

Preparation of β -sialon from Silica-gel

by

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Abstract

To prepare β -sialon ($\text{Si}_z\text{Al}_4\text{O}_4\text{N}_4$) through alumino-thermite reaction, white silica-gel with amorphous structure was reacted with aluminum at 1400 °C to 1800 °C for 0.5 to 4.0 h under nitrogen gas flow. The molar ratio of SiO_2 to Al was 12:16 and cobalt of 8 mass% against white silica-gel was added as a reaction promoter.

Sialon ($\text{Si}_{6-z}\text{Al}_2\text{O}_z\text{N}_{8-z}$) with the z-value ranging from 2.5 to 4.0 was formed at 1400 °C and 1600 °C. Aluminum compounds such as α - Al_2O_3 , AlN and others were formed along with sialon at these temperatures. The reason why many aluminum compounds were formed is considered to be caused by volatilization of silicon as SiO gas. On the other hand, $\text{Al}_2\text{O}_3 \cdot \text{AlN}$ spinel and AlN were formed at 1800 °C, except sialon.

1. Introduction

Self-propagation high temperature synthesis (SHS)⁽¹⁾ is one of the interesting methods for preparation of ceramics, because this method employs exothermic reaction among elements in raw powders and therefore has advantages in producing of high purity product and cost performance. Recently SHS method is considered to use for preparation of silicon nitride ceramics, especially for preparation of β -sialon, which has a general formula of $\text{Si}_{6-z}\text{Al}_2\text{O}_z\text{N}_{8-z}$ ⁽²⁾. The z-value in the formula is ranging from 0 to 4.2.

Umebayashi et al.^(3,7) reported that β -sialon composites could be fabricated directly from mixed powder of siliceous sands and aluminum under nitrogen gas. Uchiyama et al.^(8,9) reported that β -sialon/ β -SiC composite is fabricated directly from mixed powder of silica, aluminum and carbon under nitrogen gas. Alumino-thermite reaction was reported to occur during heat treatment above 900 °C. They found that addition of a transition metal such as iron, cobalt or nickel is effective to form β -sialon and that the most effective transition metal is cobalt. Siliceous sand and silica are an important raw material for the β -sialon fabrication reported and possess the same composition of SiO_2 . There are several materials that possess the composition of SiO_2 , including crystallite and amorphous; that is, silica, cristobalite, quartz, silica-gel and others. Structure of these materials may affect their reactivity with aluminum under nitrogen gas.

In this work, white silica-gel with amorphous structure

was used as raw material and was reacted with aluminum under nitrogen gas flow. Reaction products in the sintered compact were investigated by X-ray diffraction (XRD) method.

2. Experimental

The starting materials were white silica-gel powder with an average particle size of 4.17 μm , aluminum powder with that of 100 μm and cobalt powder with that of 2.00 μm . First, cobalt of 8 mass% against silica gel powder was added to the silica gel powder. Then, the silica gel powder with cobalt was mixed with aluminum powder in molar ratio of silica gel:aluminum = 12:16 in a mortar for 30 minutes in argon atmosphere. The molar ratio was determined to form β -sialon with the z-value of 4 by alumino-thermite reaction during high temperature heat treatment. The mixed powder of white silica-gel, aluminum and cobalt was added ethanol solution of polyethylene-glycol as a binder. After volatilization of ethanol, the mixed powder was formed into a compact of about 5×5×40 mm³ under a pressure of 1.57 MPa for 2 min and 3.92 MPa for 10 min. Then the green compact was set in graphite boat and the boat was placed at the center of electric furnace with graphite heater. The compact was heated to 1400 °C, 1600 °C or 1800 °C at a heating rate of 5.0 °C/min and then was kept at the given temperature for 0.5 h, 1.0 h, 2.0 h, or 4.0 h under nitrogen gas flow of 2.5 l·min⁻¹.

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After heat treatment, XRD analysis (equipment: RIGAKU RINT 2200 type X-ray diffraction analyzer, beam: $\text{CuK}\alpha$ with nickel filter, tube voltage: 30 kV, tube current: 16 mA) was performed for the pulverized compact and phases formed were identified. To obtain the relative intensity ratio of each phase in the sample, CaCO_3 with 20 mass% against the sample mass was added to the pulverized sample as an internal standard. Relation between lattice parameter of β -sialon and the z-value was investigated. Lattice parameter, a_0 , was calculated using 200 peak of β -sialon.

3. Results and Discussion

3.1 Phase identification

XRD profiles of the sintered compacts produced at various temperatures were shown in Figs. 1 - 3. Against our expectation, many aluminum compound phases are found as well as β -sialon.

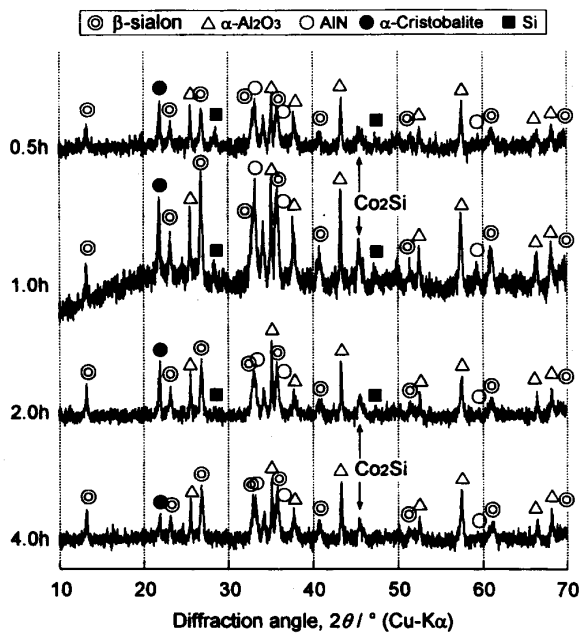


Fig.1 X-ray diffraction patterns of the compacts produced at 1400 °C under N_2 gas flow with keeping time.

From Fig. 1, in the case of heat treatment at 1400 °C, β -sialon, α - Al_2O_3 , AlN and α -cristobalite were found in all the samples. Silicon was found in the samples heat-treated for up to 2.0 h, while it was not found in the samples heat-treated for 4.0 h. From Fig. 2, in the case of heat treatment at 1600 °C, phases formed in the sample heat-treated for up to 2 h are different from those formed in the sample heat-treated for 4 h. β -sialon, α - Al_2O_3 , and 15R-AlN were formed in the sample heat-treated for up to 2 h, while AlN was formed instead of β -sialon in the sample heat-treated for 4 h. Co_2Si was formed in all the 1400 °C- and 1600 °C-treated samples.

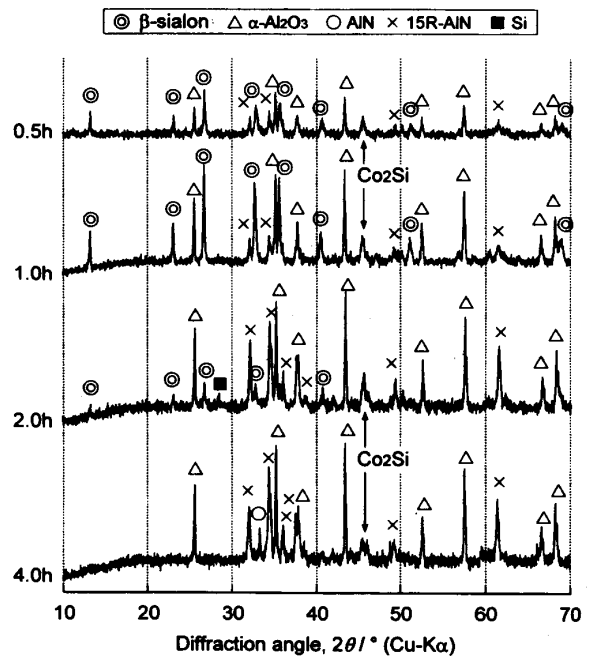


Fig.2 X-ray diffraction patterns of the compacts produced at 1600 °C under N_2 gas flow with keeping time.

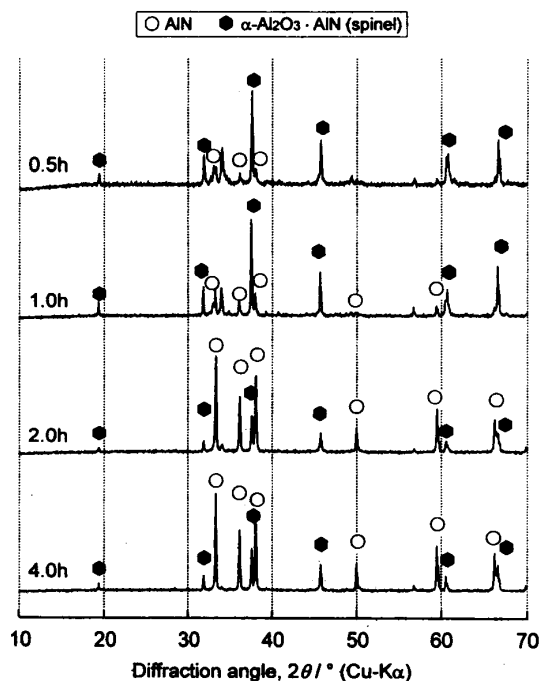


Fig.3 X-ray diffraction patterns of the compacts produced at 1800 °C under N_2 gas flow with keeping time.

From Fig. 3, in the case of heat treatment at 1800 °C, $\text{Al}_2\text{O}_3 \cdot \text{AlN}$ spinel and AlN were formed in the case of 1800 °C-treated sample.

To consider the formation process of each phase, integrated intensities of β -sialon 200 peak, α - Al_2O_3 102 peak, α -cristobalite 101 peak, AlN 101 peak, 15R-AlN 0015 peak and $\text{Al}_2\text{O}_3 \cdot \text{AlN}$ spinel 311 peak were calculated and the intensity ratio of each phase to the integrated intensity of CaCO_3 104 peak were shown in Fig. 4. From Fig. 4, slightly

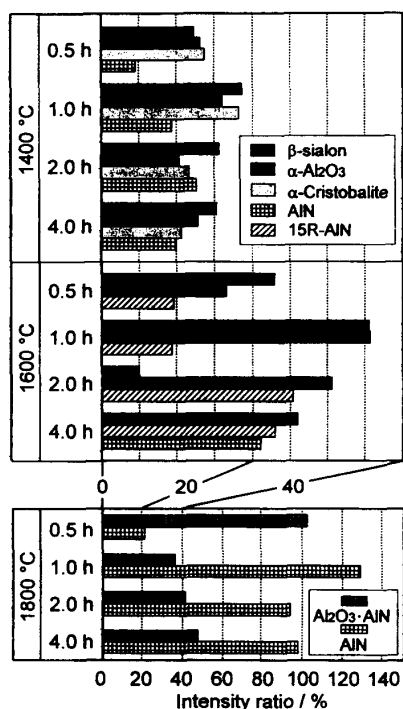
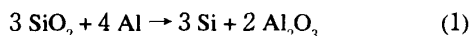


Fig.4 Keeping time dependence of XRD peak intensity ratio for various phases formed.

increasing formation of AlN was found with an increase of keeping time in the case of 1600 °C-treated samples.

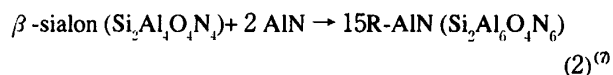
As alumino-thermite reaction is shown in eq. 1, formation



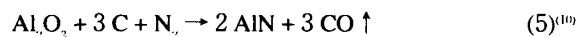
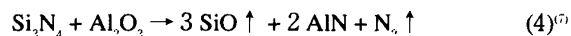
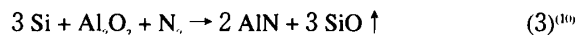
of silicon in the samples heat-treated at 1400 °C and 1600 °C suggests that the thermite reaction occurred in these samples. The reason why silicon was not formed in the sample heat-treated at 1400 °C for 4 h is considered that silicon formed reacted with nitrogen in the atmosphere into Si_3N_4 , followed by the formation of β -sialon by the reaction with α - Al_2O_3 or AlN. Co_2Si formation suggests that there is liquid phase of Co-Si binary system at reaction temperature, which was turned into Co_2Si during cooling to room temperature.

Formation of α -cristobalite in the samples heat-treated at 1400 °C and 1600 °C suggests that the thermite reaction did not occur homogeneously. Before being reacted with white silica-gel, aluminum in the sample is considered to react with nitrogen in the atmosphere into AlN, leaving SiO_2 as α -cristobalite.

From Fig. 4, β -sialon formation is remarkable in the sample heat-treated at 1600 °C for 1 h, then the fraction of β -sialon decreased and the fraction of 15R-AlN increased. This means that the following reaction occurred.



AlN formation and decreasing formation of α - Al_2O_3 in the sample heat-treated at 1600 °C for 4 h suggests that the following reaction might occurred.



Carbon in eq. (5) may come from the graphite boat used and the graphite heater of the furnace. Formation of $\text{Al}_2\text{O}_3 \cdot \text{AlN}$ spinel and AlN at 1800 °C implies that 1800 °C is too higher for sialon formation.

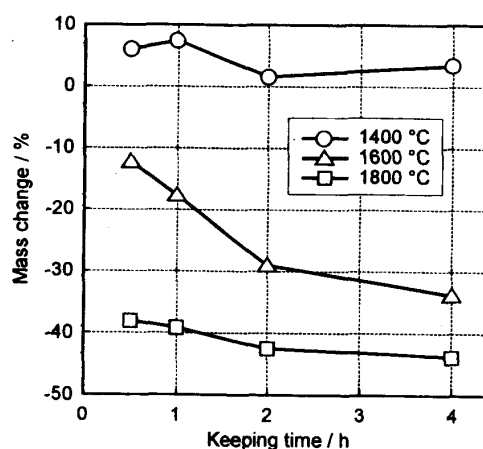


Fig.5 Keeping time dependence of mass change of the samples heat-treated at various temperatures under N_2 gas flow.

3.2 Mass change

Figure 5 shows a keeping time dependence of mass change of the samples heat-treated at various temperatures under nitrogen gas flow. Mass of the sample increased by heat treatment in the case of 1400 °C-treated sample, while it decreased in the case of 1600 °C- and 1800 °C-treated samples. Keeping time dependence is not distinguish in the case of 1400 °C- and 1800 °C-treated samples, while it is distinguish in the case of 1600 °C-treated sample. Mass of the sample heat-treated at 1600 °C decreased steeply up to 2 h and then decreased slowly.

If only nitriding occurs, mass of the sample should be increased. Mass gain by nitriding of silicon formed by the thermite reaction is calculated as 20 %. Therefore, mass loss also occurred in the sample heat-treated at 1400 °C. From XRD measurement, many aluminum compounds were formed against our expectation. This suggests that mass loss must be caused by silicon vanishment from the sample. Silicon could react with SiO_2 into SiO gas at about 1285 °C

under 1 Torr atmosphere⁽¹¹⁾. Based on this result, we can consider that silicon might vanish as SiO gas from the sample obeying the following reaction⁽⁷⁾ between silicon formed by the thermite reaction and SiO₂ from white silica-gel.



Change in keeping time dependence of the 1600 °C-treated sample may be accounted by the change in type of phases formed.

Most of silicon formed is considered to vanish from the 1800 °C-treated sample, causing formation of Al₂O₃·AlN spinel and AlN. From Fig. 5, the vanishment of silicon is considered to occur in the early stage of the reaction and keeping time dependence therefore is not distinguish in this case. Many reactions concerning SiO gas formation can be considered in this case, but without any analysis of the gas product during heat treatment the reaction process could not be considered.

3.3 Lattice parameter

Figure 6 shows lattice parameter of β-sialon calculated from 002 peak in XRD profile of some samples plotted on the data by Jack⁽²⁾. Although the z-value for the expected reaction product is 4, the z-value of the 1400 °C-treated sample is in the range of 2.5 to 4.0. Therefore, heat treatment temperature of 1400 °C is a little bit lower for β-sialon formation. On the other hand, the z-value of the 1600 °C-treated sample is 3.0 for the 0.5 h-treated sample and 4.0 for the 1.0 h-treated sample. This means that heat treatment at 1600 °C for 1 h is enough for β-sialon formation.

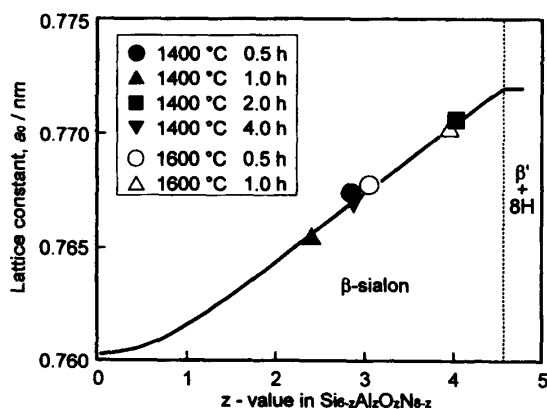


Fig.6 Lattice parameter of β-sialon in the 1400 °C and 1600 °C-treated samples. Data are plotted on the line after Jack⁽²⁾.

From our early result⁽¹²⁾ it is known that cobalt addition promotes nitriding of silicon to form Si₃N₄. It was reported by many researchers⁽¹³⁻¹⁵⁾ that nitriding of silicon was promoted by Fe addition to form Si₃N₄ through formation of liquid phase of Fe-Si. Based on the result reported, we considered that formation of liquid phase of Co-Si binary system promotes nitriding of silicon. From these experimental results, it was considered that Si formed from thermite reaction between white silica-gel and aluminum reacted with N₂ preferentially to form Si₃N₄ in the presence of cobalt, and then reacted with Al₂O₃ to form β-sialon.

4. Conclusions

Mixed powder of white silica-gel with 8 mass% cobalt and aluminum with an molar ratio of SiO₂:Al = 12:16 was heat-treated at 1400 °C to 1800 °C for 0.5 h to 4h under nitrogen gas flow and reaction product was investigated. It is concluded that:

1. Sialon (Si_{6-2z}Al₂O₂N_{8-2z}) with the z-value ranging from 2.5 to 4.0 was formed at 1400 °C and 1600 °C, along with aluminum compounds such as -Al₂O₃, AlN, and others.
2. Co₂Si was also formed at 1400 °C and 1600 °C. Formation of β-sialon is considered to be occurred preferentially through the formation of liquid phase of Co-Si binary system which changed into Co₂Si during cooling.
3. Al₂O₃ · AlN spinel and AlN were formed at 1800 °C.
4. Si volatilized from the reaction system through SiO gas.

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