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Adhesion in Ceramics and Magnetic Media

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ADHESION IN CERAMICS AND MAGNETIC MEDIA

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ABSTRACT

When a ceramic is brought into contact with a metal or a polymeric material such as a magnetic medium, strong bonds form between the materials. For ceramic-to-metal contacts, adhesion and friction are strongly dependent on the ductility of the metals. Hardness of metals plays a much more important role in adhesion and friction than does the surface energy of metals. Adhesion, friction, surface energy, and hardness of a metal are all related to its Young's modulus and shear modulus, which have a marked dependence on the electron configuration of the metal. An increase in shear modulus results in a decrease in area of contact that is greater than the corresponding increase in surface energy (the bond energy) with shear modulus. Consequently, the adhesion and friction decrease with increasing shear modulus.

For ceramics in contact with polymeric magnetic tapes, environment is extremely important. For example, a nitrogen environment reduces adhesion and friction when ferrite contacts polymeric tape, whereas a vacuum environment strengthens the ferrite-to-tape adhesion and increases friction. Adhesion and friction are strongly dependent on the particle loading of the tape. An increase in magnetic particle concentration increases the complex modulus of the tape, and a lower real area of contact and lower friction result.

1. INTRODUCTION

The high strength and wear resistance of many advanced ceramics such as silicon carbide have resulted in a steady increase in the number and extent of ceramic wear applications. These range from components of advanced engines, such as bearings and seals, to magnetic heads in magnetic storage systems. Further, the demands for operating in more extreme temperatures, chemical environments, space environments, and for longer operating times in poorly accessible locations are further accentuating the use of ceramics for high wear resistance. Although there is a significant present and future need for wear-resistant ceramics, the successful use of ceramics in these applications is limited more often by tribological requirements than by material properties or process deficiencies [1-4]. Clearly, there is a limited basic understanding of the surface interactions of ceramics with themselves and other materials [4-7].

The objective of this paper is to discuss the fundamental nature of adhesion and friction of ceramics in contact with metals and polymeric magnetic tapes.

2. MATERIALS

Hot-pressed polycrystalline magnesia-doped silicon nitride was used in the adhesion experiments. Other materials used in this investigation were (1) single-crystal silicon carbide platelets, which were a 99.9 percent pure compound of silicon and carbon with the basal plane parallel to the interface, (2) hot-pressed polycrystalline manganese-zinc ferrite and nickel-zinc ferrite platelets that were 99.9 percent pure oxide, (3) polycrystalline metals (titanium was 99.97 percent pure, and all other metals were 99.99 percent pure), and (4) magnetic tapes with different magnetic particle loadings consisting of chromium oxide powders coated on a polyester film backing. The magnetic particle loadings of the tapes (magnetic particle concentrations on a polymeric binder) were 45, 50, 55, and 58 percent. A higher particle loading results in a greater complex modulus of the tape [8]. The complex modulus was measured with a dynamic-mechanical-analysis system and was given by the ratio of the maximum stress to the maximum strain [8].

3. APPARATUS

The apparatus used in this investigation consisted of an ultrahigh vacuum system capable of measuring adhesion and friction (fig. 1). The vacuum system contained an x-ray photoelectron spectroscopy analysis system. The mechanism for measuring adhesion and friction was basically a pin-flat configuration, as shown schematically in figure 1.

For the adhesion experiments, a manipulator-mounted torsion balance was used (see fig. 1). The pin specimen was mounted on one end of a movable arm. A free-moving, rod-shaped magnetic core was mounted on the other end of the arm. The coils of a linear variable differential transformer (LVDT) were mounted on a stationary arm. There was no physical contact between the movable magnetic core and the coil structure. The movable arm was supported by a single strand of wire acting as a torsion spring. The flat specimen was mounted on a specimen holder attached to a manipulator. This torsion balance allowed measurements of pull-off force as small as 1 μN in vacuum [9].

For the friction measurements, a manipulator-mounted beam was projected into the vacuum chamber (again see fig. 1). The beam contained two pairs of flats assembled normal to each other with strain gages mounted thereon. The pair flats were parallel to each other. The end of the beam contained the pin specimen. The flat specimen was mounted on a specimen holder attached to the other manipulator. A load that was applied to the pin-flat contact by deflecting the beam was sensed by strain gages. The friction force under an applied load was measured during vertical translation by strain gages mounted normal to those measuring the load.

4. EXPERIMENTAL PROCEDURES

4.1 Specimen Preparation

The contacting surfaces of the ceramic and metal specimens, which were either hemispherical or flat, were polished with diamond powder and aluminum oxide power, each 1 μm in diameter. The specimens were rinsed with absolute ethanol prior to the experiments. The surface roughness of the polished faces (R_{max}, maximum height of irregularities) was about 0.1 μm or less. The radii of curvature of the pins were 0.8 or 1.6 mm.

The flat magnetic tape specimens, mounted on 304 stainless steel platform supporting sheets, were used only in the as-received state.

4.2 Procedures

4.2.1 Ceramic-to-Metal Contact

The metal pin and ceramic flat specimens were placed in the vacuum chamber. The system was evacuated and baked out to achieve a pressure of 30 nPa. Pin and flat surfaces of the ceramic and metal specimens were ion-sputter etched with a 3000-eV beam energy at a 20-mA beam current and a 0.7-mPa argon pressure. 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. In situ pull-off force (adhesion) and friction measurements were then made with the ion-sputter-cleaned pin and flat specimens in a 30-nPa vacuum.

In adhesion experiments, contact was maintained for 30 sec; then pin and flat specimen surfaces were pulled apart [9]. For friction experiments, contact before sliding was also maintained for 30 sec. The sliding velocity was 3 mm/min. The surface cleanliness of the pin and flat specimens was verified by x-ray photoelectron spectroscopy analysis.

4.2.2 Ceramic-to-Magnetic Tape Contact

It is extremely difficult to remove adsorbed contaminants from such magnetic media as polymeric magnetic tape surfaces. Indeed, no entirely satisfactory cleaning procedure has yet been established for magnetic tapes. Therefore, the tape specimens used both in dry nitrogen atmosphere and in vacuum were as-received. Four sets of experiments were conducted. The specimens were placed in the vacuum chamber, and for the first set of experiments, the chamber was filled with dry nitrogen. Then as-received ferrite pin specimens slid on as-received tape surfaces in the dry nitrogen atmosphere.

For the second set of experiments, the system was evacuated to achieve a pressure of 1 μPa at room temperature without baking out; then as-received ferrite pin specimens slid on as-received tape surfaces in vacuum at 1 μPa.

For the third and fourth sets of experiments, the system was evacuated and baked out to achieve a pressure of 30 nPa, and the ferrite pin specimens were argon ion-sputter cleaned. In the third set of experiments, specimens slid on tape surfaces in the system reevacuated to a pressure of 30 nPa. In the fourth set, the pin specimens were exposed to 1000-L oxygen and then they slid on tape surfaces in the system reevacuated to a pressure of 30 nPa.

5. RESULTS AND DISCUSSION

5.1 Ceramic-to-Metal Contact

5.1.1 Nonoxide Ceramics

In a vacuum environment, sputtering with rare gas ions or heating surfaces to high temperatures can remove contaminants that are adsorbed on the surface of ceramics and metals. Removing adsorbed films from the surfaces of ceramics and metals results in strong interfacial adhesion when two such solids are brought into contact [10].

Figure 2 presents the pull-off force (adhesion) for silicon nitride-to-metal contacts as a function of Young's modulus of the metals. The data of this figure for argon ion-sputter-cleaned surfaces indicate a decrease in adhesion with an increase in Young's modulus - the higher the Young's modulus, the lower the adhesion. Note that, although the behavior of iron and nickel is anomalous, the magnitude of Young's modulus is generally dependent on the electron configuration of the metal [11]; its maximum value in a given period of the Periodic Table corresponds to the metal having the maximum number of unpaired d electrons. The minimum, near the end of each period, occurs for the element that has an s^2p^1 configuration. Young's modulus is also related to such physical, chemical, and mechanical properties as shear modulus, surface and cohesive energy, chemical stability, and tensile and shear strength [11-15].

Figure 3 presents the coefficient of friction for silicon carbide-to-metal contacts as a function of shear modulus of the metals. The data for the argon ion-sputter-cleaned surfaces presented in figure 3 indicate a decrease in coefficient of friction with an increase in shear modulus of the metals. The shear modulus, like Young's modulus, has a marked dependence on the electron configuration of the metal. The similar shape of figures 2 and 3 is not surprising since $E \simeq 2.6G$ [11]. Further, all the slidings in this investigation involve adhesion at the contact area between the ceramic and metal.

On separation of the silicon carbide and metal in sliding contact, both the interfacial adhesive bonds between the silicon carbide and metal and the cohesive bonds in the metal were broken [16]. In other words, the shear forces that broke both the interfacial adhesive bonds and the cohesive bonds in the metals were primarily responsible for the frictional force. The examined metal 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 morphology revealed that all the silicon carbide surfaces contacted by the metals contained transferred films of metal. Metals that have a low shear modulus exhibit larger areas of metal transfer than those with a higher modulus. Such dependence of adhesion, friction, and metal transfer on shear modulus may arise from surface and cohesive energy as well as ductility of the metals; therefore, it is interesting to compare the foregoing friction results, for silicon carbide-to-metal contacts, with surface energy and hardness of metals.

Figure 4 presents surface energy values at room temperature from recommended values suggested by Tyson and Miedema [12,14]. The surface energy for the metals increases with an increase in shear modulus. Note that Miedema [14] estimated the values at room temperature from values of the experimental surface energy and entropy by using the temperature dependence factors. The surface energy correlated with such thermochemical parameters for metals as the electron density, the electron negativity, and heat sublimation [13,14]. The calculated ideal shear strengths of the metals were also correlated with shear modulus [15] - the higher the shear modulus, the greater the shear strength.

The adhesion and friction of the ceramic-to-metal contacts were expected to increase as the surface energy (i.e., the bond energy of metals) increased. But figures 2 to 4 show that the adhesion and friction go in the opposite direction; they decreased with an increase in surface energy of metals. In other words, the friction was reduced with an increase in shear modulus, whereas the surface energy increased as the modulus value increased. Presumably, the ductility of metals, that is, the deformation of metals, has not been considered here [6,17].

Because of the marked difference in elastic and plastic deformation of ceramics and softer metals, solid-state contact between the two materials can result in considerable plastic deformation of the softer metal. This deformation can contribute to the adhesion and friction of the materials because it increases the real contact area. To gain an understanding of interface deformation under the action of a friction force, indentation experiments were conducted with the metal pin specimens. The hardness data (fig. 5(a)) indicate that at room temperature the Vickers hardness of metals increases as the shear modulus increases. Figure 5(b) presents areas of contact, calculated from the experimental data presented in figure 5(a), as a function of shear modulus of the metal. The area of contact was determined by the ratio of normal load to hardness. The calculated area of contact is very strongly dependent on the shear modulus of the metal; it decreases with increasing shear modulus. The decrease in the area of contact with an increase of shear modulus for these metals is greater than the corresponding increase in the surface energy (bond energy) with shear modulus (see figs. 4 and 5(b)). Consequently, the shear force required to move the metal pin in a direction parallel to the surface of silicon carbide decreases with increasing shear modulus. This fact is consistent with the results of figures 2 and 3. Thus, the foregoing results show that such mechanical factors as hardness are of great importance [6,17]. During ceramic-to-metal contact, strong bonds form between the materials. These interfacial bonds are stronger than the cohesive bonds in the metal (as evidenced by the transferred metal) at the major part of the real area of contact. Hardness of metals plays an important role in adhesion and friction and exceeds that of the surface energy.

5.1.2 Oxide ceramics

The coefficients of friction for oxide ceramics such as manganese-zinc and nickel-zinc ferrites in contact with metals can also be correlated with the shear modulus of metals, as shown in figures 6. This correlation is consistent with the results indicated in figure 3. The coefficient of friction decreases with an increase in shear modulus. Again, hardness of metals is of great importance to adhesion and friction of the oxide ceramic-to-metal contacts.

Pepper [18] showed that when sapphire contacts metal a chemical bond between the metal atoms and the oxygen ions plays a role in the shear strength of the sapphire-to-metal contact. The shear strength of the sapphire-to-metal contact was correlated with the free energy of formation of the metal oxide [18]. Figure 7 presents the free energy of formation of the lowest metal oxides as a function of shear modulus of the metals [19]. The free energy of formation of the lowest metal oxides decreases with an increase in shear modulus, as does the friction. The correlations shown in figures 6 and 7 clearly indicate that the metal-to-ferrite adhesive bond at the interface, like metal-to-sapphire contact, is primarily a chemical bond between the metal atoms and the large oxygen anions of the ferrite surface. The strength of this bond is related to oxygen-to-metal bond strength in the metal oxide.

All metals shown in figure 6 adhered to and transferred to the surface of the ferrites [20]. In general, the greater the shear modulus, the less adhesion and metal transfer there is to the ferrite.

5.2 Ceramic-to-Magnetic Tape Contact

Figure 8 presents the coefficients of friction for various tapes in contact with the nickel-zinc ferrite as a function of the complex modulus of the tapes both in dry nitrogen at atmospheric pressure and in vacuum. The higher the particle loading, the greater is the complex modulus of the tape [8].

The friction properties markedly depend on the environment. In dry nitrogen at atmospheric pressure, the coefficient of friction is independent of the complex modulus of the tape (i.e., the particle loading). Since the adsorbate films remain at the interface, the bulk composition of the tapes does not have much effect on friction.

In vacuum at 1 μPa, however, the coefficient of friction for the tape is dependent on the complex modulus of the tape (i.e., the particle loading), as shown in figure 8. The data obtained from the experiments conducted in vacuum at 1 μPa reveal that the coefficient of friction decreases with increasing complex modulus. In other words, the lowering of the polymeric binder concentration of the tape surface leads to low friction. In vacuum, the adsorbate films become disrupted or dislodged. When this occurs, clean solid-state material contact can occur through the film at the sliding interface because of breakup of these surface films. Consequently, the basic material properties of the tape become extremely important in adhesion and friction. Since an increase in particle loading results in a higher complex modulus and therefore a lower real area of contact, the tape with higher particle loading has less friction.

Figure 9 presents the coefficients of friction for as-received tapes in contact with ion-sputter-cleaned ferrites and with ferrites exposed to 1000-L oxygen in vacuum at a pressure of 30 nPa. The coefficient of friction is strongly dependent on the complex modulus of tapes, as indicated in figure 9 - again, the greater the complex modulus, the lower the coefficient of friction. The data of figure 9 also indicate that the ion-sputter cleaning of the ferrite strengthened the ferrite-to-tape adhesion and increased friction. Furthermore, the adsorption of oxygen on the tape and on ion-sputter-cleaned ferrite surfaces increased the coefficients of friction. A similar friction characteristic for metal-to-ferrite contacts and metal-to-sapphire contacts was also found by Pepper and this author, respectively [18,20].

6. CONCLUDING REMARKS

Based on fundamental studies of adhesion and friction of ceramics in contact with metals and polymeric magnetic tapes, the following remarks can be made:

1. For ceramic-to-metal contacts, strong bonds form between the materials, and the interfacial bonds are stronger than the cohesive bonds in the metal at the major part of the real area of contact. Adhesion and friction are strongly dependent on the ductility of the metals. Hardness of

metals is of paramount importance to adhesion and friction, exceeding that of the surface energy of metals.

2. Adhesion, friction, surface energy, and hardness of a metal are all related to its Young's modulus and shear modulus, which have a marked dependence on the electron configuration of the metal. The decrease in area of contact with an increase in shear modulus is greater than the corresponding increase in the surface energy (bond energy) of the metals with increasing shear modulus. Consequently, the adhesion and friction decrease with increasing shear modulus.

3. The metals failed in shear or tension at the major part of the real areas of contact where the interfacial bonds were stronger than the cohesive bonds in the metal. In general, the greater the shear modulus, the less adhesion and metal transfer there is to the ceramic.

4. For ceramics in contact with polymeric magnetic tapes, environment is extremely important. For example, a nitrogen environment reduces adhesion and friction in ferrites contacting polymeric tapes, whereas a vacuum spacelike environment strengthens the ferrite-to-tape adhesion and increases friction. The adhesion and friction are strongly dependent on the particle loading of the tape. An increase in magnetic particle concentration increases the complex modulus of the tape, thereby resulting in a lower real area of contact and lower friction. Adhesion and friction for ceramic-to-tape contacts, like ceramic-to-metal contacts, are thus related to the complex modulus of the tape.

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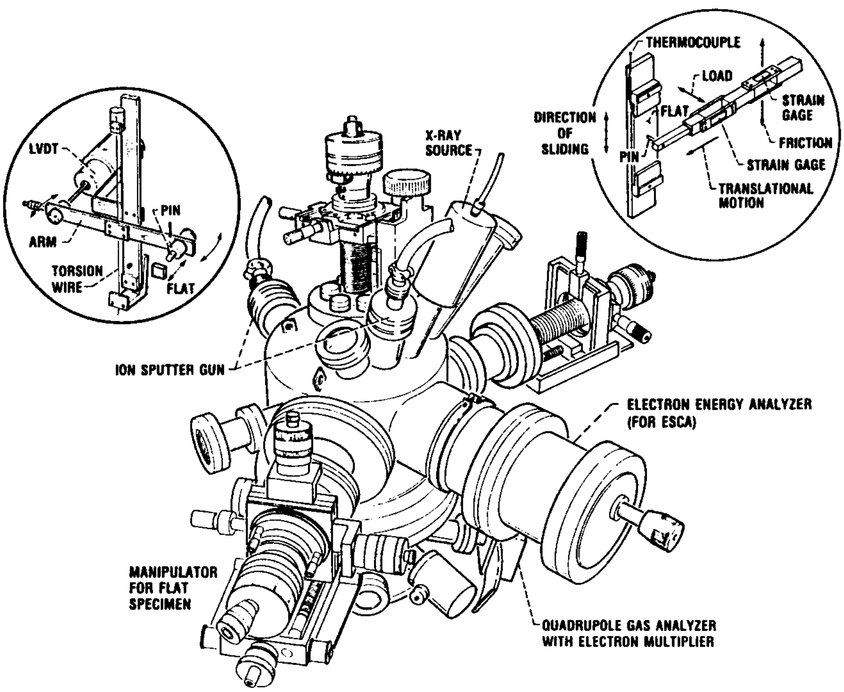

FIG. 1. - APPARATUS FOR MEASURING ADHESION AND FRICTION IN ULTRAHIGH VACUUM.

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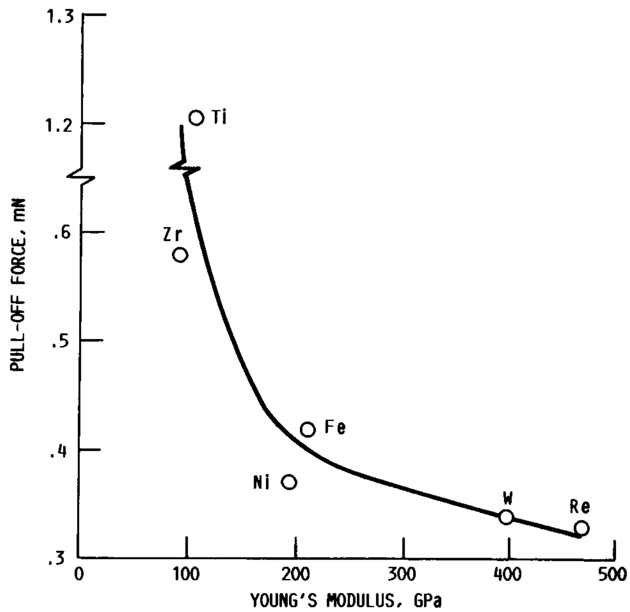

FIG. 2. - PULL-OFF FORCE (ADHESION) AS A FUNCTION OF YOUNG'S MODULUS OF METALS IN CONTACT WITH SILICON NITRIDE IN VACUUM.

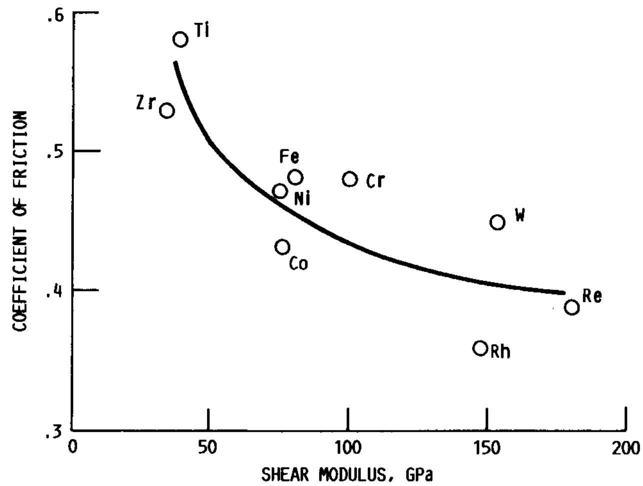

FIG. 3. - COEFFICIENTS OF FRICTION AS A FUNCTION OF SHEAR MODULUS OF METALS IN CONTACT WITH SILICON CARBIDE IN VACUUM.

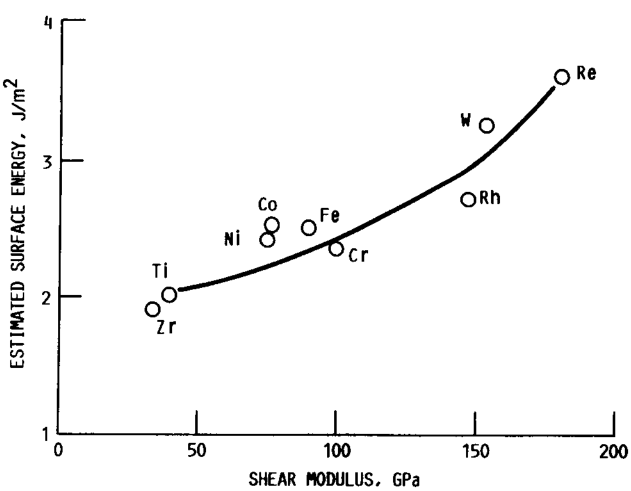

FIG. 4. - ESTIMATED SURFACE ENERGY OF METAL AS A FUNCTION OF SHEAR MODULUS.

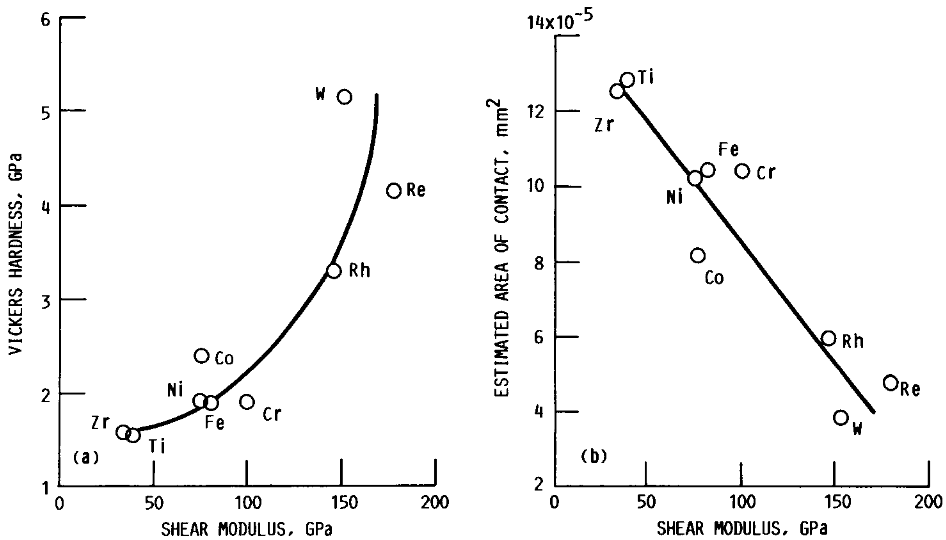

FIG. 5. - (a) VICKERS HARDNESS OF METAL AND (b) ESTIMATED AREA OF CONTACT AS FUNCTIONS OF SHEAR MODULUS.

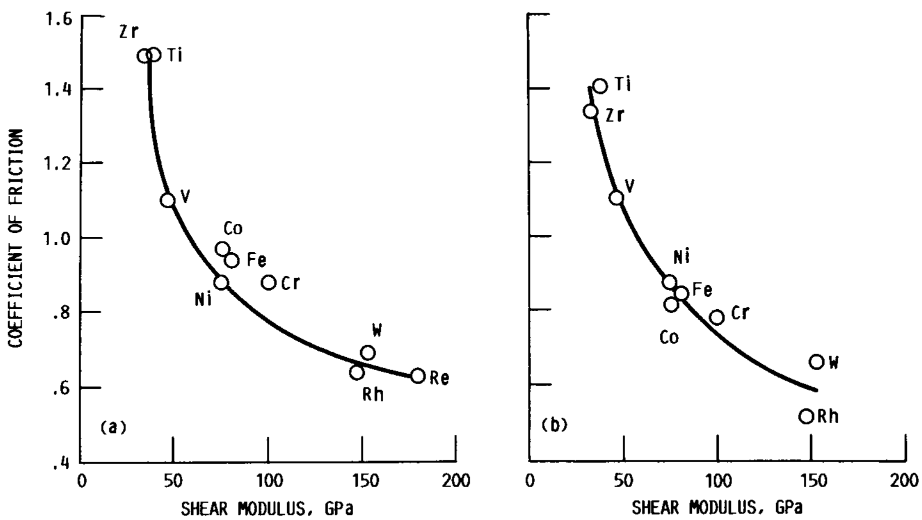

FIG. 6. - COEFFICIENTS OF FRICTION AS FUNCTIONS OF THE SHEAR MODULUS OF METALS IN CONTACT WITH (a) Ni-Zn AND (b) Mn-Zn FERRITES IN VACUUM.

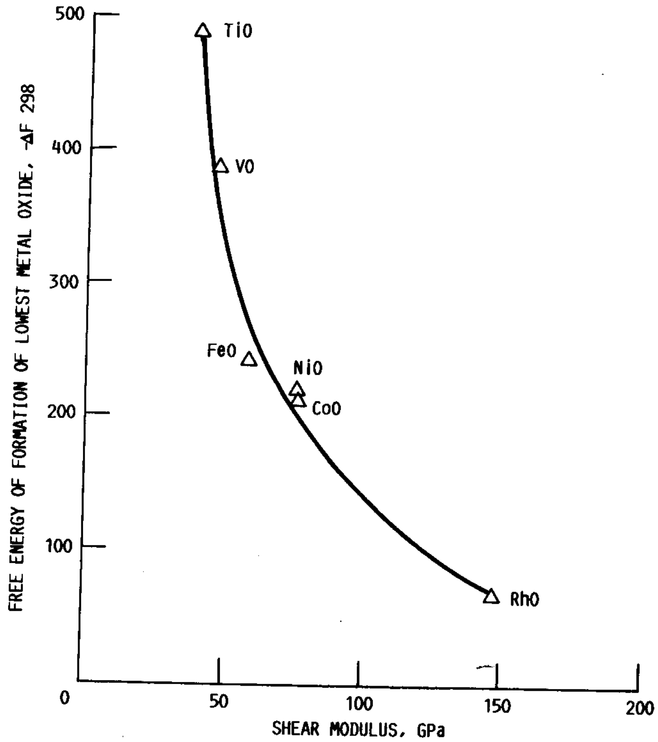

FIG. 7.- FREE ENERGY OF FORMATION OF THE LOWEST OXIDE AS A FUNCTION OF SHEAR MODULUS OF METAL.

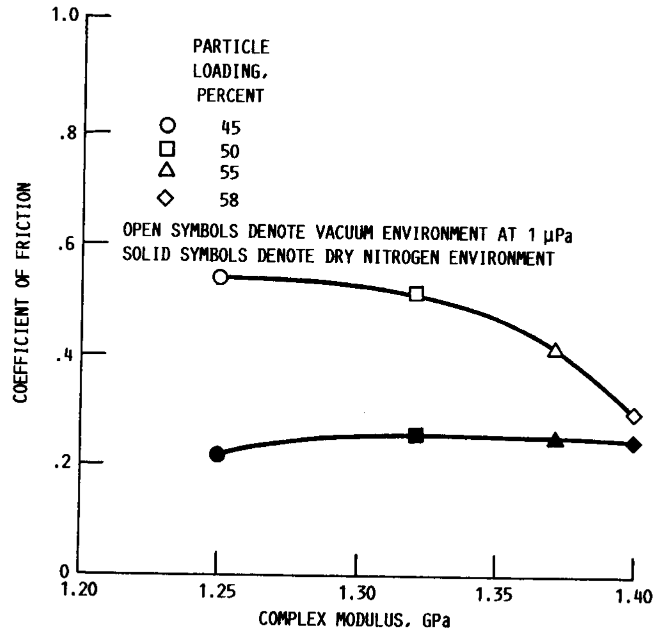

FIG. 8. - COEFFICIENT OF FRICTION FOR AS-RECEIVED Ni-Zn FERRITE PINS IN CONTACT WITH VARIOUS MAGNETIC TAPES AS A FUNCTION OF THE COMPLEX MODULUS OF THE TAPES.

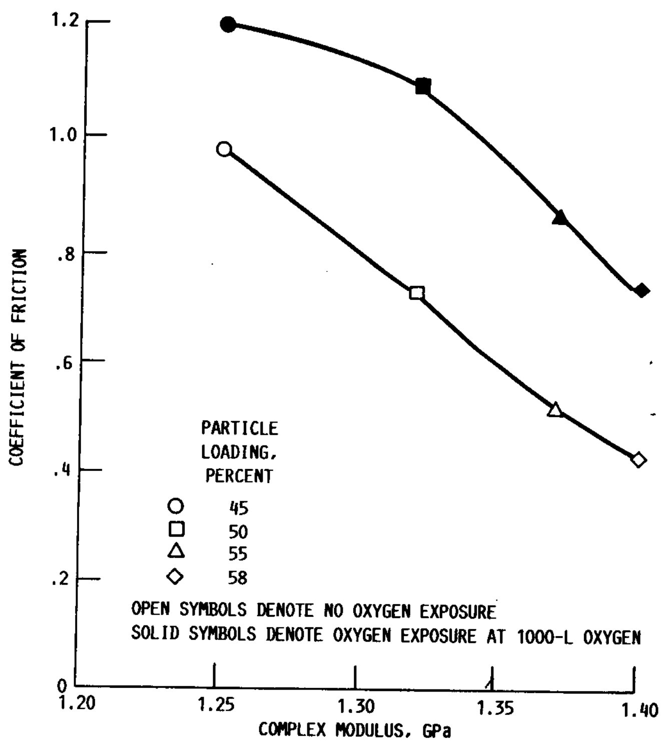

FIG. 9.- COEFFICIENT OF FRICTION FOR ION-SPUTTER-CLEANED Ni-Zn FERRITE PINS IN CONTACT WITH VARIOUS MAGNETIC TAPES AS A FUNCTION OF THE COMPLEX MODULUS OF THE TAPES IN VACUUM.

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16. Abstract

When a ceramic is brought into contact with a metal or a polymeric material such as a magnetic medium, strong bonds form between the materials. For ceramic-to-metal contacts, adhesion and friction are strongly dependent on the ductility of the metals. Hardness of metals plays a much more important role in adhesion and friction than does the surface energy of metals. Adhesion, friction, surface energy, and hardness of a metal are all related to its Young's modulus and shear modulus, which have a marked dependence on the electron configuration of the metal. An increase in shear modulus results in a decrease in area of contact that is greater than the corresponding increase in surface energy (the bond energy) with shear modulus. Consequently, the adhesion and friction decrease with increasing shear modulus. For ceramics in contact with polymeric magnetic tapes, environment is extremely important. For example, a nitrogen environment reduces adhesion and friction when ferrite contacts polymeric tape, whereas a vacuum environment strengthens the ferrite-to-tape adhesion and increases friction. Adhesion and friction are strongly dependent on the particle loading of the tape. An increase in magnetic particle concentration increases the complex modulus of the tape, and a lower real area of contact and lower friction result.

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