Disintegration Behavior of Silicon Nitride Ceramic by Hydrothermal Treatment in Aqueous HF Solution

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HF 水溶液を用いた水熱処理による窒化ケイ素セラミックスの崩壊挙動

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The possibility of recycling silicon nitride ceramic by hydrothermal treatment was investigated. A Si_3N_4 sintered compact with 0.9 mass% SrCO_3 , 3.6 mass% MgO and 4.5 mass% CeO_2 as sintering aids was used as a specimen for treatment. Hydrothermal treatment was performed using aqueous HF solution at 70–150°C for 0–120 h. The dense sintered compact was easily disintegrated into powdery particles and a core fragment by the combination of hydrothermal treatment and subsequent sonication treatment. The treated powder was identified by X-ray diffraction (XRD) analysis as $\beta\text{-Si}_3\text{N}_4$ containing CeF_3 and MgF_2 , which were formed in aqueous HF solution during hydrothermal treatment. These fluorides were completely removed by rinsing in HNO_3 solution. Then, a powder consisting only of needle like $\beta\text{-Si}_3\text{N}_4$ crystals was recovered by a series of these treatments. X-ray photoelectron spectroscopy (XPS) revealed that the surface of the recovered Si_3N_4 powder was oxidized very slightly. Hydrothermal treatment at 120°C for 24 h gave approximately 30% yield of powdery $\beta\text{-Si}_3\text{N}_4$ particles, excluding the amount of sintering aid components. In the case of hydrothermal treatment for shorter terms or at lower temperatures, the corrosion behavior of the Si_3N_4 ceramic is linearly dependent on treatment time and is controlled by surface chemical reaction. The activation energies for the dissolution of the Si_3N_4 ceramic, and the grain boundary components of strontium, magnesium and cerium were estimated as 31.9 ± 0.7 , 54.4 ± 3.6 , 74.3 ± 1.4 and 51.7 ± 3.9 kJ/mol, respectively. [Received July 1, 2003; Accepted November 27, 2003]

Key-words: Silicon nitride, Hydrothermal treatment, Disintegration

1. Introduction

Fine ceramics have been developed over the past two decades because of their superior mechanical and functional properties. Recently, the development of fabrication processes with a lower energy has been expected from environmental and economical viewpoints, since considerable energy is required for the production of fine ceramics. On the other hand, the depletion of natural resources and landfill sites is becoming a serious problem due to the discharge of a large amount of solid waste which includes various fine ceramics. To solve these problems, it is essential to develop a recycling system for these ceramics. However, research and development on the recycling of fine ceramics has not been conducted as of yet.

A dense Si_3N_4 sintered compact, a high-temperature structural material, has been sintered at high temperatures above 1700°C using metal oxides and rare-earth oxides such as Al_2O_3 , MgO , and Y_2O_3 , as sintering aids.^{1)–6)} In general, fine $\alpha\text{-Si}_3\text{N}_4$ crystalline particles are used as the starting powder and transformed to needle like crystals of $\beta\text{-Si}_3\text{N}_4$ during liquid-phase sintering. Recently, highly anisotropic silicon nitride ceramics have been developed using needle like crystals of $\beta\text{-Si}_3\text{N}_4$ as seed particles.⁷⁾ If needle like $\beta\text{-Si}_3\text{N}_4$ crystals of high purity can be recovered from Si_3N_4 ceramic waste, the use of virgin $\beta\text{-Si}_3\text{N}_4$ powder could be replaced by the recovered $\beta\text{-Si}_3\text{N}_4$ powder.

Many researchers have extensively studied the corrosion behavior of the Si_3N_4 ceramic with Al_2O_3 and Y_2O_3 sintering aids under hydrothermal conditions in pure water or in acidic solution at

moderate temperatures to develop corrosion-resistant ceramics^{6),8)–13)} because the sintering aids are unevenly segregated on the grain boundary region and form a phase which has a poorer chemical stability than the crystalline Si_3N_4 phase.⁶⁾ These results showed that the mechanical strength of the corroded Si_3N_4 ceramic was significantly degraded due to the surface defects formed by the dissolution of the grain boundary phase. In the case of corrosion tests under hydrothermal conditions in water, an oxide film was formed over the surface of the specimen.^{9)–13)} Different corrosion behaviors of the Si_3N_4 ceramic were observed, however, in the corrosion tests in aqueous HF and HCl solutions,^{6)–8)} insoluble YF_3 was formed in the HF solution, while soluble YCl_3 was formed in the HCl solution. These reports suggest that subcritical hydrothermal treatment in various solvents is an effective recycling technique for Si_3N_4 ceramic waste. The purpose of the present study is to determine the optimum conditions that can extract the grain boundary phase preferentially and recover Si_3N_4 particles efficiently from Si_3N_4 ceramic in aqueous HF solution under hydrothermal conditions.

2. Experimental procedure

2.1 Hydrothermal treatment of Si_3N_4 ceramic

Commercially available Si_3N_4 ceramic which was prepared at JFCC (Japan fine ceramics center, SN1) by adding 0.9 mass% SrCO_3 , 3.6 mass% MgO and 4.5 mass% CeO_2 as sintering aids, was used as a specimen (density: 3.21 g/cm³). For hydrothermal treatment, the Si_3N_4 ceramic was cut into 9 mm × 9 mm × 5 mm rectangular coupons. The characteristics of the grain boundary phase in the Si_3N_4 ceramic used for hydrothermal treatment are summarized in **Table 1**. Each coupon was placed in an autoclave lined with Teflon with 50 ml of 2.8 M aqueous HF solution, and then this vessel was placed in an oven maintained at a given temperature. Hydrothermal treatment was performed under autog-

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Table 1. Characteristics of Grain Boundary Phase in the Si_3N_4 Ceramics Used for Hydrothermal Treatment

Additives (mass%)	Crystallinity of grain boundary phase	Volume fraction of $\beta\text{-Si}_3\text{N}_4$, V_{SN}^{*1}	Volume fraction of grain boundary phase, V_g^{*2}	Total surface area of Si_3N_4 ceramic, S (cm^2) ^{*3}	Total surface area of grain boundary phase, S_g (cm^2) ^{*4}
0.9 mass% SrCO_3 3.6 mass% MgO 4.5 mass% CeO_2	amorphous	0.916	0.084	3.42	0.29

*1: calculated using the density of $\beta\text{-Si}_3\text{N}_4$ and the weight fraction of SrO , MgO , Ce_2O_3 and $\alpha\text{-Si}_3\text{N}_4$.

*2: $V_g = 1 - V_{\text{SN}}$

*3: calculated using the size of the Si_3N_4 ceramic ($9 \times 9 \times 5 \text{ mm}$).

*4: calculated by the product of the total surface area (S) and the total volume fraction (V_g) of grain boundary phase.

enous pressures corresponding to the reaction temperature (70–150°C) for 0–120 h. After the hydrothermal treatment under the given conditions, the vessel was cooled to room temperature, and then the solid constituents were collected by filtration. The filtered solid constituents were pulverized by sonication in pure water, filtered again and dried at 50°C for 24 h. The powder was rinsed with 50 ml of 1.4 M HNO_3 solution at 90°C for 24 h to remove the fluorides.

2.2 Characterization of the specimens

The hydrothermally treated powder and the rinsed powder were identified by X-ray diffraction (XRD; Rigaku, RINT2500H) analysis using Ni-filtered $\text{Cu K}\alpha$ X-ray radiation. The surface morphology and texture of the specimens were observed by scanning electron microscopy (SEM; JEOL, JSM-6330F). The distribution of elements on the surface of the recovered powder was analyzed by energy dispersive X-ray spectroscopy (EDS; JEOL, JFC-2140). Quantitative and qualitative analyses of strontium, magnesium and cerium ions dissolved in HF solution were performed using inductively coupled-plasma atomic-emission spectroscopy (ICP-AES; Perkin Elmer Japan, 3300DV). X-ray photoelectron spectroscopy (XPS; Shimadzu, ESCA3300) using monochromatic $\text{Mg K}\alpha$ X-ray radiation (1253.6 eV) was performed to analyze the surface state of the powder rinsed with HNO_3 . The samples were fixed on a scratched Ag plate using the Ag 3d 5/2 peak as a standard position. The accurate peak position of each peak was determined assuming that the peak was expressed by Gaussian functions.

3. Results and discussion

3.1 Recovery of Si_3N_4 powder by hydrothermal treatment

Figure 1 shows the appearance of (a) the as-received Si_3N_4 sintered compact, (b) the recovered powder (left) and the core piece (right) remaining after hydrothermal treatment at 130°C for 24 h and the subsequent hydrothermal treatment, and (c) the powder rinsed with aqueous HNO_3 solution after the above treatments. The gray as-received sintered compact became white pulverized particles. Most of the sintered compact was easily disintegrated into powdery particles by the combination of the hydrothermal treatment and the sonication treatment, as seen on the left-hand side of Fig. 1(b). However, the inner part of the Si_3N_4 compact remained as a piece of fragment, which was not disintegrated, as seen on the right-hand side of Fig. 1(b). Fragment size decreased with increasing treatment time and temperature, since the corrosion rate of the Si_3N_4 ceramic in HF solution increased with increasing treatment time and temperature. From these results, the grain boundary phase is considered to be extracted from the surface of the Si_3N_4 sintered compact by hydrothermal treatment, and then sonication treatment leads to the pulverization of the Si_3N_4 ceramic where the grain boundary phase is extracted sufficiently.

Figure 2 shows the XRD profiles of (a) the as-received Si_3N_4 sintered compact, (b) the powder recovered after hydrothermal

Fig. 1. Appearance of (a) as-received Si_3N_4 sintered compact, (b) the recovered powder (left) and the fragment (right) remaining after the hydrothermal treatment at 130°C for 24 h and sonication, (c) the powder rinsed with aqueous HNO_3 solution.

treatment at 130°C for 24 h and the subsequent sonication treatment, and (c) the powder rinsed with HNO_3 after the above treatments. All the sharp diffraction peaks of the as-received Si_3N_4 sin-

Fig. 2. XRD profiles of (a) the as-received Si_3N_4 compact, (b) the powder recovered after hydrothermal treatment at 130°C for 24 h and the subsequent sonication, and (c) the powder rinsed with HNO_3 after the above treatments. Symbols denote $\beta\text{-Si}_3\text{N}_4$ (▼), CeF_3 (●) and MgF_2 (■).

tered compact correspond to crystalline $\beta\text{-Si}_3\text{N}_4$. The broad peak at here and throughout 15° is attributed to an amorphous phase in the grain boundary. In the XRD profiles of the powder after the hydrothermal treatment and sonication, the diffraction lines of fluorides corresponding to CeF_3 and MgF_2 were confirmed, as seen in Fig. 2(b), in addition to the diffraction lines of $\beta\text{-Si}_3\text{N}_4$. Then, the broad peak as observed in the as-received Si_3N_4 sintered compact was not observed in the powder obtained after the hydrothermal treatment (compare Figs. 2(a) and (b)). This result indicates that the amorphous grain boundary phase containing sintering additives dissolved in the aqueous HF solution resulting in the production of water-insoluble fluorides. After rinsing the hydrothermally treated powder in HNO_3 solution, the diffraction peaks of these fluorides completely disappeared and only the peaks corresponding to $\beta\text{-Si}_3\text{N}_4$ were observed, as shown in Fig. 2(c). These results suggest that pure $\beta\text{-Si}_3\text{N}_4$ powdery particles could be collected by the combination of hydrothermal treatment, sonication and rinsing. The peak shift of $\beta\text{-Si}_3\text{N}_4$ to a higher diffraction angle can be observed in the as-received and hydrothermally treated samples, but the reason for this has not been clarified yet.

Figure 3 shows the SEM micrographs of (a) the powdery particles recovered after hydrothermal treatment at 130°C for 24 h and subsequent sonication, and (b) the particles rinsed with HNO_3 solution after the above treatments. SEM observation revealed that

Fig. 3. SEM images of (a) the powder recovered after hydrothermal treatment at 130°C for 24 h and the subsequent sonication and (b) the powder rinsed with HNO_3 after the above treatments.

the as-recovered powder was a mixture of needle like particles and aggregated fine particles adhered on the needle like particles with diameters below 100 nm, as seen in Fig. 3(a). On the other hand, only needle like crystals of $\beta\text{-Si}_3\text{N}_4$ with a smooth surface were obtained by rinsing with HNO_3 solution (cf. Fig. 3(b)). **Figure 4** shows the EDS images of (a) the secondary electron image (SEI) and the element maps for (b) Si, (c) N, (d) F, (e) Mg, and (f) Ce in the recovered powder. The EDS images show that the needle like crystals are basically composed of Si and N atoms. Apparently, the area corresponding to the distribution of Mg or Ce atoms overlaps that of F atoms. Moreover, fine particles are observed in this overlapped area, which can be confirmed by comparing Figs. 4(a), (e) and (f). These images led us to conclude that the fine particles observed on the surface of the needle like $\beta\text{-Si}_3\text{N}_4$ particles are fluorides of Ce and Mg. This conclusion is also supported by the results of XRD analysis in Fig. 2 and SEM observation in Fig. 3.

The XPS spectra of the rinsed powder (a) before and (b) after Ar ion etching for 600 s are shown in **Fig. 5**. In addition, the results of surface analysis by XPS for the rinsed powder before and after Ar ion etching are shown in **Table 2**. No peaks attributed to the elements, such as F, Sr, Mg and Ce, were found in the XPS spectra of the rinsed powder, as seen in Fig. 5. The peak intensity of O 1s for the etched specimen decreased apparently in comparison with that for the as-rinsed specimen. Approximately 40 atomic% oxygen was detected on the surface of the as-rinsed powder. This oxygen originates from the surface oxidation by the corrosive attack in acidic solution under the hydrothermal conditions. Based on the results of the surface analysis of the etched specimen, the

Fig. 4. EDS images of (a) secondary electron image (SEI) and the maps for (b) Si, (c) N, (d) F, (e) Mg and (f) Ce in the recovered powder.

amount of oxygen was found to decrease to 4 atomic% by etching for 600 s. It is concluded on the basis of the XPS results that most impurities can be removed by HNO_3 rinsing, but the surface of the rinsed Si_3N_4 particles is slightly oxidized by the hydrothermal treatment.

Figure 6 shows the SEM micrographs of (a) the surface and (b) the cross section of a core piece obtained after hydrothermal treatment at 100°C for 24 h and sonication treatment. The needle like $\beta\text{-Si}_3\text{N}_4$ crystals were apparently observed on the corroded surface area of a core piece, as seen in Fig. 6(a). However, these crystals could not be disintegrated into powdery particles by sonication treatment. Similar features were observed in all the specimens exposed to various hydrothermal conditions except in the case at 150°C for 120 h, when the core piece disappeared completely. SEM observation revealed that the corrosive attack of aqueous HF solution proceeds towards the inner portion by intruding through the preferential paths of grain boundary phases, as seen in Fig. 6(b). However, it was impossible to pulverize the needle like $\beta\text{-Si}_3\text{N}_4$ particles observed on the core fragment because

Fig. 5. XPS spectra of Si_3N_4 powder rinsed with HNO_3 solution (a) before and (b) after Ar ion etching for 600 s.

the grain boundary phase dissolved insufficiently.

Figure 7 shows the weight fraction of the Si_3N_4 ceramic, which dissolved in the solution, disintegrated into powdery particles or remained as a core piece after the hydrothermal treatments under various conditions. The weight fraction of the core piece decreased with an increase in treatment time and temperature. On the contrary, the weight fraction of the dissolved portion in the ceramics gradually increased with increasing treatment time and temperature. By hydrothermal treatment at 150°C for more than 60 h, most of the Si_3N_4 ceramic dissolved mostly in the solution except the water-insoluble fluorides, and only a small amount of Si_3N_4 crystals was recovered. Taking account of the total amount of added sintering aids (Table 1), the dissolution of Si_3N_4 crystals themselves cannot be negligible. The dissolution of Si_3N_4 crystals might be described as⁸⁾

Therefore, excessively long-term treatment would not be appropriate at any temperatures. In the case of extremely short-term treatment, however, only a small amount of powder would be recovered at 100 and 110°C . Consequently, a higher recovery amount of Si_3N_4 particles against the dissolved portion was achieved by the hydrothermal treatment at relatively higher temperatures for shorter times, for example at 120°C for 24 h. This condition gave approximately 30% yield of Si_3N_4 powder, extruding the amount of sintering aid components.

Table 2. Results of Surface Analysis of the Rinsed Powder by XPS

Sample	Atomic %						
	Si	N	O	F	Sr	Mg	Ce
Before etching	30.45	28.47	40.81	<D.L.*	<D.L.*	<D.L.*	<D.L.*
After etching	58.95	36.12	4.93	<D.L.*	<D.L.*	<D.L.*	<D.L.*

* D.L. means detection limit.

Fig. 6. SEM images of (a) surface and (b) cross section of a core piece obtained after hydrothermal treatment at 100°C for 24 h and sonication treatment.

Fig. 7. Weight fraction of Si₃N₄ components after hydrothermal treatment under various conditions.

3.2 Kinetics and mechanism of dissolution under hydrothermal treatment

The leaching behavior of the Si₃N₄ ceramic and the grain boundary phase was analyzed in order to recover the Si₃N₄ particles efficiently from the Si₃N₄ ceramic under hydrothermal conditions. **Figure 8** shows the weight loss ($\Delta W/S$) of the Si₃N₄ ceramic in the hydrothermal treatments at various temperatures and times. Here, the weight loss is defined as

Fig. 8. Treatment time dependence of weight loss of the Si₃N₄ ceramic by hydrothermal treatments at 70 (●), 100 (◇), 110 (◆), 120 (□) and 150 (■)°C. Broken lines show the initial slopes.

$$\Delta W/S = (W_0 - W_1)/S \quad (2)$$

where W_0 and W_1 are the weights of the specimen before and after the hydrothermal treatment, respectively, and S is the surface area of the untreated specimen (see Table 1, approximately 3.42 cm²). The surface area of the hydrothermally treated specimen was supposed to be the same as that of the untreated specimen. In the case of the short-term treatment or the treatment at lower temperatures, a linear increase in weight loss was observed (broken lines in Fig. 8). The slopes of broken lines were found to increase with increasing treatment temperature. This is because the dissolution rate of the grain boundary phase and the Si₃N₄ crystals themselves increased with increasing temperature. On the other hand, when the processing time increased, the saturation behavior of weight loss was observed. This behavior of weight loss might be caused by the considerable size reduction of the core fragment.

Since the weight loss of the Si₃N₄ ceramic was linear with treatment time (broken lines as shown in Fig. 8), the corrosion kinetics of the Si₃N₄ ceramic by aqueous HF solution in the initial stage of the reactions can be described by

$$(\Delta W/S) = kt \quad (3)$$

where k is the rate constant and t is the treatment time. The arrhenius plot of the rate constant for the dissolution of the Si₃N₄ ceramic in 2.8 M HF solution is shown in **Fig. 9**. The straight line as expected from the Arrhenius equation strictly fits the rate constants in the whole temperature range. The activation energy is 31.9 ± 0.7 kJ/mol. The corrosion reaction of the Si₃N₄ ceramic by HF seems to be controlled by the surface chemical reaction in the region where a linear relationship exists between the weight loss of the Si₃N₄ ceramic and treatment time.

The dependence of the amount of dissolved grain boundary components on treatment time by hydrothermal treatment at various temperatures is shown in **Fig. 10**. The leaching behavior of strontium and magnesium ions showed a trend similar to that of the weight loss of the Si₃N₄ ceramic, where the dissolution rate of both components increased with increasing treatment temperature. The strontium ion exhibited a higher dissolution rate than the magnesium ion (compare Figs. 10(a) and (b)). The differences in the dissolution amount between strontium and magnesium ions arise from the difference in solubility in water between the fluorides. On the other hand, the dissolution of cerium ion was negligible under the present hydrothermal conditions because cerium ions formed water-insoluble CeF₃ precipitates, as supported by

Fig. 9. Arrhenius plot of the rate constant for dissolution of the Si_3N_4 ceramic in 2.8 M HF solution.

the results in Figs. 2 and 10.

To analyze the dissolution behavior of each grain boundary component, it is necessary to know the amount of each component precipitated as fluorides as well as that of each component dissolved in the HF solution. For this reason, the total amounts of the reacted components were estimated from the components dissolved in the aqueous HF solution after hydrothermal treatment and dissolved in aqueous HNO_3 solution after rinsing.

The sintering aids react with the phases containing SiO_2 , which are always present on the particle surfaces of commercially available Si_3N_4 powders, resulting in the liquid phase during sintering.¹⁾ It was also reported that SrCO_3 and CeO_2 used as sintering aids form SrO and Ce_2O_3 during the sintering process as described in the following reactions.¹⁴⁾

According to SiO_2 existing on the Si_3N_4 powders and Eq. (5), it seems that SiO_2 would be contained in the grain boundary phase, but the amount of SiO_2 in the grain boundary phase is difficult to estimate. Here, the total amount of dissolved grain boundary components (i) is defined as

$$(\text{The total amount of dissolved grain boundary component})_i = \Delta W_i / S_g, \quad (6)$$

where ΔW_i is the amount of each dissolved grain boundary component ($i = \text{Sr, Mg and Ce}$), and S_g is the surface area of the grain boundary phase shown in Table 1. The actual composition and volume fraction of the grain boundary phase (V_g) in the Si_3N_4 ceramic are not known here, so that V_g was calculated using the following assumption. The weight fraction of $\alpha\text{-Si}_3\text{N}_4$ does not change after sintering and any SiO_2 phase is not contained in Si_3N_4 . The volume fraction of $\beta\text{-Si}_3\text{N}_4$ (V_{SN}) was then derived from the density of $\beta\text{-Si}_3\text{N}_4$ and the weight fraction of $\alpha\text{-Si}_3\text{N}_4$. Consequently, V_g can be obtained by extracting V_{SN} from unity.

The rate constants for the total reaction of each grain boundary component at various temperatures were determined using the following equation, which was obtained by a modification of Eq. (3).

$$(\Delta W_i / S_g) = kt \quad (7)$$

The arrhenius plots of the rate constant for the total corrosive reaction of grain boundary components are shown in Fig. 11. The rate constants at various temperatures and apparent activation en-

Fig. 10. Treatment time dependence of dissolution rate of grain boundary components by hydrothermal treatment at various temperatures. Symbols denote 70 (●), 100 (◇), 110 (◆), 120 (□) and 150 (■)°C.

ergies for the dissolution of the Si_3N_4 ceramics, and the grain boundary components are summarized in Table 3. The activation energies for the dissolution of the grain boundary components, strontium, magnesium and cerium ions, were 54.4 ± 3.9 , 74.3 ± 1.4 and 51.7 ± 3.6 kJ/mol, respectively. The corrosion reaction of the grain boundary phase would be also controlled by the surface chemical reaction in the shorter-term treatment or treatment at lower temperatures as is the case for Si_3N_4 ceramics. The activation energy for the strontium ion was the same as that for the cerium ion, and the activation energy for the magnesium ion was the highest. Comparing the activation energies of strontium, cerium and magnesium ions with each other, the reactivity of the components was expected to increase in this order. The difference in the rate constant for the corrosion reaction between the grain boundary components would be caused by the differences

Table 3. Rate Constants and Activation Energy for Corrosion Reaction of Si_3N_4 Ceramic and Grain Boundary Components

	Rate constant, k ($\text{g}/\text{cm}^2/\text{h}$) $\times 10^{-3}$					Activation energy, E_a (kJ/mol)
	70°C	100°C	110°C	120°C	150°C	
Si_3N_4 ceramic	1.26	3.32	4.35	5.70	10.58	31.9 ± 0.7
Sr	0.07	0.34	0.45	0.80	1.90	54.4 ± 3.9
Mg	0.10	0.66	0.76	2.08	4.06	74.3 ± 1.4
Ce	0.29	1.34	1.98	2.71	6.96	51.7 ± 3.6

Fig. 11. Arrhenius plots of the rate constant for dissolution of grain boundary components. Symbols denote Sr (■), Mg (●) and Ce (▼).

in the amount contained in the grain boundary phase, as shown in Table 1. This result indicates that corrosion reaction of the grain boundary phase in HF solution would occur by dissolving the cerium- and strontium-containing phases preferentially than the magnesium-containing phase.

The apparent activation energy for the corrosion reaction of each grain boundary component was higher than that of the Si_3N_4 ceramic, as seen in Table 3. This result indicates that the Si_3N_4 ceramic is more sensitive to the corrosion attack by HF than the grain boundary phase. On the other hand, the rate constants for the grain boundary components gradually increased with increasing treatment time, and the rate of increase in these values for the grain boundary components are larger than that for the Si_3N_4 ceramic because of their higher activation energy. Therefore, it is concluded that the higher recovery rate of β - Si_3N_4 powdery particles is achieved under hydrothermal conditions at higher temperatures for shorter times.

4. Conclusions

The possibility of recycling Si_3N_4 ceramic by hydrothermal treatment in aqueous HF solution was investigated. Pure needle like β - Si_3N_4 powdery particles were collected by a combination of hydrothermal treatment, sonication treatment, and rinsing with aqueous HNO_3 solution. The Si_3N_4 sintered compact was found to disintegrate mostly into powdery particles by hydrothermal treatment and the subsequent sonication, though the core part of Si_3N_4

ceramic still remained as a fragment. Water-insoluble fluorides, which were formed and mixed into the recovered Si_3N_4 powder during hydrothermal treatment, were completely removed by rinsing with HNO_3 after the above treatments. XPS analysis clarified, however, that the surface of the rinsed particles was slightly oxidized.

As a result of the analysis of the leaching behavior of the Si_3N_4 ceramic, the degree of dissolution of sintering aids increased with increasing treatment time and temperature. The dissolution of the silicon nitride crystals itself increased with increasing treatment time and temperature. In the case of hydrothermal treatment up to 30 h, the corrosion behavior of the Si_3N_4 ceramic is linearly dependent on treatment time and is controlled by surface chemical reactions. The activation energies for the dissolution of the Si_3N_4 ceramic, and the grain boundary components of strontium, magnesium and cerium are estimated to be 31.9 ± 0.7 , 54.4 ± 3.9 , 74.3 ± 1.4 and 51.7 ± 3.6 kJ/mol, respectively. Effective hydrothermal conditions would be treatment at higher temperatures for shorter times, such as 120°C for 24 h.

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