Microstructure and Surface Chemistry of Amorphous Alloys Important to Their Friction and Wear Behavior

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MICROSTRUCTURE AND SURFACE CHEMISTRY OF AMORPHOUS ALLOYS
IMPORTANT TO THEIR FRICTION AND WEAR BEHAVIOR

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ABSTRACT

An investigation was conducted to examine the microstructure and surface chemistry of amorphous alloys, and their effects on tribological behavior. The results indicate that the surface oxide layers present on amorphous alloys are effective in providing low friction and a protective film against wear in air. Clustering and crystallization in amorphous alloys can be enhanced as a result of plastic flow during the sliding process at a low sliding velocity and at room temperature. Clusters or crystallites with sizes to 150 nm and a diffused honeycomb-shaped structure are produced on the wear surface. Temperature effects lead to drastic changes in surface chemistry and friction behavior of the alloys at temperatures to 750 °C. Contaminants can come from the bulk of the alloys to the surface upon heating and impart to the surface oxides at 350 °C and boron nitride above 500 °C. The oxides increase friction while the boron nitride reduces friction drastically in vacuum.

1. INTRODUCTION

Metallic glasses are currently finding increased application in the aerospace industry [1]. They are used for joining internal assemblies in gas turbines. Nickel-based brazed foils of the BNi class are replacing the more expensive gold-based BAu-4 foils in engine valves and many other components. However, like BAu-4, the nickel-based filler metals have excellent flow behavior, are compatible with most stainless steels and nickel alloys, and offer an outstanding combination of high-temperature strength, fatigue properties, and oxidation and corrosion resistance [1].

A combination of favorable mechanical and physical properties makes metallic glasses candidates for other technological applications. For example, the combination of high permeability and high hardness makes these materials suitable for use in highly developed magnetic recording devices (e.g., video tape recorders). In most high-density devices, a magnetic head in sliding contact with a magnetic tape is used for recording and playback. Therefore, the magnetic head and tape must have good wear resistance.

Metallic glasses can also be used in foil bearings. The highly disordered structures of metallic glass would be resistant to radiation damage, and, thus, have potential for use where constant mechanical properties are required under irradiation. The mechanical and physical properties of metallic glasses are, therefore, of basic scientific interest.

Metallic glasses have several properties that make them attractive for tribological applications. These properties include great adhesion, shear strength, impact penetration, corrosion resistance, stiffness, and ductility. Relatively little research, however, has been done on the friction, adhesive wear, and abrasive wear properties of the metallic glasses [2-7].

This paper is principally concerned with a fundamental understanding of microstructure and chemistry of amorphous alloy surfaces, and their effects on tribological properties (friction and wear). Sliding friction experiments were conducted with three ferrous-base amorphous alloy compositions in vacuum (30 nPa) and a laboratory air or argon atmosphere. A rider of aluminum oxide was made to slide on the amorphous alloy surfaces under loads of from 0.1 to 2.5 N and at sliding velocities of from 0.033 to 0.17 mm/sec. The vacuum experiments were conducted at temperatures of from room to 750 °C.
2. MATERIALS

Three amorphous alloy compositions were examined in this investigation. The compositions and some of their properties are presented in Table I. The alloys were foils (30 to 33 μm-thick ribbon), and were used in the as-cast condition. The spherical riders that were made to slide on the foil were single-crystal aluminum oxide (sapphire) spheres and the diameter of the spheres were 3.2 and 6.4 mm.

3. APPARATUS

Two apparatuses were used in this investigation (Fig. 1). They both use a pin on flat configuration. One consists of an ultra-high vacuum system capable of measuring adhesion, load, and friction and contains an XPS spectrometer. Figure 1(a) indicates the major components, including the electron energy analyzer, the X-ray source, and the ion gun used for ion sputter etching. A manipulator-mounted beam was projected into a vacuum chamber. The beam contained two flats machined normal to each other with strain gages mounted thereon. The load was applied by moving the beam normal to the flat and was sensed by strain gages. The vertical sliding motion of the pin along the flat surface was accomplished through a motorized manipulator assembly. The friction force under an applied load was measured during vertical translation by a strain gage mounted normal to that used to measure load.

The second apparatus used in this investigation is shown schematically in Fig. 1(b). The pin was made to traverse a distance of 10 mm on the surface of the foil. Motion was reciprocal. The pin was loaded against the foil with dead weights. The arm retaining the rider contained strain gages to measure the tangential and normal forces. The entire apparatus was housed in a plastic box.

4. EXPERIMENTAL PROCEDURE

Specimen Preparation and Heating

The foil specimen was attached to an insulator flat with tantalum supporting sheets (Fig. 1). The specimen was directly in contact with the sheets. The flat and pin surfaces were rinsed with 200-proof ethyl alcohol just before they were placed in the vacuum chamber. A load of 0.2 N was applied to the pin-flat contact by deflecting the beam, as shown in Fig. 1. To obtain consistent experimental conditions, contact before sliding was maintained for 30 sec. Both the load and friction force were continuously monitored during a friction experiment. Sliding velocity was 3 mm/min with a total sliding distance of 2 to 3 mm. All single-pass friction experiments were conducted in a 30 nPa vacuum. The coefficients of friction reported herein were obtained by averaging three to five measurements.

5. RESULTS AND DISCUSSION

Amorphous Alloy Surfaces

To establish the exact crystalline state of the amorphous alloy surfaces, microstructure was examined by transmission electron
microscopy and diffraction in a microscope operating at 100 kV.

A typical example of the structure of the as-received amorphous alloy foil is shown in Fig. 2. The amorphous alloy lacks the macroscopic structural features common in crystalline metals. In the absence of macroscopic crystallinity, neither grains, grain boundaries, grain orientations nor additional phases exist. However, black spots, which are believed to be nuclei and/or crystallites with a size range to 4 nm, are apparent in the photomicrograph. Very diffused honeycomb-shaped structures formed by dark grey bands as a result of segregation and clustering of transition metals and metallic oxides are also apparent in the photomicrograph.

The electron diffraction pattern for the as-received foil presented in Fig. 2 indicates that the amorphous alloy foil was not completely amorphous but contained extremely small nuclei and/or clusters of approximately a few nanometers in size. All the XPS spectra taken from the surfaces of three amorphous alloys as received clearly revealed adsorbed oxygen and carbon contaminants in addition to the various alloying constituents of the nominal bulk composition. Beneath this layer of adsorbate there is a mixture layer of oxides of the alloying constituents. Fe_{2p} peaks of the as-received Fe_{67}Co_{16}Bi_{14}Si_{14} specimen are shown as an example in Fig. 3. The spectrum for the surface before cleaning clearly indicates that there were iron oxides such as FeO_{3} on the foil surface. The spectra taken after the foil surface had been argon sputter cleaned for 2 and 4 min reveal that the lines for Fe_{2p} were split asymmetrically into doublet peaks. The doublet peaks are associated with iron oxides and iron. The spectra taken after the foil surface had been argon sputter cleaned for 60 min clearly indicate the Fe_{2p} peaks associated with iron, while the iron oxide peak is very small. The results at 30 min sputtering were similar to those at 60 min.

The as-received Fe_{67}Co_{16}Bi_{14}Si_{14} foil contained the oxides of cobalt, boron and silicon as well [2]. The oxide layers are extremely important for amorphous alloys from a tribological point of view, because it is very hard and tenaciously bonded to the alloying constituents. This can provide good wear resistance, and will be discussed in the following section.

The XPS spectra of the surface argon sputter cleaned for 60 min contained small amounts of carbide and oxide contaminants such as silicon carbide and silicon dioxide, although the Fe_{67}Co_{16}Bi_{14}Si_{14} foil was not supposed to contain carbon and oxygen. The contaminants (i.e., oxygen and carbon) may be introduced from the environment into the bulk of the alloy and form bulk contaminants, such as carbides and oxides, in the alloy during the casting process.

The argon-ion-sputter cleaned surface conditions of the three amorphous alloy foils analyzed by XPS are summarized in Table II. The relative concentrations of the various constituents on the surfaces were different from the nominal compositions.

**Friction and Wear**

Sliding friction experiments were conducted with the three as-received amorphous alloys, where normal residual oxides were present on the surface, and in contact with an aluminum oxide ball in argon or in laboratory air. Comparative experiments were made with practical materials such as 304 stainless steel foil and 440C stainless steel. The 304 stainless steel was of equivalent foil thickness as the amorphous alloys.

When the amorphous alloys were rubbed by the 6.4 mm-diameter and 3.7 mm-diameter aluminum oxide riders at a load of 2.5 N (providing contact pressure of approximately 0.8 and 1.3 GPa, respectively) for 30 min, essentially no detectable wear existed on the surface of the three amorphous alloys. There was a complete absence of any visible wear track when examined by the optical and scanning electron microscope.

Wear tracks were, however, visible on the 304 stainless steel foil and the 440C stainless steel. The wear damage of 440C stainless steel was much less than that of 304 stainless steel. A copious amount of wear debris was generated and considerable plastic flow and wear occurred to the 304 stainless steel surface, and clumps of metal appeared in the wear track [8].

Thus, surface oxide layers present in the amorphous alloys were very effective in providing a protective film against wear.

Since no visible wear was observed on the amorphous alloys, sliding friction experiments were conducted with the 3.2 mm-diameter aluminum oxide rider at a load of 2.5 N and with the sliding time extended to 150 hr in order to provide more severe conditions and to remove the protective oxide films.

Figure 4 presents scanning electron micrographs of typical wear tracks on the amorphous alloy Fe_{67}Co_{16}Bi_{14}Si_{14} and the 304 stainless steel foil surfaces at a total sliding time of 5 hr. Oxide wear debris particles were generated on the amorphous
alloy surface, while metal wear debris particles were primarily generated on the stainless steel surface. With the amorphous alloy, microscopic brittle fracture and breaking up of oxide layers took place, and fine oxide wear debris particles were mainly produced. With the 304 stainless steel, however, rupture of the bonds of cohesively weaker 304 stainless steel occurred, cavities were formed in the material, and small platelet-type metallic wear debris particles were subsequently produced.

Figure 5 illustrates a detailed examination of the oxide wear debris (submicrons to microns in size) produced on the amorphous alloy as a result of the sliding action. The scanning electron micrographs clearly reveal powdery and whiskery (needle-shaped) oxide wear debris particles on and near the wear track after sliding contact with the aluminum oxide rider.

Figure 4(a) discussed above also clearly revealed that plastic flow occurred in the amorphous alloy. The sliding action resulted in plastic deformation not only in the wear track but also at the side of the wear track. Multiple shear deformation bands were observed on the side of the wear track (as shown in Fig. 4(a)). The plastic flow, observed on the side of the wear track, occurs in the form of highly localized shear deformation bands. Thus, a concentration of large shear strains develops in a band during sliding friction process. The shear bands are similar to those in crystalline metals [9].

Figure 6(a) clearly reveals that plastic flow occurs in the wear track of the amorphous alloy with repeated sliding. When the aluminum oxide rider in sliding contact with the amorphous alloy was examined by the scanning electron microscope, there were flow films of the alloy adhered and transferred to the aluminum oxide rider surface (as shown in Fig. 6(b)).

During a 150-hr sliding period, considerable plastic flow occurred and considerable oxide debris was generated on the amorphous alloy. Figure 7 reveals evidence of wear damage and large particles of wear debris, which were generated at local spots. Shear fracture occurs at very local areas in the amorphous alloy during repeated sliding. The wear rate is defined as the quantity of amorphous alloy removed under a unit load and with a unit distance of sliding, was 5x10^-9 mm^3/mm.

Mechanical Effects

Crystallization of amorphous alloy in mechanical contact with an aluminum oxide rider (3.2 mm-radius) has been observed to occur during sliding friction with a relatively slow sliding velocity (1.5 mm/sec), wherein frictional heating is negligible.

A typical example of the wear surface of the Fe37Co9Bi4Si1 alloy run for 150 hr is shown in Fig. 8. Dark dots and bands, which are believed to be clusters or crystallites ranging in size from 10 to 50 nm, are apparent. Diffused honeycomb-shaped structures formed by dark grey bands are due to segregation and preferential clustering of transition metals and metalloids. The electron diffraction pattern also indicates that the wear surface contained small clusters or grains.

Figure 9 presents bright and dark field images and the diffraction pattern of a local area of the wear surface on the amorphous alloy. Dark spots, believed to be clusters or crystallites ranging in size to 150 nm, observed in the bright image are reversed in the dark image. The diffraction pattern was also taken from the spots. Figure 9 clearly indicates a partially crystallized phase in the matrix. As seen from these micrographs, star-shaped crystals grow in the Fe37Co9Bi4Si1 alloy.

The diffraction pattern includes spotting rings which lose their continuity at 360° and diffuse halos. The spotty ring is essentially that for a crystalline material and most of the spot pattern of the crystallized phase was identified as α-Fe2O3. The diffuse halos indicate that the matrix contains extremely small grains of approximtely a few nanometers in size. The results suggest that crystallization may occur by nucleation and growth processes of α-Fe. The dispersed and primary crystallized α-Fe phase may act as the preferred nucleation site for crystallization of the amorphous alloy. The primary crystals, that is, α-Fe may be easily oxidized during sliding friction experiments and transform into α-Fe2O3.

Thus, a strong interaction between transition metals and metalloids such as boron results in strong segregation and provides preferential transition metalloid clustering [10,11] in the bulk of the amorphous alloy during the sliding friction process. A highly strained amorphous alloy tends to promote clustering of the amorphous alloy long before the surface may otherwise be ready for such clustering. The extent of segregation of metalloids to clusters and/or crystallites is controlled by strain and this may control the strength of the alloys, as well as friction and wear properties of the alloys.
Temperature Effects

Typical examples of the structure are shown in Fig. 10 for the amorphous alloy foils after heating to 350° and 430° C for 20 min in ultra-high vacuum. The structure of the foil heated to 350° C is similar to that of the as-received foil already shown in Fig. 2. In the structure of the foil that had been heated to 430° C, which is the so-called crystallization temperature for this particular Fe$_7$Co$_1$B$_{14}$Si$_{11}$ foil, the black spots are slightly larger than those shown in Figs. 2 and 10(a). The diffused honeycomb-shaped structure formed by dark grey bands and indicates subdivision of amorphous alloy structure as a result of decomposition and separation of amorphous phase. That is, segregation of constituents and preferential clustering are taking place at this temperature. The electron diffraction pattern also indicates the presence of an extra outer ring related to clustering or crystallinity.

Figure 11 presents microstructures of the foils heated to 500° and 750° C. They reveal two kinds of extremely fine-grained crystals: a dark grain and a light grain. Energy dispersive X-ray analysis indicated that the light grains contained about 20 times more silicon than the dark grains [3]. The dark grains contained more iron and Fe-B alloy. The transmission electron diffraction patterns for both the dark and light grains contained diffraction spots and Kikuchi lines indicating single-crystal structure [3]. The crystallized grain size was 0.7 μm at 500° C and to 1.4 μm at 750° C. Thus, the microstructure of the amorphous alloy changes continuously and drastically during the amorphous to crystalline transition. The amorphous phase separates into two crystalline phases.

Temperature effects lead to drastic changes in surface chemistry of the amorphous alloys as analyzed by XPS and not only above the crystallization temperature, but below it as well. These changes are due to segregation and diffusion of constituents, especially of metalloids such as boron and silicon.

A typical example of the XPS spectra of B$_{15}$ and Si$_{2p}$ peaks obtained on Fe$_7$Co$_1$B$_{14}$Si$_{11}$ foil surface is presented in Fig. 12. The B$_{15}$ photoelectron peaks of the as-received specimen indicate the presence of boric oxide as well as Fe$_8$B and CoB. The spectrum of the surface that had been argon sputter cleaned for 30 and 60 min reveals large peaks for boron and its alloys as well as very small boric oxide peaks.

The spectra for the foils that had been heated to 750° C clearly indicate that the foil surfaces were again contaminated with boric oxide at 350° C and boron nitride at 750° C that had migrated from the bulk of the foil specimens. The foil surfaces heated at 500° C were also contaminated with boron nitride and were the same as that for the heated surface at 750° C.

The Si$_{2p}$ photoelectron peaks of the as-received surface reveal silicides. Even the spectrum of the surface that had been argon sputter cleaned for 60 min reveals silicides as well as silicon oxide on the surface. The foil that had been heated to 350° C was contaminated with silicon oxide that had migrated from the bulk of the foil specimens. The foil heated at 750° C contains a small amount of silicon dioxide on the surface compared to that heated at 350° C.

The Fe$_{2p}$ photoelectron peaks of the Fe$_7$Co$_1$B$_{14}$Si$_{11}$ foil heated to 350° and 750° C are almost the same as that for the argon-sputter-cleaned surface shown in Fig. 3. The Co$_{2p}$ photoelectron peaks of the as-received Fe$_7$Co$_1$B$_{14}$Si$_{11}$ foil indicated cobalt oxide. The spectra for the surfaces that had been argon-sputter-cleaned and heated to 350° and 750° C revealed cobalt oxide and its alloy peaks. The cobalt oxide peak was negligible [3].

Table III summarizes the surface conditions of the foils analyzed by XPS. Generally, the XPS results indicate that the surfaces of the as-received foils consisted of a layer of oxides of alloying elements as well as a simple, adsorbed film of oxygen and carbon. The argon sputter cleaned surface consisted of the alloy and small amounts of oxides and carbides. In addition to nominal element constituents, the surface heated to 350° C contained boron and silicon oxides on Fe$_7$Co$_1$B$_{14}$Si$_{11}$ and Fe$_7$B$_{13}$Si$_{13}$ alloy, and boron oxides on Fe$_7$B$_{13}$Si$_{13}$ alloy as well as small amounts of carbides that had segregated and migrated from the bulk of the foils. The surface heated to 750° C contained boron nitride that had also migrated from the bulk of the foils as well as small amounts of oxides.

Thus, in situ examinations of the surface chemistry in the heating stage gives valuable information on the behavior of surface segregation and decomposition. The segregation and migration of compounds such as boron oxide and nitride influence the friction behavior of amorphous alloys.

Sliding friction experiments were conducted with aluminum oxide in contact with amorphous alloys in vacuum at temperatures to 750° C. Friction-force traces resulting
from such sliding were generally characterized by fluctuating behavior with evidence of stick-slip [3]. The coefficient of friction as a function of the sliding temperature of the foil specimen is indicated in Fig. 13. The aluminum oxide rider was sputter cleaned with argon ions at room temperature. The foil specimen was also sputter cleaned with argon ions in the vacuum system and then heated from room temperature to 750°C. The coefficient of friction increased with increasing temperature from room to 350°C. The increase in friction is due to an increase in adhesion resulting from segregation of boric oxides and silicon oxides to the foil surface as described earlier. Generally, the presence of oxygen does strengthen the metal-ceramic material (such as SiC) contacts and increases the friction [12].

Above 500°C the coefficient of friction decreased dramatically. The rapid decrease in friction above 500°C correlated with the segregation of boron nitride on the foil surface, as already discussed and shown in Fig. 12(c). It is also interesting in Fig. 13 that there is a considerable difference in the friction measured for variations in alloy chemistry.

6. CONCLUSION

The following conclusions are drawn from the presented data:

(1) Amorphous alloys are not completely amorphous, but contain extremely small clusters or crystallites (nuclei) of approximately a few nanometers (up to 4 nm) in size.

(2) Surface oxide layers present on the amorphous alloys are stable and very effective in providing low friction and a protective film against wear in an air atmosphere.

(3) Plastic flow occurs on an amorphous alloy surface with sliding. Multiple slip bands due to shear deformation are observed on the sides of the wear track.

(4) Enhanced clustering and crystallizing of amorphous alloys occur during the sliding process at a low sliding velocity where the temperature rise is negligible. Clusters or crystallites with sizes to 150 nm and diffused honeycomb-shaped structure formed by dark grey bands are produced on the wear surface of the amorphous alloy.

(5) Temperature effects lead to drastic changes in surface chemistry and friction behavior of the amorphous alloys in the range of room temperature to 750°C. Contaminants can come from the bulk of the material to the surface upon heating and impart to the surface boric oxide and/or silicon oxide at 350°C and boron nitride above 500°C. The segregation of contaminants is responsible for the friction behavior. The coefficient of friction increases with increasing temperature to 350°C in vacuum. The increase in friction is due to an increase in adhesion resulting from surface segregation of boric oxide and/or silicon oxide to the surface of the foil.

Above 500°C the coefficient of friction decreased rapidly. The decrease correlates with the segregation of boron nitride to the surface.

(6) The microstructure of amorphous alloy changes discontinuously from the amorphous phase to the multi-crystalline phases during the crystallization process.

REFERENCES

TABLE I. - PROPERTIES OF METALLIC GLASSES

<table>
<thead>
<tr>
<th>Nominal alloy composition, wt %</th>
<th>Crystallization temperature, °C</th>
<th>Density, g/cm³</th>
<th>Hardness, GPa</th>
<th>Ultimate tensile strength, GPa</th>
<th>Bend ductility, a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂₀Co₁₈B₁₄Si₅</td>
<td>430</td>
<td>7.56</td>
<td>10</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>Fe₈₁B₁₃.₅Si₃.₅C₂</td>
<td>480</td>
<td>7.3</td>
<td>10.3</td>
<td>0.7</td>
<td>9x10⁻³</td>
</tr>
<tr>
<td>Fe₄₀Ni₃₈Mo₄B₁₈</td>
<td>410</td>
<td>8.02</td>
<td>10.5</td>
<td>1.38</td>
<td>1</td>
</tr>
</tbody>
</table>

a = t(d - t), where t is ribbon thickness and d is micrometer spacing at bend fracture.

TABLE II. - COMPOSITION OF ARGON-SPUTTER-CLEANED SURFACE LAYER OF AMORPHOUS ALLOYS

<table>
<thead>
<tr>
<th>Nominal bulk composition</th>
<th>Composition on surface, at.%</th>
<th>at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂₀Co₁₈B₁₄Si₅</td>
<td>Fe₄₂Co₁₁B₄₆Si₁₅</td>
<td></td>
</tr>
<tr>
<td>Fe₈₁B₁₃.₅Si₃.₅C₂</td>
<td>Fe₄₈B₄₂Si₄C₆</td>
<td></td>
</tr>
<tr>
<td>Fe₄₀Ni₃₈Mo₄B₁₈</td>
<td>Fe₄₈B₁₃₀Si₈C₂₅₁₄</td>
<td></td>
</tr>
</tbody>
</table>

a Manufacturer's analysis.

b Relative concentrations of the various constituents were determined using peak area sensitivity factors and peak area.
<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Surface</th>
<th>As received</th>
<th>Argon sputter cleaned</th>
<th>Heated to 350° C</th>
<th>Heated to 750° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe67Co18B14Si1</td>
<td>Oxides of Fe, Co, B, Si, and C</td>
<td>Alloy</td>
<td>Small amount of oxides and carbides</td>
<td>Boric oxides and silicon oxides migrated from bulk</td>
<td>Boron nitride migrated from bulk</td>
</tr>
<tr>
<td></td>
<td>Adsorbed film of oxygen and carbon</td>
<td>Alloy</td>
<td>Small amount of oxides and carbides</td>
<td>Small amount of carbides</td>
<td>Very small amount of boric oxides and silicon oxides</td>
</tr>
<tr>
<td>Fe81B13.5Si13.5C2</td>
<td>Oxides of Fe, B, Si, and C</td>
<td>Alloy</td>
<td>Small amount of oxides and carbides</td>
<td>Boric oxides and silicon oxides migrated from bulk</td>
<td>Boron nitride migrated from bulk</td>
</tr>
<tr>
<td></td>
<td>Adsorbed film of oxygen and carbon</td>
<td>Alloy</td>
<td>Small amount of oxides and carbides</td>
<td>Small amount of carbides</td>
<td>Very small amount of boric oxides and silicon oxides</td>
</tr>
<tr>
<td>Fe40Ni13Mo6B18</td>
<td>Oxides of Fe, B, Ni, Mo, and B</td>
<td>Alloy</td>
<td>Small amount of oxides and carbides</td>
<td>Boric oxides migrated from bulk</td>
<td>Boron nitride migrated from bulk</td>
</tr>
<tr>
<td></td>
<td>Adsorbed film of oxygen and carbon</td>
<td>Alloy</td>
<td>Small amount of oxides and carbides</td>
<td>Small amount of carbides</td>
<td>Very small amount of boric oxides</td>
</tr>
</tbody>
</table>
(a) Ultra high-vacuum friction and wear apparatus.

Figure 1. - Friction and wear apparatuses.

(b) Friction and wear apparatus used in argon and in laboratory air.

Figure 1. - Concluded.
Figure 2. - Typical microstructure and electron diffraction pattern of an amorphous alloy (Fe$_{67}$Co$_{18}$B$_{14}$Si$_1$).
IRON OXIDES

AT ROOM TEMPERATURE
BEFORE CLEANING

Fe\textsubscript{2p\textsubscript{1/2}}

AFTER ARGON SPUTTER
CLEANING FOR 2 min

Fe\textsubscript{2p\textsubscript{3/2}}

AFTER ARGON SPUTTER
CLEANING FOR 4 min

AFTER ARGON SPUTTER
CLEANING FOR 60 min

Figure 3. - Fe\textsubscript{2p} XPS peaks on Fe\textsubscript{67}Co\textsubscript{18}B\textsubscript{14}Si\textsubscript{1} surface.
Figure 4. - Scanning electron micrographs of wear track on Fe$_{67}$Co$_{18}$B$_{14}$Si$_{1}$ amorphous alloy and wear track on 304 stainless steel. Pin, 3.2 millimeters diameter aluminum oxide sphere; load, 2.5 newtons; sliding velocity, 1.5 millimeters per second; sliding distance, 27 meters; room temperature; laboratory air atmosphere; relative humidity, 40%.
(a) Powdery debris on the wear track.

(b) Whiskery debris on the side of wear track.

Figure 5. - Scanning electron micrographs of powdery and whiskery wear debris particles produced on Fe$_{67}$Co$_{18}$-B$_{14}$Si$_1$ amorphous alloy. Pin, 3.2 millimeters diameter aluminum oxide sphere; sliding velocity, 1.5 millimeters per second; load, 2.5 newtons; sliding distance, 27 meters; room temperature; laboratory air atmosphere; relative humidity, 40%.
Figure 6. - Scanning electron micrographs of wear track on Fe\(_{67}\)Co\(_{18}\)B\(_{14}\)Si\(_{1}\) amorphous alloy and wear scar on aluminum oxide rider sliding on Fe\(_{67}\)Co\(_{18}\)B\(_{14}\)Si\(_{1}\) amorphous alloy surface. Rider, 3.2-millimeter-diameter aluminum oxide sphere; load, 2.5 newtons; sliding velocity, 1.5 millimeters per second; sliding time, 5 hours; sliding distance, 27 meters; room temperature; laboratory air atmosphere.
Figure 7. - Scanning electron micrographs of wear track on Fe$_{67}$Co$_{18}$B$_{14}$Si$_1$ amorphous alloy at sliding period of 150 hours. Rider, 3.2-millimeter-diameter aluminum oxide sphere; load, 2.5 newtons; sliding velocity, 1.5 millimeters per second; sliding time, 150 hours; sliding distance, 810 meters; room temperature; laboratory air atmosphere.
Figure 8. - Typical microstructure and electron diffraction patterns of wear surface of metallic glass \( \text{Fe}_{67} \text{Co}_{18} \text{B}_{14} \text{Si}_1 \). Rider, 3.2 millimeter-diameter aluminum oxide sphere; load, 2.5 newtons; sliding velocity, 1.5 millimeters per second; sliding time, 150 hours; sliding distance, 810 meters; room temperature; laboratory air atmosphere.
Figure 9. - Microstructure and electron diffraction patterns of wear surface of metallic glass (Fe$_{67}$Co$_{18}$Si$_{14}$). Rider, 3.2-millimeter-diameter aluminum oxide sphere; load, 2.5 newtons; sliding velocity, 1.5 millimeters per second; sliding time, 150 hours; sliding distance, 810 meters; room temperature; laboratory air atmosphere.
Metallic glass heated to 350° C: (a) microstructure and (b) diffraction pattern.

Metallic glass heated to 430° C: (c) microstructure and (d) diffraction pattern.

Figure 10. - Microstructure and electron diffraction pattern of an amorphous alloy (Fe_{67}Co_{18}B_{14}Si_{1}) heated to 350° C and 430° C in vacuum (10 nPa).
Metallic glass heated to 500° C: (a) microstructure and (b) diffraction pattern.

Metallic glass heated to 750° C: (c) microstructure and (d) diffraction pattern.

Figure 11. - Microstructure and electron diffraction pattern of an amorphous alloy (Fe_{67}Co_{18}B_{14}Si_{1}) heated to 500° C and 750° C in vacuum (10 nPa).
Figure 12. - Representative $B_{1s}$ and $Si_{2p}$ XPS peaks on $Fe_{67}Co_{18}B_{14}Si_1$ surface.
Figure 13. - Coefficient of friction as a function of temperature for aluminum oxide sliding on Fe$_{67}$Co$_{18}$B$_{14}$Si$_1$, Fe$_{81}$B$_{13}$S$_{13}$Si$_2$, and Fe$_{40}$Ni$_{38}$Mo$_{4}$B$_{18}$ in vacuum. Normal load, 0.2 N; sliding velocity, 3 mm/min; vacuum, 10 nPa.
An investigation was conducted to examine the microstructure and surface chemistry of amorphous alloys, and their effects on tribological behavior. The results indicate that the surface oxide layers present on amorphous alloys are effective in providing low friction and a protective film against wear in air. Clustering and crystallization in amorphous alloys can be enhanced as a result of plastic flow during the sliding process at a low sliding velocity, at room temperature. Clusters or crystallites with sizes to 150 nm and a diffused honeycomb-shaped structure are produced on the wear surface. Temperature effects lead to drastic changes in surface chemistry and friction behavior of the alloys at temperatures to 750°C. Contaminants can come from the bulk of the alloys to the surface upon heating and impart to the surface oxides at 350°C and boron nitride above 500°C. The oxides increase friction while the boron nitride reduces friction drastically in vacuum.