Journal of Thermal Analysis, Vol. 3 (1971) 131—136

FORMATION OF THE SOLID SOLUTION CdS/CdSe FROM CdS AND Se AND ITS THERMAL STABILITY

A THERMOGRAVIMETRIC INVESTIGATION

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(Received September 23, 1970)

Selenium and cadmium sulphide react in the temperature range 250°—350° to form a solid solution CdSe/CdS. Thermogravimetric (in N_2) and chemical analyses show that this reaction occurs with the elimination of equimolecular amounts of Se and S. The thermal stability of the s.s. (2CdS · CdSe) in an atmosphere of N_2 was studied.

Cadmium, selenium and sulphur provide a range from red to orange of pigments which have excellent colour absorption coefficients and stability to light, moisture, weathering, etc. They are not only used in the ceramic industry but also for plastics, inks, paints, enamels, etc. (though for these applications pigments with a lower thermal stability, such as Cd–Hg–S, may also be used).

Irrespective of the starting materials, Eroles and Friedberg [1] found that the Cd–Se–S pigments consist of continuous, hexagonal solid solutions (substitutional type) of CdSe and CdS.

Shade variations ranging from orange to brown (passing through various shades of red) depend on the CdSe content of the solid solution:

CdSe (mole %)	CdS (mole %)	Colour
12.6	87.4	orange
20.0	80.0	orange-red
36.0	64.0	light red
43.0	57.0	dark red
49.0	51.0	brown
54.5	45.5	dark brown

These results have been confirmed by subsequent studies [2].

The pigments can be obtained by heating the following to 450°–550°:

I) CdS or $CdCO_3$, Se and S; II) the precipitate resulting from the treatment of an alkaline sulphide and selenide solution with a solution of a cadmium salt; III) CdSe and CdS. Cadmium selenide – which is of particular interest both as a single or polycrystal semiconductor – can be obtained as follows:

a) by reducing the selenite or selenate [3]; b) by fusion of the elements [4]; c) by hydrothermal synthesis from CdO and Se at 343° and 150 atm. [5].

It has been shown [1] that the colour intensity and possible defects of the pigment are due to:

a) the grain-size of the starting materials; b) the calcination temperature and atmosphere. The presence of oxygen or air may give rise to the formation of white particles due to $CdSO_4$, while a reducing atmosphere may lead to the formation of metallic cadmium. In air, at temperatures above 600°, the solid solution rapidly decomposes first into its original components and subsequently into $CdSO_4$, Cd and then into a third phase that was not specified.

According to Chizhikov [6] cadmium selenide is the only compound in the system $Se-Cd$. It has two allotropic forms and a melting temperature of more than 1350°. According to Burmeister and Stevenson [7] CdSe vaporizes congruently, the range of congruent sublimation extending to temperatures above 1200°.

The constitution of the pigment appears to have been established, but no investigations have been made as to its formation. Hence we have examined this aspect of the problem, starting from CdS and Se.

Experimental and results

The starting materials for the present study were: Se ($>99.9\%$ hexagonal, crystalline); CdS ($>98\%$); CdSe ($>99.9\%$). Cadmium sulphide was heated to 400° to obtain its hexagonal form; this process, as well as all other experimental tests were carried out in a nitrogen atmosphere. In the industrial preparation of bhe pigment, sulphur is used in addition to CdS and Se. This third component has an indirect function: it is employed to create an oxygen-free atmosphere.

CdS and Se were mixed with the addition of absolute alcohol which was subequently eliminated by evaporation; the composition of the mixtures is listed selow:

Sample No.		Weight %	Molar %
0	CdS	64.63	50
	Se	35.37	50
1	CdS	73.27	60
	Se	26.73	40
2	CdS	84.57	75
	Se	15.43	25
3	CdS	91.64	85.7
	Se	8.36	14.3

The weight losses of ~1 g samples in porcelain crucibles were determined using a Chevenard thermobalance under anisothermal and isothermal conditions, as shown in the curves in Figs. 1a and 2. The rate of increase of the furnace temperature was 150°/h.

The sulphur contents (as $BaSO_4$ after $Na_2CO_3-K_2CO_3$ fusion and subsequent leaching with a 20% HNO_3 solution) of the products calcined at 400° are listed in column *d* of Table 1; according to these values and to the Δ weight, the reactions leading to the formation of the pigment can be formulated as in Table 1.

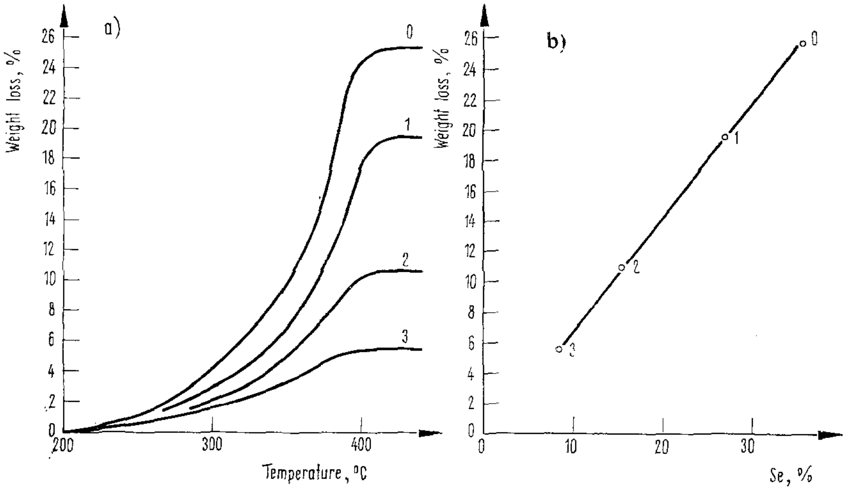

Fig. 1a) TG curves of samples 0—1—2—3 (150°/h, N_2 atm.). b) Weight loss vs. % selenium

In general, the reaction leading to the formation of the s.s. can be schematized as follows:

$$(n \geq m) \quad n\,\mathrm{CdS} + m\,\mathrm{Se} \rightarrow \left(n - \frac{m}{2}\right)\mathrm{CdS} \cdot \frac{m}{2}\mathrm{CdSe} + \frac{m}{2}\,\mathrm{Se} + \frac{m}{2}\,\mathrm{S}$$

This means that each sulphur atom replaced in the CdS lattice requires 2 selenium atoms. The vapour phase – corresponding to the weight loss – is formed by S and Se in equimolecular amounts (71.12% Se and 28.88% S).

Figure 1b shows the relationship between the selenium content and the variation in weight. This diagram justifies the loss of selenium in the pigment formation from CdS and Se.

The colours of specimens heated to 400° vary according to their Se content as indicated by Eroles and Friedberg [1]. The slopes of the TG curves (Fig. 1) clearly show that the reaction starts at a temperature immediately above the melting point of selenium (217° for the hexagonal form) and can be considered

Table 1

Sample No		*a* Δ wt% calculated	*b* Δ wt% experimental	*c* S % calculated	*d* S % experimental
0	$2CdS + 2Se \rightarrow CdS \cdot CdSe + Se\nearrow + S\nearrow$	24.85	25.20	9.55	9.62
1	$3CdS + 2Se \rightarrow 2CdS \cdot CdSe + Se\nearrow + S\nearrow$	18.77	18.95	13.85	13.26
2	$3CdS + Se \rightarrow \frac{5}{2}CdS \cdot \frac{1}{2}CdSe + \frac{1}{2}Se\nearrow + \frac{1}{2}S\nearrow$	10.83	11.05	17.55	17.70
3	$3CdS + \frac{1}{2}Se \rightarrow \frac{11}{4}CdS \cdot \frac{1}{4}CdSe + \frac{1}{4}Se\nearrow + \frac{1}{4}S\nearrow$	5.87	6.10	19.81	19.93

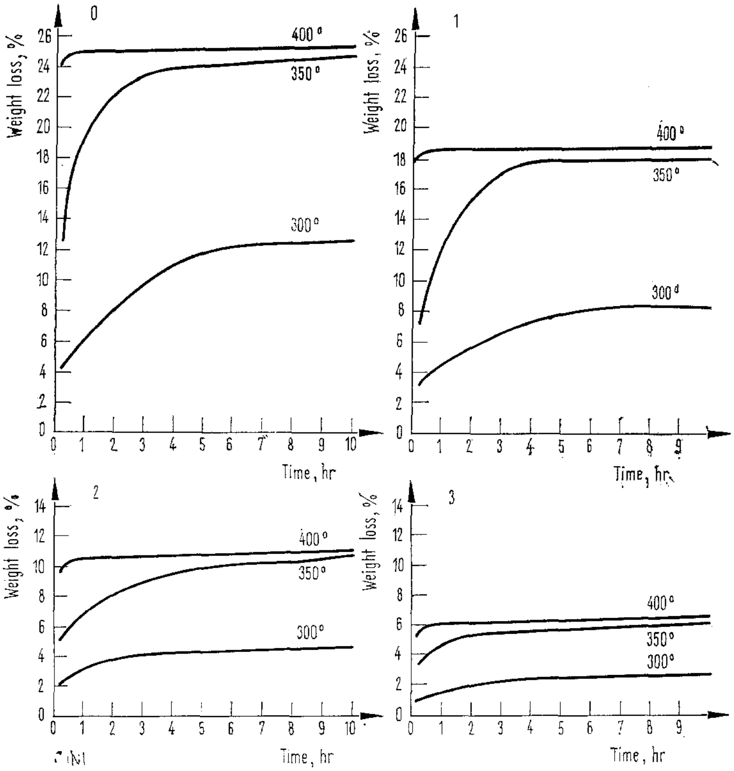

Fig. 2. Isothermal curves of samples 0—1—2—3 (N_2 atm.)

complete at about 350° (taking into account of course the other parameters affecting the kinetics of the solid-solid and solid-liquid reactions), as shown in Fig. 2.

As expected, it was found that the pigments are lighter coloured when the heating rate exceeds 300°/h since the Se volatilizes before reacting with CdS. In fact, the loss of weight increases compared with the value reported in Table 1.

On subsequent reheating at a higher temperature the solid solution first breaks down into CdS and CdSe which in air – according to [1] – are converted into $CdSO_4$, metallic Cd and a third non-identified phase. We focussed our attention in particular on the thermal stability of the solid solution in a N_2 atmosphere. For this purpose we submitted a further sample No. 1, calcined at a temperature of 400°, to thermogravimetric analysis.

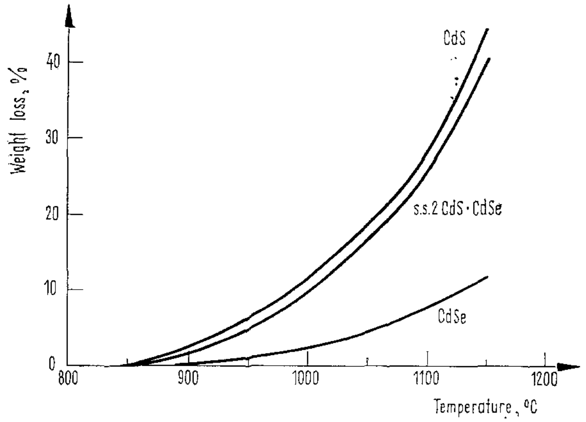

Fig. 3. TG curves of CdSe, 2CdS · CdSe s. s., CdS (150°/h, N_2 atm.)

Fig. 3 clearly shows that the loss of weight for the powdered material, heated at a furnace rate of 150°/h, begins at about 850° and increases exponentially above this temperature. At the end of the heating, the specimen had acquired a black colour similar to that of pure CdSe. The product calcined at a temperature of 1150° had a sulphur content of 7.82% (against its initial 13.26%), showing that the composition of the vapour phase differs from that of the solid phase. From the loss of weight and sulphur content data it appears that the solid solution decomposes at 850° into CdS and CdSe both congruently starting sublimation. Since CdS has a greater vapour pressure than CdSe, as demonstrated by TG curves of the two pure compounds (Fig. 3), it is clear that there will be an increase of the percentage CdSe content in the solid phase. In fact, the CdS – CdSe ratio before thermal treatment was 60.16% CdS and 39.84% CdSe (2CdS · CdSe), whereas after thermal treatment at a temperature of 1150° these values became 35.29% and 64.71%, respectively.

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Résumé — Le sélénium et le sulfure de cadmium réagissent entre 250 et 350 °C en formant une solution solide CdSe/CdS. Les analyses thermogravimétrique (dans l'azote) et chimique montrent que cette réation se produit avec élimination de Se et de S suivant un rapport équimoléculaire. On a contrôlé la stabilité thermique de la solution solide [2CdS · CdSe] dans l'azote.

Zusammenfassung — Selen und Kadmiumsulfid reagierten miteinander im Temperaturbereich von 250° bis zu 350° unter Bildung einer festen Lösung CdSe/CdS. Thermogravimetrische (unter N_2) und chemische Untersuchungen bewiesen, daß die Reaktion unter Elimination äquimolekularer Mengen von Se und S verläuft. Die thermische Stabilität der festen Lösung (2CdS · CdSe) in Stickstoff wurde geprüft.

Резюме — Сульфид селена и кадмия реагирует в температурных пределах 250°—350° C, образуя твердый раствор CdSe/CdS; термогравиметрия (в атмосфере азота) и химические анализы показывают, что эта реакция происходит с элиминированием при эквимолекулярном отношении Se и S; проверена термическая стабильность 2 CdS · CdSe в атмосфере N_2.