

Measurements of Phase Equilibria in the Aluminium–Aluminium Sulfide System

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Measurements of phase equilibria in the system Al–Al₂S₃ in the region 0.5–1.0 mol fraction Al₂S₃ were performed by using differential thermal analysis, quenching and X-ray techniques. The Al–Al₂S₃ system shows an intermediate compound, the subsulfide AlS, which seems to be stable only at high temperatures (between 1010 and 1060°C). A eutectic point exists in the Al₂S₃ rich end of the phase diagram and a peritectic point close to the AlS composition. The phase diagram proposed is different from those previously reported.

The system Al–Al₂S₃, aluminium–aluminium sulfide, is of interest both from a theoretical and from an industrial point of view. Aluminium sulfide may be an important reagent in the production of aluminium using a non-electrolytic method.^{1,2} It is fundamental for such processes to know the phase equilibria of the system Al–Al₂S₃. Moreover, the study of this system is important in the field of metal-metal salt equilibria.

There has been little experimental data reported for the system aluminium–aluminium sulfide and the phase diagrams proposed differ widely.^{3,4} The first investigators to study the change in the melting point of aluminium sulfide after the addition of aluminium were Biltz and Caspari.⁵ Murakami and Shibata³ first proposed a complete phase diagram based on chemical and X-ray studies. These authors reported two compounds in the system, AlS with a very high melting point, 2100°C, and

Al₂S₃, formed by a peritectic reaction between AlS and a liquid. These results have not been confirmed neither by other investigators^{4,5} nor by the present work. The melting point reported by these authors for the compound AlS is particularly high and this is probably due to some contamination from aluminium oxide in the samples.

The phase diagram proposed by Kohlmeyer and Retzlaff⁴ is in better agreement with our experimental data. The melting points for the compounds Al₂S₃ and AlS are given as 1100 and 1200°C, respectively. There is a liquid miscibility in this system which starts at 1070°C. The diagram is, however, only meant to be hypothetical. Some sections of the diagram violate the phase rule and the continuous liquid–Al₂S₃ region starting from pure Al₂S₃ and increasing in temperature was not observed by Biltz and Caspari⁵ and the present authors.

The subsulfide Al₂S is observed in the gas phase.^{6,7} Different modifications of Al₂S₃ are also reported.⁸

EXPERIMENTAL

Al₂S₃ was prepared by direct synthesis between sulfur(g) and aluminium(l)² employing a method similar to the one proposed by Kohlmeyer and Retzlaff.⁴ Chemical analysis showed an excess of 10 ± 2 mol % Al in the sulfide compared with stoichiometric Al₂S₃. Emission spectrographic analysis indicated impurities of Fe, Mg, and Si in the 0.5 weight % range. The excess aluminium in the sulfide was essentially metallic aluminium dissolved in the salt. Alloys of aluminium and aluminium(III) sulfide, were prepared at 1200°C

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in an ordinary laboratory furnace, which had an argon tight water cooled quenching device connected at the bottom. After quenching, the samples were examined by chemical, X-ray, and DTA studies.

DTA was carried out in a platinum furnace. The sample and reference material (Al_2O_3) were mounted in graphite and platinum crucibles, respectively, in an alsint block. A graphite crucible was necessary because the sulfide samples attack platinum. The temperature and differential temperature were measured by Pt/Pt 10% Rh thermo-couples calibrated against the melting point of silver. The DTA curves were recorded by a Varian G 2022 Dual Channel Recorder and the signal was amplified by use of DC Microvolt Amplifier, (Leeds & Northrup, USA). Sample size varied from 0.5 to 1.5 g. The heating rate was 9–10°C/min and the cooling rate 5–6°C/min.

The room temperature X-ray experiments of quenched samples were performed using a Debye-Scherrer camera. The samples were ground to a very fine particle size and filled in 0.5 mm O.D. low absorption glass capillary tubes in a dry box. Qualitative high temperature X-ray diffraction studies were carried out in a metal ribbon furnace, similar to the one described by Smith.⁹ The heating element was a platinum–10% rhodium sheet which also served as sample holder. The temperature was recorded with a Pt/Pt 10% Rh thermocouple welded to the strip.

The DTA and X-ray equipment has been described in detail elsewhere.² All high temperature work was carried out in an atmosphere of purified argon (99.99%, Norsk Hydro, Norway).

RESULTS

The phase diagram of the system Al– Al_2S_3 is presented in Fig. 1. This diagram is drawn mainly from DTA results. Both heating and cooling curves were recorded during DTA-runs, and the lower temperatures obtained for phase changes observed during cooling indicate some supercooling of the liquid in these melts. Some preliminary high temperature X-ray powder patterns obtained were in qualitative agreement with the phase change indicated at 1010°C. The phase diagram must be considered only as preliminary since precise high-temperature X-ray data are lacking. Moreover, the melting point of the pure sulfide was not obtained experimentally because of difficulties in obtaining pure Al_2S_3 . The indicated melting point of Al_2S_3 , $T_f = 1100^\circ\text{C}$, is reported elsewhere.^{3,4,10}

The solubility of aluminium in aluminium sulfide, Al_2S_3 , was determined by quenching experiments and confirmed by X-ray and chemical analysis. Aluminium dissolves very slowly in aluminium(III) sulfide, especially after the composition has exceeded 30 mol % aluminium. With alloys of more than 20 mol % aluminium stirring in periods of 48 h or more, was necessary to dissolve the metal. The maximum solubility obtained, after 10 days at 1200°C and continuous stirring, was 51.0 mol %

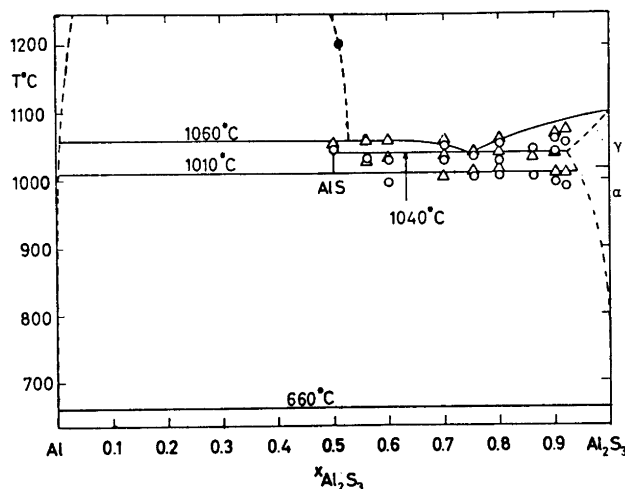


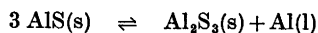
Fig. 1. Preliminary phase diagram for the system Al– Al_2S_3 . O: DTA cooling curves. Δ : DTA heating curves. \bullet : Solubility.

aluminium. The same results were obtained, with similar conditions, after one week.

After quenching of samples of different compositions, powder patterns at room temperature were obtained using a Debye-Scherrer camera. The X-ray results for the aluminium(III) sulfide rich phases showed essentially the lines given in the ASTM table 1-0726 for pure Al_2S_3 . Samples with a composition higher than 25 mol % aluminium showed some additional lines. At the composition AIS, the quenched samples showed different lines than the ones given in the ASTM tables either for pure Al_2S_3 or for aluminium (ASTM table 4-0787). It was assumed this was the X-ray pattern of the compound AIS. Also, powder X-ray diagrams were obtained for the Al_2S_3 compound which contained some Al metal (≈ 10 mol %). The lattice parameters were calculated for the α modification of Al_2S_3 (10 mol % Al in excess). These values were slightly higher than the ones determined by Flahaut.⁸

The phase diagram for the system aluminium-aluminium sulfide presented in this work, shows some new features when compared with the diagrams proposed previously.^{3,4} A eutectic point was observed in the system at composition 25 mol % aluminium and 1040°C. At the eutectic point a liquid AIS, and a mixture of Al_2S_3 and AIS should coexist in equilibrium. This finding has not previously been reported.

The system shows an intermediate compound, the subsulfide AIS, which is stable at temperatures higher than 1010°C. At 1010°C there is a peritectic transformation at which AIS decomposes to Al_2S_3 (s) and Al(l) according to the following equation:



This result agrees with a previous finding,⁴ even though the temperature is a little higher.

It was found that AIS melts at 1060°C. Its solubility in aluminium is probably very small. The melting point found for AIS is lower than that reported previously.^{3,4}

No other compounds were found in this system in the condensed state. This confirms the results of Klemm⁶ and Margrave *et al.*⁷ who reported that the compound Al_2S only exists in the gas phase.

There is a miscibility gap in the liquid state reaching from somewhere around 50 mol % Al

to the Al rich side of the phase diagram. It can be observed from the Al- Al_2S_3 phase diagram presented in Fig. 1 that at a temperature above 1010°C a mixture of Al_2S_3 and AIS coexist at equilibrium. Below 1010°C such a mixture decomposes to liquid aluminium metal and solid Al_2S_3 . It was found that the addition of about 10 mol % BaS to the Al- Al_2S_3 mixtures in the concentration range 50 to 10 mol % Al reduced the liquidus temperature to about 960°C, that is below the decomposition temperature of AIS. From these observations one may conclude that the barium sulfide containing Al- Al_2S_3 melts may be used in a preparation of aluminium metal from aluminium-silicon alloys.

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REFERENCES

1. Vereinigte Aluminium-Werke. *A-G-Brit.* 763, 709 (1955).
2. Gomez, J. Thesis, *An Investigation on the Solubility of Metallic Aluminium in Sulfides*, The University of Trondheim 1973.
3. Murakami, T. and Shibata, N. *Nippon Kinzoku Gakkaishi.* 4 (1940) 228.
4. Kohlmeier, E. J. and Retzlaff, H. W. *Z. Anorg. Allg. Chem.* 261 (1950) 248.
5. Biltz, W. and Caspari, F. *Z. Anorg. Allg. Chem.* 71 (1911) 182.
6. Klemm, W. *Z. Anorg. Allg. Chem.* 255 (1948) 287.
7. Margrave, J. L., Ficalora, P. J. and Hastie, J. W. *J. Phys. Chem.* 72 (1968) 1660.
8. Flahaut, J. *Ann. Chim. (Paris)* 7 (1952) 632.
9. Smith, D. K. *Norelco Rep.* 10 (1963) 19.
10. Klemm, W., Geierberger, K., Schaefer, B. and Mindt, M. *Z. Anorg. Allg. Chem.* 255 (1948) 287.

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