Effect of Ceramic Particle Pretreatment and Surface Chemistry on Electrocomposite Coatings

by Y. M. Henuset* & R. Menini

The quantity of embedded ceramic particles within an electroplated metal matrix plays a major role in the wear resistance of an electrocomposite coating (ECC). Increasing the ceramic content of an ECC may improve its wear resistance, and thus provide longer coating service life. There are several ways to enrich the ceramic content of an electrocomposite: optimize solution hydrodynamics, decrease current density or modify the charge of particles. This paper reports on the third method by presenting a study of the effect of various acidic particle pretreatments and the addition of anionic, cationic or amphoteric surfactants on the ceramic particle codeposition efficiency. The work focuses on two plating systems: (1) nickel/silicon carbide and (2) nickel/silicon oxide, using a sulfamate-based electrolyte. It has been demonstrated that a SiC powder pretreated with 15 vol% hydrofluoric acid (HF) and without a surfactant in the plating solution, produces coatings with the highest percentage of embedded particles. For a SiO₂ powder, the best conditions were obtained with an HNO₃ pretreatment and a cationic surfactant in the plating solution. The presence of impurities on the two types of particle influences both the particle inclusion probability and surfactant adsorption.

The replacement of hard chromium electrodeposits (because of the high toxicity of hexavalent chromium) by other coatings having equivalent properties has generated worldwide research into such surface technologies. The aerospace industry would benefit from such an alternative. Among the coatings that have been considered, cermets figure as promising substitutes.1 Cermets in general can be obtained by thermal spraying, by high velocity oxy-fuel (HVOF),² by physical vapor deposition (PVD)3 or by electroplating.49 Electroplating in particular allows one to produce composites. Hard coatings can be produced containing a wide variety of combinations of metal matrices and codeposited particles. It is also a non-line-of-sight technology. The metal constituting the matrix must be platable from an aqueous solution (e.g., nickel, cobalt, iron or their alloys). This requirement limits the choice of a matrix, but there is practically no limit concerning the particles that can be codeposited: ceramics, polymers, metal powders, among others. All types of particles, regardless of their size and shape, are superficially charged once put into an aqueous media. The overall charge of a given particle of powder will have an effect on its entrapment probability.

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Fig. 1-Particle entrapment mechanism according to Celis, et al¹⁰.



Fig. 2—Percentage of codeposited SiC particles within ECCs under various experimental conditions.

Nuts & Bolts: What This Paper Means to You

Composite coatings, that is, a mix of metals and ceramic particles, are excellent materials for high wear resistance. The more ceramic, the better the wear. Ceramic contents up to 70% are obtained by high velocity oxy-fuel (HVOF) processes. Here, the authors tried to see what plating could do, where problems line-of-sight "spraying" aren't an issue. They got up to 20% particle inclusion with nickel/silicon carbide, quite a bit for a plated coating ... and shed quite a bit of light on how to get more.



Fig. 3—Effect of acid treatment on SiC particles co-deposition efficiency: (a) untreated, condition A, (b) treated with HNO₃ 40 vol%, condition B, (c) treated with HF 15 vol%, condition C.

The work described in this paper includes the surface pre-conditioning of SiC and SiO₂ particles and surfactants added to the plating solution as a means of increasing the quantity of embedded particles in a nickel-based matrix. The impetus behind this study is motivated by the presumption that the more particles that are embedded, the better the wear resistance under certain tribological conditions. Some cermet deposits obtained by HVOF coating technology may have a metallic content as low as 30%, the remaining 70% being mainly ceramic (*e.g.*, tungsten carbide WC -12% Co). In order to reach such a high ceramic content in an ECC, ways must be found to promote particle codeposition. Surfactant addition and particle acid pretreatment are two ways to change particle charge within a given electrolyte.

Background

Particle Codeposition Mechanism & Influence of Surfactants

In order to evaluate the influence of particle surface impurities together with surfactant additions during plating, the codeposition mechanism must be understood. Inert particles added to strong electrolytes will become charged and/or hydrated up to a certain extent depending on their surface composition. Figure 1 shows a schematic of the formation of an electrocomposite coating according to Celis, *et al.*¹⁰ As seen here, the first step toward particle entrapment is the formation of an ionic cloud surrounding the particle. Following convection and diffusion, the particle contacts the cathode and is adsorbed on its surface. Simultaneously the metallic

Table

Selected Treatments & Surface Additives For the Study of the Effect of Various Conditions on Powder Codeposition Efficiency in ECCs.

Condition	Powder	Treatment	Surfactant
Α	SiC	None	None
В	SiC	40 vol% HNO ₃	None
С	SiC	15 vol% HF	None
D	SiC	15 vol% HF	Cationic
E	SiC	15 vol% HF	Anionic
F	SiC	15 vol% HF	Amphoteric
G	SiC	None	Cationic
Η	SiC	40 vol% HNO ₃	Cationic
2A	SiO ₂	None	None
3A	SiO ₂	40 vol% HNO ₃	None
4A	SiO_2	40 vol% HNO ₃	Cationic
5A	SiO ₂	None	Cationic

cations surrounding the particle are reduced. This overall process is also referred as "perfect sink conditions."

Although the convection and diffusion steps represent the key steps in bringing in the ceramic particles at an acceptable rate and velocity to produce a coating with a significant amount of codeposited particles, the nature and overall charge of the particles are also very important. This applies even for non-Brownian particles, as has been demonstrated by Fransaer, et al.¹¹ They showed that the perfect sink conditions were sometimes not respected. This is particularly true when strong electrolytes are used (as in electroplating processes) and when hydrophilic particles such as quartz and most oxides are selected. The resulting electroplated coating usually exhibits a poor particle volume fraction. In such cases and at locations very close to the cathode (on the order of nm), the hydration force is repulsive and counteracts the effect of the attractive Van der Waals forces. Attempts to overcome such repulsive forces have been performed by adsorbing monovalent cations (e.g., Tl⁺, Rb⁺ or Cs⁺) on the particle surface,^{12,13} or by surfactants added to various plating baths.¹⁴⁻²⁰

It is important to note that the addition of a cationic surfactant usually exhibits high particle inclusion rates, like the use of a silanamine compound,¹⁵⁻¹⁷ fluorocarbon types of surfactants^{14,18} or cetyl-trimethylammonium bromide (CTAB).¹⁹ As proven by Grosjean, *et al.*,¹⁸ for the Ni-SiC system, the positive charge of the particles results from the presence of electrostatically-bound Ni⁺² cations. The quantity of these cations is promoted by the adsorption of the cationic surfactant whose negative tail may point towards the solution.

Ceramic Particle Pretreatment

As mentioned above, the surface chemistry and the nature of the particle surface have a crucial effect on the degree of particle inclusion. This has been applied in the particular case of SiC particles in order to control and/or enhance the overall codeposition process. Silicon carbide powder is usually produced by SiO, reduction on activated carbon between 2000 and 2500°C (3632 and 4532°F).²¹ The commercial product is usually obtained as an aggregate of iridescent crystals. The iridescence is caused by a thin layer of silica produced by superficial oxidation of the carbide. Although manufacturers²¹ generally add a chemical treatment of the SiC particles (H₂SO₄, NaOH or HF) during processing, it is often difficult to know if this step was performed. In any case, the presence of SiO₂ must be suspected since oxides create a positive (repulsive) hydration force and may drastically decrease particle inclusion. The influence of nickel ion adsorption over the surface of the SiC particles on the codeposition kinetics was studied by Szcygiel.^{22,23} In his work, the influence of the surface purity of the SiC particles (i.e., the presence of Al, Ba, Cd, Cr and Fe) was considered when studying the deposition potential as a func-



Fig. 4—Effect of 0.5 g/L of cationic surfactant on SiC particles co-deposition efficiency, condition G.

Fig. 5—Synergetic effect of 0.5 g/L of cationic surfactant with an HF 15 vol% treated SiC powder on particles codeposition efficiency, condition D.



tion of applied current density and HNO_3 pretreatment. However, it was not considered as a factor that might affect the efficiency of ceramic particle codeposition. Moreover no attention was paid to the possible presence of a SiO₂ sheath.

Both aspects of various particle acid pretreatments and electrolyte surfactant additions were seldom studied together in the literature. For instance previous studies^{18,19} dealt only with impurity removal on the SiC surface (by HCl or H_2SO_4 pretreatments) and not with the probable presence of an SiO₂ layer. Different fresh acid treatments (HF or HNO₃) were performed on commercial SiC particles together with surfactant additions to the electroplating solution. Since silicon carbide particles are commonly oxidized at the surface, comparative studies were made with the Ni-SiO₂ system, specifically between untreated and pretreated (HNO₃) SiO₂ particles codeposited with or without the presence of a cationic surfactant. The results of such experiments were correlated with the behavior of the Ni-SiC system.

Experimental

The silicon carbide and silicon oxide powders used for the experiments were comparable in terms of particle size distribution (nominally 5ìm, ranging between 2 and 10 ìm) and shape (angular). The powders were pretreated in separate beakers with different acids according to their chemical resistance; HF and HNO₃ for SiC and HNO₃ for SiO₂. They were then thoroughly rinsed before adding to the plating solution.

Mild steel test coupons with an exposed area of 6.25 cm^2 (1.0 in.²) were used as substrates while nickel was used as the anode. The steel coupons were degreased, sand-blasted and soak cleaned before plating. The bath chemistry used was:

Boric acid	50 g/L
• pH	4.0
Bath temperature	45°C (113°F)
Particle concentration	35 vol%



Fig. 6—Percentage of codeposited SiO₂ particles within ECCs under various experimental conditions.

Experiments were conducted in one-liter beakers. Hydrodynamic conditions were kept constant for all experiments. Electrode positions were carefully maintained and the solution was magnetically stirred at a constant rate. The current density was set at 5.4 A/dm^2 (50.2 A/ft²) for three hours. Cationic, anionic and amphoteric surfactants were added separately to the baths. The various test conditions used are summarized in the table.

All chemicals and surfactants were commercially available. The cationic surfactant used was a quaternary ammonium salt of formulation $(C_4H_9)_4NCl$, tetrabutyl-ammonium chloride (TBAC). Three concentrations were studied, 0.12, 0.25 and 0.5 g/L. The anionic surfactant selected was a perfluoroalkyl sulfonic acid of formulation F_n -R-SO₂OH,* used at a nominal recommended concentration of 0.25 vol%. The amphoteric surfactant was a perfluoroalkyl betaine of formulation F_n -R-COOCH₂N(CH₃)₃** used at 1.0 g/L.

After each experiment, test coupons were cross-sectioned and mounted in epoxy polymer, then polished. The percentage of embedded particle for each specimen was evaluated with an image analysis program coupled to a scanning electron microscope. The results were given as a surface percentage occupied by the particles within the coating and based on the average value of ten measurements for each specimen.

Results & Discussion

SiC Powder

Influence of acidic treatments on particle codeposition. Figure 2 summarizes the results obtained for the silicon carbide powder pretreatment. Figure 3(a) shows a cross-section of a Ni-SiC electrocomposite coating obtained with an untreated commercial powder (condition A). Figure 3(b) shows the negative effect (low ceramic particle inclusion into the metal matrix) of a nitric acid (HNO₃) pretreatment on codeposition efficiency (condition B), while Fig. 3(c) clearly shows the positive effect of an HF pretreatment (condition C). The SiC particles were covered with impurities of iron, copper and zinc, (as determined by X-ray fluorescence) which most probably came from the ball milling process used in fabricating the powder. The silicon oxide sheath over the surface of silicon carbide was covered by these impurities, the oxide being formed underneath. With the untreated powder, impurities could bond with ionic species present in the electrolyte, which explains the signifi-

^{*} Forafac® 1033D, Elf Atochem, Philadelphia, PA

^{**} Forafac® 1157N, Elf Atochem, Philadelphia, PA



Fig. 7—Synergetic effect of 0.5 g/L of cationic surfactant with (a) an HNO_3 40 vol% treated SiO_2 powder, condition 4A, and (b) with an untreated powder, condition 5A, on particles codeposition efficiency.

cant quantity of particles embedded in the coating. Removing these impurities with an HNO₃ treatment exposed the SiO₂ sheath over the SiC particles. The silicon carbide particle thus behaved like a SiO₂ particle. Hydrofluoric acid had the ability to dissolve both metallic surface impurities and the SiO₂ sheath, which resulted in a higher percentage of entrapped particles within the nickel matrix.

Influence of surfactants on codeposition. Three different concentrations of the TBAC cationic surfactant were gradually added to the plating solution that contained untreated silicon carbide powder. Figure 4 shows the effect of the highest surfactant concentration on the codeposition efficiency (condition G, 8.5% of particles). At a lower concentration (0.12 g/L), the cationic surfactant had a negative effect (4.8% of particles) on the codeposition. At a 0.25 g/L concentration, the percentage of embedded particles (7.5%) was similar to that obtained without surfactant using the same untreated SiC powder (condition A, 7.1%). Thus TBAC had a slight positive effect on the amount of codeposited untreated SiC particles.

The influence of TBAC on the amount of codeposited SiC particles pretreated by HNO_3 was drastic. A ten-fold increase (0.8 to 10% for conditions B and H respectively) was noted when 0.5 g/L of TBAC was added to the plating bath. As mentioned before, the SiC particles were covered with a SiO₂ sheath and, with no metallic impurities on them, SiC particles behaved like SiO₂, which were highly hydrophilic. The presence of the cationic surfactant changed the hydration of the particles by charging them positively, thus, enhancing the attractive electrostatic force.

When an HF-treated SiC powder was used, the addition of 0.5 g/L (Fig. 5) of cationic surfactant did not have a beneficial effect on particle codeposition as shown in Fig. 2 (Condition C without TBAC, 25.4%; Condition D with TBAC, 21.7%). From these results it appeared that the determining factor for SiC codeposition was the nature of the particle surface. It must be free of any oxide and/or impurities. The presence of cationic surfactant did not promote the incorporation of cleaned SiC particles, which were in fact already prone to inclusion because they were hydrophobic. On the other hand only one cationic surfactant (TBAC) was tried in this work and other cationic surfactants, like fluorocarbons^{14,18} may improve the hydrofluoric acid treatment results (Condition C). In comparing conditions A (7.1%), D (21.7%) and G (8.5%), it appeared that TBAC adsorption was probably enhanced when the particle surfaces were free of contaminants.

Using an HF-treated SiC powder, the influence of anionic and amphoteric surfactants was also studied. Those types of surfactant had a drastic negative effect on codeposition as seen in Fig. 2 (Condition E, anionic and Condition F, amphoteric). Overall the classification in terms of particle inclusion efficiency was:

These surfactants did not promote particle codeposition in an electrolyte such as a sulfamate nickel bath and the determining factor for SiC inclusion was its surface composition.

SiO₂ Powder

The untreated SiO_2 powder could barely be codeposited within the nickel matrix (Fig. 6, Condition 2A). Even when treated with nitric acid, the SiO_2 particles were not significantly entrapped, as seen for Condition 3A. Comparing Fig. 2 with Fig. 6, it can be seen that the percentage of embedded par-

ticles for Conditions B (Fig. 2) and 3A (Fig. 6) is almost identical. This shows that an HNO₃-treated silicon carbide particle free of metallic impurities on its surface, exposing its silicon oxide sheath, behaved like a silicon oxide particle.

As far as the influence of the cationic surfactant is concerned, Fig. 7a shows the beneficial effect of 0.5 g/L of TBAC on the codeposition of an HNO_3 -treated SiO₂ powder (10.7%, Condition 4A). The effect of this cationic surfactant on codeposition was drastic when compared to Conditions 2A (0.05%) and 3A (1%). On the other hand, when an untreated silicon oxide powder was used, the addition of surfactant to the plating solution had no effect on codeposition (Fig. 7b, Condition 5A: 0.3%). As seen with SiC particle (Conditions A, D and G), the presence of metallic impurities strongly influenced the adsorption of the cationic surfactant (conditions 2A, 0.05%; 4A, 10.7% and 5A, 0.3%). Thus the synergetic effect of cleaning the surfactant was of primary importance. Both aspects must be considered and studied together prior to any electrocodeposition.

Conclusion

It is well known that the nature of a particle surface greatly influences its inclusion probability during an electrocomposite deposition process. Further, many authors have studied the same process while modifying the particle charge through the addition of surfactants in the plating bath. Here, it has been demonstrated that both aspects should be studied together for Ni-SiC and Ni-SiO₂ systems. It follows that other metal (or alloy) - particle systems should also be investigated in the same fashion. In fact, the presence of impurities on the particle surface influences the particle inclusion probability and the surfactant adsorption. In the case of the Ni-SiC system only an HF treatment is sufficient to obtain maximum particle inclusion. Here the determining step is the removal of the SiO₂ sheath, thus, forming a purely hydrophobic SiC surface. However, for the Ni-SiO₂ system, both an acidic (HNO₃) pretreatment and the addition of a cation surfactant (TBAC) were necessary to maximize the particle inclusion.

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