Oxygen content of reaction-bonded α-silicon nitride

From X-ray and thermodynamic studies Wild *et al* [1] and Colquhoun *et al* [2] deduced that α-silicon nitride has a range of composition lying between $Si_{11.4}N_{15}O_{0.3}$ and $Si_{11.5}N_{15}O_{0.5}$. These two compositions contain 0.90 and 1.48 wt % oxygen respectively. Recently Priest *et al* [3] reported that a sample of α-silicon nitride prepared by chemical vapour deposition had an oxygen content, as determined by neutron activation analysis, of 0.300 ± 0.005 wt %. They, therefore, concluded [3] that α-silicon nitride does not require oxygen for structural stability. In this letter observations are presented which show that the range of oxygen content of α-silicon nitride must extend to lower values than previously reported [1, 2].

Samples of reaction-bonded silicon nitride have been prepared independently at Admiralty Materials Laboratory and Leeds University using silicon powder from different sources and nitriding atmospheres of differing purity. X-ray measurements were made at both Laboratories on solid and powdered samples using a diffractometer and a high intensity X-ray source. The scanning ranges were chosen so that the strongest reflections from α- and β-silicon nitride, silicon, silica and silicon oxynitride could be observed. The relative proportions of the α- and β-silicon nitride phases present in any one sample were estimated from the peak heights of the (210) reflection for the α phase and the (210) or (102) reflections for the β phase. The ratios of these peak heights were then compared with those obtained from standards of known phase composition. In all four samples no phases other than the α- and β-nitrides and silicon were detected. Oxygen contents were measured at AML by neutron activation analysis employing 14 MeV neutrons. The experimental data are given in the Table together with the calculated oxygen contents of the α-silicon nitride in samples 1, 2 and 3, assuming all the measured oxygen is associated with that phase only. These calculated oxygen contents are about one third that required for the composition $Si_{11.5}N_{15}O_{0.5}$ (1.48 wt % oxygen) and about one half that for the composition $Si_{11.4}N_{15}O_{0.3}$ (0.90 wt % oxygen). Also included in the Table is the oxygen content of a sample (no. 4) comprising mainly β-silicon nitride. The fact that this measured oxygen content is similar to those of the samples comprising mainly α-silicon nitride shows that a considerable proportion of the measured oxygen in samples 1, 2 and 3 must be associated with phases other than α-silicon nitride (e.g. silica or silicon oxynitride) present in quantities below the limits of detection, amorphous phases, or surface silica [4]. It follows that the oxygen content of the α-silicon nitride in these samples could be lower than the calculated values quoted in the Table.

Therefore, it is concluded that α-silicon nitride does not necessarily require the level of oxygen suggested by Wild *et al*, and indeed some

TABLE I

Sample no.	Nitriding atmosphere (ppm)*		Phase composition (wt %) α	β	Si	Measured oxygen content of sample (wt %)	Calculated oxygen content of α-silicon nitride (wt %)†
1	30 600	O_2 H_2O	87	13	<1	0.53 ± 0.05	0.61 ± 0.06
2	1000 50	O_2 H_2O	81	19	<1	0.48 ± 0.02	0.59 ± 0.03
3	20 10	O_2 H_2O	58	26	16	0.26 ± 0.03	0.45 ± 0.05
4	20 100	O_2 H_2O	6	83	11	0.31 ± 0.02	—

*The stated values refer to the gas passing into the furnace; for samples 3 and 4 the local oxygen pressure was further reduced by surrounding the sample with a zirconium "getter".
†Assuming the measured oxygen to be associated with the α-silicon nitride only.

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α-silicon nitrides may not require oxygen at all. This conclusion, based on measurements on porous, reaction-bonded silicon nitride, is similar to that reached by Priest *et al* from measurements on dense, chemically vapour deposited α-silicon nitride.

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Complete indexing of electron diffraction patterns by computer

As electron microscopy is extended beyond the simple structures of metals to the more complex crystal structures of other materials, the difficulty of indexing electron diffraction patterns increases. In particular with lower symmetry structures, as found in some minerals for example, many similar but not identical diffraction patterns occur. In such cases it is important to be aware that several, non-equivalent indexing systems may fit a particular pattern within the limits of measuring accuracy. It is difficult for an operator to ensure that all possible systems have been taken into account. Such a situation is an obvious opportunity to apply a computer assisted analysis and a program has already been developed [1] which lists all possible diffraction patterns (i.e. distances and angles between them) for any given structure up to a beam direction [5 5 5].

However, in cases where only a few reflections occur from a particular specimen, it would be desirable to index the pattern directly by computer without having to complete a network of reflections from those few available. A new program has been developed which does index directly and is now available on request from the author.

The main difficulty in such a program is in the treatment of the errors. These are of two kinds: (a) an error in the camera constant (λL) due to variation in foil position and depth, (b) an error in detecting the correct position of a reciprocal lattice point from an observed reflection. The second error is not simply a result of measuring error, it arises because the reflection from a thin foil is always streaked in the direction of the foil normal (Fig. 1) and the reflection is observed at the point where the reflecting sphere intersects the streak rather than at the centre of the reflection streak which would be the true reciprocal lattice point. Operators often measure a whole row of reflections and divide by the number of intervals between points in the hope of increasing measuring accuracy. As Table I shows, such hope is illusory. In the case of planar faulted structures, with the faults lying at an angle to the foil

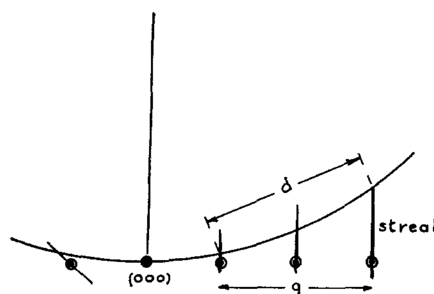

Figure 1 The intersection of the reflecting sphere with streaked reciprocal lattice reflections. The distance, *d*, measured on the diffraction pattern is different from the reciprocal lattice vector magnitude, **g**. A spot streaked obliquely due to faulting, is also shown on the left.

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