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OXYGEN AND SULFUR INTERACTIONS WITH A CLEAN IRON SURFACE AND THE EFFECT OF RUBBING CONTACT ON THESE INTERACTIONS

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16. Abstract

The interaction of sulfur and oxygen with an iron surface was studied with Auger spectroscopy analysis both statically and during sliding-friction experiments in a vacuum environment. Oxygen, hydrogen sulfide, methyl mercaptan, and sulfur dioxide were adsorbed to an iron surface. Results indicate that sulfide films formed on clean iron surfaces are completely displaced by oxygen. Hydrocarbons containing sulfur, such as methyl mercaptan, adsorb dissociatively. Less sulfur is adsorbed during sliding with hydrogen sulfide and methyl mercaptan than in the absence of sliding. With both oxygen and sulfur dioxide, sliding did not affect the amount of material adsorbed to iron.

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SUMMARY

An investigation was conducted to determine the nature of the chemical interactions of oxygen and sulfur with iron when surfaces are stationary and also during sliding in a vacuum environment. Various gases that contained sulfur, oxygen, or both were adsorbed to iron at 23° C. The gases included oxygen, hydrogen sulfide, methyl mercaptan, and sulfur dioxide. Friction experiments were conducted with a hemispherical rider sliding on a rotating disk. An Auger cylindrical mirror analyzer was used to monitor the iron surface chemistry.

The results of this study indicate that oxygen will completely displace sulfide films from iron surfaces. Hydrocarbons containing sulfur, such as methyl mercaptan, adsorb to an iron surface dissociatively. Only sulfur is detected on the iron surface. Sliding inhibits the formation of sulfide films on iron with the adsorption of hydrogen sulfide and methyl mercaptan. With oxygen and sulfur dioxide, the sliding process does not affect adsorption behavior.

INTRODUCTION

Sulfur is one of the most widely used elements in extreme-pressure lubricant additives. Despite its wide use, the exact mechanism of its interaction with metal surfaces in the presence of lubricants and normal environmental constituents (presence of air, water vapor, etc.) is still not clearly understood. Numerous works (e.g., refs. 1 to 8) have been published on the subject.

Some authors (refs. 2 to 5) have indicated that, with steel or iron surfaces, iron sulfide is formed and it is this compound which is responsible for the increased load-carrying capacity. Other authors have found no evidence for the formation of iron sulfide but rather they have found iron oxides as the principal reaction products (refs. 1

and 8). Still others have indicated that the exact mechanism is not known (ref. 7).

The real uncertainty appears to exist in whether the surface films are really sulfides or oxides. Other than reference 2, there is little or no evidence for the hydrocarbons interacting with the surface to form inorganic compounds (e.g., carbides).

The objective of this investigation was to examine the mechanism of interaction of sulfur and oxygen with a clean iron surface. The iron surface was exposed to oxygen, hydrogen sulfide, methyl mercaptan, and sulfur dioxide. Further, sulfide-covered iron surfaces were exposed to oxygen, and oxide-covered surfaces to hydrogen sulfide. The objective here was to determine if substitution reactions occur at the surface. Formation of surface films was studied with an Auger cylindrical mirror analyzer, and interactions were examined for both the static case and when the surfaces were in sliding contact.
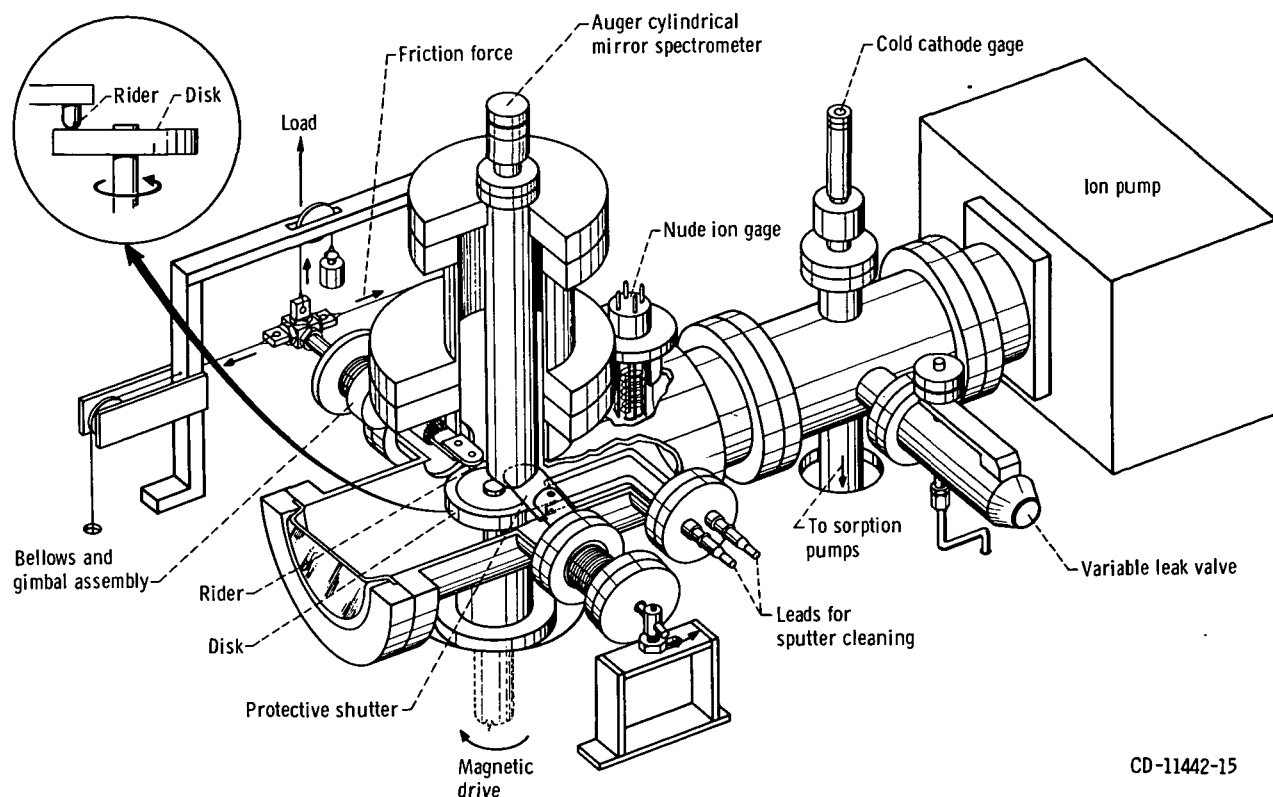
MATERIALS

The iron disk surfaces used in this investigation were fabricated from 99.99-percent zone refined iron. The surfaces were polished on metallurgical papers down to 600 grit and were then polished with 3-micron-diamond paste to produce a mirror like surface.

All of the gases used were research grades. The oxygen contained 5 ppm nitrogen, 16 ppm argon, 8 ppm krypton, and 9.4 ppm methane. The hydrogen sulfide was 99.6 percent pure. The methyl mercaptan was 99.5 percent, and the sulfur dioxide was 99.98 percent pure.

EXPERIMENTAL APPARATUS AND PROCEDURE

Specimens

The friction-and-wear specimens consisted of a disk specimen 6.5 centimeters in diameter and 1.2 centimeters in thickness and a hemispherical rider with a 0.5-centimeter radius. A schematic diagram of the specimens and the apparatus is shown in figure 1. The disk specimen is mounted on a drive shaft which is rotated with a magnetic drive assembly. The drive assembly provides for rotation at various speeds (in this study, 30 cm/min). The rider specimen (aluminum oxide coated with a thin sputter deposited metal film (1000 Å)) is mounted in a holder to one end of a stainless-steel shaft. Sliding experiments are conducted with the rider specimen loaded against the iron disk surface. As the disk is rotated, the rider scribes a circular wear track

Figure 1. - Friction apparatus with Auger spectrometer.

on the flat surface of the disk. The load used in this investigation was 100 grams, and the temperature was 23° C.

Experimental Chamber

The experiments are conducted in a vacuum chamber (see fig. 1). The vacuum system is pumped by sorption pumps and an ion pump Pressure in the vacuum system is read with a cold-cathode ionization gage. The vacuum system achieved a pressure of 1×10^{-10} torr after bakeout at 250° C.

Measurements

The friction force between the disk and rider specimen is continuously recorded during friction experiments. The beam which contains the rider specimen is welded into a bellows assembly which is gimbal mounted to the vacuum system. The gimbal

3

mounting permits deadweight loading of the rider against the disk surface (fig. 1). At right angles to the deadweight loading, the beam containing the rider can move in two directions in the horizontal plane. Movement of the rider (with the disk as it rotates) is restrained by a cable which is attached to a beryllium-copper ring. The ring contains four sets of strain gages. These gages measure the frictional force between the disk and rider specimen. The friction force is recorded on a strip chart.

Specimen Cleaning

The specimens are cleaned by ion bombardment in the experimental chamber. The disk specimen is insulated from ground on the drive shaft. Two copper rods are brought to the disk from feed-throughs insulated from ground. The end of one rod terminates 0.5 centimeter from the circumferential edge of the disk specimen. This terminal establishes the positive potential in the glow discharge. The second rod has a beryllium-copper leaf attached to it. The end of the leaf opposite its attachment to the rod makes a "wiping" type of contact with the circumferential edge of the disk. The entire flat of the disk is cleaned by the sputtering as a result of being immersed in the glow discharge. At the same time, fresh iron is deposited on the aluminum oxide from the iron disk as a result of the sputtering process. The specimens are ion-bombarded by bleeding research-grade argon gas into the system until a pressure of about 0.02 torr is achieved. A direct-current power supply is used to supply 1000 volts between the disk and the floating electrode. With the negative potential on the disk, positively charged argon ions bombard and sputter clean the specimen surfaces.

Auger Analysis

Elemental analysis of the disk specimen surface can be made before, during, and after the friction-and-wear experiment by using an Auger cylindrical mirror analyzer with an integral electron gun. The point of contact of the rider with the disk passes under the Auger beam 20 seconds after the disk moves out of the contact zone. This time element can be changed by changing the speed at which the disk rotates. The disk could rotate over a broad range of speed, and Auger analysis could still be performed. The Auger analyzer is a commercial unit, the essential elements of which are described in the literature (ref. 9).

The primary beam of electron is directed at the disk surface by a beam from the electron gun in the Auger cylindrical mirror analyzer. The beam is focused on the wear track scribed by the rider in sliding contact with the disk. The beam contact is 150°

away from the rider on the disk surface. The beam spot diameter is 0.2 millimeter. The gun contains deflection plates which allow positioning of the beam on the disk surface.

The secondary electrons come off the specimen surface, pass through the Auger can, then pass through to an energy analyzer. They are collected by the electron multiplier. Elemental identification is accomplished by detection of the Auger electron energies. The Auger electrons that appear in the secondary-electron distribution "fingerprint" the surface elements to a depth of approximately four atomic layers.

Auger traces are displayed on an oscilloscope. The sweep control module permits a full spectrum scan for those elements of interest in friction, wear, and lubrication in 0.10 second. Thus, there exists the capability of monitoring a moving or rotating surface and detecting dynamic variations in surface chemistry.

RESULTS AND DISCUSSION

Oxygen

A sputter-cleaned iron disk surface was exposed to various amounts of oxygen. Exposures are measured in langmuirs (1 langmuir = 10^{-6} torr-sec). The disk was exposed to oxygen while stationary and during a sliding friction experiment. The results, shown in figure 2, indicate that the iron surface continued to adsorb oxygen in a linear manner with increase in exposure. The relative amount of oxygen adsorbed by the surface was insensitive to the sliding process. Both static adsorption and adsorption during sliding produced the same results.
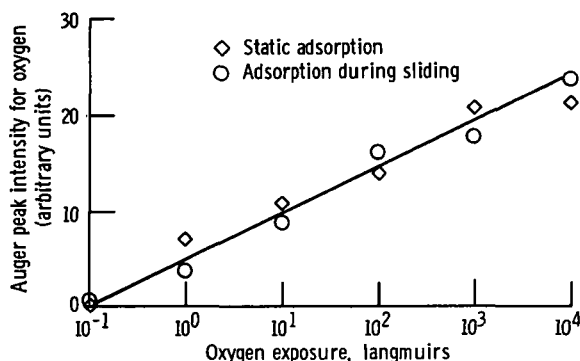

Figure 2. - Auger spectroscopy detection of oxygen adsorbed on a clean iron surface exposed to oxygen under static conditions and during sliding friction. Sliding velocity, 30 centimeters per minute; load, 100 grams; ambient temperature, 23^0 C.

Hydrogen Sulfide

A clean iron surface was exposed to hydrogen sulfide. Auger spectra are presented in figure 3 for the clean iron surface and that same surface after exposure to 10 000 langmuirs of hydrogen sulfide. In figure 3(a), the only Auger peaks are the four associated with the clean iron. After exposure to hydrogen sulfide (fig. 3(b)), there is a large sulfur peak due to the adsorption of hydrogen sulfide to the surface.

Hydrogen sulfide adsorbs to iron dissociatively (refs. 10 and 11). Only sulfur remains on the surface after adsorption. This is the case with iron as well as with other metals, such as copper.
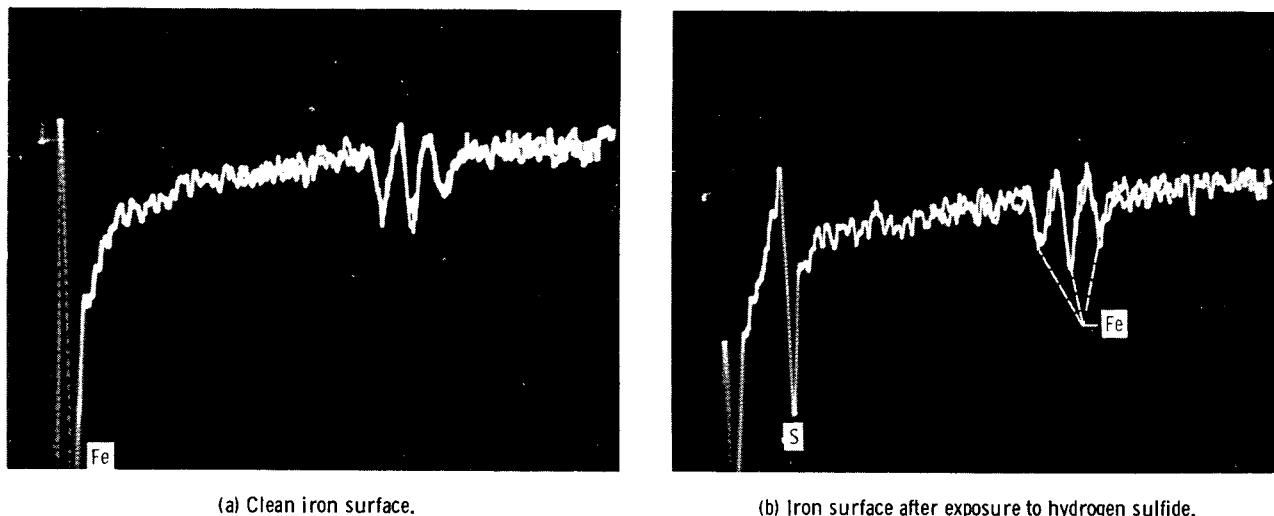

(a) Clean iron surface.

(b) Iron surface after exposure to hydrogen sulfide.

Figure 3. - Auger spectra of an iron surface before and after exposure to 10 000 langmuirs of hydrogen sulfide at 23^0 C.

Experiments were conducted with iron exposed to hydrogen sulfide in both static adsorption studies and during sliding friction experiments. The results obtained are presented in figure 4. Unlike the results obtained with oxygen (fig. 2), the results obtained with hydrogen sulfide are influenced by sliding. At exposures beyond 10 langmuirs, less sulfur is present on the sliding surface. Sliding either inhibits adsorption or induces desorption once adsorption has occurred. With sliding, the frictional heating at the interface can contribute to such desorption.
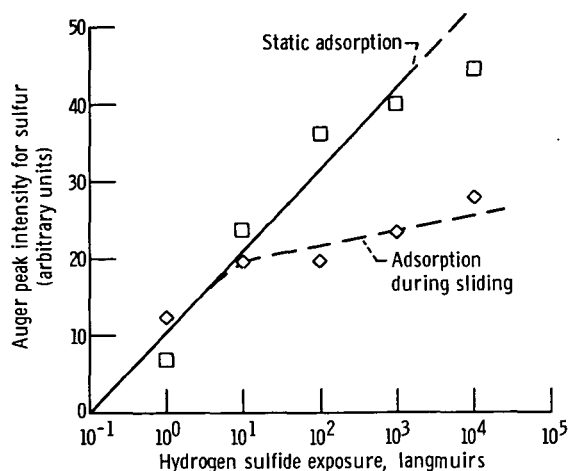
Figure 4. – Auger spectroscopy detection of sulfur adsorbed on a clean iron surface exposed to hydrogen sulfide under static conditions and during sliding friction. Sliding velocity, 30 centimeters per minute; load, 100 grams; ambient temperature, 23° C.

The sulfide films generated on the iron surface were relatively stable. Heating the iron to 250° C for 12 hours did not result in desorption of the sulfur. The sulfur Auger peak after heating had not been diminished in size by the prolonged heating.
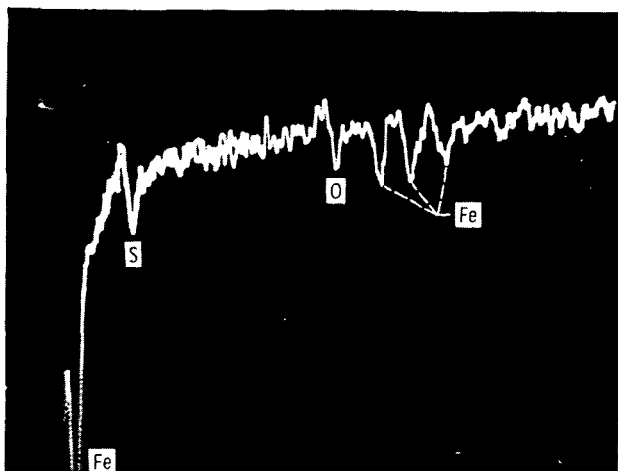
Oxygen Displacement of Sulfur

In practical lubrication systems, oxygen is nearly always present in the environment. It is of interest, therefore, to know what effect oxygen has on sulfide films such as those evidenced by the data of figure 4. The sulfide films of figure 4 were, therefore, subjected to various exposures of oxygen. Figure 5 presents Auger spectra after two different exposures of oxygen.
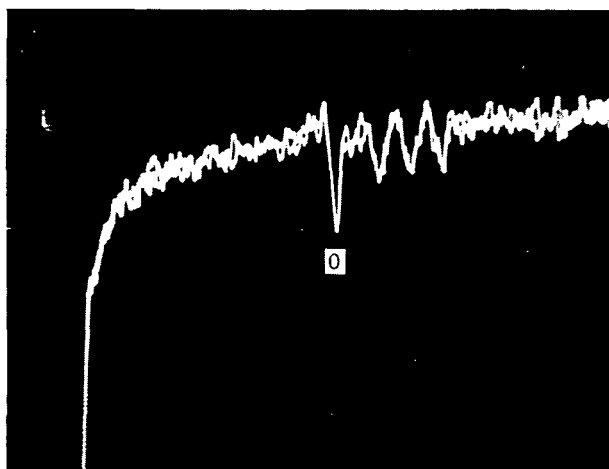
The spectrum of figure 5(a) indicates the presence of both sulfur and oxygen at 100 langmuirs of oxygen. After a total exposure of 10 000 langmuirs of oxygen, the Auger spectrum of figure 5(b) was obtained. This indicates, in addition to iron, only oxygen peaks. The sulfur is absent. Thus, there has been a total displacement of sulfur from the iron surface by the oxygen.

The change in both the sulfur and oxygen peak intensities with oxygen exposure can be seen in figure 6. The sulfur peak continues to decrease in intensity with oxygen exposure, while oxygen concentration on the surface continues to increase. At 10 000 langmuirs, the sulfur has completely disappeared.

If the oxygen Auger peak intensities of figure 2 are compared with those of figure 6, as is done in figure 7, it becomes apparent that oxygen adsorption is retarded some-

(a) Film exposed to 100 langmuirs of oxygen.

(b) Film exposed to 10 000 langmuirs of oxygen.

Figure 5. - Auger spectra for the displacement of a sulfide film from an iron surface by oxygen at 23° C.
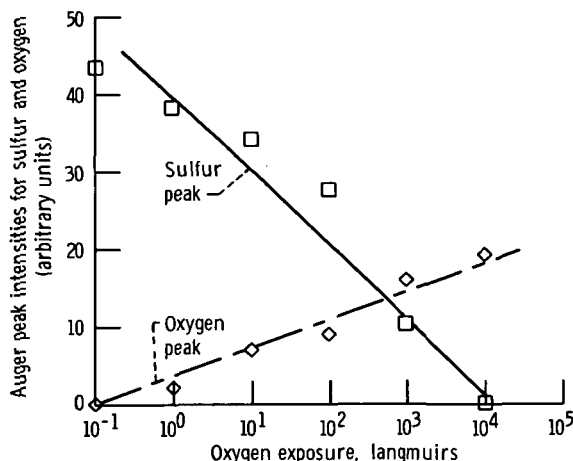

Figure 6. - Auger spectroscopy evidence for the displacement of sulfur from an iron surface by oxygen. Initial sulfide film formed by exposure of iron surface to 10 000 langmuirs of hydrogen sulfide at 23° C.
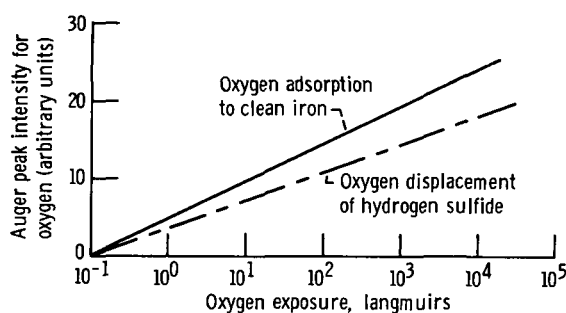

Figure 7. - Auger peak intensities for the adsorption of oxygen to clean iron and for the displacement of a hydrogen sulfide film from iron by oxygen at 23° C.

what by the presence of the sulfide film. The kinetics of the substitution reaction are slower than direct oxidation of iron.

In a different set of experiments, hydrogen sulfide was adsorbed to an oxygen-covered iron surface. The object was to determine if hydrogen sulfide chemisorbed to oxygen. The Auger emission spectroscopy results obtained are present in figure 8. The sulfur peak in figure 8(a) increases in intensity with hydrogen sulfide exposure. The oxygen peak decreases as it is covered over by the sulfur. The results of figure 8(a), then, indicate that hydrogen sulfide will chemisorb to oxygen present on an iron surface. Physical adsorption does not occur under the conditions of these experiments.
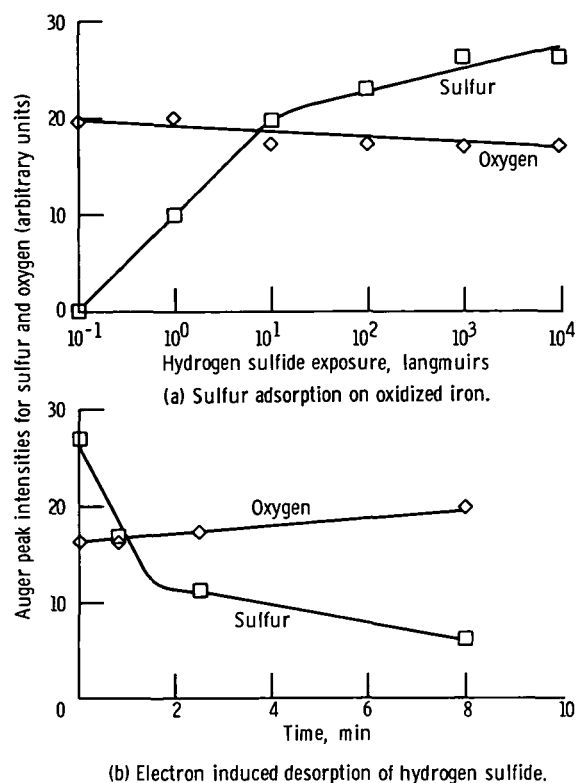
30 ┌

Auger peak intensities for sulfur and oxygen (arbitrary units)

20

Sulfur

Oxygen

10

0

10^{-1} 10^0 10^1 10^2 10^3 10^4

Hydrogen sulfide exposure, langmuirs

(a) Sulfur adsorption on oxidized iron.

30 ┌

20

Oxygen

10

Sulfur

0   2   4   6   8   10

Time, min

(b) Electron induced desorption of hydrogen sulfide.

Figure 8. – Auger spectroscopy sulfur peak intensities for
the adsorption of hydrogen sulfide on an oxide covered
iron surface at 23^0 C and electron induced desorption of
hydrogen sulfide.

The hydrogen sulfide present on the surface is subject to electron-induced desorption. That is, the electron energy associated with the Auger primary electron beam is sufficient to desorb the adsorbed species. Evidence for this is presented in the curves of figure 8(b). The sulfur peak intensity at a fixed spot on the surface decreases with time, while the oxygen peak increases slightly. The oxygen peak increases in intensity because the oxygen is being exposed as the sulfur is removed.

Methyl Mercaptan

Sulfur, when present in a lubricant as an extreme-pressure additive is usually formulated with the lubricant in the form of an organic compound. A question to be resolved is how the sulfur is liberated from the organic molecule. Adsorption studies were, therefore, conducted with the hydrocarbon methyl mercaptan (CH_3SH). Results for both static adsorption and adsorption during sliding are presented in figure 9.

In figure 9, the Auger peak intensity for sulfur is plotted as function of exposure to methyl mercaptan for both the static and the dynamic, or sliding, experiments. As with
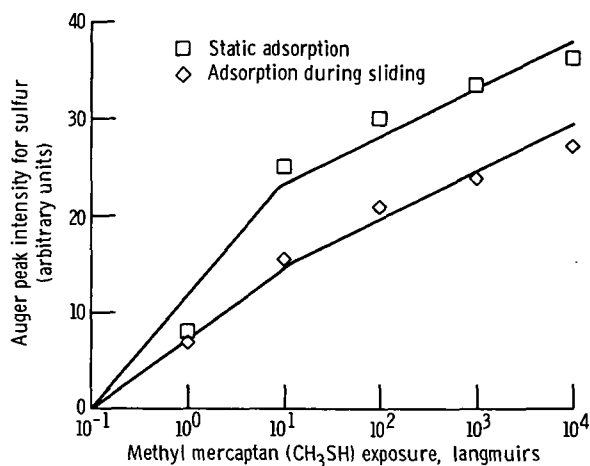
Figure 9. – Auger spectroscopy detection of sulfur adsorbed on a clean iron surface exposed to methyl mercaptan under static conditions and during sliding friction. Sliding velocity, 30 centimeters per minute; load, 100 grams; ambient temperature, 23° C.

hydrogen sulfide, the amount of sulfur adsorbed during sliding was less than with static adsorption.

The interesting aspect of methyl mercaptan adsorption to iron is that there was no evidence of carbon on the surface with adsorption. A quadrupole mass spectrometer was mounted on the vacuum system to monitor the composition of the gases in the environment and the principal M/e mass-to-charge ratios (M/e) were 48, 47, 16, and 15. These M/e values were detected with adsorption of the methyl mercaptan. The M/e value of 48 is the methyl mercaptan, the 47 value is that molecule which lacks a hydrogen atom.

The M/e values of 15 and 16 are CH_3^+ and CH_4, respectively. These originate from adsorptive dissociation of the methyl mercaptan, with sulfur adsorbing on the iron, and the methyl group passing into the vacuum system. Methane (CH_4) in all probability results from combination of the methyl group with hydrogen present in the vacuum system.

The complete absence of carbon on the iron surface even at exposures to 10 000 langmuirs of methyl mercaptan indicates that there is total dissociation of the hydrocarbon molecule. Thus, only the active sulfur in organic molecules such as methyl mercaptan remains on clean iron surfaces after adsorptive interactions. A similar observation was made in reference 12 with semiconductors.

The sulfur covered iron surface originating from the methyl mercaptan was exposed to oxygen, just as the hydrogen sulfide developed sulfur film had been. Again, the sulfur film was completely displaced from the iron surface by oxygen. Auger analysis after exposure to 10 000 langmuirs of oxygen revealed only iron and oxygen peaks.

10

Sulfur Dioxide

Since oxygen displaces sulfur from an iron surface, experiments were conducted in which both oxygen and sulfur were present in the same molecule. Sulfur dioxide (SO_2) was chemisorbed to a clean iron surface both statically and during sliding. The results obtained are indicated in the Auger spectrometer results of figure 10.

In figure 10, both the oxygen and the sulfur were detected on the surface with exposures of as little as 1 langmuir. These results indicate that adsorption is molecular. If dissociative adsorption occurred, sulfur might not have been detected.
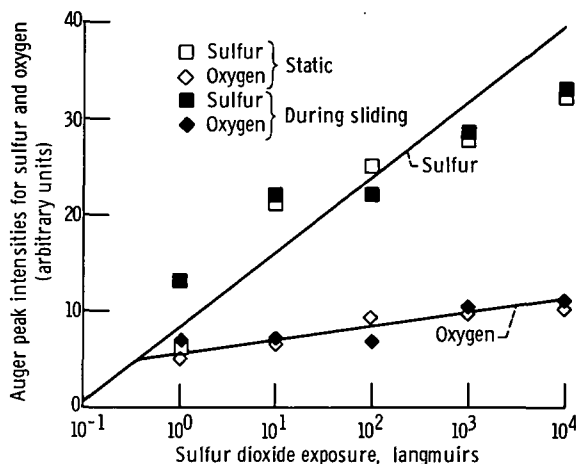

Figure 10. - Auger spectroscopy detection of sulfur and oxygen adsorbed on a clean iron surface exposed to sulfur dioxide under static conditions and during sliding friction. Sliding velocity, 30 centimeters per minute; load, 100 grams; ambient temperature, 23° C.

The data of figure 10 indicate that sliding exerts no influence on adsorption. The sulfur and oxygen data points follow the same curves. In both cases, surface uptake of sulfur dioxide increases with increasing exposure.

CONCLUSIONS

Based on the experimental results obtained in this investigation at 23° C with oxygen, hydrogen sulfide, methyl mercaptan, and sulfur dioxide adsorbed to iron, the following conclusions are drawn:

1. Sulfide films present on iron surfaces are displaced by oxygen.

2. Hydrocarbons such as methyl mercaptan adsorb to iron dissociatively. Only sulfur remains on the iron surface. The hydrocarbon radical passes into the system.

3. The sliding process inhibits the adsorption of hydrogen sulfide and methyl mercaptan to an iron surface.

4. Sliding exerts no effect on the adsorption of oxygen and sulfur dioxide to an iron surface.

5. Sulfur dioxide adsorbs to an iron surface molecularly.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, March 7, 1973,
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