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Abstract

The new phase, as prepared from the high-purity elements, is stable between room temperature and 2270 K, but decomposes between 2270 and 2370 K. The crystal symmetry is hexagonal, with \( a_0 = 3.3127(7) \) \( \text{Å} \), \( c_0 = 19.242(4) \) \( \text{Å} \), \( V = 182.9(1) \) \( \text{Å}^3 \), \( Z = 1, D_r = 2.977(2) \) g cm\(^{-3} \), Cu K\( \alpha \) radiation (\( \lambda = 1.540600 \) \( \text{Å} \)). The JCPDS Diffraction File No. for 2Al₄C₃.SiC is 35-1499.

Experimental

The new intermediate phase was initially recognized as unidentifiable lines in the diffraction patterns of some partially reacted Al–Si–C mixtures between Al₄C₃ and Al₄C₃.SiC. Numerous Al:Si:C ratios were reacted at temperatures to 2370 K for up to 2 h in attempts to determine the stoichiometry. All such samples prepared from the elements contained, at most, a trace of the new phase owing to very sluggish formation kinetics. Single-phase material with stoichiometry 2Al₄C₃.SiC was ultimately prepared by the following procedure, which comprised three consecutive stages of reaction followed by grinding and mixing. The high-purity elements (99.999% Al, 99.999% Si and spectrographic-grade graphite) were reacted in an open graphite crucible at \( \approx 1870 \) K for 2 h under an Ar atmosphere (35 kPa overpressure). 10 g charges were used containing 102% of the stoichiometric Al to allow for vaporization.

The reacted material was hand-ground to about 80 mesh, mixed thoroughly, placed in a fresh graphite crucible, and heated for an additional 2 h at 1870 K. X-ray analysis showed only a barely detectable trace (BDT) of 2Al₄C₃.SiC at this point. The material was then reground, mixed and reheated at 2270 K for 2 h to form 2Al₄C₃.SiC with a BDT of Al₄C₃. In these preparation steps the samples were cooled from 2270 to 1720 K in 2 min by cutting furnace power.

An accurate record of vaporization losses was kept, and the nominal composition was calculated from charge weights minus these losses assuming that all of the weight loss was aluminum. The average composition of three separate batches of 2Al₄C₃.SiC calculated on that assumption was 49.90(18) Al, 6.26(3) Si and 43.84(16) C, where compositions are expressed in atom %. These values compare very well with 50.00 Al, 6.25 Si, and 43.75 C (in atom %) calculated from the formula.

Small (0.5 g) samples of equilibrated material were placed in closed graphite crucibles and encapsulated in tantalum ampoules by arc welding. The ampoules were closed under about 30 kPa of argon at an estimated 1270 K. The net residual internal gas pressure was then less than 10 kPa at room temperature and about 50 kPa at 2270 K. The encapsulated samples were subjected to three different heat treatments. Two were used to determine if 2Al₄C₃.SiC was stable to room temperature by heating both to 2270 K, holding for 2 h, and cooling one slowly (12 K min\(^{-1} \)) and one rapidly (700 K min\(^{-1} \)). Both samples were unchanged after heat treatment, verifying the stability of 2Al₄C₃.SiC. The third encapsulated sample was heated to 2370 K for 2 h and cooled rapidly (700 K min\(^{-1} \)). This sample contained Al₄C₃, 2Al₄C₃.SiC, Al₄C₃.SiC, Al and Si. The evidence indicates that 2Al₄C₃.SiC decomposes by the following ternary peritectic reaction:

\[
2\text{Al}_4\text{C}_3.\text{SiC} \rightarrow \text{Al}_4\text{C}_3 + \text{C} + \text{L},
\]

where the liquid phase is a graphite-saturated Al–Si alloy. It is proposed that the dissolved carbon in the liquid alloy at 2270 K precipitated as 2Al₄C₃.SiC and Al₄C₃.SiC upon cooling, and the remaining liquid alloy solidified as the Al–Si eutectic at 850 K. Reaction (1) occurs at a temperature between 2270 and 2370 K.

The remainder of the equilibrated material was reheated to 2270 K for 2 h in an open graphite crucible. Analysis revealed a shift in composition from 2Al₄C₃.SiC with a BDT Al₄C₃ (slightly Al rich) to 2Al₄C₃.SiC with a BDT Al₄C₃.SiC (slightly Si rich). This indicates that graphite-saturated 2Al₄C₃.SiC has very little solubility for Al or Si.
X-ray powder diffraction data

X-ray diffraction patterns were obtained for single-phase, -200-mesh material in the range 5 to 140° 2θ at a rate of 0.01° s\(^{-1}\) using a 173 mm diffractometer with a graphite single-crystal monochromator and a 13.0 mm \(\theta\) compensating slit. The data were analyzed by Ito’s method (Azaroff & Berger, 1958) and found to be consistent with a hexagonal unit cell. The resulting diffractograms were subjected to the interactive computer program \(\text{INDEX}\) (Hom, Jenkins, & Ladell, 1983) to obtain the lattice parameters. No systematic extinctions were observed in this pattern.*

With one molecule per unit cell, the calculated density is compatible with the density (approximately 3 g cm\(^{-3}\)) of the other compound in this system.

*The powder data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39554 (3 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.


A comment on The peak in neutron powder diffraction by B. van Laar and W. B. Yelon. By C. J. Howard,†

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Abstract

It is shown that the neutron powder diffraction peak as computed by van Laar & Yelon [J. Appl. Cryst. (1984), 17, 47-54] can be rather well approximated using a normalized asymmetric peak profile as proposed by Howard [J. Appl. Cryst. (1982), 15, 615-620] or Prince [J. Appl. Cryst. (1983), 16, 508-511] together with an intensity correction factor from Cooper & Glasspool [J. Appl. Cryst. (1976), 9, 63–67]. Since the differences are material only at the lowest scattering angles (2θ ≤ 10°), in most cases a description of the peak by one of the simpler analytic profile functions should be adequate.

In a recent paper, van Laar & Yelon (1984) computed neutron powder diffraction peaks for the case when a detector of finite height 2H rotates around a sample of finite height 2S at a distance L. van Laar & Yelon (hereafter referred to as vLY) restricted the calculation to \(H > S\). For computation of total diffraction profiles, the diffractometer was assumed to have a resolution function \(R\), which was a symmetric Gaussian. In this communication, we employ the vLY notation throughout.

It is of interest to compare the vLY work with other recent attempts (Howard, 1982; Prince, 1983) to describe the peak profiles associated with the use of detectors of finite height. Howard (1982) has suggested that the peak profile might be approximated by a sum of Gaussians, while Prince (1983) has suggested an Edgeworth expansion be used. Prince (1983) has shown that the sum of (five) Gaussians and the Edgeworth expansion are very closely equivalent, so it suffices to compare the vLY work with that of Howard (1982).

Howard (1982) assumed the deviation from Bragg angle 2θ - 2φ remains small enough to neglect higher-order terms in 2θ - 2φ, and in particular to allow the approximation \(h \approx L [2(2θ - 2φ) \tan 2θ]^{1/2}\) in vLY equations (9). He also assumed negligible specimen height, that is 2S = 0 in vLY equations (9) and (10). Finally Howard approximated the convolution of vLY equation (16) using Simpson’s rule. The result was a sum of Gaussians involving a single asymmetry parameter \(P = \frac{3}{2} (H/L)^2\). Compared with the single Gaussian, this sum of Gaussians was shifted [the centroid being shifted by \(- (P/3) \cot 2θ\)] broadened and asymmetric. These are qualitatively the effects reported by vLY in their computed peaks. This being so, it seems worthwhile to compare the magnitudes of the peak shifts reported by vLY with the shifts of the sum of Gaussians, for the extreme case 2H = 100 mm, 2S = 40 mm, \(L = 685 \text{ mm (whence } P = 0.153\text{)}\) discussed by vLY. The shifts reported by vLY [and in parentheses the shifts calculated from \(- (P/3) \cot 2θ\) are: for 2θ = 10°, 0.24° (0.29°); for 2θ = 20°, 0.15° (0.14°); and for 2θ = 40°, 0.05° (0.06°). The agreement between the peaks computed by vLY and the sum of Gaussians in respect of peak shift is thus quantitatively good, the discrepancy at 2θ = 10° being accounted for by the fact that for a highly asymmetric peak such as shown.

References


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