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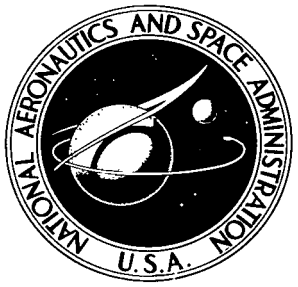

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THERMOCHEMISTRY OF BINARY ALLOYS AND ITS EFFECT UPON FRICTION AND WEAR

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16. Abstract

Friction experiments were conducted with binary alloys of the noble metals in sliding contact with iron to determine the influence of alloy thermochemistry on friction and wear. Results indicate that the greater the free energy of formation of the binary alloy, the lower the friction and wear when sliding on iron. This is believed to be due to a reduction in the valence electrons available for interaction of the alloy with the iron surface. Crystal structure exerts an influence on observed behavior.

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SUMMARY

Friction and wear experiments were conducted in an argon atmosphere with various binary noble metal alloys sliding on iron to determine the influence of alloy thermochemistry on friction and wear. The alloys investigated were the binary systems gold-indium, silver-indium, copper-indium, gold-tin, and silver-tin. Experiments were conducted with a hemisphere sliding on a flat disk at a sliding velocity of 3.8 centimeters per second in an argon atmosphere at 20° C.

Results of the investigation indicate a relation between alloy thermochemistry and friction and wear. The greater the free energy of formation of the binary alloy, the lower the friction and wear when sliding on iron. Crystal structure was observed to exert an influence on the results.

INTRODUCTION

When two metal surfaces are brought into solid-state contact, the electronic nature of the surfaces will determine the nature of the interfacial adhesion that develops. The electronic nature of the surface is reflected in such properties as surface energy and chemical reactivity. When an iron surface was contacted by various nonferrous metals in reference 1, it was shown that adhesive force was related to chemical reactivity of the clean metal surfaces contacting the iron.

Almost any foreign atomic species which will interact with the clean metal surface and the electrons available for adhesive bonding will tend to reduce adhesion of metal surfaces (refs. 2 and 3). While this is fairly obvious and understood for the interaction of nonmetallic materials with a metal, it is less clearly understood, if at all, for metal-metal systems. That is to say, if metal A has some known adhesive bonding force

to metal B, what effect will metal C alloyed with either metal A or B have on adhesion, friction, and wear?

When two metals are alloyed, electronic interaction occurs between the metals as well as it would between a metal and a nonmetal (ref. 4). The binding interaction has associated with it the liberation of energy in the form of heat when chemical binding of the metals occurs. The heat evolved can be measured just as it can for other chemical reactions (ref. 5). This heat is termed the heat of formation ΔF, and the greater the amount of heat evolved ($-\Delta F$), the stronger the binding energy.

The binding energy of the alloy with respect to mechanical behavior is somewhat analogous to cohesive binding energy of elemental metals. The greater the binding energy, the greater the resistance of the material to deformation (the higher the modulus of elasticity and bulk modulus) (ref. 6). Further, it might be anticipated that, the greater the electronic interaction between two metals in solid solution, the less the energy for adhesive bonding to a third metal across a mechanical interface.

The objective of this investigation was to determine the influence of simple binary alloy thermochemistry on the friction and wear of the alloys in contact with iron. The binary alloys examined were the noble metals alloyed with indium and tin. Experiments were conducted with a hemispherical rider specimen contacting a rotating flat disk. The binary alloys were the riders and the iron specimens were the disks. All experiments were conducted in an argon atmosphere.

MATERIALS

The alloys used in this investigation were all prepared from 99.999-percent-pure elemental metals. The proper ratios of the metals for the particular alloy composition desired were placed in carbon crucibles and vacuum-induction melted. The samples were removed from the crucibles after slow cooling to room temperature and machined into rider specimens.

The disk specimens were prepared from triple-zone-refined iron. The disk and rider contacting surfaces were rubbed on papers down to 600 grit and were then polished with polishing alumina. Prior to use the specimens were rinsed with absolute ethyl alcohol.

APPARATUS

The friction and wear apparatus used in these studies is shown schematically in figure 1. The basic elements of the apparatus consisted of the specimens, a 6.4-

centimeter-diameter disk specimen which was contacted by a 0.6-centimeter-diameter rider having a 0.48-centimeter radius on the sliding contact end.

The disk specimen was rotated by a small electric motor with a variable-speed drive. The disk was caused to rotate at a speed sufficient to produce a sliding velocity of 3.8-centimeters per second.

The rider specimen was retained in a beam which was hinged at the end opposite that containing the rider specimen. Weights were applied directly over the rider specimen to supply the required load. In this investigation the applied load was 250 grams. The beam containing the rider specimen also had a copper-beryllium ring containing strain gages in its length. The strain gages were used to measure the friction force between the disk and the rider.

A plastic cover box was employed to purge the specimen contact area with argon gas and thereby provide a controlled argon environment during the experiments. Figure 1 indicates the location of the cover box and the argon gas inlet.

RESULTS AND DISCUSSION

The most systematic experimental study of the thermochemical properties of alloy has been conducted by Kleppa (ref. 7). He has studied the heats of mixing of alloys of gold (ref. 8), silver (ref. 9), and copper (ref. 10) with cadium, indium, tin, antimony, thallium, lead, and bismuth (ref. 11). This subject has been treated theoretically by Friedel and a rule derived (ref. 12).

The heat of formation ΔF is related to the heat of mixing ΔH by the well known equation

$$\Delta F = \Delta H - T\,\Delta S$$

where T is temperature and ΔS is entropy.

Thus, with measured heats of mixing the heat of formation can be readily determined.

The alloying of indium with gold produces an appreciable variation in the heat of formation in moving from the gold-rich to the indium-rich end of the phase diagram, as indicated by the data of figure 2. The heat of formation decreases to a minimum at approximately 65 atomic percent indium and increases again. Binding and chemical stability is greatest at the largest negative free energy of formation, at 65 atomic percent indium.

Examination of the phase diagram for the gold-indium system reveals the formation of the compounds Au_3In, AuIn, and $AuIn_2$. These compounds are electron compounds.

Electron compounds in general have properties resembling those of solid solutions, including a wide range of compositions, high ductility, and low hardness. These compounds and the others discussed in this report should be distinguished from intermetallic or valency compounds. These latter compounds follow the rules of chemical valence. They form strong bonds (ionic or covalent), and their properties are essentially nonmetallic. They have poor ductility, are brittle, and are very hard (ref. 13).

Friction and wear experiments were conducted with gold-indium alloys, and the results obtained are presented in figure 2. Both friction and wear decrease with increasing concentrations of indium and thermochemical stability. At 65 atomic percent indium the minimums in both friction and wear are achieved. At concentrations of indium beyond 65 atomic percent friction and wear increase as chemical binding in the alloy decreases.

The thermochemical data of figure 2 were taken at 450° C, and consideration must be given to the crystal structures possessed by the alloys at room temperature. In figure 2 the 20-atomic-percent-indium - gold alloy has a hexagonal-close-packed structure, and this may account for the lower than anticipated friction and wear values measured and plotted in figure 2. Note that the wear scale is logarithmic. The hexagonal crystal structure is known to alter the friction and wear behavior of metals (ref. 14).

The wear mechanism in sliding is principally adhesive, as evidenced by the adherence of the binary alloy to iron. The alloy transferred to the iron surface is shown in the photograph of figure 3. The same general type of adhesive transfer was noted all compositions.

The data of figure 2 indicate a relation between the thermochemistry of indium-gold alloys and friction and wear. The question that can be asked is, why is this so? The answer to this question lies in the fact that the free energy of formation reflects the binding energy between the two metallic elements in the binary alloy. The binding energy is a function of the valence electron interaction between the metals. The greater the valency electron interaction between the two elemental metals in the binary alloy, the fewer the valency electrons available at the interface for interaction with the iron disk surface.

This concept of availability of valence electrons can best be shown by way of example. Consider the very common interaction of iron with carbon to form cementite (Fe_3C). Carbon in this instance is unquestionably quadrivalent, and in the Pauling scheme the iron-carbon bonds must have a bond number of 2/3 (ref. 15). Iron has a metallic valence of 6. Each iron atom forms a bond with bond number 2/3 with each of two carbon atoms, using up $1\frac{1}{3}$ of its total valence of 6 and leaving $4\frac{2}{3}$ for Fe-Fe bonding. If the cementite were bonding to any other material, there would be only $4\frac{2}{3}$ iron valence electrons available for interaction rather than the usual 6.

A more pertinent example is the interaction of gold and tin to form AuSn. This alloy will be discussed with respect to friction and wear later in this report. According to the method of Pauling, gold has a valence of 5.56, and tin either the metallic valence of 2.56 or the covalence of 4. Tin appears from bond distance measurements to be covalent and have a valence of 4. With this valence the Au-Sn bonds have bond numbers of 2/3 (ref. 13). The tin has four valence bonds that resonate among six positions connecting it with ligated gold atoms. These bonds use up 4 of the total of 5.56 valence electrons of gold and leave only 1.56 bonds available for the interaction with a third metal such as iron in the solid state.

If there exists a relation between the thermodynamic properties of binary metal alloys and their ability to interact with an iron surface, then systems other than the gold-indium system should exhibit a similar relation. The heats of formation and the friction and wear of silver-indium alloys are presented in figure 4. Again, just as with the gold-indium alloys, the friction and wear of the alloys follow the same general trend as the heat of formation of the alloy.

The third noble metal, copper, has also been alloyed with indium over a range of compositions to 35 atomic percent indium in copper, and the heats of formation have been measured (ref. 9). The thermodynamic data are presented in figure 5 together with friction and wear results obtained for various alloy compositions. As with gold and silver, there appears to be a relation between friction and wear and thermochemistry when alloying with indium.

In alloying all three noble metals with indium, adhesion and transfer of the binary alloy to the iron surface occurred. Transfer of a 20-atomic-percent-indium - 80-atomic-percent-copper alloy to the iron surface is shown in the surface profile trace of figure 6. The metal transfer to the iron surface of the binary alloy is the result of adhesion at the interface between the binary alloy and the iron. The greater the binding energy between the metals in the alloy, the less the energy at the interface available for interaction with the iron. The greater the energy available for interfacial interaction with the iron, the stronger the adhesive forces, the higher the friction, and the greater the probability of generating adhesive wear by subsurface fracture in the alloy.

Thus far the alloying element in the noble metals has been indium, and the question naturally arises as to whether the observations would be the same if some alloying element other than indium were used. The heats of formation have been measured for tin in copper for selected compositions, and the results obtained are present in figure 7. The free energy of formation increases in negativity with increasing amounts of tin.

The friction and wear were measured for alloys containing from 10 to 25 atomic percent tin in the copper, and the results are presented in figure 7. The friction coefficient decreases with increasing tin content. The wear also decreases with increase in tin content to 20 atomic percent tin. At 25 atomic percent tin the wear increases to a

value 10 times greater than that at 20 atomic percent. This change in wear may be associated with a phase change. At 25 atomic percent tin, and epsilon phase exists which is orthorhombic.

A question may be asked as to the apparent general applicability of alloy thermochemistry to friction and wear. Can the free energy of formation of binary alloys where one of the alloy constituents is different be compared? The friction and wear behavior of binary alloys containing silver with tin as the solute in one instance and indium in another are compared in table I. The compounds Ag_3Sn and Ag_7In_3 were examined. They contain similar amounts of solute. The free energy of formation of the Ag_3Sn is half that of the Ag_7In_3.

The friction coefficient and the wear are less for the Ag_7In_3 than for the Ag_3Sn. Unfortunately the crystal structures of the two materials are different. The Ag_3Sn is hexagonal with a c/a lattice ratio of 1.59. The lattice ratio of hexagonal metals can influence friction and wear (ref. 14).

The friction and wear characteristics were measured for two gold alloys, AuSn and $AuIn_2$, and the results obtained together with the free energy of formation for these alloys are presented in table I. The friction coefficients were the same for the two alloys dispite a difference in free energy. The rider wear was, however, less for the $AuIn_2$. Again, however, as with the silver compounds, a difference in crystal structure exists. The AuSn has an NiAs type structure with a c/a lattice ratio of 1.278, which deviates considerably from the normal ideal hexagonal stacking ratio of 1.633.

Previous friction studies have been concerned with the influence of crystal structure on friction coefficient and have examined hexagonal metals and alloys in depth (ref. 14). Table I indicates results obtained for hexagonal electron compounds (Ag_3Sn and AuSn). The mechanical behavior of these materials is not known (e.g., slip modes).

The data of table I indicate that comparisons based simply on thermochemistry may be difficult to make because other characteristics such as crystal structure may also vary. If crystal structure exerted an influence, for example, on the silver alloys of table I, it would be expected to be in the opposite direction from that observed in the friction and wear values.

The data of this investigation indicate that, with some noble metal alloys, the thermochemistry of the alloys can give insight into observed friction and wear behavior. This is another of the fundamental material properties which can influence friction and wear. It must be considered with an awareness of such properties as crystal structure, ordering, surface texturing, orientation, recrystallization, and equilibrium segregation, all of which exert an influence on friction and wear. It is another parameter to be considered in the understanding of adhesion, friction, and wear.

SUMMARY OF RESULTS

Sliding friction experiments with binary alloys of the noble metals on iron indicate that the free energy of formation of the alloys exerts an influence on friction and wear. The greater the free energy of formation in a particular binary alloy system, the lower the friction and wear when the alloy slides on iron. This is believed to be due to a reduction in the valency electrons of the alloy available for interaction with the iron surface, which in turn reduces adhesion, friction, and wear. Changes in crystal structure, however, alter observed results.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 4, 1971,
129-03.

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TABLE I. - SOME PROPERTIES OF SILVER AND GOLD ALLOYS OF TIN AND INDIUM

Binary compound	Heat of formation, ΔF kJ/g atom	Coefficient of friction[a]	Rider wear rate, mm^3/hr	Crystal structure
Ag_3Sn	-4	0.53	2.63×10^{-2}	Close-packed hexagonal
Ag_7In_3	-8	.28	9.16×10^{-3}	Cubic
AuSn	-14	.33	6.78×10^{-3}	Nickel arsenide type
$AuIn_2$	-24	.33	1.80×10^{-3}	Cubic

[a]Sliding friction experiment conducted on iron surface; sliding velocity, 3.8 cm/sec; load, 250 g; temperature, 20° C; argon atmosphere.

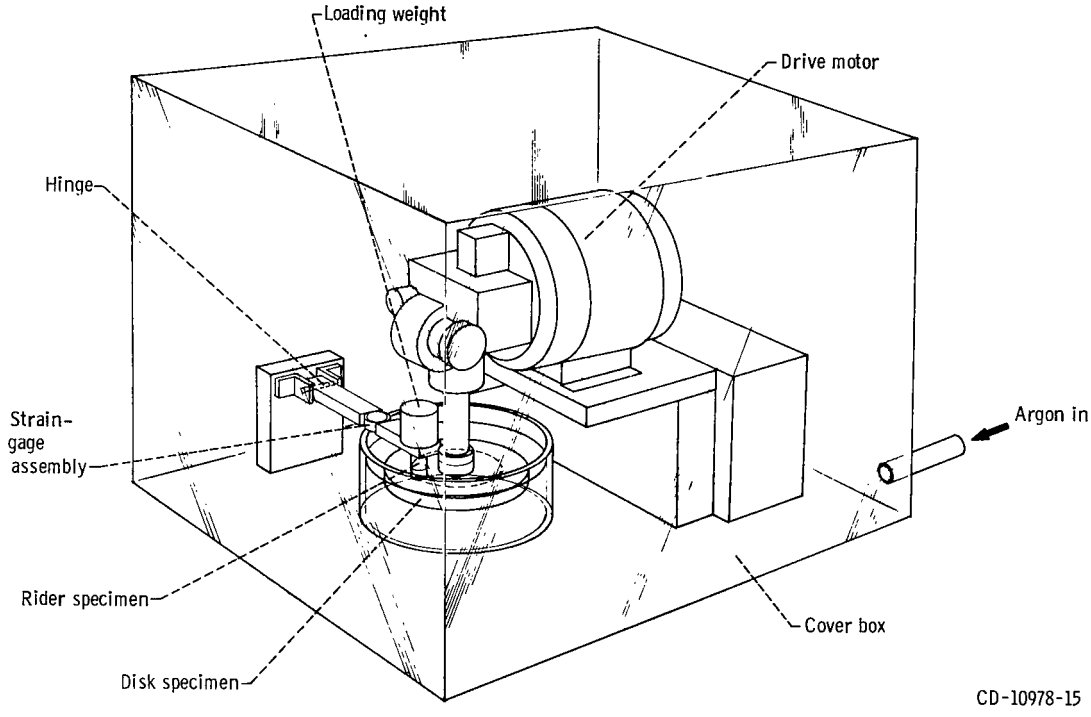

Figure 1. - Friction apparatus.

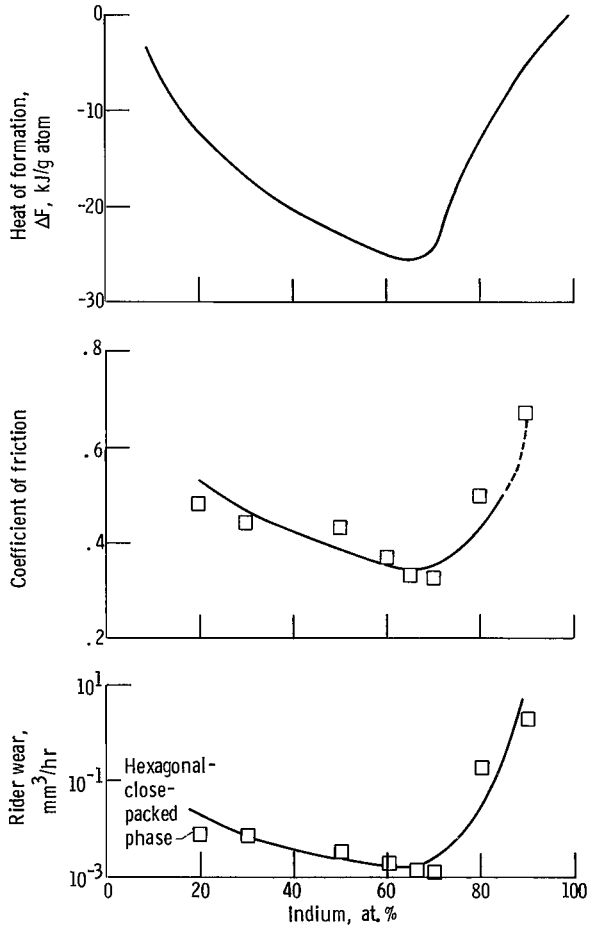

Figure 2. - Heat of formation (from ref. 8), friction coefficient, and wear for binary alloys of indium in gold sliding on iron. Sliding velocity, 3.8 centimeters per second; temperature, 20° C; argon atmosphere.

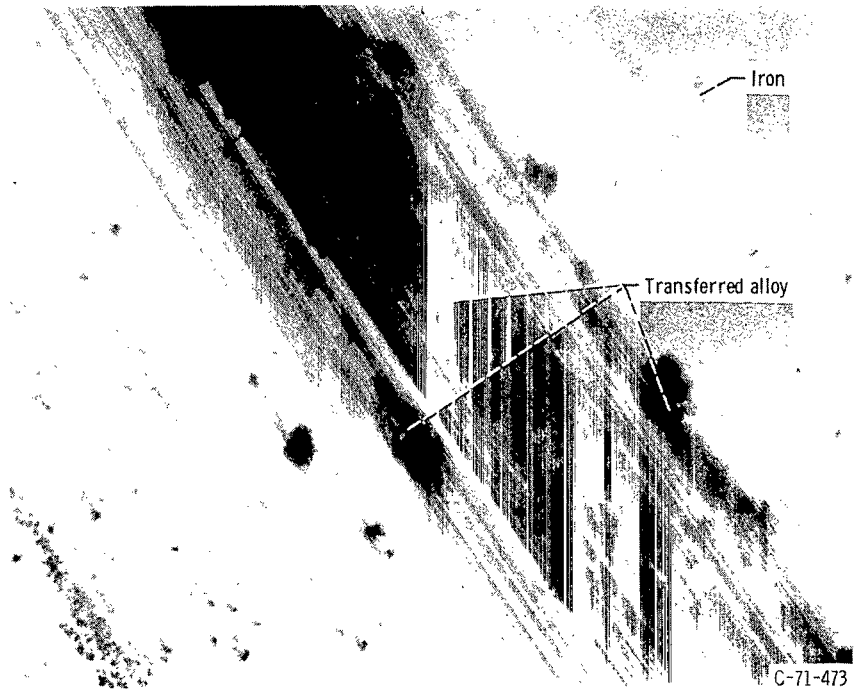

Figure 3. - Adhesion of 70-atomic-percent-indium - 30-atomic-percent-gold alloy to iron surface during sliding. Load, 250 grams; sliding velocity, 3.8 centimeters per second; temperature, 20° C; argon atmosphere.

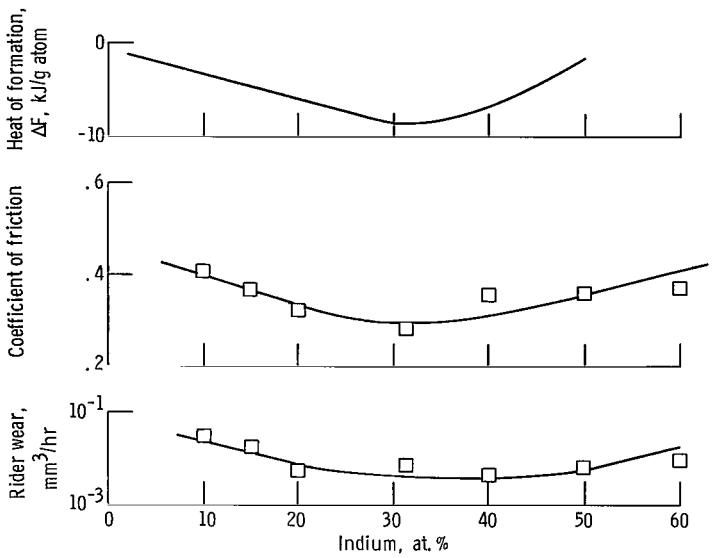

Figure 4. - Heat of formation (from ref. 9), friction coefficient, and wear for binary alloys of indium in silver sliding on iron. Sliding velocity, 3.8 centimeters per second; temperature, 20° C; argon atmosphere.

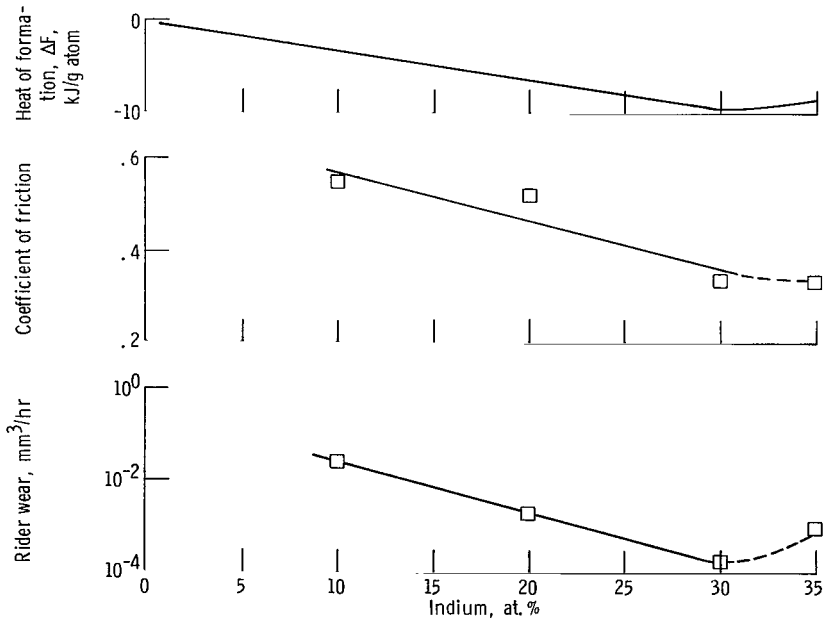

Figure 5. - Heat of formation (from ref. 10), friction coefficient, and wear for binary alloys of indium in copper sliding on iron. Sliding velocity, 3.8 centimeters per second; temperature, 20° C; argon atmosphere.

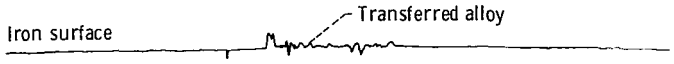

Figure 6. - Surface profile trace of iron disk surface in wear track region after sliding contact with 20-atomic-percent-indium - 80-atomic-percent-copper alloy. Load, 250 grams; sliding velocity, 3.8 centimeters per second; temperature, 20° C; argon atmosphere.

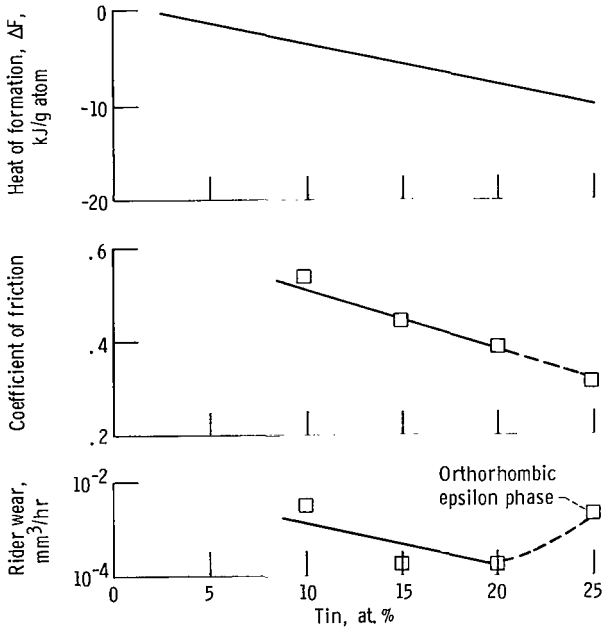

Figure 7. - Heat of formation (from ref. 10), friction coefficient, and wear for binary alloys of tin in copper sliding on iron. Sliding velocity, 3.8 centimeters per second; temperature, 20° C; argon atmosphere.

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