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BOUNDARY LUBRICATION OF CERAMIC MATERIALS BY SOFT METALLIC
COATING AND SYNTHETIC OIL*

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ABSTRACT

Boundary lubrication of metallic materials often relies on surface reaction-generated films. This approach is intrinsically more difficult for ceramic materials because of their relatively lower chemical reactivity. The present study investigates the viability of boundary lubrication of ceramics by the use of a thin soft metallic film as a boundary film. Lubrication of Si_3N_4 and ZrO_2 ceramics with coatings of Ag or Au prepared by Ion-Beam-Assisted Deposition (IBAD) and a synthetic oil was investigated. Through this method, the friction coefficient during sliding contact of ceramics was reduced (as low as 0.05) to the level that is obtained in most boundary lubricated situations. Furthermore, wear was virtually eliminated. The method was found to be effective from room temperature up to 250°C.

INTRODUCTION

Structural ceramic materials have an attractive combination of properties, notably high hardness and high thermal and chemical stability, which make them very good prospects for tribological applications. They are particularly attractive for high temperatures beyond the capability of many metallic materials. Ceramics are leading candidate materials for critical components of the low-heat-rejection engine (LHRE) which is expected to operate at peak temperatures as high as 600°C [1-3], compared to a temperature of about 200°C for existing engines. It was initially thought that these materials could be used unlubricated [4, 5]. Tribological studies, however, showed that the friction and wear rates during sliding contact are too high for engine applications [e.g., 6-8]. Consequently, efforts are now being devoted to lubrication of ceramic materials [9, 10].

During liquid lubrication, if the lubricant film thickness is large enough such that the two sliding surfaces are completely separated (hydrodynamic regime), the friction coefficient is determined solely by the viscosity of the lubricant and ideally no wear occurs. This

hydrodynamic regime of lubrication is desirable, but very difficult to maintain. It is generally achieved at low loads, using high sliding speeds with high-viscosity lubricants on smooth rubbing surfaces (conditions which are often difficult to maintain in practical applications). However, as the contact pressure increases, and/or the speed goes down and/or viscosity decreases, the lubricant film's thickness decreases. When the film is thin enough, the rubbing surfaces come into direct contact. This results in an increase in the friction coefficient and wear rate. This is the boundary regime of lubrication, which is often encountered in various practical machines. This regime is very critical because it often precedes scuffing and seizure.

For metallic materials, additives are usually incorporated into the lubricants to form a surface-reaction layer (boundary film) during boundary lubrication, which protects the rubbing surfaces by preventing metal-to-metal contact and presents an easily sheared interface between the two surfaces. A common example of an additive for ferritic surfaces is zinc-dialkyl-dithiophosphate (ZDDP), which forms a reaction layer rich in Zn, P, S, O and Fe on the rubbing surfaces [11-13]. Although the exact composition and detailed characteristics of the films are still under investigation, their roles in preventing metal-to-metal contact and providing easy shear are well known

Ceramic materials in general have low chemical reactivity when compared with metals; thus, formation of boundary films through surface reaction is more difficult. In fact, studies of ceramic-on-metal sliding couples using lubricant developed for metallic surfaces showed that the boundary films formed on the metal components but not on the ceramic ones [14]. In other studies, adsorption of some additives onto ionically bonded ceramic surfaces was found to provide limited protection while no such adsorption was observed for covalently bonded materials[15]. Even for ionic materials, adsorption of additives will have very limited practical use because desorption will occur as the temperature is increased. Since ceramics are being considered for high-temperature applications in many cases, additive adsorption will not be an effective means of their boundary lubrication. Thus a practical means of boundary lubrication of ceramics must be found.

Boundary films are known to behave in a fashion similar to soft metallic solid lubricants [16]. Recent studies have shown a significant improvement in the tribological behavior of ceramics by application of a soft metallic coating as a solid lubricant [10, 17]. The present study investigates boundary lubrication of Si_3N_4 and ZrO_2 ceramic materials by a soft metallic coating (Ag and Au) and a synthetic oil.

EXPERIMENTAL DETAILS

The ceramic materials used for this study were commercially available Si_3N_4 (SN-220) and Y_2O_3 -stabilized ZrO_2 (Z-201N) from Kyocera. Flat specimens had nominal dimensions of 50.8 x 25.4 x 6.35 mm and rods were 8 mm in diameter. Pin specimens 15 mm long were cut

from the rod. Both ends of the pin were rounded to form hemispherical caps of 127 mm radius of curvature and polished to a roughness of 0.08 $\mu\text{m Ra}$. The flat specimens were ground to a roughness of about 0.25 $\mu\text{m Ra}$.

Coating

A thin Ag film ($\approx 1.5 \mu\text{m}$ thick) was deposited on some of the Si_3N_4 and ZrO_2 flat specimens by the IBAD technique. This method involves simultaneous bombardment with energetic ions of a film growing by evaporation and often results in a substantial increase in the adhesion of the film to the substrate compared with evaporation alone [10, 18]. Prior to the deposition of the film, the surface was sputter-cleaned with a mixture of energetic Ar and O ions. IBAD of the Ag film was then done using the same ions to a film thickness of 100 nm, after which the ion source was turned off and the rest of the film thickness was deposited by vacuum evaporation. Some ZrO_2 flat specimens were also coated with Au using the same IBAD procedure.

Tests

Friction and wear tests were done with a pin-on-flat contact geometry in reciprocating sliding. The details of the test device have been described elsewhere [10]. Tests were conducted under "dry" (unlubricated) and oil-lubricated conditions using pins and flats of the same materials. Coated and uncoated flats were tested. Tests were conducted with normal loads of 10 and 50 N which impose an initial mean Hertzian pressure of about 150 and 260 MPa respectively for Si_3N_4 and 116 and 198 MPa for ZrO_2 . All the tests were done with a reciprocating frequency of 1 Hz and a stroke length of 25 mm producing an average sliding speed of 0.05 m/s. Tests were conducted at room temperature, 150°C and 250°C. The total number of cycles for 10N and 50N loads were 5000 and 2000 respectively. The oil-lubricated tests were done by immersing the flat specimens in a bath of oil during the test.

The friction coefficient was continuously monitored in all tests by a strain-gauge device. The amount of wear from the pin was calculated from the dimensions of the wear scar as measured by an optical microscope, assuming a flat wear scar [10]. The tests were interrupted after 100, 250, 500, 1000, 2000, 3000, 4000 and 5000 cycles and pin wear-scar dimensions were measured in order to determine the wear rate as a function of the number of cycles.

The worn surfaces of the pin and the flat were examined by both optical and scanning electron microscopes (SEM) equipped with an x-ray energy-dispersive spectrometer (EDAX) and a wavelength-dispersive spectrometer (WDS).

RESULTS

Friction

Figure 1 shows the frictional behavior of Si_3N_4 pairs under various conditions. At room temperature, the friction coefficient in all tests done under dry conditions showed a similar trend, irrespective of the load, i.e., a quick rise from a relatively low value over the first 100 cycles of sliding to a steady value of about 0.9 for uncoated flats and about 0.6 for Ag-coated flats (Figures 1a). In the oil-lubricated tests, however, the frictional behavior was different for coated and uncoated flats. The friction coefficient for the uncoated oil-lubricated flats showed a very quick rise over the first 10 cycles from an initial value of about 0.1 to a steady value of about 0.2. This is significantly lower than the value for dry sliding but too high for many practical applications. For oil-lubricated tests with Ag-coated flats, the friction coefficient showed a decrease from the initial value of about 0.15 to a steady value of about 0.05 at 10N load and about 0.08 at 50N load. Also, the steady friction was achieved more quickly (100 cycles) at 50N load than at 10N load (800 cycles). The steady friction levels for oil-lubricated, Ag-coated tests were comparable to or even lower than those typically obtained in lubricated metallic surfaces under boundary conditions [3, 12, 13].

The frictional behaviors at temperatures of 150°C and 250°C were similar to one another. The Ag coating under dry conditions was more effective in reducing friction at these higher temperatures. In fact, at 250°C the friction coefficients for Ag-coated flats tested dry and oil-lubricated, uncoated flats were comparable (~ 0.25, cf. Figure 1c). The lowest friction of about 0.09 was still obtained at high temperatures with the oil-lubricated Ag-coated flats.

The frictional behavior of ZrO_2 sliding pairs is shown in Figure 2. At room temperature, the friction coefficient in all the dry tests showed a quick rise from an initial value of about 0.15 to a steady value of 0.6 for uncoated flats and 0.3 for Ag-coated flats (Figure 2a). For the Au-coated flats, the friction coefficient showed only a slight increase to about 0.2. After about 1,400 cycles, however, a steady increase (to ~ 0.3 at the end of the test) was observed. This point of transition coincided with the point at which failure in the Au coating was observed. For oil-lubricated, uncoated flat tests, the friction coefficient remained virtually constant at about 0.14 throughout the tests (Figure 2a). Ag and Au coatings produced virtually identical results with oil lubrication. Sliding started with a friction coefficient of about 0.1 but this decreased gradually to a steady value of about 0.05 after 100 cycles. In general, the patterns of behavior for ZrO_2 ceramics were similar to those of Si_3N_4 under the various conditions at room temperature. The higher temperatures produced behavior very similar to that at room temperature (Figure 2b). No dry tests were run with Au films at the higher temperatures because of the quick failure of the films during sliding contact.

Wear

The variations in the "instantaneous" wear rate in the Si_3N_4 and ZrO_2 pins are shown in Figure 3. Both the Ag coating and oil lubrication when applied separately reduced the wear rate of

Si₃N₄ pins (Figure 3a) by more than an order of magnitude at room temperature. At 250°C, about a factor of 1000 reduction in the wear rate was observed. Further, with Ag coating tested dry, the wear rate at 250°C was lower than that at room temperature by about an order of magnitude; the reverse was the case with oil-lubrication without coating. In all the oil-lubricated tests with Ag coating, no measurable wear was observed on the pins.

For the ZrO₂ material (Figure 3b), a significant reduction in the pin wear rate was also achieved by oil lubrication without coating. The reduction was more pronounced at room temperature. In addition, the wear rate increased with the number of cycles for the unlubricated tests but it decreased for the lubricated tests. In all the coated cases tested dry and lubricated, no significant wear was observed on the ZrO₂ pins. When unlubricated, a significant transfer of the coating material to the pin was observed in all cases. This transfer may be responsible for the lack of wear. With lubrication, however, little (if any) such transfer occurred.

DISCUSSION

The effectiveness of a liquid lubricant film is determined by the λ ratio, defined as the ratio of film thickness (h) to the composite surface roughness of the sliding surfaces, i.e. $\lambda = h/\sigma$. The composite surface roughness $\sigma = \sqrt{\sigma_1^2 + \sigma_2^2}$ where σ_1 and σ_2 are the roughnesses of the two contact surfaces. When $\lambda < 1.5$, extensive contact of asperities of the two surfaces through the lubricant film is expected (boundary conditions). For $\lambda \geq 3$, the sliding surfaces are completely separated by the lubricant film (hydrodynamic regime). The elastohydrodynamic and mixed-lubrication regime is characterized by $1 \leq \lambda \leq 3$.

In order to determine the λ ratio, the lubricant film thickness should be estimated. There are various equations in the literature to estimate the lubricant film thickness for different contact geometries. For point contacts (similar to what was used in the present study) under isothermal, steady-state and fully flooded conditions, the Hamrock and Dowson formulation is one of the most commonly used [19, 20]. The minimum film thickness (h_m) is given as:

$$\frac{h_m}{R} = 1.118 \left(\frac{\eta v}{E^* R} \right)^{0.68} [\alpha E^*]^{0.49} \left(\frac{W}{E^* R^2} \right)^{-0.073} \quad (1)$$

where $E^* = 2 \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right)^{-1}$ is the reduced elastic modulus

η = viscosity under atmospheric pressure

v = sliding speed

R = radius of curvature of the pin

W = normal load

α = pressure viscosity coefficient.

According to Cameron [21], α can be estimated for most oils by the empirical relationship:

$$\alpha = (0.6 + 0.965 \log_{10} \eta_o) \times 10^{-8} \quad (2)$$

where α is in Pa^{-1} and η_o is the atmospheric viscosity in cP.

Also the variation of the viscosity of the oil used in the present study with the temperature can be estimated. From viscosities supplied by the manufacturer of 40°C and 99°C , using curve fitting, one obtains the equation:

$$\log \eta = -3.593 + 1739.6 (1/T) \quad (3)$$

where the viscosity, η is in cP and the temperature T is in K. The lubricant film thicknesses calculated using the above equations for the various test conditions in the present study are shown in Table 1. Also, the composite roughness σ in the present study is estimated to be about $0.26 \mu\text{m}$ for all tests. The λ ratios for the various test conditions are also shown in Table 1. The calculations show that the tests in the present study were under the boundary-lubrication regime since λ is less than 1.5 in all cases.

Results of the present study show clearly that the incorporation of a thin soft metallic film at the contact interface of ceramic materials during liquid lubrication is an effective way of reducing friction and virtually eliminating wear of the pins in these reciprocating pin-on-disc tests for boundary lubrication conditions. In addition to the separation of the sliding surfaces, the plastic deformation of the metallic coating at the points of contact resulted in the generation of a smoother surface within the contact area. For instance, a roughness of $0.03 \mu\text{m Ra}$ was measured on the contact area of an Ag-coated Si_3N_4 flat after wear testing as compared to an uncoated value of $0.23 \mu\text{m}$. This reduces the composite roughness of the surface with the metal coating and hence increases the effective λ ratio, thereby making the liquid lubricant film more effective. We believe that this modification of the λ ratio may be responsible for the observed decrease in the friction coefficient in the early part of sliding for all oil-lubricated, metal-coated flat tests.

At higher temperatures, the metal coatings get softer and shear even more easily. This is presumably responsible for the further lowering of the friction under dry contact with coatings at higher temperatures. On the other hand, the viscosity of the oil decreases very rapidly with increasing temperature (Equation 3), permitting more contact between the two surfaces. The result is an increase in friction and wear for oil-lubricated tests without metal coatings at higher temperatures (Figure 3b). These opposing effects of temperature on the oil lubrication and soft metal lubrication appear to approximately annul each other in oil-lubricated, metal-coated sliding contact.

After prolonged exposure to the oil, chemical interaction between the Ag coatings and S from the oil was observed. This could be a drawback to practical implementation of the findings of this study, since S is a very common component of oil lubricants and Ag seems to be the best metallic coating candidate from the viewpoint of the desired tribological roles for the

metallic coating [22]. Au is a potential candidate material, but the adhesion between Au and the ceramic's substrate is often poor, even with IBAD [18].

Another problem encountered in this study was the formation of carbon-rich deposits on the metal coatings at high temperatures. This will definitely modify the contact interface properties and could render the coating less effective with time. This is of particular concern for ceramics, since they are being considered primarily for high-temperature tribological applications.

Efforts are currently under way to address these problems. Oils can be formulated with additives to protect the Ag films even in the presence of S. One such additive is an alkyl derivative of 2,5-di-mercapto 1,3,4-thiadiazole [23]. Furthermore, the S content of new oils may well be reduced in order to decrease S-containing emissions as required by new U.S. standards.

CONCLUSIONS

Results of this study showed that a viable means of boundary lubrication of ceramic materials is the deposition of a soft adherent metallic film at the sliding interface. The friction coefficient was reduced to a level comparable to boundary lubrication conditions in many practical devices and the wear was virtually eliminated in Si_3N_4 and ZrO_2 sliding pairs by the synthetic-oil lubrication of Ag- and Au-coated surfaces. The improvement is brought about by the metallic coating acting essentially as a boundary film, thereby preventing direct contact between the two surfaces even under boundary lubrication conditions. The deformation of the metallic coatings leads to the reduction of the surface roughness and thus increases the λ ratio, making the lubricant film more effective. Chemical interaction between the Ag coating and S from the oil and unwanted deposit formation from the oil at high temperatures are problems that need to be overcome through improved oil formulations before a practical implementation of the findings in the study can be achieved.

Temperature	Material	10N	50N
RT	Si ₃ N ₄	h = 0.111 μm	0.099 μm
		λ = 0.43	0.38
	ZrO ₂	h = 0.115 μm	0.102 μm
		λ = 0.44	0.39
150°C	Si ₃ N ₄	h = 5.57 nm	4.69 nm
		λ = 0.02	0.018
	ZrO ₂	h = 5.49 nm	4.88 nm
		λ = 0.02	0.019
250°C	Si ₃ N ₄	h = 0.94 nm	0.835 nm
		λ = 0.004	0.003
	ZrO ₂	h = 1.026 nm	0.912 nm
		λ = 0.004	0.004

Table 1: Oil Lubricant Film Thickness and λ Ratio Calculated from EHD Equations

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Figure Captions

Figure 1: Frictional behavior of Si_3N_4 ceramic sliding pairs tested at (a) room temperature and 10N load, (b) at 250°C and 10N load.

Figure 2: Friction behavior of ZrO_2 ceramic sliding pairs tested at (a) room temperature and 50N load and (b) 150°C and 50N load.

Figure 3: "Instantaneous" pin wear rate as a function of the number of cycles under various test conditions for (a) Si_3N_4 and (b) ZrO_2 .

Figure 1a

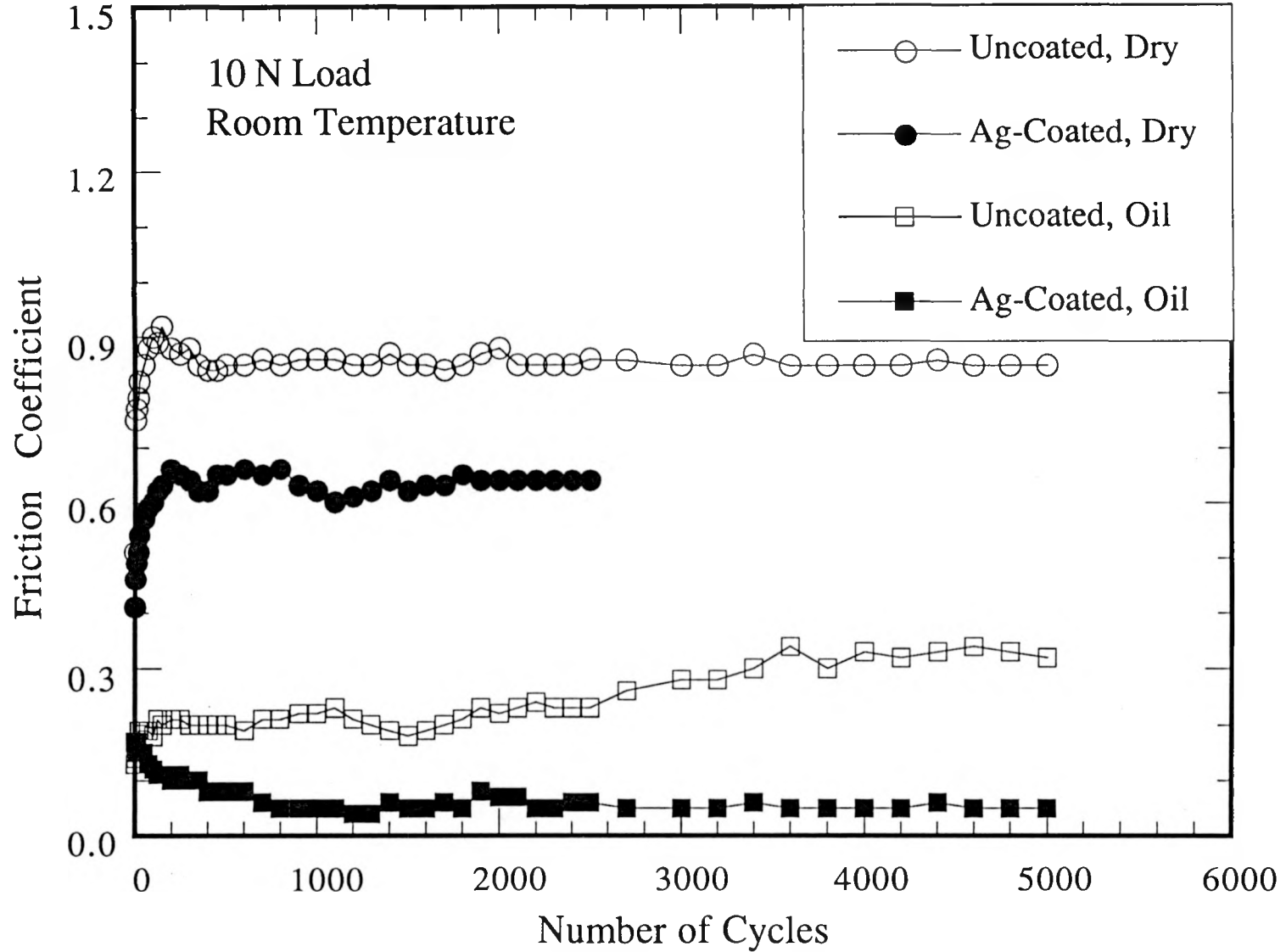


Figure 1b

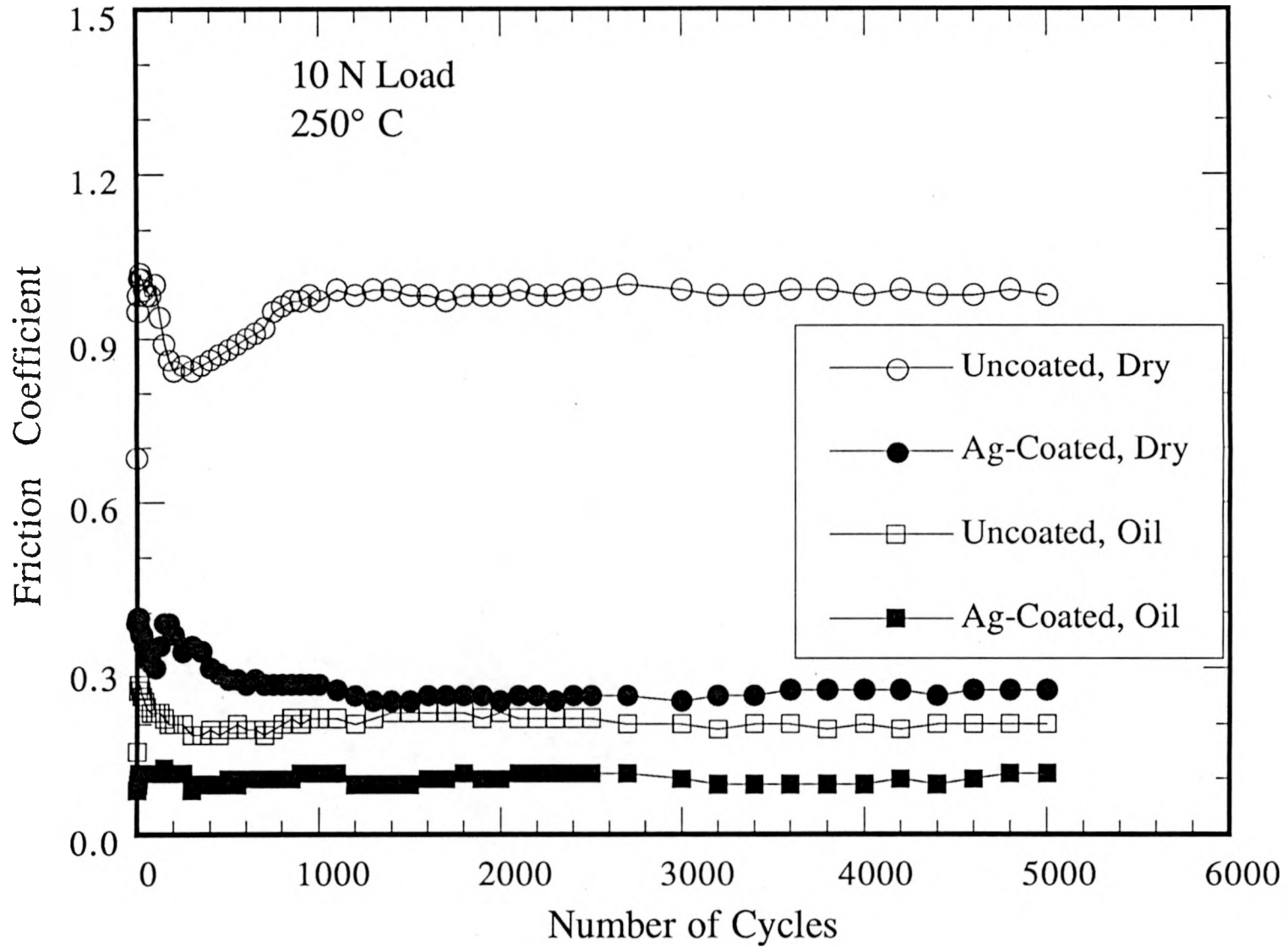


Figure 2a

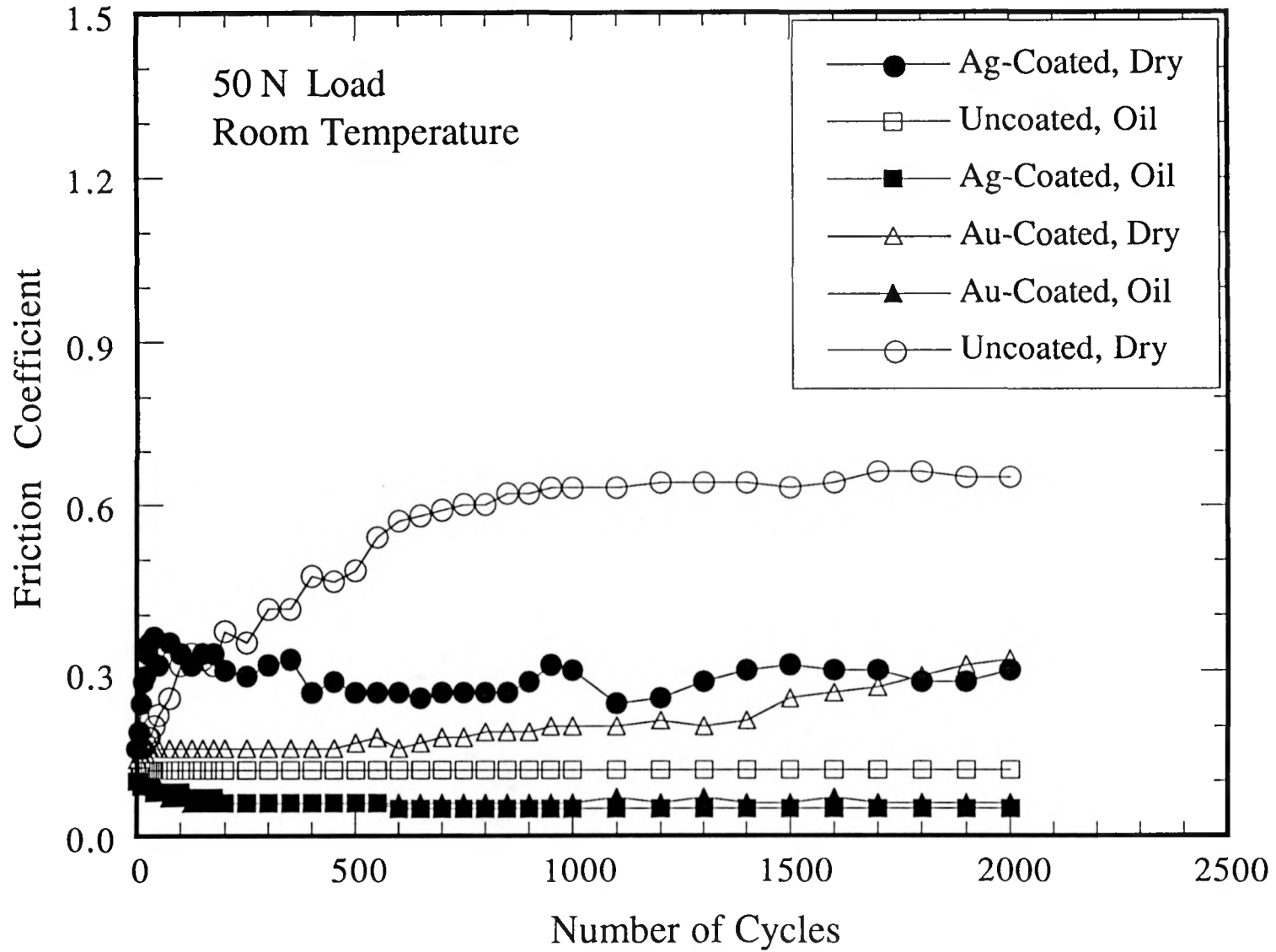


Figure 2b

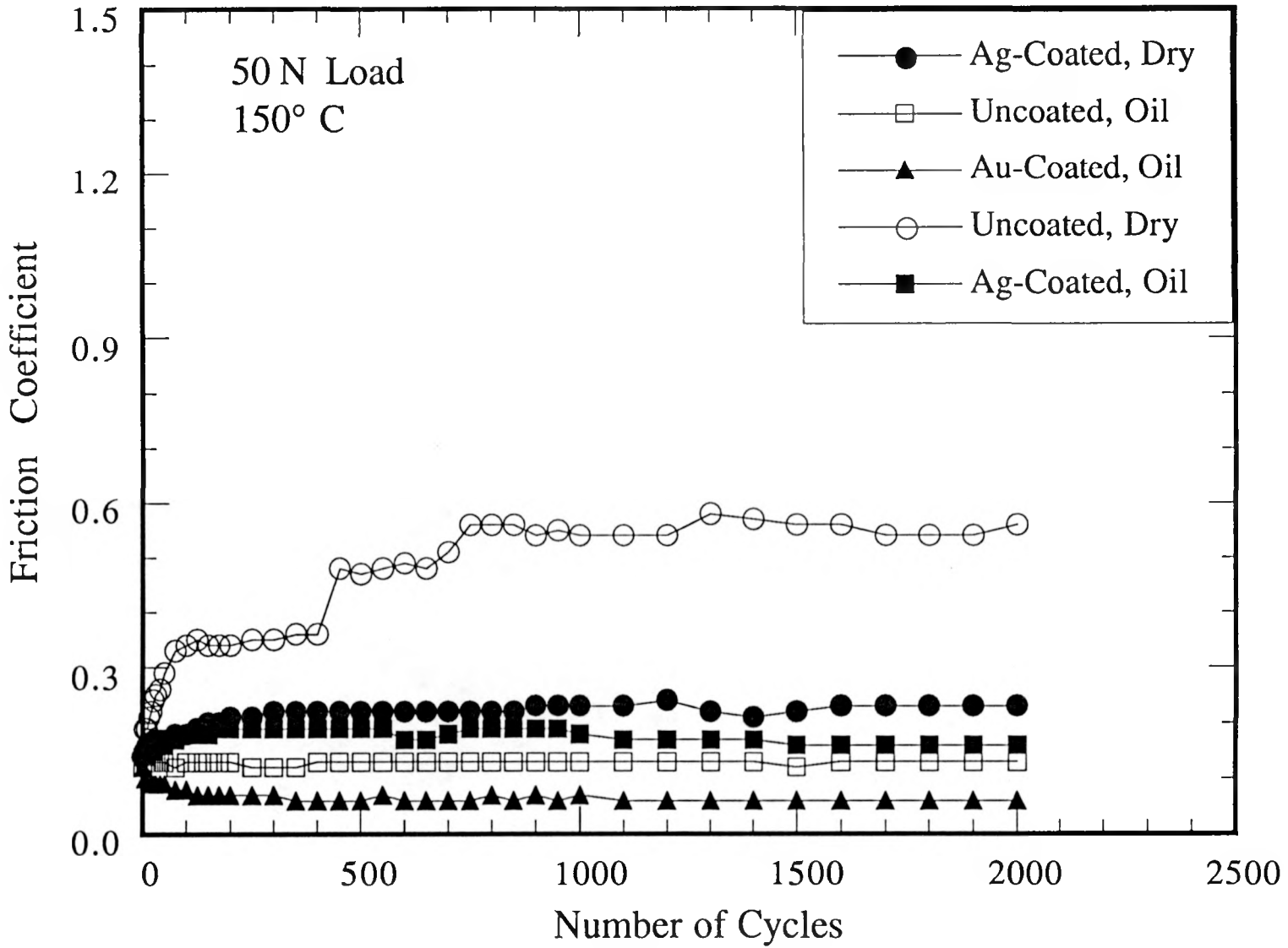


Figure 3a

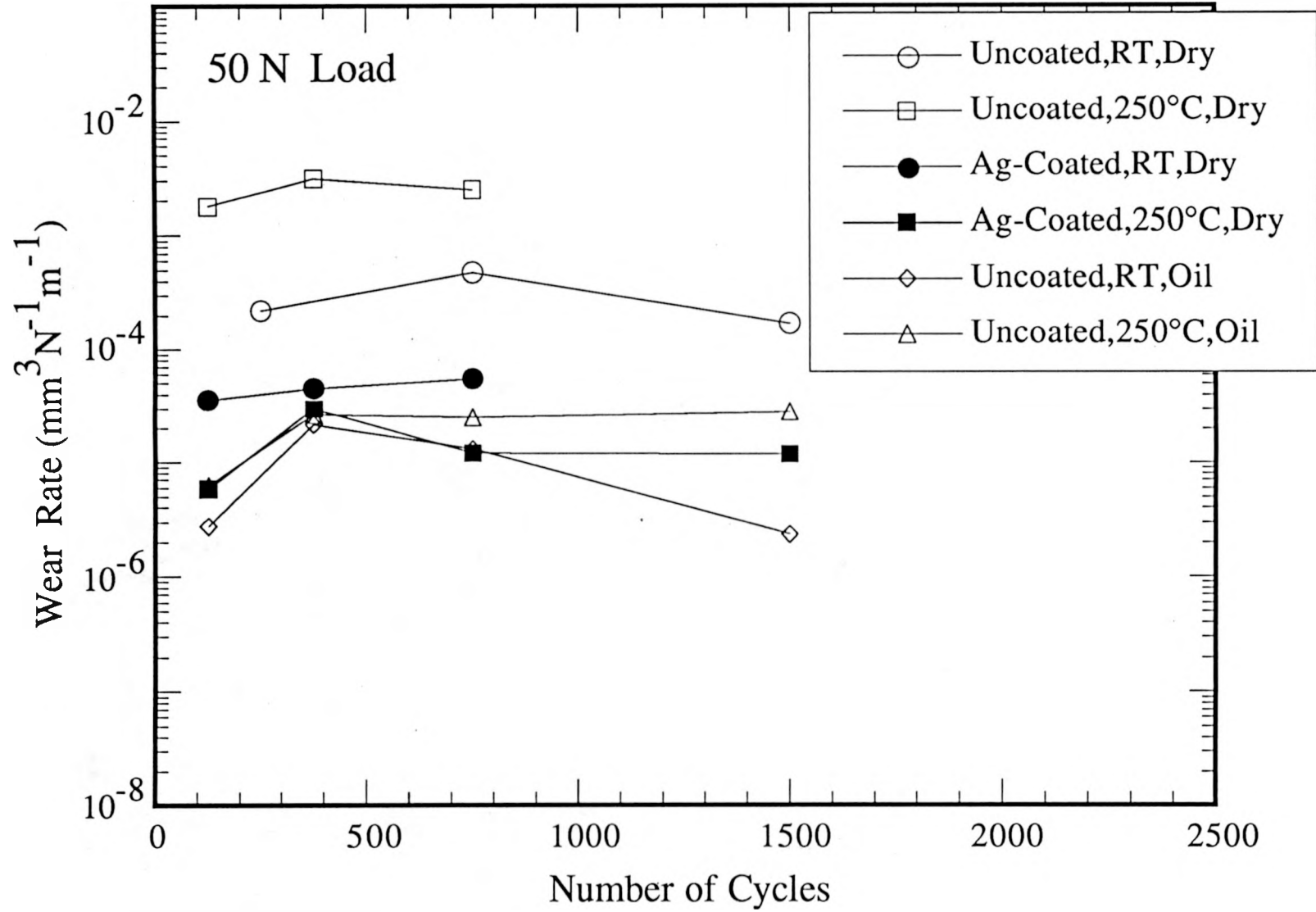


Figure 3b

