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The Influence of Substrate Material on the Formation of Silicon Nitride

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Abstract

Si_3N_4 whiskers have been grown on substrates of graphite and recrystallised alumina to determine the influence these have on product phase and morphology. Selected powders were nitrided under ammonia at 1673 K and the resulting materials analysed using TEM, EDAX and X-ray diffraction techniques. The purpose of these studies was to assess the factors which govern the nucleation and growth steps in crystal formation, in particular the role of Al and O in determining the alpha/beta-phase content.

Si_3N_4-Whisker wurden jeweils auf Graphit und auf rekristallisiertem Aluminiumoxid aufgezüchtet, um zu klären, welcher Einfluß dieser Substrate auf die Produktphase und auf deren Morphologie ausgeht. Ausgewählte Pulver wurden bei 1673 K unter Ammoniak nitriert. Die sich ergebenden Materialien wurden mittels TEM, EDAX und Röntgen-Beugung analysiert. Das Ziel dieser Untersuchungen war das Verständnis der Faktoren, welche die Keimbildungs- und Keimwachstumsschritte im Laufe der Kristallentstehung bestimmen. Von besonderem Interesse war hierbei die Rolle von Al und O bei der Bestimmung des Alpha/Beta-Phasenanteils.

On a fait croître des whiskers de Si_3N_4 sur des substrats en graphite et en alumine recristallisée pour déterminer l'influence de ces matériaux sur la phase produite et sur la morphologie. Différentes poudres ont été nitrurées sous ammoniac à 1673 K et les matériaux obtenus ont été analysés par TEM, EDAX et par diffraction de rayon X. Le but de ces études était de déterminer les facteurs qui dirigent la nucléation et les étapes de croissance durant la formation du cristal, en particulier le role de Al et O en déterminant le rapport de phases alpha/beta.

1 Introduction

Owing to the heightening industrial demand for novel engineering materials with good mechanical properties, a wide variety of ceramic/ceramic and metal/ceramic composites are being developed to meet these requirements. Si_3N_4 and SiC whisker[1,2] and platelet[3,4] forms represent possible reinforcing or toughening phases for such materials. However, the processing of these controlled morphology powders is not well understood.

Industrially, silicon nitride is most commonly produced by the direct nitridation of silicon powder at temperatures less than the melting point of the metal (1685 K). Products are typically high alpha-phase Si_3N_4, the quality of which is determined by impurities such as Fe and Ca in the starting Si. From early studies of this process it was concluded that alpha-phase whisker formation occurs via a vapour- or liquid/vapour-phase reaction.

Silicon nitride whiskers are also produced by carbothermal reduction of silica[5,6] via the chemical reaction

$$3SiO_2 + 6C + 2N_2 \rightleftharpoons Si_3N_4 + 6CO \qquad (1)$$

It has been proposed[7] that this takes place in two stages:

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \qquad (2)$$

$$3SiO_{(g)} + 3CO_{(g)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 3CO_{2(g)} \qquad (3)$$

Alternatively, it has been suggested that the second step (reaction (3)) takes place by nucleation and reaction on graphite as a substrate,[8]

$$3SiO(g) + 3C_{(s)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 3CO_{(g)} \qquad (4)$$

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This latter case, however, represents only one possibility of nucleation on a suitable substrate and, in general, heterogeneous nucleation is more probable than homogeneous nucleation from the gas phase in these systems. For example, eqn (3) requires three different gas molecules to arrive at the point of nucleation (or growth) in exactly the correct stoichiometry.

A number of effects of nucleation have been reported in the literature. The effect of heterogeneous nucleation has been demonstrated by Siddiqi[9] and by Yamada *et al.*[10] who have shown that addition of alpha-silicon nitride crystals to the carbothermal reduction mixture of $SiO_2 + C$ results in complete absence of whisker formation and increased equiaxed Si_3N_4 yield. Several other reports concerning nucleation of whiskers have been reported and include 100% alpha-phase grown on graphite in a mullite tube[11] and mixtures of beta- and beta'-phase[6] on graphite in a graphite tube. Wada & Wang[1] argue that the alpha-phase is stabilised by a higher oxygen partial pressure and it is this factor which determines the relative phase content. Platelet forms of Si_3N_4 have been produced by the ammonolysis of $SiCl_4$,[3] where the initial product was amorphous, and transformed to a platelet morphology upon calcining at 1673 K.

In the case of silicon nitride ceramics therefore, it is essential to establish the principles underlying crystal formation, in order to manufacture materials with specific chemical, physical and morphological properties. To this end the present work addresses the influence of selected substrates and starting powders on the phase and morphology of the end product.

2 Experimental Procedures

Nitriding runs were carried out in a Carbolite horizontal tube furnace using the arrangement shown in Fig. 1. The inner tube and boat act as substrates on which whiskers are grown. Ammonia was chosen as the nitriding gas owing to its high nitrogen potential when cracked at the temperatures used and the effect of the liberated hydrogen on reducing the oxygen potential. By passing the furnace output gas through a solution of boric acid, and titrating with a standard 0·1 mol HCl solution, the NH_3 content in the output gas was shown to be the order of 1%. Thus from the reaction

$$NH_3 \rightarrow \tfrac{1}{2}N_2 + 3/2H_2 \qquad (5)$$

it can be calculated[12] that the nitrogen partial pressure produced at 1673 K is approximately 0·248 atm. Nitrogen gas was used to flush the furnace before and after each run.

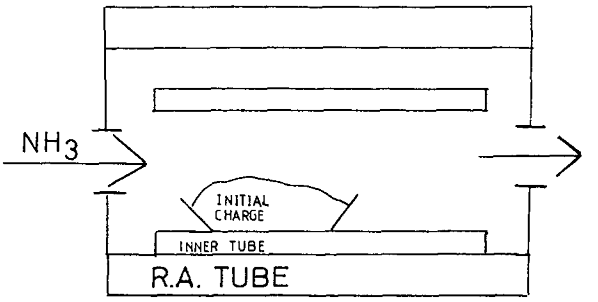


Fig. 1. Diagram illustrating the recrystallised alumina (RA) furnace tube, inner tube and boat arrangement used in the experiments.

The powders used were $Si:SiO_2$ (powder i) prepared by wet milling and drying, and $3C:SiO_2$ (powder ii) prepared by a sol–gel method (molar ratios). These were selected on the basis of their ability to liberate SiO during nitriding according to the reactions

$$SiO_{2(s)} + Si_{(s)} \rightleftharpoons 2SiO_{(g)} \qquad (6)$$

and

$$SiO_{2(s)} + C_{(s)} \rightleftharpoons SiO_{(g)} + CO_{(g)} \qquad (7)$$

which liberate equilibrium silicon monoxide partial pressures of 0·009 atm and 0·017 atm respectively.[12] The SiO thus liberated is then allowed to react with ammonia on the substrates via the overall reaction.

$$4NH_3 + 3SiO \rightleftharpoons Si_3N_4 + 3H_2O + 3H_2 \qquad (8)$$

Run conditions are detailed in Table 1.

3 Results

3.1 Reaction products

Below 1673 K, whisker growth was not observed and it was thus concluded that the P_{SiO} generated at these temperatures was too low. The results at 1673 K for various powder, boat and tube combinations are summarized in Table 2.

When powder i was used as the initial charge in experiment A, the product was a dense matt of white

Table 1. Run conditions for experiments using the arrangement shown in Fig. 1

Experiment	*Conditions*	*Flow rate (ml/min)*
A	Alumina tube/boat	400
B	Carbon tube/boat	400
C	Carbon tube, alumina boat	400

whiskers over the boat and residual charge with small amounts of whiskers grown downstream on the alumina tube. Separate XRD analysis of these materials indicated they were a mixture of alpha- and beta-Si_3N_4 with the higher beta-phase content in the residual charge and the lower on the downstream whiskers. Examples of the form these two phases take in the whisker material are shown in Figs 2 and 3.

When powder ii was used in experiment A, the products were alpha/beta-whisker mixtures occurring over and downstream from the alumina boat, and a residual charge containing beta-SiC and alpha and beta-Si_3N_4.

A significant alteration of the relative phase contents in the products was observed when different boat/tube arrangements were used. In case B (powder i), the whiskers produced were pure alpha-phase, and occurred on the graphite tube over and downstream from the initial charge, whereas the

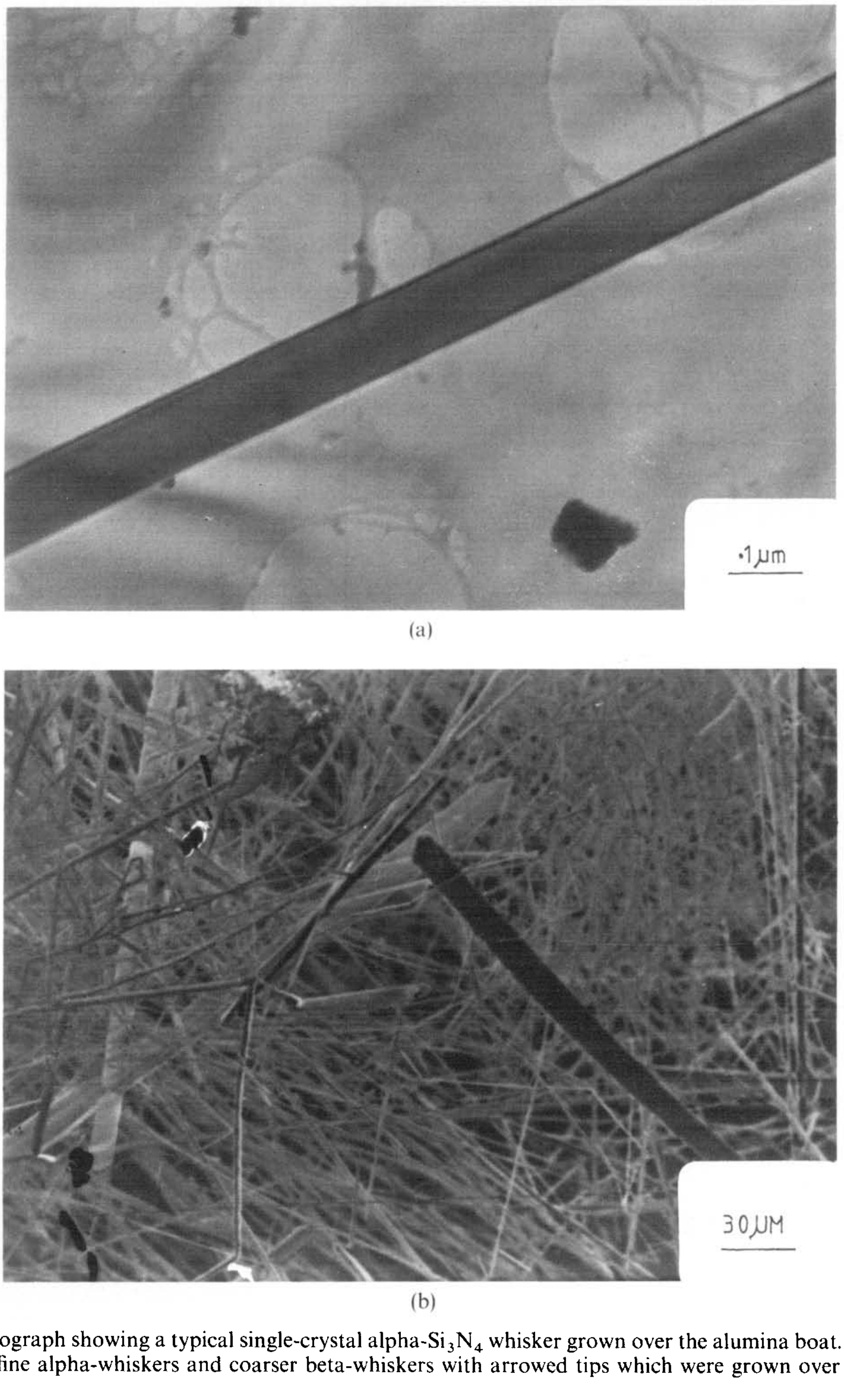
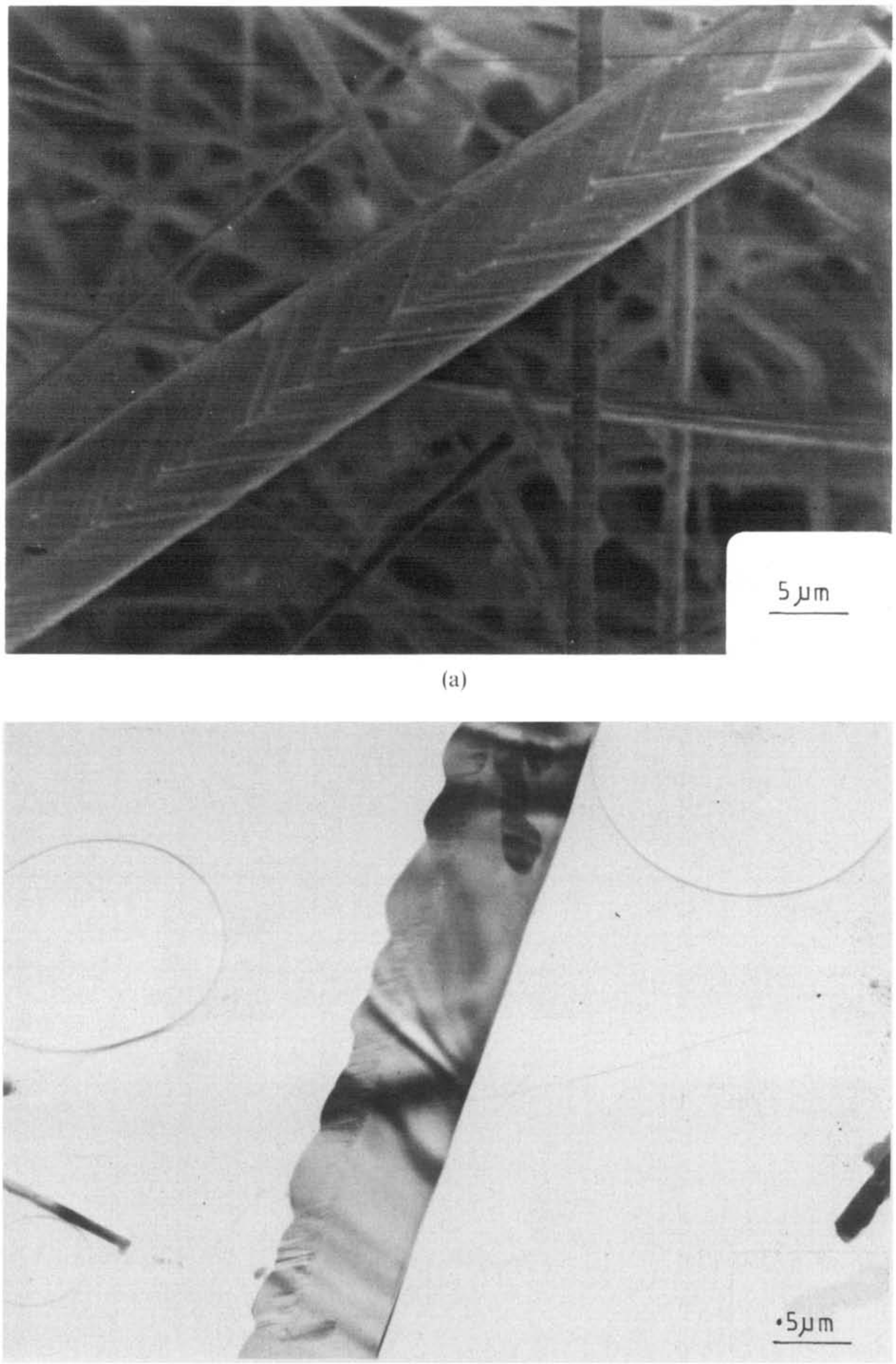


Fig. 2. (a) TEM micrograph showing a typical single-crystal alpha-Si_3N_4 whisker grown over the alumina boat. (b) SEM micrograph showing a mix of fine alpha-whiskers and coarser beta-whiskers with arrowed tips which were grown over the alumina boat.



(a)

(b)

Fig. 3. (a) SEM micrograph showing faulted growth of a beta-whisker grown over the alumina boat. (b) TEM micrograph showing the 'blade-like' shape and faulted growth of a beta-whisker grown over the alumina boat.

residual powder was a 50/50 mixture of alpha-Si_3N_4 and SiC. When an alumina boat is introduced into this arrangement, as in case C (powder i), the whiskers produced were the same, but the residual powder contained 10% beta-Si_3N_4.

It can be concluded from the latter result that, in order for SiC to form in the alumina boat, gaseous carbon species such as CO or CH_4 must be present, since the initial charge is Si:SiO_2. In fact carbon 'wool' was discovered downstream in the reaction tube, whilst the graphite reaction tube had visibly been eroded at the upstream hot zone end. The reaction

$$2H_2 + C \rightleftharpoons CH_4 \qquad (9)$$

yields a significant methane partial pressure of $4{\cdot}9 \times 10^{-4}$ atm (by assuming a hydrogen pressure of 0·75 atm from reaction (8)). Furthermore, the

Table 2. A summary of the phase composition of the products obtained when powders i and ii were nitrided under ammonia for 20 h

Product	*Experiment starting powder*	*alpha-Si_3N_4 (%)*	*beta-Si_3N_4 (%)*	*SiC (%)*
Whisker over boat	A + i	40	60	—
Residual powder	A + i	20	80	—
Whisker on carbon tube	B + i	100	—	—
Residual powder	B + i	50	—	50
Residual powder	C + i	45	10	45
Whisker on carbon tube	C + i	100	—	—
Residual powder	A + ii	10	10	80
Whisker over boat	A + ii	90	10	—
Whisker on carbon tube	A + ii	90	10	—

presence of beta-nitride in the residual powder of experiment C (powder i), suggests that P_{O_2} is not the determining parameter in altering the relative phase contents of the products, since the introduction of the alumina boat would heighten the oxygen partial pressure and, following the arguments of Wada *et al.*,[6] this would favour alpha-phase formation.

There are two main possibilities why the whiskers grown on graphite should contain no beta-phase:

(a) A difference in oxygen partial pressures between the experiments, or

(b) Al from the substrate itself stabilises the formation of beta-phase during either nucleation or growth.

To investigate these further, it was decided to calculate the expected oxygen partial pressures, carry out dew point measurements to assess the water content of the output gas (and thus the oxygen potential), and also to carry out EDAX/TEM investigations to determine the presence and distribution of Al in the whiskers produced.

3.2 Microstructure/phase analysis

Examination of the *d*-spacings from X-ray diffraction patterns gives a *z*-value for the beta-phase close to zero (the general formula for the beta'-sialon solid solution in the Si–Al–O–N system is $Si_{6-z}Al_zO_zN_{8-z}$). However, in TEM microanalysis, the beta-whiskers did show significant alumina content in their EDAX spectra. A typical example is shown in Fig. 4. The spectra showed no variation in Al content along the length of the whiskers and semi-quantitative analysis yielded a *z* value of $0{\cdot}5 \pm 0{\cdot}4$. This is within the range of error in the X-ray diffraction results.

In general the beta-whiskers were thicker and shorter than the alpha-whiskers and grew less uniformly. This can be seen by comparing Figs 2 and 3. The alpha-whiskers exhibited *c*-axis growth when observed using a goniometer stage on the microscope, while the beta-whiskers mainly grew in the [2 1 0] direction.

3.3 Equilibrium thermodynamics

Equilibrium calculations were carried out to assess the thermodynamic feasibility of the proposed SiC formation mechanism, the contribution to P_{O_2} from water and suboxide reduction, and the stability of beta'-sialon under the measured conditions over a series of low *z*-values. Standard free energies of formation were taken from the literature[12,13] whilst the values for Si_3N_4 and sialon were taken from Hendry[14] and Carr & Hendry (1991, pers. commun.).

In order to check that the proposed mechanism of formation of SiC was justified (eqns (9) and (10) in Table 3), the expected a_{SiC} was calculated on the basis of the measured P_{H_2} and a value of the activity ($a_{SiC} \sim 1{\cdot}5$) was obtained showing that formation of SiC ($a_{SiC} > 1$) was thermodynamically possible.

From Table 3 it is clear that the equilibrium between H_2O, H_2 and O_2 will produce by far the largest oxygen partial pressure. Also, eqn (8) (Table 3) shows that a water vapour pressure of less than

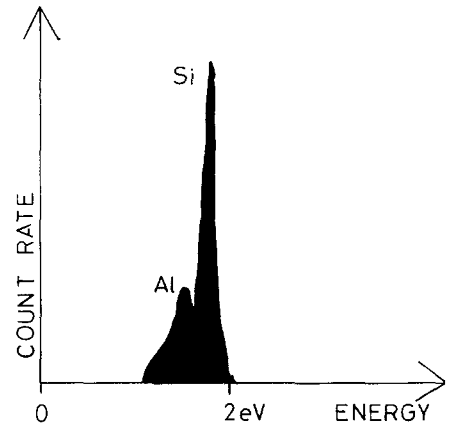


Fig. 4. Typical EDAX spectrum of the beta-whiskers showing both Si and Al peaks.

Table 3. A summary of the relevant reactions likely to affect the gas-phase composition in the experiments (based on the experimentally determined ammonia decomposition)

Reaction	*Free energy* (|*kJ*|*mol*)	*Partial pressures* (*atm*)
(6) $Si + SiO_2 \rightleftharpoons 2SiO$	130·7	$P_{SiO} = 0{\cdot}009$
(7) $SiO_2 + C \rightleftharpoons SiO + CO$	113·2	$P_{SiO} = 0{\cdot}017$
(8) $4NH_3 + 3SiO \rightleftharpoons Si_3N_4 + 3H_2O + 3H_2$	439·6	$P_{H_2O} = 0{\cdot}27$ $P_{H_2} = 0{\cdot}54$ $P_{N_2} = 0{\cdot}18$ $P_{NH_3} = 0{\cdot}004$
(9) $C + 2H_2 \rightleftharpoons CH_4$	96·9	$P_{CH_4} = 4{\cdot}8 \times 10^{-4}$
(10) $Si + CH_4 \rightleftharpoons SiC + 2H_2$	146·2	—
(11) $Al_2O_3 + 2H_2 \rightleftharpoons Al_2O + 2H_2O$	205·6	$P_{Al_2O} = 2{\cdot}7 \times 10^{-7}$
(12) $Al_2O \rightleftharpoons 2Al + 1/2O_2$	253·5	$P_{O_2} = 10^{-27}$
(13) $CO \rightleftharpoons C + 1/2O_2$	258·1	$P_{O_2} = 2 \times 10^{-19}$
(14) $H_2O \rightleftharpoons H_2 + 1/2O_2$	154·1	$P_{O_2} = 6{\cdot}2 \times 10^{-11}$

The values for reaction (8) have been normalised to 1 atm total pressure.

0·27 atm is required for successful nitriding when the measured NH_3 decomposition rate is used. The measured dew point of the furnace exhaust was below −5°C, indicating an actual $P_{H_2O} < 0{\cdot}001$ atm.

In Fig. 5, free energy is plotted against *z*-value for beta′-sialon using Carr & Hendry's equation (1991, pers. commun) based on Kaufman's model.[15] From the equation

$$(6-z)SiO + (8-z)NH_3 + (z/2)Al_2O_3 \rightleftharpoons Si_{6-z}Al_zO_zN_{8-z} + (6-z/2)H_2O + (6-z)H_2 \quad (15)$$

for nucleation of sialon on pure alumina, beta′-sialon activity (a_z) is plotted against *z*-value by assuming P_{H_2O} values of 0·001 atm and 0·0001 atm. It follows that

$$\log a_z \sim \log K - (6-z)\log\left[(P_H P_{H_2O}/(P_{SiO}P_{NH_3})\right]$$

for low values of *z*, which is close to a linear function of *z*. The results are shown in Fig. 6 and are obviously sensitive to small errors in the partial pressure measurements. Nevertheless, the results support a mechanism producing stable beta′-sialon (within the experimental error) within the range of composition indicated by the EDAX analysis reported here.

4 Discussion of Growth Mechanism

Short-term nitriding runs using powder ii produced examples within the residual powder of the early stages of nucleation on carbon. Hexagonal-like nuclei, as shown in Fig. 7, were discovered on an amorphous substrate. It has already been shown above that alpha-phase forms in the presence of graphite and these single-crystal nuclei thus support the observations of *c*-axis alpha-whisker growth on graphite in the absence of alumina species.

Oxygen partial pressures in the system are dictated by both the input gas purity and by the equilibrium reactions in Table 3. Whilst the former is constant between experiments, the differences

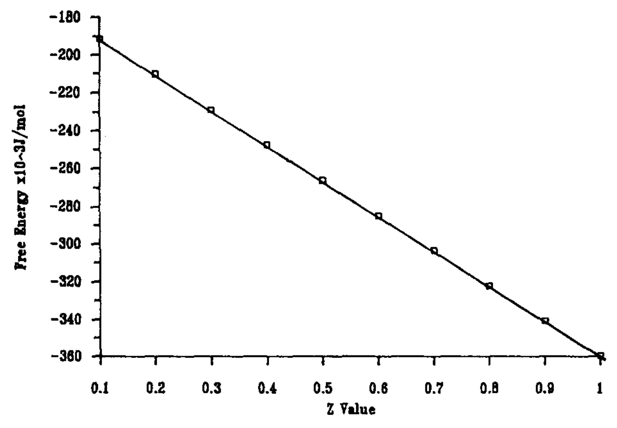


Fig. 5. A plot of the free energy of formation in kJ/mol versus *z*-value for beta′-sialon at 1673 K.

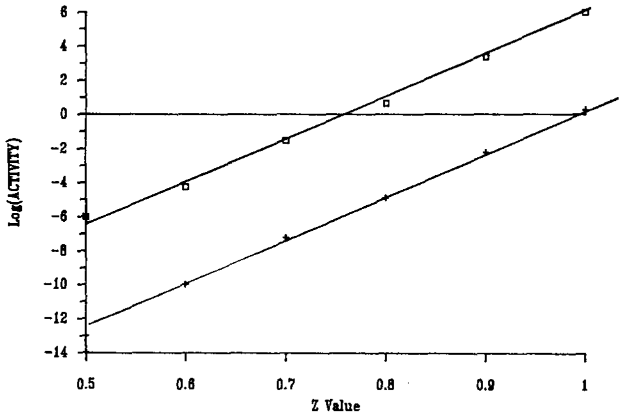


Fig. 6. A plot of log(activity) versus *z*-value for reaction 15 based on the data of Fig. 5, the measured ammonia decomposition and estimates of the dew point of the furnace exhaust. □, 0·0001 atm H_2O; +, 0·001 atm H_2O.

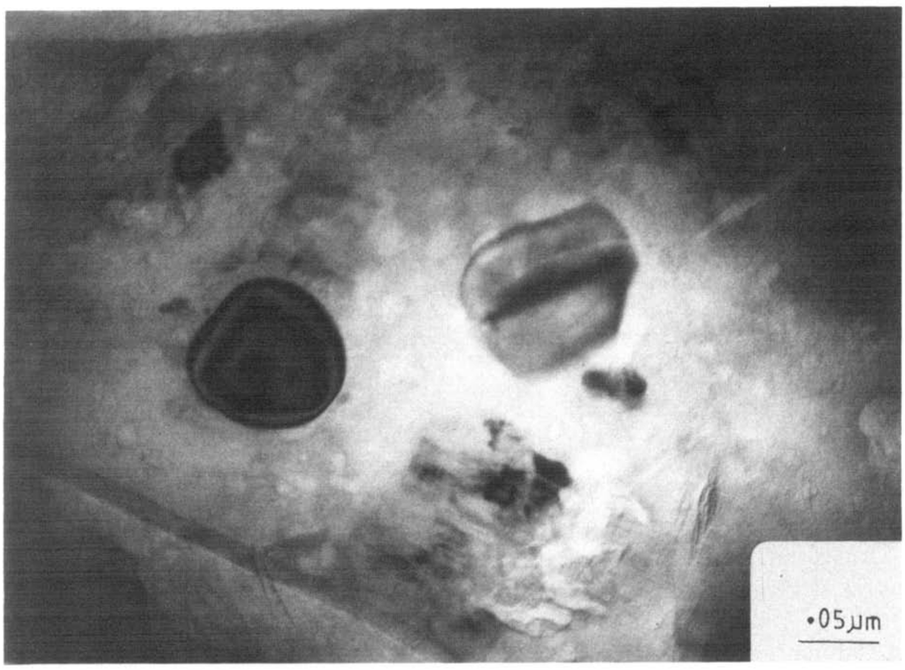


Fig. 7. TEM micrograph showing nucleation of alpha-silicon nitride on graphite.

caused by substitution of graphite for alumina must be considered. From the results of Table 3, however, it is apparent that the largest contribution arises from the reduction of water into hydrogen and oxygen, since the further reduction of suboxides such as Al_2O, SiO and CO is insignificant.[12,13]

From dew point measurements it was concluded that the water vapour pressure is much lower than that predicted by eqn (8). It should be noted, however, that a flowing system is a dynamic equilibrium, since the products are continually being removed. Thus the real water concentration from the reaction itself will be determined by kinetic rather than thermodynamic considerations.

It appears, therefore, that the phase difference in the products between experiments is caused by the influence of Al from the alumina substrate stabilising beta-phase formation through nucleation or growth. The results from TEM/EDAX would suggest the latter, since a nucleation mechanism would create localised high concentrations of Al and subsequent concentration variations along the whisker length. This has not been observed. On the other hand, the standard model of beta-nitride formation involves growth from a liquid silicide globule at the whisker tip. No such features have been observed on any of these whiskers. Also, whilst it is feasible that the liquifying and nitriding of Si could of itself promote beta-nitride formation, this does not account for beta-phase presence in the product of reacted powder ii (experiment A). Given that the tips of the beta-whiskers observed are arrowed, indicating crystal facets, it is also possible that they grow from the substrate or even sideways from an already formed whisker.

One of the original factors behind the work was that, if the principles underlying whisker formation could be understood, they could also be influenced to promote other morphologies such as platelets. Evidence of beta-platelet growth was observed by Mazdiyasni & Cooke[3] and some similarities are evident in the beta-phase shown in Fig. 3. It is invariably the case in the present work that beta-phase develops in a flat 'blade-like' morphology and the evidence of Fig. 3 is that growth occurs to a limited extent in two directions. Basal plane faulting, for example, is evident in Fig. 3(a) and (b). Thus if growth in the long direction in some way be inhibited while promoting lateral growth, then platelet morphology may be possible.

5 Conclusions

(1) The whisker morphology of beta- and alpha-silicon nitride formed from the gas-phase nitriding of SiO is primarily determined by growth in well-defined crystallographic directions.

(2) The phases nucleated are dictated by the concentration of components such as Al and O in the gas phase during nucleation and growth.

(3) Thermodynamic calculation of the partial

pressure conditions in the gas phase is consistent with the observed formation of beta-phase in the presence of an alumina substrate where the beta-phase is considered to be a dilute beta′-sialon. This is also confirmed by TEM microanalysis.

(4) Controlled platelet morphology may possibly be achieved by control of the nitride surface energy through high-temperature treatments and doping of existing powders to promote and deter growth in certain crystallographic directions.

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