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Mechanical Contact Induced Transformation From the Amorphous to Crystalline State in Metallic Glass

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MECHANICAL CONTACT INDUCED TRANSFORMATION FROM THE AMORPHOUS TO CRYSTALLINE STATE IN METALLIC GLASS

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ABSTRACT

Sliding friction and wear experiments, electron microscopy, and diffraction studies were conducted to examine the metallurgical microstructure of a metallic glass surface strained in sliding contact. Friction and wear experiments were conducted with 3.2- and 6.4-millimeter-diameter aluminum oxide spheres sliding, in reciprocating motion, on a metallic foil with a composition of $Fe_{67}Co_{18}B_{14}Si_1$ at a sliding velocity of 1.5 millimeters per second (frictional heating is negligible), with a load of 2.5 newtons, at room temperature, and in a laboratory air atmosphere.

The results of the investigation indicate that the amorphous alloy (metallic glass) can be crystallized during mechanical contact. Crystallites with a size range of 10 to 150 nanometers are produced on the wear surface of the amorphous alloy. A strong interaction between transition metals and metalloids such as silicon and boron results in strong segregation during repeated sliding and they provide preferential transition metal-metalloid clustering in the amorphous alloy. They subsequently produce the diffused honeycomb-shaped structure formed by dark grey bands and primary crystals, that is, α-Fe in the matrix. α-Fe may be easily oxidized during sliding and transformed into α-Fe_2O_3. Large plastic flow occurs on an amorphous alloy surface with sliding and the flow film of the alloy transfers to the aluminum oxide pin surface. Multiple slip bands due to shear deformation are observed on the side of the wear track. Two distinct types of wear debris were observed as a result of sliding: an alloy wear debris, and/or powdery-whiskery oxide debris. The wear rate of $Fe_{67}Co_{18}B_{14}Si_{1}$ was $5x10^{-9}$ mm^{3}/Nmm.

INTRODUCTION

Amorphous metals can be prepared by a variety of methods: Physical vapor deposition such as evaporation and sputtering, chemical vapor deposition and electroless deposition, electrodeposition, and rapid quenching from the liquid state. Amorphous alloys prepared by the latter method are so called metallic glasses or glassy metals (refs. 1 and 2).

Amorphous metal films are currently finding increased application in tribology, in order to minimize friction and wear, to maintain proper lubrication, and/or to prevent tribological failures of interacting mechanical component surfaces. For example, a spacecraft designed for planetary exploration consists of many moving mechanical components such as bearings, gears, splines, and so forth which must maintain high precisional motion. To meet the severe environmental conditions, conventional oil and grease lubricants cannot be used, and instead a solid film lubricant must be selected. Sputtered solid film lubricants have been used for example on ball bearings for solar array drives, despin and pointing mechanisms for antennas, gyroscopes and accelerometers (ref. 3). With solid film lubrication the properties (adhesive, friction, and wear) of the solid contacting surfaces are extremely important. However, we do not clearly know what actually happens on the tribological surface of amorphous solid films during the sliding, rolling or rubbing process. Does, for example, the amorphous state of solid films crystallize and become crystallographically oriented in the tribological process?

On a crystalline surface the crystallinity and crystallographic orientation can be changed markedly by the strain. The higher the degree of strain, the lower the temperature for recrystallization. Consequently, a highly strained crystalline surface tends to promote recrystallization of the solid surface long before the surface may otherwise be ready for such recrystallization. The tribological surface can also contain grains which are highly oriented as a result of the sliding, rolling, or rubbing process. In other words, the grains tend to become reoriented at the surface so as to reflect the effects of the mechanical parameters imposed on the surface. Such reorientation and recrystallization of crystalline solids in the sliding, rolling, or rubbing process are well known (refs. 4 to 6).

The objective of this investigation, therefore, is to examine the metallurgical microstructure of an amorphous alloy film strained in friction and wear experiments. A metallic glass (amorphous alloy $Fe_{67}Co_{18}B_{14}Si_1$), which was rapidly quenched from the liquid state, was used as an amorphous alloy film. The sliding friction and wear experiments simulating interfacial events of amorphous alloy film were conducted with 6.4- and 3.2-millimeter-diameter aluminum oxide spheres sliding, in reciprocating motion, on the $Fe_{67}Co_{18}B_{14}Si_1$ metallic glass at a sliding velocity of 1.5 millimeters per second (in which frictional heating is negligible) with a load to 2.5 newtons at room temperature and in a laboratory air atmosphere. Metallic glasses have several features that make them attractive for tribological applications. These features or properties include great shear strength, impact penetration resistance, corrosion resistance, stiffness, and ductility. Metallic glass coatings produced by laser glazing or electrodeposition may, because of their mechanical, wear, and/or corrosion properties, be used as protective surfacings. Aluminum oxide has been considered for use in contact with metallic glass because it has been employed in a number of practical devices and has a much higher strength in compression than metals.

MATERIALS

The composition of the metallic glass investigated herein and some of its properties are listed in Table I. The alloy was in the form of a ribbon (0.030- to 0.033-mm-thick foil) and was used in the as-cast condition. The spherical riders that were made to slide on the foil were single-crystal aluminum oxide (sapphire), and the diameters of the spheres were 3.2 and 6.4 millimeters (1/8 and 1/4 in.). The microhardness (Vickers) of the metallic glass was 980 at an indentation load of 1 newton.

APPARATUS

The apparatus used in this investigation (Fig. 1) was basically a pin (rider) on a flat configuration. The specimen was mounted on hardened steel flats and retained in a vise mounted on a screw-driven platform. The platform was driven reciprocally back and forth by a mechanical drive system containing a gear box, a set of bevel gears, and a lead screw driven by an electric motor. The rider traversed a distance of 10 millimeters on the surface of the foil. Microswitches at each end of the traverse reversed the direction of travel so that the rider retraced the original track from the opposite direction; this process was repeated continuously. The rider was deadweight loaded against the foil. The arm retaining the rider contained the strain gages to measure the tangential force. The entire apparatus was housed in a plastic box.

EXPERIMENTAL PROCEDURE

The metallic glass foil and the rider specimen surfaces were scrubbed with levigated alumina, rinsed with tap water and then distilled water, and finally rinsed with ethyl alcohol. After the surfaces were dried with nitrogen gas, the specimens were placed in the experimental apparatus. The specimen surfaces were then brought into contact and loaded, and the friction and wear experiments began. Three sets of experiments were conducted, and each one was continued to 150 hours.

RESULTS AND DISCUSSION

When the amorphous alloy was rubbed by the 6.4-mm-diameter aluminum oxide rider at a load of 2.5 newtons (contact pressure, approx. 0.8 GPa) for 30 minutes, essentially no detectable wear existed on the surface of the amorphous alloy.

Since no visible wear was observed on the amorphous alloy, sliding friction experiments were conducted with a smaller sphere (3.2-mm-diam. aluminum oxide rider) at a sliding time extended to 150 hours to provide a high contact pressure (contact pressure, approx. 1.3 GPa) and more severe conditions.

Although the coefficient of friction was initially low and was about 0.08, it increased with increasing sliding time. After some time (about 3 hr), an equilibrium condition was reached, and the coefficient of friction was 0.2 and did not change with sliding time. The coefficients of friction are generally the same as those obtained at the lower loads of 0.2 to 1.0 newton. The friction results obtained from experiments conducted with 6.4-mm-diameter aluminum oxide rider at loads of 0.1 to 2.5 newtons are also consistent with those for 3.2-mm-diameter aluminum oxide rider.

Scanning electron micrographs of a typical wear track on the amorphous alloy and a wear scar on the aluminum oxide surface are shown in Fig. 2. The experiments were conducted at a load of 2.5 newtons with a 3.2-mm-diameter aluminum oxide rider for a total sliding time of 5 hours. Oxide wear debris particles were generated on the amorphous alloy surface. Amporphous alloy as well as oxide wear debris particles were transferred to the aluminum oxide rider surface.

The sliding action resulted in plastic deformation not only in the wear track of the amorphous alloy surface, but also in the side of the wear track.

Figure 3 reveals that (a) plastic flow occurs in the amorphous alloy with repeated sliding, and that (b) the flow film of the alloy adheres and transfers to the surface of the aluminum oxide pin. Figure 3 presents scanning electron micrographs of typical wear tracks and scars in which oxide wear debris particles were removed from the surface. The wear tracks and scars were produced during a 5-hour sliding period. After the sliding friction experiment, the amorphous alloy specimen and aluminum oxide rider were cleaned with ethyl alcohol and dried.

Multiple shear deformation bands are observed on the side of the wear track, as shown in Fig. 2(a). The plastic flows, observed on the side of wear track, occurs in the form of highly localized shear deformation bands.

It is evident from Fig. 2(a) that a concentration of large shear strain develops in a band during sliding friction. The shear bands are similar to those in crystalline metals (ref. 7).

During a 150-hour sliding period, considerable plastic flow occurred and considerable oxide debris was generated on the amorphous alloy. Figure 4 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 volume was 0.01 cubic millimeter or less. The wear rate, which is defined as the quantity of amorphous alloy removed under a unit load and with a unit distance of sliding, was 5×10^{-9} mm^3/Nmm.

Figure 5 illustrates a detailed examination of the oxide wear debris (submicrometer to micrometers in size) produced on the amorphous alloy by sliding the 3.2-millimeter-diameter aluminum oxide pin on the alloy for 5 hours. The scanning electron micrographs clearly reveal powdery and whiskery oxide wear debris particles on and near the wear track.

Figure 6 reveals oxide as well as amorphous alloy wear debris (submicrometers to micrometers in size) transferred to the aluminum oxide pin.

METALLURGICAL STRUCTURE

The microstructure was examined by transmission electron microscopy and diffraction in a microscope operating at 100 kilovolts to establish the exact crystalline state of the amorphous alloy foils. Final thinning of the foils was accomplished by electropolishing.

Crystallization has been observed to occur during sliding friction with a relatively slow sliding velocity (1.5 mm/sec), in which the frictional heating is negligible.

A typical example of the structure of the as-received amorphous alloy is shown in Fig. 7, in which no dislocations or grain boundaries are evident. However, black spots, believed to be crystallites ranging in size from 1.5 to 4.0 nanometers, are apparent in the micrograph. The transmission electron diffraction patterns for the as-received foil are also presented in Fig. 7. The pattern indicates that so-called metallic glass was not completely amorphous, but contained extremely small grains of approximately a few nanometers in size.

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

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 crystallites ranging in size from 10 to 150 nanometers, 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, dendritic crystals grow in the $Fe_{67}Co_{18}B_{14}Si_1$ 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 spot pattern of the crystallized phase was identified as α-Fe_2O_3.

The diffuse halos indicate that the matrix contains extremely small grains of approximately 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-Fe_2O_3.

Thus, a strong interaction between transition metals and metalloids such as boron results in strong segregation and provides preferential transition metal-metalloid clustering in the bulk of the amorphous alloy during sliding friction. The extent of segregation of metalloids to crystallites or to clusters could be controlled by strain and could control the strength of the alloys, and friction and wear properties of the two alloys. For example, the coefficient of friction of the amorphous alloy increased with crystallization of the alloy (refs. 8 and 9).

CONCLUSIONS

As a result of transmission electron microscopy, diffraction studies, and sliding friction and wear experiments conducted with $Fe_{67}Co_{18}B_{14}Si_1$ ferrous-base metallic glass in contact with 3.2- and 6.4-millimeter-diameter aluminum oxide pins in laboratory air atmosphere, the following conclusions are drawn:

1. An amorphous alloy can be crystallized during the sliding process. Crystallites with sizes of 10 to 150 nanometers are produced on the wear surface of the amorphous alloy. A strong interaction between transition metals and metalloids such as silicon and boron results in strong segregation during sliding friction and they provide preferential transition metal - metalloid clustering in the amorphous alloy. They subsequently produce the diffused honeycomb-shaped structure formed by dark grey bands and primary crystals, that is, α-Fe in the matrix. α-Fe may be easily oxidized during sliding forming α-Fe_2O_3.

2. Large plastic flow occurs on an amorphous alloy surface with sliding, and the flow film of the alloy transfers to the aluminum oxide pin surface. Multiple slip bands due to shear deformation are observed on the side of the wear track.

3. Two distinct types of wear debris were observed as a result of sliding: an alloy wear debris and a powdery and whiskery oxide debris. The wear rate of $Fe_{67}Co_{18}B_{14}Si_1$ was 5×10^{-9} mm^3/N mm.

4. To avoid the crystallization and clustering and to achieve the desired performance level of the wear resistant metallic glass in tribological applications, it is highly desirable to optimize the sliding conditions, such as contact pressure in a particular tribological system.

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TABLE I. - PROPERTIES OF A METALLIC GLASS

Alloy composition[a]	$Fe_{67}Co_{18}B_{14}Si_1$
Vickers microhardness	980
Crystallization temperature[a], °C	430
Density[a], g/cm^3	7.56
Ultimate tensile strength[a], GPa	1.5
Bend ductility[a,b]	1
Thickness, μm	30 to 33

[a] Manufacturer's analysis.

[b] $\varepsilon = t/(d-t)$: t, ribbon thickness; d, micrometer spacing at bend fracture.

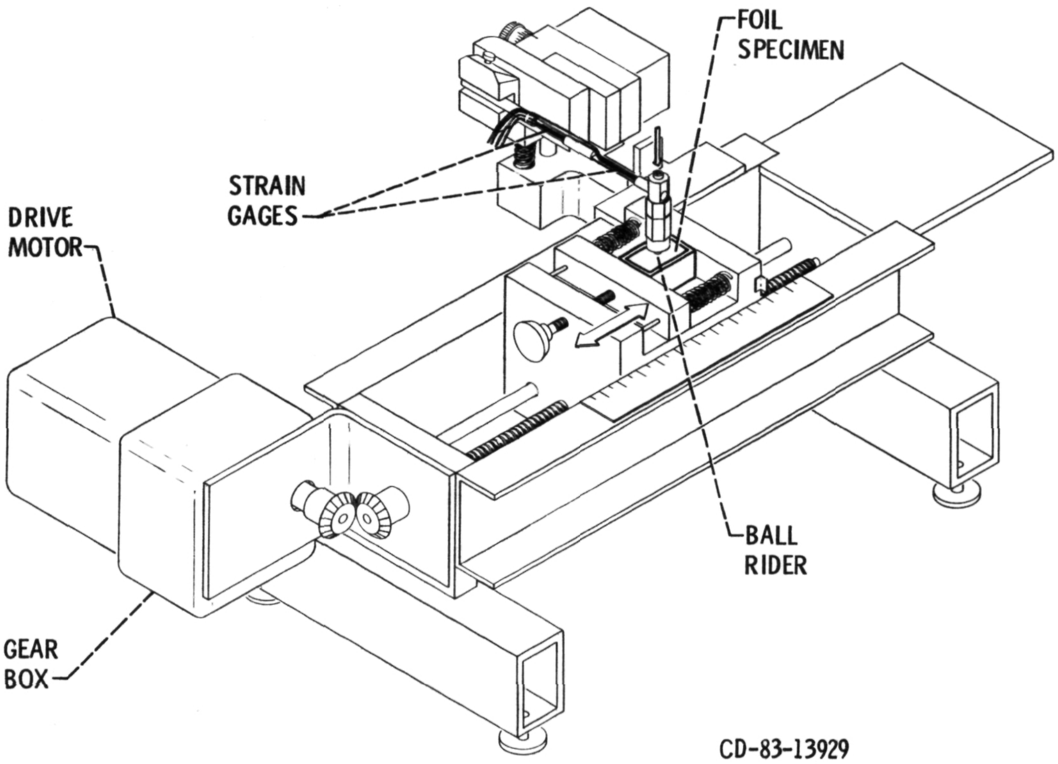
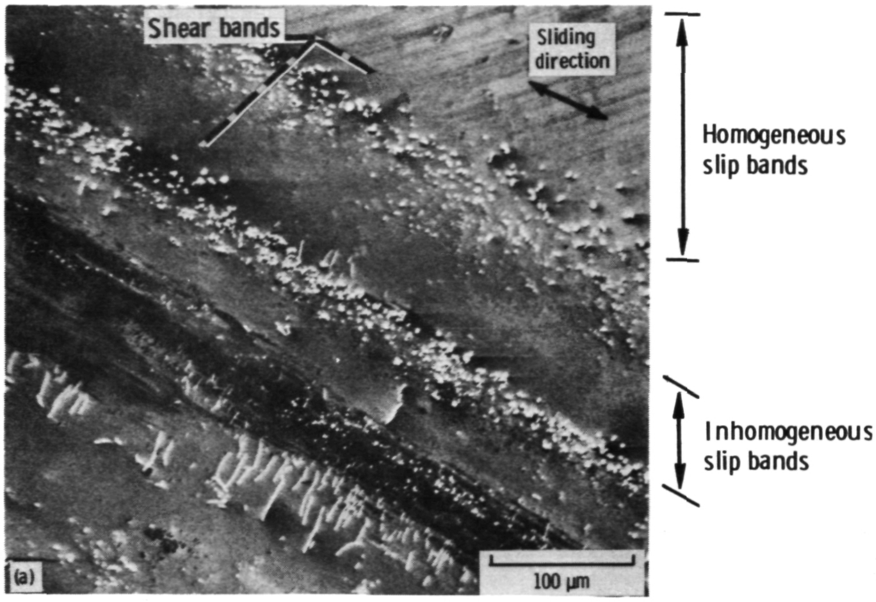
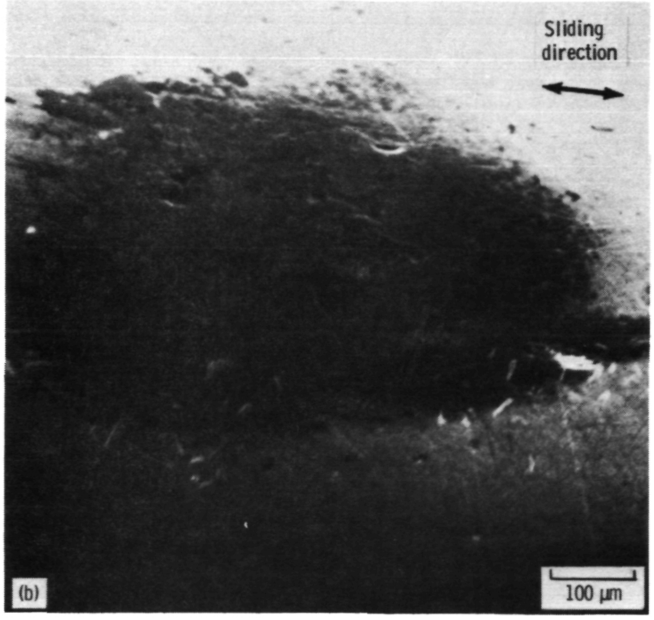


Figure 1. - Friction and wear apparatus.

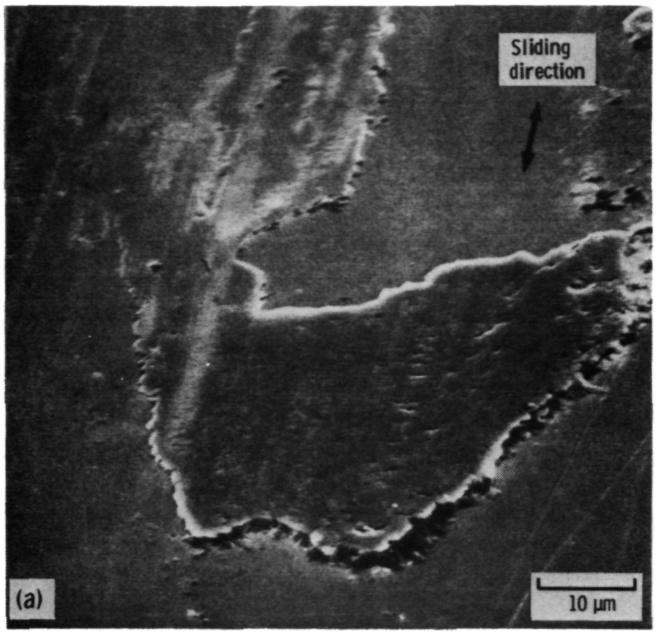


(a) Wear track on $Fe_{67}Co_{18}B_{14}Si_1$ amorphous alloy.

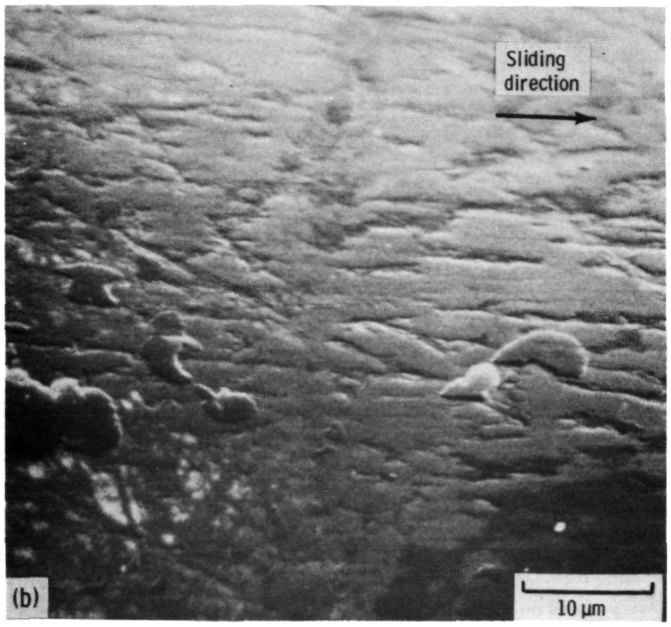


(b) Wear scar on aluminum oxide rider.

Figure 2. - Scanning electron micrographs of wear track on $Fe_{67}Co_{18}B_{14}Si_1$ amorphous alloy and wear scar on aluminum oxide rider. 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.



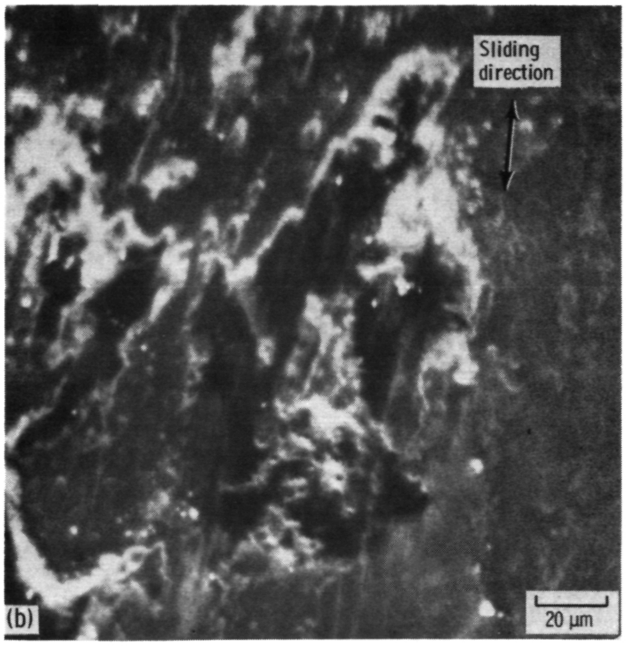
(a) Wear track.



(b) Wear scar.

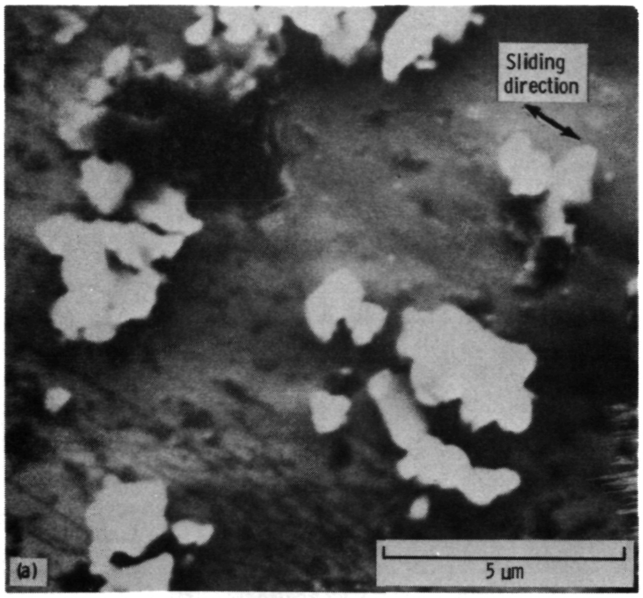
Figure 3. - Scanning electron micrographs of wear track on $Fe_{67}Co_{18}B_{14}Si_1$ amorphous alloy and wear scar on aluminum oxide rider sliding on $Fe_{67}Co_{18}B_{14}Si_1$ amorphous alloy surface. Rider, 3.2-millimeter-diameter aluminum oxide sphere; load, 2.5 newtons; sliding velocity, 1.5 millimeters per second; sliding time, 5 hours; sliding distance, 27 meters; room temperature; laboratory air atmosphere.

(a) Wear damage.

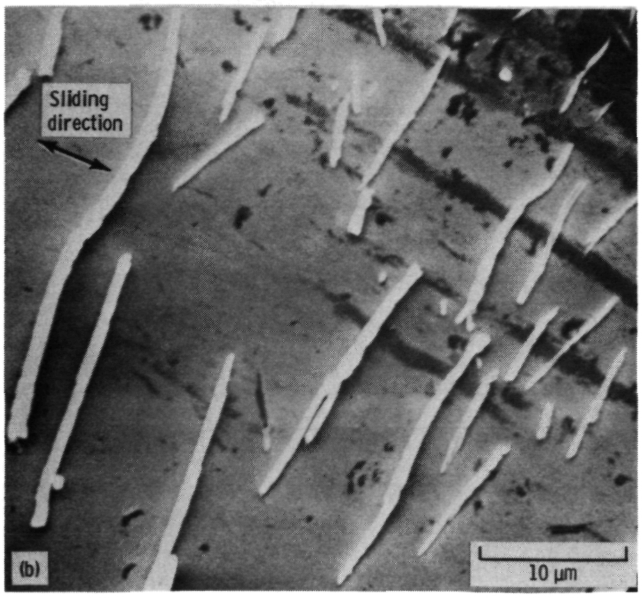


(b) Back-transferred wear debris.

Figure 4. - 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.

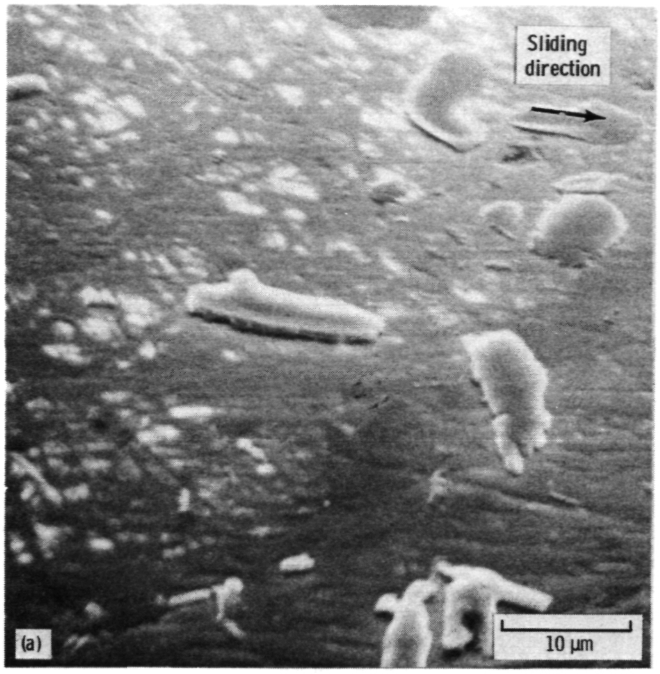


(a) Powdery wear debris particles.

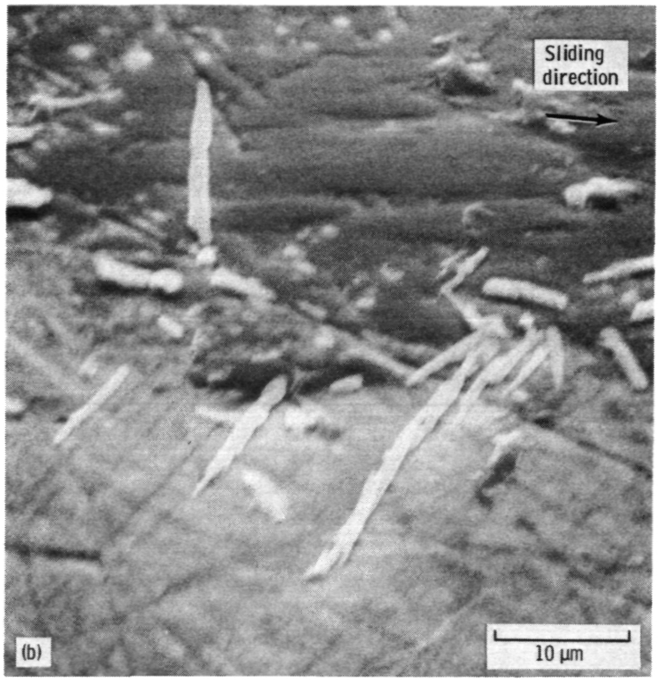


(b) Whiskery wear debris particles.

Figure 5. - Scanning electron micrographs of powdery and whiskery wear debris particles produced on $Fe_{67}Co_{18}B_{14}Si_1$ amorphous alloy. 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.



(a) Powdery wear debris particles.



(b) Whiskery wear debris particles.

Figure 6. - Scanning electron micrographs of powdery and whiskery wear debris particles produced on $Fe_{67}Co_{18}B_{14}Si_1$ amorphous alloy and then transferred to aluminum oxide rider during sliding. 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.

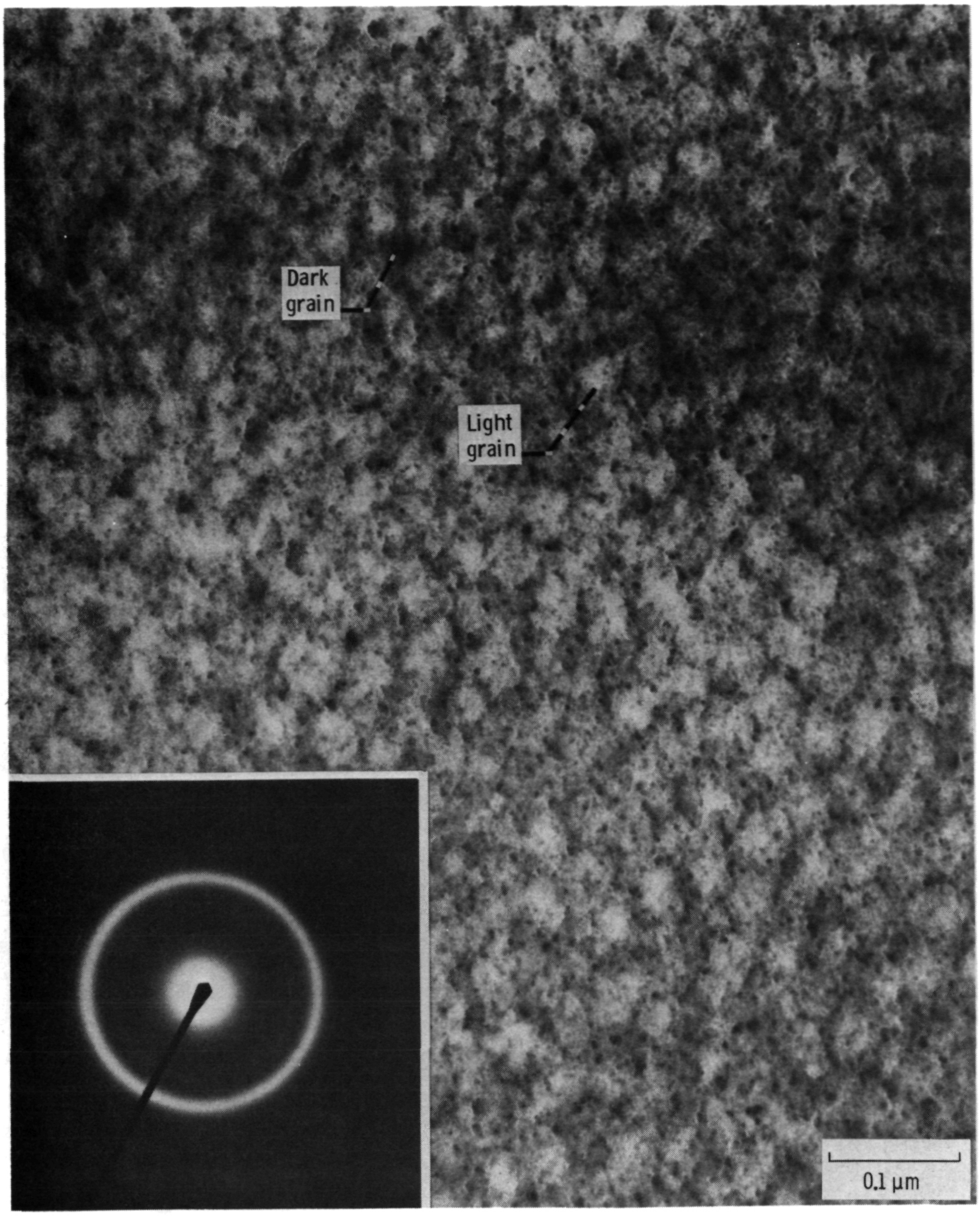


Figure 7. - Typical microstructure and electron diffraction patterns of metallic glass ($Fe_{67}Co_{18}B_{14}Si_1$).

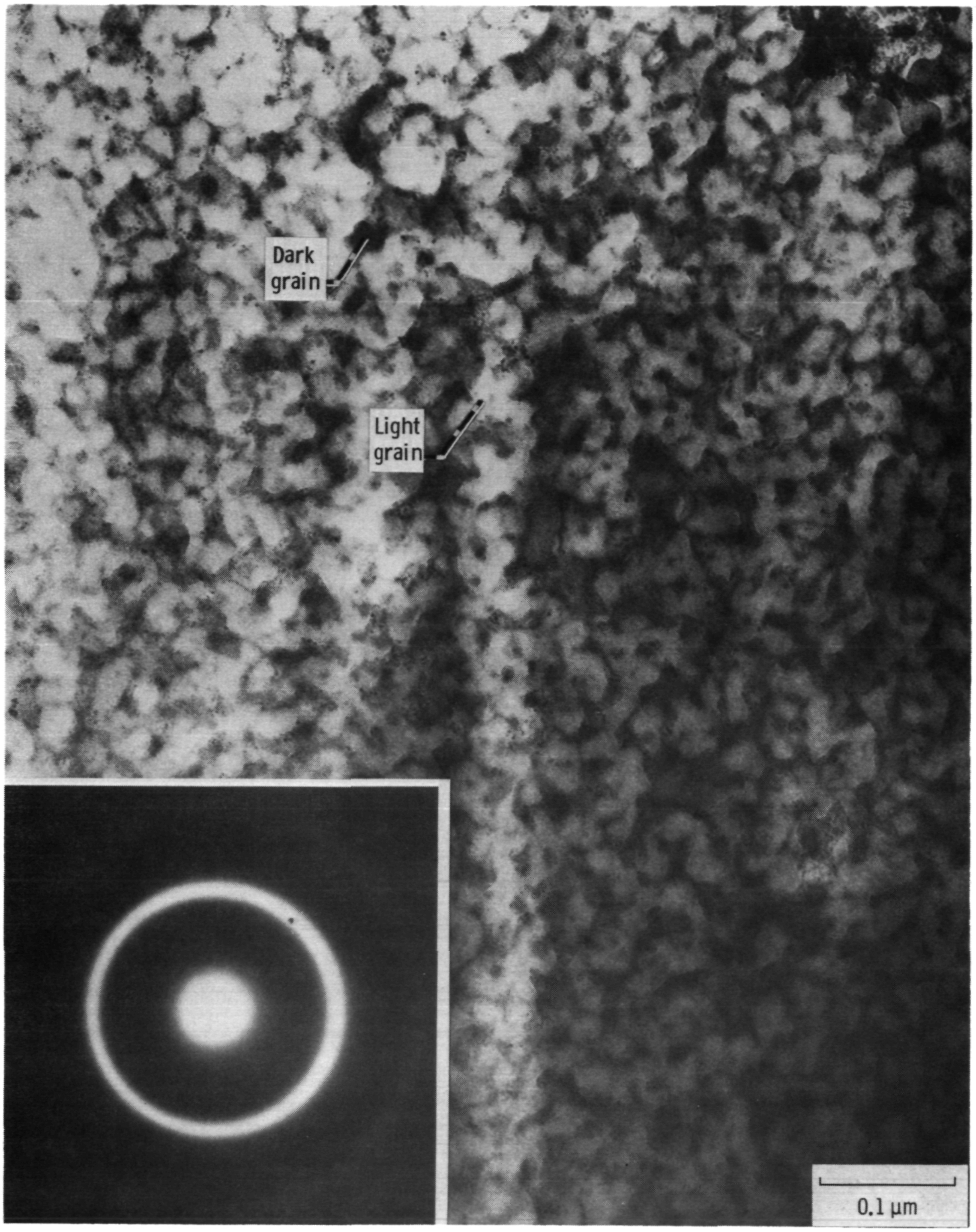
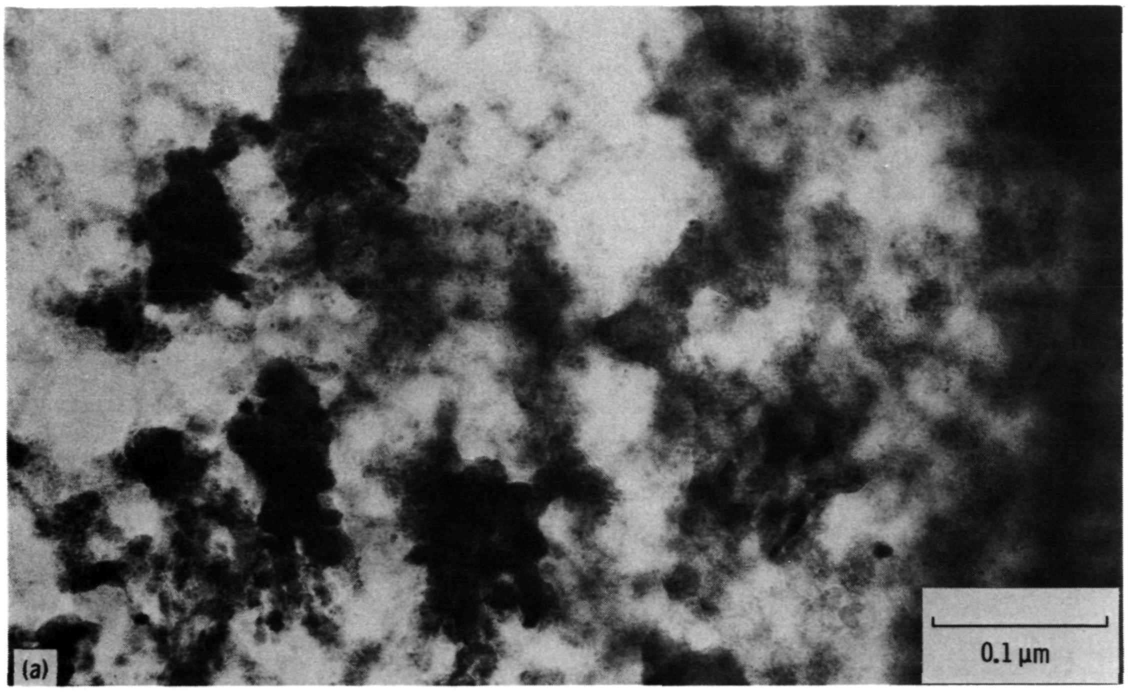
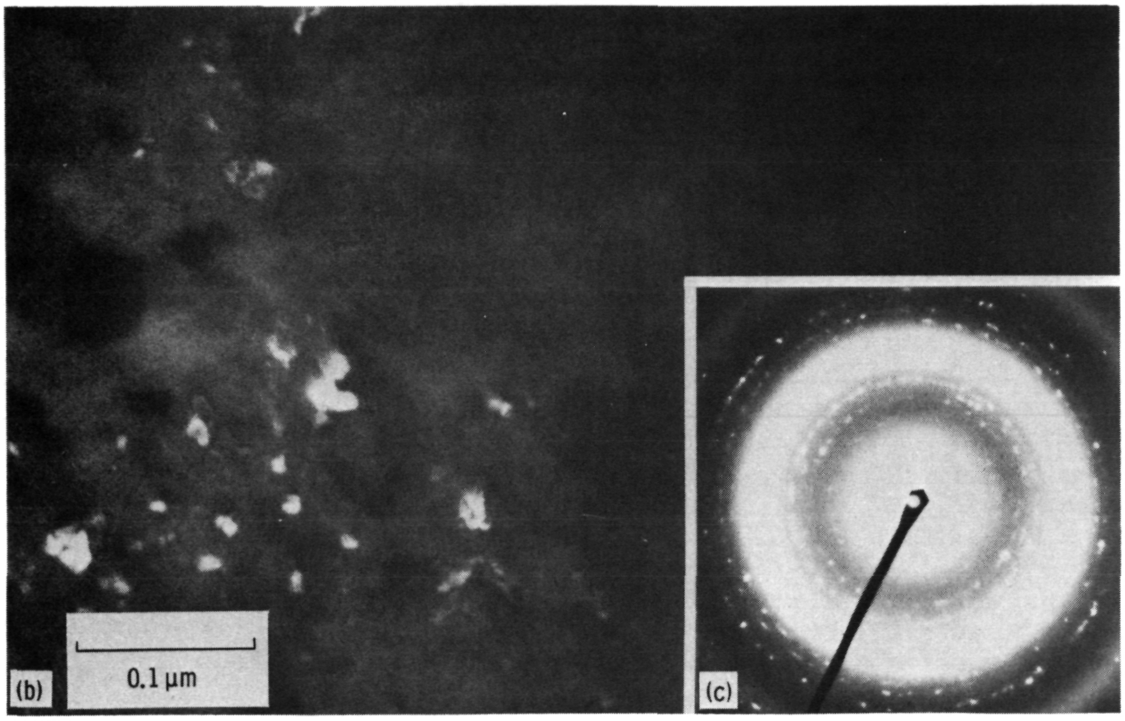


Figure 8. - Typical microstructure and electron diffraction patterns of wear surface of metallic glass ($Fe_{67}Co_{18}B_{14}Si_{1}$). Rider, 3.2 - millimeter-diameter aluminum oxide sphere; load, 2.5 newtons; sliding velocity, 1.5 millimeters per second; sliding time, 150 hours; sliding distance, 810 meters; room temperature; laboratory air atmosphere.



(a) Bright field.



(b) Dark field. (c) Diffraction pattern.

Figure 9. - Microstructure and electron diffraction patterns of wear surface of metallic glass ($Fe_{67}Co_{18}B_{14}Si_1$). 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.

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16. Abstract
Sliding friction and wear experiments, electron microscopy, and diffraction studies were conducted to examine the metallurgical microstructure of a metallic glass surface strained in sliding contact. Friction and wear experiments were conducted with 3.2- and 6.4-millimeter-diameter aluminum oxide spheres sliding, in reciprocating motion, on a metallic foil with a composition of $Fe_{67}Co_{18}B_{14}Si_1$ at a sliding velocity of 1.5 millimeters per second (frictional heating is negligible), with a load of 2.5 newtons, at room temperature, and in a laboratory air atmosphere. The results of the investigation indicate that the amorphous alloy (metallic glass) can be crystallized during mechanical contact. Crystallites with a size range of 10 to 150 nanometers are produced on the wear surface of the amorphous alloy. A strong interaction between transition metals and metalloids such as silicon and boron results in strong segregation during repeated sliding and they provide preferential transition metal-metalloid clustering in the amorphous alloy. They subsequently produce the diffused honeycomb-shaped structure formed by dark grey bands and primary crystals, that is, α-Fe in the matrix. α-Fe may be easily oxidized during sliding and transformed into α-Fe_2O_3. Large plastic flow occurs on an amorphous alloy surface with sliding and the flow film of the alloy transfers to the aluminum oxide pin surface. Multiple slip bands due to shear deformation are observed on the side of the wear track. Two distinct types of wear debris were observed as a result of sliding: an alloy wear debris, and/or powdery-whiskery oxide debris. The wear rate of $Fe_{67}Co_{18}B_{14}Si_1$ was 5×10^{-9} mm^3/N.

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