CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

THE GROWTH OF ARSENOPYRITE SINGLE CRYSTALS BY THE CLOSED-TUBE IODINE VAPOUR TRANSPORT TECHNIQUE

S. FUSHIMI AND A. H. WEBSTER

MINERAL SCIENCES DIVISION

SEPTEMBER 1969

Research Report R 216   Price 50 cents

Mines Branch Research Report R216

THE GROWTH OF ARSENOPYRITE SINGLE CRYSTALS BY THE CLOSED-TUBE IODINE VAPOUR TRANSPORT TECHNIQUE

by

S. Fushimi* and A.H. Webster**

ABSTRACT

Growth of arsenopyrite crystals was attempted by the closed-tube iodine vapour transport technique. It was necessary to choose the conditions of synthesis properly, or else loellingite and pyrrhotite would form in association with arsenopyrite. Indeed, the transported products always contained at least a trace of loellingite or pyrrhotite. Small but fairly well-shaped arsenopyrite crystals with dimensions up to 0.3 x 0.1 x 0.1 mm were obtained. It has not been possible, up to the present time, to obtain large single crystals: the product has generally consisted of agglomerated, dendritic crystals with dimensions of up to 2 mm.

*National Research Council of Canada Postdoctorate Fellow assigned to the Mines Branch. Present address: Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Musashino, Tokyo, Japan.
**Research Scientist, Physical Chemistry Section, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des mines

Rapport de recherches R 216

LA CROISSANCE DES CRISTAUX D'ARSÉNOPYRITE
PAR LA MÉTHODE DE TRANSPORT CHIMIQUE EN PRÉSENCE
D'IODE DANS DES AMPOULES SCELLÉES

par

S. Fushimi* et A.H. Webster**

RÉSUMÉ

La croissance des cristaux d'arsénopyrite a été tentée par la méthode de transport chimique en présence d'iode dans des ampoules scellées. Les conditions de croissance devraient être choisies avec soin, autrement du löllingite ou du pyrrhotine se formera. En effet, les produits transportés contiennent toujours au moins une trace de löllingite ou de pyrrhotine. Des petits cristaux bien formés d'arsénopyrite jusqu'à 0.3 sur 0.1 sur 0.1 mm de grandeur s'obtiennent. Il n'a pas été possible, jusqu'au présent, d'obtenir des monocristaux grands: le produit consiste d'ordinaire des cristaux agglomérés et dendritiques, jusqu'à 2 mm de grandeur.

---

*Boursier du Conseil national de recherches, attaché à la Direction des mines. Adresse actuelle: Laboratoire de communication électrique, Société publique de télégraphie et de téléphone du Japon, Musashino, Tokyo, Japon.
**Chercheur scientifique, Section de la chimie physique, Division des sciences minérales, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

CONTENTS

FIGURES

TABLE

==

INTRODUCTION

During the course of the continued, systematic studies performed in the Mineral Sciences Division under the Sulphide Research Project, aimed at understanding and exploiting the nature of the important naturally-occurring sulphide and related minerals, theoretical consideration was given to the structural stability of the minerals with pyrite, marcasite, arseno-pyrite and loellingite structures, with special consideration being given to the electron configurations of these minerals[1].

A project for the experimental investigation of the bonding nature of these series of minerals is under way in the Mineral Sciences Division. For this investigation, a stock of good synthetic single crystals, free from impurities, is preferable to the naturally-occurring single crystals that usually contain a significant level of impurities.

Single crystals of pyrite (cubic FeS_2) and loellingite ($FeAs_2$) have been grown in the Mineral Sciences Division by Mr. L.G. Ripley, and investigations on the growth of marcasite (orthorhombic FeS_2) crystals are under way. Since the growth of synthetic crystals of arsenopyrite ($FeAs_{1.1}S_{0.9}$) has not yet been reported, the authors undertook a study of the preparation of arsenopyrite single crystals. The crystal growth of arsenopyrite has also stimulated the authors' interest in establishing a growth technique for incongruently-melting ternary compounds that contain two volatile components, in this case arsenic and sulphur.

According to the phase diagram for the Fe-As-S system[2], arseno-pyrite decomposes by incongruent melting at 702°C to pyrrhotite ($Fe_{1-x}S$), loellingite, and a liquid phase. The phase diagram of the Fe-As-S system is shown in Fig. 1. Since it is impossible to attain the conditions for congruent melting of arsenopyrite by the presently available high-pressure techniques for crystal growth, the techniques applicable to the growth of arsenopyrite single crystals were limited to solution growth or to the chemical vapour transport technique. The authors chose the closed-tube iodine vapour transport
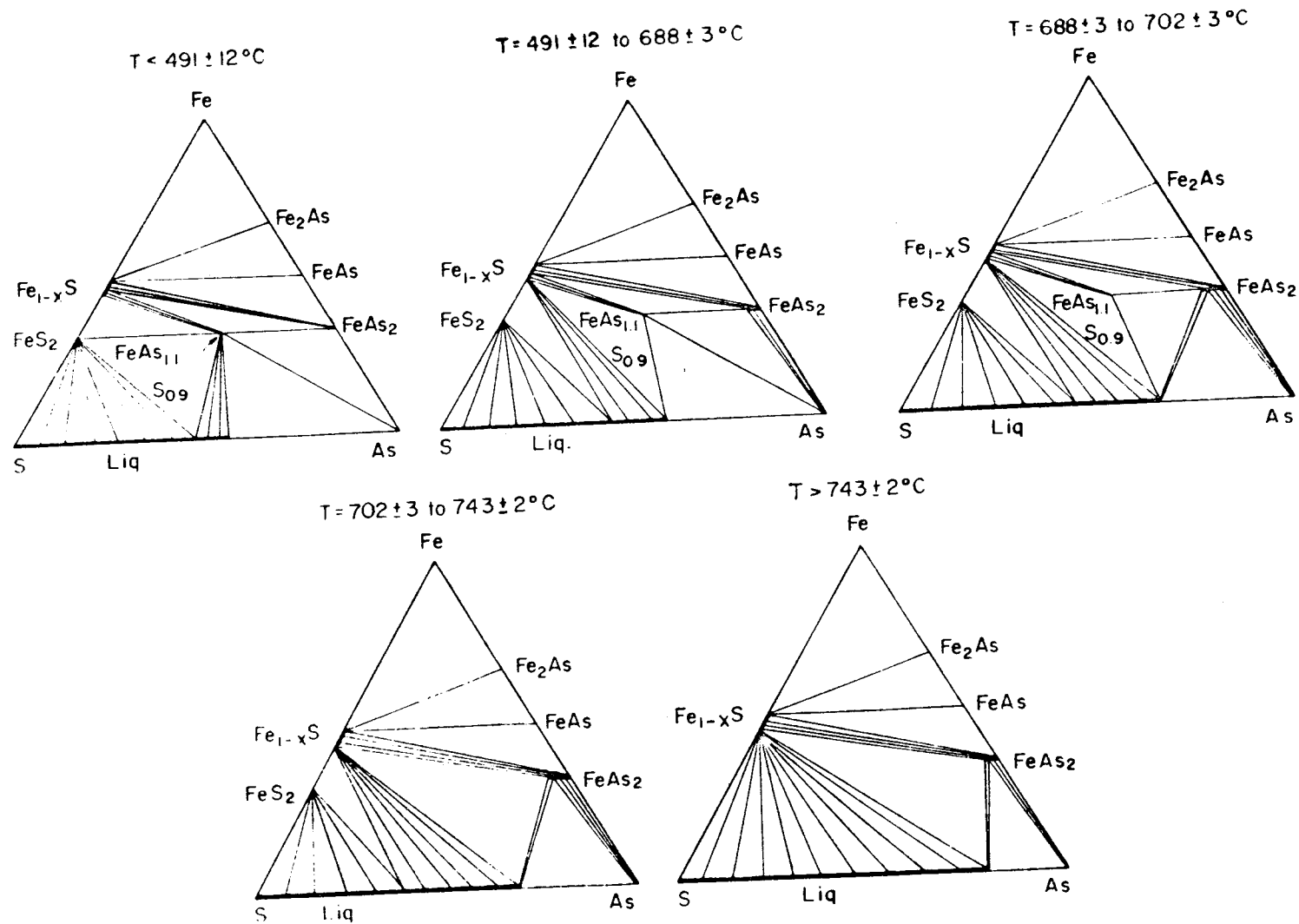
Figure 1. Phase Diagram of the Fe-As-S System, after L.A. Clark, Econ. Geol., _55_, 1376 (1960). Reproduced from "Phase Diagrams for Ceramists" edited by E.M. Levin et al., published by the American Ceramic Society, 1964.

technique on account of its potential capability of providing purer crystals than the other methods. Attempts at flux growth of arsenopyrite from molten As_2S_2 and from the KCl-LiCl eutectic mixture have failed, because of the low solubility of arsenopyrite in these fluxes.

EXPERIMENTAL

Reagent-grade iron, sulphur, and metallic arsenic from the MacArthur Chemical Co., Limited, were used for the first few runs of the synthesis of the arsenopyrite powder samples. For the other syntheses of arsenopyrite and pyrite, iron with 99.95 weight percent Fe, arsenic with 99.95 weight percent As* and sulphur with 99.999 weight percent S were used. They were purchased from Alfa Inorganic, Inc. Reagent-grade iodine from the MacArthur Chemical Co., Limited, was always used as the transportant.

Iron was deoxidized in a Pyrex tube at some temperature between 600°C and 1000°C by passing de-oxygenated, dried hydrogen gas through the tube for about 5 hours. A Pyrex tube containing arsenic at one end was positioned within a furnace, and purified hydrogen gas was passed through the tube. The arsenic was heated to some temperature between 400°C and 500°C. Arsenic metal and arsenious oxide were distilled and collected in different zones of the tube. The purified arsenic samples were stored in evacuated, sealed Pyrex tubes until they were used.

The synthesis of the powder samples of arsenopyrite and of pyrite was done using evacuated, sealed, transparent quartz tubes. The desired amounts of the elements were loaded into the tube, which was then evacuated to 10^{-5} mm Hg and sealed by a torch. The volume of free space in the tube was minimized by inserting another evacuated, sealed quartz tube into it.

---

*The purity of arsenic given here is reliable only before opening the seal. A significant level of arsenious oxide was formed when the arsenic was exposed to the air, and a distillation process for purification was always necessary.

The tubes, with the elements, were heated slowly in an electric furnace to 600°C and kept at that temperature for 10 to 25 days. In most cases, repeated grinding and heating were employed. The amounts of iron, arsenic and sulphur used for the synthesis of the arsenopyrite powder samples were chosen as 33.4, 49.4 and 17.2 weight percent for the three elements, respectively, so that single-phased arsenopyrite could be obtained at 600°C. The reported composition of arsenopyrite at 600°C is $FeAs_{1.1}S_{0.9}$[2].

The growth experiments for arsenopyrite by the vapour transport technique were done using sealed, evacuated transparent quartz tubes. The desired amounts of synthetic arsenopyrite powder and iodine were loaded at the one end of the tube, which was then evacuated to 10^{-5} mm Hg and sealed by a torch. In most runs, synthetic pyrite or sulphur was added to the arsenopyrite powder. The reason for these additions will be discussed later. The ampoules thus prepared were placed in furnaces and heated at the intended temperatures for 7 to 32 days. The temperatures of both ends of each ampoule were controlled, and the end containing the starting sample was always maintained at the higher temperature.

Two different furnaces, which provided three different temperature profiles, were used. The typical temperature profiles used in this study are shown in Figs. 2 (a) and (b).

The ampoules were either cooled slowly in the furnaces or were quenched by pulling the ampoules quickly out of the furnaces. The quenching was employed in order to ensure that the liquid phase would condense on the parts of the ampoule wall where it would not contaminate the bulk of the crystalline product.

The cool-end products yielded by the transport reactions were washed repeatedly with carbon disulphide to remove the condensed arsenic-sulphur glass. The examination of the transported phases was done by Debye-Scherrer X-ray diffraction using Co-Kα radiation, or by electron-microprobe analysis. Direct observation under the optical microscope was also employed.

Single-crystal arsenopyrite was examined, using the Buerger X-ray precession camera, to determine its phase and crystal orientation.
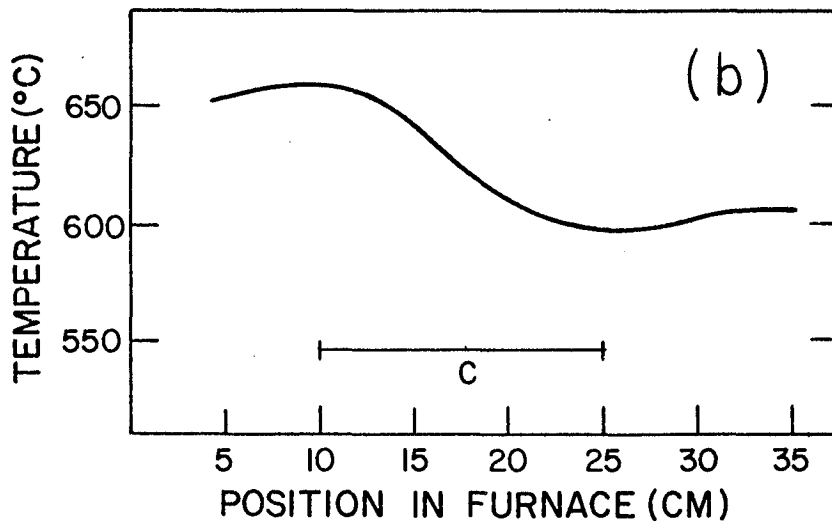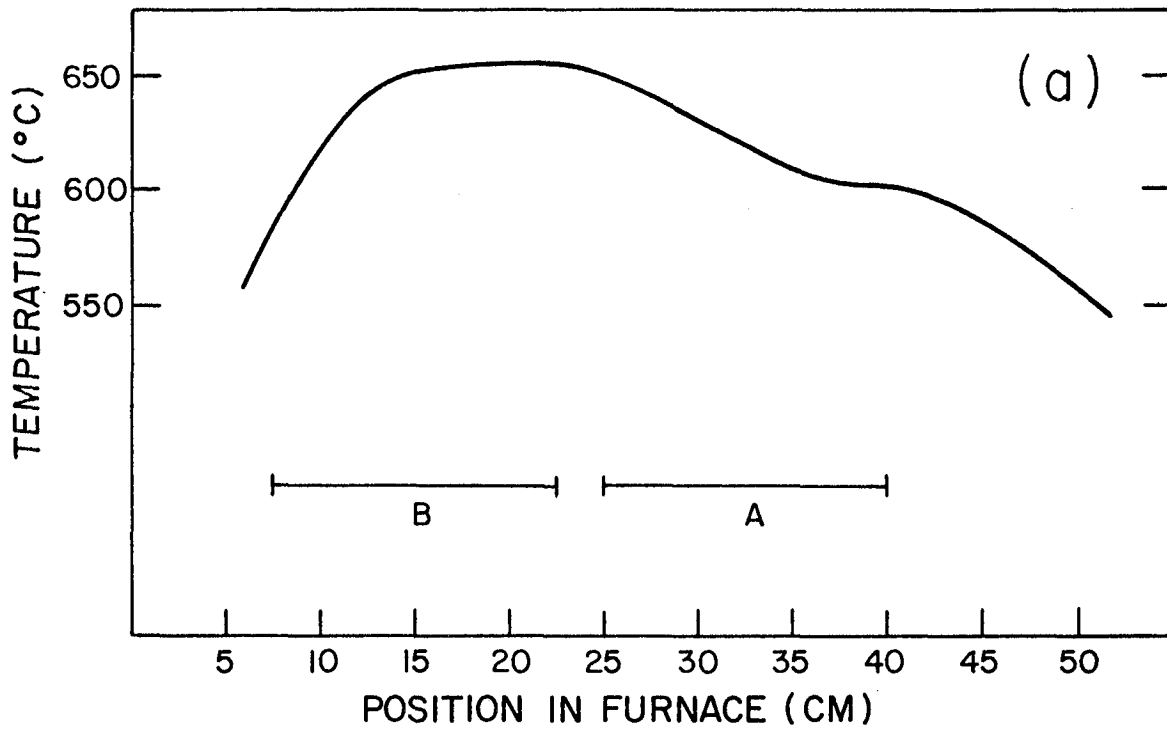
Figures 2 (a) and (b). The Typical Temperature Profiles Used in this Study. (The positions of the ampoules are indicated in the figures.)

TABLE 1

The Transport Experiments for the Synthesis of Arsenopyrite Crystals

Run Number	Starting Composition (g)			Size of Ampoule (mmϕ x mm)	T(hot) (°C)	T(cool) (°C)	Time (days)	Position** of Ampoules	Conditions*** of Cooling	Cool-end phases
#1	FeAsS* 0.50		I_2 0.12	15, 150	620	550	10	A	S	FeAsS****, $FeAs_2$*****
#5	FeAsS 0.50		I_2 0.24	15, 130	650	600	15	A	S	FeAsS, $FeAs_2$
#6	FeAsS 1.00		I_2 0.18	15, 150	650	630	15	B	S	FeAsS, $FeAs_2$
#7	FeAsS 1.00	FeS_2 0.13	I_2 0.18	15, 140	650	590	10	A	S	FeAsS, $FeAs_2$
#8	FeAsS 1.09	FeS_2 0.07	I_2 0.18	15, 140	650	590	10	B	S	FeAsS, $FeAs_2$
#9	FeAsS 1.00	FeS_2 0.24	I_2 0.18	15, 140	650	590	10	A	S	FeAsS, $Fe_{1-x}S$
#10	FeAsS 1.00	FeS_2 0.45	I_2 0.18	15, 140	650	570	10	B	S	$FeAs_2$, As
#11	FeAsS 1.00	FeS_2 0.20	I_2 0.18	15, 150	650	605	12	A	S	FeAsS, $Fe_{1-x}S$
#12	FeAsS 1.00	FeS_2 0.16	I_2 0.18	15, 150	650	620	12	B	S	$FeAs_2$
#20	FeAsS 1.00	S 0.06	I_2 0.18	15, 140	650	590	11	A	Q	FeAsS(tr.), $Fe_{1-x}S$
#22	FeAsS 1.00	FeS_2 0.18	I_2 0.18	15, 140	650	600	32	A	Q	FeAsS, $Fe_{1-x}S$ $FeAs_2$(tr.)
#23	FeAsS 1.00	FeS_2 0.18	I_2 0.18	15, 140	650	575	20	A	Q	FeAsS, $Fe_{1-x}S$

- 9 -

TABLE 1 - (Continued)

Run Number	Starting Composition (g)			Size of Ampoule (mmφ x mm)	T(hot) (°C)	T(cool) (°C)	Time (days)	Position** of Ampoules	Conditions*** of Cooling	Cool-end phases
#25	FeAsS 1.00	FeS_2 0.24	I_2 0.18	15, 140	650	580	20	C	Q	FeAsS, $Fe_{1-x}S$
#26	FeAsS 1.00	FeS_2 0.24	I_2 0.18	15, 127	650	605	20	A	Q	FeAsS, $Fe_{1-x}S$ $FeAs_2$
#27	FeAsS 1.00	FeS_2 0.10	I_2 0.18	15, 127	650	610	13	C	Q	FeAsS, $FeAs_2$
#28	FeAsS 1.00	FeS_2 0.15	I_2 0.10	15, 120	650	603	17	A	Q	FeAsS, $FeAs_2$ $Fe_{1-x}S$(tr.)
#29	FeAsS 1.00	FeS_2 0.155	I_2 0.18	15, 127	650	575	12	C	Q	FeAsS, $FeAs_2$
#30	FeAsS 1.00	FeS_2 0.135	I_2 0.16	15, 140	650	605	15	A	Q	FeAsS(tr.), $FeAs_2$
#32	FeAsS 1.00	FeS_2 0.165	I_2 0.18	15, 140	650	602	15	A	Q	FeAsS, $FeAs_2$
#33	FeAsS 1.00	FeS_2 0.165	I_2 0.18	15, 140	650	580	7	C	Q	FeAsS(tr.), $FeAs_2$
#34	FeAsS 1.00	FeS_2 0.19	I_2 0.18	15, 140	650	685	7	C	Q	FeAsS, $FeAs_2$ $Fe_{1-x}S$

*FeAsS is used for convenience and simplicity to designate $FeAs_{1.1}S_{0.9}$.

**Cf. Figs. 2 (a) and (b).

***S: Slow cooling in the furnaces; Q: Quenching.

****FeAsS is used only to designate the type of phase, not to represent its actual stoichiometric composition.

*****$FeAs_2$ is used only to designate the type of phase; it actually contained up to 6 wt. % of sulphur.

tr. = trace.

RESULTS AND DISCUSSION

The results of the transport runs are listed in Table 1. From the
first two runs (#1 and #5), it was found that arsenopyrite could be transported,
but it was also apparent that loellingite crystals were obtained as well when
the starting material had the arsenopyrite composition. In addition to
arsenopyrite and loellingite, AsI_3 crystals and red or blackish-red amorphous
precipitates were observed all over the inside of the ampoules when the
ampoules were cooled slowly, whereas amorphous precipitates and some
iodine crystals were observed when the ampoules were quenched. Since
AsI_3 is unstable at the working temperature[3], it is considered to have
been formed at lower temperatures during the cooling process. The
amorphous precipitates are considered to have the gross composition
$As_{2+x}S_2$, since the gas phases in equilibrium with arsenopyrite and pyrrhotite,
or with arsenopyrite and loellingite, at 600°C include not only As_4S_4 but
also As_4 gas.

The ideal reaction scheme for the transport of arsenopyrite by
iodine will be written as:

$$4FeAsS(s) + 6I_2(g) = 4FeI_3{}^*(g) + As_4S_4(g) \dots\dots\dots\dots (Eq. 1)$$
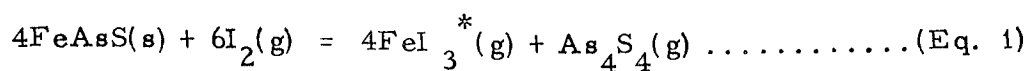
If this reaction alone takes place, then only arsenopyrite will be transported.
Contrary to the requirements of this simplified model, the results of the
runs #1 and #5 indicate that different reaction schemes were involved in
these runs.

The dissociation pressure of arsenic in equilibrium with arsenopyrite
was given by B. A. Strathdee and L. M. Pidgeon[4] as follows:

$$4FeAsS(s) = 4FeS^{**}(s) + As_4(g) \dots\dots\dots\dots\dots (Eq. 2)$$

$$\log P_{mmHg} = -\frac{6590}{T} + 9.52 \qquad (T = °K)$$
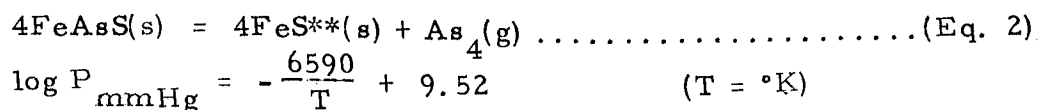
This indicates the significantly high dissociation pressure of arsenopyrite:

---

*Some FeI_2 could be present, but FeI_3 should predominate[3].
**FeS should actually be given as $Fe_{1-x}S$. Equation 2 does not imply that
the authors of reference (4) dealt with the strictly stoichiometric case.

250 mm Hg at 650°C and 100 mm Hg at 600°C. It is quite clear this reaction, shown in Equation 2, took place along with that shown in Equation 1. When this distillation reaction of arsenic from arsenopyrite takes place, the reaction

$$2Fe_{1-x}S(s) + 3(1-x)I_2(g) = 2(1-x)FeI_3 + S_2 \quad\ldots\ldots(Eq. 3)$$
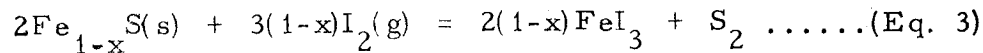
also takes place, where the $Fe_{1-x}S$ is obtained from the reaction given in Equation 2.

The lack of the data for the standard free energy of the reaction

$$As_4(g) + 2S_2(g) = As_4S_4(g)\ldots\ldots\ldots\ldots\ldots\ldots\ldots(Eq. 4)$$
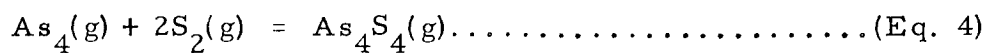
makes it difficult to estimate the standard free energy of the reaction given in Equation 1, but the results indicate that the distillation of arsenic from arsenopyrite predominated over the other reactions and, as a consequence, loellingite was formed at the cool end, leaving pyrrhotite at the hot end. It is therefore necessary to suppress the distillation of arsenic from the arsenopyrite, or, alternatively, to raise the sulphur ratio in the gas phase and compensate for the excess free arsenic gas obtained through the reaction given in Equation 2, to yield As_4S_4 gas. To suppress the distillation of arsenic from arsenopyrite, it is necessary to lower the working temperature. This method, however, would not provide an adequate rate of transport, since the temperatures employed in the Run #1 are almost at the lowest limit for the transport by iodine; also, a lower temperature difference would also decrease the rate of transport. It is more practical to find out the optimum starting composition for obtaining the arsenopyrite phase alone as a cool-end product for a particular set of the hot-and cool-end temperatures; for example, 650°C and 600°C.

Fixing the hot-end temperature at 650°C and varying the cool-end temperature from 575°C to 610°C, the relationships between the starting composition and cool-end products were investigated. It is, as mentioned earlier, necessary to raise the sulphur pressure and adjust the gas composition to that which would be in equilibrium with arsenopyrite at the cool end of the tube. This was done by adding the pyrite powder to the arsenopyrite powder samples. The dissociation pressure of pyrite was given by T. Rosenqvist [5] as follows:

$$2FeS_2(s) = 2Fe_{1-x}S(s) + S_2 \quad \dots\dots\dots\dots\dots\dots\dots(Eq.\ 5)^*$$
$$-RT\ln P_{S_2} = 87,000 - 89.7T$$
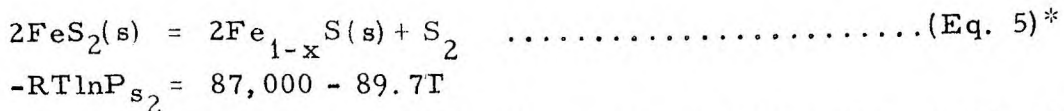
The dissociation pressure of pyrite is 76 mm Hg at 650°C and 5 mm Hg at 600°C. Pyrite is also preferable to pyrrhotite for the addition to the arsenopyrite powder, because the addition of pyrite brings the gross composition of the starting materials inside the (arsenopyrite-pyrrhotite-liquid) three-phase region and minimizes the chance of forming the troublesome (arsenopyrite-pyrrhotite-loellingite) equilibrium (cf. Fig. 1).

The results are summarized as a reaction diagram and shown in Fig. 3. Three regions, namely (arsenopyrite + loellingite), (arsenopyrite + pyrrhotite + loellingite) and (arsenopyrite + pyrrhotite), were found. In the (arsenopyrite + loellingite) region, the relative amount of sulphur in the gas phase is not high enough to convert a sufficient proportion of the arsenic gas to As_4S_4 in order to suppress the formation of loellingite. At the cold end of the tube, the relative saturation of the arsenic vapour, evolved from the decomposition of arsenopyrite, increases as the temperature difference between the hot and cold ends of the tube increases. Hence, the boundary of the (arsenopyrite + loellingite) region shifts toward the sulphur-rich side of the starting composition with increasing temperature difference between the hot and cool ends.

On the sulphur-rich side of the boundary of the (arsenopyrite + loellingite) region, the relative amount of sulphur in the gas phase is high enough to convert a large proportion of the arsenic gas to arsenic sulphide gas. The partial pressure of sulphur in the gas becomes high enough that pyrrhotite is formed at the cool end of the tube, in place of loellingite, along with arsenopyrite. The deposition of (pyrrhotite + loellingite + arsenopyrite) is probably not an equilibrium reaction, and loellingite might have been formed due to the temporarily high arsenic pressure at the beginning of the runs. The intergrowth of arsenopyrite and loellingite was observed on the crystalline bulk obtained as the product in Run #26, and the loellingite phase was covered by the arsenopyrite phase as shown in Fig. 4.

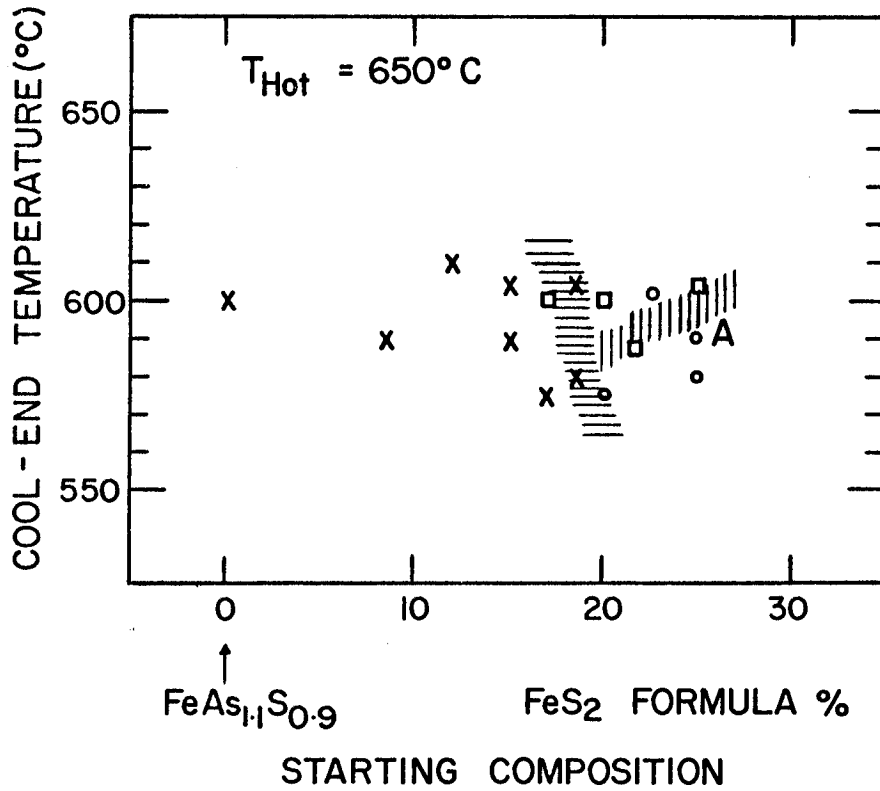*This equation is stoichiometric with respect to sulphur only.

Figure 3. Reaction Diagram of the Transport of Arsenopyrite by Iodine.

o $FeAsS + Fe_{1-x}S$

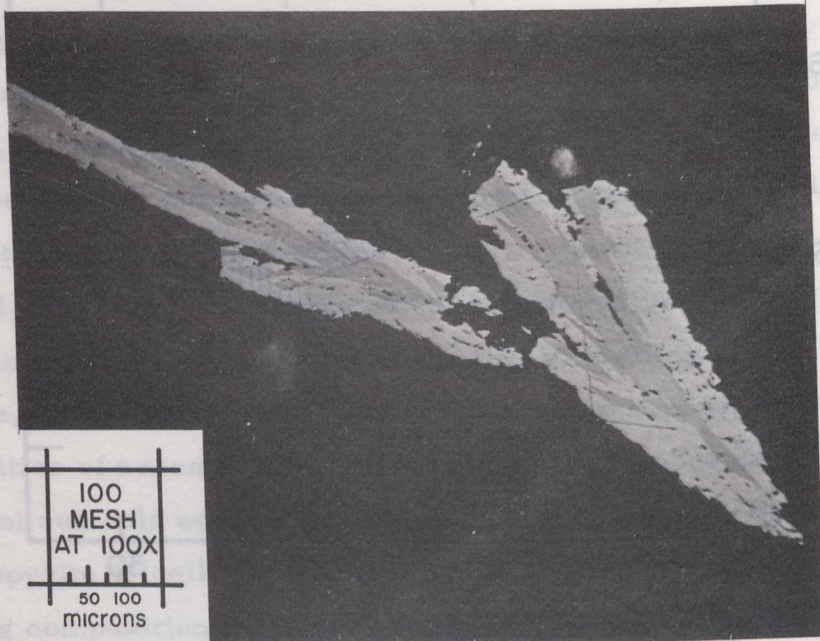x $FeAsS + FeAs_2$

□ $FeAsS + Fe_{1-x}S + FeAs_2$

Figure 4. Micrograph of the Intergrowth of Arsenopyrite and Loellingite (100x).

The boundaries, indicated in Fig. 3 by hatching, were not clearly established because of some inconsistency of the results, that might have been caused by minor changes of the conditions. The optimum conditions for transport of arsenopyrite are considered as the boundary between the (arsenopyrite + loellingite) region and the (arsenopyrite + pyrrhotite) region, but these conditions are hard to attain experimentally. It is more practical to employ the working conditions indicated as the (arsenopyrite + pyrrhotite) region and to separate the arsenopyrite crystals from pyrrhotite crystals by magnetic separation after synthesis.

Synthetic arsenopyrite single crystals, obtained by employing the working conditions indicated as A in Fig. 3, are shown in Fig. 5 (a). Well-shaped arsenopyrite single crystals obtained in this study are seen as lustrous rhombs, exhibiting the (203) and (430) faces*, with the c-axis along the direction of the rhombs, as shown in Fig. 5(b).

The other crystal data are as follows:

a = 6.35, b = 9.65 and c = 5.68 Å

Extinction rules: (Okℓ) present only with k = 2n, (hOℓ) present only with h = 2n, and (h1ℓ) present only with h = 2n + 1. These data are consistent with those for arsenopyrite, which, although actually triclinic or monoclinic[7][8], is pseudo-orthorhombic with a = 6.43, b = 9.55, c = 5.69 Å[6], and are consistent with the space group Cmmm, with extinctions (hkℓ) present only with h + k = 2n. The apparent orthorhombic symmetry has been attributed to twinning in the arsenopyrite crystals[8].

In Fig. 6, some typical agglomerations of the crystals are shown. The long direction of each crystallite will probably correspond to the c-axis, judging from their appearances.

The conditions indicated as the (arsenopyrite + loellingite) region and (arsenopyrite + pyrrhotite + loellingite) region are unfavourable for the crystal growth of arsenopyrite. In these regions, the intergrowth of arsenopyrite

*Determined by optical goniometer measurements of the interfacial angles.

- 14 -
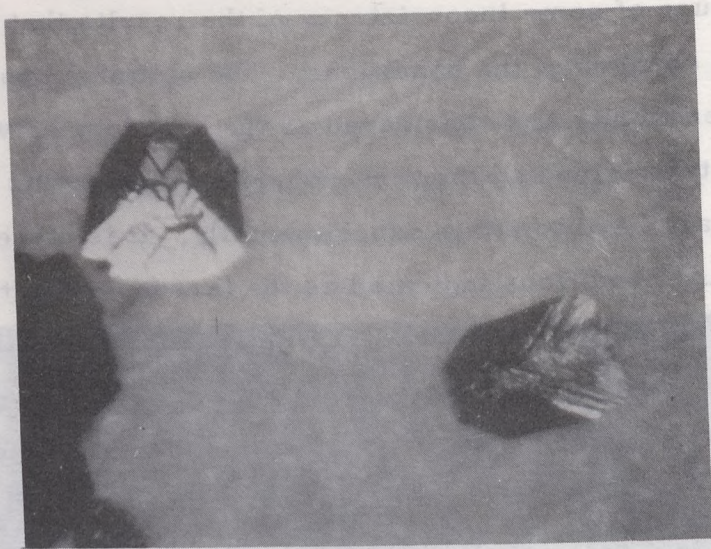
0·5 mm

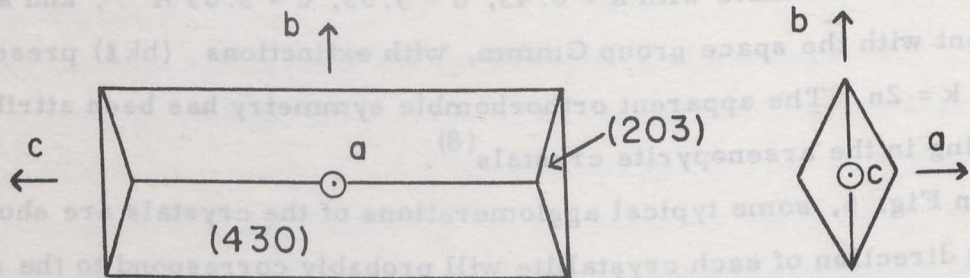Figure 5 (a). Micrograph of Synthetic Arsenopyrite Crystal (100x).

Figure 5 (b). Crystal Habit of Synthetic Arsenopyrite.

Figure 6.   Micrograph of Agglomerations of Synthetic Arsenopyrite
            Crystals (18x).

and loellingite was observed. This intergrowth is understandable on the basis of the structural similarity between arsenopyrite and loellingite.

The problem of the transport of the arsenopyrite phase has been partly solved, but obtaining good, large single crystals is another problem. Agglomerated, dendritic crystals were obtained from the runs with the working conditions quite close to the optimum conditions for the precipitation of arsenopyrite alone at the cool end of the tube, whereas from Run #9, for which the working conditions were far from the optimum, small but well-shaped arsenopyrite crystals were obtained. Judging from the complicated crystal structure of arsenopyrite, the optimum growth rate of the arsenopyrite would be very low. Even though no measurements of the transport rate of arsenopyrite were made in this study because the cool-end products were partly covered by amorphous precipitates or by AsI_3, the transport rates appeared to be considerably lower than that reported for FeS_2[9].

When the transport reaction was stopped after a short period of heating, small but well-shaped crystals were obtained, whereas the crystals were mostly dendritic when they were obtained from runs with prolonged heating.

The use of sulphur in place of pyrite was also examined (Run #20), and different results were obtained. Since the results are quite sensitive to the amount of sulphur, the use of sulphur is not recommended.

The temperature profile is important for obtaining the desired phases as the cool-end products. Amongst the temperature profiles examined in this study, the A or C type profiles, which have a smooth thermal gradient and reasonably long hot and cool ends, produced reproducible results, whereas the B-type profile, which has a drastic thermal gradient, encouraged the distillation of arsenic from arsenopyrite and was not suitable for the present purposes (Run #10).

CONCLUSIONS

Attempts at growing arsenopyrite single crystals were performed by the closed-tube iodine vapour transport technique. The reaction schemes involved in the transport of arsenopyrite are complex, due to the distillation reaction of arsenic from arsenopyrite.

The optimum working conditions for the transport of arsenopyrite were examined and a reaction diagram of the transport reaction of arsenopyrite was established for a hot-end temperature in the transport tube of 650°C. For this hot-end temperature, it is necessary to shift the starting composition toward the sulphur-rich side of the arsenopyrite composition; for this purpose, pyrite was used with reasonable success.

Small but well-shaped arsenopyrite single crystals were obtained but, in most cases, the product consisted of agglomerated dendritic crystals. The transport rate of arsenopyrite should be very small to obtain good crystals. It will be necessary to examine other hot-end temperatures lower than 650°C in order to find conditions of growth with smaller temperature differences between the hot and cool ends.

The closed-tube vapour transport technique is, however, still the most promising method for growing arsenopyrite crystals, as good fluxes for the flux-growth of arsenopyrite have not yet been found.

ACKNOWLEDGEMENTS

REFERENCES

(1) E. H. Nickel, "Structural Stability of Minerals with the Pyrite, Marcasite, Arsenopyrite and Loellingite Structures". Canad. Mineral., 9, 311-321 (1968).

(2) L. A. Clark, "The Fe-As-S System: Phase Relations and Applications", Economic Geology, 55, 1345-1381 and 1631-1652 (1960).

(3) R. F. Rolsten, "Iodide Metals and Metal Iodides", pubd. by John Wiley and Sons, Inc., New York (1961).

(4) B. A. Strathdee and L. M. Pidgeon, "Thermal Decomposition and Vapour Pressure Measurements on Arsenopyrite and an Arsenical Ore", Trans. C.I.M.M., 64, 506-510 (1961).

(5) T. Rosenqvist, "A Thermodynamic Study of the Iron, Cobalt and Nickel Sulphides", J. Iron Steel Inst., 176, 37-57 (1954).

(6) ASTM File of X-ray Powder Diffraction Patterns, Card No. 11-154.

(7) M. J. Buerger, "The System and Crystal Structure of the Minerals of the Arsenopyrite Group", Z. Krist., 95, 83-113 (1936).

(8) N. Morimoto and L. A. Clark, "Arsenopyrite Crystal-Chemical Relations", Amer. Mineralogist, 46, 1448-1469 (1961).

(9) R. J. Bouchard, "The Preparation of Single Crystals of FeS_2, CoS_2 and NiS_2 Pyrites by Chlorine Transport", J. Crystal Growth, 2, 40-44 (1968).

SF/AHW/pg