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MORPHOLOGY AND HARDNESS OF ELECTROCHEMICALLY-CODEPOSITED Ti-DISPERSED Ni-MATRIX COMPOSITE COATINGS

MORFOLOGIA I TWARDOŚĆ ELEKTROCHEMICZNIE WSPÓŁOSADZONYCH POWŁOK KOMPOZYTOWYCH Ni-Ti

The effects of current density and Ti particle loading in a plating bath on the morphology and hardness of Ni-Ti composite coatings via an electrochemical-codeposition process were investigated. The Ti-reinforced Ni-matrix composite coatings were codeposited on copper substrates using a Ni-ion electrolytic solution stably suspended with -45 micron Ti particles. Within the current studied range, the coatings' Ti contents are in the range between 46 and 62 at.%. The morphology appeared to vary with current density. Structures of the Ni-Ti composite coatings produced under low current density conditions revealed denser structures, which is in contrast to the more porous structures noted in the coatings produced under high current density. An initial increase of current density from 100 to 150 mA/cm^2 also tends to raise Ti coating content. The reinforcement of Ti particles in the coatings also increased their hardness, which is attributed to the possible role of the embedded Ti particles in hindering matrix deformation. The effect of Ti loading on the coating's Ti contents was not significant under conditions used in the present study.

Keywords: electrochemical codeposition, composite coatings, Nickel-Titanium, morphology, hardness

Badano wpływ gęstości prądu i zawartości cząstek Ti w kąpieli galwanicznej na morfologię i twardość elektrochemicznie współosadzanych powłok kompozytowych Ni-Ti. Kompozytowe powłoki niklowe zbrojone cząstkami Ti zostały współosadzone na powierzchniach miedzianych z kąpieli elektrolitycznej zawierającej jony Ni i 45 mikronowe cząstki Ti tworzące stabilną zawiesinę. Zawartość Ti wbudowanego w powłoki wahała się w granicach 46-62 at.%. Morfologia powłok zmienia się wraz ze zmianą stosowanej gęstości prądu. W przypadku kompozytowych powłok Ni-Ti wytwarzanych przy niskich gęstościach prądu stwierdzono bardziej zwarte struktury, w przeciwieństwie do bardziej porowatych struktur stwierdzonych w przypadku powłok wytwarzanych przy wysokich gęstościach prądu. Początkowy wzrost gęstości prądu od 100 do 150 mA/cm^2 również powoduje podniesienie zawartości Ti w powłokach. Ze wzrostem zawartości Ti wzrasta również twardość powłoki, co można przypisać roli osadzonych cząstek Ti utrudniających odkształcenie osnowy. W warunkach stosowanych w tej pracy wpływ zawartości Ti w kąpieli na zawartość Ti w powłokach nie był znaczący.

1. Introduction

Electrochemical codeposition is a cost effective method of producing metal matrix composite coatings. Numerous particle-dispersed metallic-matrix coatings have been successfully produced through electrochemical codeposition by electroplating the coatings from a conventional plating bath suspended with particles. By combining the electrodeposited metallic matrix such as Ni and Cu with a range of dispersed particles such as SiC [1-5], WC [6,7], ZrO$_2$ [3], or Al$_2$O$_3$ [3,4,8-10], composite coatings of improved mechanical properties have been produced.

Electrochemical codeposition was reported to have been employed to produce a high catalytic-activity layer, such as Ni-Mo, and Ni-V composite coatings, for a hydrogen-evolution process [11]. The process has also been applied to produce metallic alloy coatings via a two-stage process that includes codeposition of a composite coating and a subsequent heat treatment process for alloy homogenization [12-13]. For example, a layer of Ni-Ni$_3$Al intermetallic alloy was successfully produced by codepositing an Al-dispersed Ni-matrix composite coating and subsequently annealing the coating at 550-800°C to form the Ni$_3$Al compound [13].

Electrochemical codeposition of Ni-Ti in composite coatings has been shown to impart many useful properties. Serek and Bundniok [14] reported improved mechanical properties of a steel substrate by Ni-Ti composite coating. The results showed rough metallic coating with very good adhesion to the substrate. Panek et al. [15] found that Ni-Ti composite layers exhibited greater hydrogen-evolution activities when compared to that of pure nickel coating. Both studies reported that the changes in the mechanical and chemical properties

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The bath composition and operating conditions for the codeposition process

Bath composition	Operating conditions
Sodium acetate (CH$_3$COONa): 0.12 mol/dm^3 Ammonium chloride (NH$_4$Cl): 0.2 mol/dm^3 Nickel sulfate hexahydrate (NiSO$_4$·6H$_2$O): 0.19 mol/dm^3 Boric acid (H$_3$BO$_3$): 0.13 mol/dm^3	Ti particle size: -45 μm Particle loading: 2, 6, 8, 10 g/dm^3 Current density: 100-250 mA/cm^2 pH / temperature / duration: 3.5 / 50°C / 60 min

of Ni-Ti composite coatings depended on the amount of Ti particles embedded in the coatings. In addition, intermetallic NiTi alloy formation via codeposition was reported to strongly depend on a precise control of a Ni-Ti atomic fraction in the coatings [16].

In this study, we examine the influence of codeposition parameters including the applied current density and the Ti particle loading in an electrolytic solution on the embedded-Ti content, the rusulting composite morphology, and the hardness of the coatings. By understanding the relationship of the processing parameters to the coating characteristics, it would be possible to tailor Ni-Ti coating's properties with right design requirements for a range of applications.

2. Experimental methods

The Ni-Ti composite coating was prepared by codeposition from the nickel-plating bath containing the suspended Ti particles. Analytical-grade reagents and distilled water were used for bath preparations. The -45 μm Ti particles (Pacific Sowa Corporation, Japan) of various particle loadings (2-10 g/dm^3) were stably suspended in the solution using a magnetic stirrer, which was set to agitate the bath at 750 rpm. The plating bath was set at a pH of 3.5 and a temperature of 50°C. The bath composition and operating conditions are summarized in TABLE 1.

A Ti-dispersed Ni-matrix composite coating was deposited on a copper substrate (2.5 cm^2 working area). The deposition was carried out in a plating bath containing 300 cm^3 of the electrolyte solution. The substrate was placed horizontally inside the cell at 1 cm below the solution surface. A platinum mesh (with an approximate active area of 40 cm^2) was used as a counter electrode. The schematic illustration of the setup is shown in Fig. 1. To ensure good coating adhesion, copper plates were prepared by mechanically polishing them on abrasive papers (P 240, 400, 800, 1200, 2500 SiC) and diamond pastes (6 and 3 μm) before chemically activating them in a 10% v/v H$_2$SO$_4$. After plating, the Ni-Ti composite coating was rinsed, ultrasonically cleaned with distilled water, and dried.

The cross-sectional microstructures and chemical compositions of the coatings were analyzed using a scanning electron microscope equipped with energy dispersive spectroscopy (SEM with EDS, Phillips XL30). The coating cross-sectional areas were first mechanically polished with abrasive papers (P 240, 400, 800, 1200, 2500 SiC) and then with diamond pastes (6 and 3 μm), before ultrasonically cleaned with distilled water. The final chemical composition value was the average value of 3 random test measurements made on the

coating's cross-sectional areas using the EDS mapping analysis. The thicknesses of the coatings were measured directly from the cross-sectional microstructures; the thickness value is a mean value of 10 random thickness measurements along the coating's cross section. The phase composition of the coating was analyzed by X-ray diffractometry (XRD, Phillips X'Pert model) with CuKα radiation (U =40 kV; I = 20 mA). Diffraction patterns were recorded in the 2θ range from 30° to 90°. Phase identification was carried out based on the ICDD card standards.
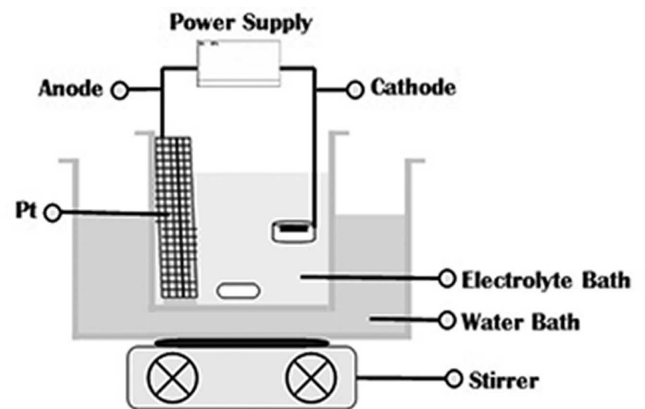

Fig. 1. Schematic illustration of the codeposition setup

Micro Vickers hardness tests were carried out to evaluate the hardness of composite coatings using Micro Hardness tester (Mitutoyo Model MVK-H1). Coating surfaces were mechanically polished first with abrasive papers and then with diamond pastes, before rinsing them in water, and indenting them with the 10 g load for 10 seconds. The final hardness value is the average value of 10 random test measurements made on each coating surface.

3. Results and Discussion

3.1. Phase analysis of the codeposited Ni-Ti coatings

The Ti-dispersed Ni-matrix composite coatings were successfully produced through codeposition. The obtained coatings have shown a uniform gray rough metallic surface with grains of incorporated Ti particles (Fig. 2). The coating's thickness increases with current density (Fig. 3), as a faster rate of Ni-ion reduction and deposition occured at higher current density resulting in a larger coating's thickness. The coatings exhibited strong adhesion to the copper substrate.
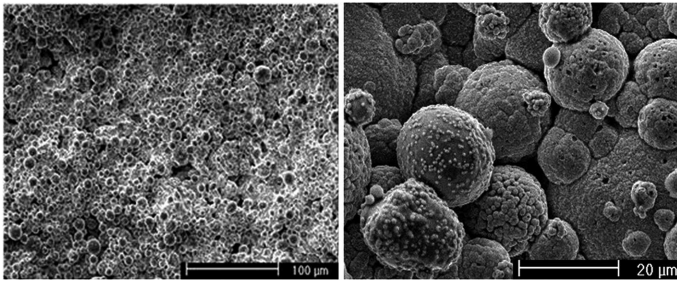
Fig. 2. Surface morphology of the Ti-dispersed Ni-matrix coating codeposited at 200 mA/cm^2 with a Ti-particle loading of 2 g/dm^3: (a) 500x magnification and (b) 2000x magnification
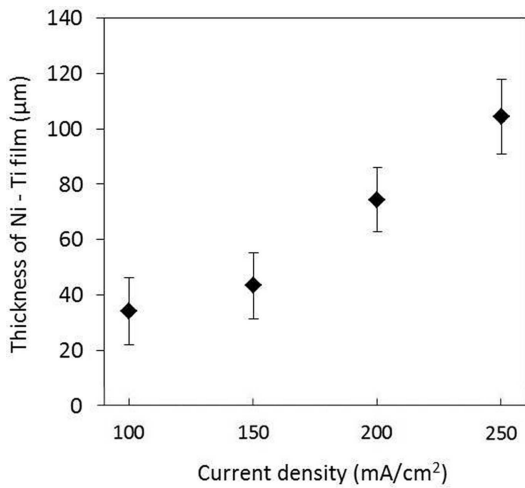
100 mA/cm^2. The tendency of the Ti loading effect, within the current studied range, is not clearly conclusive. Particle loading in the bath appears to have driven the coating's Ti content to fluctuate from 46 to 62 at.%. The relatively high Ti contents seem to suggest a possibility of the production of a NiTi alloy layer via a codeposition and subsequent heat treatment. However, the coating's Ti content must be precisely controlled to stay within the 50 at.%. Further investigations over a wider range of Ti loadings are required for a precise control of deposited Ti contents.

Fig. 3. Thickness as a function of current density with a Ti-particle loading of 8 g/dm^3

The representative XRD patterns of the Ni-Ti composite coating is shown in Fig. 4. The figure shows the peaks of Ni matrix and Ti particles in the coatings, which appear to have no sign of any contamination from other oxide compounds or metallic-compound phases.
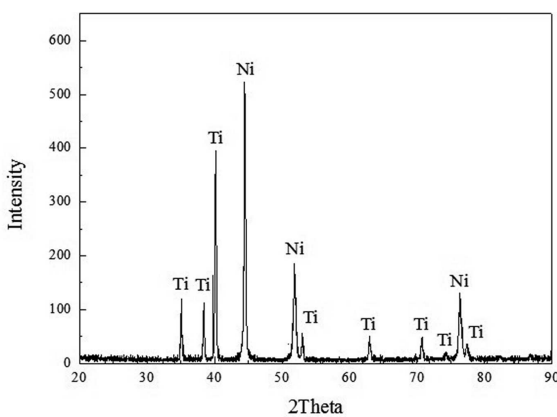

Fig. 4. The XRD patterns of the Ni-Ti composite coating deposited at 200 mA/cm^2 from the plating baths loaded with Ti particles loading at 2 g/dm^3

3.2. Effects of Ti-particle loading in a plating bath and the current density on the embedded-Ti content of the coating

Figure 5 shows the effect of Ti loading in a plating bath on the coating's embedded-Ti contents at a current density of
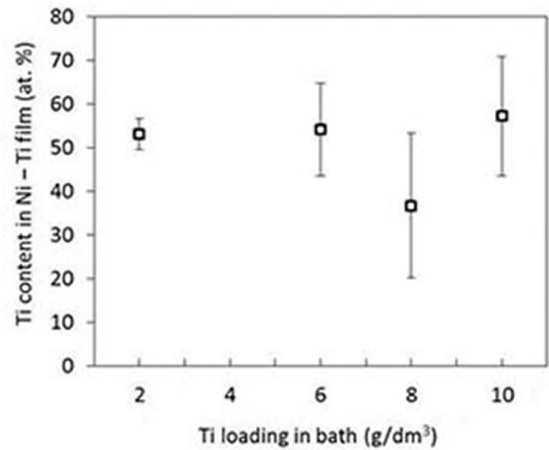

Fig. 5. The effect of Ti loading in a plating bath on the embedded-Ti contents in the Ni-Ti composite coatings codeposited under a current density of 100 mA/cm^2

Figure 6 shows the effect of the current density on the coating's Ti content, with 8 g/dm^3 particle loading in the plating bath. The results show that Ti content in the coating seems to initially increase with an increase of the current density from 100 to 150 mA/cm^2. Yet, the Ti content remains relatively constant when the current density is increased further.
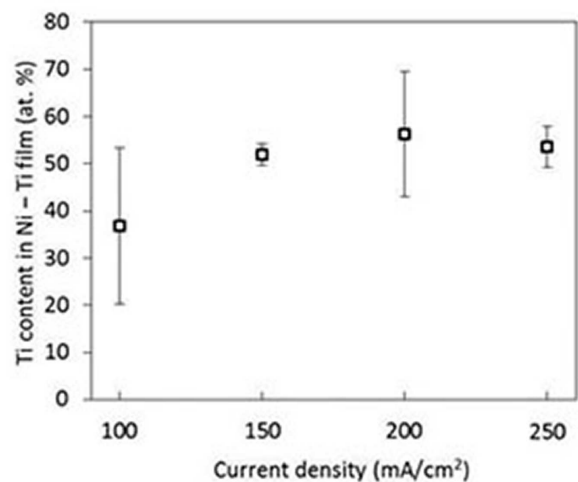

Fig. 6. The effect of current density on the embedded-Ti contents in Ni-Ti composite coating codeposited under the particle loading of 8 g/dm^3

Based on Guglielmi's model for the codeposition process, the effect of current density could possibly be explained by either of the 5 important steps that are taking place in the process namely [17]: (1) the formation of Ni-ionic clouds

around Ti particles in an electrolyte, (2) the convection of the ion-clouded particles toward the cathode, (3) the diffusion through a hydrodynamic boundary of the particles toward the cathode, (4) the electrophoretic diffusion of the particles through electrical double layers toward the cathode and (5) the adsorption of the particles to the substrate with a Ni matrix via the reduction of the Ni-ion clouds. So, knowing that the strength of the electrophoretic force is correlated with current density, an increase in current density, therefore, is likely to result in a stronger attractive force on the ion-clouded particles toward the cathodic substrate. Insufficient level of current density may result in an inefficient codeposition process. As a result, an initial current density increase from 100 to 150 mA/cm^2 significantly improves the codeposition process. However, a further increase in current density from 150 to 250 mA/cm^2 appears to have minimal effect on the Ti contents. With an increase in current density, both the rate of the bulk Ni ionic deposition and the codeposition of Ni^{2+}-clouded Ti particles may be enhanced resulting in larger coating's thickness but relatively constant Ni-Ti fraction of the coatings. Similar observations have also been reported previously by Naploszek-Bilnik et al. [18] and Panek and Budniok [11].

3.3. Hardness of the codeposited Ni-Ti coatings

Figure 7 shows the effects of Ti loading on the hardness of Ni-Ti composite coatings processed at the current density of 100 mA/cm^2. Without Ti particle loading, the hardness of the electrodeposited Ni is about 145 HV. With a presence of Ti loading in the bath, the hardness of the Ti-reinforced coatings was significantly higher than that of pure Ni coating. Further increase of Ti loading in the bath appears to have a negligible effect on the coating's hardness. The presence of dispersed particles in coatings, which has enhanced the hardness of the coatings has also been observed in composite Ni-matrix coatings with different reinforced particles such as WC, SiC, and TiO$_2$ [2,7,20].
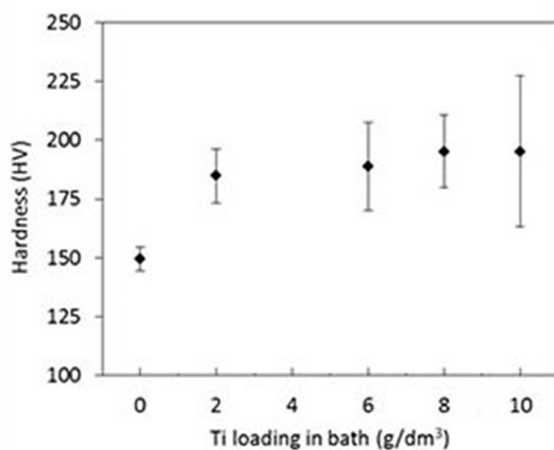
Fig. 7. The effect of Ti loading in the plating bath on the hardness of Ni-Ti composite coatings codeposited at 100 mA/cm^2 current density

Figure 8 shows the effect of the current density on the hardness of Ni-Ti composite coatings processed in a plating bath with particle loading of 8 g/dm^3. The average hardness values slightly increase from 195 to 210 HV with increasing

current density. The varying Ti contents ranged from 40-55 at.%, due to varying current density, appear to have minimal effect on the resulting coating hardness.
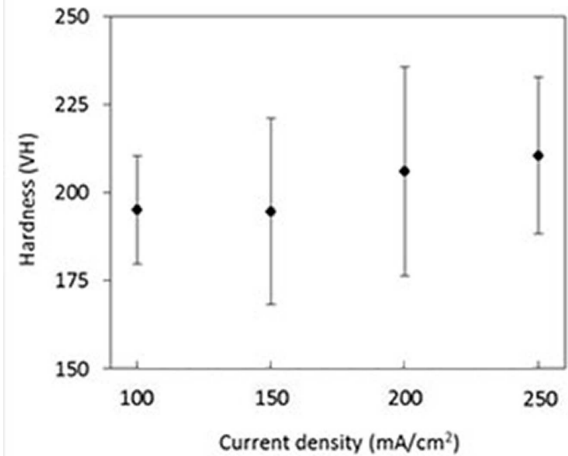
Fig. 8. The effect of the current density on the hardness of a codeposited Ni-Ti composite coatings processed in the plating bath with particle loading of 8 g/dm^3

According to R.Q. Fratari and A. Robin [21], the effects of reinforced particles on the hardness of the coating maybe explained through three possible mechanisms: (1) the particle strengthening [22-23], (2) dispersion strengthening [22,24], and (3) grain refining [25-26]. First, the particle strengthening mechanism is achieved when hard and large particles (>1 μm), present at a volume fraction above 20% in the composite coating, share the load with the metal matrix and thus hinder matrix deformation. In dispersion strengthening, fine particles (0.01-1 μm) at a volume fraction of 1-15% are uniformly distributed throughout the matrix. In this case, the matrix mainly carries the load while the dispersed particles retard the dislocation motion. With grain refining, nucleation of fine grains on the surfaces of the dispersed-particles result in an increase in hardness of the coating.

Increased composite coating hardness obtained in this study is possibly related to the particle strengthening mechanism since the particle size used in this study was relatively large (with a particle size distribution of -45 μm) and the reinforcement volume fraction used was over 20%. Thus, the hardness is enhanced with the reinforcement of the incorporated Ti particles.

3.4. Morphology of the codeposited Ni-Ti coatings

Figure 9(a)-9(d) shows that, by increasing current density from 100 to 250 mA/cm^2, Ni-Ti coating morphology changes from a dense structure to a more porous structure. For low current density (Fig. 9(a)-(b)), the Ni-Ti coatings were deposited dense structures. With increasing current density (Fig. 8(c)-(d)), the coatings show porous structures with larger thickness.
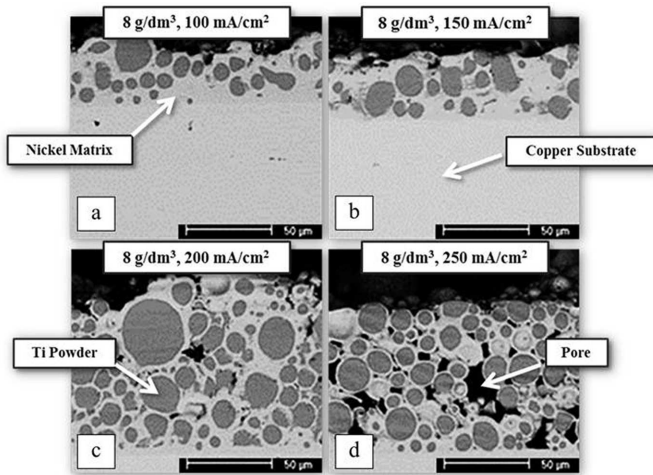
Fig. 9. Cross-sectional images (Back-scattered electron mode) of the Ni-Ti composite coatings deposited with the particle loading of 8 g/dm^3 under the following current densities of (a) 100 mA/cm^2, (b) 150 mA/cm^2, (c) 200 mA/cm^2, (d) and 250 mA/cm^2
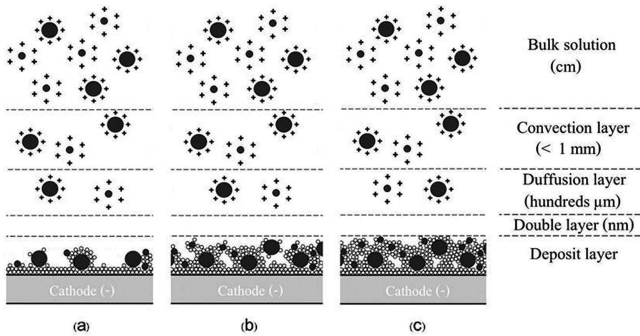

Fig. 10. The schematic illustration of the different stages of the codeposition process for: (a) initial stage, (b) intermediate stage, and (c) final stage
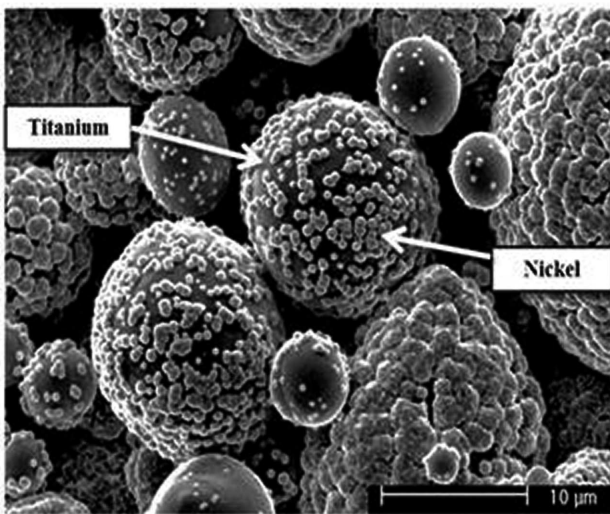

Fig. 11. Microstructure of the Ni-Ti composite coating illustrating the preferential Ni deposits on Ti particle surfaces

The morphological changes shown in Figs. 9(a) to 9(d) are possibly associated to the changes that are taking place during the codeposition process, as schematically illustrated in Fig. 10. The codeposition process is described as follows: at the initial stage, Ni-ion deposition and the codeposition of Ni^{2+}-clouded Ti particles are adsorbed on the copper substrate. Ti particles are then entrapped in the substrate, which later serve as nucleation sites for the subsequent Ni deposits as demonstrated by the microstructure of the Ni-Ti composite coating shown in Fig. 11. Ni deposits appear to favorably grow on the embedded Ti particles because of the high current density around the particle's surfaces. As the coating process continues, Ni^{2+}-clouded Ti particles are possibly deposited in the previous Ni-Ti sites that enclosed the pores, resulting in porous structures of Ni-Ti deposits appearing at the final stage of coating. Similar porous structures were also noted in the previous works on on metallic composite coatings, especially when a high current density was applied, which triggered faster deposition rate [18,27].

4. Conclusion

The Ni-Ti composite coating was sucessfully produced through the electrochemical codeposition route. The composite coating produced a gray, rough metallic surface. With thickness ranging from 40 to 120 μm and Ti content ranging at 46-62 at.%.

The amount of Ti in the coatings is initially enhanced by an increase of current density from 100 to 150 mA/cm^2. However, further increase in the current density does not affect Ti content significantly. Composite coating morphology obtained under low current density (<200 mA/cm^2) resulted in dense structures whereas, coating obtained under high current density produced highly porous structures. The porous structures have been attributed to the influence of the Ni-preferential nucleation on the embedded-Ti particles. The effect of the Ti loading in a bath on the Ti content is not significant in this study. A wider range of Ti loadings should be further investigated to analyze such effect.

The Ni-Ti composite coating appears to be harder than a pure Ni coating. The enhanced hardness of the coatings has been attributed to particle strengthening mechanism, which is achieved by sharing the load between the Ti particles and the Ni matrix.

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