Friction and Transfer of Copper, Silver, and Gold to Iron in the Presence of Various Adsorbed Surface Films

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SUMMARY

An investigation was conducted to determine the effect of metal chemistry and specie of surface film for the three noble metals, copper, silver, and gold and two binary alloys in sliding contact with iron. Friction and transfer characteristics of the noble metals to iron were examined with the surfaces saturated with oxygen, methyl mercaptan, and methyl chloride. Sliding friction experiments were conducted at a velocity of 60 millimeters per minute, a load of 100 grams, and at 25° C. Auger emission spectroscopy analysis was used to monitor the presence of the surface films and the transfer of the noble metals to iron.

Results of the study indicate that the friction and transfer characteristics of the noble metals in the presence of the various adsorbates is highly specific both with respect to the adsorbate and the surface film. With all three films present on the iron surface the noble metals transferred rapidly. Noble metals continued to transfer to the iron surface in the presence of all films except where silver and copper were sliding against iron sulfide. In the latter two cases transfer occurred rapidly initially (to 50 passes) and then no further increase in metal transfer to iron was observed.

INTRODUCTION

The adhesion and friction behavior of metals and alloys in sliding contact is dependent upon metal chemistry. A chemical effect has been observed for metals in contact with themselves (ref. 1), oxides (ref. 2), and nonmetals (ref. 3).

When dissimilar clean metals are brought into solid state contact strong adhesive bonding forces develop across the interface and these bonding forces are related to chemical reactivity (ref. 4). Thus, in dry sliding and even with sliding in the presence of a lubricant the occurrence of metal to metal contact through surface films makes metal interaction chemistry important.

In addition to metal chemistry effecting metal to metal interactions it also affects lubricant interactions with the surface. The nature of specie reaction (ref. 5) effects friction with even fractions of a monolayer of chemisorbed films having an effect (ref. 6). Thus, metal chemistry and lubricant to metal surface chemistry are both important in friction behavior.

The objectives of the present investigation were to determine the effect of metal
chemistry and lubricant surface interactions on friction behavior. Sliding friction experiments were conducted with the three noble metals, copper, silver, and gold and two binary alloys of these metals sliding against iron. Three lubricating species were examined; these included oxygen, methyl mercaptan, and methyl chloride. Friction experiments were conducted at a load of 100 grams, a sliding velocity of 60 millimeters per minute and at $25^\circ$ C. Auger emission spectroscopy analysis with a scanning sample positioner was used to monitor wear track chemistry.

MATERIALS

Only five sets of experimental specimens were used for this investigation. These consisted of a copper, silver, gold, 50 atomic percent copper in gold and 50 atomic percent silver in gold riders and iron disks upon which these riders slid. The disks and riders were refinished between experiments to ensure an absence of variation in mechanical properties from experiment to experiment. The iron specimens were 99.99 percent in purity while the copper, silver, and gold were 99.999 percent in purity. The simple binary alloys were prepared from these metals and all specimens were annealed prior to use.

The oxygen used was 99.995 percent minimum purity. Both methyl mercaptan and methyl chloride were 99.5 percent pure.

EXPERIMENTAL APPARATUS AND PROCEDURE

Experimental Chamber

The experiments are conducted in a vacuum chamber (see fig. 1(a)). The vacuum system is pumped by sorption pumps and an ion pump. Pressure in the vacuum system is read with an ionization gage.

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 2.5-centimeter radius. The specimens are shown in the apparatus schematic in figure 1. The disk specimen is mounted on a drive shaft from which it is electrically insulated and rotated with a magnetic drive assembly. The drive assembly provides for rotation at various speeds (in this study, 60 mm/min). For sputter cleaning the rider specimen is mounted in an insulated holder on one end of a stainless-steel shaft. Both disk and
rider can be sputter cleaned prior to adsorption and sliding friction studies. Friction and wear experiments are conducted with the rider specimen loaded against the disk surface. As the disk is rotated, the rider scribes a circular wear track on the flat surface of the disk. The load used in this investigation was 100 grams, and the temperature was $25^\circ$ C.

**Measurements**

The friction force between the disk and rider specimen is continuously recorded during the experiment. The beam which contains the rider specimen is welded in a bellows assembly which is gimbal mounted to the vacuum system. The gimbal 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 temperature compensated strain gage. These gages measure the frictional force between the disk and rider specimen. The friction force is recorded on a strip chart.

**Specimen Preparation and Cleaning**

The disk specimens are finish ground on metallurgical papers to a grit of 600. They are then diamond polished with 3-micrometer (micron) and finally 1-micrometer (micron) aluminum oxide. The disks are rinsed with acetone and then with absolute ethyl alcohol.

The rider specimens were acid cleaned prior to use with aqua regia to remove metal and other contaminants that may have become embedded in the surface from finishing. They were then scrubbed with levigated alumina, rinsed in water and finally in ethyl alcohol.

**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 rider to disk contact passes under the Auger beam after that point moves out of the contact zone. The Auger analyzer is a commercial unit, the essential elements of which are described in the literature (ref. 4).

The primary beam of electrons 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 $180^\circ$ 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 outer cylindrical can opening, and then pass through slits in an inner cylinder which serves as an energy analyzer. They are collected by the electron multiplier. Elemental identification is accomplished by analysis of the detected secondary-electron energies. The Auger electrons that appear in the secondary-electron distribution chemically identify the surface elements to a depth of approximately four atomic layers.

Auger traces are plotted on an x-y recorder. In this investigation, surfaces were examined before, during, and after sliding.

The Auger spectrometer had incorporated into it a sample scanning positioner. This permitted magnification of the wear track, visual display of it on a television monitor, and positioning the beam of the electron gun directly into the wear contact zone desired. Each data point acquired for Auger peak intensities consisted of three measurements in different regions of the wear track.

After the specimens were sputter cleaned, the gaseous adsorbates were admitted to the vacuum system and the system was brought up to atmospheric pressure with the adsorbing gas. When atmospheric pressure was reached, the system was held there for 20 minutes and then reevacuated. Auger emission spectra were then obtained to characterize the surface film.

The experimental procedure used in this study may be summarized in the following steps: (1) specimen preparation, (2) installation into vacuum system and evacuation, (3) AES characterization of the surface, (4) sputter cleaning of the specimens, (5) identification of surface cleanliness with AES, (6) gas adsorption, (7) reevacuation to determine the presence of adsorbed gas with AES, (8) sliding for 25 passes in vacuum continuously measuring friction, and (9) making AES measurements within the wear track.

RESULTS AND DISCUSSION

Elemental Metals

The noble metals copper, silver, and gold were selected for examination in sliding experiments because they differ in their reactions with iron. Both copper and gold have some solid state solubility while silver has very limited or no solubility (ref. 7). Solid state reactions do not predict surface behavior as indicated in the adhesion behavior of these three metals with clean iron (ref. 4). Their interactions are, however, different
with respect to the strength of the bond formed with a clean iron surface (see ref. 4).

All three noble metals differ in their interaction with oxygen (ref. 8), hydrocarbons (ref. 9), sulfur (refs. 7 and 10), and chlorine (ref. 8). Thus, by controlled experiments with these three metals in contact with iron in the presence of the different lubricating species it should be possible to determine the effect of differences in the noble metals on friction behavior.

Oxygen

After sputter cleaning of the iron disk and Auger spectroscopy characterization of that surface, the surface was saturated with adsorbed oxygen. Friction experiments were then conducted on such a surface with riders of copper, silver, and gold. Friction coefficients (mean values) measured as a function of reported number of passes are presented in figure 2. The highest friction coefficients were measured with gold, intermediate ones with copper, and the least with silver.

Examination of the amount of noble metal transferred to the iron surface with Auger spectroscopy revealed the results presented in figure 3. The amount of metal transfer for the three noble metals can be related to oxide stability. Copper which forms a protective surface oxide exhibited the least amount of transfer while gold which reportedly does not form a stable oxide transferred in the largest quantity.

The large amount of metal transfer of gold to iron in figure 3 correlates with the friction coefficients of figure 2. Heavy transfer of gold indicates that shearing is not occurring at the interface but largely in the gold. A greater amount of silver was observed to transfer to iron than copper. The lowest coefficient of friction, however, was obtained with silver. The transfer and friction behavior may be explained in terms of cohesive energy. Silver has a much lower cohesive or binding energy than do copper and gold (ref. 11). This should make shearing in the silver near the interface a much easier task which would be reflected in measured friction forces.

Methyl Mercaptan

Sulfur containing additives are very frequently present in lubricating oils where extreme pressure or antiwear action is required. The additive is generally an organic structure. The simplest structure containing both the sulfur and the carbon of the hydrocarbon is methyl mercaptan (CH₃SH). An iron disk surface was exposed to methyl mercaptan to saturation. An Auger emission spectrum taken of that surface is presented in figure 4.

Examination of figure 4 indicates the presence of both carbon and sulfur on the
iron surface. While Auger emission spectroscopy cannot identify the presence of the methyl mercaptan, it does indicate the relative ratios of carbon to sulfur. The ratio seen in figure 4 has also been observed on copper. Should molecular dissociation occur it would be anticipated that the methyl group would be lost to the environment and a decrease in carbon peak height relative to sulfur would be observed. Thus, if the molecular structure dissociates on the surface the two active species, namely carbon and sulfur remain on the surface in the same ratio for both. This appears unlikely and it is more probable that the methyl mercaptan adsorbs molecularly to the surface.

The repeated sliding of the noble metal riders across the surface did not appreciably disrupt the ratio of carbon to sulfur. This can be seen in figure 5 for silver sliding on iron. The Auger spectrum was obtained from within the wear track after 250 passes of the rider. The Auger peak height for the carbon has not changed from that of figure 4 but there is approximately a 10 percent reduction in the sulfur peak intensity. Silver is also detected in the Auger spectrum of figure 5 which resulted from transfer from the rider to the disk.

The results of friction experiments with the three noble metals sliding on iron covered with methyl mercaptan are presented in figure 6. With gold the friction coefficient was initially high as was observed with gold on iron in the presence of an oxide in figure 2. Repeated sliding, however, over the same surface resulted in a decrease in friction. This differs from what was observed in figure 2 for iron oxides. Since gold forms neither a stable oxide nor sulfide, the difference in friction behavior in figures 2 and 6 can only relate to the differing effects of iron oxides and sulfides on friction for the metal couple. The iron sulfide affords less resistance to interfacial shear. Auger emission spectroscopy traces obtained in the wear track, however, indicate more gold transfers to the iron surface in the presence of the sulfide than in the presence of the oxide. This effect can be seen by comparing the data of figure 7 with that of figure 3. The results of figures 3 and 7 indicate that metal transfer (gold) to iron is very dependent upon the nature of the surface film present. Oxides are more effective than sulfides in inhibiting the transfer of gold. As will be seen, this effect is highly specific and dependent upon both the metal contacting iron as well as the nature and chemistry of the film present on the surface.

The friction behavior for silver sliding on iron in the presence of methyl mercaptan was very similar to that observed with iron oxide (compare data of fig. 6 with that of fig. 2). The friction value varies only slightly with the sulfide but as with the oxide is unchanged over the total number of sliding passes.

Transfer of silver to the iron surface was less in the presence of the sulfide than it was in the presence of the oxide. This is indicated in the data of figures 3 and 7. In figure 3 with the oxide silver continued to transfer with repeated passes over the surface while with the sulfide in figure 7 transfer was such that after approximately 50
passes across the surface was saturated with silver. This does not mean that transfer has ceased only that the film has reached such a thickness that the Auger spectrometer is only sampling the film.

Copper behaved differently than either gold or silver in the presence of an iron sulfide with respect to friction as indicated in the data of figure 6. Friction coefficients were initially lower than was observed for oxides in figure 2. After a repeated number of passes, however, the friction coefficient increased markedly in figure 6 to values comparable to that observed for oxides in figure 2. Although copper, silver, and gold are noble metals they behaved in a markedly different manner in the presence of iron sulfide with respect to friction.

The transfer characteristics of copper to iron in the presence of the sulfide film were very analogous to that of the silver. The limited transfer of both silver and copper to iron observed in the data of figure 7 indicate why sulfides, particularly iron sulfide are such good antiwear films. The continued increase in transfer of gold in figure 7 may be explained on the basis that it does not form stable sulfides while both copper and silver do and the presence of sulfides on both surfaces may be necessary to inhibit transfer and wear.

Examination of the shear properties of the sulfides of silver, copper, and iron indicate that the sulfides of iron (FeS and FeS₂) have shear strengths approximately three times that of the copper and silver sulfides and the metals. Further, iron itself has a shear strength two and one-half times that of copper, silver, and their sulfides (ref. 12). The cohesive binding energy for iron is also greater than that for either copper or silver (ref. 11). Thus, it is reasonable to assume that interfacial shear must occur either in the copper or silver sulfide or the elemental metal of these compounds.

Methyl Chloride

In addition to sulfur, chlorine-containing compounds are widely used as antiwear additives in lubricating oils. Analogous experiments with methyl chloride to those with methyl mercaptan were conducted. Methyl chloride was selected for examination because it contained both chlorine and a hydrocarbon structure. Further direct comparisons could be made with methyl mercaptan.

An Auger spectrum for an iron disk surface saturated with methyl chloride is presented in figure 8. Both carbon and chlorine are present in the Auger spectrum in addition to iron.

Transfer of the noble metals to the iron surface was observed with sliding. Figure 9 is an Auger spectrum for the iron surface saturated with methyl chloride after
250 passes of a silver rider across the surface. A large amount of silver has transferred to the iron disk surface attenuating the intensity of the other peaks. In addition there is a decrease in the chlorine to carbon ratio when comparing the results with the data presented in figure 8 indicating a possible partial dissociation of methyl chloride. This was not observed with methyl mercaptan.

Results of friction experiments with noble metals sliding against the iron disk saturated with methyl chloride are presented in figure 10. The lowest friction coefficients were obtained with gold, intermediate with silver, and the highest friction coefficients were obtained with copper. The friction coefficient for gold sliding against the methyl chloride covered iron surface is approximately one-half that observed in figure 2 for gold sliding against oxidized iron.

Auger spectra peak intensities for the noble metals sliding against the methyl chloride covered iron surface are presented in figure 11. The least amount of metal transfer to the iron of the noble metals occurred with copper. This was observed with the oxide covered surface in figure 3, and the minimal amount observed in figure 7. Considerably more silver and gold were observed to transfer.

An analysis of the transfer data of figures 3, 7, and 11 indicate that the chemically most active metal copper of the noble metals transferred in the smallest quantities of the three noble metals to the iron surface. With methyl mercaptan in figure 7, the results appear comparable to those obtained for silver. Wear scar measurements to the rider specimens indicate, however, greater wear to the silver.

ALLOY EFFECTS

With oxygen, methyl mercaptan, and methyl chloride the amount of noble metal transferred with copper was less than the amount transferred with gold. In order to determine whether alloying would exert any influence on transfer behavior, a simple binary alloy of 50 atomic percent copper and 50 atomic percent gold was slid against iron saturated with methyl mercaptan. The presence of the copper reduced the transfer of the alloy to iron as indicated in the Auger emission spectroscopy data of figure 12. The curves for the transfer of gold, silver, and copper from figure 7 are presented in figure 12 for comparative purposes.

The wear behavior of the binary alloy of copper and gold is nicely represented by the single curve for copper from figure 7 indicating that the copper completely dominates the wear or transfer behavior of the alloy. The friction behavior, however, is markedly different than that observed for either copper or gold as indicated by the data of figure 13. The friction is lower than was observed in figure 6 with either metal and is unchanged over the entire number of repeated passes examined.
An alloy of 50 atomic percent silver and 50 atomic percent gold was also examined during sliding against iron saturated with methyl mercaptan. The transfer results observed with this alloy and its friction behavior are presented in figures 12 and 13, respectively. The transfer is analogous to that observed for silver represented by the curve of figure 7 which has been incorporated into figure 12.

The friction results obtained with the alloy in figure 13 are similar to those obtained in figure 6 for gold in that a decrease in friction occurs at passes to 100 with no further change with additional number of repeated passes. If silver were dominating the friction behavior, the friction should be similar to that seen for the gold-copper alloy in figure 13 and for silver in figure 6.

SUMMARY OF RESULTS

The results of this investigation with the three noble metals, copper, silver, and gold sliding against an iron surface saturated with films of oxygen, methyl mercaptan, and methyl chloride indicate that friction and transfer characteristics of the noble metals to iron is highly specific. Despite the fact that the surface film on the iron is the same, marked differences in friction and transfer characteristics exist for the three metals.

With all three surface films, oxides, sulfides, and chlorides, noble metal transfer to the iron occurred relatively rapidly. The metals continued to transfer with the oxides and repeated sliding passes over the same surface. This was also observed with chlorides. With sulfides, however, it only occurred with gold. Both silver and copper developed transfer films which no longer increased in thickness beyond 50 passes across the surface indicating why iron sulfide is such a good antiwear additive.

With simple binary alloys of the noble metals one of the alloy constituents can completely dominate the transfer and or friction behavior. For 50 atomic percent copper and 50 atomic percent gold the gold dominates both transfer and friction, while with 50 atomic percent silver and 50 atomic percent gold the friction behavior is dominated by the silver when sliding on an iron sulfide film.

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Figure 1. Friction apparatus with Auger spectrometer.

Figure 2. Coefficient of friction as a function of number of repeated passes for noble metals sliding on iron saturated with oxygen ($O_2$). Sliding velocity, 60 millimeters per minute; load, 100 grams; temperature, 290°C.
Figure 3. - Auger peak intensities as a function of number of passes for noble metals sliding on iron saturated with oxygen (O₂). Sliding velocity, 60 millimeters per minute; load, 100 grams; temperature, 25°C.

Figure 4. - Auger emission spectrum for iron surface saturated with methyl mercaptan before sliding.
Figure 5. - Auger emission spectrum for iron surface saturated with methyl mercaptan after 250 repeated passes of silver rider over surface.

Figure 6. - Coefficient of friction as a function of number of passes for noble metals sliding on iron saturated with methyl mercaptan (CH₃SH). Sliding velocity, 60 millimeters per minute; load, 100 grams; temperature, 25°C.

Figure 7. - Auger peak intensities as a function of number of passes for noble metals sliding on iron saturated with methyl mercaptan (CH₃SH). Sliding velocity, 60 millimeters per minute; load, 100 grams; temperature, 25°C.
Figure 8. - Auger emission spectrum for iron surface saturated with methyl chloride before sliding.

Figure 9. - Auger emission spectrum for iron surface saturated with methyl chloride after 250 repeated passes of silver rider over surface.
Figure 10. - Coefficient of friction as a function of number of repeated passes for noble metals sliding on iron saturated with methyl chloride (CH₃Cl). Sliding velocity, 60 millimeters per minute; load, 100 grams; temperature, 290°C.

Figure 11. - Auger peak intensities as a function of number of passes for noble metals sliding on iron saturated with methyl chloride (CH₃Cl). Sliding velocity, 60 millimeters per minute; load, 100 grams; temperature, 290°C.

Figure 12. - Auger peak intensities for silver and copper in binary alloys with gold sliding against iron surface saturated with methyl mercaptan (CH₃SH). Sliding velocity, 60 millimeters per minute; load, 100 grams; temperature, 290°C.

Figure 13. - Coefficient of friction for binary noble metal alloys sliding on iron saturated with methyl mercaptan (CH₃SH). Sliding velocity, 60 millimeters per minute; load, 100 grams; temperature, 290°C.
Sliding friction experiments were conducted with the noble metals copper, silver, and gold and two binary alloys of these metals contacting iron in the presence of various adsorbates including oxygen, methyl mercaptan, and methyl chloride. A pin on disk specimen configuration was used with a load of 100 grams, sliding velocity of 60 mm/min, at 25°C with the surfaces saturated with the adsorbates. Auger emission spectroscopy was used to monitor surface films. Results of the experiments indicate that friction and transfer characteristics are highly specific with respect to both the noble metal and surface film present. With all three metals and films transfer of the noble metal to iron occurred very rapidly. With all metals and films transfer of the noble metal to iron continuously increased with repeated passes except for silver and copper sliding on iron sulfide.
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