A note on the Si–Te phase diagram

Silicon telluride is a semiconducting material and although it has been assigned the formula $SiTe_2$ [1, 2] the concensus of opinion from X-ray and thermodynamic data [3–6] is that it is a complex structure of formula Si_2Te_3.

Bailey, from thermal measurements [3], evaluated the Si–Te phase diagram for values of $X_{Te} > 0.6$ and concluded that Si_2Te_3 melted incongruently at 892° C. The main aim of the present work has been the completion of the liquidus of the phase diagram at higher silicon contents, where the vapour pressures of tellurium exceed atmospheric.

Ingots of the alloys were prepared by the high-temperature method used for the rapid preparation of chalcogenide glasses [7], whereby the components of purity better than 99.999% were heated in a quartz ampoule above the melting point of silicon (1411° C) in high-pressure argon for 20 min. then cooled rapidly. The ingots of high tellurium content were matt in appearance, while those of high silicon content were shiny, homogeneous and similar in appearance to other chalcogenide glasses.

For the liquidus studies, a powdered alloy was charged into a silica ampoule which consisted of a spherical bulb (~ 3 ml volume) surmounted by a vertical tube 22 cm long, down which passed a silica thermocouple sheath. The pointed end of the latter, containing the thermojunction, was positioned centrally in the alloy, the depth of which was 1 cm.

The above arrangement was enclosed in an internally heated pressure vessel containing argon at a pressure of 30 atm. This design of the silica ampoule, in conjunction with the high-pressure argon, prevented evaporation of tellurium. This equipment was used for electrical studies of arsenic triselenide and has been described in detail [8].

To determine a point on the silicon liquidus, the alloy sample was heated to 1420° C, kept at this temperature for 10 min and cooled at the rate of 2° C min^{-1}; the appearance of the liquidus was shown by a thermal arrest in the temperature plot from the sample. The temperature was then raised and the procedure repeated. Further cooling resulted in the appearance of a weak arrest at ~ 885° C which, within the experimental errors, was considered to represent the emergence of Si_2Te_3. The results are shown in Fig. 1. For values of $X_{Te} > 0.6$ the lines are drawn from Bailey's detailed work; only a few confirmatory measurements (by heating) were considered necessary in the present study of this region. The present work confirms a eutectic at about 407° C; Bailey gives 409° C.

In contrast to the findings of Bailey and also Brebrick [5], Ploog *et al.* [6] reported that Si_2Te_3 melted congruently at 889° C but experimental details were not given. If the compound melts congruently then, for a phase diagram of this type, the melting point would be represented by a minute peak at the compound composition. This would be similar to the behaviour of the compound GeTe in the germanium–tellurium system [9]. To differentiate between congruent and incongruent melting with glassy material is difficult; however, the difference in type of melting would not greatly affect the position of the phase boundaries in Fig. 1.

The steep rise in the silicon liquidus suggested by Bailey is confirmed here; at high silicon contents, the liquidus shows a marked flattening. This flattening was originally ascribed to the presence of two liquid layers, but from the sharpness of the thermal arrests, observed from repeated determinations, it was considered that the liquid phase in this region is just on the verge of liquid–liquid immiscibility.

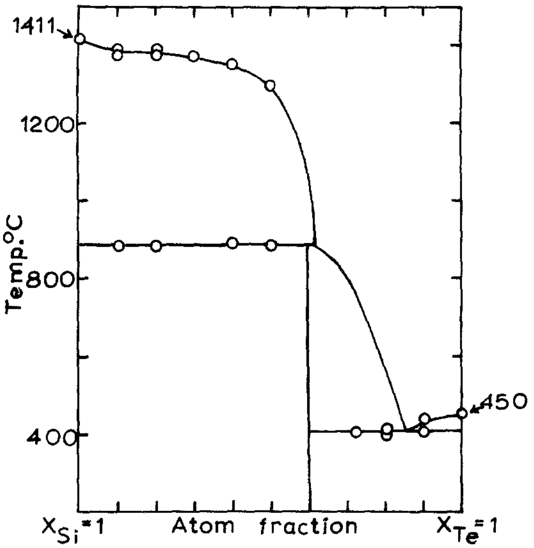

Figure 1 Completed phase diagram for the Si–Te system, assuming incongruent melting of Si_2Te_3

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