The C-Si (Carbon-Silicon) System

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Equilibrium Diagram

The assessed equilibrium phase diagram of the Si-C system is presented in Fig. 1.* The diagram indicates a peritectic transformation at 2545 ± 40 °C and a eutectic transformation at 1404 ± 5 °C. Both transformations involve the intermediate compound, SiC.

*All temperatures in this evaluation have been adjusted to the 1968 Temperature Scale (IPTS-68).
Because of difficult experimental requirements, only a few comprehensive investigations on the Si-C phase diagram have been undertaken, and their results leave much to be desired.

[54Now], based on a few measured points, tentatively proposed two versions of the diagram; both assumed a low boiling point of Si and more or less extended liquid solubility of C in Si. [58Bro] conducted more elaborate metallographic and X-ray studies to refine one of these diagrams. None of the diagrams proposed by [54Now], however, has finally proved to be quantitatively correct. [58Hall] determined the liquid solubility of C in Si at 1522, 1602, and 1728 °C by a weighing technique. His results, as pointed out by [59Sca], are probably inaccurate because of the oxidation of the dissolved C by the quartz crucible.

[59Sca] conducted a series of experiments using graphite or alumina containers placed in a graphite furnace. When the graphite container was used, the C in the alloy system came entirely from the dissolution of the container and was distributed at the operating temperature between the SiC and liquid phases; the C solubility in the liquid phase was calculated from the weight of SiC that crystallized in the bulk sample upon cooling, as determined by discarding the SiC on the surface of the sample, dissolving the matrix away, and weighing the residue. In the experiments with alumina crucibles, which were conducted below the peritectic temperature, a weighed crystal of SiC was melted with Si, and the weight loss of SiC was used to determine the solubility. The results of [59Sca] are shown in Fig. 1.

[59Sca] assumed that the SiC layer on the surface of the quenched samples represented the phase that had formed before quenching, and that the SiC formed during quenching precipitated mostly within the Si phase. These assumptions might not be valid considering the fact that the SiC forming during quenching would most likely use the existing SiC as a heterogeneous nucleating substrate to grow upon. Therefore, the present evaluators believe that the solubility results of [59Sca] might underestimate the amount of dissolved C.

The most comprehensive and probably reliable investigation of the Si-C diagram was conducted by [60Dol]. His thermal analysis results supported by metallographic and X-ray studies led to the determination of the eutectic temperature at 1404 ± 5 °C and the eutectic composition at 0.75 ± 0.5 at.% C. The peritecic transformation was, in a similar manner, determined to occur at 2545 ± 40 °C, involving SiC and a liquid of 27 at.% C. The complete results are reproduced in Fig. 1.

The phase diagram calculated by [79Kau], who has made a series of simplifying assumptions, qualitatively agrees with this diagram.

The solid solubility of C in Si has been investigated quite extensively; however, the reported data, apart from being conflicting, can hardly be used to construct an equilibrium binary phase diagram. It is nonetheless possible to conclude that the solid solubility limit for C in Si in the temperature range 1200 to 1400 °C is -10^{-3} to 10^{-4} at.% C, and that C dissolves substitutionally in Si [61New, 62New, and 71Bea]. At the eutectic temperature, the solubility assumes a value around 0.0007 or 0.00018 at.% C. The first value was determined by [70Noz] from a charged particle activation analysis, and the latter was measured by [73Vol] by using double-beam infrared spectrophotometry, metallography, and electron microprobe techniques. [70Gne] claimed the solid solubility of C in Si to be as high as 1.3 at.% C in slowly cooled samples. This value was later moderated down by [72Gne] to 0.019 at.% C, which agrees somewhat with other data. The C equilibrium distribution coefficient near the melting point of Si is probably between 0.07 [70Noz] and 0.1 [69Haa].

[73Vol] calculated the eutectic composition as 0.026 at.% C and the eutectic temperature as 0.1 °C below the Si melting point; the calculations were based on their solid solubility measurements and the distribution coefficient given by [70Noz]. The measurements by Dash employing a pedestal technique (as reported in [59Sca]) produced a eutectic point around 10^{-2} at.% C.

The atmospheric boiling point of Si has been calculated by the present evaluators as 3227 °C. The sublimation point of C at 1 bar has been estimated to be 3798 °C, compared with 3826 °C [81BAP]. The calculations have been based on the thermodynamic data discussed later. The high-pressure melting points of C have been included in Fig. 1, after [67Str].

Metastable Phases

[70Gne] reported extended solid solubility of C in Si in films prepared on quartz substrates by the pyrolysis of heptane vapor at 1252 °C. The electron-diffraction determination of the lattice parameter of the Si phase was interpreted as evidence of the formation of solid solution, containing as much as 10 at.% C; the SiC phase was also observed in the diffraction patterns.

[77Yos] and [78Yos] synthesized Si-C films by a plasma deposition process on Si and quartz substrates. The substrate temperature was in the temperature range 200 to 600 °C, and the reaction gases consisted of CH₄ and SiH₄. The authors investigated properties of the films as a function of the deposition conditions. It is not clearly specified whether the films were crystalline or amorphous. However, they referred to the formation of amorphous SiC films with a composition of 39 at.% Si and 61 at.% C, obtained by RF sputtering.

As discussed later in the section on crystal structure, aSiC and other polytypes of aSiC can be considered thermodynamically metastable at all temperatures, although some researchers believe the contrary.

Crystal Structure and Lattice Parameters

At normal pressures, Si has a cubic diamond-type structure; the high-pressure Si is tetragonal, of βSn type. The structure of C (graphite) is hexagonal.

Crystallographic data of the thermodynamically stable phases of Si-C system at 25 °C are reproduced in Table 1. The decrease of the Si lattice parameter upon substitutional dissolution of C was determined by mass spectrometry, infrared, and lattice parameter measurements by [68Bak].

βSiC with cubic structure was shown by [59Sca] to be the most stable phase at any temperature below the peritectic temperature. Thermodynamic calculations of the pres-