Coefficients of Friction in the Tin(II) Sulfide–Lead Sulfide System

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The coefficients of friction were measured over the entire tin(II) sulfide–lead sulfide system. There is a correlation between the coefficients of friction and the phase diagram and cell volume. The lowest coefficients were obtained in the PbS-rich region.

THE BINARY PHASE DIAGRAM for the system tin(II) sulfide–lead sulfide contains a compound and several areas of solid solution. From minerals collected in Bolivia, Prior (*7*) identified the compound as teallite, having the composition $PbSnS_2$. The phase diagram for the binary system has been established by means of thermal (*4,8*) and x-ray diffraction analyses (*5,6*). The solid solution between PbS and SnS exists up to approximately 10 mole % of tin(II) sulfide in lead sulfide and slightly less than 10 mole % of lead sulfide in tin(II) sulfide. The solid solutions are designated α, β, and γ for SnS, $PbSnS_2$, and PbS, respectively.

Buckley and Johnson (*3*) found that the friction and wear of metals are dependent on the crystal structure. Furthermore, the coefficients of friction of hexagonal metals decrease as the ratio of the lattice parameters, c/a, increases. The coefficients of friction in the tin(II) sulfide–lead sulfide system are dependent on the crystal phases present in the sample. The findings are in agreement with results obtained by thermal and x-ray analyses.

EXPERIMENTAL

The samples for the coefficient of friction measurements were prepared from reagent grade tin, lead, and sulfur. Appropriate amounts of the constituents were weighed into 150 x 17 mm. Vycor ampoules. The tubes were evacuated to 1 mm. of Hg or less and sealed under vacuum. The reaction tubes were placed in an electrically heated muffle furnace and held at 900° C. for 24 hours. Following the heat treatment, the tubes were removed from the furnace and allowed to air-cool. The samples were entirely, or partially, liquid at 900° C. and solidified on cooling, When cool, the samples were transferred to vials and stored in a desiccator.

The coefficients of friction were determined on an apparatus patterned after the ASTM apparatus (*1*) for measuring the coefficients of friction of polyethylene films. A cold-rolled steel rider 3 cm. in diameter weighing 508 grams was attached to a Model L-500-H Hunter mechanical force gage (manufactured by the Hunter Spring Co., Lansdale, Pa.) by means of a monofilament nylon line. A flat, cold-rolled steel plate mounted on precision bearings was moved away from the force gage at a rate of 2π inches per minute by a l-r.p.m. constant-speed motor. The plate and rider were degreased with acetone and cleaned by scrubbing them with steel wool, rinsing thoroughly with ion-exchange water, and air-drying. The force obtained with the clean rider on the clean plate was reproduced before each determination. All measurements were made at ambient temperature and humidity. The sample, ground to finer than 200-mesh, was brushed onto the plate and rider, and runs were made until constant force readings (± 10 grams) were obtained for at least three runs. Force readings were taken at five locations on the plate during each run, and each coefficient of friction point and its corresponding deviation were based on at least 15 force readings. The difference in reproducibility between the various measurements is believed to be due to slight variations in the surface condition of the steel plate and rider, such as amounts of surface oxides

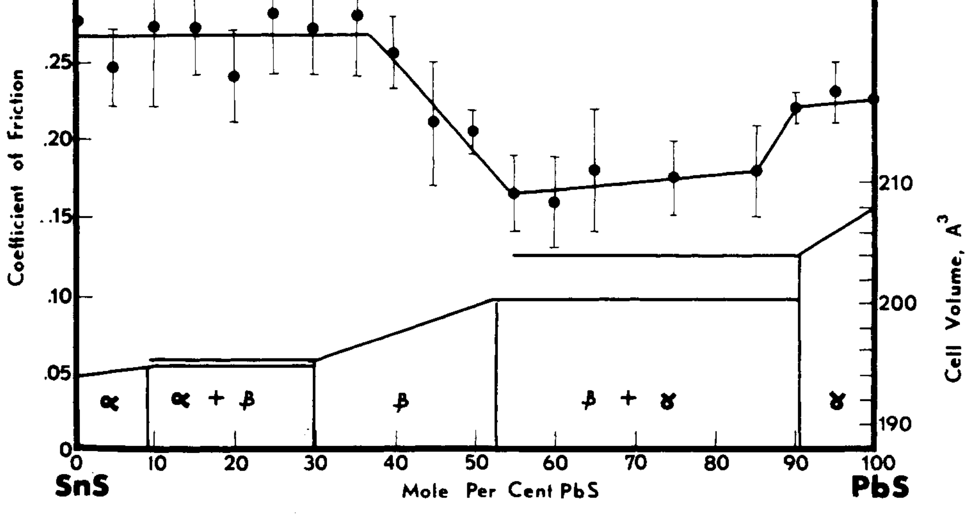

Figure 1. Composition vs. coefficient of friction and cell volume

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or adsorbed oxygen and water vapor. The reproducibility is in no way related to the composition of the sulfide sample. The coefficient of friction was calculated as the ratio of the force in grams to the load (508 grams). The coefficient of friction of graphite was measured as a check on the apparatus. Found: 0.12±0.01. Literature value: 0.1 (*2*).

DISCUSSION

Figure 1 shows the correlation between the coefficients of friction and the cell volumes of the system. The composition cell volume plot is according to Kuznetsov and Ch'ih-fa (*6*). The areas labeled α, β, and γ are the solid solution areas discussed previously.

The α and $\alpha + \beta$ areas have coefficients of friction which appear to be controlled by the α, or orthorhombic tin(II) sulfide, phase. In the β, or teallite, region, the structure of the crystal is still orthorhombic, but the coefficients of friction are decreasing owing to the increasing amounts of lead sulfide in the solid solution. That the minimum in the coefficients of friction coincides with the maximum solid solution of lead sulfide in teallite and the maximum cell volume of teallite is to be expected because, as the cell volume increases, the bonds between atoms are lengthened and weakened, making sliding or breaking of bonds between crystal planes easier. In the $\beta + \gamma$ region, the cubic γ phase has only a small effect on the coefficients of friction, as evidenced by the slight increase in the values in this region. An abrupt change in the measured values occurs between 85 and 90 mole % lead sulfide. It is thought that the change should coincide closely with the disappearance of the β phase in this area of the phase diagram.

ACKNOWLEDGMENT

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Preparation and Properties of Tropyl Selenide

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The preparation, infrared spectrum, and other physical properties of tropyl selenide are compared to those of tropyl sulfide and of tropylium salts.

THE SELENIDE, the third member of the tropyl chalcogen (*7, 8*) series and the most likely of these to be ionic, is covalent in character, like the oxide and sulfide. The infrared spectrum [3030(s), 1450(w), 1410(w), 1228(w), 1204(w), 1165(w), 1088(w), 965(w), 948(w), 923(w), 884–895(m), 844(w), 787(w), 760(m), 709(s) cm.$^{-1}$] is similar to that of the sulfide [3030(s), 1773(vw), 1695(vw), 1445(w), 1410(w), 1392(w), 1227(w), 1203(w), 1166(w), 1082(vw), 993(w), 966(vw), 951(vw), 938(w), 928(w), 895(w), 860(w), 794(w), 739(m), 717(w), 695(m − s) cm.$^{-1}$]. These spectra are very similar to that of cycloheptatriene and are not closely related to the ionic cycloheptatrienylium (tropylium) bromide (*8*) whose spectrum is akin to that of the internally ionic tropone (*5, 6*) and to that of known ionic (*1, 3, 10–12*) and π-bound (*4*) tropylium metal "sandwich" complexes. The spectra of the sulfide and selenide have fewer and less pronounced (muted) absorption bands than cycloheptatriene. The physical properties of tropyl sulfide and tropyl selenide resemble in pattern those of other analogous Group VI pairs, such as the diphenyl derivatives.

The relative instability of the covalent compounds is probably a measure of the relative bond strength of the C—X— bonds (X = O, S, or Se), as the order of decreasing stability is: C—O— > C—S— > C—Se—. Unlike the others, decomposition of the selenide is not only heat-induced but is rapidly catalyzed by sunlight, which is suggestive of a radical mechanism, possibly induced by a charge transfer excitation. The tropyl radical which would be formed evidently exists as a reactive intermediate in reductive-one-electron transfer reactions of the tropylium ion (*8, 13*).

EXPERIMENTAL

Infrared and Ultraviolet Spectra. Infrared absorption spectra were determined on a Beckman Model I.R.-4 double-beam recording spectrophotometer, in carbon tetrachloride and carbon disulfide solutions. The ultraviolet spectra were determined on a Beckman DU spectrophotometer.

Hydrogen Selenide. The hydrogen selenide was prepared by hydrolysis of aluminum selenide. Both this procedure and preparation of the aluminum selenide were carried out according to Brauer (*2*).

Cycloheptatrienylium Bromide. Essentially the method of Doering (*8*) was used. A purer tropylium bromide and better yields in purification were desired. The crude tropylium bromide was taken up in boiling ethanol (dried over magnesium sulfate) and cooled in chloroform–dry ice mixture (−64° C.) for 2 hours. The resulting yellow crystals

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