Nitridation behaviour of ZrO_2 added silicon powder with different ZrO_2 particle sizes

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Effect of zirconia particle size on the nitridation behavior of silicon powder was studied in order to assess the influence of the zirconia particle size on the nitridation of silicon powder. Thermo-gravimetric analysis revealed that for samples held at higher temperatures the addition of zirconia powder resulted in a reduction of the temperature for the onset of nitridation of the silicon powder, and the degree of silicon to silicon nitride conversion at a given temperature was higher for samples nitrided with finer particle size of zirconia. For lower temperature, the degree of nitridation was studied as a function of holding time and samples with finer additions showed a much higher initial nitridation rate than those with coarser additions.

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Key-words : Sintering, Powders-solid-state reaction, Strength, Si_3N_4 , Structural application

[Received August 11, 2008; Accepted November 20, 2008]

1. Introduction

Silicon nitride is a promising material for high-temperature and high mechanical stress applications because it offers high thermal shock resistance and high strength retention at elevated temperature as well as good erosion resistance, high corrosion resistance and low creep properties.^{1)–4)}

Amongst the different classes of silicon nitride ceramics, reaction bonded silicon nitride (RBSN) has some advantages, such as low sintering shrinkage, low raw material cost and high strength retention at elevated temperature.^{5)–7)} However, the application of these RBSN ceramics is limited due to the low fracture strength, high porosity and long processing time. The long processing time is a serious issue which is difficult to solve due to the intrinsic process of the nitridation of silicon. Generally, for obtaining RBSN ceramics, the nitridation of silicon is carried out near its melting temperature despite the fact that the reaction between silicon and nitrogen is exothermic. This means that rapid nitridation of silicon can easily lead to melting of the silicon due to the self heating reaction prior to the completion of nitridation. Melted silicon forms coarser particles, resulting in incomplete nitridation since the reaction kinetics of silicon nitridation is dependent on nitrogen diffusion from the particle surface. To overcome this problem, many researchers have reported the catalytic nitridation of silicon for fabricating raw silicon nitride powder and RBSN ceramics.^{8)–11)} Iron is a famous and well known catalyst for promoting the nitridation of silicon, and is generally contained as an impurity in the raw material of low cost grade silicon powders. However, when dense silicon nitride ceramics are required to be fabricated using reaction bonding and a post-sintering process, iron acts as a type of defect for reducing mechanical properties, such as room and high temperature fracture strength. The catalytic effect of other metals and oxides such

as chromium, calcium, copper and silver on the nitridation of silicon has also been reported.⁹⁾

ZrO_2 has been employed as a sintering additive for the densification of nitrided silicon during the post sintering process^{12)–14)} and Kleebe et al. have reported on the microstructure and mechanical properties of post-sintered RBSN ceramics with ZrO_2 and other additives, such as Al_2O_3 .¹⁵⁾ The authors have reported that the catalytic effect of ZrO_2 on nitridation of silicon powder results in a reduction of the nitridation starting temperature, and that the degree of the conversion of silicon powder is increased with increasing amount of added zirconia.^{16),17)} However, in that work the effect of ZrO_2 particle size was not clarified. In this study, the nitridation behaviour of silicon powder with various particle size of ZrO_2 was studied using thermo-gravimetric analysis under nitrogen gas flow conditions. Following nitridation, powders were measured by X-ray diffraction analysis in order to clarify the influence of zirconia particle size on nitridation of the silicon powder.

2. Experimental procedure

Three kinds of ZrO_2 powders with different particle size were used in this experiment. One was a fine ZrO_2 powder with average particle size of 70 nm (TZ-0, TOSO Co., Ltd., Tokyo). The other was a coarse ZrO_2 powder (Zirbon M, 99.3% purity, Fukushima Steel Works Co., Ltd.) prepared by electrical fused method with an average particle size of 6.1 μm . An intermediate size was produced by grinding the coarse ZrO_2 by planetary ball milling in ethanol using a ZrO_2 pot and balls. This resulted in a powder with an average particle size of 2.4 μm as measured by particle size analysis (Microtrac HRA, Nikkato Co., Ltd.). The morphology of the ZrO_2 powders used in this study are shown in Fig. 1 and the particle size and specific surface area measured by BET analysis are given in Table 1.

Each of the ZrO_2 powders was added to high purity silicon powder (Kojundo Chemical Lab. Co., Ltd., Average particle size

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Fig. 1. SEM images of the ZrO_2 starting powders.Table 1. Properties of ZrO_2 Powder using as Starting Powders

	Average particle size (μm ; microtrac)	Specific surface area (m^2/g ; BET)
ZrO_2 fine	0.7	14.0
ZrO_2 middle	2.4	7.1
ZrO_2 coarse	6.1	1.3

1 μm , Tokyo). In each case the amount of the zirconia powder added was 15.65 mass %. This amount was calculated such that the amount of ZrO_2 in the fully nitrided silicon powder would be 10 mass%, provided that the entire initial Si powder was reacted to form silicon nitride.

The powders were homogeneously mixed by planetary ball milling for 1 h in ethanol using a silicon nitride crucible and silicon nitride balls and then dried using a vacuum evaporator. The oxygen content of the silicon powder following ball milling was 1.56 mass% as determined by an oxygen analyzer (Nitrogen Oxygen Determinator, combustion type, TC436, LECO, Michigan, U.S.).

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) of the mixed powders was carried out under nitrogen atmosphere up to 1400°C in order to clarify the nitridation behaviour using TG-DTA apparatus (TGS-2000S, MAC Science Co., Ltd., Yokohama). The mixed powders were loosely packed in Al_2O_3 pans and pre-heated to 200°C under a nitrogen atmosphere. Following cooling to room temperature, two kinds of tested were carried out. In the first set of experiments, the samples were heated to 1400°C using a heating schedule of 20°C/min with no soaking time. For the second experiments, the samples were heated up to 1300°C under the same heating schedule and then held for a period of 6 h. The degree of nitridation was calculated by change in weight of the powders, taking into consideration the initial SiO_2 content of the silicon powder.¹⁸⁾ Phase identification and microscopic observations of the heat treated samples were performed using powder X-ray diffraction spectroscopy (XRD, RINT2000, RIGAKU) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS, JSM6330F, JEOL Co., Ltd.), respectively. For SEM analysis, the powder samples were first coated with a gold coating to provide electrical conductivity.

3. Results and discussions

Figure 2 shows the thermo-gravimetric behavior from 900°C to 1400°C for both Si powder only, and Si added ZrO_2 with different particle sizes. In the case of Si powder, the increase in weight began at a temperature of 955°C and a rapid gain in

Fig. 2. Thermo-gravimetric analysis results of the Si powder and samples with different particle size ZrO_2 powder additions.

weight was observed around 1365°C. In the case of the powders with ZrO_2 added, the onset of weight gain was similar at 950°C, such that no influence of ZrO_2 addition was observed for the onset of weight gain. However, the starting temperature of the main weight gain step for all of the ZrO_2 added powder samples was clearly lower than that of the Si only specimen, and this onset temperature decreased with decreasing particle size of the ZrO_2 powder.

This is supported by the differential thermal behavior of the samples at temperatures from 1100°C to 1400°C as shown in Fig. 3. In the case of Si powder, a single peak of exothermal reaction was seen at 1380°C. On the other hand, for the samples with ZrO_2 , exothermal peaks were seen at temperatures of around 1350 and 1380°C, and the lower temperature peak increased with decreasing particle size.

Figure 4(1) shows the X-ray diffraction spectra of the samples after TG analysis at 1400°C. The spectra indicated the presence of both silicon and silicon nitride for every sample. The intensity of the Si peaks decreased, and those of the crystalline silicon nitride increased, with the addition of the finer ZrO_2 powder. This trend is the same as the weight gain behavior from the thermo-gravimetric analysis, indicating that the addition of ZrO_2 to silicon powder is effective for enhancing the nitridation of silicon powder, and that this enhancement is dependent on the particle size of the ZrO_2 . Figure 4(2) shows a detailed portion of the X-ray diffraction spectra in the range from 30 to 45° for the specimens following TG analysis at 1400°C. The samples with

Fig. 3. Differential thermal analysis results samples at higher temperature.

Fig. 4. (1) X-ray diffraction spectra of samples after thermo-gravimetric analysis at 1400°C. a) Si. b) Si with coarse ZrO₂. c) Si with fine ZrO₂. (2) More detail of the X-ray diffraction spectra for 2θ angles between 30 and 45°. a) Si, b) Si with coarse ZrO₂, c) Si with fine ZrO₂.

added ZrO₂ showed the presence of tetragonal-ZrO₂, ZrSi₂ and ZrN phases in addition to the Si₃N₄ phases. The presence of these phases has been reported in previously.^{17),19)} It is thought that the reaction between ZrO₂ and Si resulting in the ZrSi₂ is responsible

Fig. 5. SEM images of the powders after thermo-gravimetric analysis at 1400°C.

for the lower temperature exothermic peak seen in the DTA results.

Figure 5 shows the SEM images of the samples following thermo-gravimetric analysis at 1400°C. In both samples of the Si and Si with fine ZrO₂, very fine particles were observed, along with whisker formation, but in the sample with fine ZrO₂ the finer particles were coarser and the amount of whisker formation and the whisker length was also decreased. EDS analysis (Fig. 6) showed that the whiskers were composed of Si, N and O elements whereas the coarser particles observed in the SEM images were silicon rich and Zr element was not detected from the whiskers. In these figures the Au peak comes from the coating material employed for SEM observation and C is derived from the SEM sample stage. The reason why coarse particle and whisker decreased in the case of Si with fine ZrO₂ is due to the enhancing effect on the nitridation of silicon at lower temperature due to ZrO₂ addition. The silicon nitride particles produced are independent of original particle size of the raw silicon powder,²⁰⁾ and the coarser particles are the unreacted silicon. It has been reported that the main mechanism of whisker formation during nitridation of silicon is VLS (Vapor-Liquid-Solid) mechanism and the whiskers are composed of the Si₂N₂O phase.²¹⁾ In the case of formation of Si₂N₂O phase, SiO vapour which is reduced SiO₂ locating on the surface of silicon, need react with nitrogen. It is considered that only reducing agent is silicon in this study. Furthermore, the considerable reactions for forming Si₂N₂O during nitridation process as follows;

The free energy change for both reactions is negative in the experimental condition of present study. It is considerable that the vapoured silicon controls the formation of Si₂N₂O because diffusion rate of gas is larger than that of solid. The vapour pressure of silicon is increased at higher temperature, and since the ZrO₂ addition to the silicon powder enhanced nitridation at lower temperature the amount of un-reacted silicon powder is decreased at a given temperature when compared with the silicon without ZrO₂ powder. As a result the amount of vapoured silicon

Fig. 6. EDS analysis results from the whiskers (a) and the particles (b) of the with fine ZrO_2 powder additions after Thermo gravimetric analysis at 1400°C .

Fig. 7. EDS analysis results of the SEM images of the Si powder added with coarse ZrO_2 powder.

was decreased, and whisker formation is decreased. On the other hand, the samples which contained both the coarse and midsize ZrO_2 added powder (Fig. 5) showed a number of coarse particles and a lot of whisker formation similar to the case of the silicon without ZrO_2 samples. EDS analysis of these samples showed that the coarse particle was composed of a Zr, Si and O rich composition (Fig. 7). This coarse particle is considered to be the ZrSi_2 phase which was detected in the XRD analysis along with some

oxide. It is considered that the reason for the whisker formation in these samples is due to a larger amount of un-reacted silicon due to a lower nitridation enhancing effect of these ZrO_2 particle sizes when compared with that of fine ZrO_2 added silicon powder.

Figure 8 shows the normalized degree of nitridation for the samples that were held at 1300°C under nitrogen flow conditions, calculated from the thermo-gravimetric analysis results. The degree of nitridation for every sample containing ZrO_2 was

Fig. 8. Normalized degree of nitridation of the Si added with various particle size ZrO_2 following a holding time of 6 h at 1300°C .

higher than the sample without ZrO_2 at all holding times. For the ZrO_2 added samples, those with the fine powder showed rapid nitridation in the initial soaking period at this temperature. For the other two powders, the degree of nitridation in the initial period was less and there was little difference between the two. The nitridation behaviour difference of the two samples was observed in the period following the initial holding, with the degree of nitridation of the coarse ZrO_2 added specimen being gradually reduced after around 30 min of holding time. This behaviour was also observed in the case of the silicon only powder sample, and in this case is attributed to the formed nitride layer that gradually covers the reacting surface.²²⁾ This behaviour is related to the powder particle size of raw silicon, but in the present study, the particle size of silicon was the same for every sample. In the case of the ZrO_2 added silicon powder, the slowing nitridation rate may be related to the contact situation between ZrO_2 and Si powders. In the initial period of nitridation, the effective catalytic behaviour of the ZrO_2 acts on the surface, where there is contact between the ZrO_2 and Si. However, as nitridation advances, the contact between ZrO_2 and silicon is decreased, particularly for the coarse ZrO_2 powder due to its lower specific area. At lower temperature below melting point of silicon, the nitridation takes place at the surface of the silicon particles through a solid-gas reaction with nitrogen, and it is considered that the enhancing effect of ZrO_2 occurs at those locations where there is contact or close between the silicon and ZrO_2 particles. For the coarse powder with a lower specific surface area, the nitridation enhancing effect was reduced due to its lower specific surface area than fine ZrO_2 powder.

4. Summary

The nitridation behaviour of silicon powder with additions of

different particle size ZrO_2 was studied using high purity silicon powder and monoclinic zirconia as starting materials. Thermogravimetric analysis revealed that the addition of ZrO_2 to Si powder promoted nitridation of the silicon at lower temperatures, and this was increased with decreasing particle size of added ZrO_2 powder. The particle size of the zirconia affected both the nitridation starting temperature and the reaction rate during holding at a constant temperature at 1300°C . The nitridation behaviour difference is attributed to differences in the solid-solid contact between silicon and ZrO_2 powders.

Acknowledgement The financial support provided by Nanotech challenge Project (NEDO, Japan) throughout this work was greatly appreciated. We thank Dr. Jones at University of Auckland (New Zealand) for helpful discussions.

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