Tribological Behavior of Ni/Sn Metallic Multilayer Composites

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The tribological behavior of Ni/Sn multilayer composites was studied. Composites with varied layer thickness and tin volume fraction were prepared by electrodeposition. The coefficient of friction and wear rate of these composites were characterized by pin-on-disk and block-on-ring tests. Both results suggested that soft tin acted as a solid lubricant between the contacting surfaces. Tin-rich films were detected on both the specimen and the steel wear pair surfaces, and wear resistance greatly depended on the thickness, area coverage, composition, and stability of this interfacial film. Specimens with a lower tin content and/or a thinner layer spacing exhibited enhanced wear resistance compared to those with a higher tin content and/or thicker layers. This was attributed to both the solid-lubricating effect of the tin and the enhanced mechanical properties of the multilayered composites.

Keywords electrodeposition, friction, multilayer composite, nickel, self-lubrication, solid lubricant, tin, wear

1. Introduction

Multilayer composites have been extensively studied in recent years. The advantage of this structure is that the composition and properties of its component layers can be adapted individually. Thus, it provides great flexibility in terms of designing and predicting the properties of the composites. Metallic multilayer composites have been studied as tribological coatings (Ref 1-3) and found to provide improved wear resistance. The improvement is generally attributed to the mechanical strengthening effect in the multilayered structure—that is, the blocking effect of the layered structure to the dislocation glide from one layer to another. This paper presents another possible wear resistance mechanism—self-lubrication—in metallic multilayer composites.

Wear is a process of surface damage and loss of material. To enhance wear resistance, the most effective approach has been to apply tribological coatings on the surfaces of materials. Traditional tribological coatings can be classified into two categories: hard coatings to prevent plastic deformation and removal of material, and soft coatings to provide low friction as solid lubricant (Ref 4). By laminating a hard coating with a soft coating, a multilayered coating can be produced that may combine these two merits. In this composite coating, soft layers offer solid lubrication and hard layers provide structural support. Consequently, this multilayered coating may exhibit self-lubricating behavior.

In this research, a novel Ni/Sn multilayer composite is designed for this purpose. This type of multilayer composite could have self-lubricating behavior (tin is a very soft metal and has been used as a solid lubricant) and enhanced wear resistance (nickel has been widely deposited as a hard coating). This paper reports the effects of layer spacing and tin content on the friction and wear behaviors of Ni/Sn multilayer composites. The wear resistance mechanisms in these multilayered structure are also discussed.

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2. Experimental Procedure

Nickel-tin multilayer composites, with different tin content or a constant tin content but different layer thickness, were electrodeposited alternatively from separate nickel and tin electrolytes. The electrochemical processing has been described elsewhere (Ref 5). Multilayered composites were deposited on a copper substrate. The total thickness of the deposits varied from 0.40 to 1.35 mm, depending on the individual sample. Figure 1 shows the microstructure of the Ni/Sn multilayered specimen, revealing that the samples have controllable layer spacing and fairly good adhesion between the layers. The dark layers are tin, etched by 2 vol% HCl in water

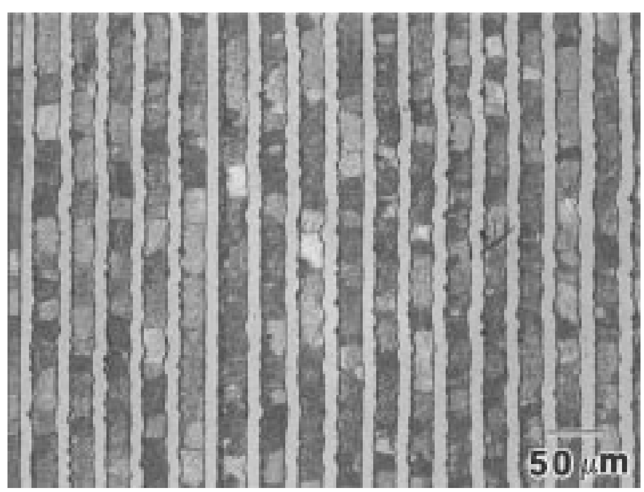

Fig. 1 Typical optical microstructure of the Ni/Sn multilayer composites. The dark layers are tin and the white layers are nickel. Etchant, 2% HCl in water solution

solution. The white layers are nickel, exhibiting good chemical resistance against the etching. The tin deposit has a coarse-grained structure, and the grain size is equivalent to the tin layer thickness.

The tribological behavior of the Ni/Sn multilayer composites was investigated using two types of wear tests. The pin-on-disk test employed two specimens, designated W1 and W2 in Table 1. They had a constant nickel layer thickness of 15 μm, but variable tin content of 33 and 57.5 vol%, respectively. Each specimen was prepared from six pieces of as-deposited multilayer samples with individual thicknesses of 1.35 mm. These pieces were mechanically clamped together and machined into a cylindrical pin with a diameter of 7.84 mm, as shown schematically in Fig. 2(a). The contacting surface of the pins was the multilayer cross section, which was worn against a 8620 tool steel disk at room temperature.

All specimens were tested under unlubricated conditions. Two slip velocities, 1.5 and 3 m/s, were chosen. The normal force was 0.9 N, and the average contact stress was 1.71 MPa. The wear rate was evaluated by the wear-in depth divided by the sliding distance of the pin on the disk. The wear-in depth was monitored in situ with a capacitance displacement probe. After the tests the worn surfaces were examined using an SEM equipped with an energy-dispersive spectrometer (EDS).

The second wear test was block-on-ring, performed in accordance with the standard method of ASTM G 77 (Ref 6). The wear specimens were rectangular blocks measuring 15.75 by 6.35 mm. The ring was made of 8620 tool steel with an outer diameter of 34.99 mm and a width of 8.74 mm. The contacting surface was parallel to the multilayers; the ring wore vertically into the multilayers and left an arc scar on the test block, as shown schematically in Fig. 2(b). The wear rate was characterized by the volume loss divided by the linear distance traveled by the ring on the block. The scar volume was calculated (ASTM G 77) by measuring the width of the scar.

Two groups of specimens, designated W3 and W4 in Table 1, were tested at room temperature and under unlubricated conditions. They had a constant tin content of 30 vol%, but the bilayer thickness varied from 16.7 to 5.0 μm. The normal load ranged from 0.5 to 1 N, and a constant linear ring speed of 2.13 m/s was employed. The wear duration varied from 5 to 15 min. The wear tracks on the blocks and surfaces of the rings were examined using SEM/EDS.

3. Results and Discussion

3.1 *Effect of Tin Content on Friction and Wear*

Nickel/tin multilayers are "two-dimensional" composites. This structural characteristic renders these composites stronger along the layers, but weaker normal to the layers. To study the solid-lubrication effect of tin, the multilayered pins were worn against the steel disks on the cross section of the layers. Thus, a compressive stress was applied along the layers and a shear stress normal to the layers. After the tests, the pins were considerably deformed (Fig. 3). The wear direction was normal to the layers and the wear track scratched the multilayers from the right side to the left. The pin expanded into an oval shape along the wear direction.

The pin-on-disk tests were performed under a constant normal load, but at two slip velocities. Figure 4 shows a typical dependence of the coefficient of friction on test duration. The initial value of the coefficient of friction was about 0.5 for specimen W1. After 230 s of wear testing, it decreased to about 0.1. This suggested that the soft tin phase had been spread onto the contacting surfaces as a solid lubricating film. As the slip velocity increased from 1.5 to 3 m/s, the coefficient of friction increased to 0.3. This result might indicate that the higher slip velocity broke through the already built-up tin lubricating film. The coefficient of friction of specimen W2 had a similar dependence on the test duration, but its initial value was about 0.3—lower than that of W1.

The solid lubricating effect was related to the tin content in the multilayers: A higher tin content led to a better lubrication effect. The wear rates for specimens W1 and W2 were 2.48 and 5.53 μm/m, respectively, which suggested that a lower coefficient of friction did not necessarily lead to a higher wear resistance—because the wear resistance also depended on the mechanical strength of the material. Since W2 had a lower

Table 1 Wear test specimens and test methods

Sample No.	Nickel layer, μm	Tin layer, μm	Tin content, vol%	Multilayer coating thickness, mm	Test method
W1	15.0	7.4	33.0	…	Pin-on-disk
W2	15.0	20.3	57.5	…	Pin-on-disk
W3	11.7	5.0	29.9	0.8	Block-on-ring
W4	3.5	1.5	30.0	0.4	Block-on-ring

Table 2 Wear test data and specimen mechanical properties

Sample No.	Coefficient of friction	Volume loss, mm^3	Wear rate	Ultimate tensile strength, MPa	Yield strength, MPa
W1	0.5-0.1	…	2.48 μm/m	498.5	301.3
W2	0.3-0.1	…	5.53 μm/m	335.8	203.4
W3	0.51	24.99	13.01×10^{-3} mm^3/m	502.7	320.1
W4	0.32	8.44	4.37×10^{-3} mm^3/m	633.1	386.5

strength than W1 (Table 2), it could be deformed more easily during the wear, so its wear-in measurement was larger. Thus, specimen W2 had a lower wear resistance than W1.

Observation by SEM confirmed the existence of tin film on the worn surface of the specimen. Figure 5 presents backscattered electron images (BEIs) of the wear tracks of specimens W1 and W2. The wear direction was from right to left. The white stripes across the wear track of W1 were tin layers. Tin was spread as a discontinuous film on the worn surfaces of both specimens, but W2 had a larger tin film coverage than W1, which explained why W2 had a lower friction coefficient than W1. Analysis by EDS indicated that in the dark areas, nickel content was higher. The atomic percentages of nickel and tin were about 80 and 20%, respectively. In the white areas, however, tin was higher. There, the atomic percentages were about 18% for nickel and 82% for tin. Thus, it was concluded that the lower friction coefficient for the layered composites was due to the solid-lubricating tin film on the contacting surfaces.

3.2 *Effect of Layer Thickness on Friction and Wear*

In the block-on-ring tests, the wear block was worn by a steel ring rotating against its surface, so that the multilayer composite was exposed to a compressive stress normal to its layers and a shear stress along its layers. As mentioned previously, the composites were relatively weak in this loading direction. Thus, the multilayers were extruded by the steel ring, and "ears" were formed on both sides of the block, as shown in Fig. 6, which offers an overall view of the worn block under a stereoscope. Some burring also was visible on the sliding-out end (right side) of the scar. Under the stereoscope or SEM, the nickel and tin layers were clearly apparent on the sliding-in side of the scar, but on the sliding-out side the boundaries of the layers were smeared. This might suggest that the wear products, including tin and nickel debris, were transported by the ring from the sliding-in side to the sliding-out side.

During the block-on-ring tests, the multilayers were worn through layer by layer, so that the coefficient of friction of the multilayers fluctuated periodically. Figure 7 shows a dependence of the friction coefficient of specimen W3 on wear duration. It is believed that the peaks and valleys of the curve correspond to the wearing-through sequence of the nickel and tin layers. Since no tin phase was exposed to the ring surface initially, the first peak, about 0.67, should correspond to the coefficient of friction of the outer nickel layer against the steel. This value is very close to the friction coefficient of pure nickel on mild steel, which is about 0.64 (Ref 7). Once this layer was worn through and the first tin layer was exposed, the coefficient of friction dropped rapidly to about 0.50, suggesting that a discontinuous tin film began to develop on the contacting surfaces at this point. After this layer of tin was penetrated and the second layer of nickel was exposed, the tin film was worn off and the coefficient of friction rose again.

This process repeated periodically. Since the contact surface area increased gradually with increasing wear depth, the time required to penetrate each layer became longer and longer. Thus, the next peak was wider than the previous one. After 6 to 8 min of testing, the variation in the coefficient of friction became less, and a constant value of 0.51 was obtained. This phenomenon suggested that a steady-state tin lubricating film had been built up on the contacting surfaces with time. Since the friction coefficient of pure tin on iron is about 0.32 (Ref 7), this constant coefficient value suggests that the surface friction condition of specimen W3 is between pure nickel and tin. The

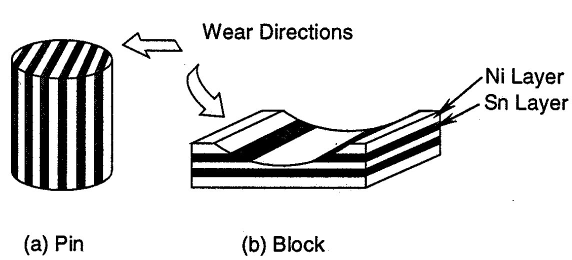

Fig. 2 Schematics of the configuration and orientation of the multilayered pin (a) and block (b) in the wear tests

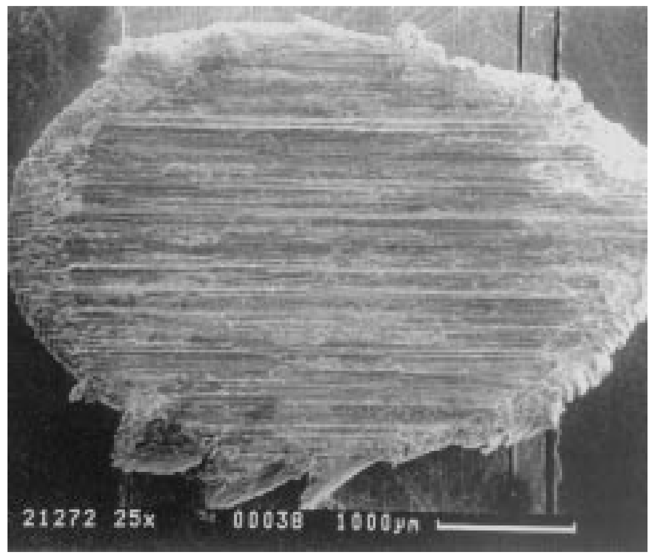

Fig. 3 Typical deformed wear pin after the pin-on-disk test

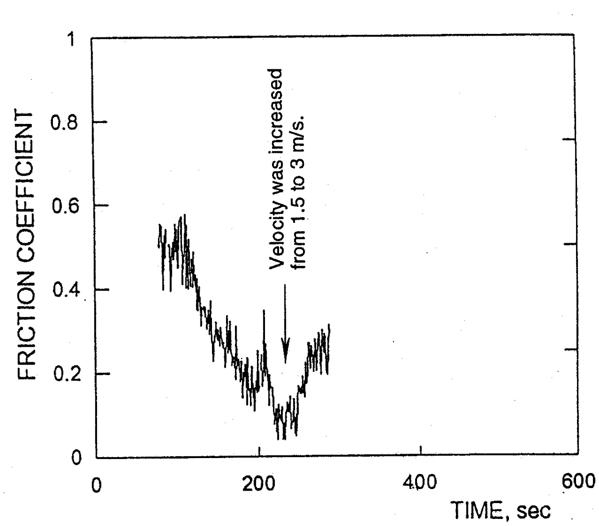

Fig. 4 Coefficient of friction of specimen W1 versus test time

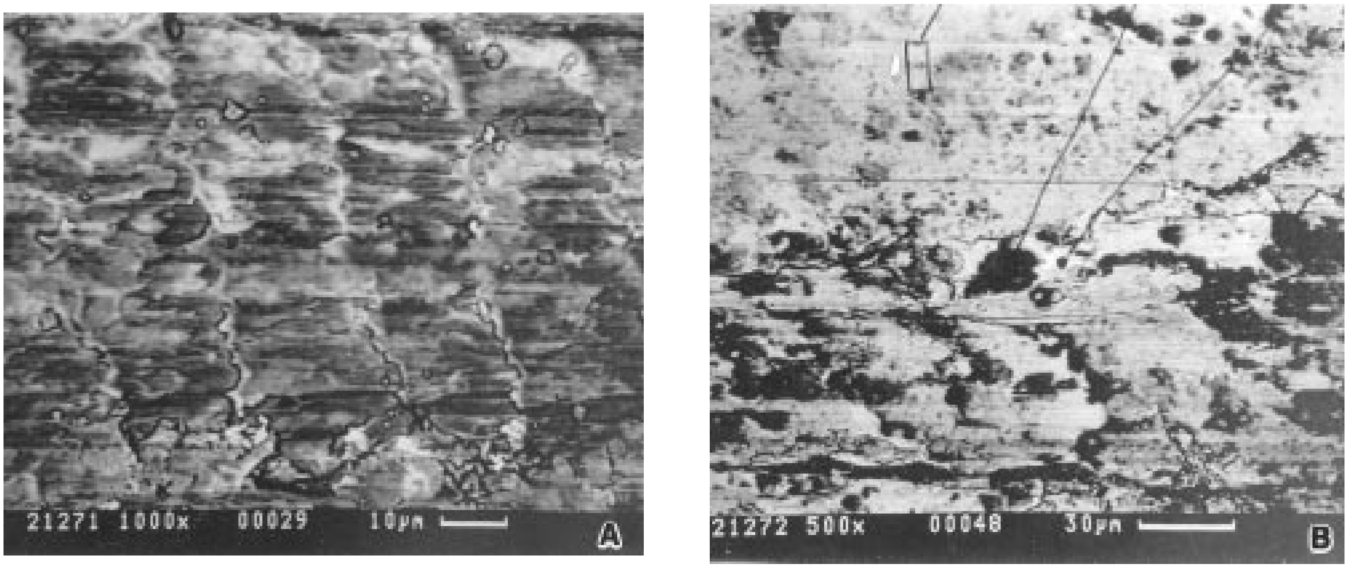

Fig. 5 SEM backscattered images of worn surfaces. (a) Specimen W1. (b) Specimen W2

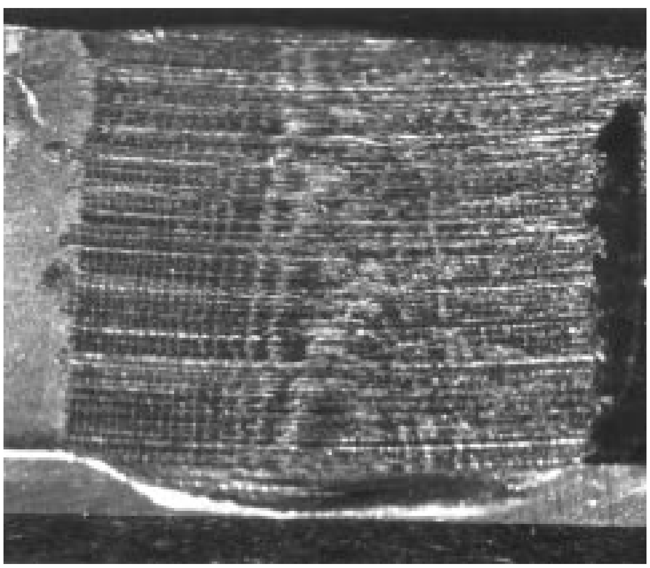

Fig. 6 Macrograph of the worn block of specimen W3. 10×

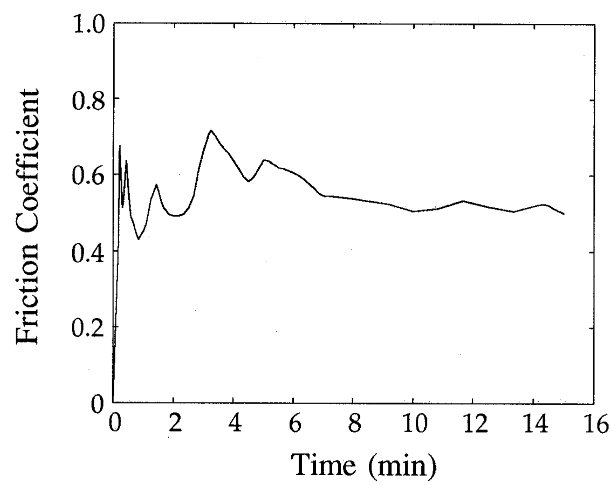

Fig. 7 Coefficient of friction of specimen W3 versus test time

friction coefficient of specimen W4 had a similar dependence on the test duration, but its final constant value was about 0.32, which equaled the friction coefficient of pure tin on iron. This result suggested that a relatively complete tin lubricating film formed on the surfaces of both specimen W4 and its steel ring wear pair.

The wear scars on specimens W3 and W4 were examined in the SEM and micrographs taken on the wear-out side of the scars. Figure 8(a) is a BEI of the wear track of specimen W3. Wear direction is from right to left. The worn surface is rough, with grooves along the wear direction. Analysis by EDS indicated that the white areas had higher tin content, and the dark areas had higher nickel content. The tin film was distributed discontinuously on the worn surface. The two white parallel stripes are exposed tin layers.

A similar wear track was observed on specimen W4, as shown in Fig. 8(b), but the worn surface was covered by an almost continuous tin film. These observations suggest that the greater tin film coverage on the surface of specimen W4 produced a lower friction coefficient than specimen W3. They might also suggest that the thinner layers favored the formation of a relatively continuous tin lubricating film.

A tin lubricating film also was detected on the surfaces of the steel rings. Figure 9(a) shows the surface morphology of the steel ring wearing against specimen W3. The surface was partially covered with a tin film, as shown in the middle portion of the image. In this area, breaking and peeling of the film are apparent, and the broken film was transferred into fine debris. In the other areas, the lapping marks of the steel ring are still clearly visible. Analysis by EDS indicated that both tin and

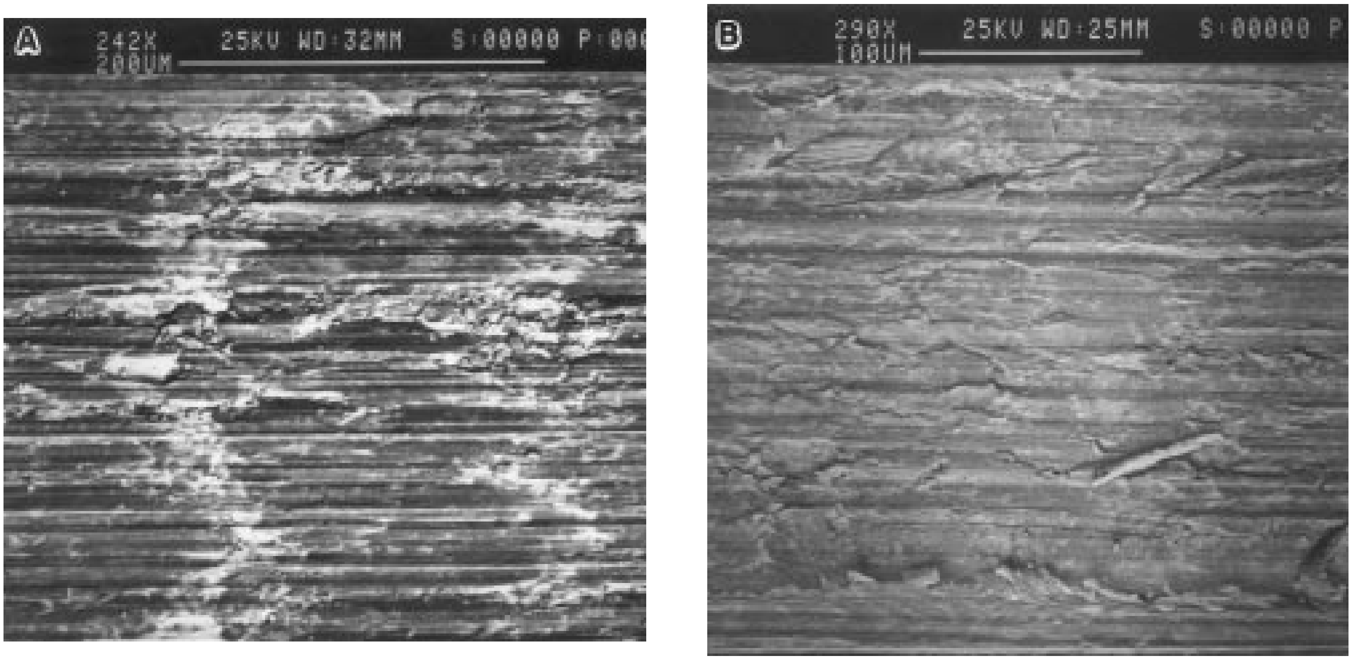

Fig. 8 SEM backscattered images of wear tracks. (a) Specimen W3. (b) Specimen W4

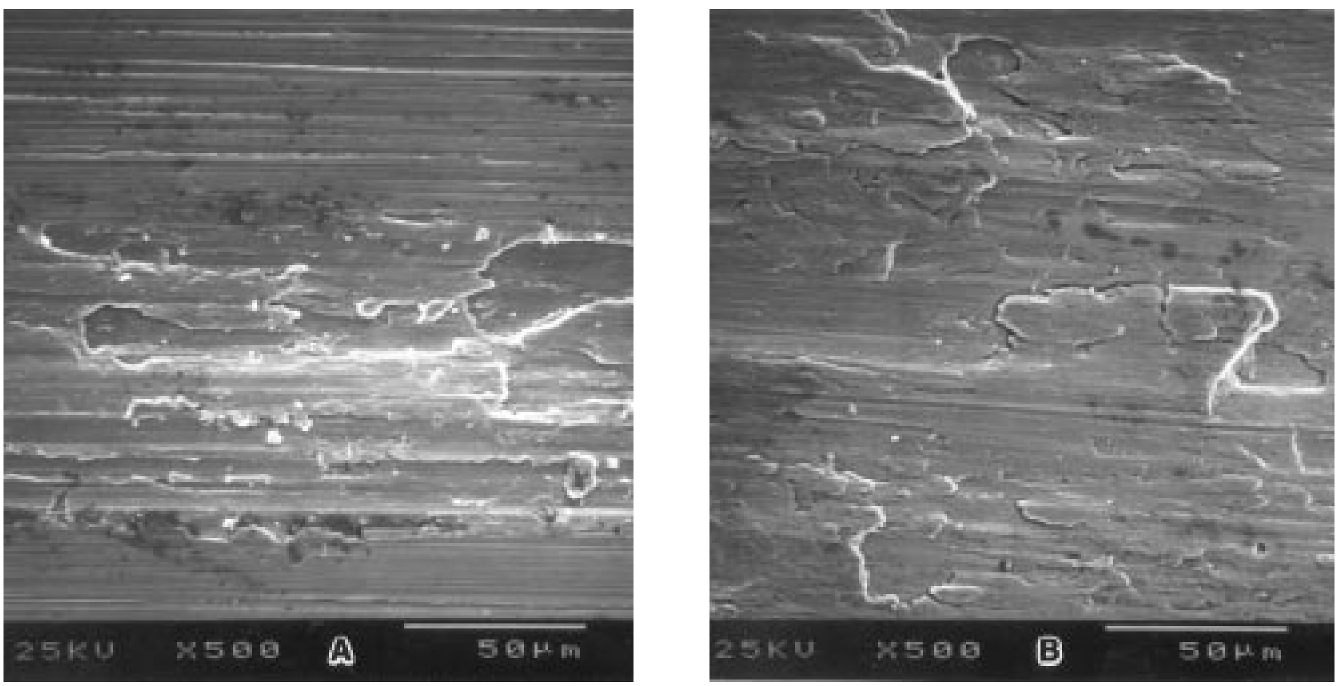

Fig. 9 SEM surface morphologies of steel rings worn against specimens W3 (a) and W4 (b)

nickel were present in the film-covered areas. The composition of this region was about 19 at.% tin, 30 at.% nickel, and the rest iron. In the uncovered areas, however, only iron peaks were detected. The surface of the steel ring wearing against specimen W4 was covered by a similar tin film, but the coverage was almost continuous, as shown in Fig. 9(b). The lapping marks on its surface were totally smeared, and only minimal debris and peeled-off film were visible.

The wear rates and tensile strengths of specimens W3 and W4 are listed in Table 2. The wear, or volume loss, rate is 13.01 $\times 10^{-3}$ mm^3/m for W3 and 4.37 $\times 10^{-3}$ mm^3/m for W4, which indicates that the thinner layered composite has higher wear resistance than the thicker layered one. This enhancement is due to not only the better tin lubrication condition in specimen W4, but also the effect of mechanical strengthening in this thinner layered specimen. The yield strength of W4 was about 21%

higher than that of W3. Consequently, its wear resistance also was higher. The dependence of mechanical strength on the layer spacing of the Ni/Tin multilayered composites is discussed elsewhere (Ref 8), and the effect of mechanical strengthening on wear resistance is interpreted in the following paragraphs.

3.3 *Lubrication and Wear Resistance Mechanisms*

The reductions in the coefficient of friction and wear rate observed in this study are attributed to two effects. First is the mechanical strengthening effect of the Ni/Sn multilayered structure. It is commonly known that surface damage in ductile metallic materials involves surface or subsurface plastic deformation. Consequently, any strengthening effect can enhance the wear resistance of the material. In metallic multilayer composites, the strengthening mechanism is due to the pinning of dislocations at the interfaces of the layers.

This barrier effect originates from two sources. One is the lattice mismatch and resultant high dislocation density at the interface zones. Here the interface blocks the movement of dislocations much as a grain boundary does. The second source is the dislocation line energy gap, or the elastic modulus difference, between the two adjacent layers. This "locking" effect exists only in composites with different phases, such as Ni/Sn multilayer composites. A thinner layer spacing creates a higher image force to restrain the dislocation motion across the interface, inhibiting the generation of new dislocations. Therefore, the specimen with thinner layers exhibits a higher strength as well as a lower wear rate than the one with thicker layers. Since the specimen with a higher tin content has a lower mechanical strength than the one with a lower tin content, its wear rate also is higher.

The second mechanism is the solid-lubrication effect due to the presence of tin film on the contacting surfaces. During wear, soft tin was sheared off and smeared onto both the specimen and the steel wear pair surfaces to form a lubricating film. Consequently, the coefficient of friction and wear were lowered. The test results suggested that the wear and damage behavior of the composites greatly depended on the thickness, area coverage, and stability of this interfacial film. The breaking and peeling of the film increased wear rates. Certain factors, such as the formation of a tin oxide film, could decrease the adherence of the tin film to the steel surface and increase the peeling tendency of the film. Thus, this lubricating film might be broken frequently and transferred into debris. The actual wear behavior depended on which process was dominant.

The test results also suggested that a smaller layer spacing favored the development of a relatively continuous tin film, so the coefficient of friction as well as the wear rate was lower for the thinner layered specimen than for the thicker layered one. Increasing the load and/or sliding velocity might break the film and lead to greater wear. The tin lubricating effect might also depend on the orientation of the wear specimens. When the wear surface was the cross section of the multilayers, the coefficient of friction was lower than when the wear surface was parallel to the composite layers—perhaps because the actual layer spacing was smaller in the former case. Consequently, a more effective tin film could be developed.

4. Conclusions

Self-lubricating behavior was observed in Ni/Sn multilayered composites. The decrease in the coefficient of friction was attributed to the presence of a solid-lubricating tin film on the wearing surfaces of the multilayered specimen and the steel pair. Greater surface area coverage of the tin film led to a lower coefficient of friction. This coverage was relatively greater in the specimen with a higher tin content and/or a thinner layer thickness.

The friction behavior of the composites depended on the orientation of the layered specimens to their steel wearing pairs. When both the tin and nickel phases were exposed to the steel simultaneously, the coefficient of friction decreased gradually with test duration. When the tin and nickel layers were worn through sequentially, the coefficient of friction fluctuated with test time.

Wear behavior depended not only on friction behavior, but also on the mechanical strength of the samples. The specimen with a higher tin content exhibited lower strength and resultant lower wear resistance than the specimen with a lower tin content. The specimen with a thinner layer thickness exhibited a higher mechanical strength as well as a lower coefficient of friction; consequently, its wear resistance was higher than that of the thicker layer specimen.

Acknowledgments

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