension compared to the electrolyte without these particles. The increase in cathodic polarization proved the SiC incorporation into the nickel matrix. Otherwise, the cathodic polarization increased with SiC suspension contents up to 20 g/L and slightly decreased at 25 g/L SiC content. This could be explained by concurrent deposition rate of discharged nickel and approached SiC particles to the cathode substrate. The extremely high SiC content in the electrolyte could slow down the particle embedding process into nickel matrix [8].

For brush plating conditions, the similar potential behavior was observed during cathodic polarization (Fig. 2). The polarization also increased with SiC content rise in the plating solution and this tendency reached the maximum value at 4 g/L SiC suspension with slight decrease afterward.

From observation of the coating's surface appearance and polarization curves presented in Fig. 1 - Fig. 2, the higher current density could be applied in the case of brush plating bath with aforementioned chemical composition compared to the conventional sulfate-chloride bath.

3.2. Effect of SiC content on Ni - SiC coating hardness

To reveal the influence of particle co-deposition on the coating hardness, the brush plating process was conducted at 70 - 80 A/dm^2 current density and 1 - 5 g/l of SiC in plating solution. Fig. 3 and Tab. 1 showed the dependence of coatings microhardness on different SiC contents with clear direct proportional relationship at the initial stage; however, a maximum microhardness was achieved at 4 g/L SiC content. With further increase of SiC content, microhardness took a fall and at 5 g/L SiC content, became even smaller than the value recorded at 2 g/L SiC content. That means abundant SiC content resulted in saturation, and therefore, under the same plating process, the concurrent incorporation of codeposition process caused possibly fewer SiC inclusion into the metal matrix, reducing the coating microhardness. This suggestion can be reaffirmed considering the dependence between incorporated SiC content in the coating and suspended SiC content in the plating solution.

Fig. 4 and Tab. 1 revealed the percentage weight of SiC content in the composite coating at different SiC contents in the brush electroplating solution. With SiC content changing from 0.5 g/l to 4 g/l, the coating's SiC percentage constantly increased reaching a maximum 4 g/L SiC content in the solution. These results were consistent with the above relationship between the coatings hardness values and the SiC concentration. The highest hardness of brush electrodeposit was 525 HV when the SiC concentration was 4 g/L and the percentage of SiC weight was 4.4%.

Table 1. *The hardness and percentage of SiC weight of brush electrodeposit at different SiC contents in solution*

No.	SiC concentration in plating solution (g/L)	Percentage of SiC weight of brush electrodeposit (%)	Microhardness of brush electrodeposit (HV)
1	1	3.62	420
2	2	4	500
3	3	4.2	505
4	4	4.4	525
5	5	3.8	455

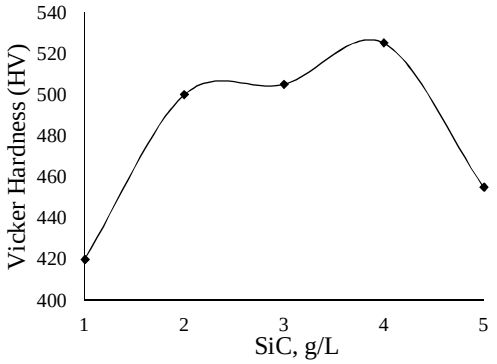


Figure 3. *The hardness of brush electrodeposit at different SiC contents in solution.*

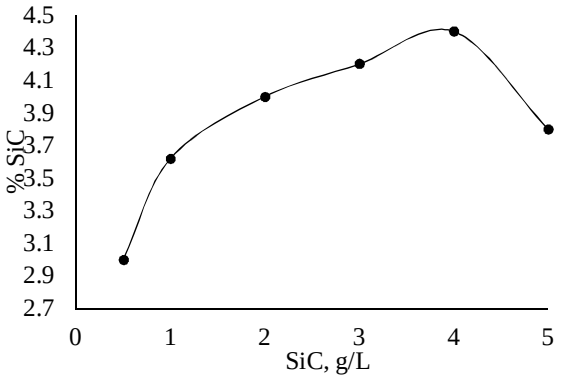


Figure 4. *The percentage of SiC of brush electrodeposit at different SiC content in solution.*

For reference, the electrodeposition process from conventional sulfate-chloride solution was also conducted with the following plating conditions: current densities in a range from 4 to 8 A/dm^2, SiC contents from 0 to 25 g/l. The presented result of 389.3 HV was produced from coating electroplated at 6 A/dm^2 in solution containing 20 g/L SiC (Fig.5 and Tab. 2). EDS spectrum in Figure 6 proved the presence of SiC on the conventional electrodeposited coating. The comparative results for conventional and brush electroplating are depicted in Fig. 7.

Table 2. *The hardness of conventional electrodeposit at different current*

No.	i (A/dm^2)	Microhardness of conventional electrodeposit (HV)
1	4	322.5
2	5	375.4
3	6	389.3
4	7	366.6
5	8	363.2

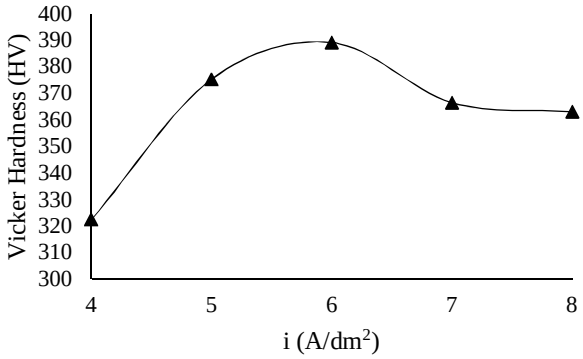


Figure 5. *The hardness of conventional electrodeposit at different current*

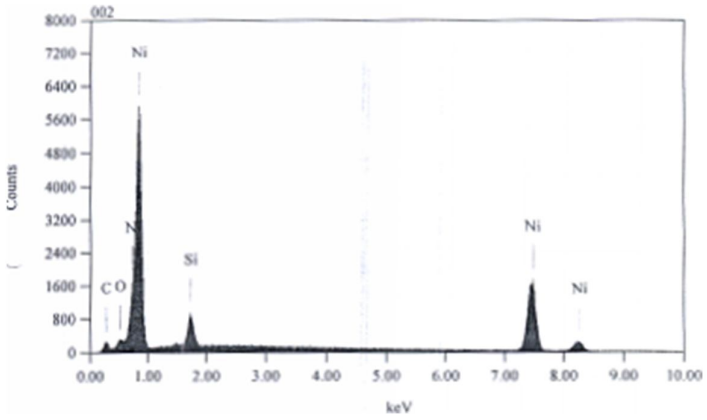


Figure 6. *EDS spectrum of conventional electroplated coatings at 6 A/dm^2 in solution containing 20 g/L SiC*

Fig. 7 revealed that the coatings formed by brush electroplating express higher microhardness than those obtained from conventional bath electroplating. Although SiC content in brush plating solution was considerably lower, compared to 20 g/L in bath plating, the higher microhardness proved the greater particles incorporation. This difference could also be observed through SEM image analysis for both types of coatings, presented in Fig. 8.

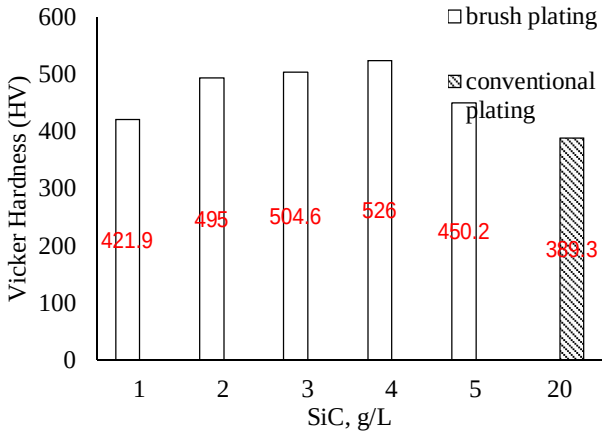
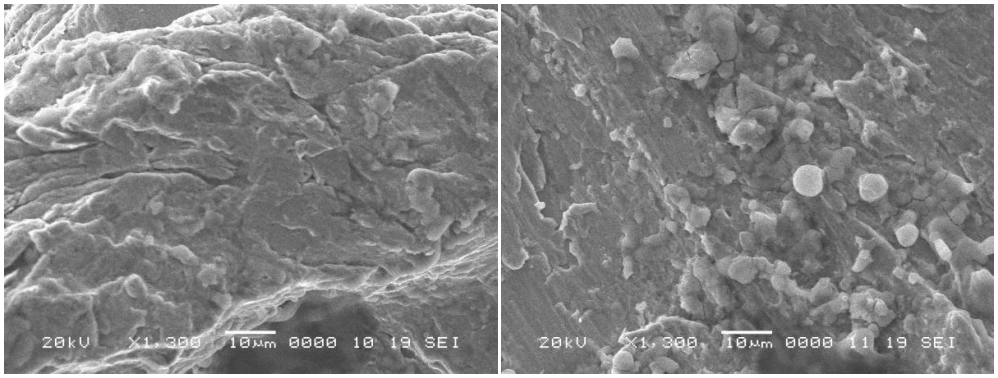


Figure 7. *The hardness of conventional and brush electroplated coating*

SEM image in Fig. 8a, derived from coating of bath plating process, reflected a smooth surface with relatively dispersed SiC particles appearance. Meanwhile, densely distributed particles were apparent on the coating surface deposited by brush plating method (Fig. 8b). These results once again could explain the higher microhardness for later mentioned electrodeposited coating.



a b

Figure 8. *SEM images of the coatings electrodeposited from: a. Conventional bath electroplating; b. Brush electroplating*

4. Conclusion

Ni - SiC composite coatings were prepared successfully from the conventional electroplating method by the standard sulfate-chloride bath and the brush electroplating method by the modified chloride bath. Compared to conventional electroplating, the coating plated from brush electroplating possessed better technological characteristics. The brush electrodeposit had 525 HV microhardness when the SiC concentration in solution was 4 g/L and the weight percentage of SiC was 4.4%. On the other hand, conventional electrodeposit achieved only 389.3 HV microhardness from coating prepared in solution containing 20 g/L SiC. From SEM images, the surface of brush electroplated coating had higher SiC density than that plated from conventional electroplating. These SEM results presented the correlation of surface properties with the hardness of the coating. In conclusion, the brush electroplated coatings were shown to possess superior characteristics versus coatings from conventional bath.

REFERENCES

[1] Benea L., Bonora P. L., Borello A., Martelli S., Wenger F., Ponthiaux P., Galland J., "Preparation and investigation of nanostructured SiC–nickel layers by electrodeposition," *Solid State Ionics*, vol. 151, pp. 89–95, 2002.

[2] Gyftou P., Stroumbouli M., Pavlatou E. A., Asimidis P., Spyrellis N., "Tribological study of Ni matrix composite coatings containing nano and micro SiC particles," *Electrochimica Acta*, vol. 50, pp. 4544-4550, 2005.

[3] Benea L., Bonora P. N., Borello A., Martelli S., "Wear corrosion properties of nano-structured SiC–nickel composite coatings obtained by electroplating," *Wear*, vol. 249, pp. 995-1003, 2002.

[4] Calderón J. A., Henao J. E., Gómez M. A., "Erosion-Corrosion Resistance of Ni Composite Coatings with Embedded SiC Nanoparticles," *Electrochimica Acta*, vol. 124, pp. 190-198, 2014.

[5] Đào Khánh Dư, Nguyễn Duy Kết, Nguyễn Đức Hùng, "Công nghệ mạ xoa với nano compozit TiO2, SiC," *Tạp chí Hóa học,* vol. 49, no. 1, pp. 79-83, 2011. (in Vietnamese)

[6] Nguyen Duc Hung, Nguyen Duy Ket, Nguyen Nhi Tru, Hoang Minh Duc, "DSA electrode rejuvenation for producing electrochemically activated solution," *Journal of Science and Technology,* vol. 47, no. 5A, pp. 415-425, 2009.

[7] Lee Hong-Kee, Lee Ho-Young, Jeon Jun-Mi, "Electrolytic deposition behaviors of Ni-SiC composite coatings containing submicron-sized SiC particles," *Metals and Materials International,* vol. 14, no. 5, pp. 599-605, 2008

[8] Gyftou P., Pavlatou E. A., Spyrellis N., "Effect of pulse electrodeposition parameters on the properties of Ni / nano-SiC composites," *Applied Surface Science,* vol. 254, pp. 5910-5916, 2008.

[9] Ger Ming-Der, "Electrochemical deposition of nickel/SiC composites in the presence of surfactants", *Materials Chemistry and Physics*, vol. 87, no. 1, pp. 67-74, 2004.

[10] Lidia Burzyńska et al, "Electrodeposition and heat treatment of nickel/silicon carbide composites," *Surface & Coatings Technology,* vol. 202, pp. 2545–2556, 2008.