Optimization of time–temperature schedule for nitridation of silicon compact on the basis of silicon and nitrogen reaction kinetics

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Abstract. A time–temperature schedule for formation of silicon–nitride by direct nitridation of silicon compact was optimized by kinetic study of the reaction, $3Si + 2N_2 = Si_3N_4$ at four different temperatures (1250°C, 1300°C, 1350°C and 1400°C). From kinetic study, three different temperature schedules were selected each of duration 20 h in the temperature range 1250°–1450°C, for complete nitridation. Theoretically full nitridation (100% i.e. 66·7% weight gain) was not achieved in the product having no unreacted silicon in the matrix, because impurities in Si powder and loss of material during nitridation would result in 5–10% reduction of weight gain.

Green compact of density < 66% was fully nitrided by any one of the three schedules. For compact of density > 66%, the nitridation schedule was maneuvered for complete nitridation. Iron promotes nitridation reaction. Higher weight loss during nitridation of iron doped compact is the main cause of lower nitridation gain compared to undoped compact in the same firing schedule. Iron also enhances the amount of β-Si_3N_4 phase by formation of low melting $FeSi_x$ phase.

Keywords. Reaction sintered silicon nitride; nitridation; reaction kinetics.

1. Introduction

Formation of reaction sintered silicon–nitride products by direct nitridation of silicon powder compact has economical advantage compared to other forming processes for near net shape formation (Haggerty 1997). The only difficulty is the requirement of long time for complete nitridation. To overcome this difficulty, methods have been developed using high purity silane derived silicon powder (Gregory *et al* 1987; Sheldon and Haggerty 1989) which produced nitridation products in short time. They are costly and relatively tough for using sub-micron size Si powder in inert atmosphere. Previous work on reaction schedule for reaction bonding formation of silicon nitride showed a long-time nitridation reaction schedule under normal nitriding condition (Mangels 1977; Danforth and Richman 1983; Heinrich 1987; Barsoum *et al* 1989; Zhang 1996). Complete nitridation (100%) of silicon via the reaction, $3Si + 2N_2 = Si_3N_4$, would occur by a theoretical weight gain of 66·7%, but the practical weight gain (after an apparently complete reaction) was found to be much lower in presence of O_2.

In the present work, a study on nitridation kinetics of silicon powder compacts of different green densities was performed in 1 atmosphere N_2 at different temperatures. Based on the results of nitridation of the compacts, the process of nitridation was optimized following three different firing schedules as discussed in the next section to complete the nitridation in short time. The process was explained in terms of compactness of the powder, additive (Fe) content and associated reaction kinetics.

2. Experimental

Commercial Si powder of ~ 97·5% purity (after milling) was used as starting Si powder containing Al_2O_3: 1·22% (from alumina ball used for grinding), Fe: 0·41%, Ti: 0·22%, Ca: 0·53%, (Na + K): 0·1% by weight as major impurities. Si powder (Indian Metals and Ferroalloys, Bhubaneswar) was ball-milled to a mean particle diameter of ~ 4·83 μm. Cylindrical pellets of ~ 20 mm dia and 5–6 mm thickness were fabricated at 15 MPa and 50 MPa pressure. Iron powder (1% by weight and 98·2% purity) was thoroughly mixed with Si powder in acetone for 1 h and pellets of iron doped Si were made at 50 MPa pressure. For kinetic study, nitridation of silicon compacts was performed at 1250°C, 1300°C, 1350°C and 1400°C in a controlled atmosphere vacuum tubular furnace. The rate of increase of temperature was kept same during the study and nitridation weight gain was determined for certain interval of time. From kinetic study, three different temperature schedules were selected as discussed in the next section. The extent of nitridation after firing in a particular schedule was determined by weight gain

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measurement. Percent weight gain was expressed as '% nitrided' (66·7% weight gain = 100% nitrided). Densities of both green and nitrided samples were determined from dimensions and water immersion technique, respectively. Quantitative estimation of phases were determined by quantitative X-ray analysis method outlined by Gazzara and Messier (1977). Microstructure of the interior surface of the polished samples was observed by incident light optical microscope (Ortholux II POL BK, Leitz, Germany).

3. Results and discussion

A linear relationship between the square of 'fraction nitrided' vs 'time' was observed by Biswas and Mukerji (1980) during the kinetic study of undoped Si powder in N_2. The reaction kinetics of Si and N_2 (Atkinson and Moulson 1976) doped with 1% Fe, Ni and Cr (at 1370°C) showed increased formation of silicon nitride compared to undoped Si. The same result was observed by Messier and Wong (1973) with 1% iron doped Si compact.

Weight gain (in terms of fraction nitrided) of Si and N_2 reaction at different temperatures and pressures of green compaction is shown in figures 1a and b in which parabolic nitriding kinetics is observed as,

$$\alpha^n = kt,$$

where α is fraction nitrided, k is a constant and t, the reaction time. The value of n, however, changes with forming pressure of pellets i.e. compactness of the Si particles. In the present case $n \approx 2$ seems to fit well for pellets pressed at 15 MPa. But for the pellets pressed at 50 MPa, the value of 'n' lies between 2 and 3. Figure 2 shows the extent of nitridation (obtained from reaction kinetics) of green compacts pressed at 15 MPa and 50 MPa at different temperatures (viz. 1250°C, 1300°C, 1350°C and 1400°C) for 10 min and 240 min duration. It is seen from figure 2 that 10 min nitriding at 1400°C would result in an additional 24% nitrided product compared to the same (pressed at 15 MPa) sample fired at 1250°C. This increment is about 32% for sample pressed at 50 MPa. When nitriding reaction time is increased from 10 min to 240 min (figure 2), increment of nitridation for sample (pressed at 15 MPa) fired at 1250° and 1300°C was about 11% and 16% respectively, whereas, such increment was about 21% and 23% for same sample fired at 1350° and 1400°C. Similar is the case for samples pressed at 50 MPa, in which more than 30% increment (nitridation gain) was observed from 10 min to 240 min reaction time. Therefore, firing temperature above 1350°C would always favour nitride formation in short duration of firing time instead of firing at lower temperature. Initial fast reaction of Si and N_2 may result in quick rise of temperature near the melting point of Si (1410°C) with a result of unfavourable melting of Si before complete nitridation,

because heat of reaction of Si nitridation is -724 KJ mol^{-1} (JANAF 1971). Further nitrogen diffusion would be stopped due to closing of pores or channels by molten Si. On considering the above fact, three different firing schedules were selected each of duration 20 h as below:

Schedule A: (1250°–1400°C) × 2 h + 1400°C × 18 h.

Schedule B: 1350°C × 17 h + 1400°C × 3 h.

Schedule C: (1250°–1400°C) × 2 h + 1400°C × 14 h
                              + 1450°C × 4 h.

In schedules A and C, slow rise of temperature from 1250°C to 1400°C was maintained (about 1°C/min rise from 1300°–1400°C) to avoid melting of Si and
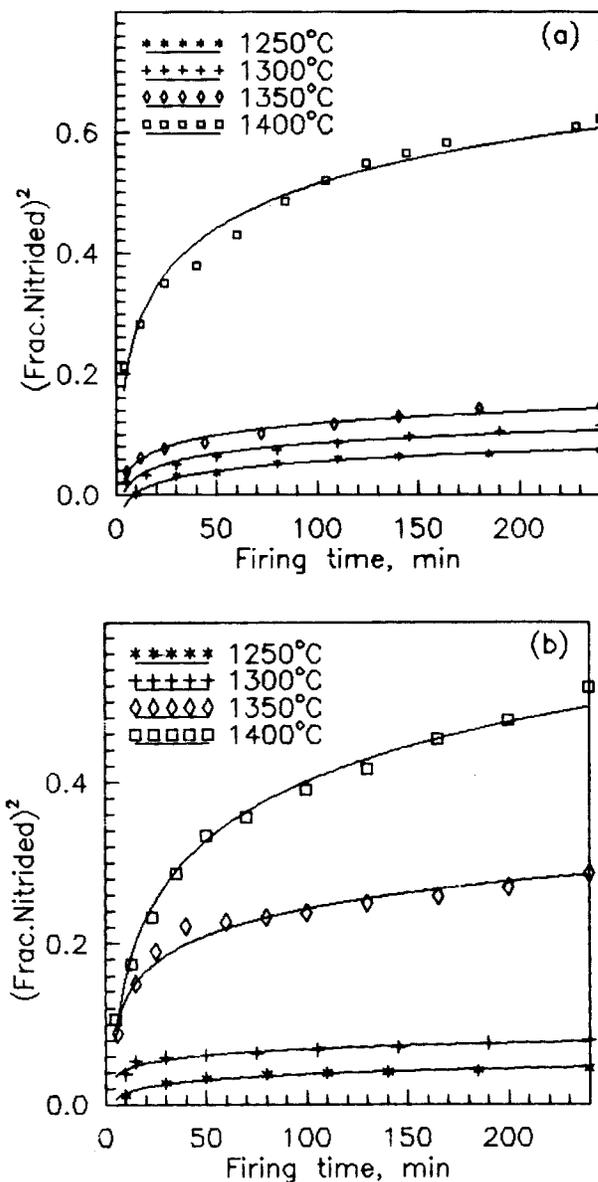

Figure 1. Nitriding kinetics of Si compact pressed at (**a**) 15 MPa and (**b**) 50 MPa at different temperatures.

completed in 2 h duration. This precaution was taken in this study to avoid fast nitridation reaction with a result of quick rise of local temperature above the melting point of Si. Schedule C differs from A as firing was done above the melting point of Si (at 1450°C) for 4 h duration to enhance nitridation.

Table 1 shows the results of nitridation in three schedules. Densities of green compact made by 15 MPa pressure are lower (< 66% T.D.) compared to compact (> 66·5% T.D.) pressed at 50 MPa. For iron doped (1%) samples, slightly higher % of relative green density was achieved compared to undoped compact. The % relative density (% T.D.) of 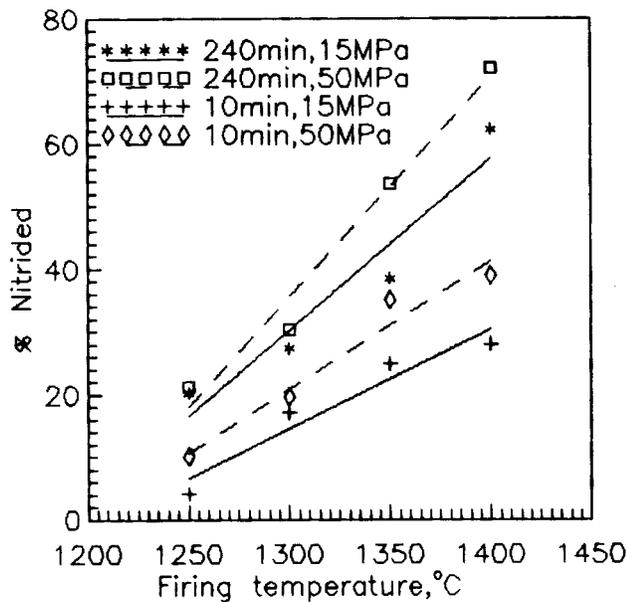nitrided products depend directly on both the green density as well as % nitridation. Nitrided density is higher for samples (of similar nitridation) having higher green density (c.f. samples 2 and 3 in table 1). The higher amount of nitridation of nitrided samples (pressed at 15 MPa) compared to nitrided samples (pressed at 50 MPa) are responsible for the lower density (i.e. higher porosity) of the green preform, which facilitates the nitrogen diffusion into the interior of the compact as a result of more nitridation. From table 1 it is evident that, compact having low green relative density (< 66% T.D.) can be fully nitrided by any one of the three firing schedules. On the other hand, for specimens of high green density (> 66·5% T.D.) schedule B is not suitable for complete nitridation and results in poor nitridation (< 80%), which indicates the presence of unreacted Si in the products (samples 6 and 10 in table 1). Theoretically full nitridation (100% i.e. 66·7% weight gain) products were not achieved in all the nitridation reactions where free silicon is nil or in negligible amount. The impurities in the Si powder (Riley 1977) and loss of materials during nitridation (Boyer *et al* 1977; Mitomo 1977) are the main causes of apparent low '% nitrided' values.

A linear and almost linear (except for samples pressed at 15 MPa) relationship between '% nitrided' vs '% T.D.' was observed for Fe-doped and undoped nitrided samples respectively (figure 3). The % T.D. of fully nitrided products depend on their green compact density as well as % nitridation as stated earlier. The wide variation of green density (64·8–65·7%) and % nitridation (89·6–92·2%) of sample pressed at 15 MPa results in a non linear relationship as shown in figure 3. Scattered low values of relative densities are observed for samples (pressed at 50 MPa) having considerable amount of unreacted Si (samples 6 and 10). Relatively high nitrided densities (80–81%) of Fe-doped samples-like (sample pressed at 15 MPa (80·2%)) reveal that Fe-doping is favourable for complete nitridation in dense green compact.

Figure 2. Extent of nitridation of green preform (pressed at 15 and 50 MPa) for 10 min and 240 min duration.

Table 1. Characteristics of nitrided samples.

Sample no.	Firing schedule	% Relative density		% Nitrided	Unreacted Si	Phases present (%)		
		Green	Nitrided			α-Si$_3$N$_4$	β-Si$_3$N$_4$	Si$_2$N$_2$O
1	A	65·6	80·2	92·2	trace	44·0	37·5	18·5
2	B	65·5	79·1	89·7	do	76·0	24·0	trace
3	C	65·7	80·0	89·75	do	62·6	32·3	5·1
4	A	64·8	77·6	89·6	do	67·0	23·1	7·9
5	A	67·3	78·75	88·9	0·6	79·5	19·9	trace
6	B	66·9	73·35	70·8	5·1	70·1	24·8	do
7	C	67·2	78·7	83·75	1·5	57·8	29·7	11·0
8	A	67·6	78·45	81·75	0·6	57·6	38·3	3·5
9	A	68·2	80·8	82·65	0·5	60·7	26·8	12·0
10	B	67·9	76·3	77·5	3·6	47·2	36·9	12·3
11	C	68·1	80·65	82·4	trace	57·0	43·0	trace
12	A	67·1	80·15	81·5	do	75·0	18·9	6·1

Sample nos 1–4 (pressed at 15 MPa), 5–8 (pressed at 50 MPa) and 9–12 (Fe-doped and pressed at 50 MPa).

3.1 *Effect of iron*

Iron-doped samples (9–12) may be compared with similar undoped samples (5–8), as both were made at same pressure (50 MPa). Apparently iron addition do not affect nitridation weight gain ('% nitrided' is low compared to undoped samples), but better nitridation would result in a particular firing schedule when followed by both doped and undoped specimens. Low nitridation gain may be accounted for by the loss of material during nitridation. Weight loss at the nitridation stage was measured by Boyer *et al* (1977) which indicated that SiO formed (in the presence of iron) via the reaction $Si + SiO_2 \rightarrow 2SiO$, does not react within the compact. So the vapour phase reactions involving SiO play no significant part in the reaction system and supposed to be condensed as α-Si_3N_4 elsewhere in the reaction system. Iron induced devitrification of silica layer resulted in active oxidation of silicon at high temperature to generate SiO, which further react with N_2 gas to form α-Si_3N_4 and/or oxynitride (Barsoum *et al* 1989). The unreacted Si is found in higher amount in nitrided samples of undoped compact rather than in Fe-doped compact (c.f. samples 6 and 10, 5 and 12 in table 1). The high '% relative density' (nitrided) also supports the possibility of complete nitridation reaction (figure 3). Most significant effect of Fe doping was observed by addition of 50 ppm to 1 w/o Fe to Si powder (Atkison and Moulson 1976). Acceleration of nitridation by Fe may be due to (i) disruption and/or removal of silica layer on the Si particles (Atkinson and Moulson 1976) and (ii) formation of a low melting (1208°C) $FeSi_x$ alloy, since it 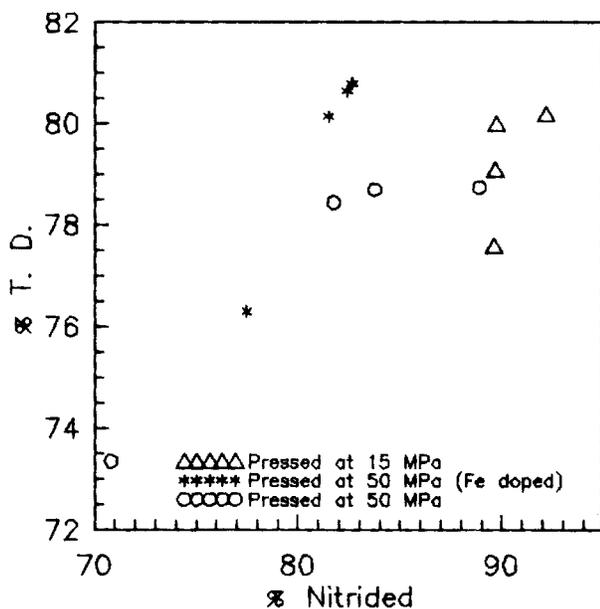has been shown that Fe-induced enhanced nitridation ceases below 1200°C, the Fe–Si solidus temperature (Jayatilaka and Leake 1977). After removal of the oxide film, iron nucleates extra nitride growth at Fe–Si melt sites (Boyer *et al* 1977). Zhang and Marino (1995) obtained ~ 6% excess nitrided product (1350°C, 20 h) using 1 vol% Ni_3Al in Si and suggested the accelerating effect of Ni_3Al is to form a low melting liquid phase of silicious intermetallics.

Optical microscopic observations of finely ground interior surface of the RBSN specimens (both undoped and Fe-doped, fired in the same schedule C) reveal that the matrix is composed of light grey silicon nitride grains with pores (black) distributed throughout the matrix. Unreacted Si particles (bright in the photograph) are found to scatter. Unreacted Si is almost negligible in Si_3N_4 matrix of Fe-doped sample (figure 5) compared to undoped sample (figure 4). The matrix of undoped Si_3N_4 is more
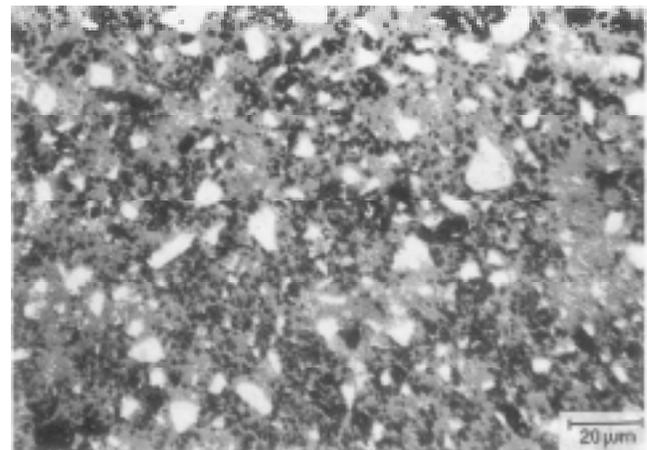

Figure 4. Optical photomicrograph of undoped (pressed at 50 MPa) nitrided (schedule C) sample, showing unreacted Si (bright) and finely distributed pores (black) in the matrix.
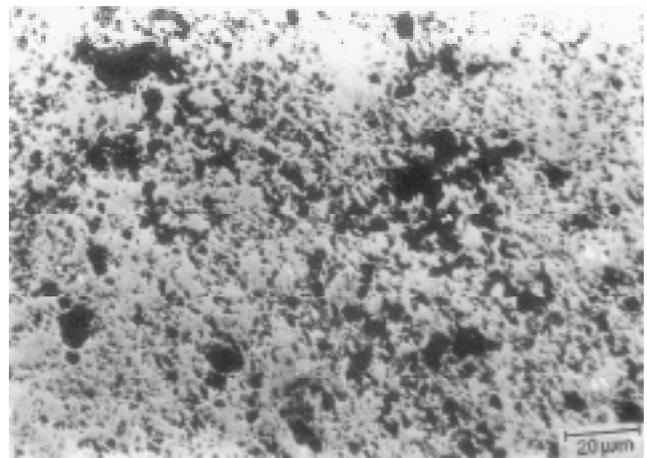

Figure 5. Optical photomicrograph of Fe-doped (pressed at 50 MPa) nitrided (schedule C) sample, showing absence of unreacted Si but some large pores (black) in the matrix.

Figure 3. Relationship between '% nitrided' vs '% T.D.' of undoped and Fe-doped RBSN specimens.

homogeneous (with finely distributed pores) compared to Fe-doped matrix in which some large pores are found to scatter and are possibly formed by $FeSi_x$ melt (Zhang and Marino 1995; Zhang 1996).

Another effect of iron is to increase the amount of β-Si_3N_4 phase in silicon nitride matrix. Amount of β-Si_3N_4 is higher in Fe-doped sample compared to undoped sample when prepared by same firing schedule (c.f. samples 5 and 9, 6 and 10, 7 and 11 in table 1). According to Longland and Moulson (1978), vapour phase reaction between Si and N_2 bearing species lead only to α-Si_3N_4 or amorphous silicon nitride, the direct reaction between solid Si and N_2 as well as reaction involving a suitable liquid phase lead to β-Si_3N_4. β-Si_3N_4 precipitates within $FeSi_x$ liquid and the rate of growth is determined by the solubility and diffusivity of N_2 in $FeSi_x$ (l). Such β-growth is directly proportional to the amount of liquid, i.e. iron content (Boyer and Moulson 1978). The same workers were able to link β-Si_3N_4 growth with the presence of an $FeSi_x$ phase by nitriding compact of high purity Si with Fe-doped. According to Messier and Riley (1977), growth of β-Si_3N_4 from a liquid phase is a process identical to the phase transformation of α- to β-Si_3N_4 from the liquid after the solution of α-Si_3N_4 in the silicate melt during hot pressing.

4. Conclusions

(I) Nitridation kinetics of compacted Si bears a relation of $\alpha^n = kt$ (α-fraction nitrided in time t, k being constant), where $n \geq 2$ when compacted at pressure more than 15 MPa.

(II) Kinetic study of silicon nitrogen reaction reveals that initial nitridation is quite rapid at 1250°C but firing temperature must be raised above 1350°C after few hours (~ 2 h) in order to increase nitridation rate and hence to reduce firing time.

(III) The extent of nitridation depend on the green density of the compact. Full nitrided products are obtained in fixed time (20 h in the present case) for green compact of low relative density (< 66% T.D.). The same observations are found for compact of high green density (> 66·5%

T.D.), when nitridation is carried out for long time (~ 18 h) at higher temperature (1400°C–1450°C).

(IV) Iron (1 w/o of Si) promotes nitridation reaction and enhances the amount of β-Si_3N_4 phase.

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