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Adhesion, Friction, and Wear Behavior of Clean Metal-Ceramic Couples

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When a clean metal is brought into contact with a clean, harder ceramic in ultrahigh vacuum, strong bonds form between the two materials. The interfacial bond strength between the metal and ceramic surfaces in sliding contact is generally greater than the cohesive bond strength in the metal. Thus, fracture of the cohesive bonds in the metal results when shearing occurs. These strong interfacial bonds and the shearing fracture in the metal are the main causes of the observed wear behavior and the transfer of the metal to the ceramic.

In the literature, the surface energy (bond energy) per unit area of the metal is shown to be related to the degree of interfacial bond strength per unit area. Because the two materials of a metal-ceramic couple have markedly different ductilities, contact can cause considerable plastic deformation of the softer metal. It is the ductility of the metal, then, that determines the real area of contact. In general, the less ductile the metal, the smaller the real area of contact.

The coefficient of friction for clean surfaces of metal-ceramic couples correlates with the metal's total surface energy in the real area of contact γA (which is the product of the surface energy per unit area of the metal (γ) and the real area of contact (A)). The coefficient of friction increases as γA increases. Furthermore, γA is associated with the wear and transfer of the metal at the metal-ceramic interface: the higher the value of γA, the greater the wear and transfer of the metal.

Keywords: Adhesion, Friction, Wear, Metal-ceramic couples, Total surface energy

1. INTRODUCTION

A contaminant layer may form on a solid surface either by the interaction of the surface with the environment or by the diffusion of bulk contaminants through the solid itself. Thin contaminant layers are unavoidably present on every surface of any solid that has been exposed to air. They are made up of contaminants such as adsorbed gases, water vapor, and hydrocarbons and have thicknesses of atomic dimensions (around 2 nm thick).

Surface analysis techniques, such as x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are well suited for examining very thin contaminant layers. Contaminant surface layers can affect the spectrum by attenuating the electron signal from the underlying surface, thereby masking spectral features related to the bulk material (1-6).

Contaminants are weakly bound to the surface, since the binding is of a physical rather than chemical nature. In vacuum, therefore, bombarding the surfaces with rare gas ions (e.g., argon ions) or heating the surfaces to a high temperature can remove the contaminants that are adsorbed on the metal and ceramic (1-6).

Contamination is an important factor to be considered in determining a solid's surface properties, such as adhesion and friction. Contaminant layers can greatly reduce adhesion and friction and, accordingly, provide lubrication. Under actual conditions of sliding, however, the contaminant surface layers are removed by the repeated sliding; thus direct contact of the fresh, clean surfaces is unavoidable. Such is the situation in space tribology as it applies to spacecraft mechanism design. This situation also applies, to some degree, in sliding contacts in an air atmosphere, where fresh surfaces are continuously produced by a counterfacing material. Obviously, an understanding of the behavior of clean surfaces in metal-ceramic couples is of paramount practical importance (1,3,7).

The objective of this paper is to review the adhesion, the friction, and the wear behavior of argon-sputter-cleaned surfaces of metal-ceramic couples in ultrahigh vacuum (10^{-8}Pa). Surface and bulk properties, which determine the adhesion, friction, and wear behavior of metal-ceramic couples, are discussed. The primary emphasis is on the nature and character of the metal, especially its surface energy and ductility. The surface cleanliness of the argon-sputter-cleaned metals and ceramics was verified by AES or XPS analysis. Some earlier data and experimental details on this research are given in references 2 to 6.

2. ADHESION

If clean, solid surfaces are brought together under a normal load, the atoms must be in contact at some points; thus interatomic forces will come into operation (1,7,8) and cause some adhesion to occur in these regions. The pull-off force, which reflects interfacial adhesion, was measured for various argon-sputter-cleaned metals in contact with argon-sputter-cleaned ferrites in ultrahigh vacuum. As Fig. 1(a) shows, this pull-off force decreases with an increase in the Young's modulus of the metal. This indicates that the bulk properties of the metal, such as the Young's modulus, affect the magnitude of the adhesive bond forces that develop at the metal-ceramic interface. Similar pull-off-force (adhesion) results were obtained for clean metal-Si_3N_4 couples (5,6).

The pull-off forces of clean metal-ferrite couples can also be correlated with the free energy of formation of the lowest metal oxides, as shown in Fig. 1(b). This correlation indicates that the adhesive bond at the metal-ceramic interface is a chemical bond between the metal atoms on the metal surface and the large oxygen anions on the ferrite (MnO-ZnO-Fe_2O_3) surface. Furthermore, Fig. 1(b) indicates that the strength of this chemical bond is related to the oxygen-to-metal bond strength in the metal oxide. Similar

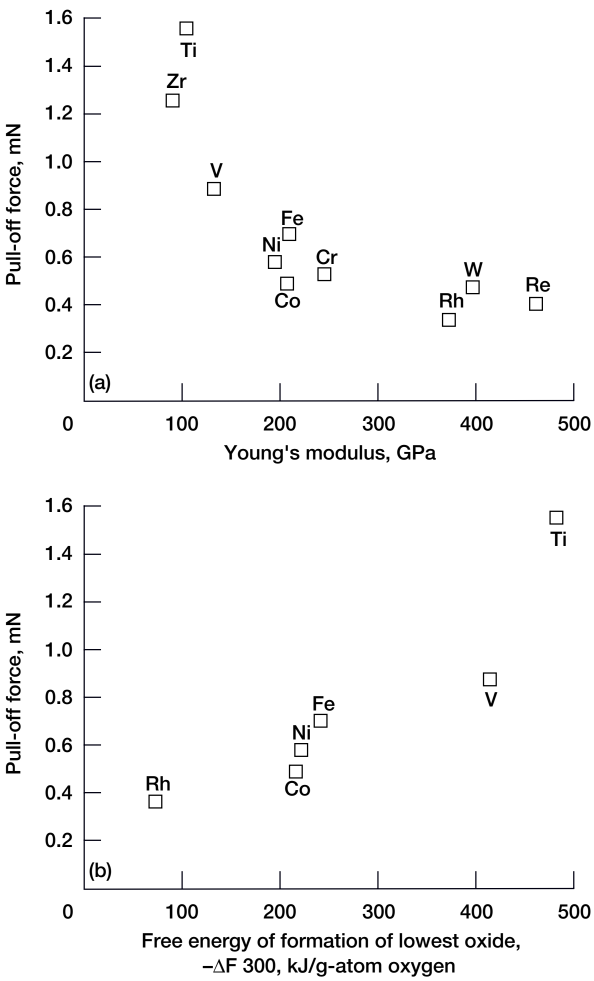

Fig. 1 Pull-off force (adhesion) for various metals in contact with ferrites (MnO-ZnO-Fe_2O_3) in ultrahigh vacuum. (a) As function of Young's modulus of metal. (b) As function of free energy of formation of lowest metal oxide.

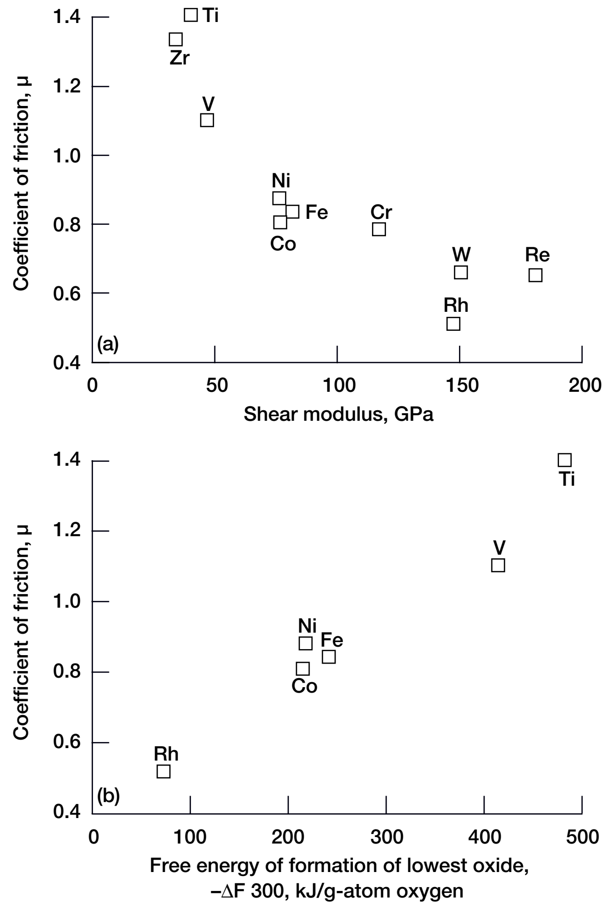

Fig. 2 Coefficient of friction for various metals in contact with ferrites (MnO-ZnO-Fe_2O_3) in ultrahigh vacuum. (a) As function of shear modulus of metal. (b) As function of free energy of formation of lowest metal oxide.

adhesion behavior has been noted with other oxide ceramics, such as Ni-Zn ferrite (NiO-ZnO-Fe_2O_3) and sapphire (Al_2O_3) (5,9).

Thus, both the surface and bulk properties of metal-ceramic couples have been shown to affect the magnitude of the adhesive bond forces that develop at metal-ceramic interfaces.

3. FRICTION

The coefficient of friction, which reflects interfacial adhesion, was measured for various argon-sputter-cleaned metals in contact with argon-sputter-cleaned ferrites in ultrahigh vacuum. It decreased with an increase in the shear modulus of the metal (see Fig. 2(a)). This shows that the shear modulus of the metal plays an important role in the friction behavior of clean metal-ferrite couples. Similar friction-shear modulus relationships have been noted with other hard materials (such as diamond, silicon carbide, Ni-Zn ferrite, and boron nitride) in sliding contact with metals (3).

The coefficient of friction of the clean metal-ferrite couple can also be correlated with the free energy of formation of the lowest metal oxides, as shown in Fig. 2(b). Clearly, Fig. 2(b) indicates that the adhesive bond at the metal-ceramic interface is a chemical bond between the metal atoms at the surface of the metal and the large oxygen anions on the ferrite (MnO-ZnO-Fe $_2O_3$) surface and that the strength of this bond is related to the oxygen-to-metal bond strength in the metal oxide. Similar relationships have been noted with NiO-ZnO-Fe $_2O_3$ (4).

Again, with the metal-diamond couples the coefficient of friction decreased with an increase in the shear modulus of the metal, as shown in Fig. 3(a).

The d-valence bands in transition metals are not completely filled. It is the filling of the d-electron bands that is responsible for the metal's surface and bulk properties such as adhesive energy, shear modulus, and chemical stability. The greater the percentage of d-bond character that a metal possessses, the less active its surface should be (10). In Fig. 3(b), the coefficient of friction for some of the transition metals in contact with a single-crystal diamond (111) surface is shown as a function of the d-bond character of the metals. The data indicate a decrease in friction with an increase in d-bond characters. Titanium and zirconium, which are chemically very active, exhibit very strong interfacial adhesive bonding to the diamond. In contrast, rhodium and rhenium, which have a very high percentage of d-bond character, have relatively low coefficients of friction; thus, the more chemically active the metals, the higher the coefficient of friction.

Again, both the surface and bulk properties of metal-ceramic couples affect the magnitude of the coefficient of friction at the

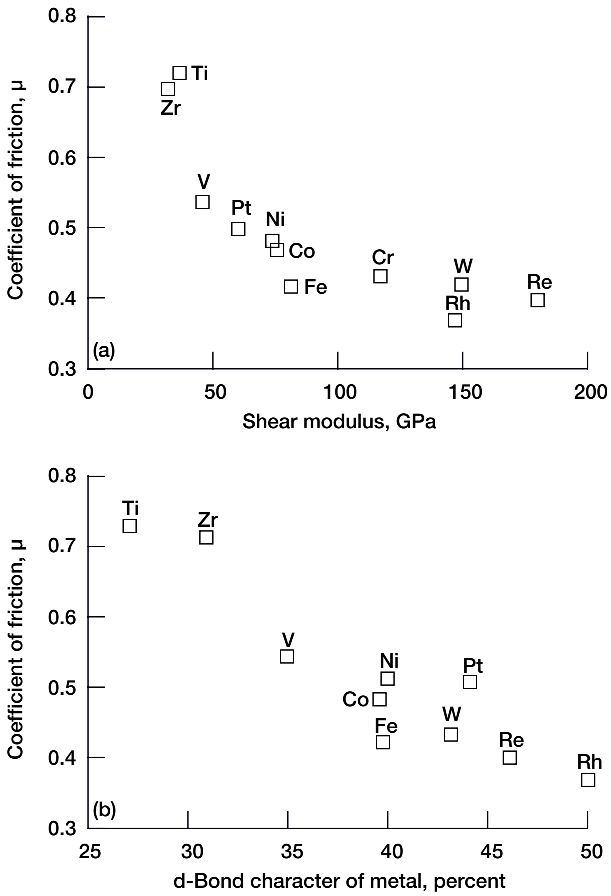

Fig. 3 Coefficient of friction for various metals in contact with diamond (111) surface in ultrahigh vacuum. (a) As function of shear modulus of metal. (b) As function of percent of metal's d-bond character.

metal-ceramic interface. This dependence of friction on the shear modulus and on the chemical activity of the metal is analogous to the adhesion behavior mentioned in the previous section.

Note that the Young's and the shear modulus values used in this paper for bulk polycrystalline metals are those reported by Gschneidner (11). He reported that a ratio of Young's modulus to shear modulus is essentially constant (nearly 2.6) for all metals and that the shear modulus, like the Young's modulus, has a marked dependence on the electron configuration of the metal.

4. WEAR

Inspection of all the metal and ceramic surfaces after sliding contact revealed that deformation of the metal was principally plastic and that the cohesive bonds in the metal fractured. All the metals that were examined failed in shear or tear and were transferred to the ceramic during sliding. The interfacial bond between the metal and ceramic is generally stronger than the cohesive bond within the metal, so when the junction was sheared, separation generally took place in the metal. Pieces of the metal were torn out and transferred to the ceramic surface. For example, when an atomically clean SiC surface was brought into contact with a clean Al surface, the interfacial adhesive bonds that formed in the real area of contact were so strong that shearing or tearing occurred locally in the Al. Consequently, the wear debris particles of Al were transferred to the SiC surface during sliding; this was verified by a scanning electron micrograph and an Al K**α** x-ray map (see Fig. 4).

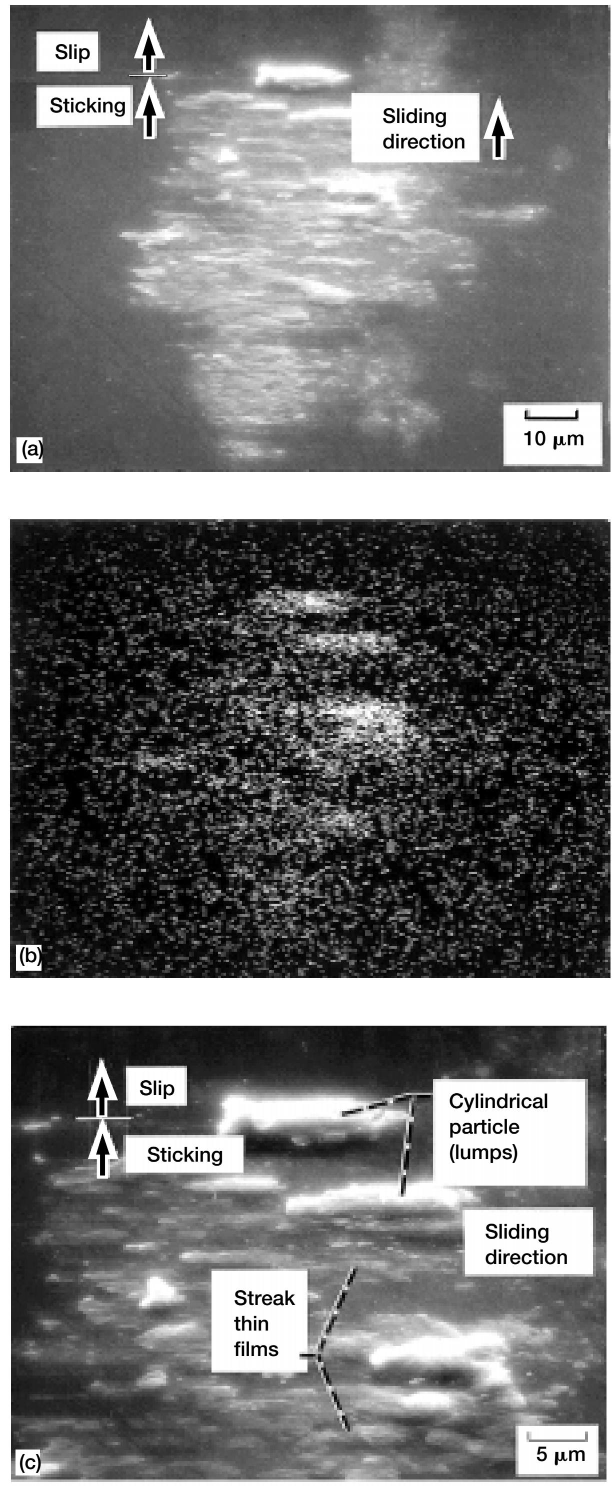

Fig. 4 Aluminum transferred to SiC (0001) surface as a result of single pass sliding in ultrahigh vacuum. (a) Metal transfer to SiC (before gross sliding). (b) Aluminum Kα x-ray map; 1.5×10^4 counts. (c) Wear debris of Al transferred to SiC.

The morphology of metal transfer to ceramic revealed that metals with a low shear modulus exhibit much more metal wear and transfer than those with a greater shear modulus. Furthermore, the more chemically active the metal, the greater the metal wear and transfer to the ceramic.

Table 1 summarizes the type of metal transfer to single-crystal SiC that was observed after multipass sliding. Generally, the metals at the bottom of table 1 had a greater shear modulus and less chemical affinity for Si and C. Therefore, those metals exhibited less wear and transferred less metal to the SiC.

Note that sometimes the strong adhesion and high friction between the metal and ceramic can produce local damages to the ceramic surface if that surface contains imperfections such as microcracks or voids (3).

bond strength per unit area is weak, but that does not mean that a low interfacial bond strength per unit area gives a mechanically weak interface in the real area of contact between the metal and ceramic surfaces.

The ductility of the metal influences the real area of contact and, accordingly, the adhesion and friction at the metal-ceramic interface. Ceramics such as Si_3N_4 and SiC, unlike metals, are not considered to be ductile; these materials behave in a ductile manner only when subjected to high compressive stresses. Because of the marked difference in the ductilities of ceramics and metals, solid-state contact between the two materials can result in considerable plastic deformation of the softer metal. The real areas of contact, then, for such couples must be calculated from the experimentally measured Vickers hardness values of various metals. In this calculation the yield pressure of the surface asperities on the metal is assumed to be approximately the same as that of the bulk metal. Furthermore, no consideration is given to the growth of the real area of contact, known as junction growth, under both the normal and shear (tangential) stresses acting at the interface. The real area of contact (A) is simply determined from the ratio of normal load to hardness. The calculated value of A is strongly dependent on the shear modulus of the metal (see Fig. 6),

TABLE 1.—METALS TRANSFERRED TO SILICON CARBIDE (0001) SURFACES AS A RESULT OF 10 PASSES SLIDING IN ULTRAHIGH VACUUM

Metal	Form (size) of metal transferred				Extent of metal transfer	Shear modulus, GPa
	Small particle (submicron)	Piled-up particle (several microns)	Multilayered agglomeration	Large lump particle (several microns)		
Al	Yes	Yes	Yes	No	Most	27
Zr	Yes	Yes	Yes	No		34
Ti	Yes	Yes	Yes	No		39
Ni	Yes	Yes	No	No		75
Co	Yes	Yes	No	No		76
Fe	Yes	Yes	No	No		81
Cr	Yes	Yes	No	No		117
Rh	Yes	No	No	Yes		147
W	Yes	No	No	Yes		150
Re	Yes	No	No	Yes	Least	180

5. ROLE OF BASIC PROPERTIES IN FRICTION AND WEAR

All the clean metal-ceramic couples, including the metal-diamond couples, exhibited a correlation between the surface and bulk properties of the metal (e.g., its Young's and shear moduli, its bond strength, and the chemistry of the contacting materials) and the adhesion, friction, and wear behavior of the metal. All of the following decrease with an increase in the Young's modulus and the shear modulus of the metal or with a decrease in the chemical activity of the metal: adhesion, coefficient of friction, metal wear, and metal transfer to the ceramic. Perhaps the metal's bulk properties depend on the magnitude of its surface properties. It is interesting, then, to consider the role that the metal's basic surface and bulk properties, as found in the literature (such as its surface energy per unit area (γ) and its ductility), play in the adhesion, friction, wear, and transfer in metal-ceramic couples.

The surface energy per unit area of the metal (γ) is directly related to the interfacial bond strength per unit area at the metal-ceramic interface (7,12). In Fig. 5, the γ values suggested by Tyson (13) and Miedema (14) for various metals at room temperature are presented as a function of the shear modulus of the metal. As γ increases, so does the shear modulus. A comparison with Figs. 2 and 3 shows γ (the surface or bond energy) behaves in the opposite manner from the coefficient of friction, which decreases with an increase in γ. Obviously, γ alone does not explain the friction trend shown in Figs. 2 and 3. Certainly, if γ is low, the interfacial

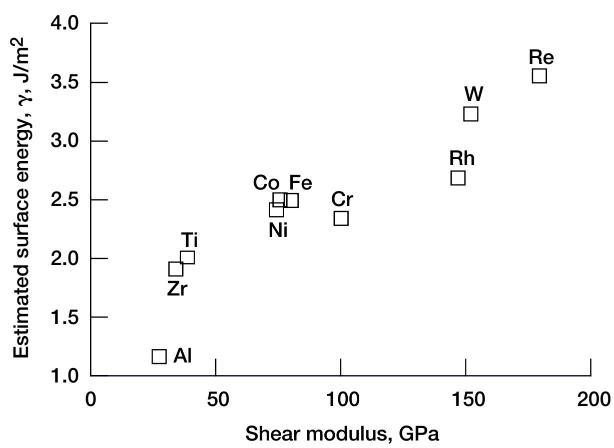

Fig. 5 Estimated surface energy values for various metals as a function of shear modulus of metal.

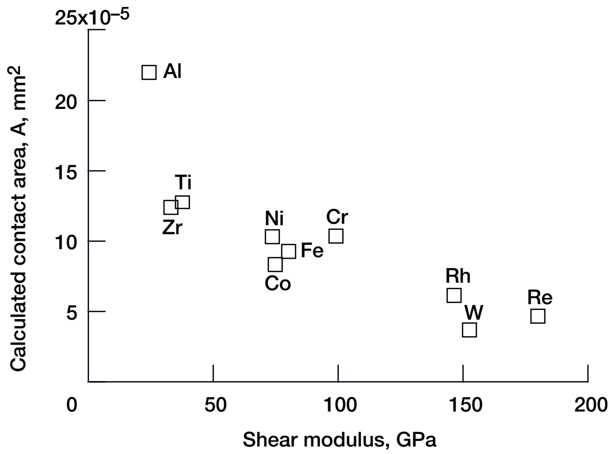

Fig. 6 Calculated areas of contact for various metals as a function of shear modulus of metal.

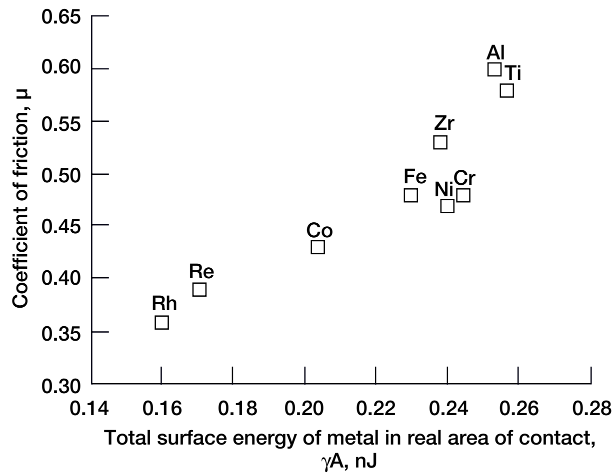

Fig. 8 Coefficient of friction for various metals in contact with SiC (0001) surface in ultrahigh vacuum as function of total surface energy of metal in real area of contact.

decreasing as the shear modulus of the metal increases. The real area of contact A obviously behaves in the same way as the coefficient of friction (see Figs. 2, 3, and 6).

The total surface energy of the metal in the real area of contact is the product of the surface energy per unit area (γ) and the real area of contact (A). It, too, decreases as the shear modulus of the metal increases. This relationship is brought out clearly in Fig.7, which shows γA plotted against the shear modulus of the metal.

A comparison of Fig. 7 with Figs. 2 and 3 shows that γA is associated with tribological behavior; the higher the value of γA, the greater the adhesion and the coefficient of friction. In addition, Fig. 8 clearly shows that the coefficient of friction for metal-silicon carbide (0001) couples increases as γA increases. A comparison of table 1 with Fig. 7 indicates that γA is also related to the wear and transfer of the metal to the ceramic (i.e., SiC); the higher the value of γA, the greater the metal wear and transfer.

The evidence from the adhesion and friction experiments reported herein points to the establishment of strong interfacial bonds in the real area of contact when clean metal-ceramic surfaces are brought into contact.

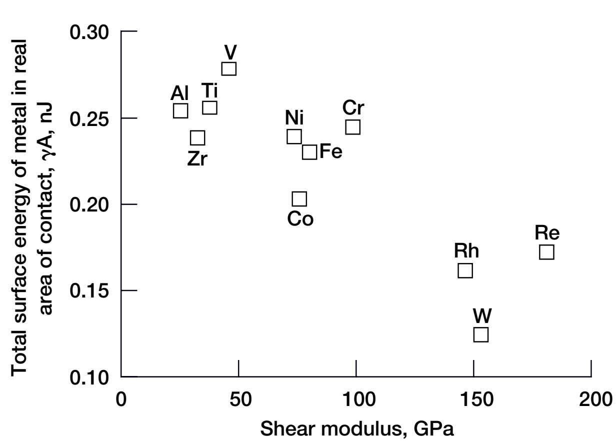

Fig. 7 Total surface energy of metal in real area of contact as function of shear modulus of metal.

6. CONCLUDING REMARKS

When a clean metal was brought into contact with a clean, harder ceramic in ultrahigh vacuum, strong bonds were formed between the two materials. The coefficient of friction for clean surfaces of metal-ceramic couples, which reflects interfacial adhesion, was found to correlate with the total surface energy of the metal in the real area of contact (i.e., the product of surface energy per unit area of the metal and the real area of contact). The coefficient of friction increased as the total surface energy of the metal increased.

The interfacial bond between the metal and ceramic surfaces was generally stronger than the cohesive bond in the metal. Thus, fracture of the cohesive bonds in the metal resulted when shearing occurred. The strength of the interfacial bonds and the shearing fracture of the metal were the main causes of the observed wear and the transfer of the metal to the ceramic. The total surface energy of the metal in the real area of contact was also associated with the wear and transfer of the metal at the metal-ceramic interface: the higher the value of the total surface energy of the metal, the greater the wear and transfer of the metal.

All of the following are related to the Young's or shear modulus of the metal: adhesion, coefficient of friction, wear and transfer of the metal, surface energy per unit area of the metal, the real area of contact, and the total surface energy of the metal in the real area of contact. With the exception of surface energy per unit area of the metal, all of these decrease with an increase in the Young's or the shear modulus of the metal. Only the surface energy (i.e., bond energy) per unit area of the metal increases with an increase in the Young's or the shear modulus.

As a practical matter, an understanding of the behavior of clean surfaces of metal-ceramic couples is relevant to the problem of forming strong bonds between metal and ceramic surfaces.

7. REFERENCES

(1) Buckley, D.H., *Surface Effects in Adhesion, Friction, Wear, and Lubrication,* Tribology Series, Vol. 5, Elsevier (1981) 631.

(2) Miyoshi, K., Advances in engineering tribology, *Proceedings of the First Int. Symp. on Ind. Tribol.,* Y-W Chung and H.S. Cheng, eds., STLE Sp-31, STLE (1991) 3–12.

(3) Miyoshi, K., Uses of AES and XPS in adhesion, friction, and wear studies, *Surface Diagnostics in Tribology,* K. Miyoshi and Y-W. Chung, eds., World Scientific Publishing Co., Inc., (1993) 93–134.

(4) Miyoshi, K. and Buckley, D.H., Properties of ferrites important to their friction and wear behavior, *Tribology and Mechanics of Magnetic Storage Systems,* ASLE SP-16, B. Bhushan, ed., ASLE (1984) 13–20.

(5) Miyoshi, K., Maeda, C., and Masuo, R., Development of a torsion balance for adhesion measurements, *Proc. 11th Triennial World Congr. of Int. Measurement Confed. (IMEKO XI),* Instr. Soc. Am. (1988) 233–248.

(6) Miyoshi, K., Design, development, and applications of novel techniques for studying surface mechanical properties, *Proc. Mat. Res. Soc. Symp.,* Vol. 153, ACS (1989) 321–330.

(7) Tabor, D., Status and direction of tribology as a science in the 80's—understanding and prediction, *New Directions in Lubrication, Materials, Wear and Surface Interactions: Tribology in the 80's*, W.R. Loomis, ed., Noyes Publications, (1985) 1–17.

(8) Georges, J.M., ed., *Microscopic Aspects of Adhesion and Lubrication:Proceedings of the 34th International Meeting of the Societe de Chemie Physique*, Elsevier, (1982).

(9) Pepper, S.V., Shear strength of metal-sapphire contacts, *J. Appl. Phys.* **47**, Mar. (1976) 801–808.

(10) Pauling, L., A resonating valence bond theory of metals and intermetallic compounds, *Proc. Roy. Soc., Ser. A,* **196** (1949) 343–362.

(11) Gschneidner, K.A. Jr., Physical properties and interrelationships of metallic and semimetallic elements, *Solid State Physics, Advances in Research and Applications,* vol. 16, F. Seitz and D. Turnbull, eds., Academic Press (1964) 275–426.

(12) Rabinowicz, E., *Friction and Wear of Materials,* Wiley, New York (1965).

(13) Tyson, W.R., Surface energies of solid state metals, *Can. Metall. Q.* **14** (1975) 307–314.

(14) Miedema, A.R., Surface energies of solid metals, *Z. Metallkd.* **69** (1978) 287–292.

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