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THE EFFECT OF SiO_2 NANOPARTICLE CONCENTRATION ON THE MORPHOLOGY, PHASE COMPOSITION AND MICROHARDNESS OF Ni-SiO_2 COATINGS PRODUCED BY SEMI-AUTOMATIC SELECTIVE ELECTROPLATING

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Abstract

Ni-SiO_2 composite coatings were produced on AISI 316L stainless steel by semi-automatic selective electroplating from electrolytes containing 0, 0.1, 0.5, and 1 wt.% added SiO_2 nanoparticles. The coatings were characterized by optical microscopy, X-ray diffraction, and Vickers microhardness testing. Increasing the SiO_2 concentration refined the surface morphology and influenced the cross-sectional structure, while the average coating thickness decreased from about 20 µm for 0 and 0.1 wt.% SiO_2 to 18 and 15 µm for 0.5 and 1 wt.% SiO_2, respectively. XRD confirmed the fcc Ni structure and showed changes in the relative peak intensities, with an increasingly pronounced Ni (111) contribution at higher nanoparticle additions. No distinct crystalline SiO_2 reflections were detected. Microhardness increased progressively from approximately 187 HV0.01 for the unmodified Ni coating to about 345 HV0.01 at 1 wt.% SiO_2, corresponding to an increase of approximately 84%. The results demonstrate that SiO_2 nanoparticle concentration strongly affects the morphology, phase development, deposition behavior, and hardness of selectively electrodeposited Ni coatings.

Keywords: Ni-SiO_2, nanocomposite coatings, selective electroplating, corrosion resistance, wettability.

INTRODUCTION

Nickel-based electrodeposited coatings are widely used for surface protection and functional surface modification because of their corrosion resistance, mechanical stability, and relatively simple deposition technology. In recent years, increasing attention has been directed toward metal-matrix composite coatings in which ceramic, oxide, carbide, or carbon-based particles are incorporated into the electrodeposited metallic matrix [1,2]. Nickel is particularly suitable as a matrix material, and particle-reinforced Ni coatings have been investigated as a means of modifying coating microstructure and improving hardness, wear resistance, corrosion behavior, and other functional properties [3,4]. The resulting performance depends not only on the characteristics of the Ni matrix but also on particle type, size and concentration, as well as on their dispersion and interaction with the growing deposit.

Among the possible reinforcing phases, SiO_2 nanoparticles are of interest for the modification of electrodeposited nickel. Recent investigations of Ni–SiO_2 coatings have shown that the presence of silica particles can affect coating morphology, microstructure, mechanical response, and corrosion behavior [5-7]. The effect of nanoparticle addition is strongly dependent on the conditions of electrodeposition. Particle concentration is particularly

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important because increasing the amount of suspended nanoparticles can modify metal nucleation and crystal growth, while excessive concentrations may promote particle agglomeration and nonuniform incorporation. Consequently, control of nanoparticle dispersion and electrolyte transport is essential for obtaining reproducible composite coatings.

Selective electroplating, commonly referred to as brush plating, provides an alternative to conventional bath electrodeposition by restricting deposition to a localized region of the component. In this process, electrolyte is continuously supplied to the contact zone between a moving anode tool and the cathodic workpiece. Recent studies have demonstrated the applicability of brush plating to Ni-based composite coatings reinforced with SiC, diamond, Al_2O_3, and other dispersed phases [8-11]. Compared with immersion electrodeposition, the continuously renewed electrolyte, localized electrical contact, and relative motion between the tool and substrate produce substantially different mass-transfer and deposition conditions. Particle dispersion is therefore particularly important; ultrasonication prior to electrodeposition has been shown to influence the structure and mechanical properties of particle-reinforced Ni coatings by improving the initial dispersion state of the suspension [12]. Brush-deposited nickel coatings have also demonstrated useful mechanical, corrosion, and wear characteristics, confirming the potential of the technique for localized surface modification [13].

Earlier investigations of conventionally electrodeposited Ni-SiO_2 nanocomposites have demonstrated that silica addition can modify the Ni microstructure and coating properties [14,15]. Nevertheless, comparatively little information is available on Ni-SiO_2 coatings produced by controlled selective brush plating, particularly concerning the effect of SiO_2 concentration on coating growth, thickness, crystallographic development, and hardness. This distinction is relevant because particle transport and incorporation during brush plating occur under continuously changing local hydrodynamic and contact conditions rather than within a conventional stationary plating bath. Increasing the concentration of SiO_2 in the supplied electrolyte may therefore affect not only the resulting coating structure but also the effective deposition rate.

The aim of the present study was to evaluate the effect of SiO_2 nanoparticle concentration on the morphology, coating thickness, phase composition, and microhardness of Ni-SiO_2 coatings produced on stainless steel by semi-automatic selective electroplating. Particular attention was given to the relationship between nanoparticle concentration, coating growth, structural development, and hardness under otherwise constant deposition conditions.

EXPOSITION

Experiment and characterization

Rectangular sheet specimens of AISI 316L stainless steel, 20 × 30 mm in size, were used as substrates. The surfaces were used in the as-received condition without additional grinding or polishing. Prior to electrodeposition, the specimens were electrochemically cleaned in an aqueous solution containing 5 wt.% NaOH and 1 wt.% citric acid, followed by surface activation in a solution containing 5 wt.% H_2SO_4 and 10 wt.% ammonium sulfate.

Pure nicklel and Ni-SiO_2 composite coatings were deposited from an aqueous nickel electrolyte containing 10 wt.% nickel formate, 20 wt.% nickel sulfate, 5 wt.% citric acid, and 1 wt.% aluminum sulfate. Four electrolytes were investigated, containing 0, 0.1, 0.5, and 1 wt.% added SiO_2 nanoparticles with a nominal particle size below 30 nm. Prior to deposition, the nanoparticle-containing electrolytes were ultrasonicated for 15 min to improve particle dispersion. During processing, continuous electrolyte circulation was provided by a peristaltic pump.

Selective electroplating was carried out using the semi-automatic system shown in Fig. 1. A nickel electrode with dimensions of 20 x 40 mm was mounted on a reciprocating linear actuator. The substrate area was masked with adhesive tape to define a 20 x 30 mm deposition region. A potential of 3 V was applied during deposition, while the actuator operated at a travel speed of 200 mm/s in a repetitive reciprocating motion. Contact pressure between the plating tool and the specimen was maintained at the minimum level necessary to ensure stable operation. Electrolyte was continuously supplied to the working zone by the peristaltic circulation system. The experiments were performed at room temperature. The deposition conditions were selected to obtain a nominal coating thickness of 20 µm for all specimens.

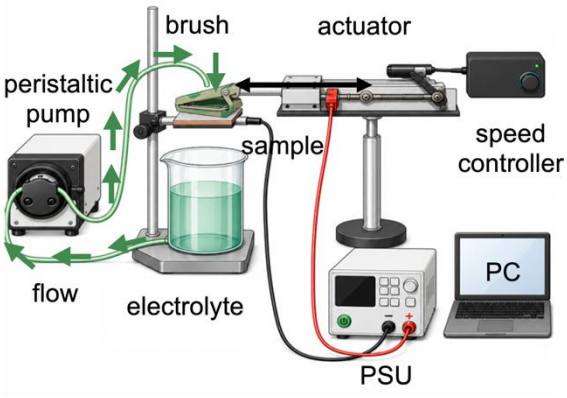


Fig. 1. *Semi-automatic selective plating setup*

For metallographic characterization, cross-sectional specimens were ground sequentially using P240, P400, P600, and P800 SiC papers and polished to a mirror finish using 1 µm diamond suspension. The polished sections were etched using 5% HNO_3. Surface and cross-sectional morphologies were examined using an LM-308 metallurgical microscope.

Phase analysis was performed using a TDM-10 diffractometer with Cu Kα radiation. Diffraction patterns were recorded over a 2θ range of 20-90° and evaluated using X'Pert HighScore software.

Microhardness was measured using an HVS-1000 semi-automatic Vickers microhardness tester with a load of 10 g and a dwell time of 10 s. Five indentations were made on each coating, and the results were evaluated as mean values with the corresponding scatter.

Morphology

Figure 2 presents the surface and cross-sectional optical micrographs of the Ni-based coatings deposited from electrolytes containing 0, 0.1, 0.5, and 1 wt.% added SiO_2 nanoparticles. The coating produced without SiO_2 exhibits a comparatively coarse and heterogeneous surface morphology, with clearly distinguishable nodular features. Addition of 0.1 wt.% SiO_2 results in a noticeably finer and more uniform surface appearance. Further increasing the nanoparticle concentration to 0.5 and 1 wt.% maintains the refined morphology, with a denser and more homogeneous distribution of surface features compared with the unmodified Ni coating.

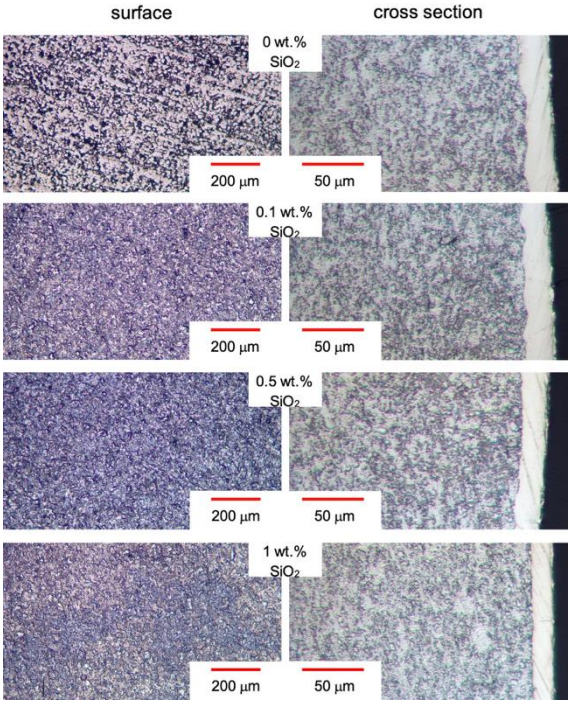


Fig. 2. *Surface and cross-sectional optical micrographs of Ni-SiO_2 coatings deposited from electrolytes containing 0, 0.1, 0.5, and 1 wt.% added SiO_2 nanoparticles.*

The cross-sectional micrographs show continuous coatings over the 316L stainless steel substrate for all investigated conditions, without obvious macroscopic cracking or delamination at the coating/substrate interface. The etched coating regions exhibit a fine heterogeneous microstructure whose appearance changes with increasing SiO_2 concentration. Because the SiO_2 particles are below 30 nm, their individual presence or distribution cannot be resolved by the present optical microscopy; therefore, the observed morphological changes should be interpreted as an effect of nanoparticle addition on the electrodeposition process rather than as direct evidence of particle incorporation.

The deposition parameters were selected to produce a nominal coating thickness of 20 µm. The coatings obtained with 0 and 0.1 wt.% SiO_2 reached approximately this target thickness, whereas the average thickness decreased to about 18 µm at 0.5 wt.% and 15 µm at 1 wt.% SiO_2. Since the remaining deposition conditions were maintained constant, this reduction indicates that increasing the nanoparticle concentration influenced the effective Ni deposition rate. At the same time, the progressive refinement of the surface morphology suggests that suspended SiO_2 nanoparticles affected nucleation and growth of the Ni matrix during selective electrodeposition.

X-ray diffraction analysis

Figure 3 shows the X-ray diffraction patterns of the coatings deposited from electrolytes containing 0, 0.1, 0.5, and 1 wt.% added SiO_2 nanoparticles. All specimens exhibit the characteristic reflections of face-centered cubic Ni, with the principal peaks located at approximately 44-45°, 51-52°, and 76-77° 2θ, corresponding to the Ni (111), (200), and (220) planes, respectively. No additional well-defined crystalline phases are evident within the investigated diffraction range.

The diffraction pattern changes progressively with increasing SiO_2 concentration. For the coating deposited without nanoparticles, the Ni (111) and (200) reflections are both pronounced, with a relatively strong (200) contribution. With increasing SiO_2 addition, the relative intensity of the Ni (200) reflection decreases, while the (111) reflection becomes increasingly dominant. At 0.5 and particularly 1 wt.% SiO_2, the diffraction pattern is therefore characterized by a stronger preferred contribution from the Ni (111) orientation. The Ni peaks also become comparatively broader at the higher nanoparticle concentrations, suggesting a reduction in the coherent crystallite size and/or an increase in lattice microstrain.

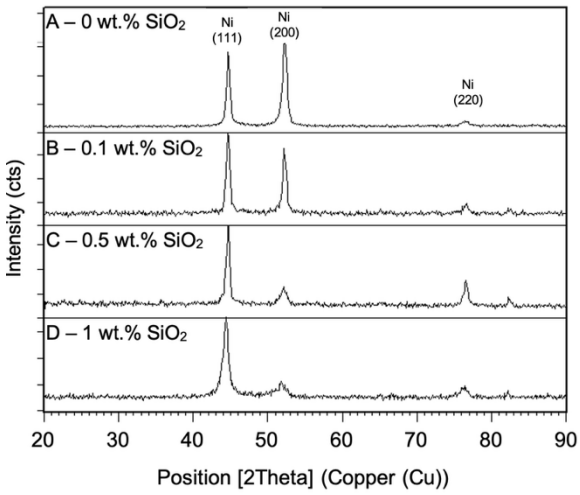


Fig. 3. *X-ray diffraction patterns of Ni coatings containing 0, 0.1, 0.5, and 1 wt.% SiO_2.*

No distinct diffraction peaks attributable to crystalline SiO_2 are observed. This does not exclude incorporation of SiO_2 nanoparticles into the coatings, since their low concentration, nanoscale dimensions, and possible amorphous character may result in diffraction signals below the detection limit of conventional XRD. Accordingly, the present diffraction data mainly demonstrate that SiO_2 addition modifies the crystallographic development of the Ni matrix rather than confirming the amount of incorporated nanoparticles.

The evolution of peak intensity and broadening is consistent with the morphological refinement observed by optical microscopy. Dispersed nanoparticles

in the electrolyte can interfere with normal Ni crystal growth and promote additional nucleation during electrodeposition, which may contribute to the development of a finer Ni matrix.

Microhardness

Figure 4 shows the Vickers microhardness of the coatings deposited from electrolytes containing 0, 0.1, 0.5, and 1 wt.% added SiO_2 nanoparticles. A clear increase in hardness is observed with increasing nanoparticle concentration. Based on the supplied measurements, the mean hardness rises from approximately 187 HV0.01 for the coating deposited without SiO_2 to about 221, 288, and 345 HV0.01 for additions of 0.1, 0.5, and 1 wt.% SiO_2, respectively.

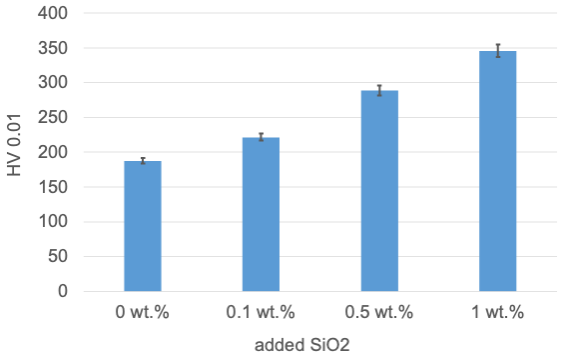


Fig. 4. *Vickers microhardness of Ni-SiO_2 coatings deposited from electrolytes containing 0, 0.1, 0.5, and 1 wt.% added SiO_2 nanoparticles.*

Relative to the unmodified Ni coating, the mean hardness increases by approximately 18% at 0.1 wt.% SiO_2, 54% at 0.5 wt.% SiO_2, and 84% at 1 wt.% SiO_2. The increase is therefore progressive over the investigated concentration range, with the highest hardness obtained for the electrolyte containing 1 wt.% SiO_2.

The hardening behavior is consistent with the morphological and XRD observations. Addition of SiO_2 nanoparticles appears to modify nucleation and growth of the Ni matrix, resulting in a finer and more strongly textured deposit. In addition, incorporation of dispersed ceramic nanoparticles into the metallic matrix may hinder dislocation motion and contribute to dispersion strengthening. Since direct compositional analysis of the coatings was not performed, the contribution of incorporated SiO_2 cannot be quantified independently; nevertheless, the systematic increase in hardness with nanoparticle addition is consistent with a combined effect of microstructural refinement and particle-assisted strengthening.

CONCLUSION

Semi-automatic selective electroplating was used to produce Ni-based coatings on 316L stainless steel from electrolytes containing 0–1 wt.% SiO_2 nanoparticles. Increasing SiO_2 concentration refined the coating morphology, producing finer, more uniform surfaces while reducing thickness from approximately 20 µm (0–0.1 wt.% SiO_2) to 18 µm (0.5 wt.%) and 15 µm (1 wt.%), indicating changes in the effective deposition rate.

XRD analysis confirmed the retention of the fcc Ni structure, with increasing SiO_2 addition modifying relative peak intensities and enhancing the Ni (111) contribution. Although no distinct crystalline SiO_2 reflections were detected, the diffraction changes suggest modified Ni nucleation and growth during electrodeposition.

SiO_2 addition significantly increased microhardness from approximately 187 HV0.01 for pure Ni to 345 HV0.01 at 1 wt.% SiO_2, representing an 84% improvement. Overall, the combined morphological refinement, crystallographic changes, and enhanced hardness demonstrate the effectiveness of SiO_2 nanoparticle addition in tailoring the structure and mechanical properties of selectively electrodeposited Ni coatings.

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