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Electrodeposition and sliding wear resistance of nickel composite coatings containing micron and submicron SiC particles

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Abstract

SiC particles of three different sizes, namely 5, 0.7 and 0.3 μm , were codeposited with nickel from Watts' solutions. It was found that for a given number density of particles in the plating solution, the number density of particles in the coating increases with decreasing particle size. The friction and wear behavior of these composite coatings was evaluated in uni- and bi-directional sliding tests against corundum balls. The best sliding wear resistance was obtained with Ni–SiC composite coatings containing 4–5 vol.% submicron SiC particles. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrodeposition; Composites; Wear; Nickel; SiC

1. Introduction

Electrodeposited composite coatings consist of a metal or alloy matrix containing a dispersion of second phase particles [1–3]. These particles can be hard oxide or carbide particles, such as Al_2O_3 , SiC, TiO_2 , WC, SiO_2 or diamond, a solid lubricant, such as PTFE, graphite or MoS_2 , or even liquid-containing microcapsules [4] to improve wear resistance and/or to reduce friction. Electroplated composite coatings containing micron-sized particles are used as wear-resistant coatings [5–7], e.g. nickel–SiC in car engines [1,8–10]. With the increasing availability of nanoparticles, there is a growing interest in the electrolytic and electroless codeposition of nanoparticles [11]. The major challenges of the codeposition of nanoparticles seem to be the codeposition of a sufficient number of particles, and avoiding the agglomeration of particles suspended in the plating solutions.

In this work, the electrolytic codeposition of micron and submicron SiC particles from nickel Watts' solutions, and the sliding wear resistance of such nickel composite coatings are investigated. The effect of particle size and number of particles suspended in the plating solution on the number of codeposited particles is reported. The codeposition results and a model based on the number density of particles codeposited are discussed. The effect of particle size on the codeposition process of micron- and submicron-sized non-Brownian particles is clarified. The effect of codeposited submicron particles on the wear resistance of composite Ni–SiC coatings is discussed.

2. Experimental

The plating solution used was a standard nickel Watts' solution. The composition of the plating solution and the plating parameters are given in Table 1. SiC particles with a mean diameter of 0.3 (BSC-21C, Performance Ceramics, Japan), 0.7 (BS 0.7, Elektroschmelzwerk Kempton, Germany) and 5 μm (E110 #4000, Norton, Norway) were used. All particles were used as received.

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Table 1
Composition of the plating solution and the plating parameters

Plating solution composition	
300 g/l NiSO ₄ ·6H ₂ O	
45 g/l NiCl ₂ ·6H ₂ O	
40 g/l H ₃ BO ₃	
Electrodeposition parameters	
pH 3.8	
50°C	
2 A/dm ²	
75 min	
Magnetic stirring	
Cathode: brass (12 cm ²)	
Anode: Ni (12 cm ²)	

For each of the plating solutions, the number density of particles, n_s , was calculated (Table 2), assuming that the particles are mono-disperse and spherical. The particle concentration in the plating solutions was varied between 0.28 and 104 g/l. Each plating solution was mixed by magnetic stirring for 24 h, and subsequently by ultrasonic agitation for 30 min just prior to electroplating. Electrodeposition was carried out on vertical electrodes, and the plating solution was agitated during electrodeposition with a magnetic stirrer.

After codeposition, some of the samples were cut and mounted in epoxy resin. Metallographic cross-sections for SEM observation were ground and polished without using SiC abrasive paper to avoid contamination. The number of SiC particles codeposited in the coatings was evaluated by EDX on these polished cross-sections. Vickers micro-hardness measurements (load, 30 g) were also carried out on these polished cross-sections. Uni- and bi-directional sliding wear tests were performed on as-plated discs. Uni-directional sliding ball-on-disc wear tests were performed at a normal load of 10 N and a sliding speed of 0.1 m/s. The number of rotations was either 15 000 or 20 000. Bi-directional sliding ball-on-disc wear tests [12] were performed at a normal load of 5 N, an oscillation frequency of 10 Hz, and a tangential displacement amplitude of 500 μ m. The number of fretting cycles was 50 000. All wear tests were performed against 10-mm corundum balls, without lubrication, at 22°C and in ambient air of 50% relative humidity. The coefficient of friction was recorded continuously during the wear tests. The volumetric material loss was determined by laser profilometry (Rodenstock RM300) after completion of the wear tests. Hereto, samples were cleaned in ethanol using ultrasonic agitation for 15 min. In order to compare uni- and bi-directional wear tests, the wear is expressed as a volumetric wear factor (cm³/N m). This wear factor was calculated by dividing the total volumetric wear loss by the total sliding distance and the applied load.

Table 2
Amounts of the SiC particles in the plating solution

Particle density, n_s (particles/m ³)	Concentration (g/l)	Diameter (μ m)
5×10^{12}	1.04	5
10^{13}	2.1	5
10^{14}	20.8	5
5×10^{14}	104	5
5×10^{14}	0.28	0.7
10^{15}	0.57	0.7
10^{16}	5.71	0.7
5×10^{16}	0.56	0.3
10^{17}	57.1	0.7
5×10^{17}	5.62	0.3
5×10^{18}	56.2	0.3

3. Results and discussion

The amount of codeposited SiC is shown in Fig. 1 for the three types of SiC particles. The volume percent of codeposited SiC in the coatings increases with increasing concentration of particles in the plating solution, which is in agreement with the literature [1,2]. The highest volume percent of codeposited SiC is achieved with the large 5- μ m particles, while the lowest code-

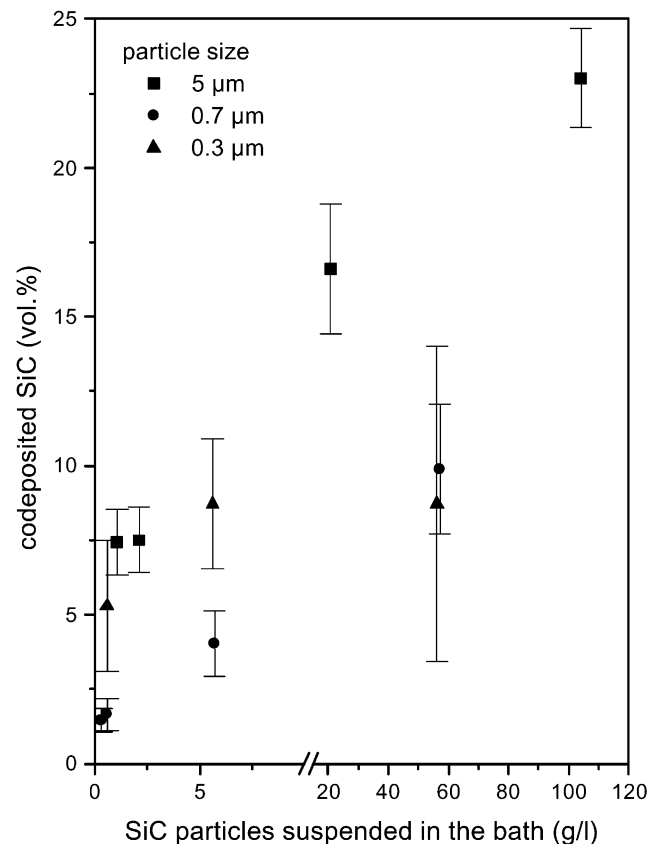


Fig. 1. Volume percent of SiC particles codeposited with nickel at different SiC particle concentrations in the plating solutions and for different SiC particle sizes.

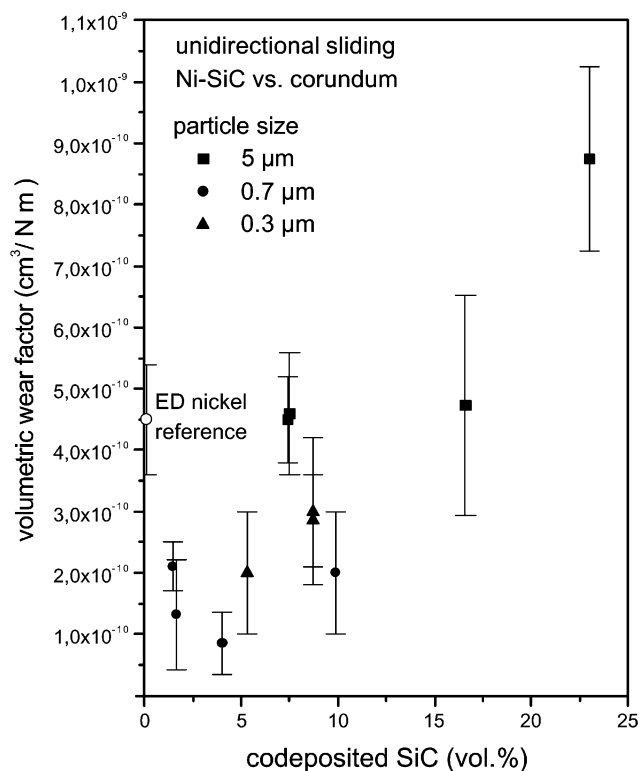


Fig. 2. Volumetric wear factor under uni-directional sliding on composite Ni-SiC coatings containing different vol.% SiC particles of three different sizes. Data for pure electrolytic nickel are also given (ED nickel reference).

position is obtained with 0.7- μm particles. Quite unexpectedly [13], the 0.3- μm SiC particles codeposit more than the 0.7- μm particles. A possible reason could be the difference in the surface condition of these SiC particles obtained from different producers. Another reason could be the agglomeration of the 0.3- μm particles in the plating solution.

The wear tracks on the composite Ni-SiC coatings after uni- and bi-directional sliding tests have a black appearance, and show scratches parallel to the direction of motion. Such scratches are typical for abrasive wear. For all Ni-SiC composite coatings tested, the coefficient of friction is approximately 0.5 during the first few sliding cycles. After the running-in phase, the coefficient of friction of nickel coatings containing 0.7- or 0.3- μm SiC particles is approximately 0.29. That coefficient of friction is lower than the value of 0.34 observed on nickel coatings containing 5- μm SiC particles at a comparable volume percent of codeposited particles. On the other hand, for each SiC particle size investigated, the coefficient of friction increases with increasing volume percent of SiC particles in the coatings, from approximately 0.34 to 0.47 in the case of 5- μm SiC particles, and from 0.28 to 0.30 in the case of 0.7- μm particles.

The wear loss on Ni-SiC composite coatings containing SiC particles of different sizes, after sliding against corundum balls in uni- and bi-directional wear tests, is shown in Figs. 2 and 3, respectively. The volumetric wear loss on pure nickel coatings and composite Ni-SiC coatings in uni-directional sliding wear tests is approximately two orders of magnitude lower than that noted in bi-directional sliding tests. This is consistent with sliding wear data obtained on hard ceramic coatings, such as TiN, showing a much lower wear rate under uni- than under bi-directional sliding test conditions [14]. However, under uni-directional sliding, composite nickel coatings containing 5- μm SiC particles exhibit a lower wear resistance with increasing amounts of SiC than pure nickel coatings (referred to as ED nickel reference in Fig. 2). On the contrary, composite nickel coatings containing 0.3- or 0.7- μm SiC particles wear less in uni-directional sliding wear tests than pure nickel, and the best results are obtained with approximately 4 vol.% of 0.7- μm SiC particles. Under bi-directional sliding, the volumetric wear loss on all the composite Ni-SiC coatings tested is lower than the wear measured on pure nickel coatings electrodeposited under similar plating conditions (Fig. 2). The lowest volumetric wear loss in bi-directional sliding tests is reached

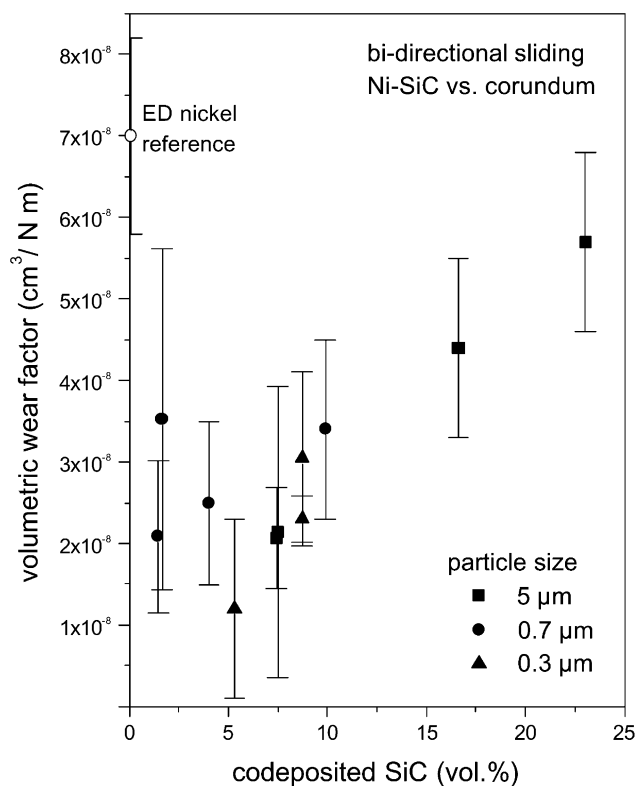


Fig. 3. Volumetric wear factor under bi-directional sliding on composite Ni-SiC coatings containing different vol.% SiC particles of three different sizes. Data for pure electrolytic nickel are also given (ED nickel reference).

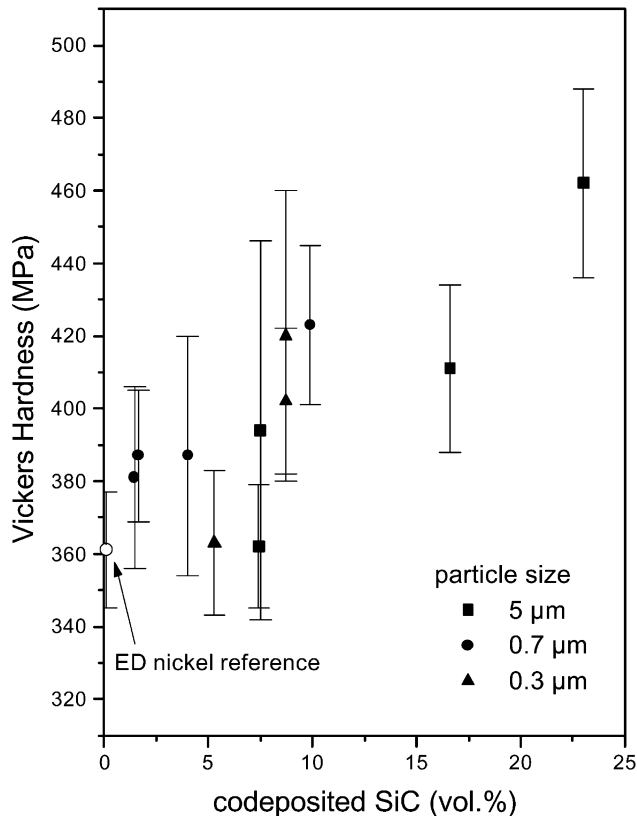


Fig. 4. Vickers hardness of pure nickel and composite Ni-SiC coatings containing SiC particles of three different sizes plotted vs. the vol.% of codeposited SiC-particles.

with composite nickel coatings containing approximately 5 vol.% of 0.3-μm SiC particles.

In an attempt to clarify the wear behavior of the composite Ni-SiC coatings tested, the Vickers hardness of these coatings was measured. That Vickers hardness is plotted as a function of the volume percent of codeposited SiC-particles in Fig. 4. For the three sizes of SiC particles investigated, the Vickers hardness increases with increasing amount of SiC particles in the nickel coatings. The Vickers hardness of all Ni-SiC coatings investigated is higher than that of pure electro-deposited nickel. A given hardness value is obtained at a lower volume percent of submicron codeposited SiC-particles than in the case of 5-μm SiC particles. Indeed, it is known that the hardness and other mechanical properties of metal matrix composites depend in general on the amount and size of the dispersed phase, apart from the mechanical characteristics of the matrix, particles and interfaces. That amount and size of particles define two kinds of reinforcing mechanisms in metal matrix composite materials, namely dispersion-strengthening and particle-strengthening. A dispersion-strengthened composite is characterized by a dispersion of fine particles with a particle diameter ranging from 0.01 to 1 μm, and vol.% ranging from 1 to 15. The optimum

performance has been found at an inter-particle spacing, λ , between 0.5 and 5 μm [15]. In this case, the matrix carries the load and the fine particles impede the motion of dislocations. A particle-reinforced composite contains more than 20 vol.% of particles larger than 1 μm. The inter-particle spacing is then larger than 5 μm, and the load is carried by both the matrix and the particles. Strengthening is achieved because particles restrain matrix deformation by a mechanical constraint. Which of these mechanisms is active in the composite Ni-SiC coatings of this work becomes evident when plotting the Vickers hardness of these coatings versus the inter-particle spacing (Fig. 5). This inter-particle spacing was calculated assuming that the SiC particles are mono-disperse, spherical and uniformly distributed in the coatings. In nickel coatings containing 5-μm SiC particles, the inter-particle spacing is greater than 5 μm, even at the highest particle volume percentage (7.5–23 vol.%) achieved (see Fig. 4). The hardness increase noted in these composite coatings containing micron-sized SiC particles can thus be linked to a particle-strengthening effect. On the contrary, in composite nickel coatings containing 2–10 vol.% of submicron SiC particles, the inter-particle spacing is below 5 μm. The

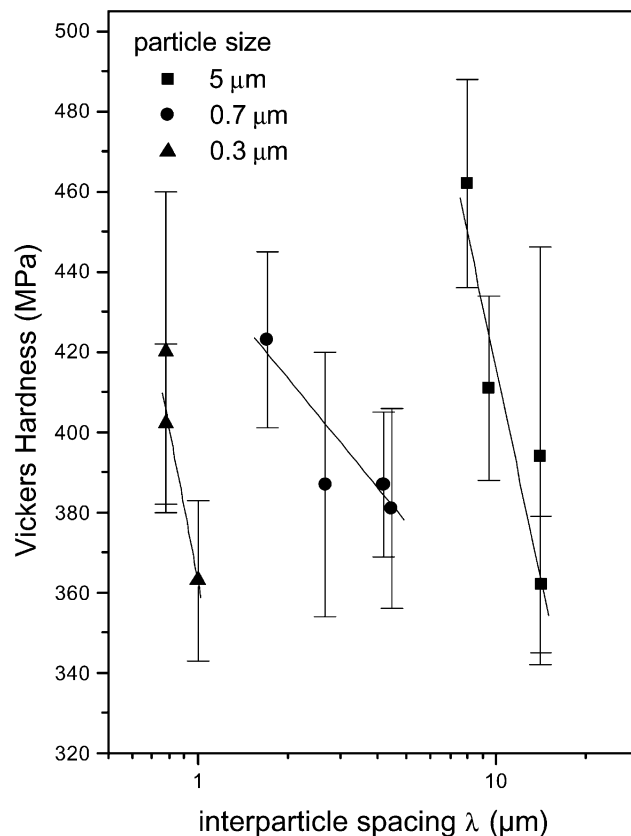


Fig. 5. Vickers hardness of composite Ni-SiC coatings containing SiC particles of three different sizes plotted vs. the SiC inter-particle distance in the coatings.

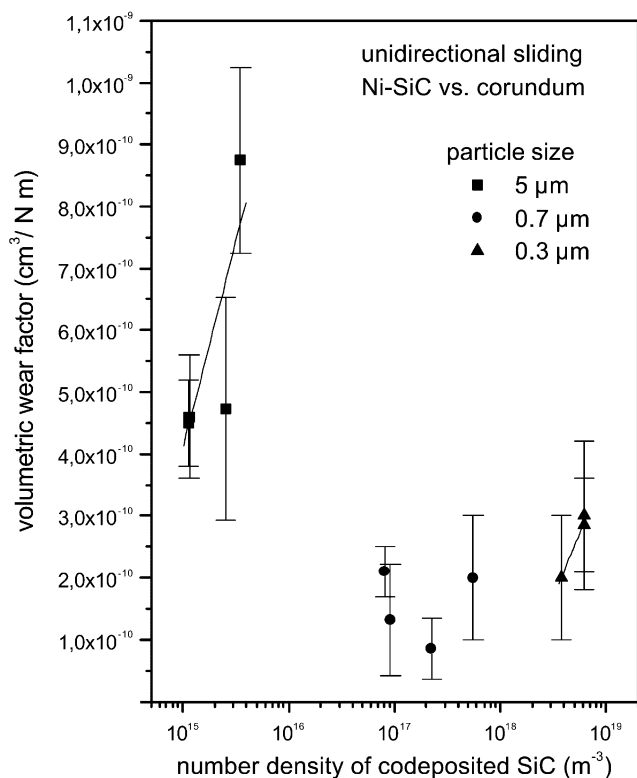


Fig. 6. Volumetric wear factor under uni-directional sliding on composite Ni-SiC coatings containing SiC particles of three different sizes, plotted vs. the number density of codeposited SiC particles.

hardness increase noted in these composite coatings can thus be linked to a dispersion-strengthening effect. This indicates the importance of achieving a uniform codeposition of non-agglomerated sub-micron particles to obtain a dispersion-strengthening effect.

The inter-particle spacing, being a parameter that depends not only on the volume percent of codeposited particles, but also on the particle size of codeposited particles, is thus more suited to analyze the mechanical properties, and thus the wear behavior, than a representation based on volume percent solely. When using number density of particles and particle size as parameters instead of volume percent and particle size, independent parameters are compared. Wear data, such as those in Figs. 2 and 3 for Ni-SiC composite coatings, become more informative when plotted versus the number density of codeposited particles (see Figs. 6 and 7, respectively). Figs. 6 and 7 show that for both uni- and bi-directional sliding wear tests, the volumetric wear factor increases, in most cases, with increasing number density of codeposited SiC particles for the three particle sizes. Furthermore, the volumetric wear factor decreases in most of the cases with decreasing particle size. This means that a low volume percent of submicron SiC particles in the composite Ni-SiC coatings results in the same wear resistance as a coating containing a higher

volume percent of micron-sized particles. The abrasive wear observed in the wear tracks after the sliding tests suggests that debris and pulled-out SiC particles have an adverse effect when they remain in the sliding contact area. A competition thus takes place between the beneficial increase in hardness due to reinforcing SiC particles codeposited in the nickel coatings, and their adverse abrasive effect. The abrasive wear of metal matrix composites increases with increasing amount and size of abrasive particles, as does the hardness of metal matrix composites. Therefore, in composite plating, a decrease in the size of the particles codeposited is, in both cases, positive. However, an increase in the number density of codeposited particles produces higher hardness and mechanical strength, but also an increase in the abrasion wear when reinforcing particles are pulled out of the composite coatings during sliding wear.

Re-plotting the codeposition data of Fig. 1 as the number density of particles in the plating solution, n_s , and in the coating, n_c , results in Fig. 8. It then appears that the number density of codeposited SiC particles is 1–100-fold larger than the number density of particles in the plating solution. The codeposition efficiency, defined as the ratio between the number density of particles in the coating and in the plating solution, increases for each SiC particle size with decreasing

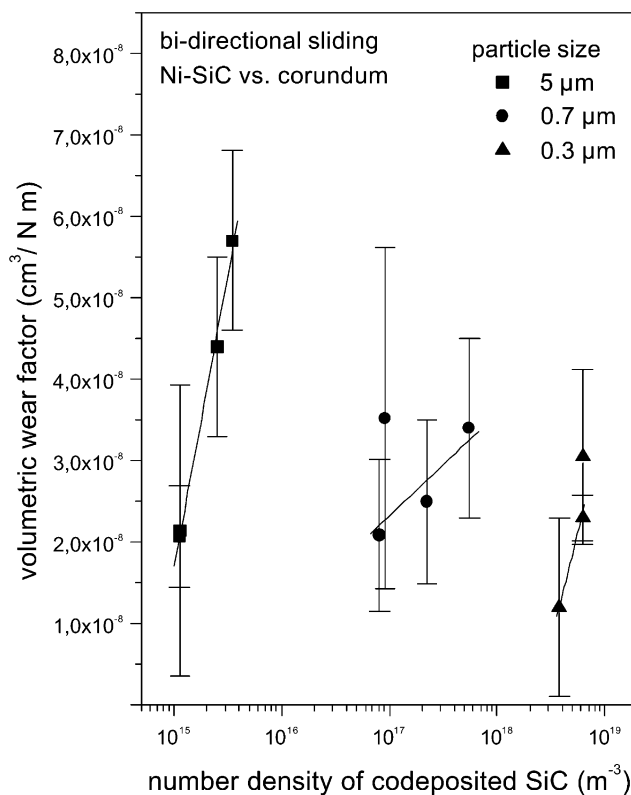


Fig. 7. Volumetric wear factor under bi-directional sliding on composite Ni-SiC coatings containing SiC particles of three different sizes, plotted vs. the number density of codeposited SiC particles.

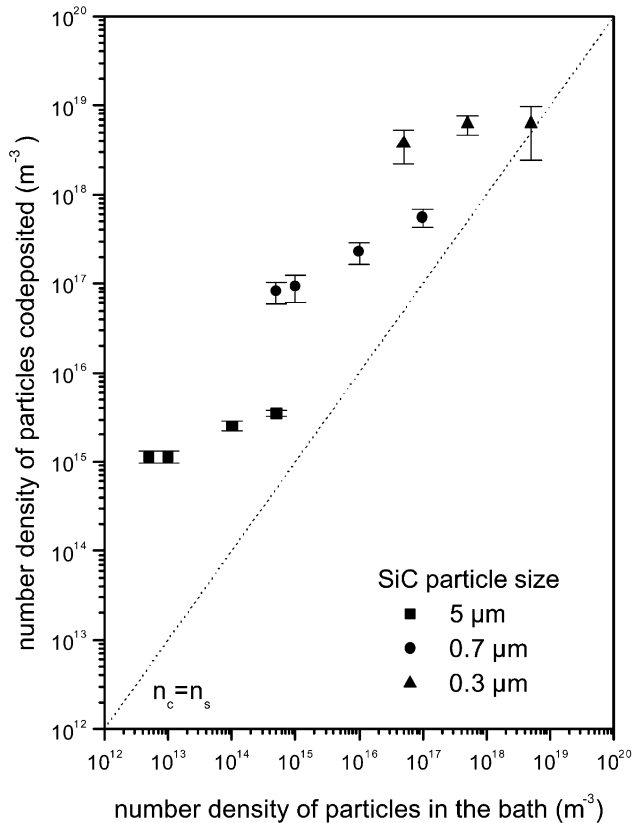


Fig. 8. Number density of particles in Ni–SiC coatings containing particles of three different sizes plotted vs. the number density of particles suspended in the plating solutions.

number density of particles in the plating solution. More important is the fact that the codeposition efficiency increases substantially with decreasing particle size. This can be noted in Fig. 8 as a jump in the number density of codeposited particles at a given number density of particles in the plating solution (see e.g. at 5×10^{14} and $5 \times 10^{17}/\text{m}^3$), but of different particle size. Therefore, in contrast to the apparent outcome of Fig. 1, the codeposition efficiency does not decrease with decreasing particle size. On the contrary, at a given number density of particles in the plating solution, the codeposition efficiency increases with decreasing particle size.

In spite the fact that the different SiC particles that were used were of high purity, it cannot be ruled out that the particles not only differ in size, but also have a different surface chemistry due to their origin. Hence, the results of Fig. 8 can be either due to a difference in surface chemistry, or to a size-dependent codeposition behavior. In order to discriminate between these two alternative explanations, a simple model was developed to see if it is possible to explain the results based on a size effect.

The number density of particles entrapped in the coating per unit volume, n_c , is assumed to be propor-

tional to the number of particles, n_s^* , that get entrapped in the coating per unit of time and surface area, divided by the volume increase, ΔV , of the coating per unit of time and surface:

$$n_c = \frac{n_s^*}{\Delta V} \quad (1)$$

The volume increase is derived from Faraday's law, taking into account the contribution of the codeposited particles, assuming they are mono-disperse and spherical:

$$\Delta V = \frac{M \cdot i}{n \cdot \rho \cdot F} + \frac{\pi}{6} \cdot d^3 \cdot n_s^* \quad (2)$$

where F is Faraday's constant, n is the valence of the metal ions, M and ρ are the atomic weight and density of the metal, respectively, i is the current density and d is the diameter of the codeposited particles. The number of particles, n_s^* , that get entrapped in the coating can be related to the number density of particles in the plating solution, n_s , by introducing a transfer rate A and a probability P :

$$n_s^* = P \cdot A \cdot n_s \quad (3)$$

where A is the total volume of particles that bump into the electrode per unit time and surface area, and P is the probability for particles to be retained on and incorporated in the cathodic deposit. This transfer rate A and probability P obviously depend on bath agitation and hydrodynamics. Substituting ΔV and n_s^* into Eq. (1), the number density of codeposited particles becomes:

$$n_c = \frac{P \cdot A \cdot n_s}{\frac{M \cdot i}{n \cdot \rho \cdot F} + \frac{\pi}{6} \cdot d^3 \cdot P \cdot A \cdot n_s} \quad (4)$$

Eq. (4) contains only one adjustable parameter, namely PA , which links the amount of particles that reach the cathode (A), and the probability that these particles remain on the cathode (P). From our codeposition experiments, it is, however, not possible to determine these two factors separately. For experiments carried out on a rotating disk electrode, A is proportional to the square root of the rotation speed, and it should be possible to obtain more information on the effect of bath agitation. In our experiments, the bath agitation and electrode configuration were kept constant, and it is assumed that the transfer rate A was constant. Eq. (4) was used to fit the experimental data of Fig. 8. The fits shown in Fig. 9 were obtained by varying PA and the value of the particle diameter. It was found that the experimental data for the three particle sizes could be fitted with a single PA value of 10^{-4} m/s. The particle diameters that yield the best fit with a PA value of 10^{-4} m/s are slightly higher, namely 8.5, 1.7 and 0.7

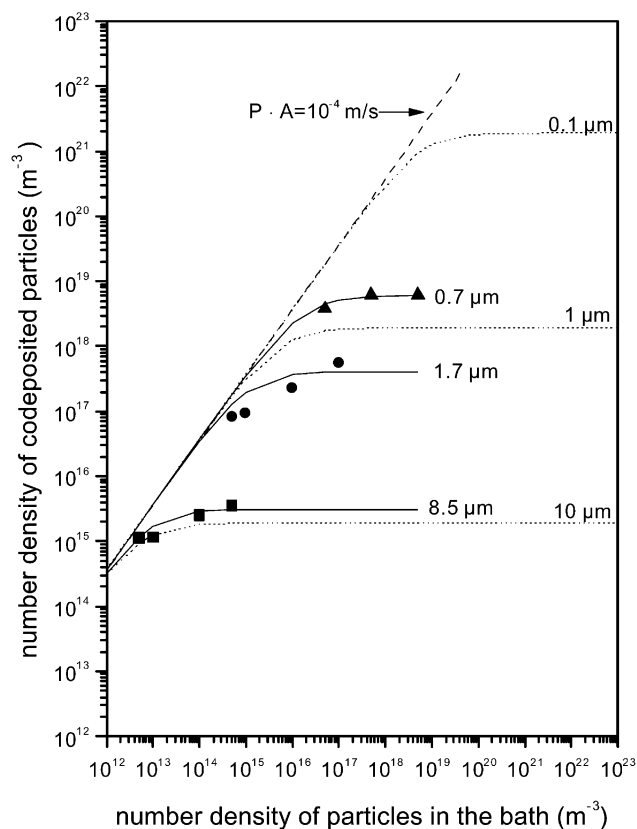


Fig. 9. Data of Fig. 8 fitted with the model expressed by Eq. (4). The particle sizes mentioned near each fit give the best fits to the experimental data.

μm , than the particle sizes mentioned by the producers of the powders, namely 5, 0.7 and 0.3 μm , respectively. The difference between the sizes specified by the producer and the fitted particle sizes is reasonable. Indeed, small particles easily aggregate in electrolytes of high ionic strength [16], and the hydrodynamic shielding between particles in the plating solution and partially engulfed particles result in a larger effective diameter in their collision interactions [17]. The fact that our results fit Eq. (4) with a single value for PA indicates that the effect is related to the size of the particles, and not to a change in surface chemistry. Extrapolating Eq. (4) to SiC particles of 0.1 μm , Fig. 9 predicts that the number density of codeposited particles in the coating will be more than two orders of magnitude larger than for particles of 0.7 μm . This opens interesting perspectives for achieving dispersion-strengthening in electrolytic composite coatings, which could have attractive wear properties.

4. Conclusions

The wear properties of Ni–SiC composite coatings were shown to depend on the volume occupied by the reinforcing particles, as well as on their number density.

The sliding wear behavior of Ni–SiC composite coatings containing different amounts of particles was the same for uni- and bi-directional sliding. The best sliding wear resistance against corundum balls was obtained for Ni–SiC coatings containing 4–5 vol.% of 0.3- and 0.7- μm SiC particles. Higher volume percent or number density of codeposited particles lowers the wear resistance. A decrease in the particle size affects the wear resistance in a positive way. This results from a beneficial strengthening effect due to codeposited particles and adverse abrasive wear due to pulled-out particles.

When comparing the effect of particle size on codeposition, it is important to express the results in terms of number density of particles, otherwise erroneous conclusions will be obtained. The benefit of presenting codeposition results based on the number density of particles was demonstrated for the codeposition of Ni–SiC with particle sizes between 0.3 and 5 μm . For this system, it was found that for a given number density of particles in the plating solution, the number density of codeposited SiC-particles increases with decreasing particle size. Hence, small SiC particles codeposit easier than large particles. Based on a relation between the number density of codeposited particles and the number density of particles in the plating solution, it was shown that the size and number density of SiC particles in the plating solution are important parameters in the codeposition process.

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