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INFLUENCE OF ALLOYING ELEMENTS ON FRICTION AND WEAR OF COPPER

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16. Abstract The friction and wear characteristics were determined for copper binary alloys containing 10 atomic percent aluminum, silicon, indium, and tin. A ternary alloy containing 10 atomic percent aluminum and 5 atomic percent silicon was also examined. The effectiveness of each of the alloying elements aluminum and silicon were very effective in reducing friction. Sili- con, however, also reduced wear appreciably. With lubrication, silicon, indium, and tin were all effective alloying elements in reducing friction and wear from values obtained for copper. Silicon was the most effective single element in reducing friction and wear in dry sliding and with lubrication.					
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SUMMARY

Friction and wear experiments were conducted with binary copper alloys. Each of the binary alloys contained 10 atomic percent of the alloying element. The elements added to copper were aluminum, silicon, tin, and indium. A ternary alloy was also examined. It contained 10 atomic percent aluminum and 5 atomic percent silicon. The alloys were examined in air and when lubricated with stearic acid in hexadecane. Friction and wear experiments were conducted with a hemispherical rider sliding on a flat disk.

Alloying elements such as aluminum and silicon which form very stable surface oxides reduce the friction of copper in air appreciably. Silicon also has a pronounced effect in reducing wear. With stearic acid lubrication, silicon, tin, and indium all improve the friction and wear behavior of copper. Silicon is the most effective single element in reducing the friction and wear of copper lubricated and in dry sliding. In air, the ternary alloy exhibited the lowest friction and wear characteristics of all the alloy compositions examined. With lubricated sliding of the aluminum containing binary alloy sliding speed and/or load must be sufficient to provide the activation energy needed for the formation of aluminum stearate.

INTRODUCTION

Copper base alloys are some of the most widely used materials in lubrication system components. In conventional lubrication systems, they rank second only to bearing steels. Despite their wide use, not a great deal is known about the influence of the alloy components in the copper on adhesion, friction, and wear.

Common elements alloyed with copper for lubrication applications include zinc, lead, silicon, aluminum, antimony, tin, and indium. Frequently, the alloy used practically is simply a binary of copper with one of these elements. While in general these elements do not drastically alter mechanical properties of the copper, they can very markedly alter friction and wear behavior of copper.

The effect of these alloy elements on lubricant behavior has been examined to some extent (refs. 1 to 3). In references 1 and 3, the alloying elements of tin, silicon, and aluminum were found to increase the critical surface temperature at which a stearic acid film no longer provided effective boundary lubrication. Some of these same elements have been shown to improve wear resistance of copper when sliding on steel in kerosene (ref. 2). They also impart to copper a high resistance to seizure (ref. 4).

The objective of this investigation was to compare the effectiveness of alloying elements in reducing the friction and wear of copper. Copper binary alloys containing 10 atomic percent of aluminum, silicon, tin, or indium were examined in friction and wear experiments both lubricated and unlubricated. By using the same concentration of alloying elements, namely 10 atomic percent, the effectiveness of each of the alloying elements in reducing friction and wear could be compared and contrasted. This had not been done previously. Compositions were such as to avoid compound formation which could alter the interpretation of friction and wear behavior. Friction and wear measurements were made in pin on disk experiments. Experiments were conducted in both air and hexadecane containing various amounts of stearic acid.

MATERIALS

The copper used in this investigation had a purity of 99.99 percent. The alloying elements of aluminum, tin, silicon, and indium were 99.99 percent or better in purity.

Alloys were prepared by melting the copper in magnesium oxide crucibles in a vacuum furnace. When the copper was in the liquid state, the alloying elements were added. Sufficient time was allowed for complete alloying and the melts were then poured into water cooled copper molds. The castings were removed from the molds after cooling to room temperature and machined into specimens. Mechanical properties of some of the alloys are presented in table I.

Alloy	Tensile strength, kg/cm ²	Elongation, percent	Yield strength, kg/cm^2	Modulus of elasticity, kg/cm ²
Cu Cu-10 at.% Sn Cu-10 at.% Al Cu-10 at.% Si	2.11×10 ³ 4.65 3.95 5.63	75 68 63 25 to 30	1.97×10 ³ 1.48 1.55	1.13×10 ⁶ 1.06 1.07

TABLE I. - MECHANICAL PROPERTIES OF COPPER ALLOYS

APPARATUS

The apparatus used in this investigation to conduct friction and wear experiments is shown schematically in figure 1. The apparatus consisted of the specimens, a 6.25centimeter-diameter disk specimen and a hemispherical rider specimen with a 0.48centimeter radius on the contacting end.

The disk specimen was mounted on a drive shaft which was driven by a variable speed electric motor. Motor speed could be varied to produce sliding velocities of from 100 to 6000 centimeters per minute.



Figure 1. - Friction apparatus.

The rider specimen was retained in an arm which was hinged to a post. In the length of arm was a strain gage assembly for monitoring frictional force. Loading was achieved by placing dead weights on the arm directly over the rider specimen.

A clear plastic cover was placed over the entire apparatus for environmental control.

EXPERIMENTAL PROCEDURE

The disk and rider specimens (pin and disk) were in all experiments the same composition, that is, the alloys were sliding on themselves. The machined specimens were polished on metallurgical paper to 600 grit. They were then diamond polished with 3 micron diamond paste.

After diamond polishing, the specimens were rinsed with acetone to remove the diamond paste and then cleaned with ethyl alcohol. They were dried in a stream of dry nitrogen and then placed into the friction apparatus of figure 1.

In those experiments conducted with stearic acid in hexadecane, the specimen contact surface was covered with the fluid. A dish containing the fluid was placed under the disk and rider, and the dish was filled with fluid until the fluid covered the top surface of the disk. A clear plastic cover was placed over the apparatus and the system was continuously purged with argon during the experiment to minimize the effect of atmospheric contaminants.

Each experiment in which wear measurements were involved lasted 1 hour in duration. Wear scar diameters on the rider specimens were measured; and from these, wear volume was calculated. The wear to the disk surfaces was examined with a surface profilometer. Friction force was continuously monitored during the experiment. The friction coefficients reported are average values.

RESULTS AND DISCUSSION

In order to compare the relative effectiveness of alloying elements on the friction and wear behavior of copper, four alloys were prepared containing 10 atomic percent solute with the balance of the alloy being the solvent copper. The solute elements were aluminum, silicon, tin, and indium. A fifth, ternary alloy was also prepared. It contained 10 atomic percent aluminum and 5 atomic percent silicon. The silicon content was limited to 5 atomic percent to avoid compound formation. The objective in examining the ternary alloy was to determine its friction behavior relative to the two binary alloys containing the same solute elements.

Friction and wear results for these five alloys in air are presented in figure 2 with data for elemental copper. The first observation to be made from the data is that the lowest friction coefficient and rider wear rate were obtained with the ternary alloy. This alloy exhibited lower friction and wear than either the binary copper-10 atomic percent aluminum or the copper-10 atomic percent silicon alloy.

A second observation that can be made from the data of figure 2 is that the friction coefficient for the copper alloys containing 10 atomic percent aluminum and silicon were





less than those containing tin and indium. All of the friction coefficients were less than that observed for copper. These differences may be due to two factors, oxidation char-acteristics of the alloying elements and surface segragation of those same elements.

All of the alloying elements employed in figure 2 form more stable oxides than copper as indicated by the data of table II (ref. 5). From the data of table II, it can be seen that the oxides of copper are the least stable while those of aluminum and silicon have the greatest stability. The friction results of figure 2 follow in the same order as the relative stability of the oxide of the alloying element. With elemental copper, friction is the greatest. With the tin and indium containing alloys, it is intermediate; and it is least with the aluminum and silicon alloys.

The alloying elements used were present in copper in concentrations of only 10 atomic percent. Generally, it would, therefore, be assumed that only one out of every ten surface atoms would be of the alloying element. Oxidation of the surface

TABLE II. - FREE ENERGY OF

FORMATION OF VARIOUS

METAL OXIDES

[kcal/g-atom of oxygen, 300 K (ref. 5).]

Metal oxide	Free energy of formation
Al ₂ O ₃	-125
SiÕ2	-98
SnO_{2}	-63
SnO	-62
In ₂ O ₃	67
InÕ	-58
Cu ₂ O	-35
CuÕ	-31

might, therefore, be expected to produce a surface oxide which is a mixture of copper plus the alloying element oxide with the copper oxide predominating. This is, however, not what is observed.

Oxidation studies on copper-aluminum alloys with aluminum concentrations less than the 10 atomic percent employed herein indicate the initial surface oxide to be γ -aluminum oxide. This occurs despite the small bulk concentration of aluminum (ref. 6).

The presence of γ -aluminum oxide on the surface of the copper-aluminum alloys is due to segregation of aluminum to the surface of the alloy. Surface studies using the Auger spectrometer and Low Energy Electron Diffraction (LEED) indicate surface concentrations of aluminum far in excess of bulk concentrations (refs. 7 and 8).

The segregation of aluminum on the surface of the copper alloys results in an increase in the adhesive forces between two surfaces when the alloys have atomically clean surfaces (ref. 9). Increases in friction and wear have also been observed when aluminum segregates to the surface of iron (ref. 10). The segregation of aluminum to clean metal surfaces, therefore, appears to be detrimental to adhesion, friction, and wear in vacuum.

The extremely reactive nature of aluminum with oxygen provides for a very effective nonmetallic surface film in air which reduces gross adhesion and friction as indicated by the data of figure 2. The wear in figure 2 for the copper-aluminum alloy is principally abrasive wear of the alloy surface by the aluminum oxide film formed.

With silicon in copper, the behavior is much the same as with aluminum as determined by LEED and Auger analysis. The silicon segregates to the surface forming a protective silicon dioxide film. The film forms readily and is very effective in reducing friction (fig. 2). The wear, much like that with the aluminum oxide film present, is primarily abrasive. This can be seen from the photomicrograph in figure 3. In figure 3(a) the wear track is smooth, with no evidence of adhesive transfer. For purposes of contrast in figure 3(b) a wear track on the copper-indium alloy surface is included. Examination of that photograph indicates large areas of transfer to and removal of material from the wear track.

Both indium and tin containing alloys exhibited adhesive wear when sliding in air. Despite the differences in the wear mechanism between these alloys and the silicon con-





taining alloy, the wear rates are comparable. Friction coefficients are, however, markedly different. With the copper alloys containing indium and tin, the less stable and less readily formed oxides are more easily penetrated allowing greater metal to metal contact. This results in increased metallic adhesion and accordingly higher friction coefficients.

Surface segregation of indium and tin in copper alloys has been observed with Auger surface analysis (ref. 11). Thus, as with aluminum, the surface can be expected to be rich in the oxides of these metals.

Friction and wear experiments were conducted with the copper alloys lubricated with 0.1 volume percent stearic acid in hexadecane. The results obtained in these experiments are presented in figure 4. It should be noted that the wear scale in figure 4 is different from that used in figure 2.

In air the unlubricated copper alloys containing tin and indium exhibited the highest friction coefficients. When lubricated with stearic acid, these alloys exhibit the lowest



friction coefficients. Wear rates when lubricated for the silicon, indium, and tin containing binary alloys and the ternary alloys are comparable. They are approximately two orders of magnitude less than that obtained with the copper-aluminum alloy and with elemental copper.

In reference 1, tin in copper was found to afford a greater increase in the temperature at which the lubricant film broke down than did aluminum in copper. The results presented in figure 4, also using stearic acid as the lubricant, indicate that tin is also more effective in reducing friction and wear than aluminum when alloyed with copper.

Aluminum stearate itself is an effective boundary lubricant (ref. 12). Aluminum on the copper alloy surface in the presence of stearic acid should, under sliding conditions, result in the formation of aluminum stearate. Such a film may not have formed in these experiments because the energy put into the interface may not have been sufficient to reach the activation energy necessary for soap formation. Sliding friction experiments were therefore conducted over a range of sliding velocities to increase interfactial energy. Copper alloys containing aluminum, silicon, and tin were examined and the results obtained are presented in figure 5.

With both aluminum and silicon in figure 5, a decrease in friction is observed with an increase in sliding velocity. This decrease is believed to be due to the formation of



Figure 5. - Coefficient of friction as a function of sliding velocity for various copper alloys sliding on themselves. Lubricant, 0. 10 volume percent stearic acid in hexadecane; load, 250 grams; temperature, 23⁰ C.

protective stearate films. The ternary copper-aluminum-silicon alloy also exhibits a decrease in friction with sliding velocity.

The copper-tin alloy unlike the other three alloys does not change in friction behavior with changes in sliding velocity. The friction coefficient was approximately 0.1 over the range of sliding velocities investigated. The copper-indium alloy behaved in an analogous manner to the copper-tin alloy. When the sliding velocity was sufficiently high, all four alloys exhibited friction coefficients of approximately 0.1.

The effect of load on the friction coefficient of the copper-aluminum and copperindium alloys lubricated with stearic acid in hexadecane was determined. The friction results obtained with loads of from 20 to 300 grams are presented in figure 6. Unlike with sliding velocity, no change in friction behavior was observed with increases in load



Figure 6. - Coefficient of friction as a function of load for two copper alloys sliding on themselves in 0. 1 volume percent stearic acid in hexadecane. Sliding velocity, 300 centimeters per minute; temperature, 25⁰ C; steady-state load conditions.

for the copper-aluminum alloy. The total load used may not have been sufficient to initiate the changes seen in figure 5 with changes in sliding velocity.

With the copper-indium alloy, a modest decrease in friction coefficient was observed at a load of 100 grams. The copper-indium alloy is being effectively lubricated by the stearic acid while the copper-aluminum alloy is not.

In order to determine whether the concentration of stearic acid in hexadecane had an effect on wear behavior, the copper-aluminum and the copper-indium alloys were examined in hexadecane containing various amounts of stearic acid. The results obtained are presented in figure 7. With an increase in stearic acid concentration of from 0.01 to 0.05, the wear rate for the copper-aluminum alloy decreased tenfold. Further increases in stearic acid concentration produced no further reduction in wear. Thus, a



Figure 7. - Rider wear rate for two copper alloys sliding on themselves with various concentrations of stearic acid in hexadecane as lubricant. Load, 500 grams; sliding velocity, 300 centimeters per minute; temperature, 25⁰ C.

copper-aluminum alloy could be adequately lubricated with 0.05 volume percent stearic acid under the sliding conditions reported herein.

The copper-indium alloy required a stearic acid concentration of 0.10 percent before no further reduction in wear was observed. The wear rate at all stearic acid concentrations was less for the copper-indium than for the copper-aluminum alloy.

SUMMARY OF RESULTS

Sliding friction studies conducted with copper and copper alloys indicate that alloying elements which form very stable oxides have the greatest effect in reducing the friction of copper in air. Both aluminum and silicon are effective in this regard. Silicon, however, also reduces wear appreciably. A ternary alloy containing both aluminum and silicon was more effective than either alloying element alone in reducing friction and wear.

With stearic acid in hexadecane, silicon, tin, and indium in copper all improved observed friction behavior. Wear was approximately a hundredfold less with these elements present in copper than it was for elemental copper.

The addition of aluminum to copper did not reduce the lubricated friction and wear of copper at the low interfacial energies associated with low speed sliding. When the speed is increased, the necessary activation energy is supplied to form aluminum stearate which reduces friction. When a small concentration of silicon was added to the binary copper-aluminum alloy, both friction and wear decreased.

Lewis Research Center,

National Aeronautics and Space Administration, Cleveland, Ohio, June 6, 1972, 114-03.

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