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TRIBOLOGICAL PROPERTIES OF BORON NITRIDE SYNTHESIZED BY ION BEAM DEPOSITION

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SUMMARY

An investigation was conducted to examine the adhesion and friction behavior of boron nitride films (BN coating, 2 μm thick) on 440 C - bearing stainless steel substrates. The thin films containing the boron nitride were synthesized using an ion beam extracted from a borazine ($B_3N_3H_6$) plasma. Sliding friction experiments were conducted with BN in sliding contact with itself and various transition metals (Ti, Zr, V, Fe, Ni, Pd, Re, and Rh) at a sliding velocity of 3 mm/min with a load to 0.2 N at room temperature and in a vacuum of 30 nPa. The results of the investigation indicate that the surfaces of atomically cleaned BN coating film contain a small amount of oxides and carbides, in addition to boron nitride. The coefficients of friction for the BN in contact with metals are related to the relative chemical activity of the metals. The more active the metal, the higher is the coefficient of friction. The adsorption of oxygen on clean metal and BN increases the shear strength of the metal - BN contact and increases the friction. The friction for BN-BN contact is a function of the shear strength of the elastic contacts. Clean BN surfaces exhibit relatively strong interfacial adhesion and high friction. The presence of adsorbates such as adventitious carbon contaminants on the BN surfaces reduces the shear strength of the contact area. In contrast, chemically adsorbed oxygen enhances the shear strength of the BN-BN contact and increases the friction.

INTRODUCTION

In recent years, the increasing potential for the use of ultrahard and high temperature materials such as ceramics in tribological systems and in thermodynamically efficient engines (stirling, adiabatic diesel, and gas turbine) in both ambient and space environments has emerged as representing critical needs for NASA, industry, DOE, and DOD.

Following the successful synthesis of diamond in 1955, stable phase of cubic boron nitride has also been produced in bulk form (ref. 1). In the 1970's it was recognized that unusual phases can be synthesized by particle fluxes containing energetic, ionized species in deposited coating material. Transparent carbon films with diamond like properties formed by direct C^+ ion beam deposition were demonstrated in 1971 (ref. 2). Further, cubic phase boron nitride (CBN) thin films were produced by ion beam plating or ion beam deposition (refs. 3 to 5).

The objective of the present investigation was to examine the adhesion and friction of BN films (2 μm thick) on metal substrates. The thin films were synthesized using an ion beam extracted from a borazine ($B_3N_3H_6$) plasma (ref. 5). Shanfield and Wolfson reported evidence for the presence of CBN in films produced by this deposition method. They also indicated a film stoichiometry corresponding to boron nitride. Sliding friction experiments were conducted with the BN films on 440 C bearing stainless steel substrates in sliding contact with BN itself and various transition metals (Ti, Zr, V, Fe, Ni, Pd, Re, and Rh) at a sliding velocity of 3 mm/min with a load to 0.2 N at room temperature and in an ultrahigh vacuum system (30 nPa). X-ray photoelectron spectroscopy (XPS) analysis of the BN films were also conducted.

MATERIALS

Thin films (2 μm thick) containing BN have been synthesized using an ion beam extracted from a borazine ($B_3N_3H_6$) plasma. The substrates were 440 C bearing stainless steel. The metals were all polycrystalline. The titanium was 99.97 percent pure; the vanadium was 99.95 percent pure; and all the other metals were 99.99 percent pure.

APPARATUS

The ion source used to deposit BN films is presented in figure 1 and is described in reference 5. The tribological apparatus used in this investigation was an ultrahigh-vacuum system capable of measuring adhesion, load, and friction and conducting XPS analysis. The mechanism for measuring adhesion, load, and friction is shown in figure 2. The friction apparatus was basically a pin on a flat configuration. The major components for the XPS analysis shown in the figure include the energy analyzer, x-ray source, and the ion gun used for ion sputter etching. The x-ray source contained a magnesium anode.

EXPERIMENTAL PROCEDURES

Specimen Preparation

The 440 C bearing stainless steel substrates were flats and hemispherical pins (see fig. 1). The flat and pin specimens were polished with diamond powder (of particle diameter 3 μm) and with aluminum oxide powder (diameter, 1 μm). The ion beam synthesis was conducted on these surfaces. The ion beam synthesis procedure for the deposition of BN is described in reference 5. The radius of 440 C bearing stainless steel pin with the deposited film of BN was 4.8 mm.

The sliding surfaces of the polycrystalline-transition metal pin were hemispherical and were polished first with diamond powder 3 and 1 μm in diameter and then with Al_2O_3 powder 1 μm in diameter. The radii of curvature of the metal pins were 0.79 and 1.58 mm. The surfaces of the pin specimens were rinsed with absolute ethanol before the friction experiments.

PROCEDURE

For the experiments in vacuum the specimens were placed in the vacuum chamber, and the system was evacuated and baked out to achieve a pressure of 30 nPa (10^{-10} torr).

In situ friction experiments were conducted with a load to 0.2 N applied to the pin-flat contact by mechanically deflecting the beam through precision manipulators. Sliding was initiated by moving the beam in a vertical direction parallel to the flat surface. To obtain consistent experimental conditions, the time in contact before sliding was kept constant at 30 s. The friction force was continuously monitored during a friction experiment. The sliding velocity was 3 mm/s with a total sliding distance of about 5 mm. All in situ experiments were conducted in a vacuum of 30 nPa or lower at room temperature. The values of coefficients of friction reported herein were obtained by averaging four or more measurements.

Ion-sputter etching was performed with a beam energy of 3000 eV at 20-mA beam current with an argon pressure of 0.7 mPa. The ion beam was continuously rastered over the specimen surface. After sputter etching, the system was reevacuated to a pressure of 30 nPa or lower. The surface cleanliness was verified by XPS analyses.

In those experiments designed to examine the adsorbed-oxygen effect on friction, atomically sputter-cleaned specimens were exposed to 1000 L ($L = 1\times10^{-6}\cdot$torr s) of O_2 with an oxygen pressure of 0.7 mPa (5×10^{-6} torr). At completion of the exposure, the vacuum system was reevacuated to a pressure of 30 nPa or lower. The surface chemistry of the specimens was then examined again by XPS analysis.

The XPS instrument was calibrated regularly. The analyzer calibration was determined by assuming the binding energy for the gold 4f 7/2 peak to be 83.8 eV. The MgKα x-ray was used with an x-ray source power of 400 K (10 kV-40 mA). The spectra were obtained with a pass energy of 25 eV and 50 eV.

RESULTS AND DISCUSSION

The Boron Nitride Surface

Since XPS-survey spectra, scans of 1100 eV, of BN surfaces obtained before argon ion sputter cleaning revealed oxygen and carbon peaks, individual XPS spectra of B_{1s}, N_{1s}, C_{1s}, and O_{1s} were taken and are presented in figure 3 (top traces). The BN was in the as-received state after it had been baked out in the vacuum system. In addition to boron nitride, the XPS peaks indicate adventitious adsorbed-oxygen and carbon on the surface.

The surface was next argon ion sputter cleaned for 70 min. The adsorbed carbon and oxygen contamination peaks nearly disappeared from the survey spectra after 20 and 30 min sputter cleaning, respectively. Typical examples of the individual XPS spectra of B_{1s}, N_{1s}, O_{1s} and C_{1s} obtained from narrow scans on the sputter cleaned BN surface are presented in figure 3 (bottom traces).

The B_{1s} photoelectron emission lines of the BN are primarily peaked at 190 eV which is associated with BN. They also include a small amount of B_4C, labeled as such in figure 3(a).

The N_{1s} photoelectron lines for the BN peaked primarily at 397.9 eV, which is again associated with BN.

The C_{1s} photoelectron lines taken from the as-received surface at 284.6 eV are the adsorbed carbon contamination with a small amount of carbides present. After sputter cleaning the adsorbed carbon contamination peak disappears from the spectrum and the relatively small carbide peaks are seen in the spectrum of the sputter cleaned surface.

The O_{1s} photoelectron lines of the as-received BN surface peaked at 531.6 eV are the adsorbed oxygen contamination and oxides. After sputter cleaning the adsorbed oxygen contamination peak disappears from the spectrum, but the oxide peaks remain.

The peak intensity for both boron and nitrogen associated with BN increased with argon ion sputter cleaning, while that for carbon and oxygen decreased markedly. The XPS analyses clearly indicate the presence of a small amount of oxides and carbides on the BN surface even after argon ion sputter cleaning for 30 min or more. The contaminants such as carbides (e.g., B_4C) and oxides may be introduced to the BN film during the ion beam synthesis process.

For the adhesion and friction experiments reported herein, the surfaces of the BN were argon ion sputter cleaned and the XPS spectra of the surfaces were very similar to those shown in figure 3.

Friction

BN-BN contact. - Single pass sliding friction experiments were conducted with BN coated on 440 C bearing stainless steel flat in contact with itself on 440 C steel pin in vacuum at a pressure of 30 nPa. The surfaces of BN coated flat and pin specimens were in three states of as-received, argon ion sputter cleaned, and exposed to 1000 L oxygen after sputter cleaning.

Friction force traces resulting from sliding were primarily characterized by both stick-slip and randomly fluctuating behavior.

The coefficients of friction measured for the surfaces at various normal loads are presented in figure 4. The basic friction characteristics for the surfaces in the three states were similar. That is, the coefficient of friction is not constant but decreases as the load increases under all three surface conditions. To a first approximation for the load range investigated, the relation between coefficient of friction (μ) and load (W) is given by an expression of the form $\mu = kW^{-1/3}$. The inverse minus 3 power may be interpreted most simply as arising from an adhesion mechanism, the area of contact being determined by elastic deformation (refs. 6 and 7). Friction is a function of the shear strength of the elastic contact area. The shear strength of the elastic contact area is strongly affected by adsorbates. The adsorbates such as carbon contaminants present on the as-received surfaces exhibit uniformly low shear strength over the entire load range. The coefficients of friction for the sputter cleaned surfaces of BN are higher than those for the as-received surfaces. Thus, the presence of the adsorbates on the BN surfaces reduced the shear strength of the contact area.

In contrast, contacts of the BN surfaces, which were exposed to oxygen after sputter cleaning, exhibited that the chemically adsorbed oxygen enhanced shear strength of the contact area and increased coefficient of friction. In this case strong oxide - BN or oxide - oxide bonding between oxidized BN surfaces was taking place at the interfaces and raised the shear strength.

Metal-BN contact. - Both nitrogen and boron interact with most metals. It may, therefore, be possible by the removal of adsorbates from BN and metal surfaces to achieve strong bonding between BN and metal surfaces. Further, it may be possible to determine whether the chemical activity or inactivity of a metal plays a role in the adhesion and friction of BN to metals.

Sliding friction experiments were conducted with BN sliding against various transition metals (metals with partially filled d shells) with loads of 0.05 to 0.2 N.

The friction traces were primarily characterized by stick-slip behavior over the entire load range to 0.2 N with all the metals. This type of friction is anticipated where strong adhesion occurs at the interface. Further, there was no change in coefficient of friction with applied normal load indicative of occurrence of plastic deformation in metals at the real area of contact. In fact, the wear scar on the metal pin, after it slid against BN coating, revealed evidence of plastically deformed grooves and indentations. The metals examined failed in shear or tension at some of the real areas of contact where the interfacial bonds were stronger than the cohesive bonds in the metal.

The relative chemical activity of the transition metals as a group can be ascertained from their percent d valence bond character after Pauling (ref. 8). The greater the percent d bond character, the less active is the metal. Adhesion and friction properties of the transition metals sliding on the surfaces of bulk metals and nonmetallic materials (diamond, SiC, Mn-Zn ferrite, and pyrolytic hexagonal BN) have been shown to be related to this character (refs. 9 to 13). The greater the percent d bond character (the less active the metal), the less the coefficient of friction. Whether a similar concept applies to the interactions of ceramic coating thin film-to-metal interfaces is a matter of interest.

The coefficients of friction for a number of transition metals with BN coating are presented in figure 5 as a function of the d bond character of the transition metal. There appears to be good agreement between friction and chemical activity of the transition metal. Titanium and zirconium both having strong chemical affinity for boron and nitrogen (ref. 14) exhibit considerably high friction in contact with BN than do rhenium and palladium metals having lesser affirmity for these same two elements.

The morphology revealed that the BN surfaces contacted by all the transition metals were found to contain on the surfaces transferred films of metals. Similar transfer characteristics for metal on diamond, metal on Mn-Zn ferrite, and metal on silicon carbide were found (refs. 10 to 12). In the case of pyrolytic boron nitride, however, Buckley found that pyrolytic boron nitride transferred to the surface of all the transition metals examined (ref. 13).

Figure 5 also presents the coefficients of friction for the metals in contact with the BN in which other clean metal and BN specimens were exposed to oxygen gas. The data reveal the adsorption of oxygen on argon-sputter cleaned metal and BN coated surfaces produce two effects: (1) the metal and BN oxidize and form an oxide surface layer, and (2) the oxide layers increase the coefficient of friction for metal-to-BN interfaces.

The oxygen exposure did strengthen the metal-to-BN adhesion and increased the friction. The enhanced bond of the oxides between metal to BN may be due to the formation of complex oxides on establishing contact.

Lastly, it is interesting to compare the foregoing friction results for BN-BN coating and metal-BN coating contacts with those for other ceramic-ceramic, metal-metal, and metal-ceramic contacts.

Figure 6 summarizes friction properties for ceramic-ceramic, metal-metal, and metal-ceramic contacts in vacuum environments. In addition to BN coating, ceramics of concern include SiC, Si_3N_4, SiO_2, ferrite in bulk form. Metals of concerned include Ti, Zr, Ta, Mo, Pt, Pd, Ir, Rh, and Fe.

The data presented in figure 6 indicate the marked difference in friction for the combination of solids. The coefficients of friction due to adhesive bonding for ceramic-ceramic and metal-ceramic contacts were much lower than those for metal-metal contacts. The coefficients of friction for metal-metal contacts are extremely high. In general, coefficient of friction for BN-BN contact can fit into the category of ceramic-ceramic contact. The coefficient of friction for metal-BN contact can also fit into the category of metal-ceramic contact.

Figure 6 suggests that use of ceramic materials including bulk and coating like forms in space and vacuum environments are beneficial from tribological considerations.

CONCLUSIONS

As a result of sliding friction experiments conducted with a boron nitride coating in sliding contact with BN itself and various transition metals, the following conclusions are drawn:

1. When the radius of curvature of the BN coated spherical pin is 4.8 mm, deformation of BN is principally elastic. The relation between coefficient of friction (μ) and load (W) is given by an expression of the form $\mu = kW^{-1/3}$. The friction for BN-BN contact is a function of the shear strength of the elastic contacts. Atomically clean BN exhibited strong interfacial adhesion and high friction. The presence of adsorbates such as adventitious carbon contaminants on the BN surfaces reduced the shear strength of the contact area. In contrast, the chemically adsorbed oxygen enhanced shear strength of the contact area and increased coefficient of friction.

2. The coefficients of friction for BN in contact with metals were related to the relative chemical activity (d valence bond character) of the metals. The more active the metal, the higher the coefficient of friction. There was no change in coefficient of friction with applied normal load indicative of occurrence of plastic deformation in metals at the real area of contact.

3. The surfaces of sputter cleaned BN coating film contained a small amount of oxides and carbides, in addition to boron nitride.

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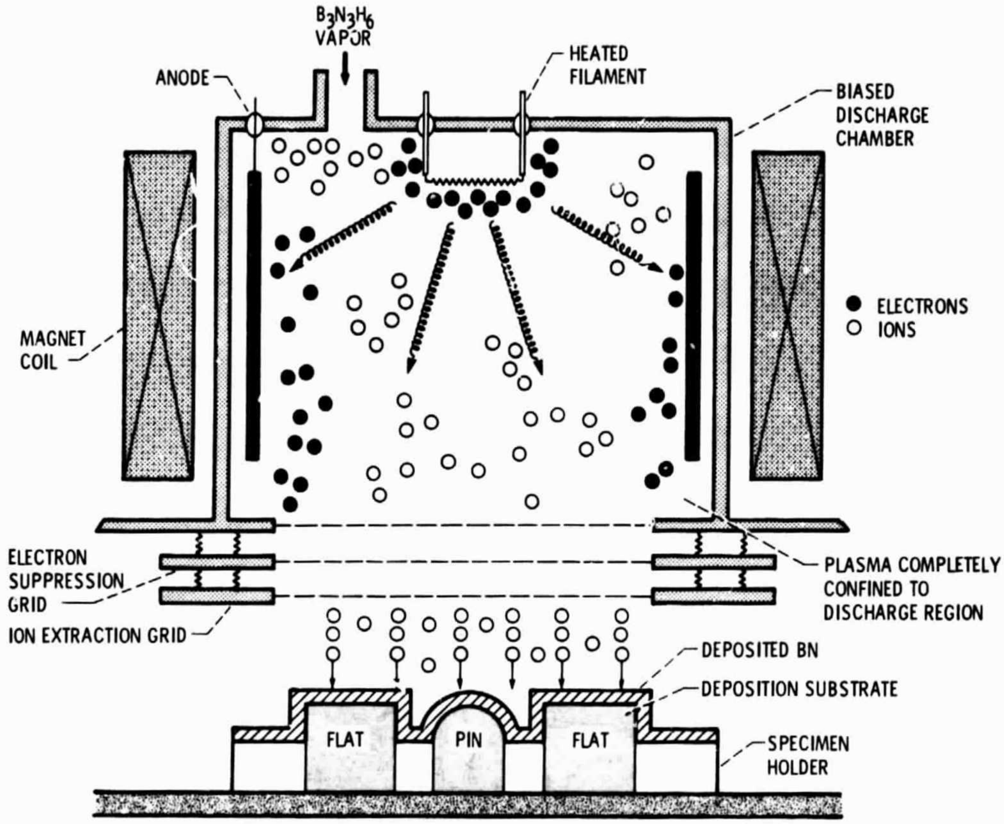


Figure 1. - Ion source configuration used to deposit BN. Procedure: Deposition of boron nitride thin films using an ion-beam from a borazine ($B_3N_3H_6$) plasma. Beam diameter: 10 cm.

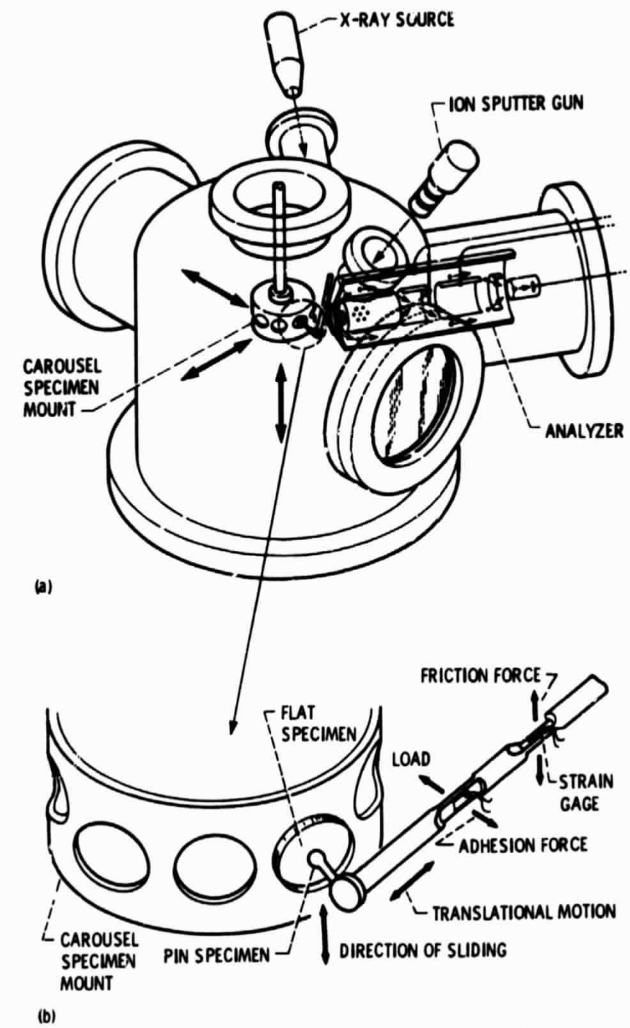
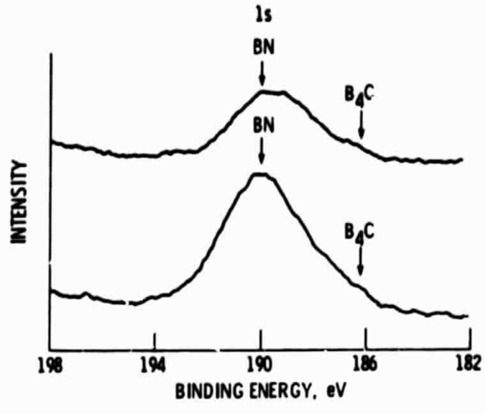
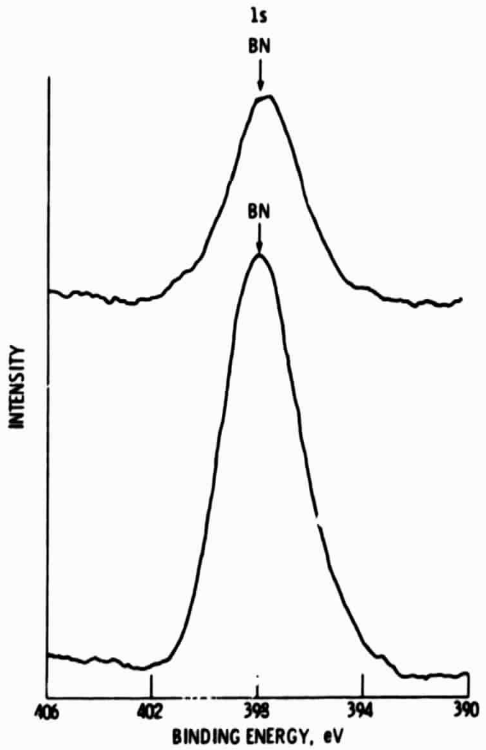


Figure 2. - Ultrahigh-vacuum friction and wear apparatus.

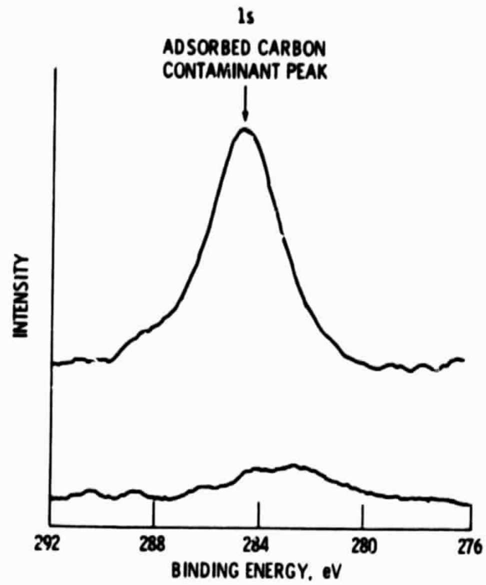


(a) B_{1s}.

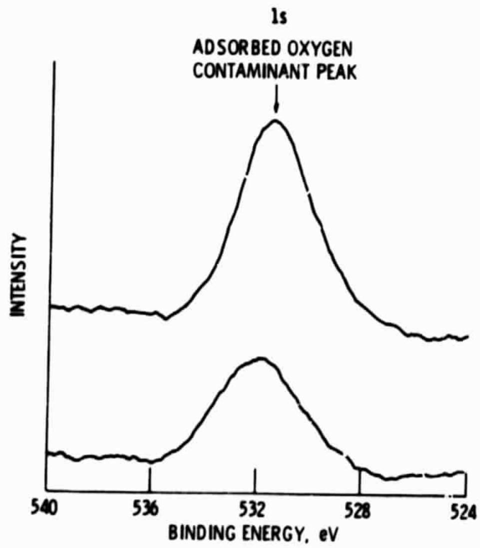


(b) N_{1s}.

Figure 3. - XPS peaks of BN films deposited on 440-C bearing stainless steel. (Top traces taken before sputtering; bottom traces, after sputtering for 45 min.)



(c) C_{1s}.



(d) O_{1s}.

Figure 3. - Concluded.

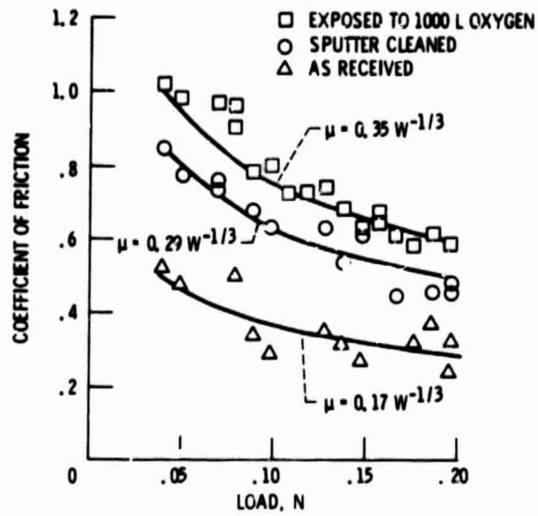


Figure 4. - Coefficient of friction as a function of load for hemispherical BN pins in sliding contact with BN flats. Single-pass sliding; sliding velocity, 3 mm/min; vacuum, 30 nPa; room temperature.

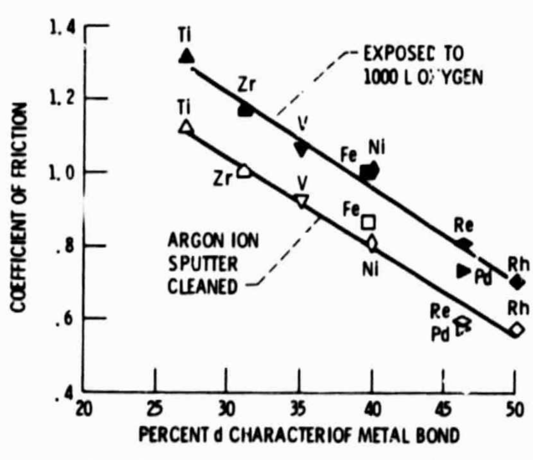


Figure 5. - Coefficient of friction as a function of the percentage d-bond character of various metals in sliding contact with BN and effect of adsorbed oxygen on friction. Single-pass sliding; sliding velocity, 3 mm/min; load, 0.05 to 0.2 N; vacuum, 3 nPa; room temperature.

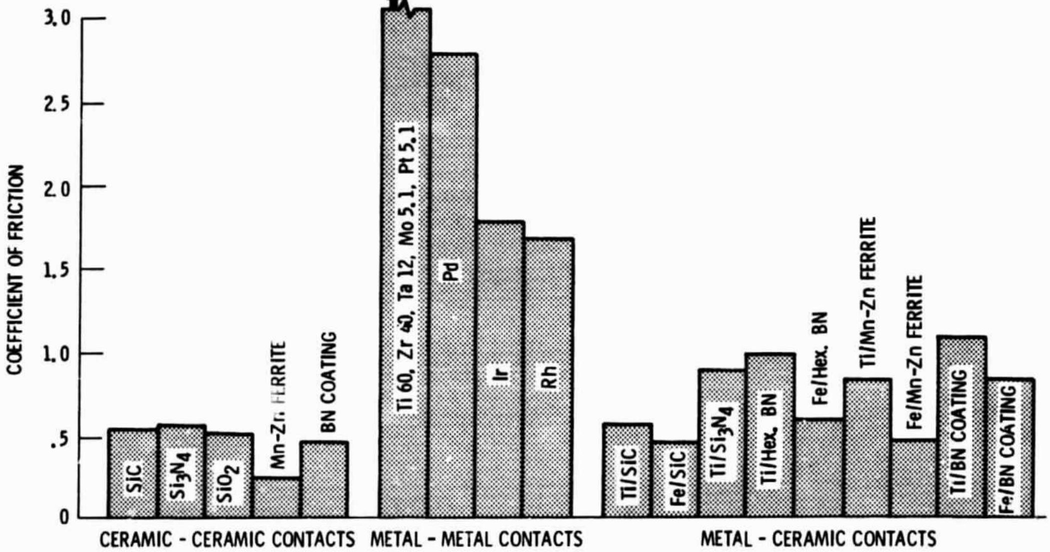


Figure 6. - Coefficients of friction for clean solid-to-solid interfaces. Single pass sliding in vacuum (30 nPa).