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FRICTION AND WEAR OF SINGLE-CRYSTAL MANGANESE-ZINC FERRITE

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ABSTRACT

Sliding friction experiments were conducted with single-crystal manganese-zinc ferrite in contact with itself and with transition metals. Results indicate matching highest atomic density directions ((110)) on matched crystallographic planes exhibit the lowest coefficient of friction indicating that direction is important in the friction behavior of ferrite. Matched parallel high atomic density planes and crystallographic directions at the interface exhibit low coefficients of friction. The coefficients of friction for ferrite in contact with various metals are related to the relative chemical activity of these metals. The more active the metal, the higher the coefficient of friction. Cracking and the formation of hexagonal- and rectangular-shaped platelet wear debris due to cleavages of (110) planes are observed on the ferrite surfaces as a result of eliding.

INTRODUCTION

Manganese-zinc ferrite is becoming increasingly important as a typical magnetic material used for highly developed magnetic recording devices, e.g., video tape recorders. Most of the high recording-density devices are the system in which the recording and playback are conducted with a magnetic head in sliding contact with a magnetic tape. Therefore, the magnetic head and tape are required to have good wear resistance and low friction.

The manganese-zinc ferrite is used practically in both single-crystal and polycrystalline form. The composition and hardness data on manganese-zinc ferrite are presented in table I. The spinel crystal structure of manganese-zinc ferrite is illustrated in figure 1. The crystal is that of spinals in which the oxygen ions are in a nearly close-packed cubic array. In the unit cell, which contains 32 oxygen ions, there are 32 octahedral sites and 64 tetrahedral sites; of those, 15 of the octahedral sites are filled with divalent (Mn $^{2+}$, Zn$^{2+}$, Fe$^{2+}$) and trivalent (Fe$^{3+}$) ions which are equally divided, and 8 of the tetrahedral sites are filled with trivalent ions (Fe$^{3+}$). All of the metals were polycrystalline. The titanium was 99.97 percent pure, and all the other metals were 99.99 percent pure, as presented in table II.

EXPERIMENTAL APPARATUS AND PROCEDURE

Apparatus

The experiments were conducted in a vacuum chamber. The vacuum chamber contains a system capable of measuring adhesion, load and friction as well as providing Auger surface analysis. The mechanism for applying load and measuring adhesion and friction is shown in figure 2. A gimbal-mounted beam projected into the vacuum system. The beam contained two flats.
The surfaces of the single-crystal manganese-zinc ferrite and the polycrystalline metal pin specimens (riders) were hemispherical and were polished with approximately 3-μm-diameter diamond powder and then 1-μm-diameter aluminum oxide (Al₂O₃) powder. The orientation of the ferrite riders are shown in figure 3(a) and are within ±10 of the indicated orientation. For the (100)-orientation at the interface, the (100) plane of the rider specimen was oriented such that it was nearly parallel to the sliding interface. For the (110)- and (111)-orientations, rider specimens were also oriented as indicated in figure 3(a). The radius of curvature of the ferrite and metal riders was 0.79 mm (1/32 in.).

The surfaces of disk specimen of the single-crystal manganese-zinc ferrite were also polished with 3-μm-diameter diamond powder and then 1-μm-diameter aluminum oxide powder. The orientation of the ferrite disks are shown in figure 3(b) and are within ±10 of the indicated orientation. For the (100)-orientation at the interface, the (100) plane of the disk specimen was oriented such that it was nearly parallel to the sliding interface. For the other, the (110)-, (111)-, and (211)-orientations, disk specimens were also oriented as indicated in figure 3(b). The method used for determining the orientation of single-crystal was the back-reflection Laue technique.

Both disk and riders of ferrite were also chemically polished with hydrochloric acid at 50% C for 2 minutes after mechanically polishing as mentioned above in order to establish the effect of the deformed layer of the surface on friction behavior.

Procedure

The surfaces of the disk and rider specimens were rinsed with absolute ethyl alcohol before the experiment.

For the experiments in vacuum, the specimens were placed in the vacuum chamber and the system evacuated and baked out to achieve a pressure of 1.3x10⁻⁸ N/m² (10⁻¹⁰ torr). When this vacuum was achieved, argon gas was bled back into the vacuum chamber to a pressure of 1.3 N/m². A 1000-volt, direct-current potential was applied to the specimens (disk and rider) and was argon sputter bombarded for 30 minutes. The vacuum chamber was then reevacuated and Auger spectra of the disk surface were obtained to determine the degree of surface cleanliness. When disk surface was clean, friction experiments were conducted.

Loads of 0.05 to 0.5 N were applied to pin (rider)-disk contact by deflecting the beam of figure 2. Both load and friction force were continuously monitored during a friction experiment. Sliding velocity was 3 millimeters per minute with a total sliding distance of 2.5 millimeters. All friction experiments were conducted with the system reevacuated to a pressure of 10⁻⁸ N/m².

RESULTS AND DISCUSSION

Auger Analysis of Manganese-Zinc Ferrite Surfaces

Auger spectra of the as-received single-crystal manganese-zinc ferrite surface were obtained before and after sputter cleaning. The spectra obtained before sputter cleaning revealed that, in addition to the oxygen and iron, a carbon contamination peak was evident (5). An Auger spectrum for ferrite (110) surface after sputter cleaning, is shown in figure 4. The carbon contamination peak has completely disappeared from the spectrum. In addition to oxygen and iron, Auger peaks indicate small amounts of manganese, zinc on the surface. If the oxygen peak was compared to that of the iron peak on the (100), (110), (111), and (211) surfaces, the oxygen to iron peak height ratio indicated that the surface accommodation for oxygen was in the order for the various planes of, (110) > (211) > (111) > (100).

Friction and Wear Behavior of Ferrite in Contact with Itself

Deformation effects of mechanical polishing on friction. Sliding friction experiments were conducted with an etched surface of (100) rider in contact with both etched and mechanically polished surfaces of (110) disk specimens in the (110) sliding direction. An examination with high-energy reflection electron diffraction revealed a single-crystal spot pattern or Kikuchi lines, which indicates perfection of the crystal structure, from the etched (110) disk surfaces. Debye ring (mostly diffuse) pattern generally appeared on the mechanically polished surfaces. This pattern might indicate a oriented layer or texture of the mechanically polished surface.

Friction force traces of both etched and mechanically polished surfaces of ferrite in contact with itself are generally characterized by marked stick-slip behavior. This type of friction is expected where strong adhesion occurs at the interface.

Figure 3 presents the coefficients of friction, calculated from maximum peaks in the friction traces, as a function of angle between (100) plane of the rider and (110) sliding surface of the disk. The (110) disk specimen was inclined at various angles with respect to the mating rider. The disk were turned relative to the rider on an axis in the (110) direction. Sliding was in the (110) direction on both rider and disk. The data of figure 3 indicate that the coefficients of friction for both etched and mechanically polished surfaces are not significantly different and the trend of the data are similar. Thus, the succeeding experiments were conducted with mechanically polished ferrite surfaces.

Influence of crystallographic plane on friction.

Slding friction experiments were conducted with the (100), (110), and (111) planes of riders in contact
with those planes of disks. The disks were inclined at various angles with respect to the mating riders. All disks were turned relative to the rider on an axis in the (110) direction of the rider to achieve the desired orientation. All sliding was in the (110) direction on both riders and disks. The data of figure 6 indicate that the coefficient of friction is lowest with the (100), (110), and (111) planes of the rider parallel to the interface, that is, at an angle of zero to the sliding mating surface. This is due to the interface of higher atomic density achieved with parallel planes than with surfaces inclined at various angles. This is consistent with earlier studies (6, 7). The coefficients of friction reported herein were obtained from the results of measurements of three to five friction traces. The deviation in friction with repeated experiment was ±10 percent of that indicated in the figure.

The coefficients of friction for three crystallographic planes of ferrite, (100), (110), and (111), in contact with themselves were not significantly different. It might be anticipated from these results that the atomic density for (100), (110), and (111) planes would be nearly the same because the distribution of the cations in the available sites is very complicated in a spinel crystal, as shown in figure 1. Sliding friction experiments were also conducted with the (110) plane of ferrite riders in contact with (100), (111), and (211) planes of the disks, respectively. The disks were inclined at various angles with respect to the mating riders. Disks were turned around on an axis in the (110) direction of rider, and sliding was in the (110) direction on both rider and disks. The data of figure 7 reveal that the coefficients of friction for three mated dissimilar crystallographic planes on the (100), (110), (111), and (211) planes were nearly the same as those for matched crystallographic planes in contacts in figure 6. However, in figure 7, as anticipated, there is an absence of a friction minimum at an angle of zero to the interface.

Influence of crystallographic direction on friction. It might be anticipated from preceding results shown in figure 5 that the mating crystallographic direction of both rider and disk would give rise to a significant difference in the coefficient of friction. Therefore, the influence of crystallographic direction on friction is a matter of interest. The coefficients of friction for three matched crystallographic planes in same and dissimilar directions are plotted in figure 8. In the experiments herein, the (110) rider slid on the flat surfaces of the (110), (111), and (211) planes in the same and dissimilar crystallographic directions to that of the rider. Sliding in the same direction was in the (110) directions on both the riders and disks, as already shown in figures 6 and 7. The sliding of dissimilar direction was in the (110) direction on the rider, and in the (100) direction on the (110) surface of the disk, (211) on (111) disk and (111) on (211) disk. The differences in coefficients of friction with respect to the mating crystallographic directions are significant, as expected. The coefficients of friction for the three matched crystallographic planes in the dissimilar directions are generally higher than those in the same directions and vary according to the indication of the surface of the disk at various angles.

The coefficient of friction is lowest with (110) plane of rider parallel to the interface, namely at the angle of zero to the sliding mating surface. Thus, mating highest atomic density directions on matched crystallographic planes exhibits the lowest coefficient of friction, and mating higher atomic density planes may also exhibit lower coefficient of friction. These results indicate that mating the crystallographic direction can specially play a significant role in friction behavior of ferrite. Sliding along the direction, which is most closely packed, may minimize the adhesive friction.

Anisotropic wear behavior. Following the single pass experiments in the former section, multipass experiments were conducted to establish steady state conditions. When repeated passes were made of the ferrite rider over the same ferrite at a load of 0.2 N (20 g), the coefficient of friction was constant or slightly increased with the number of passes. The friction traces under repeated passes were characterized by stick-slip behavior over the entire number of passes.

Anisotropy of wear behavior of the ferrite surface is observed with (1) cracking and (2) the wear debris generated by fracture.

(1) Cracking - The sliding of ferrite results in surface cracks along the (110) planes. Figures 9(a) and (b) show scanning electron micrographs of the wear debris. The wear debris are produced by fracture pits primarily due to cleavage-cracking of the (110) planes. Figures 9(a) and (b) reveal the wear debris generated by fracture on the surfaces of other riders and disks, namely, (100) and (111). The second type of wear debris is rectangular in shape. The second type of wear debris is rectangular in shape. Figure 10 contains a scanning electron micrograph of the cracks propagated along the (110) planes and a fracture pit on the rider as a result of 20 passes over the ferrite (110) surface. The formation of a fracture pit is primarily due to cleavage-cracking along (110) planes and sub-surface cracking along (110) planes. The smooth surface at the bottom of fracture pit is due to sub-surface cleavage of the (110) planes. Thus, the fracture behavior of the ferrite crystal during sliding, is significantly dependent on the cleavage systems of (110) planes.
smothe and the formation of the ledge may be due to sub-surface cracking of (110) planes in the disk. The 
formation of a rectangular-shaped platelet is also due to cleavage of (110) planes, where the values of angle 
between different (110) planes on the (100) sliding 
surface are 90° or common multiples thereof. "Thus, hexagon- and rectangular-shaped wear debris may be 
produced by cleavage systems of (110) planes under high 
sliding friction and shearing forces. This is also consis-
tent with an earlier study (8). In that study, 
sliding friction experiments were conducted with 
single-crystal, hexagonal silicon carbide sliding 
against itself and against titanium. The results 
indicated that wear debris is fractured of silicon car-
bide and the formation of platelet hexagonal-shaped wear 
debris of silicon carbide due to primary cleavages of 
both prismatic and basal planes when silicon car-
bide was sliding against itself.

Friction and Wear Behavior of Ferrite in Contact with Various Metals

Effect of metal activity on friction. The relative 
chemical activity of the transition metals 
(metals with partially filled d shells) as a group 
can be ascertained from their percent d bond char-
acter after Pauling (9). The friction properties of 
metal mating contacts and metals have 
been shown to be related to this character (10,11). 
The greater the percent of d bond character, the 
less active is the metal. The more active the metal, 
the higher the coefficient of friction.

Sliding friction experiments were conducted with 
ferrite in contact with a number of transition metals. 
The friction traces with metal-ferrite couples are 
generally characterized by smoothly fluctuating be-
behavior with no evidence of stick-slip, but the traces 
with ferrite against itself contained frequent stick-slip behavior. With the chemically more active metal ti-
tanium, more marked stick-slip behavior appears at a 
load of 0.2 N (20 g). With the chemically less ac-
tive metal rhodium, stick-slip behavior appears under 
higher loads of 0.35 N or more. The coefficients of 
friction for various metals sliding on ferrite were 
unaffected by load in the range of 0.05 N to 0.5 N.

The coefficients of friction for various metals 
with ferrite are presented in figure 12 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 metals. Ti-
tanium, having strong chemical affinity for iron and 
oxygen in ferrite, exhibits considerably higher friction 
behavior in contact with ferrite than does rhodium, which 
has a lesser affinity for those same two elements.

Wear behavior. Examinations of the wear track 
on ferrite surfaces after sliding with metals revealed 
extremely occasional evidence of fracture in ferrite. Figure 13 
is scanning electron micrographs of wear tracks on 
ferrite. In figure 13, three types of cracking in 
the wear track are observed. One type is character-
fized by a small crack propagating perpendicular to 
the sliding direction. The second type is a crack 
propagating at an inclination of about 45° to the 
sliding direction, that is, along cleavage planes of 
(110). The third type observed is a crack propagating 
parallel to the sliding direction, that is, along the 
cleavage planes of (110). Thus, the cracking 
of ferrite in sliding contact with metal is also 
significantly dependent on the cleavage system of 
(110) planes as well as ferrite-ferrite contacts as 
alread discussed in the former section.

The three types of cracking were observed with 
single-crystal manganese-zinc ferrite in sliding con-
tact with spherical diamond riders in nitrogen at 
atmospheric pressure (1) and with single-crystal silica-
cone carbide in sliding contact with spherical and 
conical diamond riders in argon at atmospheric pres-
sure (12). Under such conditions, sliding occurred at 
the interface and friction primarily involved shearing 
at the interface and plowing (plastic deformation) in 
the single-crystal manganese-zinc ferrite and silicon carbide. It is of interest that similar cracking 
occur in nominally brittle materials regardless of 
mixed differences in friction behavior and environ-
ments.

The fracturing and formation of wear debris of 
ferrite in contact with metal are the result of cracks 
being generated, propagating and then intersecting.
Figure 14 presents a scanning electron micrograph and 
and X-ray map of a wear scar of metal rider generated 
by five passes sliding on ferrite disk. The wear scar 
on metal rider may generally contain small wear debris 
particles generated by the fracture of the ferrite 
surface, as shown in figure 14. Titanium, having 
strong chemical activity, exhibited considerably more 
wear debris particles of ferrite transferred (em-
bedded) to metal surface than did rhodium or iron, 
having lesser chemical activity. Thus, wear debris 
of ferrite may be produced by cleavage cracking and 
be transferred to or embedded in the metal during 
sliding.

Lastly, all examinations of the wear track on 
ferrite surfaces after sliding with metals revealed 
evidence of metal transfer to ferrite. The transfer 
and wear behavior of various transition metals was 
similar to those in sliding friction experiments con-
ducted with single-crystal silicon carbide sliding 
against various transition metals in vacuum (11); that 
is, the more active the metal, the greater the trans-
fer to ferrite and the rougher the wear scar on the 
surface of the metal.

CONCLUSIONS

As a result of the sliding friction experiments 
conducted in this investigation with single-crystal 
manganese-zinc ferrite (100), (110), (111), and (211) 
surfaces in sliding contact with themselves and with 
various metals, the following conclusions are drawn:

1. Matching highest atomic density (most closely 
packed) directions (110) on matched crystallographic 
planes exhibit the lowest coefficient of friction indi-
cating that direction is important in the friction 
behavior of ferrite.

2. Matched parallel high atomic density planes 
and crystallographic directions at the interface ex-
hibit low coefficients of friction. Matching dissimilar 
crystallographic planes, however, does not give a 
significant difference in friction from that observed 
with matched planes.

3. The coefficients of friction for ferrite in 
contact with various metals are related to the rela-
tive chemical activity of these metals. The more 
active the metal, the higher the coefficient of frac-
tion.

4. Cracking, and the formation of hexagon- and 
rectangular-shaped platelet wear debris are observed 
on the ferrite surfaces as a result of sliding. The 
cracking and formation of such wear debris particles 
are primarily due to cleavage of (110) planes on the 
surface and in the bulk of ferrite.

5. All metals examined transferred to the sur-
faces of ferrite in sliding.
ACKNOWLEDGEMENT

The authors wish to thank Prof. Kyuichiro Tanaka of Kanazawa University in Japan for supplying the materials.

REFERENCES


TABLE I. - COMPOSITION AND HARDNESS DATA ON MANGANESE-ZINC FERRITE

<table>
<thead>
<tr>
<th>Composition, wt %</th>
<th>Fe₂O₃, 71.6</th>
<th>MnO, 17.3</th>
<th>ZnO, 11.1</th>
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</thead>
<tbody>
<tr>
<td>Surface</td>
<td>(100)</td>
<td>(100)</td>
<td>(110)</td>
</tr>
<tr>
<td>Direction</td>
<td>[001]</td>
<td>[011]</td>
<td>[001]</td>
</tr>
<tr>
<td>Knoop hardnessº</td>
<td>630</td>
<td>560</td>
<td>630</td>
</tr>
<tr>
<td>Vickers hardness¹</td>
<td>630</td>
<td>665</td>
<td>645</td>
</tr>
</tbody>
</table>

ºKnoop hardness measuring load was 300 grams.
¹Vickers hardness measuring load was 50 grams.

TABLE II. - CRYSTAL STRUCTURE AND PURITY OF VARIOUS METALS

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal structure</th>
<th>Purity, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>Body-centered cubic</td>
<td>99.99</td>
</tr>
<tr>
<td>Fe</td>
<td>Body-centered cubic</td>
<td>99.99</td>
</tr>
<tr>
<td>Ni</td>
<td>Face-centered cubic</td>
<td>99.99</td>
</tr>
<tr>
<td>Rh</td>
<td>Face-centered cubic</td>
<td>99.99</td>
</tr>
<tr>
<td>Ti</td>
<td>Close-packed hexagonal</td>
<td>99.97</td>
</tr>
<tr>
<td>Co</td>
<td>Close-packed hexagonal</td>
<td>99.99</td>
</tr>
</tbody>
</table>
Spinel structure.

- Cation in octahedral site (\(\text{Mn}^{2+}, \text{Zn}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}\))
- Cation in tetrahedral site (\(\text{Fe}^{3+}\))

Layers of atoms parallel to (100) plane.

Figure 1. - Spinel structure. (From refs. 1 and 2.)
Figure 2. - High-vacuum friction-and-wear apparatus.

Figure 3. - Orientation of single-crystal manganese-zinc ferrite riders and disks for sliding friction and wear tests in vacuum. "A" plane parallel to sliding interface.

<table>
<thead>
<tr>
<th>Plane designation</th>
<th>Crystallographic plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(100)  (110)  (111)  (211)</td>
</tr>
<tr>
<td>B</td>
<td>(110)  (100)  (211)  (111)</td>
</tr>
<tr>
<td>C</td>
<td>(111)  (110)  (110)  (110)</td>
</tr>
</tbody>
</table>

Figure 4. - Auger emission spectroscopy spectrum for manganese-zinc ferrite (110) surface after sputter cleaning.
Figure 5. - Coefficients of friction for both mechanically polished and chemically etched surfaces of disks. Sliding direction of rider, <100>; sliding directions on disk, <110> and <100>; single pass sliding.

Figure 6. - Coefficient of friction as function of angle between \(h, k, l\) plane of rider and \(h, k, l\) plane of disk, \(\theta\), deg. Sliding direction for both riders and disks, <110>; single pass; rider and disk material, manganese-zinc ferrite.
Figure 7 - Coefficient of friction as function of angle between (110) plane of rider and (h, k, l) plane of disk. Sliding direction for both riders and disks, (110); single pass; rider and disk material, manganese-zinc ferrite.
Figure 8. - Coefficients of friction for mating same and dissimilar directions of rider and disk. Sliding direction of rider, (110); single pass, rider and disk material, manganese-zinc ferrite.
a) Rider, with \{110\} plane parallel to interface.

Figure 9. - Scanning electron micrographs of cracking of single-crystal manganese-zinc ferrite \{110\} rider after 5 passes in sliding contact with single-crystal manganese-zinc ferrite \{211\} disk. Sliding direction for rider and disk, \{110\}. 

Wear debris 

Sliding direction 

Cracks along \{110\} 

Cracks along \{110\} 

10 \mu m
Cracks along \{110\}

Sliding direction

(b) Disk, with \{211\} plane parallel to interface.

Figure 9. - Concluded.
Figure 10. - Scanning electron micrograph of fracture pit and cracks on single-crystal manganese-zinc ferrite \{110\} rider after 20 passes in sliding contact with single-crystal manganese-zinc ferrite \{110\} disk. Sliding direction for rider and disk \(\{110\}\).
Figure 11. Scanning electron micrograph of wear track on single-crystal manganese-zinc ferrite (110) disk, showing transfer of hexagonal wear debris from single-crystal manganese-zinc ferrite (110) rider after 10 passes. Sliding direction for rider and disk, (110).
(c) Dislodged rectangular wear debris.

Figure 11. - Concluded.

Figure 12. - Coefficient of friction as function of percent of $d$ bond character of various metals in sliding contact with single-crystal manganese-zinc ferrite (110) surface in vacuum ($10^{-8}$ N/m²). Single pass; sliding velocity, 3 mm/min; load, 30 grams; temperature, 25°C.
Figure 13. Scanning electron micrographs of wear track and cracking of single-crystal manganese-zinc ferrite (110) surface after five passes of cobalt rider in high vacuum ($10^{-8}$ N/m²). Sliding velocity, 3 mm/min; temperature, 25°C.

(a) Cracks propagating perpendicular to, parallel to, and at an inclination of about 45° to sliding direction.

(b) Cracks propagating perpendicular to and at an inclination of 45° to sliding direction.
Figure 14. - Scanning electron micrograph and energy dispersive X-ray analysis of wear debris of single-crystal manganese-zinc ferrite transferred to iron rider as result of five passes in high vacuum (10⁻⁸ N m²). Sliding velocity, 3 mm min; temperature, 25°C.

(a) Wear debris.

(b) Manganese Kα X-ray map; 4.5X10³ counts.