The Stability of $\alpha$-sialon at High Temperatures

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$\alpha$-サイアロンの高温での安定性

Key-words: $\alpha$-sialon, Stability, Thermal decomposition, N$_2$ pressure, Sintering

The formation of $\alpha$-sialons was reported previously$^{33}$. The mechanical and electrical properties of some $\alpha$-sialons were also investigated$^{33}$. But there was no thermochemical data on $\alpha$-sialons, so that it is not possible to calculate the stable temperature range of $\alpha$-sialons. The information on the stability of $\alpha$-sialons at high temperatures is very important for the sintering and the application of $\alpha$-sialons.

Present note intends to know the stable temperature range of Y-$\alpha$-sialon under 1 atm N$_2$ and show the condition to stabilize the sialon at high temperature, experimentally.

The general formula for $\alpha$-sialons is $M_x(Si,Al)_{12}(O,N)_{16}$, where M is Li, Mg, Ca, Y and rare-earth elements except La and Ce, and $0 < x \leq 2$. In $\alpha$-sialon, Si and N sites in
\[ \alpha - \text{Si}_3\text{N}_4 \text{ structure are partly replaced by Al and O respectively as in } \beta - \text{Si}_3\text{N}_4. \]  

The dissolution of M metal in \( \alpha - \text{Si}_3\text{N}_4 \) structure was supposed to be at the interstitial sites.

### Table 1. The weight loss and the composition after 1 h.

<table>
<thead>
<tr>
<th>( \text{N}_2 ) pressure (atm)</th>
<th>Temperature (°C)</th>
<th>wt. loss (%)</th>
<th>composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1700</td>
<td>8.7</td>
<td>( \alpha - \text{sialon} \rightarrow \text{Y}_2 \text{Si} \left( \text{Si}_2\text{O}_3\text{N}_4 \right) )</td>
</tr>
<tr>
<td></td>
<td>1750</td>
<td>33.6</td>
<td>( \beta - \text{Si}_3\text{N}_4 )</td>
</tr>
<tr>
<td>1</td>
<td>1800</td>
<td>35.0</td>
<td>( \text{Si} \rightarrow \text{YSi}_2 \rightarrow \text{ALN} \rightarrow \alpha - \text{sialon} )</td>
</tr>
<tr>
<td>10</td>
<td>1800</td>
<td>1.1</td>
<td>( \alpha - \text{sialon} \rightarrow \beta - \text{Si}_3\text{N}_4 )</td>
</tr>
<tr>
<td>30</td>
<td>1900</td>
<td>2.0</td>
<td>( \alpha - \text{sialon} \rightarrow \beta - \text{Si}_3\text{N}_4 )</td>
</tr>
</tbody>
</table>

### Fig. 1. The change in weight loss with time at 1700°, 1750° and 1800°C.

\( \alpha - \text{Si}_3\text{N}_4 \) structure are partly replaced by Al and O respectively as in \( \beta - \text{Si}_3\text{N}_4 \). The dissolution of M metal in \( \alpha - \text{Si}_3\text{N}_4 \) structure was supposed to be at the interstitial sites.

An \( \alpha - \text{Y-sialon} \) was fabricated by hot pressing the powder mixture of \( \text{Si}_3\text{N}_4 \) and \((\text{Y}_2\text{O}_3 + 9\text{AlN}) \) at 1700°C for 1 h under a pressure of 200 kg/cm². The composition used in the present work was,

\[
31\ \text{Si}_3\text{N}_4 + 3(\text{Y}_2\text{O}_3 + 9\text{AlN})
= 10\ \text{Y}_5\left(\text{Si}_{1.3}, \text{Al}_{2.7}\right)\left(\text{O}_{0.9}, \text{N}_{15.1}\right)
\]

The sintered materials were then pulverized to the powder \(< 50 \mu\text{m}. \) The powder mostly composed of \( \gamma - \text{Y-sialon} \) (>95%). The unit cell of hexagonal \( \gamma - \alpha - \text{sialon} \) was \( a = 7.827 \) Å and \( c = 5.704 \) Å, which agreed well with that by Hampshire and co-workers.

About 0.8 g of the \( \alpha - \text{sialon} \) powder was heated in the temperature range 1700°~1800°C for 0.5~2 h under 1 atm \( \text{N}_2 \) in a carbon crucible coated with BN powder. The crucible was open to the atmosphere. The weight loss after heating the specimen was plotted in Fig. 1. At 1700°C, the weight loss was less than 10% after heating for 2 h. At 1750 and 1800°C, the other hand, it was very large (>35%) after heating for 2 h. The results show that \( \alpha - \text{sialon} \) is stable at lower temperatures than 1700°C under 1 atm \( \text{N}_2 \).

The weight loss and the crystalline composition detected by X-ray diffraction of specimens after heating for 1 h are listed in Table 1. The formation of \( \text{Y}_2\text{Si} \left(\text{Si}_2\text{O}_3\text{N}_4\right) \) was observed after heating at 1700° and 1750°C. This phase was formed by the reaction of \( \text{Si}_3\text{N}_4 \) with \( \text{Y}_2\text{O}_3 \). There was no diffraction peak of \( \text{Y}_2\text{Si} \left(\text{Si}_2\text{O}_3\text{N}_4\right) \) in the starting powder. The table suggests that the part of \( \text{Y}_2\text{O}_3 \) remained at grain boundaries as glassy phase and crystallized as \( \text{Y}_2\text{Si} \left(\text{Si}_2\text{O}_3\text{N}_4\right) \) by the heat treatments. At 1750°C and 1800°C, \( \text{Si}, \text{YSi}_2, \) and \( \text{AlN} \) were detected as reaction products. It is the most likely that gaseous products were \( \text{SiO and N}_2 \) as in the thermal decomposition of sialons.

The thermal decomposition of \( \gamma - \alpha - \text{sialon} \) may be inferred to be,

\[
\text{Y}_5\left(\text{Si}_{1.3}, \text{Al}_{2.7}\right)\left(\text{O}_{0.9}, \text{N}_{15.1}\right)
= 7.2\ \text{Si} + 0.6\ \text{YSi}_2 + 2.7\ \text{AlN}
+ 0.9\ \text{SiO} + 6.2\ \text{N}_2
\]

The evaporation of \( \text{SiO and N}_2 \) from \( \alpha - \text{sialon} \) may contribute to the weight loss during heating. The calculated weight loss based on the equation is 34.8% which was shown in Fig. 1 by a dotted line. Larger weight loss observed at 1750° and 1800°C than calculated one might be attributed to the evaporation of Si from molten Si. The equation suggests that the dominant gaseous product was \( \text{N}_2 \). The molar ratio for \( \text{SiO/N}_2 \) in the equation \( \left(\text{2}\right) \) is about 1/7, which is smaller than that in \( \beta - \text{sialon} \) of 2.5 or 3. \( \beta - \text{sialon} \) at high temperatures is more significant than that of \( \text{SiO} \) pressure.

The stability of \( \alpha - \text{sialon} \) was also examined at 1800° and 1900°C under 10 and 30 atm \( \text{N}_2 \), respectively. The results were added in Table 1. The table shows that \( \alpha - \text{sialon} \) was stabilized under high \( \text{N}_2 \) pressures.
Y₅Si(Si₂O₃N₄). It means that the degree of solid solubility in α-sialon was increased at high temperatures.

Present work showed that Y-α-sialon Y₅₆(Si₉₃, Al₂₇) (O₀₉, N₁₅) was stable up to about 1700°C under 1 atm N₂. Under high N₂ pressures, α-sialon was stable at higher temperatures. The stability of α-sialon was related to the pressure of ambient N₂. The results suggest that α-sialon could be sintered at high temperatures under high N₂ pressures at which the amount of residual intergranular phase might be decreased by its dissolution in α-sialon grains.

References

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Crystallographic Study of Potassium Tetratitanate

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四チタン酸カリウムの結晶学的研究

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1. Introduction

Potassium hexa- and tetratitanate are well-known artificial minerals of fibrous-shape. Among them, potassium tetratitanate has only a preliminary X-ray powder diffraction data. Berry et al. reported the X-ray powder diffraction data and lattice parameters for a potassium oxyfluotitanate (K₅Ti₄O₁₀F₂₂) in 1960. Those data are not considered to be precise enough\(^9\). Easteal and Udy (1972) reported the X-ray powder diffraction data and lattice parameters but did not give indices\(^9\). Dion et al. obtained the lattice parameters on the potassium tetratitanate which was obtained by the exchange reaction of melt KCl or melt mixture KCl-KNO₃ with thallium tetratitanate (Tl₄Ti₄O₁₀) at 800°C, but reported no X-ray powder diffraction data in 1978\(^9\).

The present authors synthesized a high-quality crystals of potassium tetratitanate obtained form of the whisker-like potassium titantate "Fur-fibers" by the KDC (Kneading-Drying-Calcination) method, from which lattice para- meters, indices of X-ray powder diffraction data and infrared spectra were obtained\(^9\).

2. Experimental

Titanium dioxide (mixture of 89% rutile and 11% anatase) and anhydrous potassium carbonate of guaranteed reagent grade were