The catalytic role of additive components for the nitridation of silicon/additive mixture

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The nitriding behavior of silicon/additives mixture with varied composition was investigated by focusing on the catalytic effect of sintering additives (Y2O3 and Al2O3) and diluents (Si3N4). While sintering additives have originally been mixed to form a liquid phase to promote both densification and grain growth during post-sintering, it was revealed that the addition of Y2O3 enhances the nitriding reaction by eliminating the SiO2 and Si3N4 layer on the surface of silicon particles. Further, a synergistic effect resulting in an increased nitridation was verified by concurrent addition of sintering additives and diluents. The contribution of each component of the compact to the promoted nitriding reaction was elucidated in quasi in-situ manner by the combination of phase analysis and thermogravimetric analysis.

1. Introduction

The breakthrough in Si3N4 ceramics have been pursued by researching new applications and novel cost-effective fabrication methods. Since the early 1990’s, there have been research activities into the development of non-conventional structural applications, which included their usage as substrates in devices, as machinable ceramics, and as filtering media. Technological investigations have concentrated on enhancement of thermal conductivity and development of porous bodies with controlled microstructures, e.g. crystallinity, texture, grain morphology and pore size distribution.

A significant disadvantage of engineering ceramics is their difficulty in machining after sintering, which leads to high machining costs and keeps them from wide spread usage. As a solution to this obstacle, various machinable ceramics have been developed, including porous Si3N4 materials. Recent studies have suggested that the presence of pores might improve machining performance if the ceramic microstructure is carefully controlled. By adjusting the characteristics of sintering additives, such as type and amount, porous Si3N4 ceramics were developed by the same sintering process used to obtain dense Si3N4 ceramics. Reaction-bonding route covered in this research is one of the representative near-net processings.

Though the reaction-bonding method is relatively old sintering technology used to fabricate Si3N4 ceramics, it is regaining attention since pore-free densification has been achieved by subsequent post-sintering. An unusual and attractive feature of reaction-bonding fabrication is that very little size change occurs between green body and sintered body. Thus close tolerances (~0.1%) on the dimensions of a finished component can be achieved, thereby avoiding expensive machining cost. Final shrinkage of sintered reaction-bonded silicon nitride ceramics (SRBSNs) is substantially smaller than that in conventionally sintered ceramics.

The reaction-bonding process intrinsically results in porous Si3N4 ceramics because the reaction mechanism involves a gas phase. Therefore, a key issue in development of advanced engineering SRBSN parts has been the elimination of pores in the RBSN microstructure. A large amount of knowledge has been accumulated regarding the nitriding behavior of silicon particles. Several researches also have been done focusing the catalytic effect of a single additive on the nitridation. However, little research has been done on silicon mixture containing sintering additives and/or other components. Diluents, such as Si3N4, contribute not only to control of the exothermal nitriding reaction, but also they increase strength due to the creation of an agglomeration-free homogenized microstructure. A practical way to incorporate sintering additives and diluents for post-sintering is to blend raw silicon with other components during mixing step prior to forming the compact. Thus, understanding of nitriding behavior of the mixture compact has important engineering implications. In this research, the effect of component powders on the nitriding behavior of the silicon/additive mixture compact was investigated by quasi in-situ manner aided by combination of phase analysis and thermogravimetric measurement.

2. Experiment

The commercially available silicon powder was >98.6% pure grade (Sicomm Mill Grade 2, Vesta Ceramics, Ljungaverk, Sweden; 0.4 wt% Fe, 0.2 wt% Al, 0.2–1.0 wt% O, d50 = 7 μm). Commonly adopted oxide sintering additives, Y2O3 (Grade C, H. C. Stark, Goslar, Germany; 99.99%, d50 = 0.7 μm) and Al2O3 (AKP-30, Sumitomo Chemical, Tokyo, Japan; 99.99%, d50 = 0.3 μm), were used. Si3N4 [E-10 grade, Ube Industries, Ube, Japan; α/(α+β) >95%, d50 = 0.5 μm] was blended as diluents to prevent an explosive exothermic nitriding reaction. Compositions of specimens and associated nomenclatures are summa-
rized in Table 1. The total amount of sintering additives was fixed at 7 wt% both for either single addition of Y₂O₃ (SiY) or concurrent addition of Y₂O₃ and Al₂O₃ (SiYA, SiSNYA). Weight percentages of sintering additives were calculated based on total Si₃N₄, and assumed perfect nitridation of raw silicon powder into Si₃N₄. Specimens blended with Si₃N₄ were designated as SiSN and SiSNYA. For the convenience of phase analysis, twice the Y₂O₃ amount was employed in SiY* compared to that in SiY. The amount of sintering additives and diluents per 100 g of silicon in the powder mixture are specified in Table 1.

Approximately 50 g of powder mixture was thoroughly mixed in a nylon jar with Si₃N₄ balls and ethanol as a milling medium for 4 h using a planetary milling machine. After mixing, the powder mixture was dried using a rotating evaporator, and sieved to a particle size <150 μm. The sieved powder mixture was uniaxially pressed into rectangular pellets and then cold isostatically pressed at 200 MPa to create specimens measuring 10 mm in a horizontal tube furnace. For the upper 5 specimens listed in Table 1, the nitriding reaction was conducted at 1150°C for 1 h or at 1350°C for 1 and 3 h. For Si and SiY*, nitriding temperatures varied from 1100 to 1350°C for fixed 2 h. A maximum of 8 specimens from the various trials were placed upon a suspended BN-coated graphite plate inside an Al₂O₃ tube furnace.

The nitridation rate (RN) was calculated from the weight change before and after nitriding and was compared to that in perfect nitridation of Si into Si₃N₄, which yields a weight increase of 66.5%. It was assumed that there was no change in weight of the other components in the specimens. The shrinkage after nitridation was calculated via measuring the diameter and the thickness of each specimen 3 times by a micrometer and a vernier calipers expected due to the presence of impurities in the raw powders which lower the eutectic temperature of the mixed composition. The contaminating elements, especially Fe, Al, and O, were reported to vary the composition, eutectic temperature, viscosity, and amount of liquid phase during heating. The w sintering additives are active components in the nitriding reaction (see compound formation at low temperature, Fig. 7), the diluents Si₃N₄ is inert owing to its stability at the nitriding temperatures (≤1350°C in this research). The increased nitridation rate by diluents Si₃N₄ (SiSN, SiSNYA) is attributed to the stable passage of nitrogen provided by the inertness of Si₃N₄. The harmful effect of the pore-blocking on the entire nitridation of Si compacts was reported by J. S. Lee et al. The highest nitridation rate was measured in the SiSNYA specimen, which contained both sintering additives and diluents Si₃N₄.

Porosity and shrinkage of RBSNs are summarized in Fig. 2. The highest porosity in the specimen Si (Si only) reflects the lowest nitridation rate in Fig. 1. With an increase in nitriding temperature from 1150 to 1350°C, porosity level decreased due to the enhanced nitriding reaction [Fig. 2(a)]. An increase in specimen weight resulted in a decrease in porosity, because the volume of specimens was nearly fixed at that of the green compacts [Fig. 2(b)]. Shrinkages for all specimens were less than ±1%, which is typical to near-net shape RBSNs.

Figure 3 are the SEM photographs of fractured RBSNs representing the middle stage of nitriding reaction (i.e., 1350°C–1 h). Microstructures consisting of both fine grain Si₃N₄ and whisker-like Si₃N₄ were observed, which exhibit a substantial reduction in grain size from metal silicon. The large flat particles marked by arrows indicate residual silicon.

The composition SiY* was designed to investigate the effect of Y₂O₃ in exaggerated manner. Plots of nitridation rates for both Si and SiY* indicate the positive role of Y₂O₃ on the nitriding reaction (Fig. 4). The results yielded that ~10% higher values for SiY* specimen during nitriding at 1200°C or higher temperatures.

4. Discussion

4.1 Catalytic effect of additives on nitridation

All components in the powder mixture in this research enhanced the nitriding reaction regardless of the composition.

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Table 1. Composition and nomenclature of the specimens

| Specimen | Si (g) | Si₃N₄ (g) | Y₂O₃ (g) | Al₂O₃ (g) | Additives in weight percentage |
|----------|--------|-----------|----------|-----------|-----------------------------|
| Si       | 100    | 0         | 0        | 0         | 0                           |
| SiSN     | 100    | 20        | 0        | 0         | 0                           |
| SiYA     | 100    | 0         | 9.7      | 2.7       | 7                           |
| SiSNYA   | 100    | 20        | 10.3     | 3         | 3                           |
| SiY*     | 100    | 0         | 12.4     | 0         | 7                           |
| SiY      | 100    | 25        | 0        | 0         | 13                          |

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Thermogravimetric (TG) analysis using nitrogen gas elucidated the nitriding mechanism by analyzing weight gain profiles. Pure nitrogen gas was employed for the TG experiment due to the apparatus safety, while nitrogen/hydrogen mixed gas was applied for the nitriding of other specimens in the tube furnace. The percentages in the inset exhibit nitridation rates after 1 h of isothermal holding at 1350°C in the TGA apparatus (Fig. 5). Relatively large variations in nitridation rate were noted in Fig. 5, while hydrogen containing atmosphere used to produce the data in Fig. 1 yielded only small fluctuation in reactivity, presumably because hydrogen dominated the compositional differences. That is, TG analysis carried out in a pure nitrogen atmosphere revealed the effect of composition. In order to verify this effect of hydrogen, nitriding reactions in the tube furnace were conducted at 1350°C for 1 h under pure nitrogen gas (Fig. 6). In a comparison of Figs. 1 and 6, higher nitridation rates were achieved in the mixed gas reaction, with a maximum difference of ~10% between Si and SiSNYA. In the pure nitrogen atmosphere, smaller nitridation rates were measured owing to the lack of hydrogen which acts as a nitriding promoter. As expected, larger differences in nitridation rates under pure nitrogen were apparent with ~20% fluctuation between Si and SiSNYA.

The mechanism by which each component enhances the nitriding reaction was deduced from analysis of the curves in Fig. 5. The weight gain profiles are categorized into two distinctive groups. Profiles of Si and SiSN describe a weight gain which started above 1300°C, while those of SiYA, SiSNYA, and SiY exhibit an earlier weight gain, starting around 1200°C. It has been reported that inert components in silicon mixture increase nitridation rates by stabilizing gas channels.\(^{19,26}\) Si\(_3\)N\(_4\) in the SiSN specimen is stable under the experimental conditions in isothermal holding at 1350°C in the TGA apparatus (Fig. 5).

Fig. 2. (a) Porosity and (b) shrinkage of RBSNs nitrided at various temperatures and time.

Fig. 3. SEM microstructures of fracture surface of RBSNs nitrided at 1350°C for 1 h. Cleavage-like large particles (arrow) are the fractured residual metallic silicon. (a) Si, (b) SiSN, (c) SiYA, (d) SiSNYA, (e) SiY.

Fig. 4. The nitridation rate of Si and SiYN* nitrided at 1100 to 1350°C for 2 h.
of SiO₂, Y₂O₃ and Si₃N₄. The enhanced nitriding reaction and
accompanying formation of secondary phases comprised
of Y₂O₃ and silicon were selected and its peak ratios were
detected in the nitrided samples revealed that a decrease in residual Y₂O₃ is
not detectable after nitriding at and over 1300°C. Phase analysis
additives such as Y₂O₃ and Al₂O₃. As mentioned earlier in Fig. 4,
initiation of weight gain at lower temperatures contains sintering acceleration of nitriding. The second group, characterized by the
temperature from 1100 to 1200°C, respectively. Peaks of Y₂O₃ were
ratio decreased from 0.11 to 0.05 with increase in nitriding tem-
perature is illustrated in Fig. 5. Nitridation rate and relative peak
nitridation rates among specimens is apparent for pure N₂ atmosphere.

Phase analysis of the nitrided SiY+SiSn+SiYa specimen nitrided at various temperatures for 2 h. For green compact of SiY*, Y₂O₃/(Y₂O₃+Si) ratio is 0.26.

4.2 Effect of liquid phase
Although there were substantial differences in eutectic temperatures, similar nitridation rates were measured between SiYA and SiY. The phase ratio, however, of α-Si₃N₄ in both specimens was quite different (Fig. 8). The highest β-Si₃N₄ content was found in SiYA, while the lowest content was observed in SiSN. The latter is attributed to the initial dose of α-Si₃N₄ (E-10 grade, α-Si₃N₄ fraction >0.95, Ube Industries) in the starting powder mixture. The phase diagrams indicated that the eutectic temperature for the SiO₂–Y₂O₃ and the SiO₂–Y₂O₃–
Al₂O₃ systems are 1660 and 1370°C, respectively. Considering the existence of minor impurities in the powder mixture (>98.6% pure grade Si), which would lower the liquidus temperature, formation of the liquid phase was possibly involved in the SiYA specimen nitrided at 1350°C. Watari et al. have observed the existence of liquid phase at lower temperatures than used in common nitriding processes, i.e. between 1300 and 1400°C.

Phase analysis of the nitrided SiY* specimen at various temperatures is illustrated in Fig. 7. Nitridation rate and relative peak height of Y₂O₃ are also specified in the figure. Major peaks of Y₂O₃ and silicon were selected and its peak ratios were calculated. These ratios are indicative of relative differences among specimens fabricated at different temperatures. The Y₂O₃/(Y₂O₃ + Si) ratio in the starting powder mixture was 0.26. This ratio decreased from 0.11 to 0.05 with increase in nitriding temperature from 1100 to 1200°C, respectively. Peaks of Y₂O₃ were not detectable after nitriding at and over 1300°C. Phase analysis of nitrided samples revealed that a decrease in residual Y₂O₃ is accompanied by the formation of secondary phases comprised of SiO₂, Y₂O₃ and Si₃N₄. The enhanced nitriding reaction and lowered reaction starting temperatures in Fig. 5 is related to a chemical reaction between the SiO₂ layer on the silicon particles, the Y₂O₃ sintering additive and newly formed Si₃N₄. Thus, earlier weight gain at lower temperatures in the specimens containing sintering additives (i.e., SiYA, SiSNYA, SiY) is mainly attributed to elimination of SiO₂ surface layer on the silicon particle by reacting with Y₂O₃ into Y₂SiO₃ silicate phase. While the amount of Y₂SiO₃ phase reduced as increasing temperature, other secondary phases containing nitrogen, YSiO₂N (K-phase) and Y₄Si₂O₇N₂ (J-phase), formed at 1300 and 1350°C. This phenomenon is consistent with the report by Zhu et al. which revealed that YSiO₂N was observed by the reaction between Y₂O₃, SiO₂, and newly formed Si₃N₄. Based on the slope of weight change at 1350°C in Fig. 5, the nitriding reaction of Y₂O₃ containing group (SiYA, SiSNYA, and SiY) is faster than that of the other group (Si, SiSN). J. Koike et al. suggested that continuous nitriding of pure Si can occur via the sequential spallation of the Si₃N₄ layer from the Si surface due to the lattice misfit between the Si substrate and thermally-grown Si₃N₄ layer. Thus, the most reasonable explanation why the higher rate of nitriding reaction in SiYA/SiSNYA/SiY than the rate in SiSN/Si during soaking at 1350°C in Fig. 5 is thought that the bare surface of Si is exposed to N₂ atmosphere due to both the spallation of Si₃N₄ layer by thermally-activated lattice misfit and the removal of Si₃N₄ layer by the formation of YSiO₂N and Y₄Si₂O₇N₂ from the chemical reaction between Y₂O₃, Y₄Si₂O₇ and the newly formed Si₃N₄ layer.

this research, thereby explaining the higher nitridation rate in SiSN compared to that in Si. Furthermore, with or without Si₃N₄, weight gain started at nearly the same temperatures. Therefore we postulate that Si₃N₄ addition only affects physical configuration of microstructures with no indication of a chemical basis for the acceleration of nitriding. The second group, characterized by the initiation of weight gain at lower temperatures contains sintering additives such as Y₂O₃ and Al₂O₃. As mentioned earlier in Fig. 4, addition of these sintering additives resulted in an increase in nitridation rate even at lower temperatures than used in common nitriding processes, i.e. between 1300 and 1400°C.

Phase analysis of the nitrided SiY+SiSn+SiYa specimen at various temperatures is illustrated in Fig. 7. Nitridation rate and relative peak height of Y₂O₃ are also specified in the figure. Major peaks of Y₂O₃ and silicon were selected and its peak ratios were calculated. These ratios are indicative of relative differences among specimens fabricated at different temperatures. The Y₂O₃/(Y₂O₃ + Si) ratio in the starting powder mixture was 0.26. This ratio decreased from 0.11 to 0.05 with increase in nitriding temperature from 1100 to 1200°C, respectively. Peaks of Y₂O₃ were not detectable after nitriding at and over 1300°C. Phase analysis of nitrided samples revealed that a decrease in residual Y₂O₃ is accompanied by the formation of secondary phases comprised of SiO₂, Y₂O₃ and Si₃N₄. The enhanced nitriding reaction and lowered reaction starting temperatures in Fig. 5 is related to a chemical reaction between the SiO₂ layer on the silicon particles,
$\beta$-Si$_3$N$_4$ content observed in Si and SiY supports the mechanism discussed herein. Furthermore, based on the similar shrinkage and porosity between SiYA and SiY, the spatial distribution of the liquid phase in SiYA may not be continuous but scattered.

5. Conclusions

It is generally agreed that the SiO$_2$ surface layer on the silicon particle should be removed by evaporation in the form of SiO(g), then the exposure of non-oxidized, bare silicon surface leads to enhancement in nitriding reaction. In this study, the addition of Y$_2$O$_3$ sintering additives contributes to an accelerated nitriding reaction and the final nitridation rate. That is, the formation of secondary phases among the initial SiO$_2$ surface layer, the Y$_2$O$_3$ sintering additives and the newly formed Si$_3$N$_4$ surface layer, promotes the accessibility of nitrogen gas to bare silicon. The formation of those phases has been confirmed through X-ray diffraction. Thermogravimetric analysis has discriminated the formation of those phases has been concretely presented through X-ray diffraction and RBSN analysis. Thermogravimetric analysis has discriminated the formation of those phases has been concretely presented through X-ray diffraction and RBSN analysis. Thermogravimetric analysis has discriminated the formation of those phases has been concretely presented through X-ray diffraction and RBSN analysis. Thermogravimetric analysis has discriminated the formation of those phases has been concretely presented through X-ray diffraction and RBSN analysis. Thermogravimetric analysis has discriminated the formation of those phases has been concretely presented through X-ray diffraction and RBSN analysis. Thermogravimetric analysis has discriminated the formation of those phases has been concretely presented through X-ray diffraction and RBSN analysis.

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