Phase Relations in the System Ag-Sb-S at 400°C

JAN BARSTAD

Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

The coexisting phases in the three-phase fields of the system Ag—Sb—S at 400°C within the region AgS—Sb₂S₃—Ag have been determined by means of X-ray identification in samples annealed at 400°C and quenched to room temperature. In addition, the reactions between pellets of silver-antimony alloys and silver-antimony sulfides at 400°C have been investigated. The results are in agreement with the isothermal section of the ternary phase diagram deduced from X-ray investigations.

In conjunction with kinetic investigations on solid state reactions in the quasi-binary system Ag₂S—Sb₂S₃, it was found desirable to reexamine the isothermal section of the phase diagram of the ternary system Ag—Sb—S at 400°C. Previously this ternary system was investigated by Schenck, Hoffmann, Knepper and Vögler with the help of measurements of the H₂S/H₂ ratio during the reduction of sulfides of the quasi-binary system Ag₂S—Sb₂S₃ with H₂ at 400°C. From the obtained staircase curves the boundaries of two-phase and three-phase fields were deduced. As the H₂S/H₂ ratios for some of the steps of the staircase curves were close together, the reality of some steps may be questioned. The composition of the silver-antimony sulfide phases was given as Ag₂S·Sb₂S₃, 4Ag₂S·Sb₂S₃, and 2Ag₂S·Sb₂S₃. This is in disagreement with thermal studies by Jaeger and van Klooster and by Jensen where only the phases Ag₂S·Sb₂S₃ and 3Ag₂S·Sb₂S₃ were observed. The work was confined to the region Ag—Sb—Ag₂S—Sb₂S₃ of the system Ag—Sb—S. The nature of the coexisting phases was ascertained by the following methods.

1) Samples whose compositions were presumably in three-phase fields were prepared from the elements, annealed at 400°C, and quenched. In addition, two samples in two-phase fields were investigated. The phases present were identified by means of X-ray powder diagrams with the help of a General Electric diffraction unit with Cu-radiation and Ni-filter.

2) Pressed and sintered pellets of Ag₂S, Ag₃SbS₃, AgSbS₂ and Sb₂S₃ and pellets of Ag, Ag₃Sb, and Sb solidified from melts were prepared. Two pellets

* Present address: Forsvarets Forskningsinstitutt, Kjeller pr. Lillestrøm, Norway.
of different composition 2—3 mm thick were pressed together and heated at 400°C for several days in a N₂ atmosphere. Observation of a reaction zone involving new phases indicates that the phases initially present do not coexist under equilibrium conditions.

The following informations on the crystal structures and homogeneity ranges of the phases in the binary systems were used.

1) The binary system Ag—Sb

By means of metallographic examination and X-ray diffraction identification, Weibke and Effinger studied the system Ag—Sb in detail. Their results agree in principle with previous X-ray diffraction investigations by Broderick and Ehret and by Westgren, Hägg, and Eriksson. At 400°C, the following phases exist:

α-Phase. Homogeneity range 0—6.2 atom % Sb. Face-centered cubic structure with a lattice constant increasing from a = 4.086 Å for pure silver to a = 4.121 Å. Lattice constant for pure silver is given on the ASTM data card as a = 4.0862 Å at 27°C.

ζ-Phase. Homogeneity range 9.4—14.9 atom % Sb. Hexagonal close-packed structure with lattice constants increasing from a = 2.927 Å, c = 4.784 Å, c/a = 1.634 to a = 2.961 Å, c = 4.797 Å, c/a = 1.620.

ε-Phase. Homogeneity range 21.3—26.2 atom % Sb. Orthorhombic structure which can be considered as a slightly distorted ζ-phase structure. The change in lattice constants within the homogeneity range for alloys annealed at 400°C is from a = 2.986 Å, b = 5.180 Å, c = 4.774 Å to a = 2.996 Å, b = 5.246 Å, c = 4.854 Å.

The lattice constants given by Westgren, Hägg, and Eriksson for the lower limit of the homogeneity range of the ε-phase are considerably higher than those given by Weibke and Effinger. Only the latter authors give the annealing temperature of the alloys and report differences in lattice constants for alloys annealed at 400°C and 500°C and thus their values are considered to be more accurate.

Sb-Phase. The dimensions of the hexagonal unit cell of pure Sb are given on the ASTM data card as a = 4.307 Å, c = 11.273 Å. The solubility of Ag in Sb and its effect on the lattice constants are not yet known.

2) The binary system Sb—S

As shown already by Jaeger and van Klooster, Sb₂S₃ is the only stable compound in the system Sb—S. The compound Sb₂S₃ has been obtained only by precipitation from aqueous solutions. The ASTM data card gives the following dimensions of the orthorhombic unit cell of Sb₂S₃: a = 11.229 Å, b = 11.310 Å, c = 3.839 Å.

The homogeneity ranges of the Sb phase and the Sb₂S₃ phase must be considered as very limited, but actual data are missing.

3) The binary system Ag—S

There is only one compound Ag₂S, which has a cubic structure at 400°C, called α Ag₃S or argentite. Transformation to the low temperature modification, called β Ag₃S or acanthite, takes place spontaneously near 178°C even on rapid quenching. According to Ramadell acanthite is monoclinic, a = 9.47 Å, b = 6.92 Å, c = 8.28 Å, β = 124°. The homogeneity range of α

Acta Chem. Scand. 13 (1959) No. 8
Ag₉S was deduced by Wagner 12 at 200° and 300°C from electrochemical measure-
ments and can be given as Ag₂₈₀₀₀S to Ag₂₉₀₂S.

The solubility of S in Ag is negligible.

4) The quasibinary system Ag₃S–Sb₂S₃

A thermal study of the system Ag₃S–Sb₂S₃ was first made by Jaeger and
van Klooster 2. The most detailed investigation has been made by Jensen ³.
Two intermediate compounds with a narrow homogeneity range are reported,
AgSbS₂ and Ag₃SbS₃.

αAgSbS₂. This modification is stable above 380°C. The crystal structure is
 cubic with a lattice constant a = 5.653 Å according to Graham 14. The
 transformation to the low temperature modification β AgSbS₂, miargyrite,
takes place on slow cooling whereas α AgSbS₂ is preserved on quenching.

Ag₃SbS₃, pyrargyrite. The structure of this phase was determined by Har-
er 14. The dimensions of the hexagonal unit cell are a = 11.06 Å, c = 8.74 Å.

In addition, there have been reported the minerals polyargyrite,
11 Ag₃S·Sb₂S₃, polybasite, 8Ag₃S·Sb₄S₃, pyrostitlpite, 3Ag₃S·Sb₂S₃, and
stephanite, 5Ag₃S·Sb₂S₃. Polybasite and pyrostitlpite were prepared by Weil
and Hoeart ¹⁵ by heating the components in glycerol.

IDENTIFICATION OF PHASES BY X-RAY DIFFRACTION

In Fig. 1 the compositions of the samples in the ternary system are indicated
in the phase diagram. The exact composition and the phases identified
in each sample are given in Table 1.

The interpretation of the X-ray diffraction diagrams was complicated
because overlapping of diffraction lines from different phases often occurred.
The β Ag₉S, Sb₂S₃ and Ag₉SbS₃ phases give very complex patterns. The com-
plex β Ag₉S pattern could have been avoided by using a high temperature
camera where the specimen was kept at a temperature above 178°C, but in
the present investigation a high temperature camera was not used.

The accuracy of the lattice constants is estimated to be 0.2 % unless other-
wise stated.

The lattice constants of the individual phases found in the various samples
were compared with values available in the literature with the following results.

Sb₂S₃-Phase. Within the limits of error, complete agreement was found
between the Sb₂S₃ phase in sample G and pure Sb₂S₃ ⁹.

Sb-Phase. Within the limits of error the lattice constants of Sb in the
samples G, A, and B agreed with those of pure Sb ⁹.

α AgSbS₂-Phase. The samples G, A, B, K, and C contain α AgSbS₂ with
a lattice constant equal to the value given for pure α AgSbS₂ ¹⁹.

ε-Phase. The calculated lattice constants in samples B and K are
a = 2.992 Å, b = 5.244 Å, c = 4.852 Å. In sample C considerable overlapping from
Ag₉SbS₃ interferes with an accurate evaluation of the lattice constants, but
they are within a limit of error of ± 0.4 % the same as in samples B and K.
Upon comparing these values with the lattice constants of the ε-phase in
the system Ag–Sb ⁶ within the homogeneity range, nearly complete agreement
with the values for the Sb-rich limit of the ε-phase is found. In sample L where

*Acta Chem. Scand. 13 (1959) No. 8*
both the $\varepsilon$-phase and the $\zeta$-phase are present, nearly complete overlapping of the reflections from these phases is observed.

$Ag_3SbS_3$. Within an estimated error of $\pm 0.4 \%$, agreement of the lattice dimensions of the $Ag_3SbS_3$ phase in the samples C, L, D with synthetic $Ag_3SbS_3$ prepared from $Ag_2S$ and $Sb_2S_3$ was obtained.

$\zeta$-Phase. The following lattice constants were obtained:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>2.965 Å</td>
<td>4.783 Å</td>
</tr>
<tr>
<td>D</td>
<td>2.963 Å</td>
<td>4.780 Å</td>
</tr>
<tr>
<td>E</td>
<td>2.940 Å</td>
<td>4.792 Å</td>
</tr>
<tr>
<td>H</td>
<td>2.924 Å</td>
<td>4.763 Å</td>
</tr>
</tbody>
</table>

Table 1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ag</th>
<th>Atom % Sb</th>
<th>S</th>
<th>Phases present</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>9.4</td>
<td>41.9</td>
<td>48.7</td>
<td>$Sb_2S_3$, Sb, $\alpha$ AgSbS$_2$</td>
</tr>
<tr>
<td>A</td>
<td>18.8</td>
<td>43.8</td>
<td>37.4</td>
<td>Sb, $\alpha$ AgSbS$_2$</td>
</tr>
<tr>
<td>B</td>
<td>33.3</td>
<td>33.3</td>
<td>33.3</td>
<td>Sb, $\alpha$ AgSbS$_2$, $\varepsilon$</td>
</tr>
<tr>
<td>K</td>
<td>55.0</td>
<td>35.0</td>
<td>10.0</td>
<td>Sb, $\alpha$ AgSbS$_2$, $\varepsilon$</td>
</tr>
<tr>
<td>C</td>
<td>47.5</td>
<td>21.5</td>
<td>31.0</td>
<td>$\alpha$ AgSbS$_2$, $\varepsilon$, $Ag_3SbS_3$</td>
</tr>
<tr>
<td>L</td>
<td>76.5</td>
<td>16.5</td>
<td>7.0</td>
<td>$\varepsilon$, $Ag_3SbS_3$, $\zeta$</td>
</tr>
<tr>
<td>D</td>
<td>69.3</td>
<td>7.7</td>
<td>23.0</td>
<td>$Ag_3SbS_3$, $\zeta$, $Ag_2S$</td>
</tr>
<tr>
<td>E</td>
<td>79.0</td>
<td>5.3</td>
<td>15.7</td>
<td>$\zeta$, $Ag_2S$</td>
</tr>
<tr>
<td>H</td>
<td>87.7</td>
<td>7.4</td>
<td>4.9</td>
<td>$\zeta$, $Ag_3S$, Ag</td>
</tr>
</tbody>
</table>

*Acta Chem. Scand.* 13 (1959) No. 8
\( \alpha \text{Ag}_2\text{S} \). The diffraction lines of \( \text{Ag}_2\text{S} \) in the alloys D, E, and H were identified by a comparison with those of pure \( \text{Ag}_2\text{S} \). Due to the transformation to \( \beta \text{Ag}_2\text{S} \) on cooling, the lattice constant of \( \alpha \text{Ag}_2\text{S} \) has not been obtained.

**Ag-Phase.** The lattice constant of the silver-phase in alloy H was found to be \( a = 4.112 \text{ Å} \) compared with the value \( a = 4.121 \text{ Å} \) given as the upper limit for the \( \alpha \) phase in the system Ag—Sb.

The following conclusions can be drawn:

There is no indication of more than very limited homogeneity ranges of the phases \( \text{Sb}_2\text{S}_3 \), \( \text{Sb} \), \( \text{AgSbS}_2 \), and \( \text{AgSbS}_3 \) as deviations from the lattice dimensions of the pure stoichiometric phases have not been observed.

No significant solubility of sulfur in \( \alpha \text{Ag} \), \( \zeta \) and \( \varepsilon \) seems to occur as the three-phase samples have lattice constants which do not differ from the lattice constants at the phase boundaries in the corresponding binary system Ag—Sb.

As sample D contains \( \zeta \)-phase with lattice constants nearly equal to the lattice constants at the Sb-rich end of the \( \zeta \)-phase in the system Ag—Sb, the tie lines from nearly the whole phase area must be directed towards the \( \text{Ag}_2\text{S} \) phase. The tie lines from the \( \alpha \text{Ag} \) phase area are also directed towards the \( \text{Ag}_2\text{S} \) phase.

Sample C contains \( \varepsilon \)-phase with lattice constants nearly equal to the lattice constants at the Sb-rich end of the \( \varepsilon \)-phase in the system Ag—Sb. The tie lines from nearly the whole \( \varepsilon \)-phase area are thus directed towards the \( \text{AgSbS}_3 \) phase.

There is no indication of a phase with the approximate composition 31 \( \text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3 \) as reported in the paper by Schenk et al.\(^1\)

The experimental data given by Schenck et al.\(^1\) are not in obvious conflict with the phase diagram in Fig. 1 although they have been interpreted differently. It must be recalled, however, that some of the reported steps of the \( \text{H}_2\text{S}/\text{H}_2 \) vs. composition plots are not very distinct and, therefore, do not permit a definite construction of the phase fields.

**REACTION BETWEEN PELLETS OF DIFFERENT COMPOSITION**

The pellet combinations \( \text{Sb—AgSbS}_2 \), \( \text{AgSbS}_2 \), \( \text{AgSbS}_3 \), \( \text{AgSbS}_3 \), \( \text{AgSbS}_3 \), and \( \text{AgSbS}_3 \) gave no indication of a reaction after heating 170 h at 400°C. Except for the combination \( \text{AgSbS}_3 \), the phases involved are connected by tie lines in the Fig. 1 and thus coexist at 400°C. After 170 h at 400°C, the pellets of the combinations \( \text{Sb—AgSbS}_3 \) and \( \text{AgSbS}_3 \) were easily separated, but a thin reaction layer could be observed at the contact surfaces. The pellet combination \( \text{AgSbS}_3 \) showed a more pronounced reaction; the pellets stuck together. Reactions between the phases \( \text{Ag} \) and \( \text{AgSbS}_3 \), \( \text{Ag} \) and \( \text{AgSbS}_2 \), and \( \text{Ag} \) and \( \text{Sb}_2\text{S}_3 \) take place very rapidly. After 100 h virtually only the reaction products could be observed on staining polished transverse sections according to Gaudin and McGlashan.\(^1\)

In all the pellet combinations where a reaction was observed, the two initial phases do not coexist according to the phase diagram in Fig. 1.

**Acknowledgement.** The author wishes to express his thanks to Professor Carl Wagner for the interest in this work and for his valuable suggestions and to Professor John T. Norton for making X-ray equipment available. My work at M.I.T. was made possible by

*Acta Chem. Scand.* 13 (1959) No. 8
a fellowship granted by Per Frelich. The author wishes also to express his thanks to Norges Teknisk-Naturvitenskapelige Forskningsråd, Norge Amerika Foreningen and United States Educational Foundation in Norway. The investigation has been sponsored by Office of Ordnance Research, U.S. Army under Contract DA-19-020-ORD-3661.

REFERENCES


Received June 19, 1959.