Codeposition of Mixtures of Dispersed Particles With Nickel-Phosphorus Electrodeposits

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Codeposition of SiC, ZrO_2, Cr_2O_3, TiB_2 and MoS_2 powders and their mixtures with a Ni-P coating has been investigated. With the mixtures, more conductive and hydrophobic particles intensified the codeposition of non-conductive and hydrophilic particles; the reverse effect was observed also. This phenomenon suggests an additional possibility for control of the dispersed phase content and composition by selecting the components of powder mixtures. Compared with the matrix, the hot-oxidation resistance at 950 °C increased to the greatest extent in the presence of Cr_2O_3 and ZrO_2 together in the electrolyte.

Interest in electrochemical composite coatings (ECC) containing dispersed phase has persisted for more than 20 years, and new possibilities for ECC are now being considered.[1-3] For instance, the alloying effect of ECC can be achieved by introducing mixtures of particles of various natures, similar to dispersion strengthening of thermostable metallurgical alloys. In the opinion of the authors, this aspect has not been studied sufficiently with reference to ECC. Moreover, it would be productive to include the mixtures of hard, refractory and dry-lubricant particles in order to reinforce both mechanical, thermostable and antifrictional properties of ECC.

In this study, composite nickel-phosphorus coatings, containing mixtures of various kinds of ultrafine dispersed particles, were deposited; then some of these ECC were treated at 950 °C to determine the oxidation rate.

Experimental Procedure

The coatings were deposited from a nickel-phosphorus plating bath containing (in g/L) nickel sulfate, 180; sodium sulfate, 70; boric acid, 30; sodium hypophosphite, 5.0; acetic acid, 5.0; and sodium lauryl sulfate, 0.2. The bath was maintained at a current density of 50 A/m², with pH of 4.0 to 4.5, at a temperature of 55 to 60 °C, and was stirred mechanically.

The ultrafine powders chosen for codeposition were produced by plasma technique and included silicon carbide, titanium boride, chromium and zirconium oxides. Molybdenum disulfide particles were 0.5 to 1 µm in size and, according to USSR Technical Standard TU 49-19-193-85, were 98.5 percent MoS_2. To increase the SiC content in the coatings, a silicon-containing cationic agent (CA) of the class of silanamines was added, with the ratio of 0.03 g/g of SiC.[4] The MoS_2 powder was given preliminary treatment with nitric acid. Dispersed phase densities (p_{dp}), conductivities (γ) and particle sizes (d) are listed in Table 1. The values of d were calculated from powder-specific surfaces (S_s) indicated by the suppliers.

The sign of the particle charge in the electrolyte was analyzed by absorption of a cationic dye, methyl violet (MV), by the powders. MV concentrations in the electrolyte were determined by photocolorimeter, measuring the optical density *(D),* then calculating the concentrations by using the corresponding calibration curve. Values of D were measured before adding a powder to the electrolyte and after filtration of the suspension. From the difference of these two values, the percentage *(A)* of MV that was not adsorbed on the powder, but remained in the electrolyte, was calculated. If *A* was close to 100, that indicated that the particles did not absorb the dye because of their large positive charge. By contrast, the particles were charged negatively if *A* was equal to zero. The suspension stabilities were also studied by means of a photocolorimeter, determining the light transmission coefficients (K_{10}), which were measured 10 min after adding a powder to the electrolyte.

Table 1
Properties and Measured Parameters

	SiC	ZrO_2	Cr_2O_3	TiB_2	MoS_2
P_{dp}, kg/m³	3.2	5.9	5.15	4.5	4.8
γ, $Ohm^{-1}m^{-1}$	10^{-10}-10^{-8}	3.3 10^{-3}	7.8 10^{-2}	1.1 10^{3}	10^{-2}-10^{-3}
S_s, m²/g	24	19	27	35	2.5-1.25
d, µm	0.08	0.10	0.04	0.35	0.5-1.0
A, %	99	96	51	73	0
K_{10}, %	0	13.7	10.0	4.2	24.5

Dispersed phase densities (p_{dp}),conductivities (γ) and specific surfaces (S_s), particle sizes (d), percentages of non-adsorbed cationic dye (A), light transmission coefficients (K_{10}), measured 10 min after suspension preparation.

The dispersed phase volume percentages (a_v) were calculated from the weight percentages (a_w), determined from the concentrations of elements in the coatings by means of microzond analysis. Phosphorus weight percentages *(P)* were measured by the same technique. To evaluate the ability for inclusion, the relative content of particles in the coatings were calculated from the ratio of a_v to the particle volume percentages in the electrolyte (c_v).

When studying the hot-oxidation resistance, the coatings were deposited on steel substrates 150 µm thick and given preliminary treatment in argon at 400 °C for 1 hr, then at 950 °C for 10 hr in air. The coating weight gain resulting from oxidation was calculated as the difference between the weight after heating for γ hr and the initial weight.[4]

Results and Discussion

Influence of Surface Properties on Codeposition

Surface properties acquired by particles in liquid media depend on their nature and have a noticeable influence on the codeposition process.[5-7] The chemical composition of particles and electrolyte predetermines a kind of potential-decisive ion in the outer layer of ion shells. The MeO^+ and Me^+ ions play a leading part on the surface of amphoteric Al_2O_3 and some other oxides and, therefore, these particles often acquire a positive charge.[7] When the ions of discharged metal are absorbed on dispersed phase, the similar composition of ion shells and the near-cathode layer hinders a repelling action of the thin liquid layer between two solid bodies. In addition to the positive charge of the particles, this also favors an increase in their codeposition.[5,6] As a rule, anions possess larger dipole moments than cations, thus are polarized to a greater extent. Consequently, anions can also act as potential-decisive ions in the shells. As a result, dispersed particles often acquire a negative charge; for example, SiC particles are not easily included in Ni coatings.[7] In this case, the forces of adhesion appear to be insufficient to overcome the electrical and molecular repulsive forces, which exist between particles and the cathode. To include such particles, the composition of the ion shells should be modified.

Particle hydrophobic/hydrophilic properties also depend on the composition of ion shells. For example, a protonic bond is formed between SiO_2 and water, causing the presence of a large amount of H_3O^+ in the ion shells and high hydrophilic tendency of the particles.[7] SiC particles also possess hygrophilic properties because of SiO_2 admixtures on their surfaces. As a result of strong interaction of hydrophilic particles with the liquid medium, their surface energy is reduced. This favors, on the one hand, a greater suspension stability and prevents particle adhesion on the cathode. Therefore, to include highly hydrophilic particles, modification of their surface properties should be implemented, just as with negatively charged particles. Because of dependency on the composition of ion shells, particle inclusion depends also on the composition and pH of the electrolyte.

On the other hand, adhesion of highly hydrophobic particles to the cathode is very strong and, therefore, can affect cathodic process rates and can lead to deposition of rough, porous and non-compact layers. As an example, non-compact powder Ni layers are deposited in the presence MoS_2 in the electrolyte.[8] The particle properties must be changed also in this case.

Weight gains of ECC deposits from Ni-P bath after heating at 950 °C in air. Bath composition (powder, g/L): 1. Cr_2O_3, 20; 2. TiB_2, 20; 3. ZrO_2, 70; 4. Cr_2O_3, 20 and ZrO_2, 70; 5. Cr_2O_3, 20, ZrO_2, 70 and TiB_2, 20; 6. Cr_2O_3, 20 and TiB_2, 20; 7. ZrO_2, 20 and MoS_2, 20; 8. SiC, 20 and MoS_2 20; 9. Without dispersed phase.

Table 2
Particle Contents in Electrolyte (c, c_v)

	SiC		**ZrO_2**		**Cr_2O_3**	**TiB_2**	**MoS_2**
	Contents, percent						
c, kg/m^3	20	70	20	70	20	20	20
c_v	6.8	22.2	3.4	11.8	3.9	4.1	4.2
a_v	1.3	5.1	1.7	4.2	6.1	7.9	18.8
a_v/c_v	0.2	0.2	0.4	0.4	1.6	1.9	4.5
P	12.4	8.4	11.0	11.3	7.5	6.9	4.6

Phosphorus weight percentages (P) in the coatings, particle volume percentages (a_v) and particle relative contents (a_v/c_v).

The modification of particle surface properties consists in either adding the relevant surface active agents to the suspension,[5,7,8] or in the preliminary chemical treatment of the powder.[9] Both methods have been applied in this study to negatively charged silicon carbide and to high-hydrophobic molybdenum disulfide particles.

Making use of the previous data on ECC deposition, the following particle properties were taken into account in this study, in analyzing the ability for inclusion—the conductivity, the sign of the particle charge in the electrolyte and hydrophobic/hydrophilic properties. Based on the data of suspension stabilities, the conclusion about particle hydrophobic/hydrophilic properties was drawn. The point is that both these phenomena depend on the presence and structure of ion shells. The hydrophilic nature of particles is connected with existence of the shells saturated by H_3O^+. This results in strong interaction of the particles with the liquid medium and, as a consequence, increase in stability of the suspension.

Using the data of Tables 1 and 2, the powders were arranged in Table 3 according to increase in conductivity, ability for inclusion, percentages of non-absorbed cationic dye, and light transmission coefficients of suspensions. The data of Table 3 show that codeposition of ultrafine particles depends noticeably on their conductivities and hydrophobic/hydrophilic properties and depends less on the sign of their charge. This can be explained by high dispersions and high surface energy level of the particles under consideration, which provide strong adhesion to the cathode independently of the sign of their charge.

Judging by complete absorption of cationic dye ($A = 0$), TiB_2 particles had a large negative charge in the electrolyte, but despite this, the highest ability for inclusion. By contrast, SiC particles modified by cationic agent CA did not absorb the cationic dye MV ($A = 99$). Consequently, they acquired a large positive charge after the modification but, being highly hydrophilic in this electrolyte (Table 1), the SiC particles were inadequately included in the coatings and the a_v values were less than in Watts electrolyte.[4]

It is interesting to note that the inclusion of dispersed phase reduced the phosphorus content in the coatings. The latter was equal to 12.5 percent in the absence of dispersed phase and decreased with the increase in particle quantity in the coatings (Table 2). This is surely connected with the structure

Table 3
Powder Position by Parameter Increase

Parameter	Corresponding property	Position according to increase in the property				
a_v/v_v	Ability to include	SiC	ZrO_2	Cr_2O_3	TiB_2	MoS_2
γ	Conductivity	SiC	ZrO_2	(MoS_2,	Cr_2O_3)*	TiB_2
A	Positive charge	MoS_2	Cr_2O_3	TiB_2	ZrO_2	SiC
k_{10}	Hydrophobicy	SiC	TiB_2	Cr_2O_3	ZrO_2	MoS_2

*Similar values

Particle relative content in the coating (a_v/c_v), powder conductivity (γ), percentage of non-adsorbed cationic dye (A), light transmission coefficient (K_{10}), measured 10 min after suspension preparation.

of nickel-phosphorus coatings, which has been found to be a supersaturated solution of phosphorus in the matrix.[10] In this case, inclusions seem to be competitors in occupying active centers in the matrix.

Codeposition of Particle Mixtures

When codepositing mixtures of various types of particles, interaction between them seems to take place and this changes the percentages of inclusions (Table 4). Accordingly, all tested powders hindered codeposition of molybdenum disulfide, and this occurred despite the fact that they had larger positive charges than MoS_2. The most obvious reason for this phenomenon was that all other powders were more hydrophilic than MoS and, with the exception of TiB_2, less conductive. The most hydrophilic SiC hindered MoS_2 codeposition to a greater extent than the less hydrophilic ZrO_2. The SiC percentage increased noticeably when interacting with MoS_2, whereas the percentage of TiB_2 did not change in the similar case insofar as both TiB_2 and MoS_2 were conductive. This shows that the play of hydrophobic/hydrophilic properties of the particles is rather great, but in all cases, the powder conductivities influenced the codeposition process to the greatest extent. Accordingly, TiB_2, being negatively charged, but more conductive, raised the amount of positively charged but non-conductive and highly hydrophilic SiC.

Table 4
Volume Percentages of Particles (a_v) and Particle Mixtures ($\sum a_v$) in Deposits

SiC		ZrO_2		Cr_2O_3		TiB_2		MoS_2		
c_v	a_v	c_v	a_v	c_v	a_v	c_v	a_v	c_v	a_v	$\sum a_v$
6.4	2.4							4.2	4.2	6.6
22.2	9.3							4.2	1.2	10.5
		3.4	2.6					4.2	9.5	12.1
		11.8	6.9					4.2	2.5	9.4
				3.9	1.5			4.2	0.1	2.6
						4.1	7.6	4.2	1.5	9.1
		11.8	6.8	3.9	2.6					9.4
6.4	4.1					4.1	4.0			8.1
6.4	6.3			3.9	2.0	4.1	2.3			10.6
6.4	6.4	3.4	2.6			4.1	1.2			10.2
		11.8	11.0	3.9	2.3	4.1	4.6			17.9

Volume percentages of particles (c_v) in the electrolyte.

The influence of particle surface charges was not appreciable in this study. It was indicated, for instance, from codeposition of the chromium and zirconium oxide mixture. The addition of more positively charged ZrO_2 to Cr_2O_3 resulted in increase in the ZrO_2 percentage but not that of Cr_2O_3, which amount even decreased. The only case when the influence of particle charge was observed was codeposition of Cr_2O_3 and MoS_2 together. The negative charges of both powders can be the reason for the decrease in their percentages in the deposit. The conclusion can be drawn from the data considered that the presence of more conductive and hydrophobic particles in an electrolyte increases the inclusion of non-conductive and hydrophilic particles, and that the reverse process can take place as well.

In the triple mixtures, an inhibiting effect of hydrophilic and non-conductive SiC on the behavior of other particles was manifest (Table 4). Codeposition of ZrO_2 and TiB_2 was hindered when the mixture of these powders was together with SiC in the electrolyte; the SiC percentage became even larger. Greater influence of hydrophobic/hydrophilic properties, as compared with the sign of the surface charge, was noted in this case also. In the double mixture of SiC and TiB_2, the percentage of the latter was twice as small, compared with TiB_2 deposited alone. In the triple mixture, both non-conductive SiC and ZrO_2 hindered the inclusion of TiB_2 to a much greater extent, specifically, by a factor of 6.6.

As this study shows, one can control dispersed phase content in ECC by selecting components of powder mixtures. For instance, in the absence of SiC in triple mixtures, a larger content of other particles was achieved (Table 4). When depositing ECC with dry-lubricant MoS_2 particles, the most suitable ratio between the components was achieved by the presence of ZrO_2 or SiC in the electrolyte.

High-Temperature Oxidation of the Coatings

Because of being affected by high temperatures, some kinds of ECC show a higher oxidation resistance than “pure” metal deposits.[4,11-13] It was found in the previous study[4] that ECC with ultrafine Cr_2O_3 and Si_3N_4 exhibits a lower oxidation rate than a nickel matrix. When operating with only the type of particles used in this study, the hot-oxidation resistance also improved in the presence of chromium oxide particles (Figure, curve 1), whereas other powders under investigation worsened the resistance of the nickel-phosphorus matrix.

The coatings containing MoS_2 particles were distinguished by low thermostability and were destroyed earlier than other ECC (curves 7 and 8). This can be connected with MoS_2 oxidation as well as with SiC interaction with the matrix at temperatures over 400 °C.[14] Interphase interactions also seemed to be responsible for the coating resistance worsening also in some other cases. For example, the oxidation rate of ECC with a mixture of Cr_2O_3 and TiB_2 was greater (curve 4) than that of ECC with only one of these powders (curves 1 and 2). At the same time, when adding ZrO_2 to the above mixture, the negative influence of TiB_2 was suppressed (curve 5). The highest hot-oxidation resistance found in this study was for the coatings containing the mixture of Cr_2O_3 and ZrO_2, as well as for Cr_2O_3, ZrO_2 and TiB_2 particles (curves 4 and 5). Experiments with ECC containing MoS_2 in the mixtures with other particles failed to show good results.

Conclusions

The codeposition of ultrafine SiC, ZrO_2, Cr_2O_3, TiB_2 and MoS_2 with Ni-P coatings has depended to a greater extent on the powder conductivities and hydrophobic/hydrophilic properties than on the sign of the particle charge in the electrolyte. Various types of particles in the electrolyte have exerted mutual influence on the capability for inclusion. More conductive and hydrophobic types have increased inclusion of nonconductive and hydrophilic types; the reverse effect has been observed also.

Codeposition of the mixture of ultrafine Cr_2O_3 and ZrO_2, with and without TiB_2, has led to improvement in ECC hot-oxidation resistance, compared with the Ni-P matrix.

Editor's Note: *This research was completed in September, 1993. In the first report by the authors (Oct., 1993, p. 73) interparticle distances are given in millimeters. These distances should be in µm.*

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