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DETERMINATION OF THE K-Se PHASE DIAGRAM IN THE RANGE FROM 55 TO 100 ATOMIC PERCENT SELENIUM

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ABSTRACT

The phase diagram of the system K-Se has been determined by differential scanning calorimetry (DSC) in the composition limits 55 - 100 at.% Se. The liquidus curve obtained by these measurements indicated the existence of K_2Se_3, having a melting point of 648 K. The range of liquid immiscibility was found to exist from 86 and 98 at.% Se, with a monotectic temperature of 494 K. Furthermore the studies establish the existence of an additional compound, probable K_2Se_4, which is formed peritectically at 479 K. The eutectic on the Se-rich side of the phase diagram is formed at 432.7 K, the eutectic composition is 78 at.% Se.

INTRODUCTION

Large single crystals of trigonal selenium are grown from thallium - as well as from potassium-doped melts (ref. 1). In order to obtain appropriate growth conditions the knowledge of phase equilibrium data of the Tl-Se and K-Se systems is important (ref. 1). Until now the Tl-Se phase diagram has been subject of several investigations (ref. 2 - 8). On the other hand only one determination of the K-Se phase diagram is known (ref. 9). According to the latter authors their study needs clarification with regard to the extension of the liquid immiscibility region. Therefore a reinvestigation of the K-Se phase diagram appeared advisable.

RESULTS

Sample preparation

The samples used for DSC measurements were prepared in the following way: A proper amount of selenium (99.999 %, Asarco) and K_2Se (99.9 %, Zinsser) in a desired composition is sealed in an evacuated quartz ampoule, of which dimensions are 10 mm in dia. and 80 mm length. The ampoule is heated gradually up to 820 K and held at this temperature for 4 hours. After this procedure the sample was annealed at 300 K for one day. All subsequent sample preparations were carried out in a glove box (Mecaplex) containing special pure argon

(99.99, Linde). In order to prevent sample reaction with the atmosphere the samples were also packed in hermetically sealed aluminum pans.

DSC measurements

The differential scanning calorimeter experiments were carried out on a Perkin-Elmer DSC 2. The DSC traces at different compositions in the range from about 70 at.% Se to 100 at.% Se reveal the same features as those found in the case of the Tl-Se system (ref. 6,8). In the composition range, in which the miscibility gap appears, two endothermic peaks are detected. These peaks are due to the three-phase invariant eutectic and monotectic reaction, respectively (ref. 8). From about 60 at.% Se to 69 at.% Se DSC heating and cooling curves were obtained indicative of an incongruently melting system (ref. 10).

In fig. 1 the measured enthalpies of the monotectic, eutectic and peritectic reactions - denoted by ΔH^M, ΔH^E and ΔH^P, respectively - as a function of the initial sample concentration x^o_{Se} are shown.

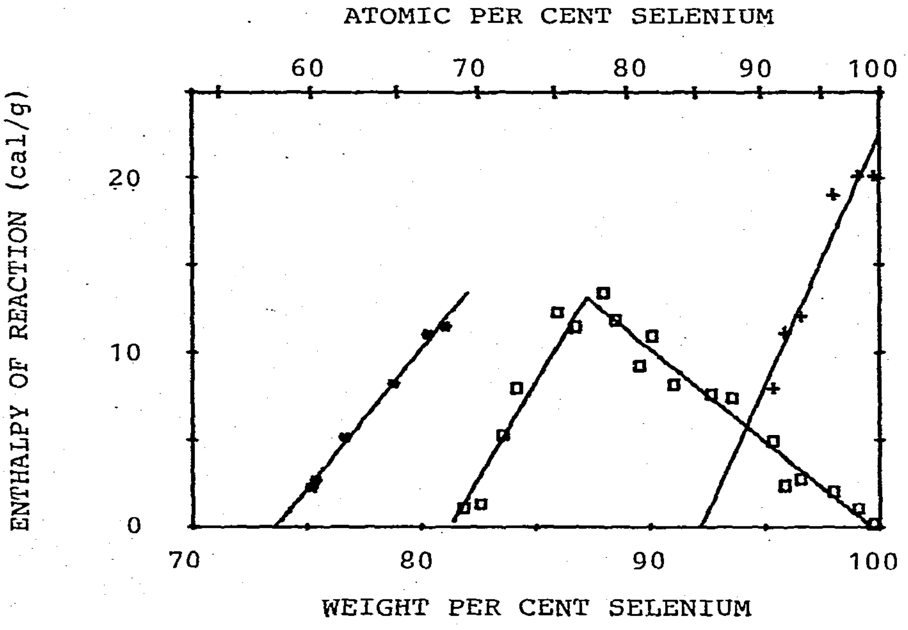

Fig. 1 Enthalpies of the peritectic (*), eutectic (□) and monotectic reaction (+)

A representation of ΔH^E vs. x^o_{Se} by two straight lines gives quite a good fit of the experimental data. The intersection point yields the eutectic concentration (ref. 6), which is 78 at.% Se. In the case of ΔH^M vs. x^o_{Se} also a linear dependence is expected (ref. 8). ΔH^M as a function of

x_{Se}^{o} is given by following equation:

$$\Delta H^{M} = H_{Se}^{f} \left(\frac{x_{Se}^{o} - x_{Se}^{I}}{x_{Se}^{II} \quad x_{Se}^{I}} \right)$$

where H_{Se}^{f} is the enthalpy of fusion of pure selenium, x_{Se}^{I} and x_{Se}^{II} are the mass fractions of the two liquid phases at the monotectic temperature, respectively. From this equation it follows that the straight line ΔH^{M} vs. x_{Se}^{o} intersects the concentration axis at x_{Se}^{I}. Because H_{Se}^{f} is known (ref. 8) also x_{Se}^{II} is calculable. According to our measurements we obtain:

x_{Se}^{I} = 86 at.% Se, x_{Se}^{II} = 98 at.% Se

Fig. 1 finally reveals that ΔH^{P} vs. x_{Se}^{o} becomes zero at x_{Se} = 58.2 at.% Se instead of 60 at.% Se which corresponds to the composition of K_2Se_3. This discrepancy still needs clarification.

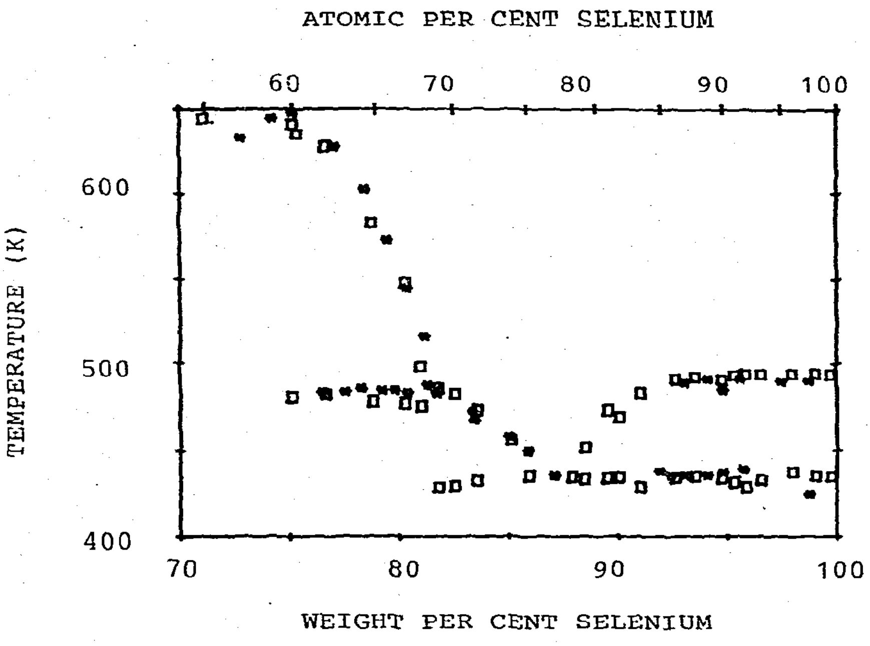

Fig. 2. Phase diagram K-Se: present work (□), Klemm et al. (✻) (ref. 9)

In fig. 2 the phase diagram of K-Se according to our DSC measurements is represented. For comparison also the results reported by Klemm et al.(ref.9) are shown. It is obvious that there is a substantial agreement between both investigations. Deviations are found only with respect to the extension of the liquid immiscibility region. Furthermore a second peritectic reaction reported by Klemm et al.(ref.9) has not been detected.

It may be mentioned that the results given here are preliminary. X-ray structure analyses of K_2Se_3 single crystals and K-Se-alloys at different concentrations as well as atomic absorption measurements are to be performed.

ACKNOWLEDGEMENT

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