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Some effects of Al and O_2 on the nitridation of silicon compacts

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The influence of a simultaneous decrease of the nitrogen partial pressure and increases of the oxygen potential on the nitridation of Si and Si-6% Al powders has been investigated. The highest final weight gains and densities have been obtained when Si–Al compacts were nitrided in an oxygen enriched atmosphere. These samples were also found to exhibit the most homogeneous microstructures. X-ray diffraction analysis shows that they consist of a β'-Si–Al–O–N solid solution. It is also shown that obtaining only this phase depends, once the nitrogen pressure of the reaction atmosphere has been set, on the adjustment of its oxygen content. Finally, some of the important steps of the overall process, which in the present case appears to be gas flow controlled, are identified and discussed.

1. Introduction

Although a sizeable body of information is available about the preparation of reaction-bonded silicon nitride ceramics, the detailed mechanisms of their formation are still not fully understood, especially with regard to impurity effects, either in the nitriding gas or as additives to the starting silicon powder. Attempts to interpret experimental observations of the overall kinetic behaviour of the compacts [1–6] in terms of models that had been developed for the oxidation of metals [7–9], have been largely inconclusive. It has now become clear [10, 11] that the nitridation of silicon proceeds via some gas-phase reaction(s) as well as solid state diffusion through more or less continuous nitride layers. The active silicon-bearing molecule, however, is still unidentified. Silicon monoxide has for a long time been considered to participate in the formation of α-Si_3N_4 [10, 12–14], but it has also been proposed [15] that the formation of gaseous silicon mononitride was the essential step.

The possible inhibiting effect of oxygen impurities has been pointed out [16, 17] and shown to be related to the presence of protective silica layers on the silicon particles [18]. Proper adjustment of the oxygen partial pressure in the furnace atmosphere allows these layers to be vaporized off and clean silicon to be exposed to the nitriding agent. Similarly, the apparent catalytic action of some impurities of the starting silicon powder (e.g. transition metals) has been noted [19], and recent work suggests that they help in the removal of surface silica as volatile SiO [18, 20]. The influence of aluminium and Al_2O_3 has also been of interest. Si + Al compacts have been nitrided under 1 atm "oxygen free" nitrogen [21]. Aluminium nitride was formed and claimed to be responsible for the somewhat lower bend strength of such samples [21]. The presence of aluminium, on the other hand favours, the formation of the β crystal structure, in preference to α [22] and more recently, it was suggested that the presence of Al_2O_3 in the starting powder could lead to β'-Si–Al–O–N solid solutions [23]. But to our knowledge, no experimental evidence has yet been given.

From the preceding, it seems that the nitridation of pure silicon requires as low as possible an oxygen partial pressure. Experiments suggests that under such conditions, suboxides and volatile impurities are transferred from the tube, muffle or other ceramic ware of the furnace (usually resistance heated), to the samples [11]. This is not constant with time, hardly controllable and, probably one source of property dispersion.

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TABLE I Characteristics of starting powders

Powder	Residual impurties (ppm by weight)
Silicon* ~ 10 μm 99.96% pure	B : 2 Ca : < 10 Cd : 1 Co : < 10 Cr : < 10 Cu : 1 Fe : 10 Mg : 10 Ni : < 15 Pb : < 5 Sn : < 10 Ti : < 10 V : < 5 Zn : 10
Aluminium† ~ 8 μm 99% pure	B : 2 Ba : < 30 Be : < 3 Ca : < 30 Cd : < 4 Co : 13 Cr : 6 Cu : 40 Fe : 220 Ga : 45 Mg : 15 Mn : 35 Mo : 10 Na : < 50 Ni : 30 Pb : 15 Sn : < 5 Ti : 75 V : 15 Zr : 55

*Cerac Inc, Menomonee Falls, Wisc., USA.
†Baudier, Senecourt, France.

It then appears that a suitable oxygen getter, if present within the compacts, might allow the corresponding pressure in the flowing gas to be raised and kept at a high enough level for undesirable interactions between the compacts and their environment to be minimized. The present paper will show that aluminium added to the silicon powder, can play such a role. An alpha-free β'-Si–Al–O–N ceramic is formed and no excess AlN remains in the nitrided samples.

2. Experimental procedure

Chemical analyses and particle sizes of the starting powders are given in Table I. Isostatically pressed compacts (196 MN m^{-2}) were prepared, either from pure silicon or from Si-6 wt % Al, blended 24 h in a "Turbula" mixer. The characteristics of the nitriding atmospheres and temperature programmes are given in Table II as determined during blank runs. In the presence of samples, the same operating conditions were *a priori* chosen, but the temperature and oxygen pressure varied during the reaction as will be discussed. Experiments were conducted with either of two nitriding agents: "pure" N_2 (O_2 and H_2O: 10 ppm each, determined at the tank valve) and a 70% N_2 30% argon mixture. The oxygen content of the latter was set by the equilibrium:

$$2CuO = Cu_2O + \tfrac{1}{2}O_2$$

as the gas passed over a CuO/Cu_2O mixture at 450° C. This temperature, corresponding to an equilibrium $p_{O_2} = 10^{-4}$ atm [24] was arbitrarily chosen so as to provide the compacts with just the theoretical number of O_2 molecules necessary to transform all the Al into Al_2O_3 during our 100 h experiments.

Weight changes during nitridation were recorded. Fig. 1 shows a sketch of the thermobalance*, and of sample position and dimensions.

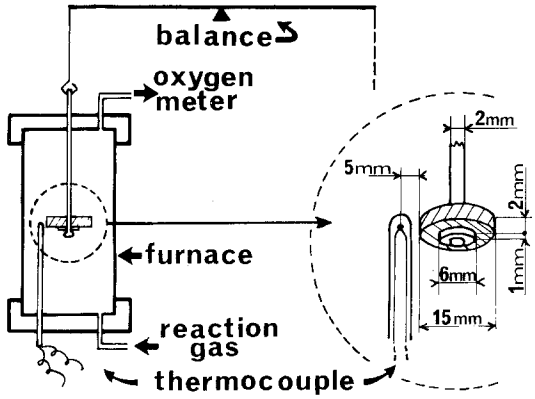

Figure 1 Schematic drawing of thermobalance and sample position.

TABLE II Nitriding conditions during blank runs

Atmosphere	Temperature programme
Total pressure: 1.2 ± 0.02 atm Flow rate: 5 renewals h^{-1} Outflowing N_2 : 18 to 20 ppm O_2 Outflowing 0.7 N_2 –0.3 Ar*: 95 to 100 ppm O_2	heat at constant rate (± 5%): 600° C h^{-1} hold at 1250 ± 3° C heat at constant rate (± 5%): 200° C h^{-1} hold at 1450 ± 3° C cool at 700° C h^{-1} to 600° C

*Oxygen enriched as described in text.

*Ugine-Eyraud, type B60, relative precision: 0.1%.

TABLE III Final densities

Sample	Si + Al(N_2 + Ar)	Si + Al(N_2)	Si(N_2)	Si(N_2 + Ar)
density (g cm^{-3})	2.50 ± 0.05	2.40 ± 0.05	2.35 ± 0.05	2.0 ± 0.05

The same commercial alumina rods and tubings were used throughout†. A sheathed Pt–Pt 10% Rh thermocouple read temperatures at a distance from the sample surface no greater than 5 mm. Oxygen partial pressures of the outflowing gases, were also systematically measured with a ZrO_2 cell meter‡. To test the influence of the furnace environment, the first experiment of the series was repeated at the end and both results will be presented.

Bulk densities of the nitrided samples were measured by a standard water displacement method, after dipping in liquid parafin. Cut surfaces were diamond polished for microstructure observation. X-ray diffraction patterns were recorded on a CGR "theta 60" goniometer, using Cu$K\alpha_1$ radiation on the crushed and ground samples. Accurate positions were determined for the β diffraction peaks, with unreacted silicon serving as an internal standard. Diffracted X impulses were counted for 10 sec at each θ position, this being automatically increased (10^{-2}°) after counting. Microstructural observations and X-ray analyses were always made on parts of the samples that had not been in contact with Al_2O_3 devices.

3. Results

The time variations of sample weight, temperature and oxygen partial pressure of the outflowing gas

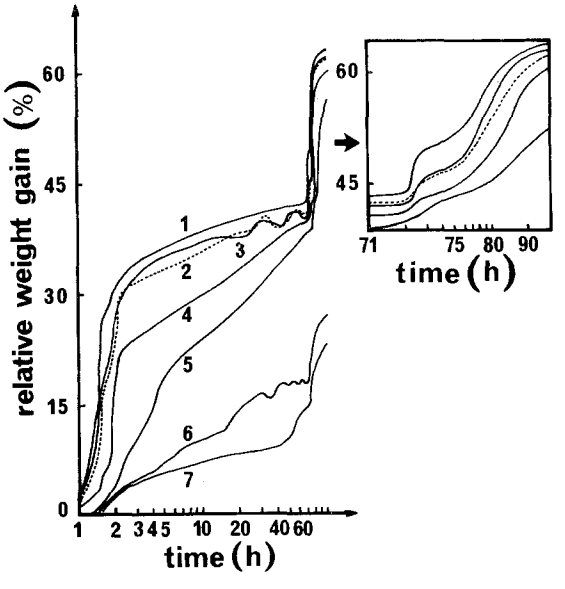

Figure 2 Thermobalance recordings. 1 : loose Si–6% Al (0.7 N_2 + 10^{-4} O_2); 2 and 3 : Si–6% Al (0.7 N_2 + 10^{-4} O_2); 4 : Si–6% Al (1.N_2 + 2 × 10^{-5} O_2); 5 : Si (1.N_2 + 2 × 10^{-5} O_2); 6 : Si (0.7 N_2 + 10^{-4} O_2); 7 : loose Si (0.7 N_2 + 10^{-4} O_2).

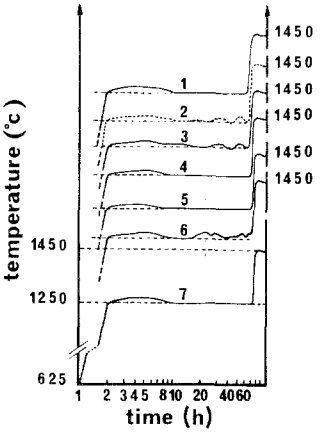

Figure 3 Time variations of temperature during nitridations (1 to 7 as on Fig. 2).

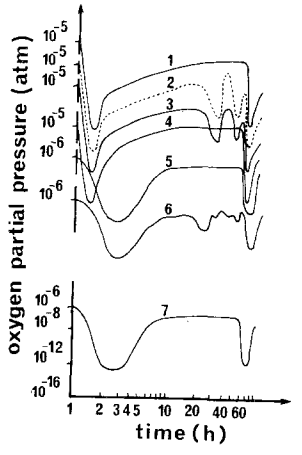

Figure 4 Oxygen partial pressure variations during nitridations (1 to 7 as on Fig. 2).

†Desmarquest et C.E.C., 27000 Evreux, France.
‡Thermo-Lab Instruments, Inc, Glenshaw, Pa, USA.

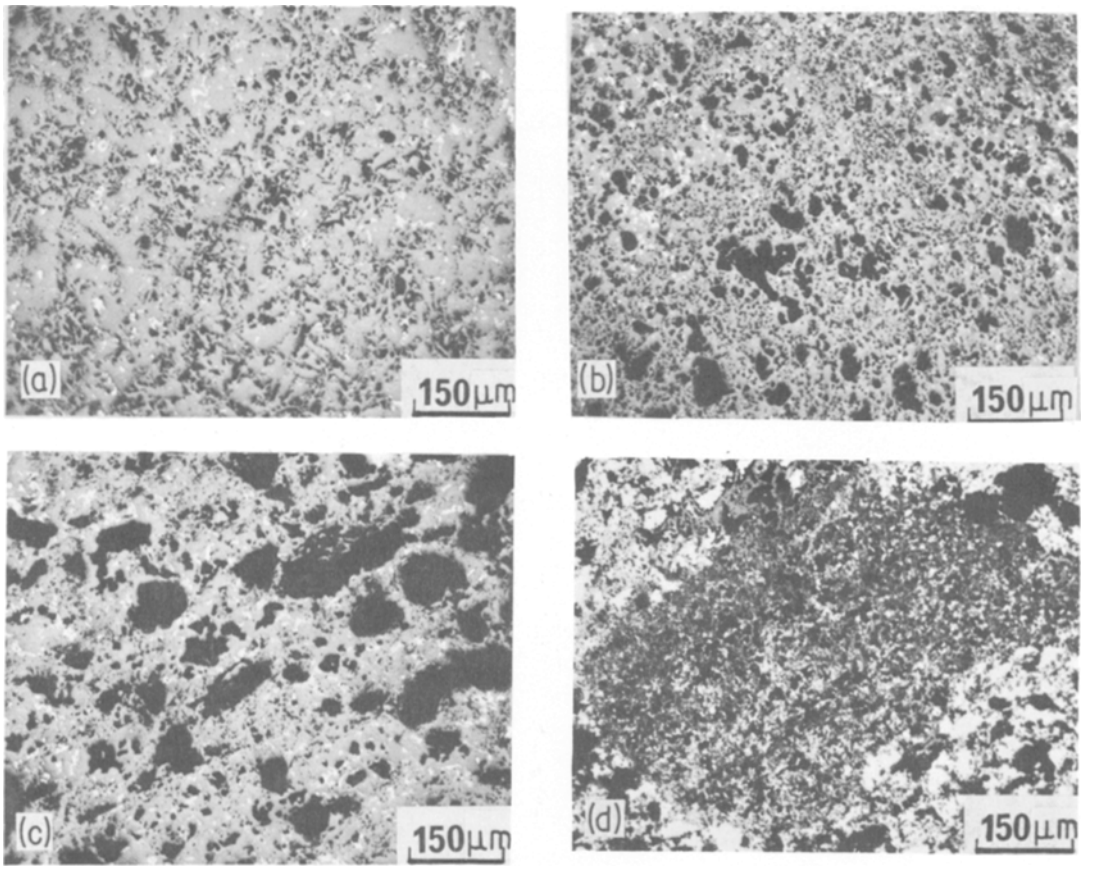

Figure 5 Microstructures of nitrided samples. (a) Si–6% Al ($0.7\ N_2 + 10^{-4}\ O_2$); (b) Si–6% Al ($1.N_2 + 2 \times 10^{-5}\ O_2$); (c) Si ($1.N_2 + 2 \times 10^{-5}\ O_2$; (d) Si ($0.7\ N_2 + 10^{-4}\ O_2$).

during two-stage nitridation experiments, 72 h at 1250° C plus 24 h at 1450° C, are shown in Figs. 2 to 4 respectively. It is clear from Fig. 2, that the reaction kinetics are complex and do not correspond to what could be expected from simple models such as those developed for the oxidation of metals. Alternating weight losses and gains are occasionally observed in some of the samples. This confirms previous findings [1] and again shows the importance of gas-phase reaction contributions [10]. The TGA curves (Fig. 2) and the results of density measurements after nitridation (Table III) show that adding aluminium to the initial silicon powder allows higher final weight gains and densities to be reached. This effect is still more pronounced when the nitridation is carried in the oxygen enriched gas, whereas that mixture appears to be detrimental to pure silicon. The latter observation has already been made [16 17] but the former one will be discussed further. It is also interesting to note that both the promoting (Si + Al) and inhibiting (Si) effects of the oxygen enriched gas are more marked when uncompacted powders are nitrided.

Temperature increases, most probably corresponding to heat evolution from the samples are noticeable at times, during the course of the reaction (Fig. 3). Such increases which can amount to $\simeq 15°$ C (pure Si) or 20° C (Si + Al) can be correlated with oxygen consuming reactions as suggested by Fig. 4. More oxygen is consumed in the aluminium-containing samples than in pure silicon.

The micrographic aspects of the nitrided compacts are illustrated in Fig. 5. The aluminium-containing samples exhibit, a finer, more homogeneous and regular microstructure than those developed from pure silicon. This is particularly striking in the case of nitridation with an oxygen enriched gas. No qualitative difference could be noted between two such samples prepared under the same operating conditions at the beginning and at the end of the present programme respectively. It is thus tentatively concluded that furnace and

TABLE IV X-ray diffraction analyses

	Si (N_2)			Si (N_2 + Ar)			Si + Al (N_2)			Si + Al (N_2 + Ar)			loose Si (N_2)			loose Si + Al (N_2 + Ar)		
Reaction time (h)	2	72	100	2	72	100	2	72	100	2	72	100	2	72	100	2	72	100
Qualitative analyses																		
"AlN"	–	–	–	–	–	–	–	+	+	–	–	–	–	–	–	–	–	–
Al	–	–	–	–	–	–	+	+	–	+	+	–	–	–	–	+	+	–
SiO_2	–	–	–	+	+	+*	–	–	–	–	–	+*	+	+	+	–	+*	+*
AlO_3	–	–	–	–	–	–	+*	+*	–	+*	+*	–	–	–	–	+*	+*	–
Quantitative analyses																		
"β" (%)	0	30	50	0	5	10	40	65	> 95	50	60	> 95	0	< 5	5	50	65	> 95
α (%)	25	30	45	10	20	40	0	0	0	0	0	0	10	> 15	30	0	0	0
Si (%)	75	40	5	90	75	50	60	35	< 5	50	40	< 5	90	80	65	50	35	< 5

*Traces.

environment ageing had no influence on the course of the process in that particular case.

The results of both qualitative and quantitative X-ray analyses performed on the samples at various stages of nitridation, are summarized in Table IV. In every case, information was obtained after 2 h and 72 h at 1250° C and also after 72 h at 1250° C, followed by 24 h at 1450° C. The concentrations of α- and "β"-Si_3N_4 and free silicon are given in mol %, irrespective of sample porosity. When pure Si is nitrided in an O_2-poor atmosphere, some α-Si_3N_4 is formed once and for all during the first few hours of reaction. Oxygen enrichment of the gas yields a higher α/β ratio and even some silica as could be expected. In the Si + Al samples, on the other hand, no trace of α was found after a 2 h nitriding at 1250° C, which of course does not rule out its possible formation at still earlier stages. Aluminium oxide is detected instead, together with β-Si_3N_4 and has disappeared from the diffraction patterns of the final product. Depending on the oxygen content of the nitriding gas, minor amounts of either SiO_2 or of an AlN-type phase are also found in the final products. The β-phase Bragg angles were determined, at the end of the reaction, in the Si + Al samples. Fig. 6 and 7 and Table V show systematic shifts (about -10^{-2}°) with respect to their positions in a pure β-Si_3N_4 standard*, corresponding to a cell constants increase. Such shifts taken indivually are of the

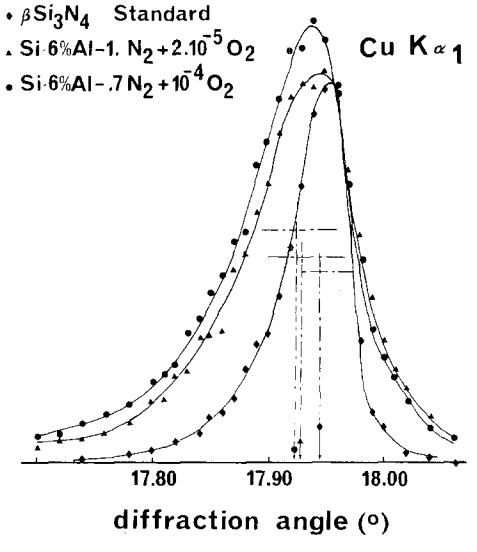

Figure 6 Intensity profiles of β-Si_3N_4-type (2 1 0) lines.

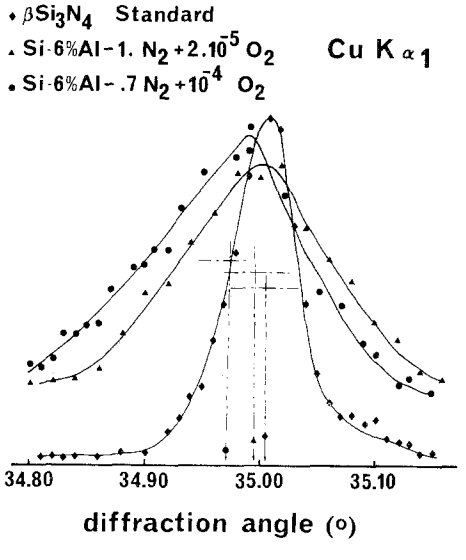

Figure 7 Intensity profiles of β-Si_3N_4-type (3 2 1) lines.

*Cerac Inc, Menomonee Falls, Wisc., USA.

TABLE V Experimental Bragg angles for the β phase in Si + Al samples

(h k l)	$\theta_{observed}$ Si_3N_4 standard*	Observed angle shifts ($\theta_{standard} - \theta$)	
		Si + Al(1.N_2 + 2 × $10^{-5}O_2$)	Si + Al(0.7N_2 + $10^{-4}O_2$)
(2 0 0)	13.438	0.008	0.012
(1 0 1)	16.747	0.020	0.032
(2 1 0)	17.945	0.014	0.016
(3 0 1)	26.010	0.014	0.028
(3 2 0)	31.580	0.010	0.014
(0 0 2)	31.920	0.020	0.026
(3 2 1)	35.005	0.009	0.033
(4 1 1)	36.654	0.010	0.028
(3 3 0)	37.366	0.010	0.018
(2 1 2)	37.787	0.032	0.046

*Cerac Inc, Menomonee Falls, Wisc., USA.

order of the experimental uncertainties, but in the authors' opinion it is quite unlikely that all experimental errors should have fallen in the same direction. It also does not seem fortuitous that the use of an oxygen enriched atmosphere seemingly amplifies them.

4. Discussion

4.1. Phase and microstructure control

The experimental results show that a β'-Si–Al–O–N solid solution is formed during the nitridation of Si + Al compacts when some oxygen is also present in the reaction atmosphere. The corresponding samples exhibit the highest densities and contain the smallest amount of unreacted silicon of the present series. At fixed temperature and total pressure, application of the phase rule to the pseudoquarternary Si_3N_4–AlN–Al_2O_3–SiO_2 shows [25] that equilibrium of β' having a fixed Si/Al ratio with any other condensed phase depends upon one parameter only and may therefore be determined once the nitrogen partial pressure has been chosen. Similarly, given that pressure, the composition of β' in equilibrium with, e.g. an AlN type phase [27] is fixed. A gradual increase of the oxygen partial pressure will therefore tend to shift the equilibrium, first towards an enrichment of β' in AlN and Al_2O_3: the amount of the AlN-type phase will be reduced and an oxygen-rich phase such as SiO_2 may even be formed, if the oxygen partial pressure becomes too high to allow equilibrium coexistence between β' and one of the other oxynitride phases [27, 28]. An oxygen potential decrease on the other hand, will have opposite effects and AlN-type phase(s) will be stabilized and co-exist with an oxygen-poor β'-Si–Al–O–N.

Fig. 8 shows the diffraction patterns of Si–6% Al compacts nitrided as previously described in the 0.7 N_2 0.3 Ar mixture with different residual oxygen pressures. It is clear that a single phase ceramic may be obtained when the oxygen content of the reactive gas has been properly adjusted. It must, however, be pointed out that the optimum oxygen potential corresponding to given nitrogen pressure and aluminium content of the powder, cannot *a priori* be determined. It must be adjusted by trial and error for each type of compact, powder or shape. In the present case, the transfer of the reacting gas within the porous samples played a dominant role: more silica was found after nitridation of loose Si + Al powders, than in the corresponding compacts, everything else being the same.

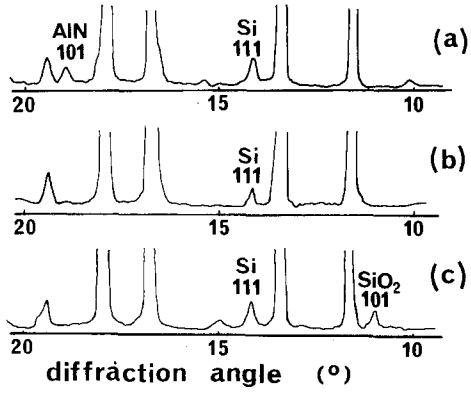

Figure 8 Diffraction patterns of nitrided Si–6% Al compacts (Cu$K\alpha_1$). (a) 5 × 10^{-5} atm O_2; (b) 8 × 10^{-5} atm O_2; (c) 10^{-4} atm O_2.

It is beyond the scope of this paper to give a detailed account of microstructure development in our Si + Al samples, which would necessitate a discussion on the influence of nitrogen pressure. It may simply be pointed out that a reduced N_2 partial pressure allows fine homogeneous microstructures to be produced. Other samples have been prepared under one atmosphere N_2 containing various amounts of oxygen. Larger pores and sometimes gross structural heterogeneities between the surface and interior of the samples have been observed, presumably due to erratic kinetics. It is our feeling that the same kind of interpretation that has recently been proposed [11] for microstructure development in pure silicon compacts is also qualitatively applicable to our case.

4.2. Comments on the reaction mechanism

The detailed chemical steps that lead to reaction bonded silicon nitride ceramics still seem insufficiently understood. It is however, confirmed here that α-Si_3N_4 is formed first in pure Si compacts, β-Si_3N_4 appearing only when the reaction has advanced somewhat, as recently suggested [14]. The inhibiting effect of oxygen, thought to form protective silica layers [18] is also confirmed by our observed correlation between larger SiO_2 and smaller nitride contents in loose silicon than in the same compacted powder.

When aluminium is added to silicon, a first important step in the nitridation process takes place at relatively low temperatures ($\approx 660°$ C) when some of the molten aluminium particles oxidize (cf. Table IV). Then, knowing the gas flow rate and assuming that oxygen participates in no other reaction, from the initial p_{O_2} decrease of the outflowing gas (Fig. 4) it is possible to distinguish between the contributions of silicon nitride and Al_2O_3 formation to the overall weight increase. Fig. 9 shows the resulting curves when Si.6% Al is nitrided in an oxygen enriched atmosphere. After only a 3 h soaking time at 1250° C, 1/3 of the initial aluminium content of the sample has already been converted*. This interpretation is consistent also with the temperature increase, recorded in the close vicinity of the sample surface (Fig. 3). As Table VI shows, there is a good agreement between the observed ΔT values which have been found reproducible in other systematic

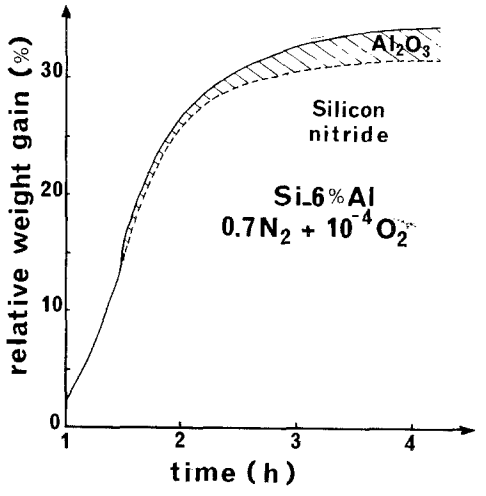

Figure 9 Respective contributions of silicon nitride and alumina to the overall weight gain.

experiments and those estimated from the approximate equation [26]:

$$\Delta T \approx \frac{(r+h)Q_v}{8\sigma T^3}$$

where σ = Stefan's constant; r and h = sample radius and height respectively (Fig. 1); Q_v heat released by the reaction in the unit of sample volume and time. The above relation assumes that steady state has been established and all the calories are radiated off. In our experimental set up, heat can be evacuated conductively to the alumina device used as a sample holder (Fig. 1). Steady state is thus reached only after a few hours, corresponding to the time needed to thermally equilibrate both sample and holder.

The alternating weight gains and losses which are observed (Fig. 2) during the second half of the 1250° C stage when an oxygen enriched atmosphere is used, are paralleled by similar temperature and oxygen pressure fluctuations. The overall behaviour can presumably be interpreted as follows. Consider an element of the reaction front, e.g. the end of a pore channel. Oxygen is eaten up first to form Al_2O_3 or SiO_2 as just described. The p_{N_2}/p_{O_2} ratio then increase up to a value allowing silicon nitride to be formed. There is subsequently a local depression and more gas is supplied from the outside, making the p_{N_2}/p_{O_2} ratio to decrease again down to a value where nitridation stops.

*A qualitatively similar behaviour is noticeable when pure Si is nitrided in the O_2 enriched gas: SiO_2 is formed.

Then a new oxidation step sets in as before, provided there is still enough gettering element available (i.e. Al or Si to form Al_2O_3 and SiO_2 respectively), and so on. So far the system should have experienced no weight loss but a time will come when the oxygen getter will be used up at that very place which we are considering. The previously formed silicon nitride will, therefore, have to act as a replacement for Al or Si and will be oxidized according to:

$$Si_3N_4 + \tfrac{3}{2}O_2 \rightarrow 3SiO + 2N_2. \quad (1)$$

Assuming that the maximum SiO partial pressure in the system is fixed at 1250° C by the equilibrium:

$$Si(s) + SiO_2(s) = 2SiO(g),$$

i.e. $\approx 2 \times 10^{-3}$ atm [18], then Reaction 1 may occur if:

$$\frac{(p_{O_2})^{3/2}}{(p_{N_2})^2} \geqslant (2 \times 10^{-3})^3 \times K_1 \quad (2)$$

where K_1 is the corresponding equilibrium constant; $K_1 = 10^{-14}$ at 1250° C [29]. Condition 2 then becomes:

$$p_{O_2} \geqslant 10^{-15} \times (p_{N_2})^{4/3}.$$

This shows that if $p_{N_2} = 1$ atm, then 10^{-15} atm oxygen would be sufficient to allow Reaction 1 go from left to right. If p_{N_2} decreases, so does the corresponding equilibrium oxygen partial pressure. Reaction 1 is thus thermodynamically possible in our system, at least locally, and brings about a weight loss until it stops because enough nitrogen has been generated to bring chemical equilibrium back. Such a mechanism may also be responsible for the development of microstructural heterogeneities (Fig. 5d) when inadequately controlled. It is macroscopically observable because of the sizeable compact resistance to gas flow. The marked differences between the behaviour of loose and compacted powders under otherwise identical operating conditions, are thought to support this conjecture.

5. Conclusion

The experimental evidence presented in this paper is believed to show that:

(1) nitriding an Si + Al mixture can lead to a β'-Si–Al–O–N solid solution as a result of reaction between alumina formed at the beginning of the nitridation and simultaneously formed β-Si_3N_4;

(2) obtaining only the β'-phase depends, once the nitrogen partial pressure has been fixed, on the choice of the oxygen partial pressure. A lack of oxygen leads to an additional "AlN" type phase, whereas too much oxygen leads to silica;

(3) in the present experimental conditions, the process appears to be gas flow controlled;

(4) in practice, aluminium additions to the starting silicon powder help relieve some operating difficulties: the oxygen content of the reacting gas can be reaised to easily controllable levels.

Acknowledgements

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TABLE VI Observed and estimated maximum temperature differences.

Sample	Observed (° C)	Estimated from reaction (° C)		
		$3Si + 2N_2 \rightarrow Si_3N_4$	$Si + O_2 \rightarrow SiO_2$	$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3$
Si ($0.7 N_2$ 0.3 Ar + $10^{-4} O_2$)	15 ± 3	~ 1	15	–
Si–6% Al ($0.7 N_2$ 0.3 Ar + $10^{-4} O_2$)	20 ± 3	~ 1	–	22

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