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Role of anodic time in pulse-reverse electrocodeposition of nano-SiC particles

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Abstract

This work focused on the significance of the particles residence time in composite electrodeposition. Ni-SiC were produced using different pulse-reverse (PR) waveforms based on the particles average diameter (60 nm). The waveform was designed to deposit a metal thickness equivalent to the average diameter during the cathodic pulse and strip half during the anodic pulse. The shape of the waveform was modified to study its effect on particles codeposition by changing the cathodic and anodic pulse current density peaks and cycle time while maintaining the same charge. For benchmark, samples were also produced under direct current (DC), matching the cathodic pulse current density peaks and average. The electrodeposition was done in an additive-free and SDS-Watts bath. ζ -potential measurements were employed to determine the interaction between particles and electrolyte. A relation was established between particle incorporation rate and residence time at the electrode interface, examining. The microhardness of the deposits was also studied. The SiC content was more than doubled by PR compared to DC, from 2 vol.% to 5.5 vol.% even after SDS addition. The increase in codeposition rate was related to the anodic pulse time, supported by the existing models on the mechanisms of particles codeposition.

Keywords: Pulse reverse current; Nanocomposite coatings; Surfactant; ζ -potential; Residence time; Electrophoresis

1. Introduction

The benefits of including hard nanoparticles as the second phase in metal-matrix composites rest in the sufficient incorporation volume and distribution within the matrix necessary to enhance the deposits' final properties. High content of particles have a beneficial effect on composites, improving their coating hardness and wear protection ¹. Furthermore, nanoparticles have also been linked to grain refinement ²⁻⁴, thus, promoting grain boundary-strengthening in addition to strengthening by particles, improving hardening. Therefore, the main goal of previous scientific research ^{5, 6} can be summarised as the optimisation of parameters to control and increase nanoparticle inclusion.

Nevertheless, due to its complexity, the electrodeposition process is sensitive to any change in the process parameters ^{6, 7}. The optimisation process results have been limited to specific experimental conditions, and thus, a generalisation of the optimisation methods or the parameters control has not been achieved. As a result, the codeposition process is not controlled, resulting in scattered and sometimes contradictory results. In the last decades, different theoretical models have been proposed as an attempt to describe the mechanisms of particle transport and codeposition by electrophoresis, mass transport, hydrodynamics or convection-diffusion ⁶, and predict the codeposition rate. These models, however, are often limited by not considering all the systems mechanisms as a whole but as single instances.

Guglielmi ⁸ described codeposition as two consecutive steps: adsorption and electrophoresis but without considering the effects of flow. In the first step, described as physical-based, a layer of loosely absorbed particles is built at the cathode's surface. Secondly, the electric field promotes a strong adsorption at the interface, leading to their entrapment by the growing metal. Celis et al. ⁹ proposed that particles transport was proportional to the mass transport of ions toward the working electrode. The model suggests that an adsorbed layer of ionic species is built around the particles after their addition to the plating solution. Particles are then transported by convection-diffusion to the cathode, and their incorporation depends on the number of transported particles and which metal ions, the ones adsorbed ions on the surface of the particle or free in the electrolyte, are reduced. Celis et al. suggested that the probability of particles entrapment increases when the adsorbed ions on the surface of the particle are preferentially reduced. However, concentration nor overpotential variations were considered in the model. Vereecken et al. ¹⁰ also described the transport of particles as controlled by convective-diffusion, but the model considered hydrodynamics as well and assumed that particle incorporation rate increases by their residence time at the cathode's surface. The model proposes that particles will diffuse away if a critical time is not met before the metal entrapment occurs. Fransaer et al. ¹¹ model use trajectory analysis to describe the favourable conditions, given by tangential forces acting on the particle, to decrease the removal rate of particles away from the cathode. In essence, if the forces acting on the particle allow its immobilisation at the cathode's surface, the particle residence time will increase, improving the chance of the particle being entrapped by the growing metal.

Essentially, models mainly agree on two common factors: (i) particles must be efficiently transported from bulk electrolyte to the cathode's surface, and (ii)

particles must stick adequately at the surface for a critical time so the growing metal matrix can entrap them. The present study examines the role that the shape of the anodic pulse during pulse-reverse plating play in promoting these two factors: transport and residence time.

ζ -potential measurements were used to examine the SiC particles surface charge in a diluted Watts bath ¹², and after the addition of sodium dodecyl sulfate (SDS). The surfactant type was preferred anionic over other classes to promote a negative surface charge in SiC particles ^{13, 14}, so the electrophoretic transport capability of the anodic pulse during pulse reverse could be examined.

Ni-SiC (60 nm) composite coatings were produced by different current set-ups. The net charge of the process was kept constant, allowing the same metal deposition rate in all samples. Samples were produced under two different direct currents (DC) densities, 4 and 10 A dm⁻², as benchmarks. Samples were also produced under an adapted pulse-reverse (APR) waveform, taken from Pinate et al. ¹⁵. The APR from the previous study was designed to plate a thickness equivalent to the particle diameter during the cathodic pulse and strip half the diameter during the anodic pulse. The APR waveform had the advantage of releasing some of the particles during the anodic pulse, permitting the particles to remain in the surface's vicinity, increasing the number of particles near the cathode surface. As a result, the subsequent layer of growing metal has a higher chance to entrap particles. The time or current density of the anodic pulse was adjusted in the present work, allowing the study of their effect on the released particles. Microhardness was also examined to determine the significance of controlled codeposition and verify if the particles' content was directly related to the final hardness.

2. Experimental and characterisation details

2.1. Electrolyte composition and experimental set-up

The electrodeposition was carried out at different current types: direct current (DC) or adapted pulse-reverse (APR), in a thermally controlled (45 °C) cell with 2 L bath volume from two electrolyte compositions: Additive-free Watts bath ¹² and after SDS (0.4 g L⁻¹) addition, as listed in Table I. The powder load was 20 g L⁻¹ of SiC nano-size powder (Iolitec GmbH #NC-0002 β -SiC 60 nm). The configuration of the electrodes was in parallel vertical with a distance between the cathode (low carbon steel, 0.25 dm²) and anode (pure Ni, 0.90 dm²) of 12 cm, and the suspension was continuously stirred at 200 rpm by a cylindric-shaped rotating magnet (0.7 cm diameter and 6 cm in length) placed in the bottom of the cell. Fransear et al. ¹¹ and Berçot et al. ¹⁶ pointed at the influence of hydrodynamic velocities and flow regime in particles codeposition. In order to take into account their impact, the cell geometry, bath agitation and operating conditions were kept constant for all samples.

Before electroplating, the low carbon steel substrates were mechanically ground with SiC grade #1000, cleaned ultrasonically in an alkaline soap (5% diluted, TICKOPUR R 33; DR H STAMM GmbH) and activated by pickling for 8 min in 2.5 M H₂SO₄. The electrolyte was stabilised at pH 3.0 before electrodeposition by sulfuric acid or sodium hydroxide. Additionally, the solution was agitated by ultrasound (Hielscher, 24 kHz, 0.087 W cm⁻³) for 30 minutes before electroplating to avoid the agglomeration of particles.

Table I. Plating bath parameters

NiSO ₄ ·7H ₂ O	240 g L ⁻¹	Temperature	45 °C
NiCl ₂ ·6H ₂ O	45 g L ⁻¹	Stirring speed	200 rpm
H ₃ BO ₃	30 g L ⁻¹	Particles concentration	20 g L ⁻¹
SDS (Sodium dodecyl sulfate)	0.4 g L ⁻¹	SiC particles average size	60 nm
pH	3.0		

2.2. Direct current and pulse-reverse waveform set-up

The different electrodeposition conditions were modified following the parameters described in Table II. Considering the role of the current density in particles codeposition reported by Hwang et al. ¹⁷, the set-ups were designed to maintain the same process' net charge (≈ 1800 C) to prevent differences in their faradaic electrodeposition. The electrodeposition was done on a 5 cm x 5 cm cathodic surface area for all samples.

Table II. Electrodeposition parameters

Direct Current (DC)			
Total deposition time (min)	12; 30	DC deposition net charge	1800 C
Current density (A dm ⁻²)	10; 4	Cathode area	0.25 dm ²
Anode area	0.90 dm ²	Anode material	Nickel 99.9% purity
Adapted pulse reverse waveforms			
APR deposition net charge		1800 C	
Cathodic current density peak (A dm ⁻²)	$i_c = 10; 4$ in APR _{ic4} only	Anodic current density peak (A dm ⁻²)	$i_a = -5$ in APR _{hia} ; -4 in APR _{ic4} and APR _{ic10t} ; -2 in APR _{hat}
Cathodic duration (ms)	$t_c = 1780; 4450$ in APR _{ic4} only	Anodic pulse duration (ms)	$t_a = 3744$ in APR _{hia} ; 5040 in APR _{ic4} and APR _{ic10t} ; 8190 in APR _{hat}
Plating thickness per cathodic cycle	≈ 60 nm	Stripping thickness per anodic cycle	≈ 30 nm
Number of cycles	800	Approximate total deposition time (min)	69 in APR _{hia} ; 127 in APR _{ic4} ; 91 in APR _{ic10t} ; 133 in APR _{hat}

Two of the set-ups were under DC with electric current densities of 4 and 10 A dm⁻², and four were under APR waveforms, designed after a previous work ¹⁵. The APR waveform was adapted to deposit a metal thickness equivalent to the particles' diameter (60 nm) during the cathodic pulse and strip half (30 nm) during the anodic pulse, as depicted in Figure 1. As described by Pinate et al. ¹⁵, a train of anodic pulses with intervals of short cathodic train pulses (6 ms and 2 A dm⁻²), shown in Figure 2, was required to modify the reverse pulse to avoid metal passivation.

Figure 1. Adapted Pulse-reverse plating representing the incorporation of 60 nm SiC particles.

Figure 2. Adapted Pulse-reverse waveform (APR) (a) Cathodic and anodic pulse of a single cycle (b) Reverse pulse train within the anodic pulse as designed by Pinate et al. ¹⁵.

The different APR waveform shapes are depicted in Figure 3. In two of the APR waveforms, APR_{ic4} and APR_{ic10}, the cathodic pulse was modified by setting the current density peak at 4 and 10 A dm⁻², respectively, to match the DC densities. The cathodic pulse times were adjusted to maintain the same net charge of the process while maintaining the same anodic current density (-4 A dm⁻²), anodic total pulse time (5040 ms) and anodic train pulse (10 ms).

In the adapted pulse-reverse with high anodic current (APR_{hia}), the anodic current density peak was increased to -5 A dm⁻² and the anodic total pulse time shortened (3744 ms) without modifying the anodic train pulse time. While in the adapted pulse-reverse with longer anodic time (APR_{hat}), the anodic current density peak was decreased to -2 A dm⁻² and the anodic pulse time raised to 8190 ms by increasing the anodic pulse train time from 10 ms to 20 ms. The cathodic pulse in both APR_{hia} and APR_{hat} was kept the same as in APR_{ic10} for comparison. Three samples for each electric current type and current density condition were electrodeposited from the additive-free electrolyte and after SDS addition.

The current efficiency (CE) of the processes was calculated as the ratio of the deposited mass minus the particles' mass (measured by WDS) compared to the theoretical deposited mass as predicted by Faraday's law.

Figure 3. Scheme of APR waveforms.

2.3. ζ -potential

The ζ -potential was measured in a diluted (25%) variant of the working electrolyte with and without SDS. Both were measured at the conditions described in Table I, changing the concentration of the SiC particles to 0.2 g L^{-1} . The values were determined by a Zetasizer Nano ZS (Malvern Instruments, Herrenberg) by laser Doppler velocimetry. The refraction index of the SiC particle was set to 2.610 and the electrolyte adsorption index to 0.900. The particles were kept in suspension by continuous agitation and before measurements and US for five minutes. The ζ -potential was expressed as the average value of three different sets of ten ζ -potential measurements.

2.4. Coating characterisation

The cross-section of the deposits was analysed by scanning electron microscopy (SEM, TESCAN Lyra 3). The composition analyses and quantification of SiC particles were done by Wavelength dispersive X-ray spectroscopy (WDS, EDAX-TSL) in preference over energy-dispersive spectroscopy (EDS) due to the better resolution of light elements at a low content. Pure Si standards were used to quantify the Si weight %. The analysis of each specimen was performed over a surface area of $75 \times 75 \mu\text{m}^2$ using an acceleration voltage of 10 kV and a beam current ranging from 13.2 nA to 18.1 nA. The SiC volume content is calculated starting from Si wt% data and considering the particles to be stoichiometric and with a density of 3.22 g cm^{-3} . The values are expressed as the mean average of five different WDS area measurements of two different specimens.

The microhardness of the deposits was obtained from load-displacement curves by microindentation (NanoTestTM Vantage) with a Berkovich pyramidal-shaped diamond tip. The measurements were done on the cross-section with an indentation load of 100 mN and a dwell time of 10 s. Fifteen repetitions were done on two samples

for each condition, and the values were expressed as the average and standard deviation.

3. Results and discussion

3.1. ζ -potential

Particle addition to an electrolyte leads to the interaction between particle surface and the elements that constitute the electrolyte. In suspension, the surface of the particles adsorbs ions forming an ionic cloud¹⁸. The type of adsorption is dependant on the particle surface charge¹⁹. Thus, the potential at the topmost layer of the ionic cloud, referred to as ζ -potential²⁰, is used to characterise the behaviour of the particles in suspension.

SiC particles showed a negative and close to zero ζ -potential value ($-0.09 \text{ mV} \pm 0.74$ ²¹) in the additive-free Watts bath. Although previous studies^{13, 22} also reported negative ζ -potentials for nano-sized SiC in Watts based baths, ζ -potential values are dependant on the environment where the measurement is done. For instance, measurements taken on SiC particles in nickel sulfamate or KCl electrolyte showed positive ζ -potential values^{23, 24}. The addition of SDS increased the SiC ζ -potential absolute value, becoming more negative ($-10.66 \text{ mV} \pm 0.74$). Lari et al.¹³ also reported an increase in absolute value and more negative values in SiC ζ -potentials after adding SDS to Watts-Co bath. Kenjiro et al.¹⁴ as well, reported negative ζ -potential for β -SiC in the presence of SDS.

3.2. Particles codeposition

Most codeposition models are built upon the interaction between particles and electrolyte²⁵. The cloud of ionic species surrounding the particle influences their transport from the bulk electrolyte to the cathode. Therefore also affecting their incorporation. Fransaer et al.¹¹ model considered the influence of the ionic cloud on the particles transport by approximating ζ -potential measurements to the electrophoretic force acting on the particles. Ultimately, the model proposed that codeposition occurs if all forces are favourable for the particle entrapment. In practice, the codeposition results from a series of input variables that affects codeposition as a whole⁶, and not necessarily explicitly due to the presence of synergistic or antagonistic inter-linked effects.

The increase of electric current inefficiencies due to side reactions in nickel electrodeposition is anticipated. The pH increase due to the hydrogen reduction on the cathode surface²⁶ is an indication of this. Side reactions influence the current efficiency (CE) of the process leading to a drop in efficiency, ranging from 90-98% in Watts baths²⁷. Celis et al.⁹ model placed special attention on the efficiency of the metal deposition. Particle codeposition was described as the weight increased by particle entrapment, probability of entrapment, and transported particles. The first term, weight increase by particle entrapment, only ensues if the growing metal covers the particle. In the model, the current efficiency was assumed as 100%. Thus, in real electroplating conditions, drops in CE might hinder particle codeposition.

The correlation between CE, pH variation and SiC codeposition rate (Figure 4) varied between conditions. The process average pH change (ΔpH) was calculated by measuring the pH before and after each electrodeposition. In samples produced under DC, the ΔpH was never higher than ≈ 0.07 , even after SDS addition. The CE of

the process in these samples ranged from 94 to 98%, indicating some influence of hydrogen reduction in the metal deposition efficiency.

The relation between ΔpH and CE was not clear in the APR samples. The ΔpH ranged from values of ≈ 0.4 to around ≈ 0.7 , with a maximum of ≈ 1.0 in APR_{ic10} after SDS addition. However, contrary to an expected low metal deposition efficiency, all CE APR ranged from 95 to 98%, except in $APR_{ic10}+SDS$ reporting $\approx 92\%$. The lack of correlation between ΔpH and CE was due to the different efficiency at each electrode and the hydrogen reduction occurring during each waveform pulse at each electrode. On the cathode during the forward cycle or the counter electrode during the reverse cycle. Hence, hydrogen evolution took place for the total duration of the process. Thus, promoting further pH changes, but with a Ni mass deposition similar to DC, thereby reporting comparable CE values. The same phenomenon was observed in a previous work of Pinate et al. ¹⁵.

Although CE values were similar between conditions, and all samples were produced under the same set-up to guarantee a similar effect from hydrodynamics, the SiC incorporation rate (Figure 4) varied between samples, pointing to an additional element influencing the mechanisms of transport and entrapment.

Figure 4. Codeposited SiC volume content (%) in Ni/SiC composites from additive-free Watts bath and SDS, as determined by WDS.

In DC samples, the codeposition rate was similar independently of the current density, reporting a codeposition of around 2 vol.% under both 4 and 10 A dm⁻². Eroglu et al. ²⁸ also reported ≈ 1.7 vol.% in SiC particles with similar size (45-55 nm) in Ni-SiC nanocomposites produced under DC (5 A dm⁻²) from Watts bath with the same powder load (20 g L⁻¹). While Gyftou et al. ²⁹ reported about ≈ 3 vol.% content in Ni-SiC nanocomposites produced under similar conditions. Although samples were produced from similar baths compositions and showed similar codeposition values, it is essential to remark that the stirring system in these studies was different. Therefore, it is not possible to compare the codeposition mechanisms since the hydrodynamics were not considered. As suggested by Berçot et al. ¹⁶, stirring by a

magnetic rotator is not adequate when carrying out a comparative study to other systems.

Figure 5a depicts how particles are transported as the result of their interaction with the additive-free Watts. With ζ -potentials values close to zero, the electrophoresis does not play an active role in the transport of the particles compared to other transport mechanisms such as convection and diffusion. More importantly, the electrostatic attraction between particles and the cathode's surface, as described by Guglielmi ⁸, would also be minimised. Therefore, any favourable condition for codeposition in DC electrodeposition was achieved by the combination of metal growth and entrapment and fluid dynamics. Despite not modifying the current density or agitation, SDS addition had a slightly negative effect on the particle codeposition rate, proving the influence of surface charges with the same sign in electrostatic attraction.

Figure 5b depicts how particles are transported due to their interaction with the electrolyte after SDS addition. In the presence of the surfactant, the SiC vol.% slightly decreased. In both DC 4 and 10 A dm⁻², the content dropped from ≈ 2 vol.% to 1.4% and 1.2 vol.%, respectively. Opposite to the interaction between the particles and additive-free Watts, the resulting ζ -potential value after SDS addition was more negative. Therefore, any possible electrophoretic effect in transport from the bulk electrolyte to cathode should be disregarded. After the particles are transported by convection-diffusion to the cathode's vicinity, the electrostatic attraction at the cathode surface described by Guglielmi ⁸ is instead repulsion between the negatively charged particles and the negative electric field. For instance, the opposite effect can be achieved. Kılıç et al. ²² reported initial negative ζ -potential values for SiC in a Watts-based bath. The values were shifted to positive after cetyltrimethylammonium bromide (CTAB) addition. The authors reported a linear increase in SiC vol.% connected to the positive ζ -potential values and CTAB addition.

Figure 5. Electrophoresis of SiC particles during cathodic current in (a) additive-free Watts and (b) Watts with SDS.

The negative effect of SDS addition in DC electrodeposition was not limited only to the interaction between particle and electrolyte. A second response, physical in nature, the release of H₂ bubbles, could also have disturbed the particles as they stick to the surface of the cathode. SDS is a surfactant that modifies the surface tension of the electrolyte, thus decreasing the cathode's wettability and preventing the bubbles from clinging. The displacement of the bubble can be a tangential force, enough to remove particles from their sticking place, hindering entrapment as described by Fransear et al.¹¹, or create a turbulent flow that can disturb particle codeposition. Berçot et al.¹⁶ reported a decrease in incorporation rate due to pure turbulent flow. In essence, any response that decreases residence time will impact the incorporation rate, as pointed by Vereecken et al.¹⁰.

APR deposition reported a significant increase in SiC codeposition rate compared to DC, showing that a waveform adapted to the particles average diameter influenced the particles codeposition. Similar studies with PR waveforms³⁰⁻³², where the deposited thickness of the metal per cycle approached the particles diameter size, also reported a considerable increase of particle content compared to DC. For instance, in a previous study, Pinate et al.¹⁵ reported an increase of SiC particles with an average size of 50 nm from ≈ 0.8 vol% using DC4 to 4.1% with a PR adapted to the particles average diameter.

The variation in the cathodic pulse current density peak from 4 to 10 A dm⁻² in APR_{ic4} and APR_{ic10} had minimal influence on the codeposition as comparable contents were observed, $\approx 3.4 \pm 0.4$ and $\approx 3.8 \pm 1.1$ vol.%, respectively. This proves that the anodic pulse and the waveform design had ultimately impacted the particles codeposition.

Figure 6 depicts an N cycle of the adapted pulse-reverse waveform. During the cathodic pulse (Figure 6a), the transport and codeposition were like those described in DC plating. A physical transport move particles through the convective layer and diffusive transport over the concentration boundary^{9,10}. However, not all particles are successfully transported, and thus, the number of particles shows a decreasing gradient after each successive layer. Similar to the Nernst diffusion layer model for the concentration of ions, where the concentration decreases closer to the electrode.

Celis et al.⁹ described the incorporation rate as a function of the probability of the particles to be entrapped by the metal growth and the number of particles that were successfully transported. These two factors are essentially equivalent during the cathodic current of DC or APR since the set-up was constant. Celis et al. expressed the probability of entrapment as the chance of reducing the ions at the particles' surface. Since ion reduction is correlated to the cathodic current density by Faraday's law, the probability of entrapment is therefore linked to the cathodic current. In both cases, DC and APR, the variation of current density between 4 or 10 A dm⁻² had no noticeable impact in SiC codeposition, i.e. the cathodic current did not provoke any change in the probability of entrapment. The other factor, the chance of transport, is ruled by the hydrodynamics of the system, which was constant for all samples. Furthermore, the electrolyte composition, varied by SDS, did not affect the codeposition negatively in samples produced using APR, opposite to the results observed under DC deposition. Therefore, considering that the cathodic current did not modify the probability of entrapment or particles transport, it indicates that the codeposition was encouraged solely by the reverse pulse introduced in the APR electrodeposition.

Figure 6. Schematic illustration of the mechanisms of particle incorporation during electrodeposition. Under the (a) cathodic current, electric migration takes place toward the deposit. Particles are transported from bulk (∞) by convective movement through the convective layer (c); diffuse through a concentration layer (δ); arriving at the electrical double layer (ψ) where adsorption and entrapment take place. Similar to the Nernst diffusion layer, where ion concentration (C_i) decreases in the region closer to the electrode. Particles concentration (C_p) is also reduced closer to the cathode since not all particles are successfully transported. Under the (b) anodic current, electric migration advances away from the deposit and particles are released back to the electrolyte. Particles concentration (C_p) is immediately increased at the electrical double layer (ψ), some particles may be removed and diffuse-convect away (δ , c) from the surface to the bulk (∞). Ion concentration (C_i) decreases farther from the deposit.

In the anodic pulse of the cycle (Figure 6b), particles are released back to the electrolyte, increasing their number across the layers close to the deposit. Under the anodic current, electrons flow out of the deposit, changing its sign to positive. At this moment, the released particles might be subjected to migration toward the deposit driven by the electric field (Figure 7), promoting an electrostatic attraction because of the difference in sign between electrode and particles, more significant after SDS addition (Figure 7b). Diffusion could transport released particles away from the deposit toward the bulk electrolyte. However, this would be minimal because of the bulk's higher particle concentration. Since the convective transport depends on the fluid dynamics of the system, constant during the process, any benefits or hindrance from convection is similar to the ones present on the cathodic pulse. Any further considerations on the hydrodynamics were limited since stirring by a magnetic rotator does not allow complete control of the hydrodynamic flow.

Even though convective-diffusive transport might have worked against codeposition during the anodic pulse, the inclusion rate was improved due to electrostatic attraction as described by Guglielmi⁸. Successive pulses recaptured particles where

the electrostatic attraction was sufficient to keep the particle stuck to the deposit, along with capturing new ones. In the next cathodic pulse (in the following N+1 cycle), the number of particles in the diffusion layer is higher than in the cathodic pulse (from the N cycle). Therefore, as described by Celis et al. ⁹, codeposition would be increased due to new particles crossing the diffusion layer, besides the ones that were released in the anodic pulse. Furthermore, due to the continuous entrapment-release and subsequent electrostatic attraction, particle incorporation was increased due to the increased chance of particle entrapment since more particles are readily available.

Figure 7. Electrophoresis of SiC particles during anodic current in (a) additive-free Watts and (b) Watts with SDS.

The anodic pulse was modified to determine the influence of the anodic current density in the particles' electrostatic attraction and the influence of the anodic pulse time in the particles residence time. In APR_{hia} the anodic current density was increased (-5 A dm⁻²), shortening the anodic pulse (≈3.8 s), while in APR_{hat} the anodic time was increased (≈8.2 s), decreasing the anodic current density (-2 A dm⁻²).

APR_{hia} reported a slightly lower SiC content (2.9 vol.%) than APR_{ic10} (3.8 vol.%), also showing similar SiC codeposition independently of the electrolyte composition (2.7 vol.% in SDS). The increase in anodic current density might have caused a negative effect by releasing the particles too rapidly. The electrostatic attraction was not sufficient to keep the particles in the cathode vicinity for the critical time to ensure the recaptured of particles in the next cathodic pulse, despite the more negative values of the particles ζ-potential after SDS addition. Analogously, Vereecken et al. ¹⁰ described that codeposition is prompted if the residence time of particles is increased. A higher anodic current for APR_{hia} was attempted but resulted in passivation and delamination of the deposit.

On the contrary, APR_{hat} with a longer anodic pulse time reported the highest content compared to any other electric current parameter. Thus, showing that a slower release of particles and an increase in the time that permit particles to stuck to the

deposit promoted SiC inclusion. Therefore, promoting a higher chance to entrap particles in the successive cathodic pulses. These results agree with the models that related incorporation rate to residence time ^{10,11}. Xiong-Skiba et al. ³² also reported using an adapted pulse-reverse plating based on particles diameter, an increase in particle content (Al_2O_3 50 nm), as high as 22 wt.%, when the anodic pulse was 10,000 ms long. Instead of 7.5 wt.% content with a 7,000 ms anodic time.

The method where the pulse-reverse waveform is adapted to the particles average diameter shows good reliability, considering that the present study and Pinate et al. ¹⁵ used the same APR waveform design and that both studies showed similar codeposition rates (4.1 vol.%¹⁵ and 3.8 vol.%).

Cross-section imaging by SEM indicated minimal particles agglomeration in the deposits independently of the current type: DC (Figure 8a) or APR (Figure 9a), showing agglomerate sizes smaller than 500 nm in all cases. The lack of sizeable agglomerates in the deposits produced by APR proves that the increase in particles content observed in this condition was not due to an increase in agglomerations. The change in the current type did not modify the particles entrapment. Furthermore, The addition of SDS did not affect the entrapment of particles within the matrix (Figures 8b and 9b), showing similar characteristics to the additive-free deposits.

Figure 8. SEM cross-section image of Ni-SiC 60 nm produced using DC4. (a) additive-free and (b) with SDS. SiC particles are indicated by the white-coloured circles. The insets show high magnification images of the particles encircled in yellow.

Figure 9. SEM cross-section image of Ni-SiC 60 nm produced using APRic10. (a) additive-free and (b) with SDS. SiC particles are indicated by the white-coloured circles. The insets show high magnification images of the particles encircled in yellow.

3.3. Microhardness

The microhardness tests showed hardening by particle strengthening, revealing that hardness increased linearly with the codeposition increments. Figure 10 includes all composites produced from the additive-free Watts solution. Pure nickel produced under the conditions described in Table I and using APR_{ic10} was also included to benchmark the composites hardness values. Ni-SiC electrodeposited under APR_{ic10} from the Watts and SDS solutions were included to compare composites with different electrolyte compositions and the same electric current parameters (APR_{ic10}).

Figure 10. Microhardness (GPa) vs codeposited SiC volume content (%) as determined by WDS for all additive-free composites, accompanied for benchmark, by Pure Ni (X) and Ni/SiC+SDS (◇) both produced under APR_{ic10} .

Pure Ni showed similar values (2.30 ± 0.31 GPa) compared to pure nickel deposits from a previous study (2.58 ± 0.25 GPa¹⁵), also produced under an APR, revealing consistency of the method in producing nickel deposits with similar behaviours. The addition of SiC (60 nm) hardened all the electrodeposits, following the already established relationship between increments of codeposition and hardness¹. Composites produced by DC10 showed higher hardness, up to 13% higher, compared to DC4 despite presenting similar particles content. In a previous study, Pinate et al.¹⁵ also observed similar results where the differences between hardness values of nickel deposits produced by using DC4 and DC10 were attributed to the combined effect of particles content and the matrix microstructure resulting from different current densities. Furthermore, Gül et al.³³ also observed in Ni-Al₂O₃ electrodeposits higher hardness values with increasing direct current densities but similar vol.%, attributed to the grain refinement.

In the APR composites, a linear increase in hardness was evident with the increase of SiC particles (Figure 8). APR_{hat} reported the highest codeposition, along with the highest hardness value. The composites produced under APR_{ic10} displayed the reliability of the APR method in producing Ni-SiC composites with similar behaviours. Although the composites were produced from different electrolytes compositions, both reported similar SiC content and hardness values.

4. Conclusions

The interaction between particles and electrolyte varied after the addition of SDS. The ζ -potential value of SiC in a diluted variant of an additive-free Watts was negative and close to zero, whereas, in diluted a Watts with SDS, the values were ten times more negative. All adapted pulse-reverse waveforms based on particles average diameter successfully increased the SiC codeposition rates compared to DC electrodeposition, independent of the electrolyte composition.

The addition of SDS decreased SiC content under DC 4 A dm⁻² around 25%, and 35% under DC 10 A dm⁻², compared to the additive-free plating. SDS had no influence on the SiC deposition rate when APR was used. Under DC, two factors were identified as responsible for the reduction in SiC content. Due to the more negative ζ -potential value, SiC particles were exposed to electrostatic repulsion, reducing the electrophoresis's contribution in the particles entrapment. Lastly, SDS also affected the electrolyte's surface tension, aiding in the release of hydrogen bubbles. Particles entrapment was disturbed by these bubbles, reducing the time particles stick to the cathode surface, agreeing with the theoretical models that link particles inclusion to residence time.

The cathodic current density did not modify the codeposition rate. The changes in cathodic current density peak, 4 and 10 A dm⁻², in APR_{ic4} and APR_{ic10}, respectively, had no impact on the SiC content. This indicates that the anodic pulse was responsible for the increase in SiC codeposition compared to DC plating. In the anodic pulse, particles were released back to the electrolyte, with some remaining close to the cathode. The particles that did not diffuse away enriched the cathode's vicinity and were re-entrapped in addition to the ones that crossed the diffusion layer in the subsequent cathodic pulse. Thus, agreeing with the mechanisms proposed by Celis et al. model where the incorporation rate was related to the probability of the particle successfully crossing the diffusion layer, i.e. the number of particles available to be entrapment: newly transported and previously released.

The increase of the anodic current density peak in APR_{hia} showed that a rapid release of particles during stripping of the metal led to a decrease in SiC content. The longer anodic time in APR_{hat} promoted an increase in particle content, reporting the highest vol.%, in agreement with the hypothesis where prolonged residence time was correlated to higher incorporation rates.

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