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Properties of Ferrites Important to Their Friction and Wear Behavior

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FRICTION AND WEAR BEHAVIOR

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ABSTRACT

This paper reviews environmental, chemical and crystallographical effects on the fundamental nature of friction and wear of the ferrites in contact with metals, magnetic tapes and themselves. The removal of adsorbed films from the surfaces of ferrites results in very strong interfacial adhesion and high friction in ferrite-to-metal and ferrite-to-magnetic tape contacts. The metal-ferrite bond at the interface is primarily a chemical bond between the metal atoms and the large oxygen anions in the ferrite surface, and the strength of these bonds is related to the oxygen-to-metal bond strength in the metal oxide. The more active the metal, the higher is the coefficient of friction. Not only under adhesive conditions, but also under abrasive conditions the friction and wear properties of ferrites are related to the crystallographic orientation. With ferrite-to-ferrite contact the mating of highest atomic density (most closely packed) direction on matched crystallographic planes, that is, <110> directions on {110} planes, results in the lowest coefficient of friction. The mating of higher density directions and planes results in lower coefficient of friction. Under abrasive conditions the anisotropic friction of ferrites do not correlate with the hardness, while anisotropic wear is inversely proportion to the hardness of wear surface on the abraded ferrites.

INTRODUCTION

In most devices of magnetic recording and playback, recording is conducted with a magnetic head (slider) in sliding or intermittent contact with a

magnetic medium. Typical magnetic head materials are either the ferrites or laminated metallic variety. The present authors have particularly been interested in the ferrites such as Mn-Zn and Ni-Zn mixed ferrites. Mn-Zn ferrites have been used for videoand audio-tape recorders, while Ni-Zn ferrites have been used for computer-memory systems, such as magnetic-recording-disk files. The most common medium is tape and disk, in which a suspension of magnetic powder in a binder is coated on a flexible backing (substrate) used for strength.

A small amount of wear of the magnetic head and medium may render the recording process unreliable. The magnetic head and medium therefore must have good wear resistance and low friction. The difficulty with tribological studies and understanding in practical situations of magnetic recording and playback devices is that the conditions at and below the sliding interface are very complex and it involves the effects of the topographical, physical, mechanical, chemical and crystallographical nature of materials.

The objective of this paper is to discuss the fundamental nature of friction and wear of the ferrites in contact with metals, magnetic tapes and themselves with respect to environmental, chemical and crystallographical effects.

BACKGROUND: WEAR OF FERRITES WITH MAGNETIC MEDIA

Magnetic tapes normally consist of $\gamma - Fe_2O_3$ or CrO_2 powder (small particles 1 μm or less in size) held in a polymeric binder, as typically presented in Fig. 1. Composed largely of oxide particles, the magnetic layer bears a certain resemblance to emery, a familiar abrasive.

The sliding of magnetic tape on a ferrite generates abrasion. Figure 2 presents electron micrograph and diffraction pattern of the {110} plane of a Mn-Zn ferrite simulated head sliding against the magnetic tape shown in Fig. 1. The experimental apparatuses and procedure are described in Ref. 1.

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The wear surface of ferrite revealed a large number of plastically deformed grooves formed primarily by the plowing actions of oxide particles held in the magnetic tape. The grooves are formed in the sliding direction of the head. The width of the grooves formed on the wear surface was almost the same as the diameter of oxide particles (less than 0.1 μm). The electron diffraction pattern of the wear surface (fig. 2(a)) indicates that the surficial layer was nearly amorphous, but contained fine grains of approximately a few nanometers in diameter. The surface after etching at a depth of a few hundreds angstroms from the wear surface had an enlarged streak spot pattern, as shown in Fig. 2(b). The streaking indicates the imposition of a large amount of plastic deformation. The amount of line defects can lead and give rise to streaking in diffraction patterns.

The surface etched to 0.3 μm in depth had a sharp spot pattern without streaking. Further, the surface etched to a depth of 0.6 μm from the wear surface had Kikuchi lines consisting of pairs of black and white parallel lines, which are an indication of the bulk crystalline structure of the ferrite specimen.

The abrasiveness of a magnetic tape containing needlelike ferric oxide $\gamma - Fe_2O_3$ particles (0.7-μm long and 0.07 μm diameter) was almost the same as that for lapping-tape, which is an abrasive impregnated tape containing 1.5-μm silicon carbide abrasives (mesh no. 6000), as presented in Fig. 3. Note that lapping-tapes normally use silicon carbide (SiC), aluminum oxide (Al_2O_3) or chromium oxide (CrO_2) powder of various grit sized held in a nonmetallic binder [1].

The lapping-tapes are very similar to the magnetic tapes and both tapes are very flexible. The specific wear rates shown in Fig. 3 were strongly dependent upon abrasive grit size. The specific wear rate and the coefficient

of friction is variable and depends on the kind of abrasive grit. The specific wear rates for grits of the same kind decreased rapidly with a decrease in grit size. A decrease in the specific wear rate for lapping-tapes with SiC was almost the same as that for lapping with tapes containing Al_2O_3 with the exception of 1.5 μm SiC.

Another interesting point to be observed from Fig. 3 is that, in spite of the nearly same grit size, of 7.1 μm for Al_2O_3 and 6.3 μm for SiC, the abrasiveness of Al_2O_3 is approximately five times higher than that of the SiC. This may be related to the shape of particles and their distribution on the tape as well as the degree of enclosure of the particles by the binder.

Thus, abrasion can arise when a magnetic tape slides against a ferrite surface. The abrasion and groove formation on the ferrite surface strongly depends on the nature of the surface, the tribological properties, bulk properties of both the ferrite and the tape, and on the environment.

ADSORBATE AND ENVIRONMENTAL EFFECTS

Ferrite-to-Metal Contact

The two apparatuses which were used in sliding friction experiments both used a pin on a flat configuration. The first apparatus, which is capable of measuring adhesion, load, and friction, was mounted in an ultrahigh vacuum system. The vacuum system contained tools for surface analysis, XPS and AES. An ion gun was used for cleaning ferrite specimens. The second apparatus consists of a system capable of measuring friction in dry argon, or in dry nitrogen. The entire apparatus was housed in a plastic box, which was filled with dry argon, or dry nitrogen. The details of the sliding friction experiments are described in Refs. 2 and 3.

With oxide ceramic materials such as Mn-Zn and Ni-Zn ferrite adsorbates are present on the surface from the environment, and these include water vapor

and carbons, as typically shown in Fig. 4(a). With metals, in addition to the presence of adsorbate films, beneath this layer of adsorbate is generally a layer of metal oxide [4].

The adsorbed films on ferrites and metals as well as oxides on metals can generally be removed by sputtering or heating [2,4]. For example, in Fig. 4(a) the adsorbates have disappeared form the spectrum taken after sputter-cleaning. In addition to oxygen and iron, which are associated with the composition of Mn-Zn ferrite, the XPS peaks obtained from the sputter cleaned surface indicate manganese and zinc, but there is no adsorbate.

The adsorbates play a very large role in mechanical and chemical behavior of ferrite surfaces in tribological systems. Typical friction results with single crystal Mn-Zn ferrite-to-metal couples are presented in Fig. 4(b). The marked difference in friction for the two environments, i.e. in vacuum and in argon at atmospheric pressure indicates the effects of adsorbate and environ-ment on friction properties. The removal of adsorbed films from the surface of ferrites as well as that of adsorbed films and oxide layers from metals results in very strong interfacial adhesion and high friction.

The data obtained from the experiments in vacuum are to be anticipated from chemical interactions and the important role they play in the friction of clean ferrite-to-metal couples. This subject is explained in detail in the following section.

The coefficients of friction for various metals sliding on ferrites in argon atmosphere were all nearly 0.1 to 0.2. The chemical activity or inac-tivity of metal does not appear to play a role as to friction in argon. A prerequisite for this sameness in friction is that the metals form a stable metal oxide, and the environment is responsible for providing the adsorbates on the surface.

Ferrite-to-Magnetic Tape Contact

With polymeric magnetic media, much as with oxide ceramics, the outermost surface layer may not be an oxide as it is in the case of metals. But adsorbates are certainly present on the solid surface, and again they may include water vapor and carbon compounds from the environment [4].

It is extremely difficult to remove adsorbates from the polymeric magnetic tape surface, and no entirely satisfactory cleaning procedure has yet been established for magnetic tape.

Figure 5 presents the coefficients of friction for various as-received tapes in contact with the Ni-Zn ferrites as a function of particle loading (magnetic particle concentration). The experiments were conducted in vacuum and in dry nitrogen at atmospheric pressure. The Ni-Zn ferrite specimens were polished first with Al_2O_3 powder 1 μm in diameter and then rinsed with absolute ethanol before the experiments. But even in vacuum the ferrite specimens were not sputter cleaned.

The as-received tape specimens were used both in dry nitrogen and in vacuum. When tape and ferrite surfaces are placed into contact, the adsorbed layers deform with the materials. The mechanical properties of the adsorbate films markedly depend on the environment.

In vacuum the adsorbate films become disrupted or dislodged. When this occurs, solid-state clean material contact can occur at the sliding interface through the film because of the breakup of these surface films. The basic material properties of the tape become extremely important in adhesion and friction. For example, the coefficient of friction for tape is strongly dependent on the particle loading (magnetic oxide particle concentration in a polymeric binder), as indicated in Fig. 5. The data obtained from the experiments conducted in vacuum reveal that the coefficient of friction decreases

with increasing magnetic particle concentration of the tape surface in the range of 45 to 58 percent, that is, the lowering of the polymeric binder concentration of the tape surface leads to low friction.

In dry nitrogen at atmospheric pressure the adsorbate films remains at the interface. The coefficient of friction, is therefore, independent of the bulk composition of the tape (see the effect of particle loading, in fig. 5).

CHEMICAL EFFECTS

Ferrite-to-Metal Contact

The coefficients of friction for polycrystalline Ni-Zn and Mn-Zn ferrite in contact with metals can be correlated with the free energy of formation of the lowest metal oxides, as shown in Fig. 6. The correlation shown in Fig. 6 clearly indicates that the metal-ferrite bond at the interface is primarily a chemical bond between the metal atoms and the large oxygen anions in the ferrite surface, and the strength of this bond is related to oxygen to metal bond strength in the metal oxide [3].

All metals indicated in Fig. 6 transferred to the surface of the ferrites. In general the less active the metal, the less transfer there is to the ferrite. Titanium, having a much stronger chemical affinity to the elements of the ferrite, exhibited the greatest amount of transfer [2].

The relative chemical activity of the transition metals (metals with partially filled of shells) as a group can be ascertained from their percentage d-bond character, as established by Pauling [5]. The frictional properties of metal-metal and metal-nonmetal contacts have been shown to be related to this character [6-9]. The greater the percentage of d-bond character, the less active is the metal, and the lower is the friction. Conversely, the more active the metal, the higher is the coefficient of friction.

The coefficients of friction for various metals in contact with Ni-Zn ferrites are replotted with solid symbols in Fig. 7 as a function of the d-bond character of the transition metal. Titanium, which is a chemically active metal, exhibits a considerably higher coefficient of friction in contact with ferrite than does rhodium, which is a metal of lesser activity. This result is consistent with the author's earlier studies conducted with single-crystals of SiC, diamond, and Mn-Zn ferrite [7-9].

Figure 7 also presents the coefficient of friction for various metals in contact with the ferrites, in which both metal and ferrite specimens were exposed to O_2 gas (99.99 percent pure). The data reveal a decrease in friction with an increase in d-bond character. The adsorption of oxygen on argon-sputter cleaned metal and ferrite surfaces produces two effects: (1) the metal oxidizes and forms an oxide surface layer, and (2) the oxide layer increases the coefficients of friction for Ni-Zn ferrite-to-metal interface. This result is consistent with that of the Mn-Zn ferrite-to-metal interface. The coefficients of friction with single-crystal Mn-Zn ferrite shown in Fig. 4(b) were lower than those of the hot-pressed polycrystalline Mn-Zn ferrite [3]. This difference in friction may be in accord with effects of crystallographic orientation and grain boundary as well as impurities contained in the crystals.

The oxygen exposures did strengthen the metal-to-ferrite adhesion and increased the friction. The enhanced bond of the metal oxide to ferrite may be due to the formation of complex oxides on establishing contacts [3].

Ferrite-to-Magnetic Medium Contact

Figure 8 presents the coefficients of friction for various tapes in contact with ferrites as a function of particle loading in vacuum. 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). The

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ferrite specimen was then ion-sputter cleaned. The data shown with solid symbols in Fig. 8 presents the coefficients of friction for the tapes sliding against sputter cleaned ferrite pins. Sliding friction experiments were also conducted with ferrite specimens, which were first argon-ion sputter cleaned, exposed to 1000 L oxygen, and then were brought into contact with magnetic tapes in the system reevacuated to a pressure of 30 nPa (10^{-10} torr). The results are presented in Fig. 8 with open symbols.

The data of Fig. 8 reveal that the adsorption of oxygen on tape and on sputter cleaned ferrite surfaces increases the coefficients of friction for ferrite-to-magnetic tape interfaces. The oxygen exposures did strengthen the ferrite-to-tape adhesion and increased friction. The coefficient of friction is also strongly dependent on the particle loading. Again the greater the magnetic particle concentration (particle loading), the lower the coefficient of friction.

CRYSTALLOGRAPHICAL EFFECTS

Under Adhesive Conditions

The anisotropic nature of friction and wear of single-crystal Mn-Zn ferrite surfaces such as {100}, {110}, {111}, and {211} planes in sliding contact with themselves has been examined from consideration of adhesion between the sliding surfaces in vacuum [2]. Typical examples of data obtained are presented in Fig. 9. The coefficients of friction for three matched crystallographic planes in the same and different directions are plotted in Fig. 9. In these experiments the {110} pin (rider) slid on the flat surfaces of the {110}, {111}, and {211} planes in the same <110> crystallographic direction as that of the rider and in dissimilar crystallographic directions. The difference in the coefficients of friction with respect to the mating crystallographic directions are significant.

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The coefficients of friction for the three matched crystallographic planes in dissimilar directions are generally higher than those in the same directions and vary according to the orientation of the surface of the flat. The coefficient of friction is lowest with the {110} plane of the pin parallel to the interface, that is, at an angle of zero to the sliding mating surface. The mating of highest atomic density (most closely packed) direction on matched crystallographic planes, that is, <110> directions on {110} planes, results in the lowest coefficient of friction. The mating of higher density directions and planes generally results in lower coefficient of friction than those in dissimilar directions.

Examination of the wear track on ferrite surfaces after sliding under adhesive condition revealed occasional evidence of cracking and fracture in ferrite and hexagonal and rectangular platelet wear debris on the ferrite surfaces. The cracking and formation of such wear debris particles were primarily due to cleavage of {110} planes on the surface and in the bulk of ferrite [2].

Under Abrasive Conditions

Under abrasive conditions just as under adhesive conditions, the friction and wear properties are related to crystallographic orientation. Abrasion occurs when a hard grit or hard asperity slides on ferrite surfaces. The sliding involves plastic flow and the generation of ferrite wear debris [10]. For example, with a spherical diamond pin on ferrite the sliding action resulted in a permanent groove, with a considerable amount of deformed ferrite piled up along the sides of the groove on the ferrite surface.

The coefficients of friction were measured as function of the crystallographic direction of sliding on the {100}, {110}, {111} and {211} planes of Mn-Zn ferrites for the diamond pin in air atmosphere. The results presented in

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Fig. 10 indicate that the coefficient of friction and hardness are influenced by the crystallographic orientation.

Figure 10(b) also presents the Knoop hardness. The <001> directions on the {100} and {110} planes have the greater hardness, and they are the direction of lower friction for {100} plane, while they are those of higher friction for {110} plane. The <$0\bar{1}1$> direction on the {111} and the <$0\bar{1}1$> on the {211} planes have greater hardness and are the directions of higher friction, when compared with the <$11\bar{2}$> on the {111} planes and the <$\bar{1}11$> on the {211} plane. The anisotropies of friction are as follows:

μ <011> / μ <001> = 1.2 on the {100},

μ <001> / μ <$\bar{1}10$> = 1.2 on the {110},

μ <$1\bar{1}0$> / μ <$11\bar{2}$> = 1.1 on the {111},

and

μ <$0\bar{1}1$> / μ <$\bar{1}11$> = 1.1 on the {211}.

An interesting point of observation from Fig. 10 is that the anisotropies of friction do not correlate with the Knoop hardness. This is due to the complexity of slip systems and cleavage systems in ferrites.

With single-crystal silicon carbide the present authors found that the <$10\bar{1}0$> directions on the based plane of SiC would exhibit the lowest coefficient of friction and greatest hardness. The anisotropies of friction on the {0001}, {$10\bar{1}0$}, and {$11\bar{2}0$} surfaces do inversely correlate with the Knoop hardness. The anisotropic friction and hardness are primarily controlled by the slip system {$10\bar{1}0$} <$11\bar{2}0$> [11].

From the above facts the anisotropic friction and hardness (plastic deformation) of the ferrites are quite unique and complex.

Figure 11 presents wear volume for four crystallographic planes of ferrite {100}, {110}, {111}, and {211} sliding against an abrasive impregnated lapping-

tape, as a function of Vickers hardness of wear surfaces. A modified commercial two-head helical scan video tape recording system was used for wear experiments [1]. The wear is influenced by the crystallographic orientation and Vickers hardness. The wear of the ferrite surfaces was lower in the order {211} > {111} > {100} > {110}. The slip planes (most closely packed planes) of Mn-Zn ferrite {110} exhibits the highest resistance to the abrasion.

Khrushchov and Babichev found that the resistance of metals to abrasive wear are related to their static hardness under two-body conditions, that is, the inverse of the abrasive wear rate is proportional to the hardness for a large number of annealed pure metals [12]. Avient et al. have theoretically and experimentally indicated that the resistance of metals to abrasive wear is inversely proportional to the Vickers hardness of the fully work-hardened surface region on the abraded metal [13]. Similar results have been obtained by Rabinowicz et al. for three-body conditions [14]. In Fig. 11 the wear volume is inversely proportional to the Vickers hardness of the wear surface region on the abraded ferrites.

CONCLUSIONS

The following conclusions are drawn from the presented data herein:

(1) The removal of adsorbed films from the surfaces of ferrites results in very strong interfacial adhesion and high friction in ferrite-to-metal and ferrite-to-magnetic tape contacts.

(2) The metal-ferrite bond at this interface is primarily a chemical bond between the metal atoms and the large oxygen anions in the ferrite surface, and the strength of these bonds is related to the oxygen-to-metal bond strength in the metal oxide.

The coefficient of friction for ferrites in contact with metals is correlated with the free energy of formation of the lowest metal

oxides and the d-bond character of the transition metal. The more active the metal, the higher is the coefficient of friction.

(3) Oxygen exposure did strengthen adhesion and increased friction in the metal-to-ferrite and magnetic tape-to-ferrite contacts.

(4) The coefficient of friction for ferrite in contact with magnetic tape in vacuum is strongly dependent on the particle loading (magnetic particle concentration). The greater the particle loading, the lower the coefficient of friction.

(5) Not only under adhesive conditions, but also under abrasive conditions the friction and wear properties of ferrites are related to the crystallographic orientation.

With ferrite-to-ferrite contact the mating of highest atomic density (most closely packed) direction on matched crystallographic planes, that is, <110> directions on {110} planes, results in the lowest coefficient of friction. The mating of higher density directions and planes results in a lower coefficient of friction.

Under abrasive conditions the anisotropic friction of ferrites do not correlate with the hardness, while anisotropic wear is inversely proportional to the hardness of wear surface on the abraded ferrites.

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(a) Scanning electron micrograph.

—MAGNETIC LAYER
(MAGNETIC OXIDE,
BINDER, AND LUBRICANT)

— BACK FILM

— BACK COATING LAYER
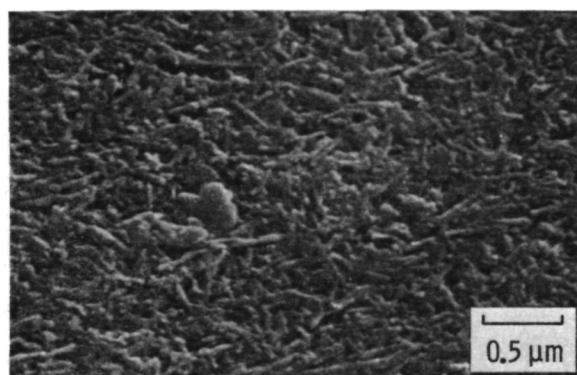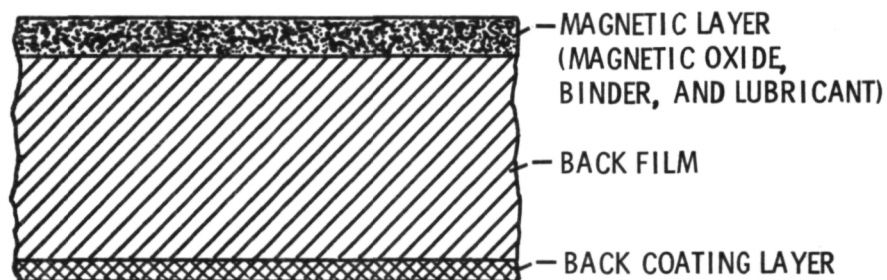
(b) Schematic.

Figure 1. – Scanning electron micrograph and schematic of magnetic tape.
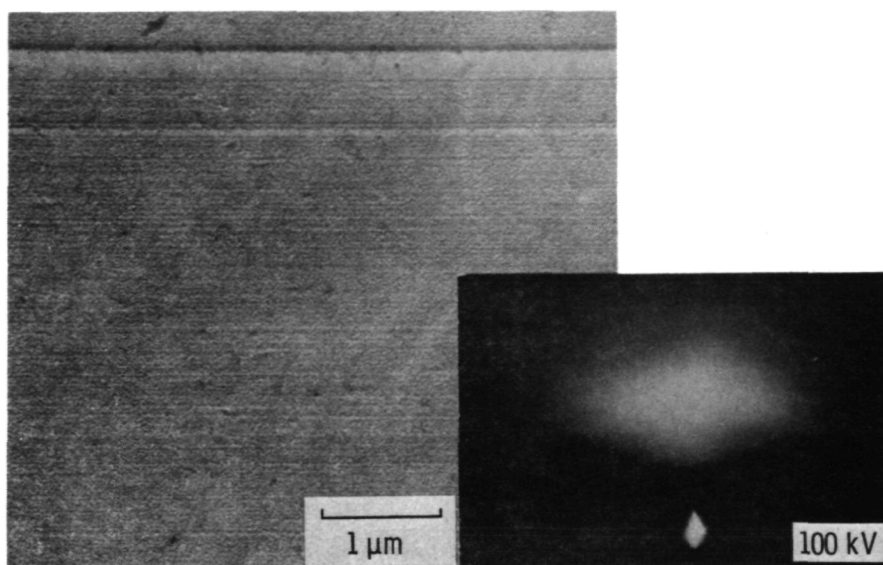
(a) Wear surface.
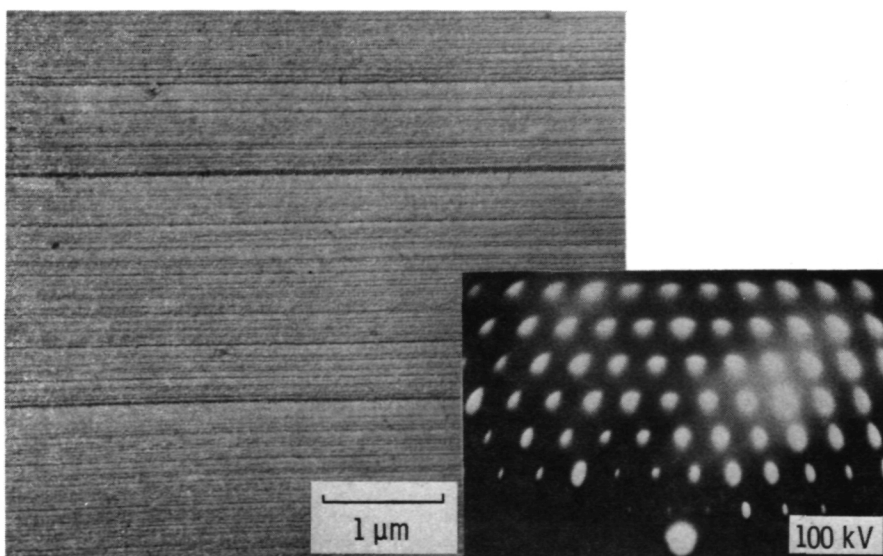
(b) Etched surface (etching depth: few hundreds Å).

Figure 2. - Wear surface of Mn-Zn ferrite in sliding contact with a ɣFe$_2$O$_3$ magnetic tape. Sliding surface, {110}; sliding direction, <110>; sliding velocity, 11 m/s; laboratory air; room temperature.
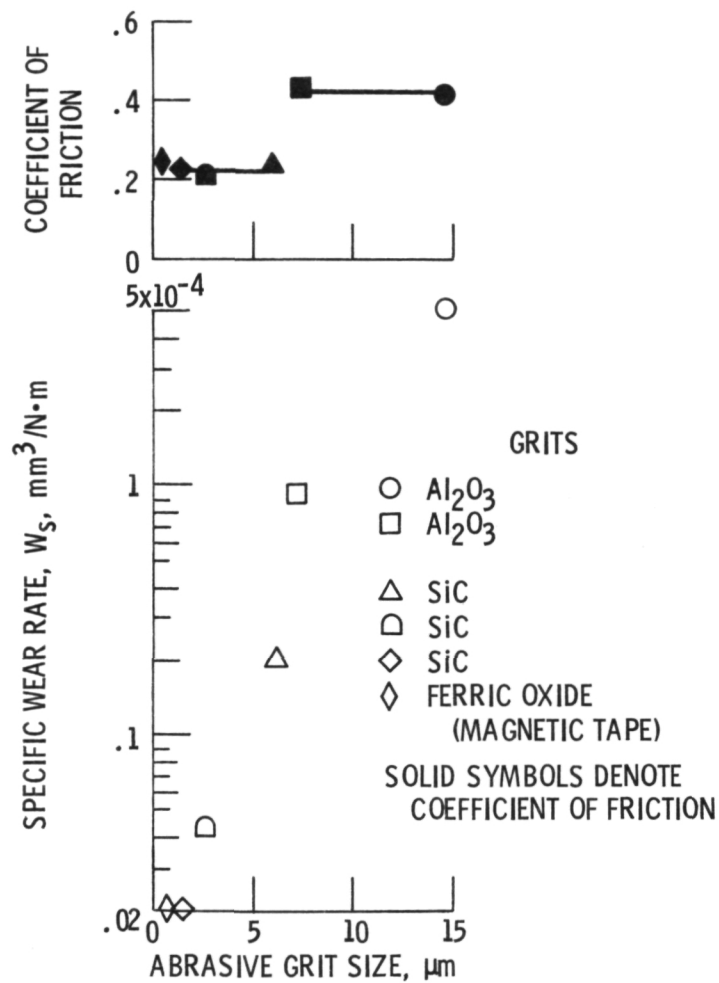
Figure 3. – Specific wear rates (abrasiveness) and coefficients of friction for various lapping tapes in lapping process of drum ferrite specimen. Initial tape tension, 2N; rotation speed of drum, 0.5 m/s; tape speed, 0.02 m/s; wrap angle, $\pi/2$; laboratory air; room temperature.
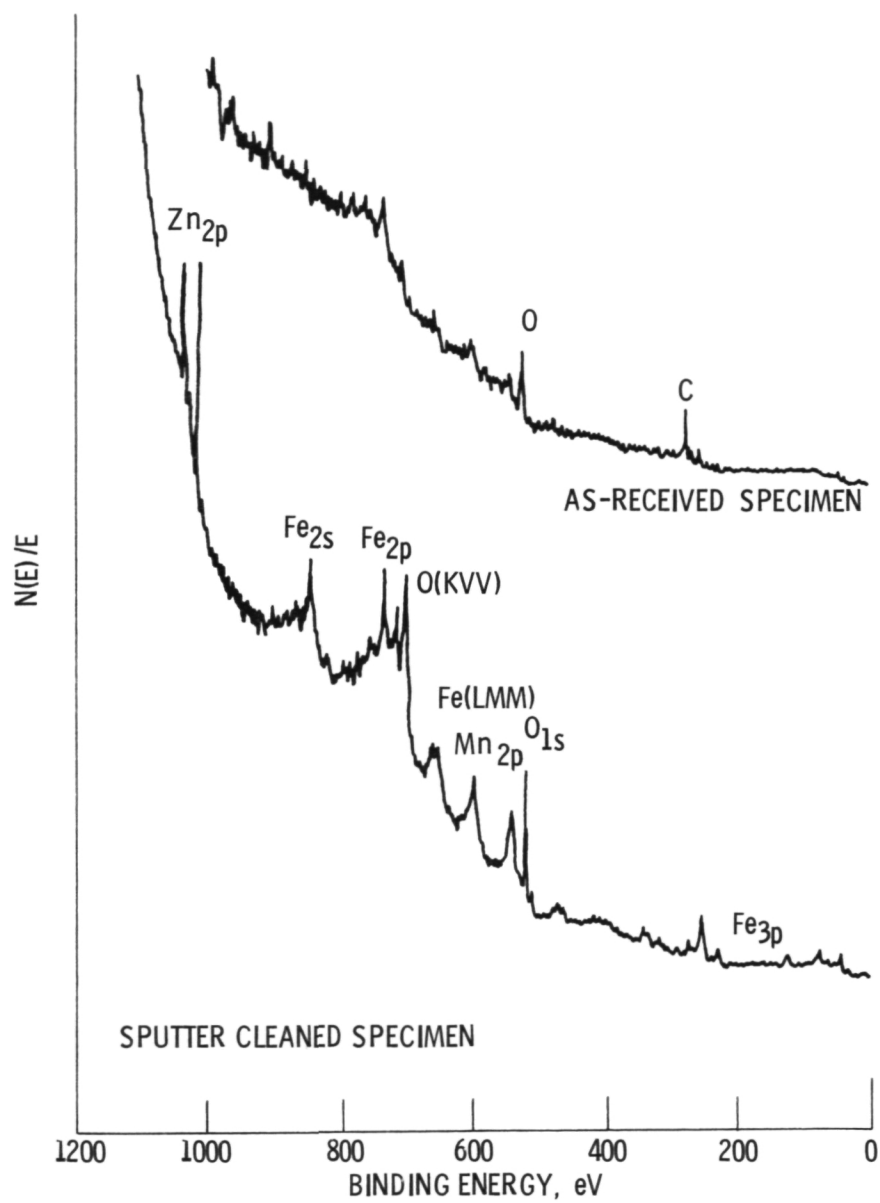
(a) XPS-survey spectra of the Mn-Zn-ferrite surfaces.

Figure 4. - Surface chemistry and friction of Mn-Zn ferrite.
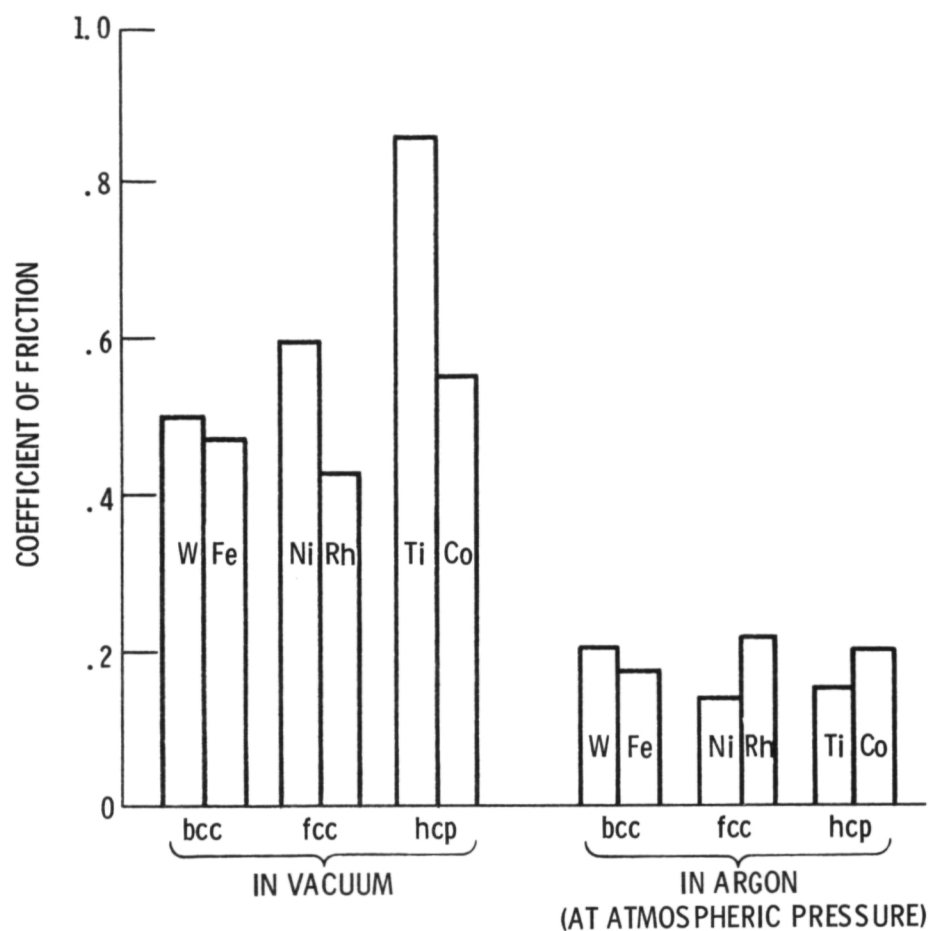
(b) Coefficient of friction as a function of the percentage of d-bond character of various metals in sliding contact with Mn-Zn-ferrite (110) surface in vacuum (30 nPa) and in argon at atmospheric pressure. Sliding velocity, 3 mm/min: load, 0.05 to 0.5 N; room temperature.
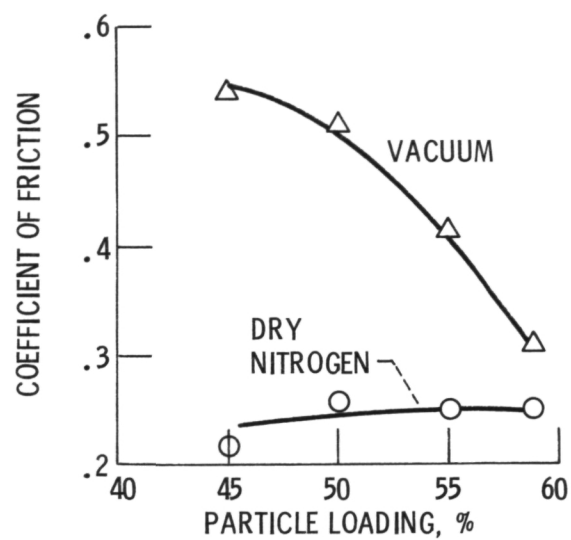
Figure 4. - Concluded.

Figure 5. - Coefficients of friction for various magnetic tapes in contact with Ni-Zn ferrite as a function of the particle loading (magnetic particle concentration). Single-pass sliding; sliding velocity, 3 mm/min; load, 0.5 N; dry nitrogen at atmospheric pressure and vacuum (1 μPa), room temperature.
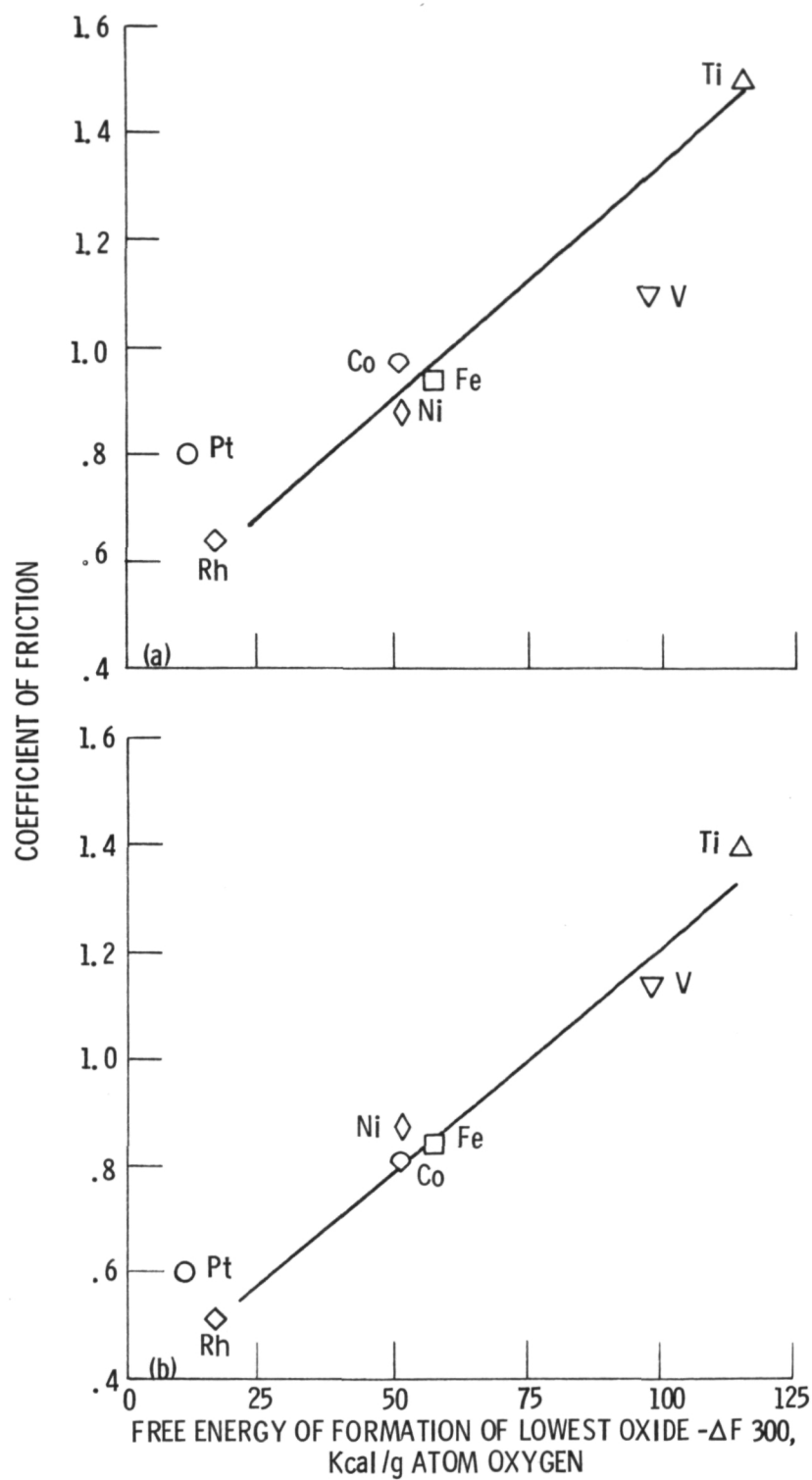
Figure 6. - Coefficients of friction for various metals in contact with (a) Ni-Zn and (b) Mn-Zn ferrites as a function of the free energy of formation of the lowest oxide. Single-pass sliding; sliding velocity, 3 mm/min; load, 0.05 to 0.2 N; vacuum, 30 nPa; room temperature.
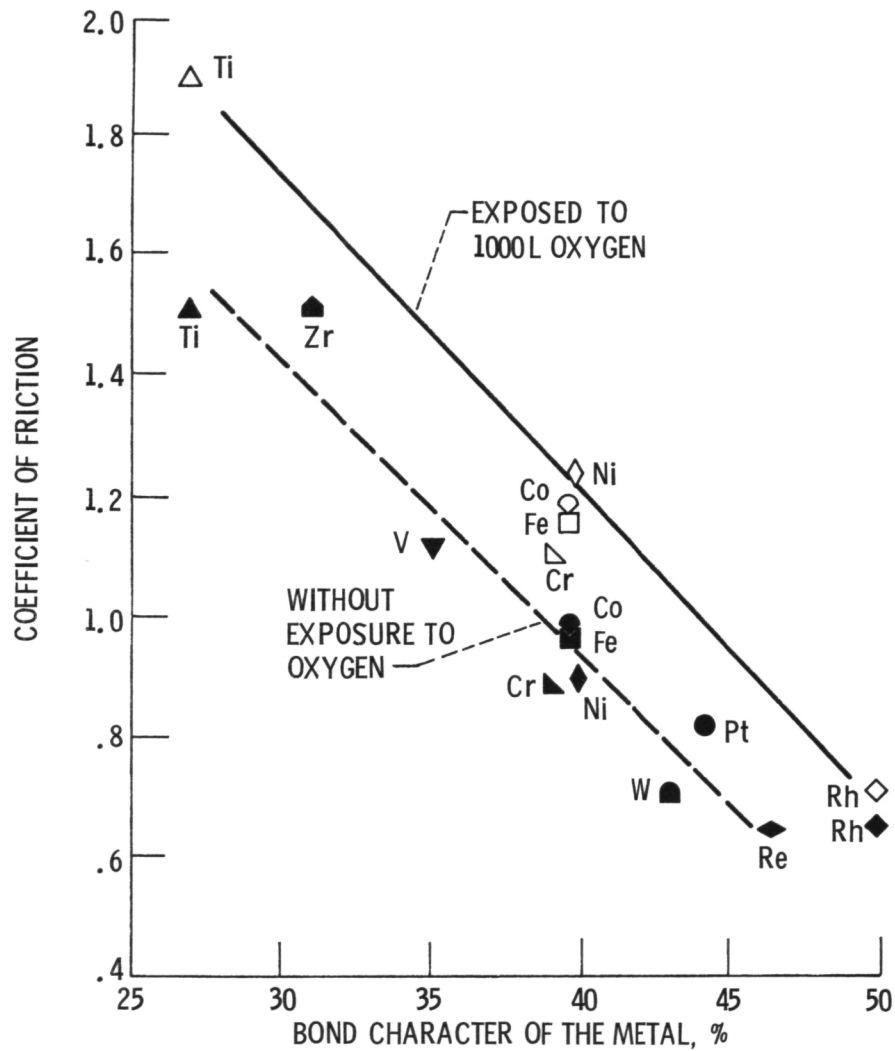
Figure 7. – Effect of adsorbed oxygen on the friction for various metals in contact with Ni-Zn ferrite. Exposure, 1000L of oxygen gas; sliding velocity, 3 mm/min; load, 0.05 to 0.2 N; vacuum, 30 nPa; room temperature.
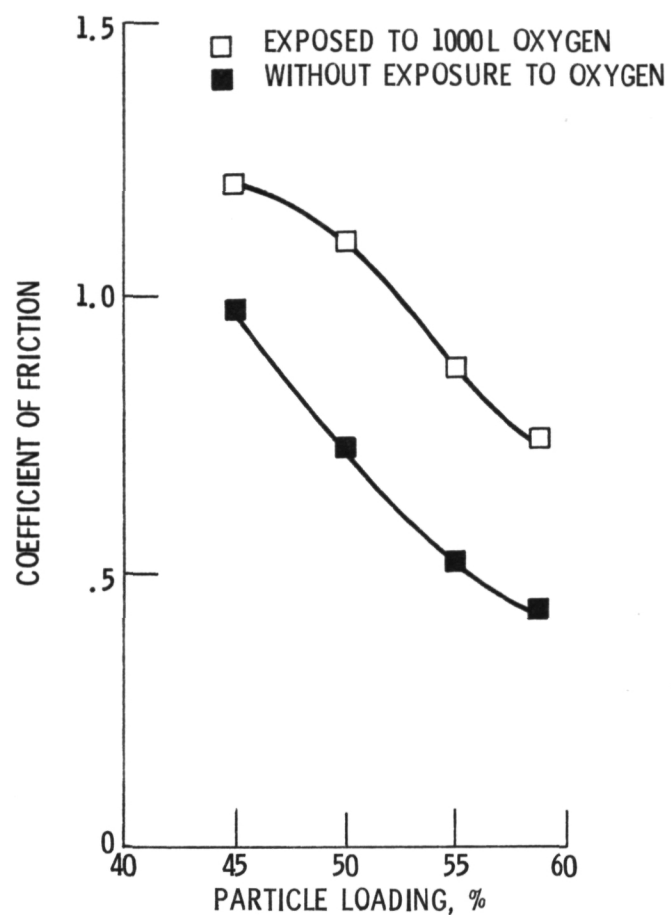
Figure 8. – Coefficients of friction for
various magnetic tapes in contact
with Ni-Zn ferrite as a function of
the particle loading (magnetic particle
concentration). Effect of adsorbed
oxygen on friction for various tapes.
Exposure, 1000 L of oxygen gas; slid-
ing velocity, 3 mm/min; load, 0.5 N;
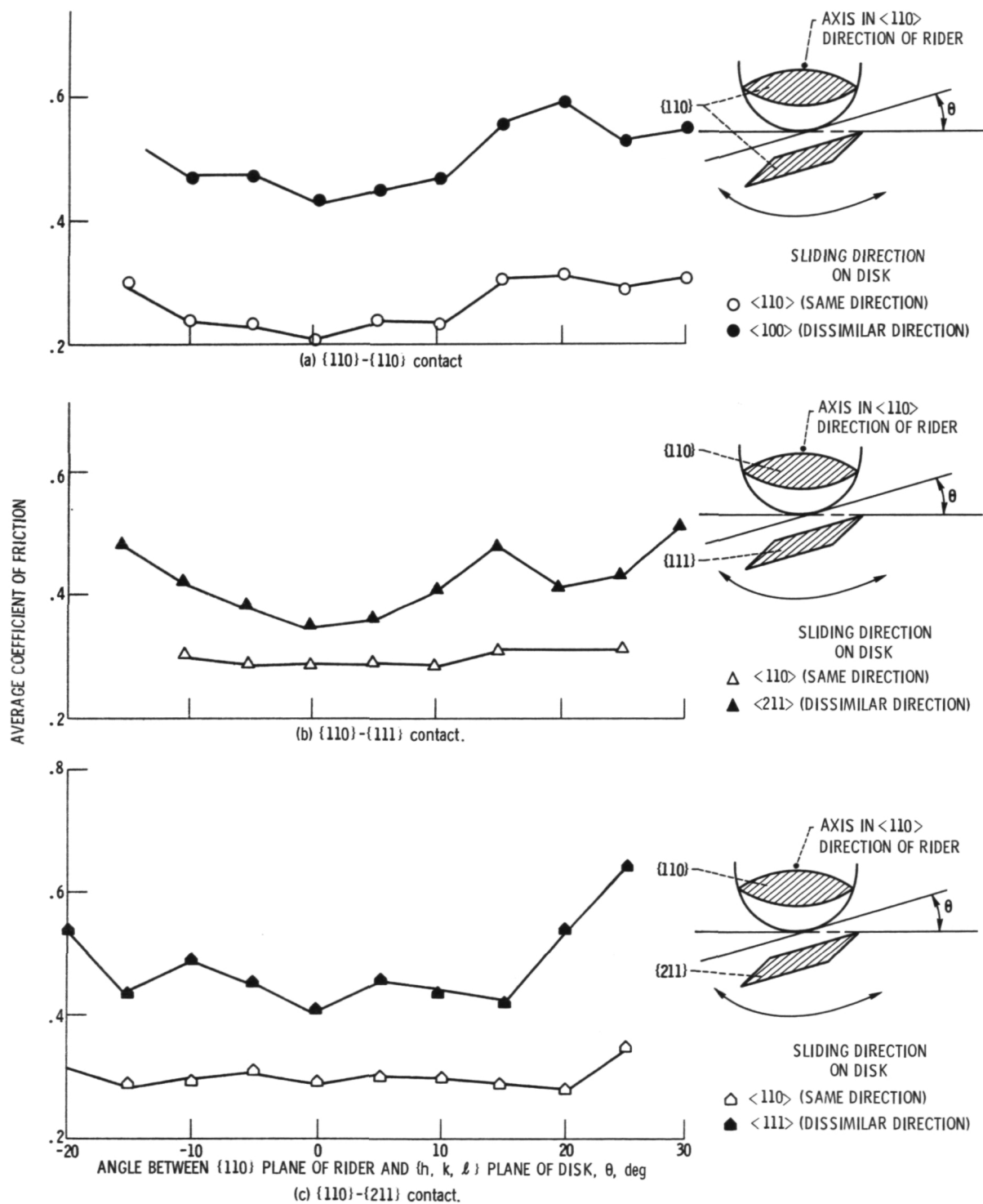vacuum, 30 nPa; room temperature.

Figure 9. – Coefficients of friction for mating the same and different rider and disk directions (sliding direction of the rider, <110>; single-pass sliding; manganese-zinc ferrite riders and disks); single-pass sliding; sliding velocity, 3 mm/min; load, 0.05 to 0.5 N; vacuum, 30 nPa; room temperature.
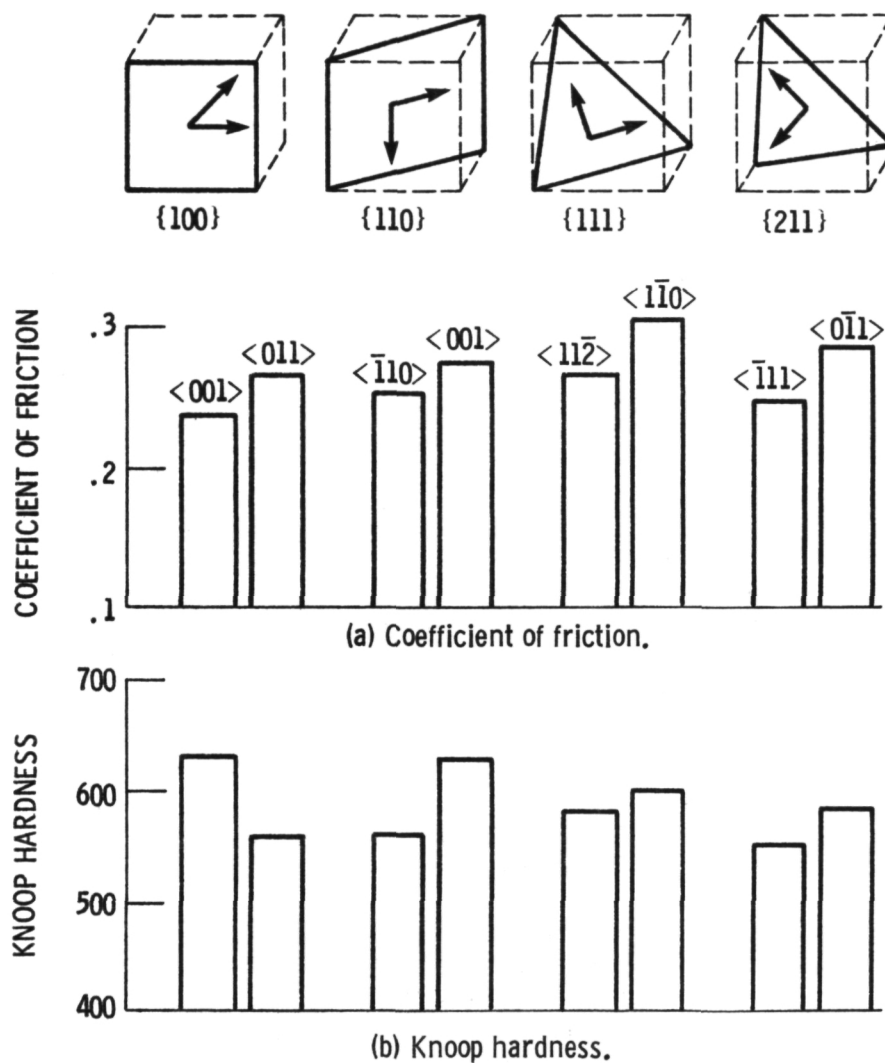
Figure 10. - Anisotropies on {100}, {110}, {111}, and {211} surfaces of Mn-Zn ferrite: (a) coefficient of friction, single pass sliding of a diamond pin (20μm-radius), sliding velocity, 3 mm/min; load, 1 N; laboratory air; room temperature; (b) Knoop hardness; load, 3 N;laboratory air; room temperature.
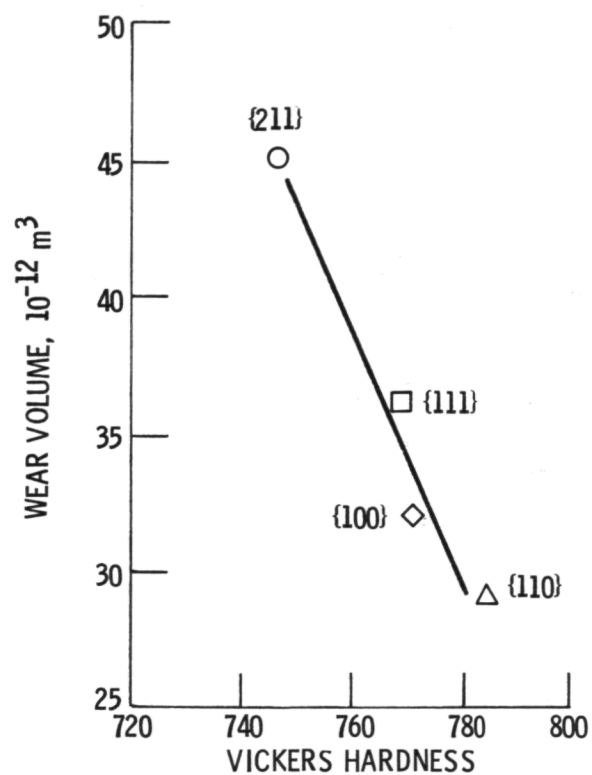
Figure 11. – Anisotropy of wear for {100}, {110}, {111}, and {211} planes of Mn–Zn ferrite as a function of Vickers hardness. Sliding direction, <110>; lapping-tape, Al_2O_3 number 2000; sliding velocity, 11 m/s; laboratory air; room temperature; Vickers hardness measuring load, 0.25 N.

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16. Abstract

This paper reviews environmental, chemical and crystallographical effects on the fundamental nature of friction and wear of the ferrites in contact with metals, magnetic tapes and themselves. The removal of adsorbed films from the surfaces of ferrites results in very strong interfacial adhesion and high friction in ferrite-to-metal and ferrite-to-magnetic tape contacts. The metal-ferrite bond at the interface is primarily a chemical bond between the metal atoms and the large oxygen anions in the ferrite surface, and the strength of these bonds is related to the oxygen-to-metal bond strength in the metal oxide. The more active the metal, the higher is the coefficient of friction. Not only under adhesive conditions, but also under abrasive conditions the friction and wear properties of ferrites are related to the crystallographic orientation. With ferrite-to-ferrite contact the mating of highest atomic density (most closely packed) direction on matched crystallographic planes, that is, $\langle 110 \rangle$ directions on $\{110\}$ planes, results in the lowest coefficient of friction. The mating of higher density directions and planes results in lower coefficient of friction. Under abrasive conditions the anisotropic friction of ferrites do not correlate with the hardness, while anisotropic wear is inversely proportion to the hardness of wear surface on the abraded ferrites.

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