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Composition of Single Crystal of Iron Sulfide Grown by Normal Freezing

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Synopsis. The composition of a single crystal of iron sulfide was determined as a function of position along the growth axis using atomic absorption spectrophotometry. The observed composition was consistent with the phase diagram for the iron-iron sulfide pseudo binary system and the results of physical measurements.

Single-crystal ingots of iron sulfide, FeS, are grown from iron-rich nonstoichiometric melts by normal freezing.[1] The maximum size of crystals obtained is 10 mm in diameter and 30 mm in length. To investigate the physical properties of this material, the composition must be determined as a function of position along the growth axis of the crystal. In this paper, a method using 25 mg of samples in each analysis is described. The sample is dissolved in nitric acid containing bromine and sulfur is precipitated as barium sulfate by adding a known amount of barium chloride. After filtration, iron is determined directly by its atomic absorption, and sulfur, indirectly by the atomic absorption of an excess barium content in the filtrate.[2]

Experimental

Reagents. The standard barium solution was prepared by dissolving barium chloride dihydrate in deionized water and standardized by chelatometry using EDTA (5 mg Ba/ml). The standard iron solution was prepared by dissolving iron metals (99.9% up) in hydrochloric acid and stocked as 0.1 M hydrochloric acid solution (1 mg Fe/ml). Reagents used were of analytical reagent grade.

Atomic Absorption Measurements of Iron and Barium. Atomic absorption measurements were made at 372.0 nm for iron and 553.6 nm for barium in a nitrous oxide-acetylene flame using a Hitachi model 208 atomic absorption spectrophotometer and hollow cathode lamps HLA-3. The nitrous oxide-acetylene flame is recommended over an air-acetylene flame for reducing or eliminating the chemical interference by coexisting elements.[3] However, barium has a relatively low ionization potential (5.21 eV) and is readily ionized in the nitrous oxide-acetylene flame, unless a large amount of an easily ionized element is added to suppress the barium ionization.[4] In this work, lanthanum chloride was used as the suppressor. We already described the usefulness of this reagent in the measurements of several rare earths[5] which have ionization potentials (5.67—6.8 eV) similar to barium. As shown in Fig. 1, the barium absorption was increased with an increase of the lanthanum chloride concentration. For example, in the presence of 5000 ppm of lanthanum chloride, the barium absorption is about 2.3 times greater than without this reagent. The iron absorption was not generally affected by the presence of lanthanum chloride. In this lanthanum chloride matrix, iron did not affect the barium absorption and *vice versa.*

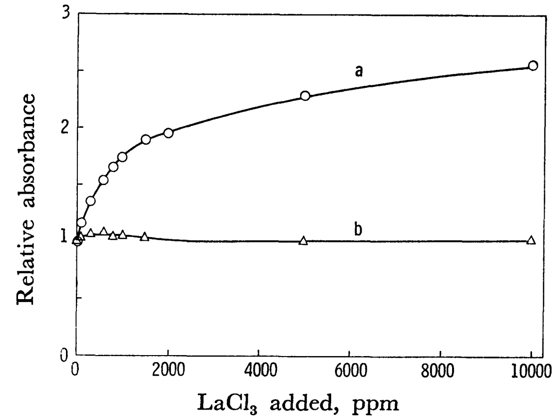

Fig. 1. Effects of lanthanum chloride on atomic absorptions of barium and iron in 0.1 M hydrochloric acid.
a: Ba 50 ppm, b: Fe 20 ppm.

Analysis of Single Crystals. Samples, 1.0—2.0 mm thick, were sliced from the single-crystal ingot of iron sulfide perpendicular to the growth axis for each analysis. Twenty-five mg of crystals were dissolved in 2 ml of concentrated nitric acid containing bromine. After the removal of nitric acid by evaporation with hydrochloric acid, the sample solution was diluted to about 40 ml and warmed to about 80 °C. The ferric ions were reduced to ferrous ions by adding ascorbic acid. The solution was adjusted to 0.05 M hydrochloric acid and sulfur was precipitated as barium sulfate by adding 9 ml of the standard barium solution (5 mg Ba/ml). The precipitate was allowed to settle for 1 hr on a hot water bath. After aging for more than 40 hr at room temperature, the precipitate was filtered and washed with six 5-ml portions of boiling water. The filtrate was adjusted to 0.1 M hydrochloric acid and 5000 ppm

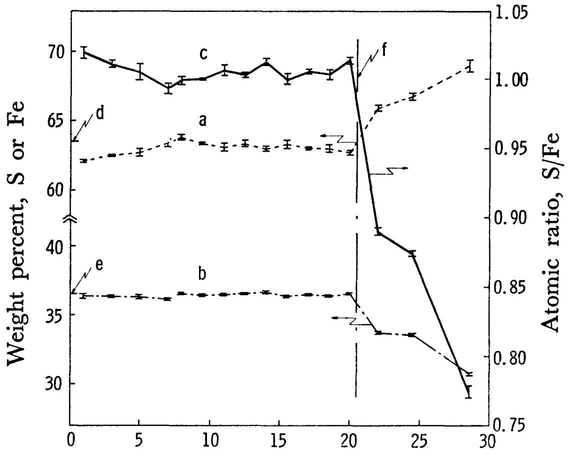

Fig. 2. Composition of the crystal as a function of position along the growth axis.
a: Fe wt%, b: S wt%, c: Atomic ratio S/Fe, d: Fe wt% expected for the composition FeS, e: S wt% expected for the composition FeS, f: Interphase boundary in crystal.

of lanthanum chloride. A similar adjustment was made for the iron and barium standards. Iron was determined directly by atomic absorption, and sulfur, indirectly by the atomic absorption of an excess of barium in the filtrate.

The results are shown in Fig. 2, where the observed wt% values of iron and sulfur are plotted as a function of position along the length of the crystal growth axis. The distance is measured from the bottom of the long single crystal. From the observed wt% values the calculated atomic ratio S/Fe is also plotted. The variation of the observed values for each analysis was usually ±0.3 wt% for iron and ±0.1 wt% for sulfur, so that the atomic ratio can be determined within ±0.004. The sum of the wt% values for iron and sulfur ranged from 98.5 to 100.3 in all analyses. As can be seen in Fig. 2, the chemical composition at the bottom is slightly sulfur rich ($\sim FeS_{1.02}$), but is almost stoichiometric ($FeS_{1.00} \sim FeS_{1.01}$) starting from approximately 7 mm and up to the interphase boundary which appears at a height of 20.5 mm. Above the interphase boundary the composition becomes abruptly iron-rich. This compositional variation is consistent with the solidus curve in the phase diagram for the iron-iron sulfide system,[1,6] and also with the results of physical measurements, such as the transition temperature from hexagonal NiAs structure to distorted NiAs structure and metallographic observations.[1]

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