Ceramics International 22 (1996) 27–31
© 1996 Elsevier Science Limited and Techna S.r.l
Printed in Great Britain. All rights reserved
0272-8842(95)00049-6
0272-8842/96/$15.00

Role of Pore Structure in the Nitridation of Silicon/Silicon Nitride Compacts

Jow-Lay Huang, Shun-Wen Chen & Horng-Hwa Lu

Department of Material Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan

&

Wen-Hu Chan

Department of Mechanical Engineering, Chinese Military Academy, Taiwan

(Received 19 September 1994; accepted 14 April 1995)

Abstract: The effects of the pore-size distribution in silicon compacts on the nitridation kinetics were investigated. Various compositions of silicon nitride inert filler materials were added to silicon compacts to control pore structure. Samples having a higher pore volume and a larger pore diameter reacted faster at temperatures below 1200°C, the reaction started at lower temperatures and the samples showed more weight gain and less residual silicon. The pore value was reduced and the strength was improved by decreasing nitridation rate.

1 INTRODUCTION

One obstacle to the commercial application of advanced structural ceramics is their expensive post-machining cost. For this reason the near-net shape-forming capability of the reaction bonding technique has attracted a significant amount of attention during the past decades. Reaction sintering of silicon is of particular interest to ceramic researchers not only because of the good mechanical and chemical properties of reaction bonded silicon nitride (RBSN) but also because silicon is a model material utilized for other covalent bonded non-oxide ceramics.

One drawback of the reaction bonded silicon nitride is its porous structure upon nitriding that degrades strength, toughness and oxidation resistance. Two different approaches have been made recently to resolve this problem. One is the incorporation of a second-phase material, such as SiC whiskers[1] or fibres,[2,3] in order to improve strength, stiffness, toughness, creep resistance and to enhance reproducibility and defect tolerance. The other approach is directed towards the improvement of the microstructure by controlling the particle size distribution and the purity of the raw material,[4] catalyst,[5] atmosphere,[6] sintering routes,[7,8] or the post-sintering process.[9]

The formation of Si_3N_4 from silicon is accompanied by a volume expansion of 22% which is primarily internal. This expansion causes a closure and a change of the internal porous network during nitriding, which reduces the penetration of the nitriding gas into the compact and the ability of gaseous reaction products to escape. The pore-size distribution of the compact is therefore the dominant factor which controls the permeability and the completion of the reaction.[8]

Some reports involving the effect of porosity on nitridation have been published.[10–12,15–17] Gregory and Riceman[12] were able to enhance the reaction rate through the use of large Si_3N_4 particles as an inert filler to keep the nitridation paths open during nitridation. A substantial decrease in reaction time was observed by Huang and Simms[10] by the incorporation of MgO/CeO dopants and SiC whiskers into silicon powders prior to nitridation. A different approach was used in this study in order to investigate further the effect of the pre-nitriding pore-size distribution on the nitriding kinetics. Instead of using silicon powders with different particle size distributions as reported elsewhere,[16,17] various compositions of fine silicon nitride particles (0·6 μm in size) were added as inert filler to control the pore structure in the silicon compacts. The influence of pore volume and size distribution on weight gain, residual silicon and reaction rate were studied in this report.

2 EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Silicon (Cerac Inc., 99·999 purity) powder was attrition milled in ethanol with high purity alumina balls until an average size of 5 μm with a narrow size distribution was obtained. Various fractions of fine Si_3N_4 powder (Herman C. Starck, LC 12, 0·6 μm) corresponding to 10, 20 and 40 wt% of silicon powder, and Fe_2O_3 (0·5 wt.%, Wako Pure Chemical Industries Ltd) were added to the silicon and milled in a polyethylene container for one hour with a ball : charge : ethanol ratio of 7.5 : 1 : 10. The fine Si_3N_4 powder was added as an inert filler in order to control the pore-size distribution. Fe_2O_3 was used as a nitridation catalyst. The slurry was dried in a rotating evaporator, ground with an alumina mortar and pestle, and screened through a 100-mesh screen in order to reduce the agglomerate size.

Samples containing 0, 10, 20 and 40 wt% of Si_3N_4 in equivalent amount of silicon (1 gram) were cold isostatic pressed to fabricate pellets of 12·7 mm in diameter and 4·5 mm in height.

2.2 Nitridation

Samples were placed in a hot-pressed Si_3N_4 crucible and nitrided in an alumina tube furnace in a flowing gas mixture of 4% H_2, 21% H_e and 75% N_2.[10]

The gas mixture was purified by passing it through a U-tube containing P_2O_5 and silica gel to remove moisture. The amount of gas prior to and after passing through the furnace was monitored by two separate mass flowmeters (Teledyne HFM-201) which were also interfaced with a personal computer. In this way it was possible to acquire, store and analyse nitriding data such as nitrogen gas consumption and corresponding temperatures, accumulated time, reaction rate and percentage of completed reaction.

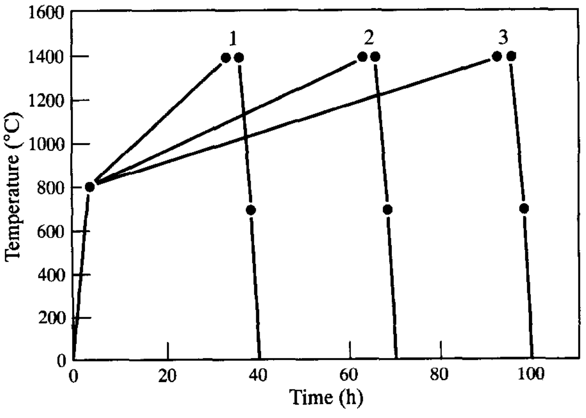

Fig. 1. Temperature profiles in nitridation.

Samples were nitrided at a heating rate of 20°C h^{-1} up to 1400°C until no further nitrogen gas consumption was detected. The nitriding profiles are shown in Fig. 1. Route 1 in Fig. 1 was the major profile used in this study unless otherwise specified. Routes 2 and 3 were used for investigating the effects of nitridation rate on the pore structure.

2.3 Measurement of pore-size distribution

Pore-size distribution of samples before and after nitriding were measured using mercury porosimetry (Micromeritics Instrument Corp. AUTO PORE II 9220). The Washborn equation was used for calculation.

2.4 Determination of residual silicon

Nitrided samples were pulverized and ground to fine particles, then soaked in nitric acid until the residual Si was completely dissolved. The quantity of residual Si was then calculated from the weight difference before and after the acid treatment.

2.5 Strength

Green compacts with dimensions of 3 × 4 × 40 mm were nitrided for 40, 70 and 100 h (Fig. 1). Flexural strength (four-point) was measured with a universal testing machine (Instron 8562) at a cross-head speed of 0·5 mm min^{-1}. The inner and outer spans were 20 mm and 40 mm, respectively.

3 RESULTS AND DISCUSSION

3.1 Stability of Si_3N_4 filler

Silicon nitride filler was pressed and sintered under the same experimental conditions (Fig. 1, Route 1)

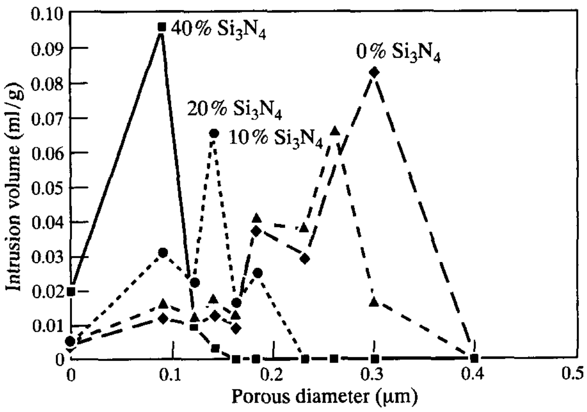

Fig. 2. Intrusion volume of mercury versus pore diameter for Si compacts containing various amounts of Si_3N_4

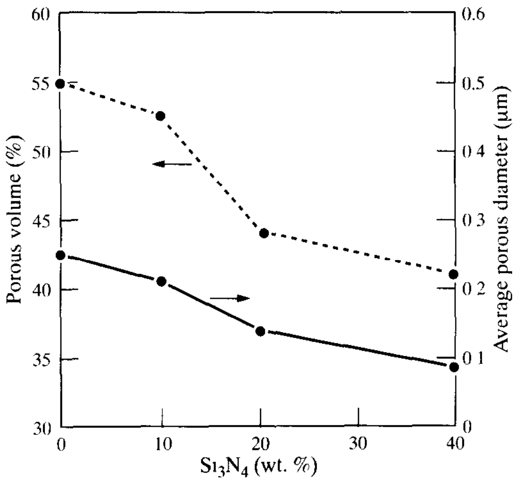

Fig. 3. Average pore volume and pore diameter of silicon compacts containing various concentrations of Si$_3$N$_4$ filler.

to investigate its chemical stability in the nitridation process. No trace of a nitrogen consumption was detected by mass flow meter during the nitridation process, and no phases other than the original silicon nitride were detected by XRD in the nitrided samples. The Si$_3$N$_4$ filler was apparently quite chemically stable during the nitridation process.

3.2 Pore-size distribution

The intrusion volume of mercury in the green silicon compacts which contained various fractions of Si$_3$N$_4$ is shown in Fig. 2.

The average pore volume and pore size for silicon compacts with various silicon nitride filler content are plotted in Fig. 3. The tendency to decrease in pore volume as the Si$_3$N$_4$ inert filler content is increased is clearly illustrated in Figs 2 and 3.

The pore volumes of non-nitrided and nitrided silicon compacts containing different concentrations of Si$_3$N$_4$ filler are illustrated in Fig. 4. The pore volume apparently decreases dramatically after nitridation. Only a slight difference is noticeable in the pore volume of nitrided samples if the Si$_3$N$_4$ content exceeds 10%.

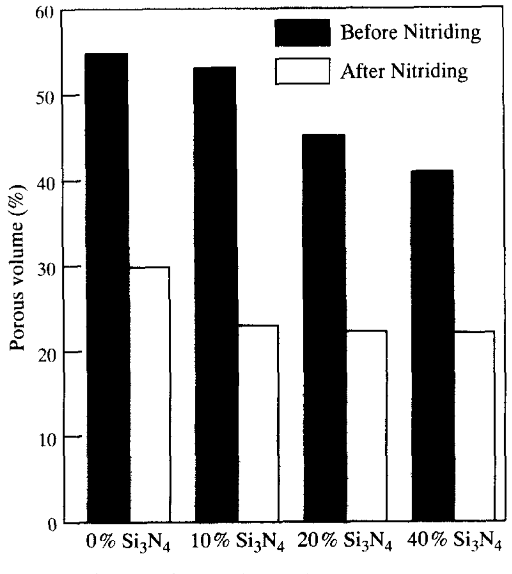

Fig. 4. Pore volume of samples before and after nitridation containing various concentrations of Si$_3$N$_4$.

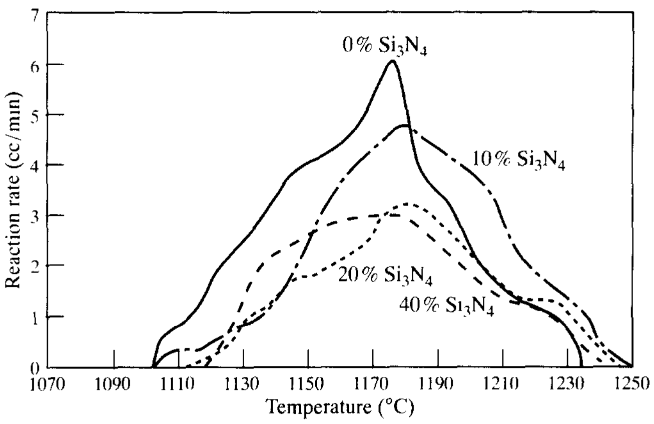

Fig. 5. Reaction rates of silicon with various Si$_3$N$_4$ filler content versus reaction temperature.

3.3 Nitridation kinetics

The nitridation rates were calculated from the nitrogen gas consumption/time curves. The nitridation rates of samples with various Si$_3$N$_4$ filler concentrations at different temperatures are plotted in Fig. 5. Samples with a higher pore volume (less Si$_3$N$_4$ filler) also tend to have higher maximum reaction rates at the early and medium stages of the nitridation process (below 1200°C). Not much difference in the nitridation rate occurred in the final stage of the nitriding process (above 1200°C). No further gas consumption was detected at temperatures above 1250°C, which is probably due to the closing of the pore structure by the reaction-formed Si$_3$N$_4$.

The temperatures for the start-up of the reaction for samples containing various concentrations of Si$_3$N$_4$ filler are plotted vs the silicon nitride content in Fig. 6. This temperature is shown to increase as

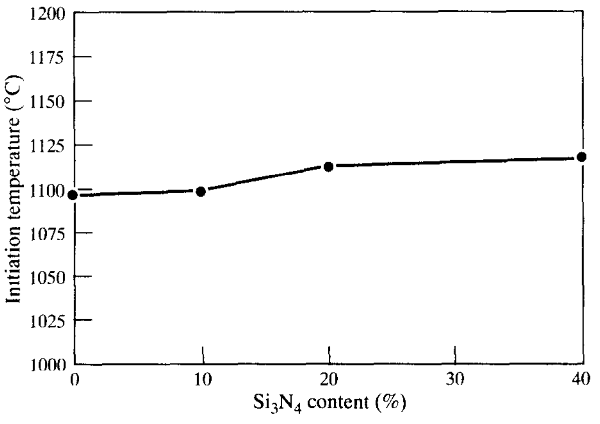

Fig. 6. Temperature of reaction start-up vs Si$_3$N$_4$ content.

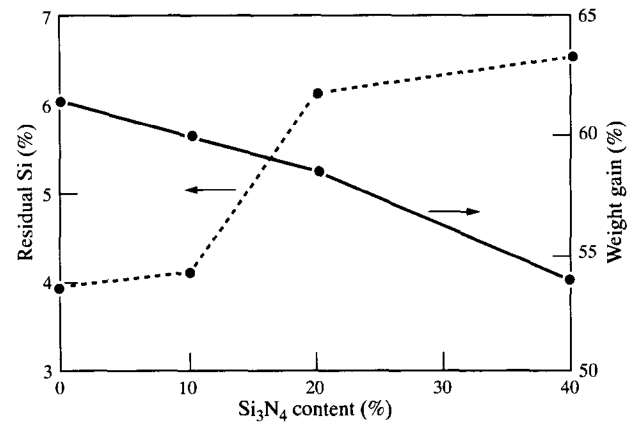

Fig. 7. Residual silicon and weight gain of nitrided compacts vs Si_3N_4 content.

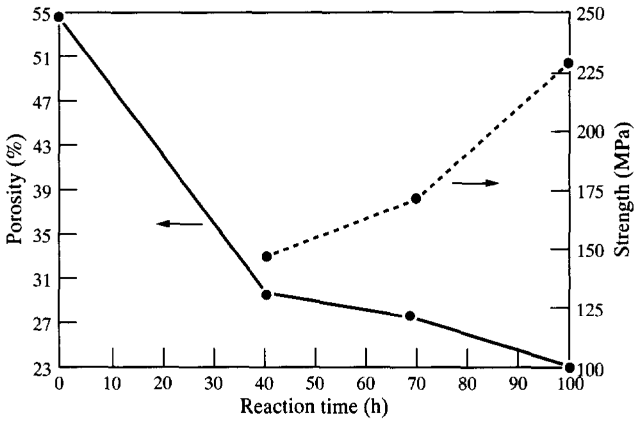

Fig. 8. Porosity and flexural strength vs reaction time.

the Si_3N_4 filler content increases. It was previously reported that the pressure gradient increases with decreasing pore volume and pore diameter.[13] A higher local nitrogen partial pressure must therefore be maintained above the reacting surfaces as the Si_3N_4 filler content increases. This relatively high N_2 partial pressure at equilibrium is probably related to the higher temperature required to initiate the nitridation.

The weight gain and the residual silicon content for silicon compacts containing different amounts of Si_3N_4 filler are plotted in Fig. 7. A higher weight gain and less residual silicon occur as the amount of Si_3N_4 filler decreases, as clearly indicated in this figure. Similar results can be obtained by comparing the area under the curves in Fig. 5 which also indicates that more N_2 gas was consumed for samples containing less Si_3N_4 filler despite the fact that all samples contained an equivalent amount of Si prior to nitridation.

Profiles with slower heating rates (Fig. 1, Routes 2 and 3) were used to nitride silicon compacts in order to examine how the pore structure and the mechanical properties change with nitridation rates. The pore volume and the flexural strength vs total nitriding time are shown in Fig. 8. Preliminary results indicated that the pore volume was reduced and the strength was substantially improved as the nitridation time was increased from 40 h to 70 and 100 h.

4 SUMMARY AND CONCLUSIONS

Silicon nitride particles were incorporated into silicon compacts as an inert filler in order to control the pore-size distribution prior to nitridation. Both pore volume and average pore diameter showed dramatic effects on the nitriding kinetics which might also be related to the pressure gradient.

Samples having a higher pore volume and a larger pore diameter reacted faster at temperatures below 1200°C, the reaction started at lower temperatures, and showed a higher weight gain and less residual silicon.

The pore volume was substantially reduced and the flexural strength was improved with increasing nitridation time.

ACKNOWLEDGEMENT

The authors would like to thank the National Science Council of Taiwan for financial support under Contract no. NSC80-0405-E006-25.

REFERENCES

1. WHITEHEAD, A. J. & PAGE, T. F., Degradation of SiC whiskers at elevated temperatures. *Ceram. Eng. Sci. Proc.*, **10** (7-8) (1989) 986–97.
2. BHATT, R. T. & PHILLIPS, R. E., Laminate behavior for SiC fiber-reinforced reaction-bonded silicon nitride matrix composites. *NASA AVSCOM Technical Report* 88-C-30, October 1988.
3. BHATT, R. T. & PHILLIPS, R. E., Thermal effects on the mechanical properties of SiC fiber-reinforced reaction bonded silicon nitride matrix (SiC/RBSN) composites. *NASA AVSCOM Technical Report* 88-C-028, October 1988.
4. SHELDON, B. W. & HAGGERTY, J. S., The nitridation of high purity, laser-synthesized silicon powder form reaction bonded silicon nitride. *Ceram. Eng. Sci. Proc.*, **9**(7-8) (1988) 1061–72.
5. BOYER, S. M. & MOWSON, A. J., A mechanism for the nitridation of Fe-contaminated silicon. J. *Mater. Sci.*, **13** (1978) 1637–46.
6. DERVISBERGOVIC, H. & RILEY, F. L., The role of hydrogen in the nitridation of silicon powder compacts. *J. Mater. Sci.*, **16** (1981) 1945–55.
7. NYBERG, B., FALK, L. K. L., POMPE, R. & CARLSSON, R., Some features of nitrided pressureless sintered (NPS) silicon nitride materials made by modified preparation routes. *Cer. Master Comp. for Eng. Proc. and Int. Symp.* Apr. (1986) 155–63.
8. MANGELS, J. A., Effect of rate controlled nitriding and nitriding atmospheres on the formation of reaction-bonded Si_3N_4. *Ceram. Bull.*, **60**(6) (1981) 613–17.
9. PIECARLO MARTINENGO, Process for sintering reaction bonded silicon nitride. US P 4,351, 787 (1982).
10. HUANG, J. L. & SIMMS, F. E., Nitridation of Mgo/CeO_2-doped silicon containing SiC whiskers. *J. Am. Ceram. Soc.*, **75**(6) (1992) 1662–5.

11. WILLIAMS, R. M. & EZIS, A., Slip casting of silicon shapes and their nitriding. *Am. Ceram. Soc. Bull.*, **62** (1983) 607.
12. GREGORY, O. J. & RICEMAN, M. H., The role of Si_3N_4 additions in the reaction bonding of silicon compacts. *J. Mater. Sci. Letter*, **3** (1984) 112–16.
13. POISEUILLE, J. L. M., *Inst France Acad. Sci.*, **9** (1846) 433.
14. KANI, A., OSADA, H., KATAYAMA, S. & HIRABAYASHI, H., Gas permeability and bending strength of porous SiC ceramics. *J. Jap Ceram Soc.*, **99**(1) (1991) 63–7.
15. ATKINSON, A., LEATT, P. J. & MOULSON, A. J., The role of nitrogen flow into the nitriding compact in the production of reaction-sintered silicon nitride. *Proc. Brit. Ceram. Soc.*, No. 22 June (1973) 253–74.
16. HUGHES, G. S., McGREAVY, C. & MERKIN, J. H., A theoretical model of the manufacture of reaction-bonded silicon nitride with particular emphasis on the effect of ambient reaction temperature and compact size *J Mater. Sci.*, **15** (1980) 2345–53
17. MANGEL, J. A., In *Progress In Nitrogen Ceramic*, ed. F. L. Riley. The Netherlands, Martinus Nijhoff, pp. 135–40.