Composite Nickel Coatings Containing Lubricating Oil Microcapsules and Their Tribological Properties

by Liqun Zhu & Liu Feng and Yinghe He*

Surface engineering has been widely used to improve the wear and friction properties of articles. A frequently used technique to achieve such a goal is co-electrodeposition of a metal with solid particles such as SiC, Al_2O_3, BC and ZnO_2. In this paper, we present a new technique for the preparation of composite coatings of nickel and liquid lubricating oil microcapsules, and the test results on the wear and friction properties of the coatings. The results demonstrate that the wear resistance is greater and kinetic friction coefficients substantially lower for the composite coatings than those for coatings with only nickel.

One of the major objectives of electrodeposition of composites is to enhance the wear resistance of the deposited film. Methods for enhancing wear resistance of composite coatings so far include the use of relatively hard materials such as Ni-Co, Ni-Mn and Ni-P alloys. The addition of hard solid granules, which are approximately spherical in shape, such as SiO_2, SiC and WC, are codeposited with a matrix metal to form a composite film.[1-5] A major drawback for this type of surface modification is that it substantially increases the surface friction. To combat this problem, solid lubricants such as graphite, MoS_2 and PTFE have also been incorporated into composite coatings. However, the friction coefficient for composite coatings containing solid lubricants still ranges from 0.2 to 0.6.[6-8]

It is well known that liquid lubricants significantly reduce both friction and wear. However, a practical inconvenience in the use of liquid lubricants is the need for a constant supply of the lubricants, a mundane chore often carried out manually. If this supply can be manipulated such that it becomes self-lubricating throughout the life of the parts, it would make a significant saving in running costs. Such a function may be achieved by forming a composite coating on the surface of the part in which evenly distributed liquid droplets or capsules containing liquid cores serving as mini-reservoirs of the lubricant are incorporated. This approach has been used in the pharmaceutical and food industries where microcapsules, *i.e.*, capsules of sizes in the micrometer range are produced to control the release of their liquid content.[9-15]

The authors have been among the first to fabricate successfully composite coatings containing liquid capsules by electrodeposition.[16-19] In the process, the liquid-containing capsules are codeposited with a metal ion during electrodeposition. Organosilicone-based oils have been used as the core material, and have been codeposited with Ni, Cu and Fe-P to form nickel, copper or Fe-P alloy-based liquid-containing composite coatings. Depending on the liquid core used, these coatings can exhibit good tribological and/or anti-corrosive properties.

In this paper, a method for the preparation of composite nickel coatings containing capsules with liquid lubricating oil cores will be presented. These coatings are fabricated

Nuts & Bolts: What This Paper Means to You

An electrodeposited nickel composite containing codeposited particles has been a useful concept to tailor deposit properties to challenging applications. Reported here is a rather novel approach where the particles are actually microcapsules containing lubricants. This has all the makings of a self-lubricating electrodeposited coating. This budding concept exercises the mind as to possibilities.

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with the aim of achieving self-lubrication for moving parts. The results from the structure and morphological characterization and tribological tests on the composite coatings are also reported.

Experimental

Preparation of liquid microcapsules

Microcapsules used for composite Ni-microcapsule electrodeposition with gelatin as the envelope (wall material) and lubricating oil as the core were prepared by the phase separation method. Specifically, lubricating oil was added dropwise into a 2 vol% aqueous gelatin solution, which was stirred at 1200 rpm. After a few minutes, a few drops of a liquid surfactant, sorbitan monooleate (Span 80), were added with a 1 mL burette. Phase separation, *i.e.*, precipitation of gelatin from its aqueous solution to form the wall of the microcapsules enveloping the liquid lubricant, was achieved by addition of anhydrous ethanol in an oil-in-water emulsion. This procedure produced microcapsules in a dispersion in the size range between 4 and 16 μm (157 and 630 μ-in.) in diameter with a wall thickness of 2 to 8 μm (78 to 314 μ-in.), which, after many trial-and-error runs, were found to be the most desirable sizes for their inclusion into the layer during nickel electrodeposition to form a composite Ni-microcapsule coating. Observation under an optical stereomicroscope revealed that, in dispersion, the microcapsules were almost perfectly spherical in shape which, after codeposition with nickel, became slightly distorted into ellipsoids in the composite coating.

Cathode plate, electrolyte and electrodeposition

The base cathodes used for both the simple electrodeposition of nickel and the simultaneous electrodeposition of nickel and the microcapsules were low carbon steel plates. The dimensions of the plates were all 30 × 20 × 1 mm (7.6 × 5.1 × 0.25 in.). The electrolyte was an aqueous solution of nickel sulfamate, 800 g/L (107 oz/gal), nickel chloride, 15 g/L (2.0 oz/gal) and boric acid, 45 g/L (6.0 oz/gal). For the codeposition of nickel and lubricant oil microcapsules, a volume of microcapsule suspensions prepared by the above procedure was added to the bath to make up the required microcapsule volume fraction in the solution of 5, 15 and 25%, for the three levels of study chosen. The microcapsules were suspended in the bath during electrodeposition by mechanical stirring at a speed of 100 rpm. All electrodeposition was performed at a solution temperature range of 50 to 60°C (122 to 140°F), a solution pH between 4.5 and 5.0 and a cathode current density of 10 to 15 A/dm^2 (93 to 139 A/ft^2).

To ensure adhesion between the Ni-microcapsule composite coating and the substrate, the plain carbon steel plates were first electroplated in a Watts type nickel bath for 2 min followed by the codeposition of the microcapsules and nickel in a bath containing the nickel electrolyte and the microcapsule dispersion.

Tribological property tests

Wear tests were conducted on both nickel and composite Ni-microcapsule coatings using a planar reciprocation wear machine. In the tests, #600 waterproof sanding papers were used. The wear load (dead weight) was 7.5 kg (16.5 lbf). The following equation was used to evaluate the wear resistance of the coating:

$$W_R = \frac{N}{(W_1 - W_2)/S} \quad \text{or} \quad \Delta m = \frac{W_1 - W_2}{S} \qquad (1)$$

where: W_R is the number of cycles required for a specific surface weight loss, cm^2/mg,

W_1 is the sample weight before the wear test, mg,
W_2 is the sample weight after the wear test, mg,
Δm is the specific surface weight loss, mg/cm^2,
N is the number of cycles of the sample has been abraded and
S is the wear area of the sample, cm^2.

The higher the W_R, or the lower the Δm, the better was the wear resistance of the coating.

A microtribometer was used to measure the friction properties. The applied load was 3 N (0.67 lbf), the frictional diameter was 1.329 cm (0.52 in.) and the test frequency was 3.0 cycles/sec. For each test, the microtribometer measured the maximum, minimum and average friction forces and calculated the kinetic friction coefficients.

Surface morphology, microstructure and composition

The surface morphology of the samples before and after the wear tests was studied with both an optical microscope for an immediate observation of the surface conditions and a scanning electron microscope for a more detailed morphological inspection. The microstructures and composition of the coating were investigated using the SEM and an energy dispersion spectrometer (EDS).

Results and discussion

Ni-microcapsule composite coatings

Figure 1 shows an SEM micrograph of the cross-section of the composite nickel coating containing microcapsules. It can be seen that the microcapsules were enveloped in the composite nickel coating. Although not very clear in this particular photograph, the microcapsules were in fact deformed from their original spherical shape in suspension into ellipsoids in the coating. This is likely because, after adhesion of the microcapsules to the cathode, the subsequent deposition of nickel around the microcapsules created localized pressure, causing the deformation. X-ray energy dispersion spectrum analysis detected C, O, Al, Si, Ca and S in the ellipsoids, as seen in Fig. 2. They are the same as the major components of the lubricating oil as shown in Fig. 3. This confirms that the microcapsules containing lubricating oil were codeposited with nickel metal to form a composite Ni-microcapsule coating.

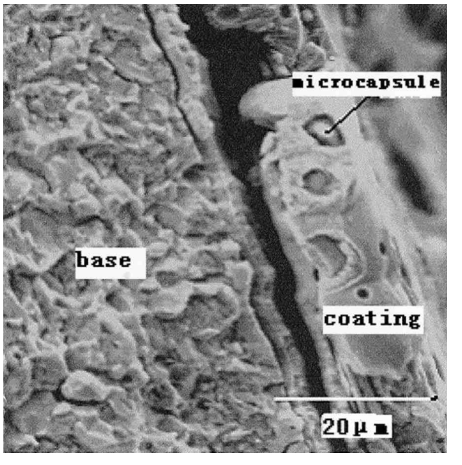

Figure 1—SEM micrograph of a cross-section of the composite Ni-microcapsule coating.

It should be noted that, in the micrograph, the coating is seen to be slightly detached from the substrate. This is because the cross-section of the sample was exposed by fracture (bending), instead of the usual sanding and polishing, to ensure the integrity of the microcapsules. In the process of bending, the excess strain on the sample caused a slight detachment of the coating.

Wear resistance

Before discussing the wear test results, it is worth pointing out a major deviation in our test procedure from the standard one. In a

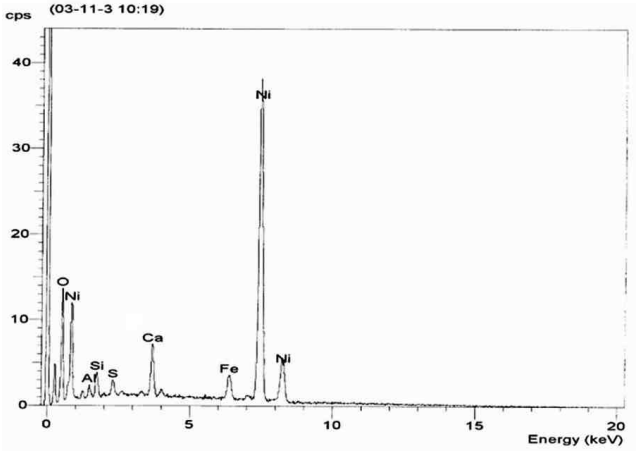

Figure 2—EDS spectra of a microcapsule in the composite coating.

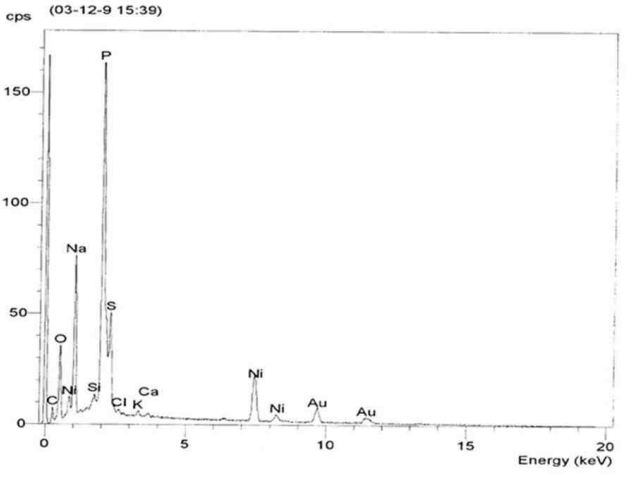

Figure 3—EDS spectra of liquid lubricant oil.

standard wear test, the samples should be washed and dried after each test to obtain the weight loss. However, this procedure could not be applied directly in our work as washing altered the surface characteristics of our Ni-microcapsule samples, as lubricant oil is intended to be released on breakage of the microcapsules as a result of wear. Consequently, the weight for both the nickel and Ni-microcapsule coated samples after each wear test was measured directly without washing.

Table 1 presents the weight loss data from wear tests for both the nickel and Ni-microcapsule coatings. The weight loss was calculated with Equation (1), above. It can be seen that there was a major difference between the results for the nickel coating and those for the Ni-microcapsule coating. The nickel coating consistently lost weight throughout the test period whereas the Ni-microcapsule coating exhibited an apparent overall weight gain at the end of the tests. Clearly, the apparent weight gain for the Ni-microcapsule coating sample was caused by the adhesion of sand grains from the sand paper to the sample surface when the microcapsules were broken and lubricant oil released from them. The greatest weight gain occurred after the first 1200 cycles of abrasion. It then began to lose weight after 3600 cycles. The loss, however, was consistently less when compared to that for the nickel coated samples. These results confirm that (1) the microcapsules in the Ni-microcapsule coating could easily be broken by light abrasion, and therefore could be used as mini-reservoirs of liquid lubricants in self-lubricating moving parts and (2) the overall wear of the Ni-microcapsule coating was less than that of the nickel coating, due mainly to a reduction in friction (as will be seen in the next section).

Kinetic friction coefficients

Figure 4 shows the kinetic friction coefficients for the coatings obtained by microtribometry. In Fig. 4(a), it can be seen that the kinetic friction coefficient of the nickel coating was about 0.3 whereas that of the Ni-microcapsule coating obtained from the bath containing 15 vol% microcapsules in the electrolyte was nearly zero. Another significant difference between the two curves in Fig. 4(a) was that there were noticeable fluctuations in the curve for the nickel coating while the curve for the Ni-microcapsule composite coating was much smoother. This was likely caused by the difference in the micro-roughness of the surfaces after wear as will be discussed in the next section.

In Fig. 4(b), the kinetic friction coefficients are presented for Ni-microcapsule coatings obtained from electrodeposition from solutions containing 5, 15 and 25 vol% microcapsules. The coefficient for the coating from the solution containing 5 vol% microcapsules, while still far below that for the nickel coating at the end of the test period, gradually increased over time. This was possibly because the total amount of lubricant oil contained in the microcapsules was insufficient to sustain the lubrication for the entire surface and test period. By contrast, the coefficients for the 15 and 25 vol% microcapsule coatings were essentially zero, and remained virtually constant for the test period. The practical implication of this is that, to achieve complete self-lubrication, a sufficient amount of lubricating oil must be incorporated into the coating.

Table 1
Reciprocating wear test data

Coating Type	Cumulative Weight Loss after N cycles (mg/cm^2)							
	N=1200	2400	3600	4800	6000	7200	8400	9600
Nickel coating	0.017	0.033	0.117	0.200	0.233	0.250	0.283	0.317
Ni-capsule coating	-0.383	-0.567	-0.467	-0.433	-0.433	-0.417	-0.400	-0.383

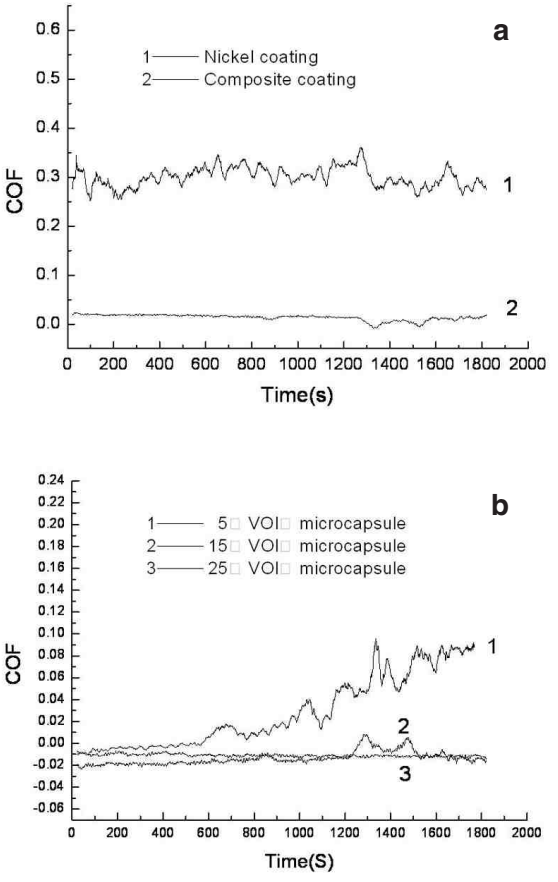

Figure 4—Kinetic friction coefficient of coatings: (a) Ni coating vs. Ni-microcapsule coating; (b) Ni-microcapsule coatings with different volume fractions of microcapsules.

Surface morphology after wear testing

The surface morphology of the simple nickel coating and the Ni-microcapsule coating before the wear tests is shown in Figs. 5(a) and (b), respectively. In Fig. 5(c), the surface of the nickel coating after the wear test (bottom portion) is seen to be fairly rough and irregular, with pieces of nickel remaining on the surface. This helps to explain the fluctuations in the measurement of kinetic friction coefficients for the nickel coatings. Inclusions of the microcapsules in the composite coating, shown as surface bulges in Fig. 5(b) and the top part of Fig. 5(d), are evident. Compared with the nickel coating, the worn surface of the Ni-microcapsule composite coating was smoother. Cavities left by the broken capsules as well as traces of lubricant oil can be seen in the lower part of Fig. 5(d). Undoubtedly, the release and rapid spread of lubricant oil on the surface through rupture of the microcapsules was the major reason for the significant reduction in the friction coefficient.

Conclusion

A method has been developed to fabricate a composite coating incorporating microcapsules containing liquid lubricant oil. The technique involves the preparation of microcapsules with gelatin as their envelopes and lubricating oil as their cores by an aqueous phase separation method. A composite Ni-microcapsule coating can be formed on a cathode plate by electrodeposition in a bath containing both a nickel solution and microcapsules which are suspended in the bath. When subjected to wear, the microcapsules in the composite coating ruptured, resulting in the release of lubricant oil from the capsule to the wearing surface. Results from tribological tests on the composite coatings show that they exhibit greater wear resistance and offer much lower friction. This type of composite coatings has application in anticorrosion as well as self-lubricating applications.

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References

1. F. Hu & K.C. Chan, *Applied Surface Science*, **233**, 163 (2004).
2. K.H. Hou, M.D. Ger, L.M. Wang & S.T. Ke, *Wear*, **253**, 994 (2004).
3. B. Jugović, J. Stevanovic & M. Maksimovic, *J. Applied Electrochem.*, **34**, 175 (2004).
4. F. Plumier, E. Chassaing, G. Terwagne, J. Delhalle & Z. Mekhalif, *Applied Surface Science*, **212**, 271 (2003).
5. C. Muller, C. Sarret & M. Benballa, *Surface & Coatings Technology*, **162**, 49 (2003).
6. I. Garcia, J. Fransaer & J.P. Celis, *Surface & Coatings Technology*, **148**, 171 (2001).
7. M. Ghorbani, M. Mazaheri, K. Khangholi & Y. Kharazi, *Surface & Coatings Technology*, **148**, 71 (2001).

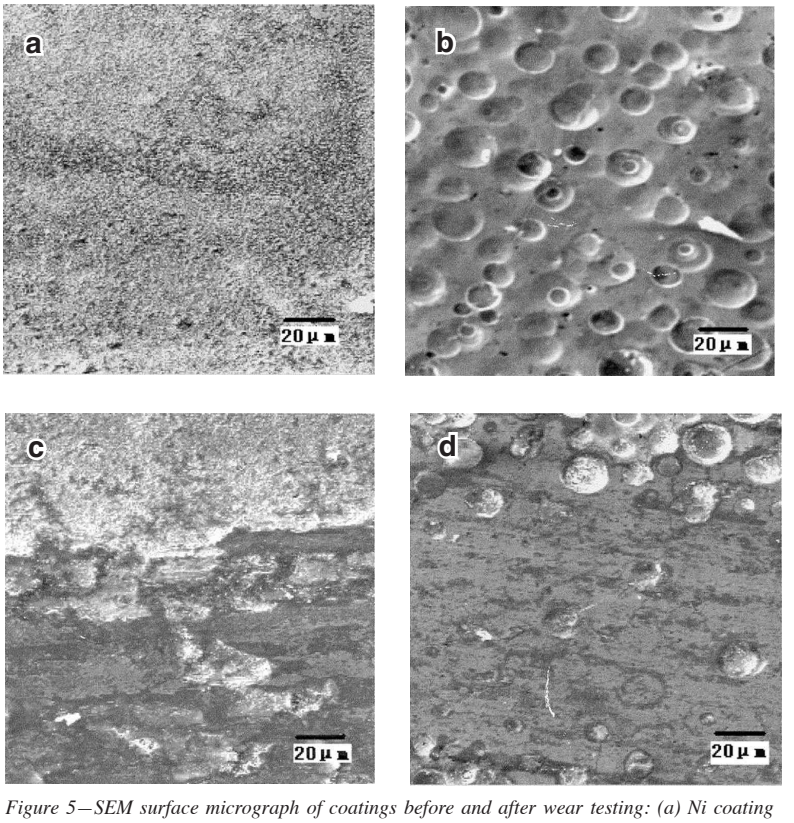

Figure 5—SEM surface micrograph of coatings before and after wear testing: (a) Ni coating before test; (b) Ni-microcapsule composite coating before test; (c) Ni coating after test; (d) Ni-microcapsule composite coating after test.

8. M. Surender, B. Basu & R. Balasubramaniam, *Tribology International*, **37**, 743 (2004).
9. S. Freitas, A. Walz, H. Merkle & B. Gander, *J. Microencapsulation*, **20**, 67 (2003).
10. C. Berkland, M. King, A. Cox, K. Kim & D.W. Pack, *J. Controlled Release*, **82**, 137 (2002).
11. C. Berkland, K. Kim & D.W. Pack, *J. Controlled Release*, **73**, 59 (2001).
12. Y. Matsunami & K. Ichikawa, *Int'l. J. Pharmaceutics*, **242**, 147 (2002).
13. B.F. Gibbs, S. Kermasha, I. Alli & C.N. Mulligan, *Int'l. J. Food Sciences & Nutrition*, **50**, 213 (1999).
14. M.M. Kenyon, in *Encapsulation and Controlled Release of Food Ingredients* (S.J. Risch & G.A. Reineccius Eds.), ACS Symposium Series No. 590, American Chemical Society, Washington, DC, 1995; p. 42.
15. F. Shahidi & X.Q. Han, *Critical Reviews in Food Science & Nutrition*, **33**, 501 (1993).
16. S. Alexandridou, C. Kiparissides, J. Franser & J.P. Celis, *Surface & Coatings Technology*, **71**, 267 (1995).
17. L. Zhu, W. Zhang, F. Liu & Y. He, *J. Material Science*, **39**, 495 (2004).
18. L. Zhu, W. Zhang & F. Liu, *J. Materials Engineering*, **1**, 12 (2004) (in Chinese).
19. M. Itagaki, I. Shitanda, K. Watanabe & H. Koyano, *Surface Technology*, **54**, 230 (2003) (in Japanese).

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