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BOUNDARY FILM FOR STRUCTURAL CERAMIC MATERIALS*

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ABSTRACT

Structural ceramic materials, like metals, will require lubrication if they are to be used extensively for tribological applications. The use of thin soft metallic coatings (specifically Ag) as a boundary film during mineral oil lubrication of silicon nitride (Si_3N_4) and zirconia (ZrO_2) ceramic materials was investigated in this study. With a pin-on-flat contact configuration in reciprocating sliding, the steady friction coefficient was reduced by a factor of 2 (0.14 -0.16 vs. 0.06 - 0.07) when the flats were coated with Ag. Also, with Ag coatings the wear of pins was reduced to an unmeasurable level, whereas, in the absence of Ag coatings specific wear rates of $\approx 2 \times 10^{-9}$ - 4×10^{-8} mm^3/Nm and $\approx 7 \times 10^{-8}$ - 2×10^{-7} mm^3/Nm were measured for Si_3N_4 and ZrO_2 pins respectively. In addition to preventing direct contact between pins and flats, thereby reducing wear, the Ag coatings also act as a solid lubricant, help dissipate flash heating, and accelerate modification of the λ ratio.

INTRODUCTION

Structural ceramic materials are increasingly being used for tribological applications, such as nozzles, cutting tools, mechanical seals, etc. These materials are also being proposed as replacements for metallic materials in applications that involve sliding and rolling contacts, which are often lubricated. Some of these applications include automotive components like cylinder liners, bearings, etc. An extensive amount of work has been done on the tribological behavior of ceramic materials in dry-sliding contact [e.g. 1-4, 17]. Under such conditions, the wear in most ceramic materials is much less than that of metallic materials tested under the same conditions of e.g. 10N load and 0.77 ms^{-1} speed at room temperature [9]. A wide range of behavior has been reported in the friction characteristics of ceramic sliding pairs. Some materials exhibit lower friction than ferrous materials (which constitute a large majority of metallic materials currently being used for tribological applications), others exhibit higher friction coefficients under similar test conditions. Friction coefficients ranging from 0.2 to >1.0 have been reported for various ceramic materials [5, 6, 21]. Nevertheless, the tribological characteristics of ceramic materials with the lowest wear and friction under dry conditions are unacceptable for most applications. Thus, there is a need to find ways of effectively lubricating structural ceramic materials if they are to be used extensively in tribological applications.

To date, only a limited amount of work has been done on lubrication of ceramic materials [e.g. 7-10]. Some of these studies utilized hydrocarbon oil without any additives as lubricants, others used formulated lubricants. Results of these studies clearly show the deficiencies of the current state of knowledge of ceramic materials' lubrication. While some investigators reported significantly improved tribological characteristics of ceramics through lubrication [7, 10], others reported little or no improvement at all [8, 11]. Furthermore, the same lubricants produced significantly different results with different ceramic materials [8, 11]. One conclusion from these early works on ceramic lubrication is that the oils that successfully lubricate metallic materials may not work as well for existing ceramic materials, at least under non-hydrodynamic conditions. Thus exploration of other adequate means of lubricating ceramics is necessary.

During liquid lubrication, the critical regime is the boundary one, wherein tribological behavior is determined by the properties of both the lubricant and the material surface. This is a consequence of the extensive direct contact between the lubricated surfaces in this regime. With ferritic materials, the lubricants are formulated with a blend of additives that interact chemically with the wearing surfaces to create a new layer, commonly referred to as a boundary film. This film separates the two contacting surfaces (thereby preventing direct interaction) and reduces wear and friction [12, 13]. Although some investigators have reported limited interaction between Si_3N_4 material and additives in current commercial oils [14], the extent of such interaction was so small, compared to the ferrous surfaces, that it could not be considered adequate for boundary lubrication. This is not unexpected in view of the relatively low chemical reactivity of ceramic materials when compared to metallic materials.

Boundary lubrication of ceramic materials must be addressed. One can use the approach of designing a lubricant specifically for ceramics by using more reactive additives, which can readily form boundary film. To the best of our knowledge, no such lubricant has been designed yet. An inherent problem with such an approach is the wide variety of available structural ceramics. Due to the specificity of interaction between additives and wearing surfaces, it is very unlikely that one or two additives could be found that will work well with the wide variety of current ceramics. In fact, significant differences in chemical adsorption of the additives in oil onto ionic and covalent ceramic materials have been reported [11].

An alternative approach is to modify the surface of ceramic materials in such a way as to provide a good boundary film. Studies have shown that boundary-film behavior during lubrication is very similar to that of soft solids [15, 16]. Other studies have also shown that a well-adhering soft metallic coating can be deposited on different ceramic materials [17-19]. Conceivably, one could use such a metallic coating as a boundary film for ceramic materials. This study investigates the feasibility of using Ag coatings as a boundary film for silicon nitride (Si_3N_4) and zirconia (ZrO_2) ceramic materials during oil lubrication.

EXPERIMENTAL DETAILS

Material - The materials used in this study were commercially available Si_3N_4 (SN-220) and ZrO_2 (Z-201N) structural ceramics from Kyocera Corporation. Some properties of these materials, as supplied by the manufacturer, are given in Table 1. The microstructure of the Si_3N_4 consists primarily of elongated β-Si_3N_4 grains with an aspect ratio (width:length) of about 1:4. Average grain diameter was about 0.8 µm, and average grain length was about 3.5 µm. The material was processed with a Y_2O_3 sintering aid, resulting in the presence of a grain-boundary phase of amorphous yttrium silicate glass and crystalline $Y_2Si_2O_7$ grains [22]. The ZrO_2 material was stabilized with about 6 mol. % Y_2O_3; its microstructure consists primarily of tetragonal phase and a few cubic-phase grains. Average grain size was about 0.5 - 1 µm.

Flat specimens with nominal dimensions of 50 x 25 x 6.5 mm and pin specimens with 15-mm length and 8-mm diameter were prepared from both materials. One end of each pin was rounded to a radius of curvature of 127 mm and finished to a surface roughness of 0.08 µm R_a. The flat specimens were ground to a surface roughness of about 0.25 µm R_a.

Coating - A thin Ag film (≈1.5 µm thick) was deposited on some of the flat specimens by ion-beam-assisted deposition (IBAD). This method involves simultaneous bombardment of a growing film with energetic ions and results in a substantial increase in the adhesion of the film to the substrate. Details of the IBAD procedure and the characteristics of the films produced have been previously described in detail [17-19]. Only some of the flat specimens were coated; none of the pin specimens were coated.

Tests - Friction and wear tests were done with pin-on-flat contact geometry in reciprocating sliding. A schematic diagram of the test device is shown in Figure 1. A loaded pin, firmly attached to the loading arm by a pin holder, is moved back and forth on the surface of a stationary flat, which has been placed and firmly secured in a lubricant cup. The friction force was measured by a strain gage device attached to the loading arm. Lubricated tests were done using the same material sliding pairs, with and without Ag coatings on the flats. The lubricant cup was filled with the oil after the flat specimens had been secured in place. White (light) paraffin (mineral) oil with room-temperature viscosity of about 25.6 cSt was used as the lubricant. The oil contained no additives. In our previous study with a fully formulated oil lubricant, the occurrence of chemical interaction between the Ag coatings and the S additive in the oil had a detrimental effect on the effectiveness of the coating [23]. All the tests were done with a normal load of 50 N (giving an initial nominal mean Hertzian pressure of 166 and 132 MPa for Si_3N_4 and ZrO_2 respectively), stroke length of 25 mm, reciprocating frequency of 1 Hz, resulting in an average speed of 0.05 m/s. Tests were performed at room temperature (≈23°C) and 150°C for a total of 2000 cycles.

The friction coefficient was continuously monitored in all tests. The amount of wear from the pin after each test was calculated from the dimensions of the wear scar, as measured by optical microscope. The wear volume in the pin was estimated by the equation $V_p = (\pi r^4)/4R$, where r is the radius of the wear scar and R is the radius of curvature [20]. An attempt was made to estimate the wear in the flats using a stylus-type surface profilometer. Traces of the surface profile were taken across the wear track, from which the cross-sectional area of the wear track can be determined. The volume of material removed is the product of the average measured cross-sectional area and the stroke length.

The worn surfaces of the pin and the flat were examined with an optical microscope and a scanning electron microscope (SEM). The pin and uncoated flat specimens were sputter-coated with a thin layer of carbon before examination to prevent charging during SEM analysis.

RESULTS

Figure 2 shows the frictional behavior of various sliding couples. For Si_3N_4 couples (Figure 2a), the friction coefficients during the first cycle of sliding for both the uncoated and Ag-coated flats at room temperature were the same at 0.12. The friction coefficient increased gradually in the test with an uncoated flat, reaching a steady value of about 0.14 after 600 cycles. With an Ag-coated flat, however, the friction coefficient decreased rapidly, after an initial value of 0.12 to 0.04 over the first 200 cycles, and then showed a modest increase to a steady value of 0.06 after ≈600 cycles of sliding. At the higher temperature of 150°C, the frictional behavior with uncoated and Ag-coated flats showed the same trend but the value of the friction coefficient was lower for the coated flat. In both cases, the friction coefficient increased slightly over the first 20 cycles to a peak value of about 0.16 for the uncoated flat and about 0.14 for the Ag-coated flat; it then fluctuated for the uncoated flat, attaining what appears to be a steady value of about 0.15. For the coated flat, the friction coefficient showed a gradual decrease from the peak value to about 0.11 at the end of the test.

The frictional behavior of the ZrO_2 sliding pair is shown in Figure 2b. At room temperature, the friction coefficient during the first cycle of sliding was about 0.16 for an uncoated flat. The friction coefficient increased, attaining a peak value of about 0.18 before it eventually decreased to a steady value of 0.15 after about 800 cycles. With the Ag-coated flat, sliding started with a friction coefficient of 0.09, increased slightly to a peak value of 0.12 and then finally decreased to a steady value of about 0.07 after 700 cycles of sliding. At 150°C, the trend of frictional behavior was very similar to that at room temperature for both the uncoated and the Ag-coated flats. For the uncoated flat, the friction coefficient at the start of the test was about 0.17. It increased to a peak value of about 0.23 and finally decreased to a steady value of about 0.15. With the Ag-coated flat, the initial friction coefficient was 0.08, increasing to a peak value of 0.11, and eventually decreased to a steady value of about 0.07.

The specific wear rates for the pin, averaged over the duration of each test, are shown in Table 2. For both Si_3N_4 and ZrO_2 materials, some wear occurred in the pin that was rubbed against the uncoated flats.The wear at 150°C was higher than that at room temperature by about an order of magnitude for both materials. It was also observed that more wear occurred for the ZrO_2 pins than for the Si_3N_4 pins under the same test conditions. In both materials, there was no measurable wear in any pins tested against Ag-coated flats at room temperature or 150°C. Although the wear tracks were identifiable in all the uncoated flats, the amount of wear was so small that it could not be adequately measured by surface profilometry. The Ag coatings were not worn through in any of the coated flats; thus the ceramic substrates were well protected from wearing.

Figure 3 shows the typical microscopic appearance of the wear tracks on the pin that had been rubbed against uncoated flats. The wear areas of both the Si_3N_4 and ZrO_2 pins showed some dark coloration. A similar observation has been attributed to the formation of carbon deposits from the lubricating hydrocarbon oil [9]. In the Si_3N_4 pin, scratches running in the direction of reciprocating sliding were seen in the worn area (Figure 3a), suggesting abrasion as one of the wear mechanisms during the test. In the ZrO_2 pin, the worn area was also rough but not as much as in Si_3N_4 (Figure 3b). The characteristics of the typical wear track on the uncoated flat are shown in Figure 4a. Although the wear track can clearly be identified, the original grinding marks are still visible. In the coated flats, however, a very smooth area was generated on the Ag coating (Figures 4b and 4c). Roughness measurements on the wear track of coated ZrO_2 flats in the sliding direction after the test gave an Ra number of 0.03 µm, compared to a value of 0.23 µm outside the wear track.

DISCUSSION

The fluid-film thickness during boundary lubrication is very small, leading to extensive direct contact and interaction of asperities on the lubricated surfaces. This interaction usually results in high friction, high wear and significant flash heating at the asperity points of contact. In metallic (especially ferritic) material lubrication, the formation of a boundary film by chemical interactions between the lubricated surface, lubricant additive and the operating environment, serves the primary purpose of preventing direct contact and interaction between the two surfaces.

In the present study, the Ag coating effectively served the primary function of a boundary film by preventing direct contact between the wear surfaces of ceramic material. The effectiveness of the coating was seen in the fact that no measurable wear occurred during any of the tests that involved a coated specimen. In addition to preventing direct contact, the Ag coatings functioned in the following ways to improve the tribological behavior of ceramic materials during lubricated sliding contact.

(1) Synergism of solid and liquid lubrication: Ag coatings have been shown to be an effective solid lubricant for different structural ceramic materials [17, 19]. A significant decrease in friction and wear has been observed by coating one of the sliding couples with Ag. The lubricating action of the coating was due to its softness and low shear strength, thereby creating an easily sheared interface when present. Results of the present study also showed that the use of a mineral oil lubricant can significantly reduce both the friction coefficient and wear of Si_3N_4 and ZrO_2 ceramic materials when compared to dry sliding. For the oil-lubricated tests involving an Ag-coating, one would have expected a combined action of both the solid lubricant (Ag coatings) and the liquid lubricant under boundary conditions. This synergism of the two kinds of lubricants was seen in the fact that the friction coefficients were significantly lower when both were present as compared to when only one of the two was present.

(2) Modification of the λ ratio: The regime of liquid lubrication and to a large extent the effectiveness of a lubricant is determined by the lambda ratio (λ), defined as the ratio of minimum EHD fluid film thickness (h_m) to the composite surface roughness of the contacting surfaces (σ), i.e., $\lambda = h_m/\sigma$ [24]. When $\lambda>3$, lubrication is hydrodynamic; for $\lambda<1$, boundary lubrication exists. In general, the higher the λ ratio, the more effective the fluid film lubrication. In the present study, a smooth contact area was generated on Ag-coated flats during friction and wear testing. This is due to the softness of the coating material. The effect of this smoothing of the contact area will be an increase in the λ ratio. For instance, the estimated λ ratio for the Ag-coated ZrO_2 at the start of the test was

0.43, which clearly is in the boundary regime. An estimate of the λ ratio at the end of the test was about 1.3. This modification of the λ ratio by the Ag coating will make the liquid lubricant more effective.

(3) Dissipation of flash heating: One of the functions of liquid lubricants is the control of bulk temperature resulting from frictional heating. Under boundary lubrication, however, a significant amount of heating occurs at the few asperity contacts. This often produces localized high temperatures at such contact points, the so-called flash temperatures. The flash heating could cause thermal degradation of the lubricant. On the other hand, it could increase the reaction rate of boundary film formation. An important detrimental effect of flash heating for boundary lubricated ceramics is the possible occurrence of localized thermal shock. It has been suggested that this localized thermal shock was responsible for extensive cracking in lubricated ZrO_2 material [8]. A similar kind of cracking was also observed during unlubricated sliding contact [19]. The use of Ag coatings as a boundary film could alleviate the problems associated with flash heating. Due to its excellent thermal conductivity, the coating can easily dissipate the heat laterally, thereby preventing the localized increase in temperature. An estimate of the flash temperature under the present test conditions using Ashby T-maps gave a value of about 300°C for ZrO_2 [25, 26]. When coated with Ag, the estimated flash temperature is less than 30°C. This function of the Ag coating is particularly important for ceramic materials with very low thermal conductivity (such as ZrO_2), since they are more susceptible to thermal shock, and the flash temperature is usually very high in such materials.

CONCLUSIONS

Structural ceramic materials, like metals, need effective lubrication in order to find extensive use in tribological applications. Results of the present study showed that thin soft metallic coatings (Ag in this study) can serve as an effective boundary film during liquid lubrication of ceramic materials. Friction coefficients for Si_3N_4 and ZrO_2 materials were decreased by a factor of about 2 during mineral-oil lubrication when one component (the flat) was coated with Ag. Wear in both sliding components was reduced to an unmeasurable level. The presence of Ag coating improved the oil-lubricated tribological characteristics of the tested materials by preventing direct contact between the ceramic couples. The coatings were also beneficial by acting as a solid lubricant, modifying the operating λ ratio and laterally dissipating the flash heating during boundary lubrication.

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Property	Si_3N_4	ZrO_2
Bulk Density (x10^3 kg/m^{-3})	3.2	6.0
Young's Modulus (GPa)	294	206
Hardness (GPa)	17.41	13.2
Fracture Toughness (MPa$\sqrt{m}$)	4.25	6.0
Flexural Strength (MPa)	590	980
Poisson's Ratio	0.28	0.31

Table 1 - Some properties of the Si_3N_4 and ZrO_2 ceramic materials

Temperature		Si_3N_4	ZrO_2
RT (23°C)	Uncoated	2.35×10^{-9}	6.92×10^{-8}
	Ag-coated	NMW *	NMW
150°C	Uncoated	3.62×10^{-8}	2.03×10^{-7}
	Ag-coated	NMW	NMW

* NMW means no measurable wear

Table 2 - Average pin specific wear rate (mm^3/Nm) after sliding against uncoated and Ag-coated flats.

CAPTIONS FOR FIGURES

Figure 1: Schematic diagram of sliding reciprocating contact of the friction and wear testing device.

Figure 2: Variation of the friction coefficients with the number of sliding cycles (sliding distance) during various test conditions for (a) Si_3N_4 sliding pairs, (b) ZrO_2 sliding pairs.

Figure 3: Optical micrograph of worn areas on pins tested against uncoated flats at 150°C (a) for Si_3N_4 showing dark coloration and scratches, (b) for ZrO_2 also showing dark coloration.

Figure 4: (a) Optical micrograph of wear track on uncoated Si_3N_4 flat, (b) optical micrograph of wear track on the Ag-coated ZrO_2 flat showing smooth contact area, (c) SEM micrograph of track on Ag-coated Si_3N_4 flat also showing smoothing of the contact area.

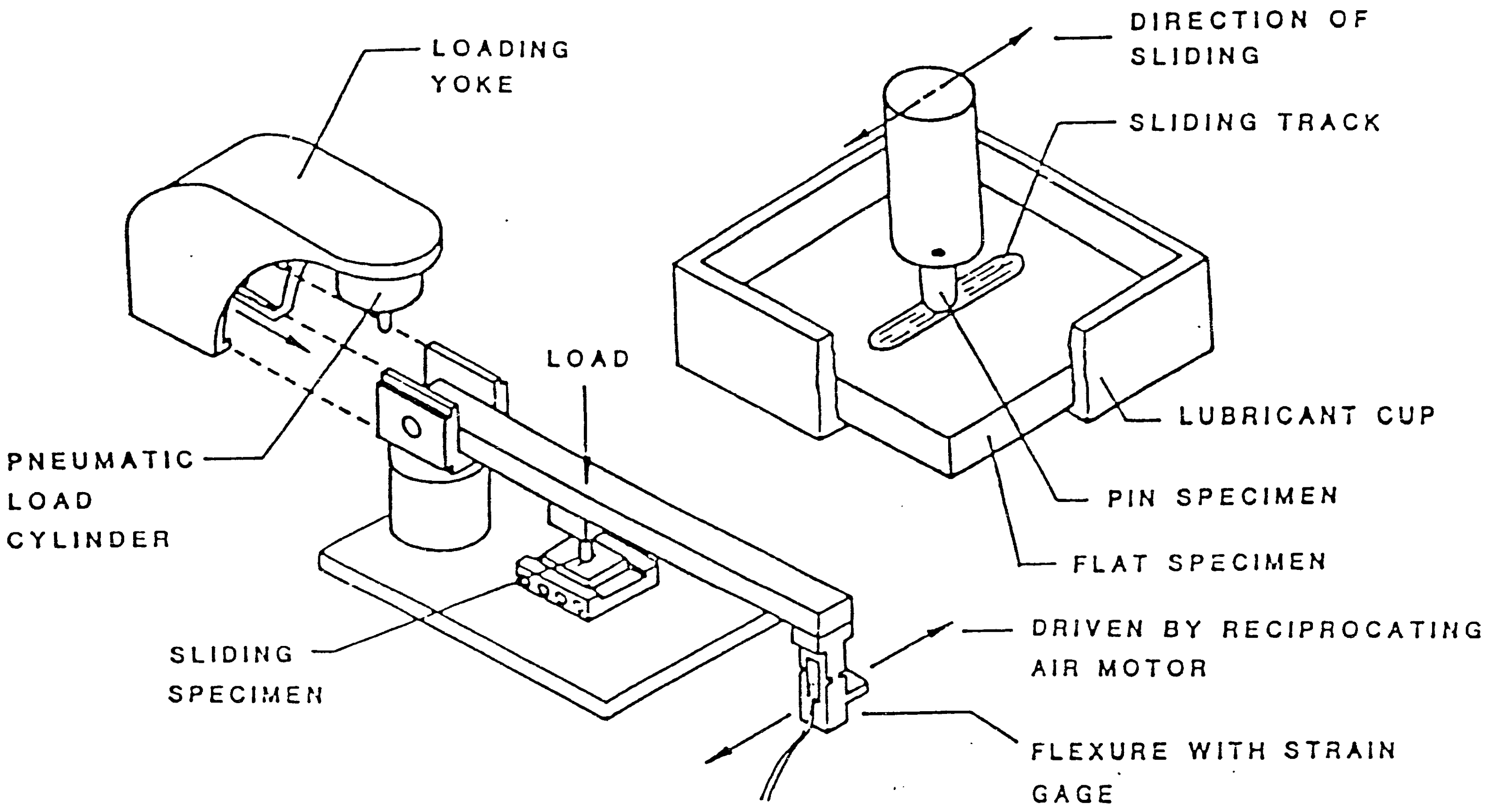
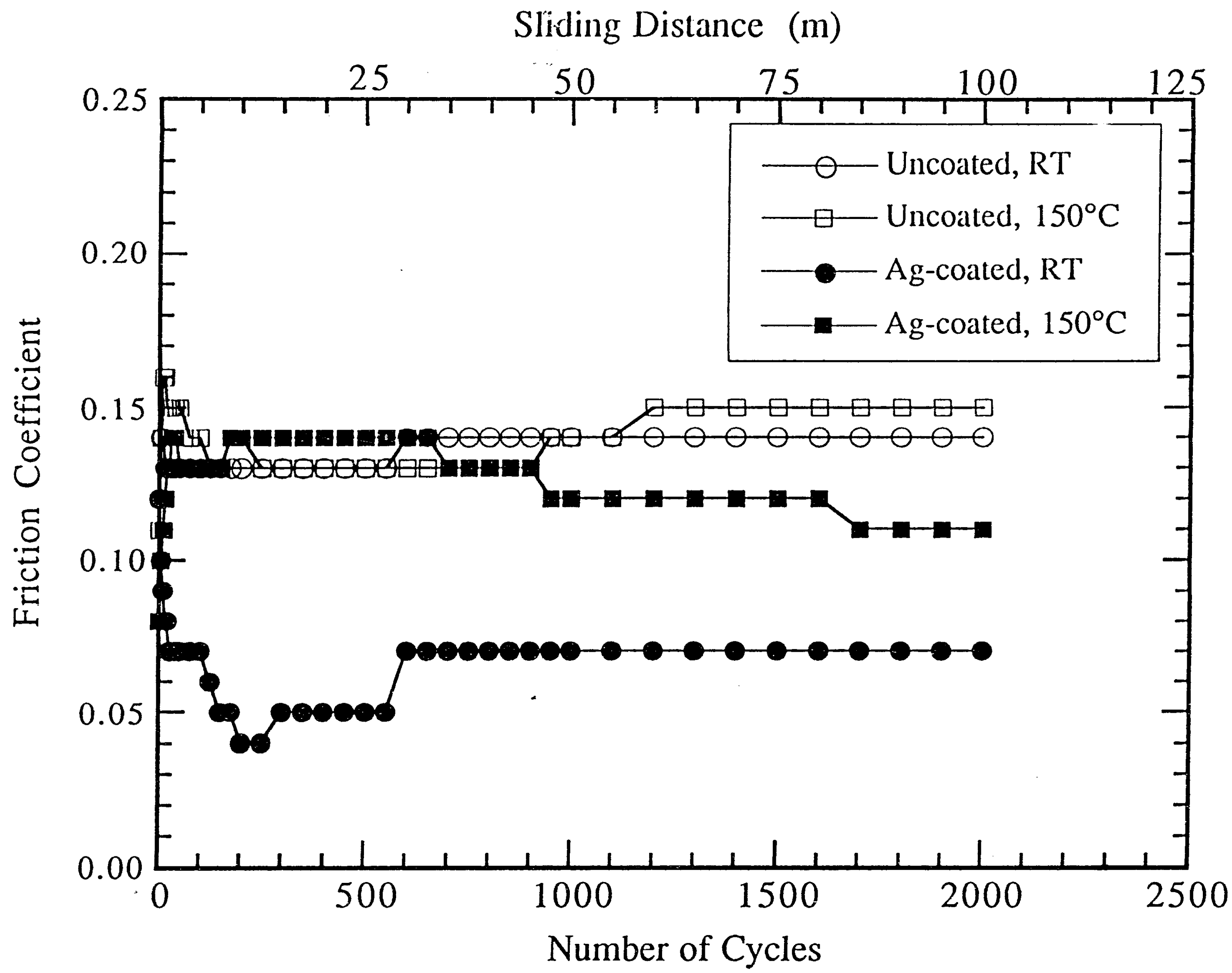

LOADING
YOKE
DIRECTION OF
SLIDING
SLIDING TRACK
LOAD
LUBRICANT CUP
PNEUMATIC
LOAD
CYLINDER
PIN SPECIMEN
FLAT SPECIMEN
DRIVEN BY RECIPROCATING
AIR MOTOR
SLIDING
SPECIMEN
FLEXURE WITH STRAIN
GAGE

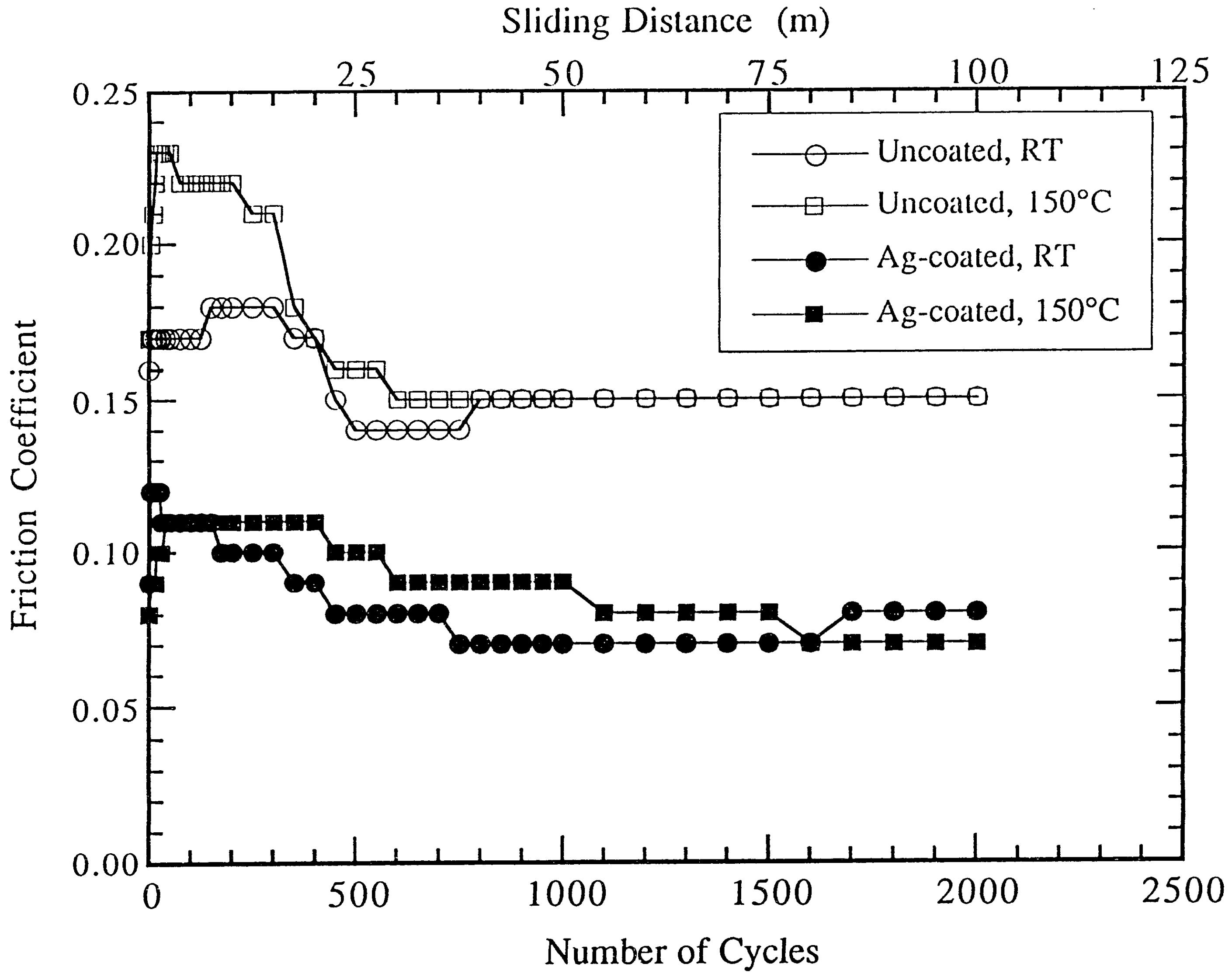
Figure 1

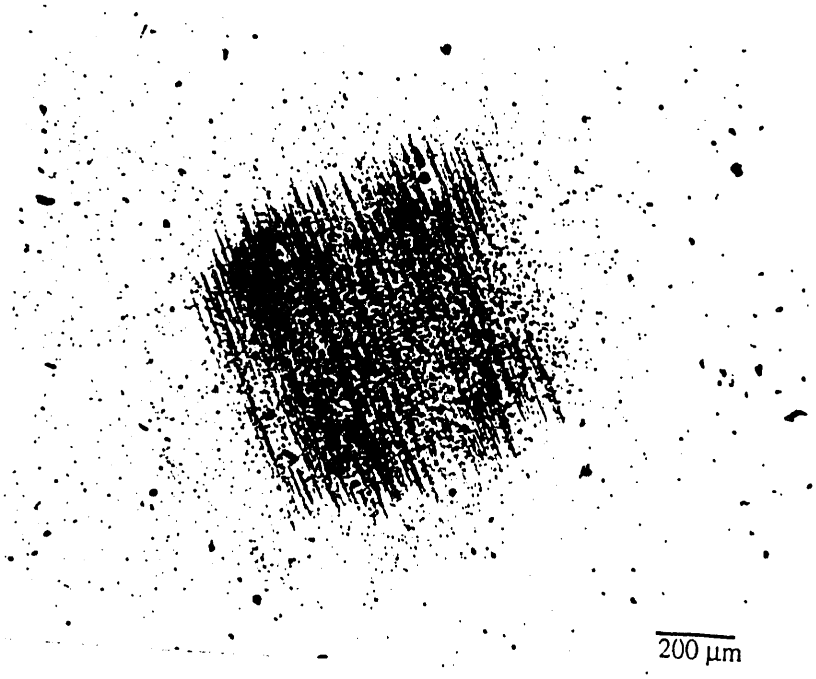
Figure 2a



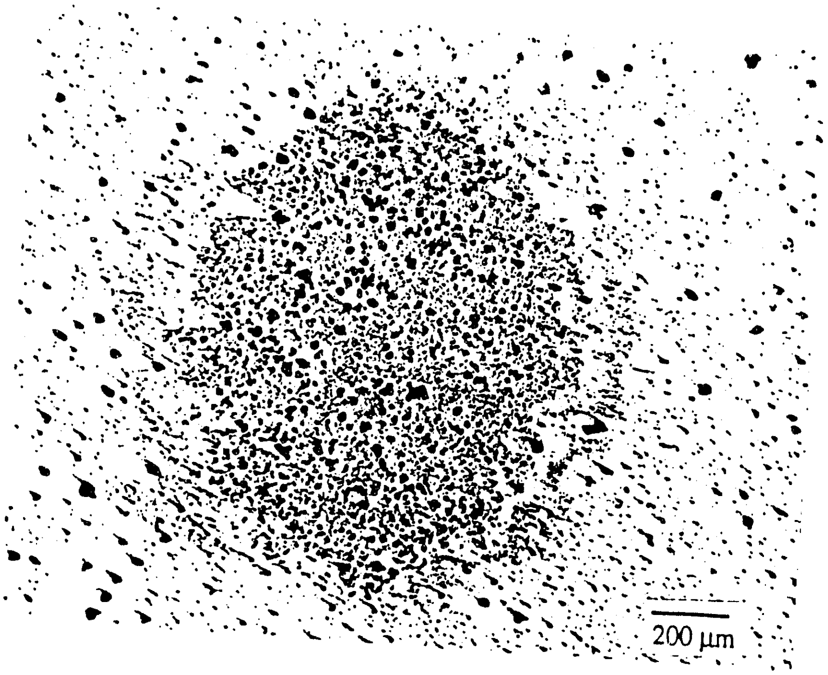
Sliding Distance (m)
25
50
75
100
125
0.25
0.20
0.15
0.10
0.05
0.00
Friction Coefficient
0
500
1000
1500
2000
2500
Number of Cycles
Uncoated, RT
Uncoated, 150°C
Ag-coated, RT
Ag-coated, 150°C

Figure 2b


Sliding Distance (m)
25
50
75
100
125
Uncoated, RT
Uncoated, 150°C
Ag-coated, RT
Ag-coated, 150°C
Friction Coefficient
0.25
0.20
0.15
0.10
0.05
0.00
0
500
1000
1500
2000
2500
Number of Cycles

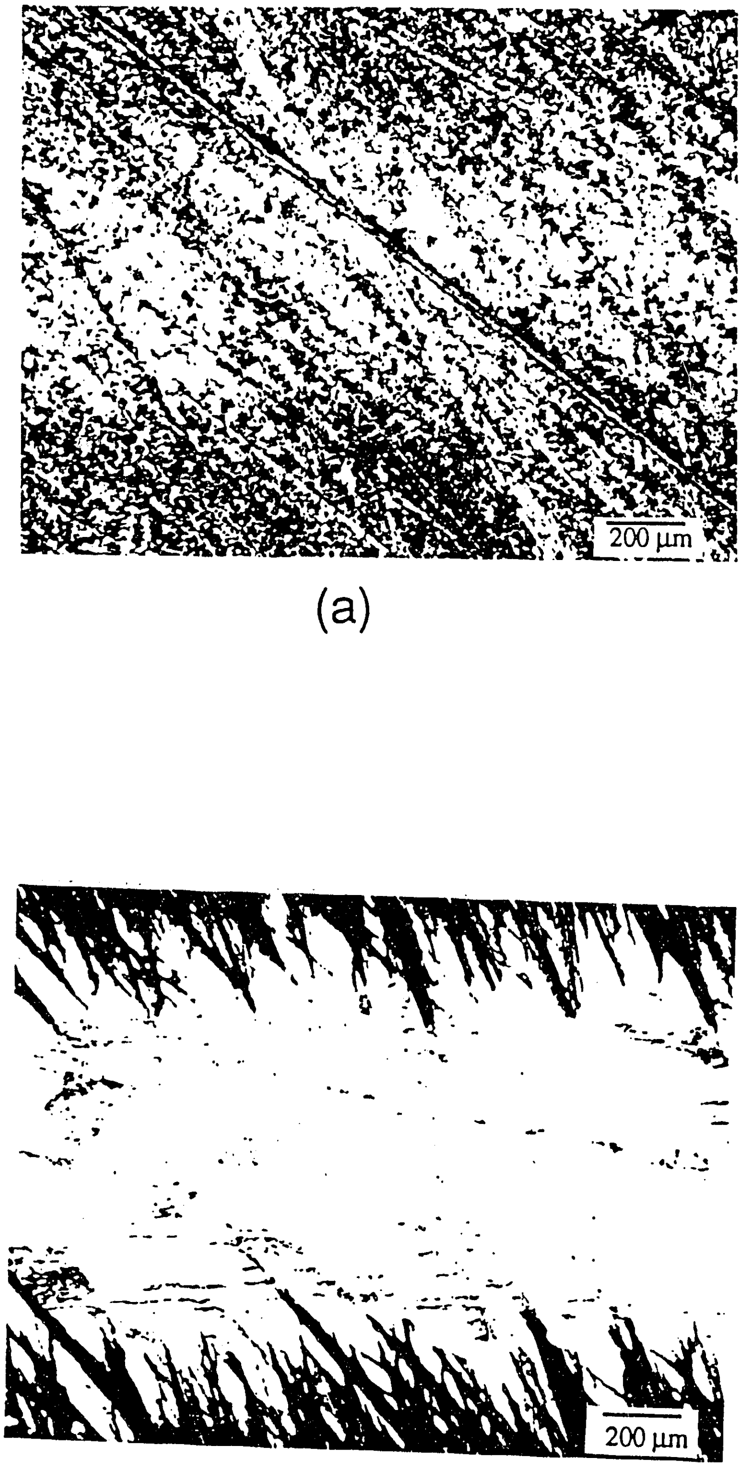


(a)



(b)

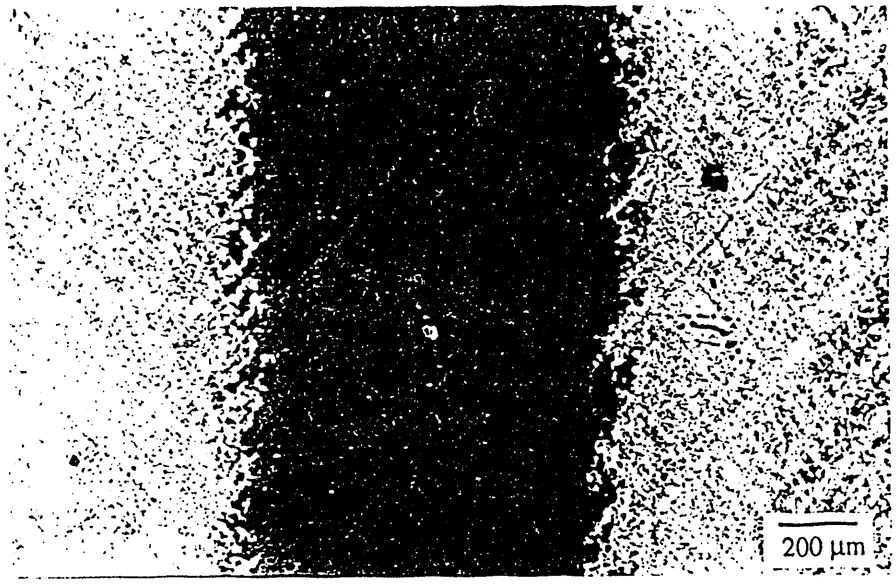
Figure 3



(a)

(b)

Figure 4



(c)

Figure 4

END

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