Thermal Stability of Phases in \( \text{Si}_3\text{N}_4(-\text{SiO}_2) - \text{AlN}-\text{Y}_2\text{O}_3 \) System

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This paper discusses the thermal stability of phases in the system \( \text{Si}_3\text{N}_4(-\text{SiO}_2) - \text{AlN}-\text{Y}_2\text{O}_3 \). The total amount of \( \text{AlN} \) and \( \text{Y}_2\text{O}_3 \) varied from 5 to 11 wt\% and the molar ratio of \( \text{AlN}/\text{Y}_2\text{O}_3 \) was 0 to 11. Specimens were prepared by hot-pressing, and then were heat-treated for 50h. The phases formed by hot-pressing changed during the heat treatment. The fraction of \( \alpha' \)-Sialon was decreased by the heat treatment. This decrease was remarkable, when the solubility of \( \alpha' \)-Sialon was small. Due to the heat treatment, the solubility of \( \beta' \)-Sialon changed to a constant value, while that of \( \beta' \)-Sialon showed little change.

Key-words: \( \alpha' \)-Sialon, \( \beta' \)-Sialon, Phase relation, Solubility, Heat treatment

1. Introduction

Sialon is a solid-solution material with the same structure as \( \text{Si}_3\text{N}_4 \). In \( \beta' \)-Sialon, Al and O atoms replace Si and N atoms, respectively. In addition to these replacements, \( \alpha' \)-Sialon dissolves a metal element M (such as Y, Mg or Ca) in the interstitial sites. The general formulas of \( \alpha' \) - and \( \beta' \)-Sialon are described as \( \text{M}_x(\text{Si}, \text{Al})_{12-x}(\text{O}, \text{N})_{16-x}(x \leq 2) \) and \( \text{Si}_{6-z}\text{AlN}_z\text{O}_{12-z} \) \((0 < z \leq 4.2)\), respectively.\(^1\) Sialon can dissolve oxides and nitrides into its grains, and the glassy phase at grain boundaries can be diminished. Consequently, Sialon is expected to have good mechanical properties at high temperatures. We have obtained Sialon composites composed of \( \gamma' \)-Y-Sialon and \( \beta' \)-Sialon by sintering powder mixtures of \( \text{Si}_3\text{N}_4 \), \( \text{AlN} \), and \( \text{Y}_2\text{O}_3 \), which showed good mechanical properties at elevated temperatures.\(^2\),\(^3\)

In their practical application to gas turbine components operating above 1400°C, the thermal stability of Sialon seems very important. Crystalline phases in the \( \text{Si}_3\text{N}_4-\text{AlN}-\text{Y}_2\text{O}_3 \) system were reported by Mitomo et al.,\(^4\) Huang et al.,\(^5\) and Fukuhara.\(^6\) However, it was not clear whether the phases were in equilibrium, because they identified the phases which formed after sintering for only 1 or 2h. The phases in the specimen obtained by hot-pressing for 1h in the \( \text{Si}_3\text{N}_4-\text{AlN}-\text{Y}_2\text{O}_3 \) system were also discussed in our previous work.\(^7\) The results did not agree with the phase diagram (Fig. 1) proposed by Mitomo et al. and Huang et al. It was considered that one of the reasons for this disagreement was that the reaction did not reach to equilibrium after hot-pressing for 1h. To clarify this, Sialon composites, obtained by hot-pressing mixtures of \( \text{Si}_3\text{N}_4 \), \( \text{Y}_2\text{O}_3 \) and \( \text{AlN} \) powders at 1850°C for 1h, were annealed at 1850°C for 50h. The changes in crystalline phases and solubilities of \( \alpha' \)-and \( \beta' \)-Sialons were examined by X-ray diffraction (XRD) method.

2. Experimental procedure

2.1 Specimen preparation

As was the case in our previous work,\(^7\) \( \text{Si}_3\text{N}_4 \) (Ube Industry Co., Ltd., SN-E10), \( \text{Y}_2\text{O}_3 \) (Mitsubishi Chem. Co., Ltd.) and \( \text{AlN} \) (Tokuyama Soda Co., Ltd.) were used as raw powders. The total amounts of \( \text{Y}_2\text{O}_3 \) and \( \text{AlN} \) were 5, 7 and 11 wt\%. In each case, the molar ratio of \( \text{AlN}/\text{Y}_2\text{O}_3 \) \((=r)\) varied from 0 to 11. The mixtures were hot-pressed in \( \text{N}_2 \) atmosphere at 1850°C under a pressure of 20 MPa for 1h. The sintered bodies were 60 mm in diameter and 6 mm in thickness. They were heat-treated in a graphite crucible at 1850°C (the same temperature as that for hot-pressing) for 50h in a \( \text{N}_2 \) of 10 atm. The sintered bodies were buried in the powder with the same compositions as the starting mixture during the heat treatment to prevent changes in the composition of the sintered body. The specimens were cooled down in the furnace.

Specimens for X-ray diffractometry (approximately 10 mm × 15 mm × 2 mm) were cut from the heat-treated bodies.

![Fig. 1. Correlation diagram of Si3N4-AlN-Y2O3.](image-url)
2.2 Determination of crystalline phases and lattice parameters

Phases and lattice parameters were determined by XRD analysis (Mo Kα, 40 kV, 80 mA). The fractions of α'- and β'-Sialons were calculated from XRD peak intensities. The fraction of α'-Sialon was determined using the following equation.

\[
\alpha' (\text{vol}%) = \frac{I_{(102)} + I_{(210)}}{I_{(102)} + I_{(210)} + I_{(101)} + I_{(210)}} \times 100
\]

The changes in the solubilities of α'- and β'-Sialons were investigated by measurement of lattice parameters and discussed in comparison with the results of our previous work.7

3. Results

3.1 Crystalline phases

The summary of phases determined after the heat treatment is shown in Table 1, being compared with those of sintered bodies before the heat treatment. Y2O3·SiO2 (A in Table 1) and 10Y2O3·9SiO2·Si3N4 (B), which were not seen in the phase diagram (Fig. 1), were detected before the heat treatment. The existence of these phases cannot be predicted from the phase diagram proposed by Mitomo et al.4 and Hu-ang et al.5 In our previous work, the main reason for this was estimated to be the existence of SiO2 on the surface of Si3N4 powder. After the heat treatment, these phases disappeared, and 4Y2O3·SiO2·Si3N4 (C) and 5Y2O3·Si3N4·Al2O3 (F) were observed in turn. The region where Si3N4·Y2O3 was formed was extended by the heat treatment. On the other hand, the region of α'-Sialon occurrence was confined to the composition with a larger amount of additives and a higher value of \( r \), compared with those before the heat treatment (Fig. 2).

The fractions of α'-Sialon obtained after the heat treatment are given in Fig. 3. As may be seen from this figure, the fraction was largest at the stoichiometric composition \( r=9 \) and the amount of α'-Sialon was decreased significantly by the heat treatment.

3.2 Lattice parameter (solid-solubility)

The lattice parameters of α'- and β'-Sialons determined after the heat treatment are shown in Fig. 4 and Fig. 5, together with those of the specimens before the heat treatment. The lattice parameters of α'-Sialon were scattered in a range of 0.562–0.566 nm (at c-axis) with their compositions before the heat treatment. However, they were constant at nearly

Table 1. The Summary of Phases Detected Before and After Heat Treatment

<table>
<thead>
<tr>
<th>t</th>
<th>r</th>
<th>0</th>
<th>1</th>
<th>3</th>
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<td>5 wk</td>
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<td>( \beta + A )</td>
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<td>( \beta + C )</td>
<td>( \beta + P )</td>
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<tr>
<td>7 wk</td>
<td>(b)</td>
<td>( \beta + B )</td>
<td>( \beta + C )</td>
<td>( \beta + P )</td>
<td>( \beta + P )</td>
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<td></td>
<td>(a)</td>
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<td>10 wk</td>
<td>(b)</td>
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<td>( \beta + P + D + E )</td>
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<td>Mitomo</td>
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<td>( \beta + D + E )</td>
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A : Y2O3·SiO2, B : 10Y2O3·9SiO2·Si3N4, C : 4Y2O3·SiO2·Si3N4, D : Si3N4·Y2O3, E : AlN, F : 5Y2O3·Si3N4·Al2O3. Mitomo : Phases expected from Mitomo's diagram (b) before heat treatment, (a) after heat treatment

r : Molar ratio of AlN/Y2O3, t : Total amount of AlN and Y2O3

Fig. 2. The region of α'-Sialon occurrence in the Si3N4-AlN-Y2O3 system before and after heat treatment.

Fig. 3. The fraction of α'-Sialon before and after heat treatment plotted against the composition.

Fig. 4. The lattice parameters of α'-Sialons before and after heat treatment plotted against the composition.
0.566 nm irrespective of the compositions after the heat treatment, $\alpha'$-Sialons with low solubility disappeared during the heat treatment. This indicates that $\alpha'$-Sialons with low solubility as well as $\alpha$-Si$_3$N$_4$ were not stable at high temperature and that it was transformed to $\beta'$-Sialon. On the other hand, the lattice parameters of $\beta'$-Sialon did not change at around 0.291 nm (at $c$-axis).

4. Discussion

4.1 Phase analysis

In our previous work,$^7$ we have reported that the differences between the phases expected from the Si$_3$N$_4$-AlN-$Y_2$O$_3$ diagram proposed by Mitomo et al. and those obtained by hot-pressing for 1h were as follows:

1. $\beta'$-Sialon, instead of $\beta$-Si$_3$N$_4$, was formed in the compositions where AlN was added.
2. The region where only $\alpha'$- and $\beta'$-Sialons exist has some spread in the diagram.
3. When the amount of additives and the value of $r$ were small, $\alpha$'-Sialon was not formed, but compounds containing SiO$_2$, which were not seen in the diagram, were formed.

It was considered that these differences depended on whether SiO$_2$ on the surface of Si$_3$N$_4$ powder was taken into account and whether the reaction reached equilibrium. In this study, therefore, heat treatment was employed to make the reaction close to the equilibrium.

$\beta'$-Sialon, which was formed before the heat treatment, existed stably after the heat treatment. There was little change in the solubility of $\beta'$-Sialon. $\beta'$-Sialon is considered to be formed according to the following equation, as described in the previous paper.$^7$

$$ (2 - z/2) \text{Si}_3\text{N}_4 + z\text{AlN} + z/2\text{SiO}_2 \rightarrow \text{Si}_6\text{AlO}_4\text{N}_8 - z \quad (2) $$

According to the diagram, the solubility of $\alpha'$-Sialon must be constant when $\alpha'$-Sialon co-exists with $\beta$-Si$_3$N$_4$. If the composition is on the plane of Si$_3$N$_4$-AlN-$Y_2$O$_3$ system, $\alpha'$-Sialon with various solubilities cannot exist. However, the solubilities of $\alpha'$-Sialon obtained before the heat treatment varied with the compositions, as shown in Fig. 4. This suggests that the phases obtained in practice were shifted from those on the plane of the Si$_3$N$_4$-AlN-$Y_2$O$_3$ system.

The fraction of $\alpha'$-Sialon decreased and the region where $\alpha'$-Sialon existed became narrower due to the heat treatment. In particular, the fraction of $\alpha'$-Sialon decreased remarkably in the region where $\alpha'$-Sialon had low solubilities. $\alpha'$-Sialon is considered to have dissolved or disappeared according to the following equation.

$$ Y_x(\text{Si, Al})_{12}(\text{O, N})_{16} \rightarrow (4 - 3x/2)\text{Si}_3\text{N}_4 + 9x/2\text{AlN} + x/2\text{Y}_2\text{O}_3( + \text{SiO}_2) \rightarrow \beta' + \text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3 \quad (3) $$

The two-phase region of $\alpha'$ and $\beta'$-Sialons, was limited to the stoichiometric composition ($r = 9$) after the heat treatment, as shown in the phase diagram.

$\text{Y}_2\text{O}_3 \cdot \text{SiO}_2$ and $10\text{Y}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot \text{Si}_3\text{N}_4$, which were formed before the heat treatment in the cases where the amount of additives and the value of $r$ were small, disappeared. Also, $4\text{Y}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{Si}_3\text{N}_4$ and $5\text{Y}_2\text{O}_3 \cdot \text{Si}_3\text{N}_4 \cdot \text{Al}_2\text{O}_3$ were formed by the heat treatment. Figure 6 shows the phase diagram of Si$_3$N$_4$-$\text{SiO}_2$-$Y_2$O$_3$ system proposed by Wills et al.$^9$ and Lange et al.$^{10}$ Considering these compounds in the view of the contents of SiO$_2$ and Y$_2$O$_3$, it is clear that the SiO$_2$ content in the crystalline phase decreased during the heat treatment and that the Y$_2$O$_3$ content increased contrarily. This is also true in the case of $5\text{Y}_2\text{O}_3 \cdot \text{Si}_3\text{N}_4 \cdot \text{Al}_2\text{O}_3$, which is not on the plane of Si$_3$N$_4$-$\text{SiO}_2$-$Y_2$O$_3$ system. This compounds can be described as follows.

$$ 5\text{Y}_2\text{O}_3 \cdot \text{Si}_3\text{N}_4 \cdot \text{Al}_2\text{O}_3 = 3/2\text{SiO}_2 \cdot 5\text{Y}_2\text{O}_3 \cdot 2\text{AlN} \cdot 1/2\text{Si}_3\text{N}_4 \quad (4) $$

This phase also has lower SiO$_2$ content and higher Y$_2$O$_3$ content. Si$_3$N$_4$-$Y_2$O$_3$ was found in the region where $\alpha'$-Sialon disappeared. These facts indicate that crystalline phases with low SiO$_2$ content and high Y$_2$O$_3$ content were formed by the heat treatment. The results showed that silicon oxides left the system during the heat treatment and the content of Y$_2$O$_3$ in the crystalline phase became higher.

4.2 Lattice parameter (solid solubility)

Figure 4 shows that the solubility of $\alpha'$-Sialon con-

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Fig. 6. Correlation diagram of Si$_3$N$_4$-$\text{SiO}_2$-$Y_2$O$_3$. 

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verged to a constant value by the heat treatment and that α’-Sialon with low solubility could not exist stably at high temperatures. Mitomo et al.\(^4\) reported the solubility of α’-Sialon obtained with various amounts of additives at stoichiometric composition \((r=9)\). According to their paper, the solubility of α’-Sialon co-existing with β-Sialon was constant at \(x=0.3\). The solubility determined after the heat treatment was \(x=0.3\), which was the same as that of Mitomo et al. From these results, it is obvious that the solubility of α’-Sialon is constant after the heat treatment, independently of not only the total amount of additives but also the composition of additives. When the change in the fraction of α’-Sialon was small (the value of \(r\) and the total amount of additives were large), the change in the solubility was also small. On the other hand, the fraction of α’-Sialon decreased significantly at the composition where the solubility increased remarkably (the value of \(r\) was small). That is, α’-Sialon with low solubility was decomposed into β’-Sialon or Si\(_3\)N\(_4\)-Y\(_2\)O\(_3\) during the heat treatment.

We reported the transformation of α’-Sialon into β’-Sialon during heat treatment.\(^8\) When the transformation of α’-Sialon into β’-Sialon proceeds, the element such as Y and N will be excluded to grain boundaries and the concentrations of these elements at grain boundaries will increase during heat treatment. These elements will then diffuse to the remaining α’-Sialon and dissolve again. Therefore, the lattice parameters of the remaining α’-Sialon increased.

The equation of α’-Sialon formation can be expressed as follows, when the solubility is \(x=0.3\) as derived from this experimental result.

\[
3.55\text{Si}_3\text{N}_4 + 0.15(9\text{AIN} + \text{Y}_2\text{O}_3) \rightarrow \text{Y}_{0.3}\text{Si}_{10.65}\text{Al}_{3.65}\text{O}_{6}\text{N}_{15.55}
\]

The amount of AIN contained in α’-Sialon can be estimated using this equation. For example, we consider the case of \(r=9\) and the total additive amount of 11 wt\%, where only α’- and β’-Sialons were formed. Figure 4 shows that 45 vol\% α’-Sialon and 55 vol\% β’-Sialon exist in the composition. Assuming that the densities of α’- and β’-Sialon are equal and that AIN is consumed according to the Eq. (5) in advance, 66% AIN is contained in α’-Sialon and the remaining 34% is in β’-Sialon. Based on these considerations, the solubility of β’-Sialon is estimated to be \(z=0.3\). This value is approximately equal to the solubility determined by the lattice parameters in this experiment, according to Ref. 1.

In the experiment of Mitomo et al., the solubility of α’-Sialon reached equilibrium (\(x=0.3\)) after hot-pressing. On the other hand, equilibrium was attained only after the heat treatment in our experiments. The difference is considered to be caused by the character of the raw material used in the experiments. The oxygen content and its distribution in Si\(_3\)N\(_4\) powder depend on the production process and the grade. The Si\(_3\)N\(_4\) powder (Starck LC-10) used by Mitomo et al. and SN E-10, which was used in this work, contain 1.3 wt\% and 0.8 wt\% oxygen, respectively.\(^11\) That is, SN E-10 has less oxygen than LC-10. Also, Greil et al. stated that most of the oxygen in SN E-10 was distributed on the surface, compared with LC-10. These characteristics of the powders, which determine the viscosities of liquid phase in sintering, must be related to the difference in reaction rate.

5. Conclusions

The thermal stability of phases in the Si\(_3\)N\(_4\)–Y\(_2\)O\(_3\)–AIN system was examined by the heat treatment at 1850°C for 50h of the hot pressed bodies. The results obtained in this work are as follows:

1. The phases detected by XRD changed during the heat treatment. 10\(Y_2O_3\); 9SiO\(_2\); Si\(_3\)N\(_4\) and Y\(_2\)O\(_3\); SiO\(_2\), which were observed before the heat treatment, disappeared and 4Y\(_2\)O\(_3\); SiO\(_2\); Si\(_3\)N\(_4\) and 5Y\(_2\)O\(_3\); Si\(_3\)N\(_4\); Al\(_2\)O\(_3\) were formed.

2. The content and region of α’-Sialon were decreased and limited drastically by the heat treatment.

3. The lattice parameters (solubilities) of α’-Sialon, which varied with the compositions before the heat treatment, increased and converged to a constant value of 0.566 nm after the heat treatment. On the other hand, that of β’-Sialon was almost constant before and after the heat treatment.

References