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Corrosion of Oxygen and Sulfur Systems in Al, Zn, In

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Abstract

Phase relationships of Al_2O_3 - Al_2S_3 were investigated between 300 C and 1200 C. The solid solutions of $Al_2(O, S)_3$ were found to be water soluble. As an exploratory work the Al_2S_3 -ZnS system was studied resulting in the fact that $ZnAl_2S_4$ is spinel and wurtzite forms. Furthermore subsolidus phase relations in $ZnAl_2S_4$ - $ZnIn_2S_4$ were studied.

초 록

Al_2O_3 - Al_2S_3 의 相 관계를 300°C에서부터 1200°C 사이에서 조사했으며 Al_2O_3 의 유황 고용체 ($Al_2(O, S)_3$)가 물에 녹는 현상을 발견했다. Al_2S_3 -ZnS의 상관계를 초기적인 단계에서 실험했으며 $ZnAl_2S_4$ 의 intermediate 相을 합성했으며 이것은 spinel과 Wurtzite의 결정 구조를 가졌다. $ZnAl_2S_4$ 와 $ZnIn_2S_4$ 의 相 관계를 조사했다.

I. Introduction and Literature

Al_2O_3 is the most favorable material for the lining of the coal liquefaction and gasification reaction chamber. The hostile atmosphere inside the chamber will possibly corrode the even Al_2O_3 which is known as a chemically stable material (1).

The possible corrosion reaction can occur between Al_2O_3 and by-product materials including sulfur (SO_2 , H_2S forms) during the coal liquefaction and gasification. The literature on the structure of Al_2O_3 is extensive, well known, and need not to be discussed here. Aluminum sulfide, Al_2S_3 , was reported by Flahaut et al. (2) to exist in two stable modifications, a low temperature form isostructure with wurtzite and a high temperature form isostructural with corundum.

The limited data on the system ZnS- Al_2S_3 have been summarized by Flahaut (2). The principal features of the system include one intermediate compound, $ZnAl_2S_4$

Lappe et al. (3) found $ZnIn_2S_4$ to have rhombohedral symmetry and described its structure as slightly distorted close-packing of sulfur with zinc occupying slightly enlarged tetrahedral interstices and indium occupying both tetrahedral and somewhat compressed octahedral

sites. Range et al. (4) synthesized $ZnIn_2S_4$ with the spinel structure by heating pressure and quenching to low temperature and pressure.

No previous data are available on the system $ZnAl_2S_4$ - $ZnIn_2S_4$.

The present work was taken to provide background data on corrosion of Al_2O_3 in sulfur existence, and included the structure of $ZnAl_2S_4$ and Zn (In Al_2S_4 solid solution which resulted in a bright yellow and red colors. These compounds indicated a potential to be important inorganic pigments.

II. Experimental Procedure

(1) Raw materials and Sample Preparation

Chemically pure Al_2O_3 , Al_2S_3 , ZnS, In_2S_3 were used to prepare the samples for this study. Materials were weighed to an accuracy of 0.1 mg to make 0.5 to 2.0 gm batches which were manually mixed in agate mortars under acetone and dried completely in air. Pellets which were 3 mm in diameter and 5mm in length were made using the mixed batches. Lengths of fused silica tube (ID 5mm and OD about 9mm) were sealed at one end in an oxygen-gas flame. After the pellets were inserted, the open ends connected to a vacuum hose, and the system

evacuated by a mechanical pump capable of attaining a vacuum of 10^{-4} Torr. The capsules were sealed by collapsing the capillaries in the oxygen-gas flame while the pump was maintaining vacuum. A more detailed discussion of this technique has been given by Kullerd (5).

(2) Heat Treatment and Phase Identification

The capsules were placed in electric furnaces and heated from the room temperature to the desired equilibrium temperatures by the heating rate about $10\text{--}20^\circ\text{C}$ per hour. After soaking 24–240 hrs at the equilibrium temperature, capsules were quenched by removing from the furnace with tongs and plunging in cold water.

Nickel filtered CuK radiation from a diffractometer operated at 40 KV and 15mA was used to identify phases present in quenched samples.

III. Results and Discussion

A. The system $\text{Al}_2\text{O}_3\text{--Al}_2\text{S}_3$

Since all the fired and quenched samples were finely powdered, phase identification was dependent on the use of X-Ray diffraction.

It presented no problems in the high- Al_2O_3 portion of the system because Al_2O_3 yielded strong, well-defined corundum diffraction peaks. On the other hand, the presence of Al_2S_3 was very difficult to detect but poorly showed the wurtzite solid solution form. As indicated the phase relationship in Fig. 1, about 30% of oxygen

at 710°C could be substituted with sulfur.

B. Corrosion of Al_2O_3

The wurtzite structure of Al_2S_3 and its solid solution ($\text{Al}_2(\text{S}, \text{O})_3$) are ready to be solved in water. The sulfur, solid solution form ($\text{Al}_2(\text{O}, \text{S})_3$) of corundum structure was not soluble in water. A solid solution compound which contained 20% of sulfur and quenched from 1000°C was kept for 7 days in a steam injected chamber maintained 500°C and about the atmospheric pressure.

The solid solution was found to be 15% of the weight loss, and still kept well defined corundum structure in XRD pattern. The weight loss of $\text{Al}_2(\text{O}, \text{S})_3$ (corundum structure) significantly indicated a fashion of Al_2O_3 corrosion in the presence of sulfur and H_2O . Firstly Al_2O_3 will react sulfur to form the solid solution and then the reaction with H_2O will give rise to gas and water soluble forms. The reactions between $\text{Al}_2(\text{O}, \text{S})_3$ and water under the experimental conditions have not been reported, but the extended experiments of the present study for the reaction mechanism will be published elsewhere. For the time being, however, the possible mechanism for the weight loss in the solid solution can be deduced; the formation of H_2S and $\text{Al}(\text{OH})_3$ or $\text{AlO}(\text{OH})$ as gel during the reaction between $\text{Al}_2(\text{O}, \text{S})_3$ solid solution and steam (H_2O).

C. Al-Zn-S system

A complete phase diagram has not been constructed but the present study includes the following (a) the occurrence of spinel ZnAl_2S_4 to wurtzite ZnAl_2S_4 phase transition at 720°C (b) complete intersolubility of ZnS (wurtzite) and ZnAl_2S_4 (wurtzite, high temperature form) (c) solubility of Al_2S_3 in ZnAl_2S_4 (spinel) of 56 mole % between 800 and 950°C .

In the subsolidus system of ZnAl_2S_4 and Al_2S_3 the solid solution indicated water soluble compounds.

D. The system $\text{ZnAl}_2\text{S}_4\text{--ZnIn}_2\text{S}_4$

It was found necessary to perform the end member compounds, ZnAl_2S_4 and ZnIn_2S_4 , from the starting materials and subsequently to mix these to yield intermediate compositions. The $\text{ZnAl}_2\text{S}_4\text{--ZnIn}_2\text{S}_4$ mixtures were then encapsulated, equilibrated, and quenched as previously described. Even with this procedure a small amount of a non-equilibrium phase (6) was detected in compositions ranging from 10 to 40 mole % of ZnIn_2S_4 . The addition of 2 wt % of 50 NaCl–50 KCl

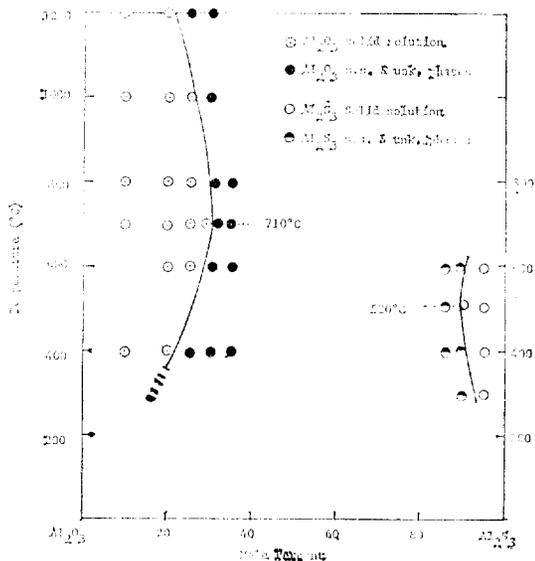


Fig. 1 Mutual Solubility between Al_2O_3 and Al_2S_3

mineralizer aided in the attainment of equilibrium in these samples.

The complete phase diagram will be published elsewhere, but the results of the current experiments are following (a) melting point of ZnI_2S_4 $1125 \pm 25^\circ C$. (b) 20 mole % of ZnI_2S_4 eutectic composition at $940^\circ C$ (c) solubility of $ZnAl_2S_4$ in $ZnIn_2S_4$ 56 mole % from $800^\circ C$ to $900^\circ C$ (d) little solubility of $ZnIn_2S_4$ in $ZnAl_2S_4$. No corrosion behavior of the solid solution of $Zn(Al, I)_2S_4$ was observed in the presence of steam.

The $Zn(Al, I)_2S_4$ showed a bright yellow color which can be an alternative less toxic inorganic pigments.

IV. Summary

- (1) Phase relationship in the system $Al_2O_3-Al_2S_3$ were determined.
- (2) From the weight loss of the solid solutions ($Al_2(O, S)_3$ -corundum structure) a possible Al_2O_3 corrosion behavior was deduced in the presence of sulfur and water
- (3) Tentative phase relationship in the systems of $Al-Zn-In-S$ was investigated
- (4) In the $Zn(Al, I)_2S_4$ compound, a possibly less toxic yellow pigment was observed.

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