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STUDY OF THE FORMATION OF CADMIUM SULFOSELENIDE

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ABSTRACT

The formation of cadmium sulfoselenide from cadmium sulfide and selenium has been studied using differential scanning calorimetry (DSC). The formation of a solid solution begins following the melting of selenium and is seen as a broad endothermic peak centered around 320°C. The influence of pressure on the peak temperatures was also studied.

INTRODUCTION

Cadmium sulfoselenides provide a wide range of heat-stable pigments ranging from light orange to deep maroon. The color of the pigment is controlled by the amount of selenium present. These pigments are used extensively in the plastics industry and in many high temperature applications.

These pigments can be prepared by calcining any of the following to 450–600°C.

(1) Cadmium sulfide and selenium.

(2) Cadmium carbonate, selenium and sulfur.

(3) The precipitate resulting from the treatment of a cadmium salt with an alkaline selenide and sulfide solution.

The calcination step is important in the pigment manufacture as the pigmentary properties are developed during this stage. Also in processes using elemental selenium, the proper choice of calcining conditions is important to keep the volatilization of selenium at a minimum level and to obtain good pigmentary properties. Eroles and Friedberg [1] found that these pigments consist of continuous solid solutions of hexagonal cadmium sulfide and cadmium selenide.

The formation of cadmium sulfoselenide (also referred to as the solid solution $CdS \cdot CdSe$) has been studied by many workers using thermoanalytical techniques. Thermogravimetric investigation by Cini and Melandri [2] shows that the reaction between cadmium sulfide and selenium starts immediately following the melting point of selenium and can be considered

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complete at about 350°C. Beltran et al. [3] have reported DTA, TG and DTG for four mixtures of cadmium sulfide and selenium in different proportions diluted with alumina. DTA shows a broad endotherm between 375 and 529°C without any strong peaks. The general reaction leading to the formation of the solid solution $CdS \cdot CdSe$ according to refs. 2 and 3 is

$$n\ CdS + m\ Se \rightarrow (n - m/2)CdS \cdot m/2\ CdSe + m/2\ Se + m/2\ S \qquad (1)$$

Jernejcic's study [4] is based on precipitated cadmium sulfoselenide. According to him the composition of the calcined products is determined by the y-values of the original precipitates (eqn. 2) and is independent of the heating rate. This is explained by the assumption that the structure design of the future calcined product is already present in the precipitate. On heating

$$CdSeS_y \rightarrow CdS_xSe_{(1-x)} + (1 - x)S + (x + y - 1)Se \qquad (2)$$

excess sulfur and selenium escape, in a ratio dependent on the composition of the starting precipitate, and the hexagonal lattice gains in its order.

In the present investigation we have studied the formation of cadmium sulfoselenide from cadmium sulfide and selenium by DSC and the effect of pressure on the peak temperature.

EXPERIMENTAL

The starting materials for the study were cadmium sulfide and selenium (elemental)

Cadmium sulfide was prepared by reaction of cadmium nitrate and sodium sulfide in aqueous medium at 80°C. Elemental selenium of purity > 99.5% was obtained from Aldrich Chemical Co. A mixture of cadmium sulfide and selenium in the proportion 88 : 12 was prepared by mixing the two with the addition of methanol, which was subsequently eliminated by evaporation.

A DuPont 1090 thermal analyzer was used to record the DSC thermograms. Sample sizes varied between 2 and 8 mg. The thermograms were obtained in closed and open sample pans (Perkin-Elmer Cat No. 219-0062) from 160 to 460°C at a heating rate of 20°C min^{-1} in a flowing nitrogen atmosphere at 30 ml min^{-1}.

The X-ray diffraction patterns of the heated products were obtained using a General Electric XRD-5 spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the thermograms of the starting materials, cadmium sulfide and selenium, and the mixture of the two in open sample pans.

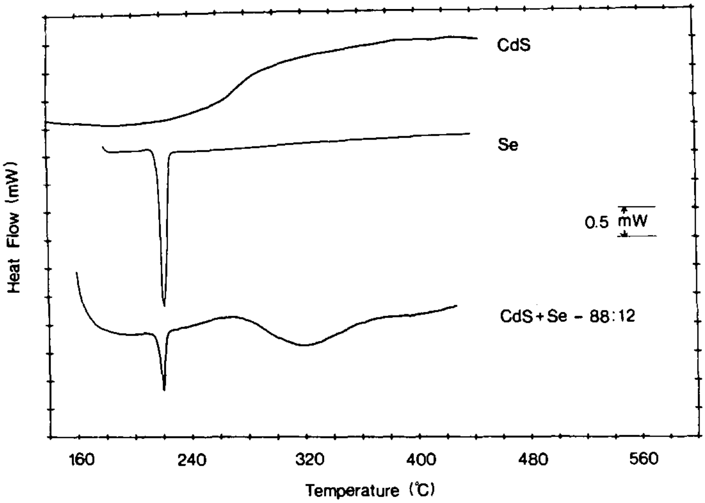

Fig. 1. DSC thermograms of cadmium sulfide, selenium and CdS + Se mixture.

Cadmium sulfide shows a change of baseline at 270°C. This is probably a second-order heat capacity transition. Selenium shows a sharp endothermic peak at 220°C corresponding to its melting. The mixture shows a sharp endothermic peak at 220°C and a broad endotherm centered at 320°C. The sharp endotherm at 220°C is due to the melting of selenium. The broad endotherm centered at 320°C represents the reaction between cadmium sulfide and selenium, i.e., formation of the solid solution CdS · CdSe. The reaction starts at ~ 265°C as indicated by the descending baseline, and can be considered practically complete at 380°C.

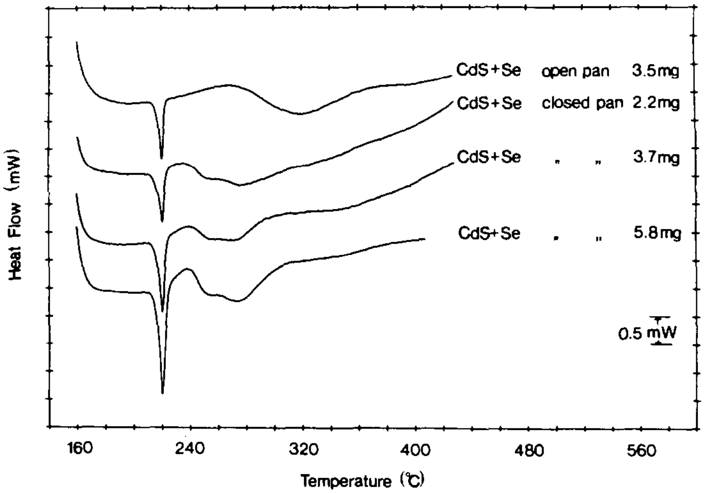

Fig. 2. DSC thermograms of CdS + Se mixture in open and closed sample pans.

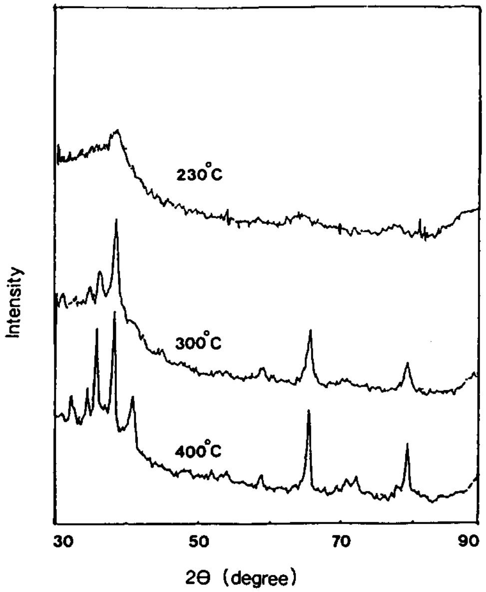

Fig. 3. X-ray diffraction patterns of CdS + Se mixture calcined at the temperatures indicated.

The influence of pressure on peak temperature is shown in Fig. 2. The pressure increase was effected by varying the sample sizes and closing the sample holders to retain the evolved gases. The increase in pressure has no effect on the melting of selenium. The broad endotherm corresponding to the formation of the solid solution is shifted to a lower temperature. The open-pan DSC thermogram shows a broad endotherm at 320°C, in the closed-pan DSC thermograms this peak is shifted to 275°C. Further increase in pressure (by virtue of increased sample size) does not appear to have a significant effect on the peak position, but the endotherm is well defined. A possible explanation for this is that with an open sample pan, the evolved gases are swept away by flowing nitrogen, whereas, by closing the sample holder, there is an increase in the vapor pressure of the evolved gases, viz. selenium sulfides, which facilitate the introduction of selenium into the cadmium sulfide crystal lattice.

The X-ray diffraction patterns of samples calcined at 230, 300 and 400°C are shown in Fig. 3. The X-ray diffraction pattern of the sample calcined at 230°C is diffuse with no measurable reflection. The samples calcined at 300 and 400°C show reflections corresponding to the solid solution CdS · CdSe. The sample calcined at 400°C has more hexagonality.

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