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THE GROWTH OF SILVER SULPHIDE CRYSTALS

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ABSTRACT

Crystals of Ag_2S were grown from the vapour phase reaction under H_2S–H_2 atmospheres. Morphological symmetry and X-ray rotation photographs showed that they are acanthite crystals which are formed under metastable conditions. This indicates that the phase transformation temperature of silver sulphide is dependent on the gaseous medium surrounding it and the stoichiometry.

INTRODUCTION

THERE are large discrepancies in literature on the equilibrium diagram of Ag–S system. Jeannot, Perrot and Tridot[1] reinvestigated this system in the temperature range of 170–800° C in H_2S–H_2 atmospheres. They reported the existence of the compound, Ag_4S, which they confirmed by thermoanalytical and electrical conductivity measurements. In the present investigation we tried to grow crystals of this metal-rich silver sulphide (Ag_4S) under the same set of conditions reported by the above authors. Ag_2S and Ag have been found to be the eventual products. However, Ag_2S grows into fine whiskers and quite often as well-grown tablets and larger needles with well-bounded faces exhibiting the monoclinic prismatic symmetry. In this report, we would like to communicate our observations on the crystal growth of Ag_2S in H_2S–H_2 atmospheres.

EXPERIMENTAL

Silver foil of high purity with 0·5 mm thickness was cut into 5 × 3 mm rectangles. A small amount of gold can be expected as impurity in this material. The metal was mixed with sublimed sulphur (Fluka, AG, 99·99 purity) such that the mole ratio was varied from Ag_4S to Ag_2S. The mixtures were taken in pyrex-glass ampoules and evacuated to 10^{-5} mm of Hg. The ampoules were subsequently filled with H_2S–H_2 gas mixtures which had a composition of 1 : 3 mole ratio. The total pressure was adjusted such that at 450° C the internal pressure was 760 mm of Hg, as calculated from the measured volume of the ampoule. Each ampoule had a narrow tube portion fitted with a stopcock. After filling the gas mixture, the ampoule was isolated from the rest of the vacuum system by closing the stopcock. The ampoule was sealed at the narrow tube part, while cooled in liquid nitrogen. It was possible by this procedure to keep a constant H_2S : H_2 ratio at the time of filling. The ampoules were transferred to a horizontal tube furnace and slowly heated to 450° C. The furnace (50 cm long) had a constant temperature zone of about 10 cm in the middle, while about 5 cm on each side of this had a drop in temperature of about 5° C. The lengths of all ampoules were within 15 cm. The ampoules were kept at 450° C for 7 days and subsequently taken out. The growth of silver sulphide crystals as well as the growth of silver "hair" could be observed within a day, by illuminating from one end of the furnace through the loosely packed quartz-wool.

RESULTS

Irrespective of the nett composition of the initial charge with respect to silver and sulphur, the resulting products were Ag_2S crystals (whiskers, larger needles and tablets) and hair-like growth of silver. As the composition approached Ag_2S, the amount of silver separating as filaments was negligible. With slightly more sulphur than 2 : 1 ratio

for silver and sulphur, no metallic particles were observed. Figure 1 shows the whiskers of Ag_2S and in contrast, the growth of silver hair can be clearly seen in Fig. 2. The nett composition for the charge in these cases was Ag_4S. The crystals of Ag_2S with morphologically bounded faces did not show cubic symmetry. Examination of a large number of crystals which were upto 5 mm in length revealed only monoclinic morphology. However, it is well known that under normal conditions, above 173° C, Ag_2S is formed as cubic argentite (α-Ag_2S with BCC structure)[2,3]. Below this temperature, it transforms to monoclinic acanthite (β–Ag_2S). Freuch[2] reported that argentite transforms below 173° C into a polycrystalline body of acanthite which retains the cubic morphology. However, in the present case, the crystals had non-cubic morphology and the X-ray diffraction patterns revealed that they were not polycrystalline. Besides, the X-ray rotation photographs indicated monoclinic symmetry. Figure 3 illustrates the morphology of a crystal of Ag_2S growing on the side of a silver platelet. The crystal is monoclinic, prismatic in the direction of the orthoaxis, flattened parallel to (010) faces and bounded by pyramidal (111) and unit (110) faces. It is evident, therefore, that under H_2S–H_2 atmosphere at 450° C, monoclinic acanthite crystals are metastably formed.

The appearance of silver in the form of many centimeter length aroused some interest. The silver grew always at the two ends of the charge which can be expected to be at a lower temperature than the central part of the ampoule. It recalls the older report of Ercker (1574) about the occurrence of silver whisker in nature, and is mentioned by Sisco and Smith[4]. Recently, controlled filamentary growth of silver from silver compounds has been reported by Ohachi and Taniguchi[5] and also by Corish and O'Briain[6,7]. Silver hair obtained by us appeared as bundles of elongated silver crystals. The rotation photograph showed that they are polycrystalline. The arcs in the Debye-Scherrer pattern had more intensity at the centre than at the edges which indicates a certain preferred orientation for the crystallites in each silver hair. In many cases, side growths of cubelets of silver could be observed under higher magnification.

X-ray rotation photographs indicated that the longer axis of the Ag_2S crystals were nearly parallel to the *c*-axis. The value of the *c*-axis cell edge varied from 7·8 to 8·18 A for a number of crystals examined. The change in cell dimensions may be due to a change in stoichiometry which in turn is dependent on the initial sulphur content. Layers corresponding to a superstructure lattice could be observed as weak reflections in the rotation photographs, particularly when the nett composition was about Ag_3S.

Discussion

It is a matter of surprise how the low temperature acanthite is formed under the conditions used for the present crystal growth. Observations show that Ag_2S crystals are not formed as cubic phase which subsequently transformed into monoclinic crystals. Polycrystalline mass or multitwinned crystals should be the product of such an event. It may be mentioned that natural crystals of acan-

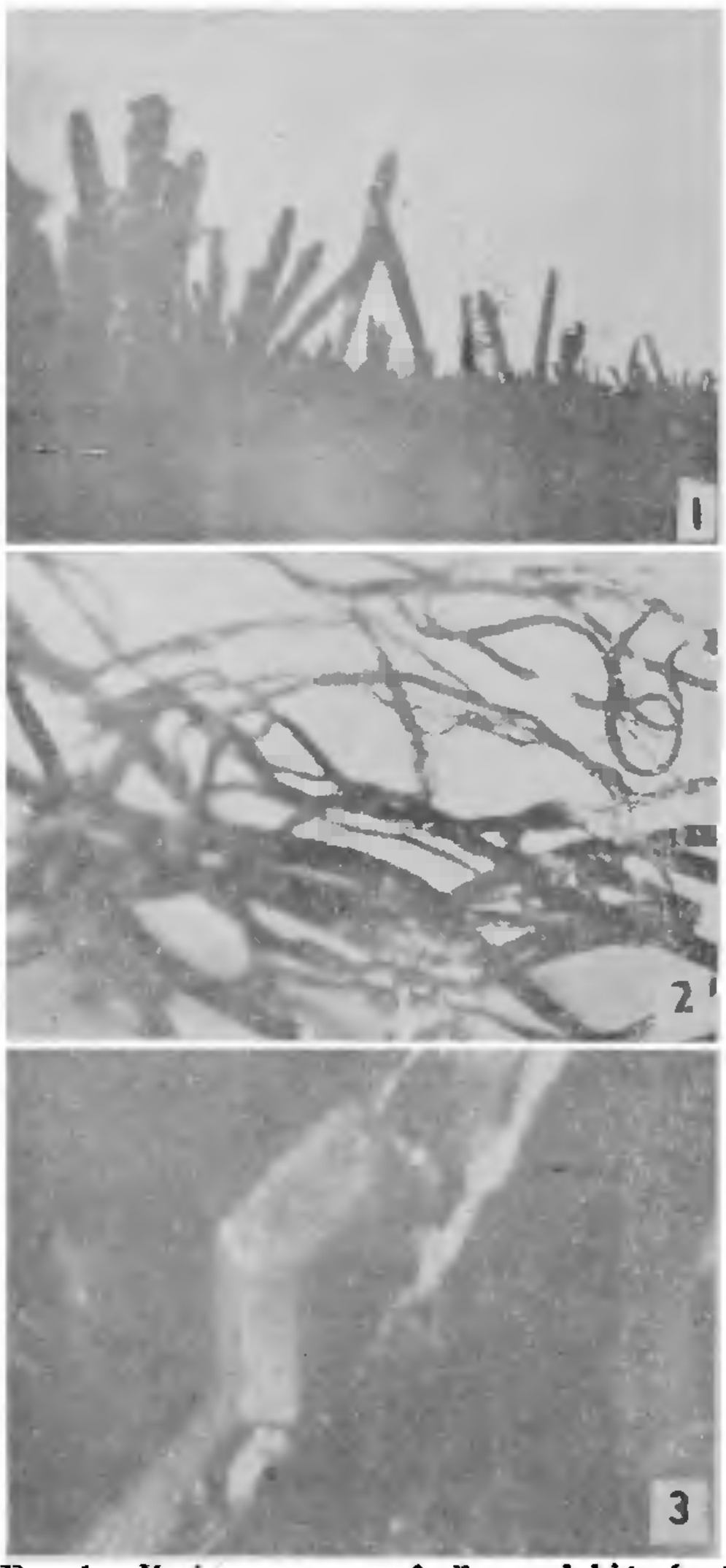

FIG. 1. Whisker growth of silver sulphide (× 15).
FIG. 2. Hair-like growth of metallic silver (× 6).
FIG. 3. Ag_2S crystal with monoclinic morphology (× 15) (*see* text).

thite do exist which have no twinning characteristics. These crystals can only be formed by a different pathway under metastable conditions. If the observations of Tridot *et al.*[1] is considered as valid, Ag_4S may be a transient phase, having no stability in the other ranges of the phase diagram, both along the temperature and the composition axes. The variation in temperature and $H_2S : H_2$ ratio in the gas phase from the value reported by Tridot *et al.*[1] will result in the conversion of Ag_4S to Ag_2S and Ag. The Ag_2S thus formed may be growing as an acanthite phase possibly due to the crystallochemical similarities between Ag_4S and acanthite. Silver extruded in such a reaction in the solid phase grows in the form of hair-like filaments. The presence of H_2S–H_2 mixture facilitates such a transformation since equilibrium can be easily attained by the supply of sulphide ion through the reaction,

$$H_2S \rightleftharpoons HS^- + H^+ \rightleftharpoons S^= + H_2.$$

This conclusion is supported by the observation that no crystal growth took place when the gas phase contained only pure H_2. Similar was the effect when the amount of sulphur was in excess of the composition, Ag_2S which prevents the transient formation of the metal-rich sulphide.

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