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Electrocodeposition of nano-SiC particles by pulse-reverse under an adapted waveform

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Abstract

This work has explored the potential of using pulse reverse (PR) plating for increasing the deposited fraction of SiC nanoparticles. Two PR waveforms were selected, a short pulse (500 Hz) waveform and a newly modified and adapted pulsed sequence that equals the plating thickness to the particles' diameter (50 nm) for the on-time and half-diameter during the anodic time. The pulse waveforms were designed with 4 and 10 A·dm⁻² as the average current density and cathodic peak current density, respectively. Direct current (DC) deposits at the same values were also produced as reference. In all cases, the codeposition of nano-SiC particles influenced the microstructure. The electroplating under DC 10 A·dm⁻² showed the strongest grain refinement and increased the content of the particles (up to 2% vol.) PR using high-frequency achieved a similar codeposition. The maximum particle incorporation was achieved by the proposed adapted pulse waveform, doubling the SiC content produced by other set-ups (up to 4% vol.); increasing the microhardness of the deposits to 400 HV, despite no grain refinement compared to the pure metal. From these results, it was observed a relationship between the influence of the plating method on the microstructure, the particle content, and the material's hardness.

Keywords: Electroplating; Pulse reverse current; Composite coating; EBSD

1. Introduction

The electrodeposition of composite coatings reinforced by nanoparticles have attracted industrial and research interested in substituting the use of microparticles due to the improvement of the coating's properties, such as hardness, wear resistance and corrosion resistance ¹⁻⁵. For decades electrodeposition of nanocomposites has been a target of scientific research by studying the impact of multiple electrodeposition parameters, and how they affect the different characteristics of the deposits ⁵⁻⁷. Often the main focus is on a high content of nanoparticles since it is mainly believed that a large content of particles is responsible for the improvement of the properties of the deposit. Therefore, the main focus has been on parameters optimisation to increase the quantity of codeposited nanoparticles ^{2,8,9}. However, due to the complexity of the electrodeposition process, the influence of the different parameters ¹⁰ on the particle content is not fully understood as well as their impact on the overall coating properties. All this is leading to a lack of robustness in the production of nanocomposites, difficulties in designing and predicting coating properties, and scattered content of nano-particles, especially when compared to the reported content of microparticles ^{1,9,11}.

This lack of understanding of the governing mechanism of codeposition of nanoparticles and lack of control has limited the industrial exploitation. In general, it has been observed that the physicochemical properties of the particles and their interaction with the plating bath chemistry play an important role in the quantity of entrapped particles ^{10,12}. Likewise, the effect of the current type ¹³⁻¹⁵ and density ^{16,17} has also been studied, proving their influence on the codeposition process. Nevertheless, most of the results do not show a substantial increase in the content of nano-particles, which in essence is the first step to allow a comparison to microcomposites.

Pulse-reverse (PR) plating has been explored as a method to increase the content of nanoparticles. Podlaha et al. ^{18,19} reported a noticeable increase of particle content in a copper metal matrix using PR when the plating thickness corresponding to each cathodic period is similar to the particle diameter. Likewise, Xiong-Skiba et al. ²⁰ achieved a very high alumina nanoparticle content, up to 23 wt.%, in a nickel matrix by plating thickness steps that correspond to multiple (N) of the particle diameter during the cathodic pulse and stripping N-1 times the diameter during the anodic pulse. In the reverse pulse, some of the particles are released and remain in the vicinity of the surface, enriching the content of the particles in the electrolyte on the surface. In the following cathodic pulse, the particles are recaptured, enriching the particle content of the growing layer.

The present study aims to develop a PR plating waveform based on Xiong-Skiba et al. ²⁰ work, that can consistently produce nanocomposite coatings containing carbides with a higher content than other methods available in the literature. Nevertheless, the application of a similar waveform described by the authors for nickel plating resulted in the passivation of the electrode and therefore to the production of faulty coatings. To prevent the passivation of Ni, Aroyo et al. ²¹ suggested a train of short anodic pulses during the reverse pulse. Inspired by this work, a modified pulse-reverse cycle was re-designed with an anodic pulse train with the inclusion of

intervals of short cathodic pulses. The use of these high-frequency pulses benefited the dissolution of Ni, therefore avoiding passivation ²².

SiC nanoparticles with a diameter of 50 nm were selected to be combined with Ni from a Watts bath and deposited according to the designed pulsed waveform and by direct current (DC) as reference. Particles content, as well as microstructure and microhardness, were studied properties.

2. Experimental and characterisation details

2.1. Electrolyte composition and experimental set-up

Four specimens for each condition were electrodeposited by DC and by PR from an additive-free Watt's bath ²³ on low carbon steel plates, 3 cm x 5 cm (Table I). The DC densities were set to 4 and 10 A · dm⁻² to match, the average current densities and the cathodic peak density of the pulse-reverse (PR) plating, respectively. Pulse reverse (PR-HF) with high-frequency pulses (500 Hz) was used as a traditional PR waveform in order to benchmark the deposits made by pulse reverse with a tailored long cycle (PR-LF). This waveform used an adapted N diameter plating thickness and N-1 diameter stripping thickness set-up. The reverse cycle included was also modified by a train pulse with intervals of short cathodic pulses (Figure 1).

The electrodeposition was performed in a thermally controlled cell with 500 mL bath volume and with a parallel vertical electrodes configuration with a distance between cathode and anode of 7 cm. Before plating, the steel substrate was mechanically ground with SiC grade #1000, cleaned ultrasonically in an alkaline soap and activated by pickling for 8 min in 2.5 M H₂SO₄. All electroplating baths were set at pH 3 before electrodeposition, using sulfuric acid or sodium hydroxide. Composite coatings were produced adding 20 g · L⁻¹ of SiC nano-size powder (gnm© #SiC-110 β-SiC 50 nm). The bath suspension was continuously stirred by a rotating magnet and additionally agitated with ultrasound (US) for 30 minutes prior to electroplating to avoid agglomeration of particles.

The current efficiency (CE) of the process was obtained by comparing the theoretical deposited mass calculated by Faraday's law to the weight of the deposited mass minus the particles' mass. An oscilloscope was used to verify the pulsed waveform.

Figure 1. Pulse-reverse tailored pulses (PR-LF). (a) Forward and reverse waveform of a cycle (b) Reverse pulse train design within the reverse waveform.

Table I. Plating bath composition and parameters

Electrodeposition parameters			
NiSO ₄ ·7H ₂ O	240 g · L ⁻¹	Pulse Reverse current – Low Frequency, i.e. 1D – ½D (PR-LF) (Figure1)	
NiCl ₂ ·6H ₂ O	45 g · L ⁻¹	Total deposition time	83 min
H ₃ BO ₃	30 g · L ⁻¹	<i>Forward cycle</i>	
pH	3.00	Cathodic current density (i _c)	10 A·dm ⁻²
Temperature	45 °C	Cathodic duration (t _c)	1500 ms
Anode	Ni sheet; 99.9% purity	Plating thickness	≈ 50 nm
Stirring	200 rpm	<i>Reverse cycle – Train pulses</i>	
Particle concentration	20 g · L ⁻¹	Peak Cathodic current (i _{tc})	2 A·dm ⁻²
SiC particle size	50 nm	Train-Cathodic duration (t _{tc})	6 ms
Coating thickness	25 μm	Peak Anodic current (i _{ta})	4 A·dm ⁻²
Direct Current (DC)		Anodic duration (t _{ta})	10 ms
Total deposition time	12 min; 30 min	Total train time (t _a)	4000 ms
Current density	10 A·dm ⁻² ; 4 A·dm ⁻²	Frequency	62,5 Hz
Pulse Reverse current – High Frequency (PR-HF)		Stripping thickness	≈ 25 nm
Total deposition time	40 min		
Peak Cathodic current	10 A·dm ⁻²		
Cathodic duration	1 ms		
Peak Anodic current	4 A·dm ⁻²		
Anodic duration	1 ms		
Frequency	500 Hz		

2.2. Coating characterisation

Wavelength dispersive X-ray spectroscopy (WDS, EDAX-TSL) was preferred over energy-dispersive spectroscopy (EDS) for the composition analyses and quantification of SiC particles due to the better resolution of light elements at a low content. The weight % of Si was quantified based on pure Si standards. The analysis of the standard and each specimen was performed using an acceleration voltage of 10 kV and beam current ranging from 22 nA to 24 nA. The volume content of SiC is calculated starting from Si data and considering the particles to be stoichiometric and is expressed as the average value of five different WDS area measurements of two different specimens.

The surface morphology was observed by scanning electron microscopy (SEM, JEOL 7001F). The samples were also prepared as cross-sections by mechanical polishing for the electron backscattered diffraction (EBSD, EDAX-TSL) analysis. The measurements were performed with an electron probe current of 4.23 nA at an acceleration voltage of 15 kV, with a magnification of X6000, and a step size of 80 nm. The OIM 5™ software was used for the analysis of the EBSD maps in the growth

direction; all the data points with coefficient index (CI) < 0.1 were disregarded. The analysis was performed on two samples for each plating condition. A grain was defined as a region consisting of at least three similarly oriented connected points with a misorientation $< 5^\circ$. The grain area was calculated by the number of data points contained in this region. The grain diameter was calculated from the area by considering the grain as a circle.

The microhardness of the coatings was measured on cross sections by Vickers micro indenter (NanoTestTM Vantage) with an indentation load of 100 mN and a dwell time of 10 s. Fifteen repetitions were done on each of two specimens for each plating condition, and the hardness was expressed as the average and standard deviation.

3. Results and discussion

3.1. Coatings electrodeposition

The variation of pH during electrodeposition was calculated by measuring it before and after. In all cases, the pH increased; this was due to the hydrogen reduction on the cathode surface ²⁴. The Ni electrodeposited by DC showed a current efficiency (CE) higher than 98% with a slight change in pH. The particles addition lead to a decrease in the CE to 92% with a minor increase in pH (< 0.1). Nevertheless, the results were in agreement with what had been reported as cathode efficiency for Watts baths ²⁵.

The samples produced by pulse reverse with high-frequency pulses (PR-HF) had a similar change in pH ($\Delta \text{pH} \approx 0.1$). However, the measured deposited mass was higher than the theoretical mass calculated by Faraday's law, for both nickel and composite deposits. This was due to a difference between the planned pulse parameters and the real current flowing through the cell as determined by an oscilloscope (Figure 2). The data showed that the transient response of the cell had the same time scale of the pulse duration. Therefore the average current density was lower for both the cathodic and anodic part, resulting in a total average current density higher than the planned. Hence, the theoretical mass was recalculated based on the oscilloscope data, showing a CE drop-down close to 92% for both pure Ni and composite coatings for PR-HF.

Figure 2. Pulse reverse – High-frequency waveform: Cathodic and Anodic pulse, programmed and as determined by an oscilloscope.

In the case of the long pulses, the transient is negligible. The nickel deposits produced by PR-LF had a significant change in pH, up to 0.60. The composite produced by PR-LF had a similar ΔpH and a drop of the CE down to almost 90%, similar to the CE of the other composite electrodeposits. For PR-LF, there was a limited correlation between ΔpH and CE because of the presence of a pulse train. The total deposited mass did not vary with the application of the pulse train, but the hydrogen evolution was. Hydrogen is produced at each pulse of the train, either on the cathode (during deposition) or the counter electrode (during stripping). Therefore, the addition of the pulse train increased the overall hydrogen production.

The PR-LF electroplating was used to deposit a thickness with approximately the particle theoretical diameter size and strip half of the particle diameter size ($1D - \frac{1}{2}D$), as illustrated in Figure 3. It is presumed that the plated thickness would initially capture some of the particles that were in contact with the cathode. During the stripping cycle, only a few of the entrapped particles are released back to the electrolyte. The next plating cycle could recapture the nearby particles released in the previous stripping cycle and also newly attracted ones, without losing many of the already entrapped particles. Therefore, producing an enriched composite coating.

Figure 3. Scheme for pulse-reverse plating illustrating the incorporation of particles by plating one diameter and stripping half.

In Table II is reported the content of codeposited SiC. The composites produced under DC at $10 \text{ A} \cdot \text{dm}^{-2}$ had a vol.% content close to 2%, similar to the results presented by Lee et al.¹¹ at the same pH. This content represents more than double when compared to DC at $4 \text{ A} \cdot \text{dm}^{-2}$. On account of that a faster-growing metal, resulting of a higher current density could lead to a more rapid entrapping of the nearby nanoparticles. The samples produced by pulse plating with high-frequency (PR-HF) reported a negligible increase in SiC content, compared to DC10. Nevertheless, it is often reported in the literature an increase in content in composited produced by PR over DC^{7, 14, 20, 26, 27}.

As it was reported by Podlaha et al.^{18, 19} and Xiong-Skiba et al.²⁰ the highest vol.% content of particles was achieved in samples produced by a cathodic pulse where the thickness of the deposit per cycle approached the particles diameter size ($1D - \frac{1}{2}D$), increasing the content of nanoparticles up to 4%.

Table II. Codeposited SiC volume content (%) as determined by WDS

	DC4	DC10	PR-HF	PR-LF
SiC vol.%	0.78	1.90	2.07	4.07
<i>St. dev</i>	<i>0.13</i>	<i>0.51</i>	<i>0.30</i>	<i>0.51</i>

3.2. Microstructure

The distribution of grain size and number of grains was calculated from the EBSD maps (Figure 5), and the average grain area (GA) is reported in Figure 4. A columnar growth was dominant in all the pure nickel samples, independently on the process parameters. The high current density on DC10 modified the large columnar grains seen in DC4 to a thinner and elongated structure. The fraction of smaller grains was also increased (Figure 4a); thus showing a grain refinement. The use of PR current with high-frequency also slightly refined the microstructure. Still, the refinement was less when compared to DC10. This was because, in practice, the cathodic output current density was lower than $10 \text{ A} \cdot \text{dm}^{-2}$ (Figure 2). Therefore, the average experimental cathodic current had a closer value to DC4 than DC10; hence, the microstructure is more comparable to the one reported in DC4 (Figure 5). The use of tailored long pulses (low-frequency) increased the number of smaller grains (Figure 4a). Thus, a more refined microstructure was achieved compared to the high-frequency waveform.

Figure 4a. Distribution of the grain number in relation to the grain area – Pure Ni

The addition of 50 nm particles did not modify the columnar shape of the grain growth observed in the pure nickel deposits (Figure 5). However, the SiC codeposition did modify the grain size by refining the microstructure of the samples produced by DC and PR-HF, particularly for the latter where there was an increase in the number of nano-sized grains (Figure 4b), which considerably decreased the average grain area. It is possible that the nanoparticles acted as nucleation sites, therefore promoting multiple growing sites along the larger columnar growth. There was an exception in the samples produced by PR-LF where there was a decrease in the number of nano-sized grains after the addition of particles (Figure 4b). However, the microstructures appeared to be similar (Figure 5), and the average grain size did not change significantly.

Figure 4b. Distribution of the grain number in relation to the grain area – Ni/SiC.

The EBSD maps in cross-section (Figure 5) and the inverse pole figures reported in Figure 6 showed a preferred growing $\langle 100 \rangle$ direction for all the deposition conditions. This grow direction is typical of the so-called ‘free mode’ nickel crystal uninhibited growth²⁴. Nevertheless, the different methods of electrodeposition produced different degrees of textured microstructure. This is evident when comparing the inverse polar figures of the pure Ni samples produced under DC4 and DC10 (Figures 6a and c). As a result of the high current density in DC10, there was a decrease in the texture intensity in the $\langle 100 \rangle$ direction. The multiple nucleation sites prompted by a higher current density, led to a microstructure that did not allow the normal nickel growth of larger columns, leading to an increase in the nucleation rate and growth of smaller, more randomly oriented grains. The reduction of H^+ into H_2 could have had also contributed to reducing the preferential crystal growth orientation. H_2 is a known Ni growth inhibitor²⁴, and the local alkalization during electroplating would also favour the formation of $Ni(OH)_2$, a strong growth inhibitor²⁴. The ΔpH shows an alkalization of the bulk electrolyte after the electroplating, which would indicate an even higher local pH at the electrode surface during electroplating. A similar effect was seen in the samples produced by PR-HF, where the ΔpH was slightly higher to the one reported for DC4. Hence, the $\langle 100 \rangle$ texture intensity in the PR-HF deposits (Figure 6e) was slightly lower compared to DC4 (Figure 6a). This was in agreement with the results reported by Kollia et al.²⁸ where the $\langle 100 \rangle$ texture persist as dominant even at high values of pulse frequency.

As mentioned, the ΔpH of the PR-LF was close to 0.60; having a final pH of the bulk of 3.6. Hence, the local pH variation at the cathode surface-electrolyte interface during the electrodeposition is supposed to be higher than the one reported at DC and PR-HF. Consequently, the formation of $Ni(OH)_2$ and the reduction of H^+ were the highest during the electrodeposition leading to higher growth inhibition (Figure 6g).

The presence of nanoparticles during the electrocrystallisation decreased even further the preferential crystal growth direction of the metal deposits for the samples

produced by DC and PR-HF. It has been suggested in previous studies ¹⁴ that the particles could promote a higher H⁺ reduction rate favouring growth inhibition. For the samples produced under PR-LF the texture intensity remained the same as in the pure nickel deposits, independently of the SiC content; showing that the crystal orientation in these samples was governed by the plating parameters and not the particles.

Figure 5. Orientation map, colour-coded in relation to the electrodeposits' growth direction, shown by an arrow in the figure. (a) Ni-DC4 (b) SiC-DC4 (c) Ni-DC10 (d) SiC-DC10 (e) Ni-PR-HF (f) SiC-PR-HF (g) Ni-PR-LF (h) SiC-PR-LF.

Figure 6. Inverse polar figures, including the max texture intensity in units of multiples of random distribution (mrd) as indicated by the colour bar. (a) Ni-DC4 (b) SiC-DC4 (c) Ni-DC10 (d) SiC-DC10 (e) Ni-PR-HF (f) SiC-PR-HF (g) Ni-PR-LF (h) SiC-PR-LF.

3.3. Microhardness

The microhardness tests showed a grain size correlation, comparable to Hall-Petch strengthening, between hardness and the microstructure of the deposits (Figure 7) and content of codeposited SiC (Figure 8).

The hardness of the pure Ni coatings was directly proportional to the grain refinement. The deposits where large columns were dominant (e.g. nickel at DC4 and PR-HF, Figure 5a and e) showed typical hardness values of pure nickel of about 280 HV. The use of the tailored long pulse reverse waveform decreased the grain size, thus increasing the hardness up to 315 HV. Nevertheless, the maximum hardness was attained in the samples produced by DC10, where the grain refinement was most distinct.

The addition of nanoparticles contributed directly to the increase in hardness for all the samples. However, the samples were strengthened differently, and two hardening effects were identified. The first type is the hardening by the combination of the grain refinement caused by the selection of the electroplating method, and the decrease of the grain size provoked by the increase of nucleation sites caused by the particles codeposition. The second type is by the increase in particle content alone.

The hardness of the samples produced by DC and PR-HF was a product of the first hardening effect, the contribution of both microstructure and codeposited SiC. For these samples, Figure 7 shows that the increase in hardness was accompanied by the grain refinement provoked by the codeposition, as reported in previous studies^{4, 29, 30}. Therefore, the hardness was maximum when the electroplating method provoked the highest grain refinement in the metal matrix (DC10), which is further refined by the particles' codeposition. The addition of particles in the deposits produced by PR-LF had no impact on the grain size. Still, the increase in hardness was considerable (70 HV) due to the hardening effect caused by the particles' content alone.

Figure 8 shows the hardness as a function of particle content. The composite produced by DC4 and PR-HF had the lowest hardness increase, compared to the pure Ni counterpart, due to the combination of larger grain size and low content of codeposited SiC. When comparing PR-HF and DC10, it was evident how significant to the hardness increase is the contribution of the grain refinement caused by the electroplating parameters, and by the codeposition. Even though the vol%. content of SiC was similar the hardness was increased by more than 25%. This strengthens the assumption that the total hardness of these deposits was a function of the first type of hardening: the synergistic effect between the resulting microstructure, refined by the electroplating method and the codeposition of particles.

The particles alone also had a hardening effect on the composites. However, the increase in hardness varies between content (Figure 8). There was only a minor improvement in hardness ($\Delta HV \approx 40$) over the pure metal in the composites produced by DC10 and PR-HF; while PR-LF achieved the highest increase ($\Delta HV \approx 70$) due to a higher content of particles. Even further, when comparing PR-LF with DC10, the hardness was similar even though the matrix microstructure was different. Although the metal matrix produced by DC10 was well refined, the higher the particles' content in PR-LF provoked an equivalent hardening effect. This shows that the final properties could benefit from both the microstructure and codeposited particles, or by a high content of nanoparticles alone, reliably codeposited by PR.

Figure 7. Microhardness vs Grain size relationship measured for the electrodeposited pure Ni and composite with SiC 50 nm at different current set-ups.

Figure 8. Microhardness vs codeposited SiC volume content (%) for the electrodeposited pure Ni and composite with SiC 50 nm at different current set-ups as determined by WDS.

4. Conclusions

The use of PR with a waveform where the plating and stripping thicknesses were based on the particle size ($1D - \frac{1}{2}D$), was proven effective in increasing the nanoparticles deposition. In order to avoid passivation, the anodic pulses were designed as a pulse train with intervalled short cathodic pulses. The combination of these pulses during reverse cycles may increase the particles' sitting time at the composite's surface, aiding to their recapture by the composite in the following plating cycles. The composite produced by this waveform doubled or quadrupled the SiC content, up to 4 vol.%, compared to other methods. This also provided the highest increment in hardness compared to pure metal coatings.

The pure Ni coating produced by DC10 had a refined microstructure and a non-dominant preferential $\langle 100 \rangle$ crystal growth. The high current density presumably led to a decrease in the grain size and high local alkalization; therefore, encouraging more randomly oriented grains. The addition of particles slightly modified the microstructure, decreasing the grain size area and preferred growth direction.

Compared to DC4, the use of PR with high frequency produced deposits with a similar large columnar microstructure and a more dominant preferential $\langle 100 \rangle$ crystal growth. This correlation was due to a similar average current density. In both methods, the addition of nanoparticles decreased the average grain size, compare to pure Ni counterpart, by increasing the number of smaller grains.

The pure Ni samples produced by PR with tailored pulses, i.e. $1D - \frac{1}{2}D$ thickness, also had a columnar microstructure. However, crystal growth inhibition was stronger compared to other methods. The lower CE played a significant role in growth inhibition by increasing the reduction of hydrogen and the formation of $\text{Ni}(\text{OH})_2$. Opposite to the composites produced by other methods, the addition of the particles did not have any effect on the microstructure.

This study revealed that the hardness of the composites is a function of the synergistic relationship between the matrix microstructure caused by the codeposition, or the particle content alone. The hardness of the samples produced by DC and PR-HF was proportional to the grain refinement of the metal caused by the electroplating method and the refinement caused by the particle codeposition. However, the hardness of the samples produced by a non-traditional PR with tailored pulses was not the result of a grain boundary strengthening but solely due to particle codeposition.

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