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DTA-CONTROLLED REACTIONS AND PHASE RELATIONS IN THE TERNARY SYSTEM Sn—Te—I

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The system Sn—Te—I was investigated by DTA and X-ray powder methods. No intermediate ternary phase exists in the respective phase diagram. Reactions of the components on pseudobinary joins are easily explained by the phase relations. Liquidus isotherms of the ternary system are given.

The present investigation is part of a systematic study of binary VI—VII [1—3] and ternary IV—VI—VII systems [4] (IV = Sn; VI = Se, Te; VII = Cl, Br, I). The system Sn—Te—I is interesting because the existence of a ternary phase $SnTeI_6$ has been reported [5], while the reaction of SnI_2 with TeI_4 has been found to take place by formation of SnI_4 and the subiodide TeI (α and/or β-modification) [4]. Hence, the join SnI_2-TeI_4 of the ternary system is not quasibinary with an intermediate phase $SnTeI_6$, but pseudobinary. Therefore, a possibly existing phase $SnTeI_6$ should be metastable with regard to the respective phase diagram.

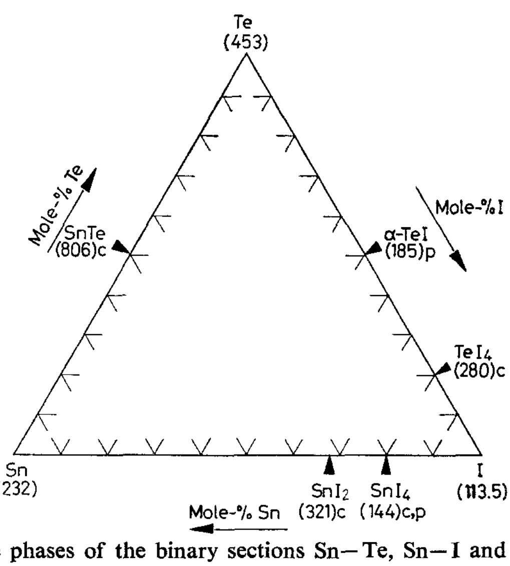

Fig. 1. Intermediate phases of the binary sections Sn—Te, Sn—I and Te—I of the ternary system. Numbers in parentheses represent melting temperatures (°C)·c = congruently melting; p = peritectically melting

The complete ternary system Sn–Te–I was investigated by DTA and X-ray powder methods in order to yield a deeper insight into the respective phase relations and reactions. Figure 1 shows the intermediate phases of the binary sections Sn–Te [6], Sn–I [7] and Te–I [1] of the ternary system. Melting temperatures and the melting behaviour of the binary phases are given.

Binary phases (see Fig. 1) (except for TeI_4) were prepared from the elements; TeI_4 was obtained by dehydration of freshly-prepared $H_2TeI_6 \cdot 8\,H_2O$ [8].

DTA measurements were carried out using a Braun DTA (R. Kniep). Mixtures of the respective components were sealed off in DTA tubes of quartz glass by simultaneous evacuation and cooling with liquid nitrogen. Reactions of the components during heating were controlled by DTA. Subsequently, the samples were quenched from the melt and annealed below the first melting temperatures for several weeks. The annealed samples were again investigated by DTA during heating; phase equilibria in the solid state were studied by the Guinier technique (camera Enraf-Nonius FR 552) using monochromated nickel-filtered $Cu-K_{\alpha 1}$ radiation.

Results and discussion

Figure 2 shows the five quasibinary cross sections of the ternary system. They represent two-phase equilibria in the solid state; the respective phase diagrams are simple eutectic without intermediate ternary phases. Figure 3 shows the system SnI_4-TeI_4 as a representative example of the various quasibinary sections.

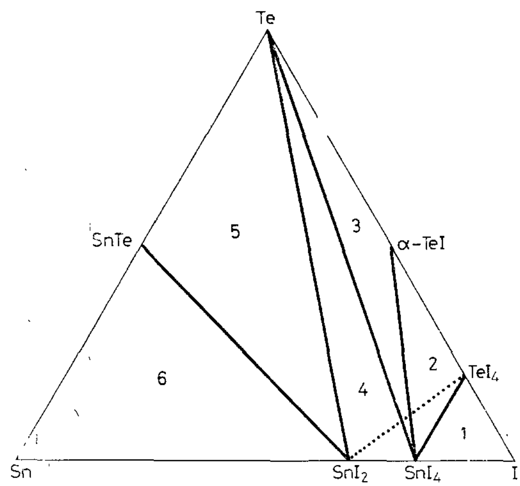

Fig. 2. Quasibinary cross sections of the ternary system Sn–Te–I. The dotted line shows a pseudobinary section including reactions between SnI_2 and TeI_4. 1. SnI_4, TeI_4, I; 2. SnI_4, α-TeI, TeI_4; 3. SnI_4, Te, α-TeI; 4. SnI_2, SnI_4, Te; 5. SnTe, SnI_2, Te; 6. Sn, SnTe, SnI_2

Three-phase equilibria (indicated and explained by the numbers 1–6 in Fig. 2) are separated by the two-phase equilibria.

The join SnI_2-TeI_4 (dotted line in Fig. 2) is pseudobinary. There are five different phase equilibria in this section:

I: $SnI_4 + TeI_4 + I_2$ (2 in Fig. 2)
II: $3\,SnI_2 + 2\,TeI_4 \rightarrow 2\alpha\text{-TeI} + 3\,SnI_4$ [4]
III: $SnI_4 + Te + \alpha\text{-TeI}$ (3 in Fig. 2)
IV: $2\,SnI_2 + TeI_4 \rightarrow 2\,SnI_4 + Te$ [4]
V: $SnI_2 + SnI_4 + Te$ (4 in Fig. 2)

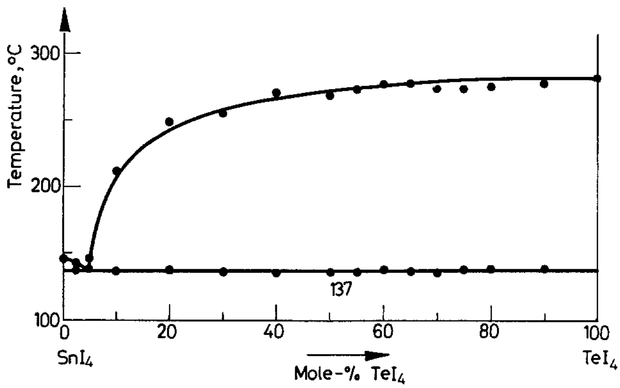

Fig. 3. The quasibinary system SnI_4-TeI_4

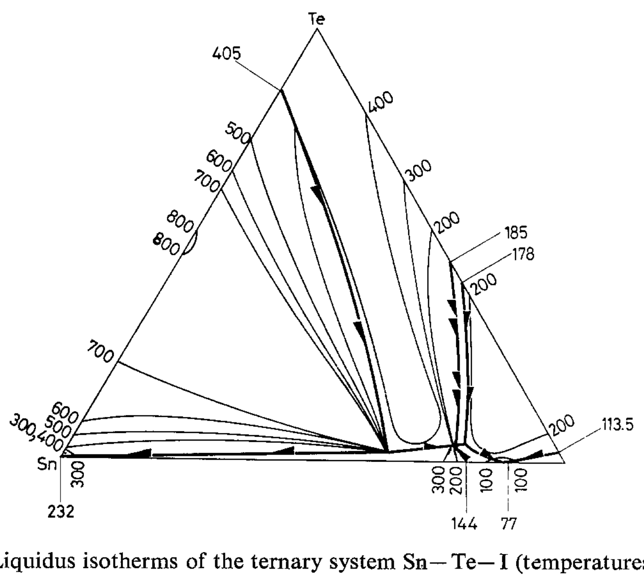

Fig. 4. Liquidus isotherms of the ternary system Sn—Te—I (temperatures in °C)

In this way, the reduction of tellurium from the formal oxidation state +4 (TeI_4) to +1 (TeI) or 0 (Te), and the dependence of the degree of reduction on the amount of SnI_2 involved in the reactions, are quite easily explained by the phase relations of the ternary system.

Progressive reduction of tellurium from the formal oxidation state +4 in TeI_4 down to −2 in SnTe takes place in the pseudobinary section Sn − TeI_4 with increasing amounts of Sn (see also Fig. 2).

Liquidus isotherms of the complete ternary system are given in Fig. 4. Subtraction curves (starting from the eutectics of the binary sections) are marked by a single arrow and indicate "thermal valleys". Reaction curves are marked by a double arrow and indicate a break in the slope on the liquidus surface. The lowest melting temperature of the ternary system is near the eutectic at 88 at. % I and 77° in the binary section Sn − I.

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Résumé — Le système Sn—Te—I a été étudié pa ATD et rayons X sur poudre. Il n'existe pas de phase ternaire intermédiaire dans le diagramme de phases correspondant. Les réactions des composants en systèmes pseudobinaires s'expliquent facilement par les relations de phases. Les isothermes des liquidus du système ternaire sont données.

Zusammenfassung — Das System Sn—Te—I wurde durch DTA- und Röntgenmethoden untersucht. In dem Phasendiagramm existiert keine intermediäre Ternärphase. Die Reaktionen der Komponenten der pseudobinären Koppelungen können durch die Phasenverhältnisse leicht erklärt werden. Flüssigkeitsisothermen des Ternärsystems werden gegeben.

Резюме — С помощью ДТА и порошковой рентгенографии исследована система Sn—Te—I. В соответствующей фазовой диаграмме не установлено существование промежуточной трехкомпонентной фазы. Реакции компонент с псевдобинарными соединениями хорошо объяснимы на основе фазовых соотношений. Представлены изотермы ликвидуса этой трехкомпонентной системы.