次のようにまとめられる。

(1) ガラス量が多い場合はそのガラスの屈伏点以上の温度で加圧焼結すればほぼ完全に密化した混合焼結体が得られた。

(2) 微粒の銅粉を混合する方が比較的少量の混合で混合焼結体中の銅相のつながりができるから、熱伝導率の向上に効果的である。粗粒の銅粉を混合した場合は銅が熱伝導率の悪いガラス中に分散するため、熱伝導率の向上は悪い。

(3) 微粉の銅を用いた混合焼結体では、銅粉の混合量が少量の時は、混合熱伝導率の一つである対数則に従ってその熱伝導率は変化し、ある程度以上の混合量となると銅相が連続化するため、対数則よりはるかに急激に大きくなる。しかし熱伝導の良い銅が連続相であるモデルから予想されるほどには大きくならない。一方粗粒の銅粉を用いた場合は、熱伝導の良い銅が分散しているモ

デルによる熱伝導率とよい一致を示した。

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論文・Paper

Thermal Decomposition Reaction of Sialon

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Thermal decomposition of sialon was performed by heating two-phase sialon consisting of both β -sialon with $z=2.3$ and X-sialon and single-phase β -sialon ($z=2$, $\text{Si}_4\text{Al}_2\text{O}_7\text{N}_6$) at 1800°C under 1 atm N_2 . Changes in composition and phase were studied by means of X-ray diffraction and chemical analysis.

The reactions are inferred to be,

for the two-phase sialon and,

for the single-phase sialon.

The region of SiO pressure for the stable single-phase β -sialon under total pressure of 1 atm was calculated to be from 6.0×10^{-1} to 3.9×10^{-1} atm at 1800°C assuming intermediate stages.

The methods to fabricate β -sialon by reaction sintering, published up to date, were discussed in terms of SiO pressure around the compact. The method to sinter the compact in loose powder of Si_3N_4 and SiO_2 , which was developed by present authors, was the most successful because of the formation of sufficient pressure of SiO (4.8×10^{-1} atm at 1800°C) to prevent the thermal decomposition of β -sialon described above.

The result of present study enables the fabrication of high density β -sialon with small amount of intergranular phase by the reaction sintering.

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サイアロンの熱分解反応

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β -サイアロン ($z=2.3$) と X-サイアロンからなる 2 相サイアロン及び単相の β -サイアロン ($z=2$, $\text{Si}_4\text{Al}_2\text{O}_7\text{N}_6$) の粉末を 1 気圧の窒素中で加熱することにより熱分解を行った。組成及び相の変化を X 線回折及び化学分析で調べた。

2 相サイアロンの熱分解反応は、

単相サイアロンは、

と推定された。

中間状態を仮定することにより β -サイアロンの安定な SiO 分圧は 1800°C で、 6.0×10^{-1} と 3.9×10^{-1} 気圧の間であると算出できた。

今までに報告されている β -サイアロンの反応焼結法を成形体上の SiO 分圧という観点から検討した。著者らが開発した Si_3N_4 と SiO_2 の混合粉末でおおう方法が最も有効であった。それは成形体上に 1800°C で 4.8×10^{-1} 気圧の SiO が存在し、 β -サイアロンの熱分解を抑えるためである。

本研究の結果、粒界相が少量しか存在しない高密度 β -サイアロンの反応焼結が可能となった。

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Key-words : Sialon, Thermal decomposition, SiO pressure, Reaction sintering, Weight loss

1. Introduction

A solid solution of Si_3N_4 with $\text{AlN} \cdot \text{Al}_2\text{O}_3$, which has $\beta\text{-Si}_3\text{N}_4$ structure, is called as β -sialon in present work to avoid a confusion with other sialons. Number of works have been done on fabrications and measurements of mechanical properties of β -sialon^{1)~3)}. The materials were mostly obtained by hot pressings.

Attempts have been made to fabricate β -sialon by the reaction sinterings or the pressureless sintering to apply it as high temperature engineering materials^{4)~6)}. The method would enable to supply sintered β -sialons with high density and complex shapes. But a lack in information on thermochemical properties of β -sialon prevented us to fabricate it under stable conditions.

Goursat⁷⁾ recently reported that sialons decomposed thermally and formed gaseous products containing Si, O and N. The formation of SiO by the thermal decomposition of β -sialon was already assumed^{8),9)}. The equilibrium partial pressure of SiO was not esti-

mated, because thermochemical data on sialons were not available yet.

The sintering of Si_3N_4 with additives were successfully carried out under high nitrogen pressures¹⁰⁾. The method made possible to decrease the amount of weight loss due to thermal decomposition by depressing an equilibrium Si vapor pressure at high temperatures^{10),11)}. It is due to the fact that the stability of Si_3N_4 at high temperature is directly related to N_2 pressure on Si_3N_4 as shown by thermal decomposition reaction,

No attempt has been made to sinter β -sialon under sufficient pressures of gaseous species which are formed by the thermal decomposition of β -sialon.

The present work intends to estimate equilibrium pressures of SiO on β -sialon under a total pressure of 1 atm by approximate calculations. The necessity to sinter β -sialon under sufficient SiO pressure will be discussed with respect to the weight loss during sintering and resulting changes in composition.

2. Experimental

2.1 Materials

Two kinds of sialon powder were obtained by heating the powder mixtures of Si, AlN and/or Al_2O_3 at 1350°C for 20 h and 1450°C for 5 h in N_2 containing 20 vol% H_2 . These sialon powders were (1) "two-phase sialon" containing both β -sialon with $z=2.3$ in general formula $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ and X-sialon, the composition of which is represented by "A" in Fig. 1, and (2) "single-phase sialon" with $z=2$ ("B" in Fig. 1).

The contents of Si, Al and N were determined by chemical analyses and shown as "original" in Table 1.

2.2 Thermal decomposition

The powder specimen was heated at 1800°C for 1 h in N_2 to investigate the thermal decomposition process of sialons. The composition and crystalline phases in residual solid were determined by X-ray diffraction and chemical analysis.

The thermodynamic calculation for SiO pressure on sialons was performed by assuming intermediate stages.

3. Results and discussions

3.1 Thermal decomposition of sialons

The chemical analysis of thermally decomposed sialon powders revealed the decrease in Si and O content as shown in Table 1. The shifts in composition from the originals were shown in Fig. 1 as arrows in the Si_3N_4 - SiO_2 - Al_2O_3 -AlN phase diagram¹²⁾. The figure clearly showed that the compositions of sialons were shifted toward AlN or AlN- Si_3N_4 line from the original positions by the thermal decomposition.

Phase analyses of the original and the thermally decomposed sialons showed the decrease of X-sialon in the two-phase material and the

Table 1. The results of chemical analyses of original and thermally decomposed sialons.

Sample		Analytical value (wt %)			
		Si	Al	N	O*
Two-phase sialon	original	35.9	21.2	23.7	19.2
	decomposed	34.0	23.3	24.8	17.9
Single-phase sialon	original	41.2	18.0	28.5	12.3
	decomposed	34.1	25.8	31.1	9.0

* by difference.

Fig. 1. The change in composition by thermal decomposition of two-phase sialon (A → A') and single-phase sialon (B → B').

formation of 15 R-sialon in the single-phase sialon by the thermal decomposition. The increased z value of β -sialon compared to the original after the decomposition of the two-phase sialon and the formation of 15 R-sialon from the single-phase sialon with $z=2$ was consistent with phase diagram (Fig. 1).

The reverse extrapolation of arrows to a Si_3N_4 - SiO_2 axis in Fig. 1 showed that materials evaporated during the heating at 1800°C correspond to the composition $A_0(\text{Si}_3\text{N}_4 + 3 \text{SiO}_2)$ and $B_0(\text{Si}_3\text{N}_4 + 2 \text{SiO}_2)$ in the two-phase and the single-phase sialon respectively.

3.2 Thermal decomposition of two-phase sialon

The evaporation of materials from the two-phase sialon might be due to the formation of gaseous species⁹⁾,

The reaction actually observed might be,

The z value of β_1 -sialon was 2.3 and that of β_2 -sialon was larger than 2.3.

The reaction can be divided into two reactions assuming an intermediate state as follows,

Partial pressure of SiO in reaction (3) is calculated by,

$$\ln k_p = \ln(p_{\text{SiO}})^6 (p_{\text{N}_2})^2$$

$$= -\frac{\Delta G_3}{RT} = -\frac{(\Delta G_4 + \Delta G_5)}{RT} \quad (6)$$

and,

$$p_{\text{SiO}} + p_{\text{N}_2} = 1 \quad (7)$$

where ΔG_3 , ΔG_4 and ΔG_5 are the free energy change for the reaction (3), (4) and (5), respectively. The value of ΔG_5 is the same as ΔG_2 and calculated as 17.1 kcal/mol at 1800°C using JANAF thermochemical data¹³⁾. Phase studies on the system Si_3N_4 - SiO_2 - Al_2O_3 - AlN ^{11,8)} suggest that the free energy change for solid state reaction (4), ΔG_4 , is >0 . But the value itself might be small compared to ΔG_5 , because the free energy changes in solid state reactions are generally very small. For example, free energy changes for formation of silicates from constituent oxides are,

$\Delta G = -0.29$ kcal/mol at 1800 K for andalusite

$\Delta G = -4.75$ kcal/mol at 2000 K for mullite,

(The calculations were made using JANAF data¹³⁾ and standard free energies for silicates¹⁴⁾). This suggests that ΔG_4 might be neglected for approximate calculation of the SiO pressure by Equations (6) and (7). The pressure of SiO vapor, thus obtained, is 6.0×10^{-1} atm at 1800°C.

3.3 Thermal decomposition of single-phase sialon

The thermal decomposition of single-phase β -sialon ($z=2$) is considered to correspond to a reaction,

The thermal decomposition of β -sialon was observed to form 15 R-sialon and Si,

The calculation of SiO pressure was made by the same procedure as for the two-phase sialon by assuming the intermediate stage, 15 R-sialon + $(\text{Si}_3\text{N}_4 + 2 \text{SiO}_2)$.

The calculated value of SiO pressure was 3.9×10^{-1} atm at 1800°C.

The calculated results suggest that the single-phase β -sialon is more stable than the two-phase sialon when the vapor pressure of SiO on sialon powder is lower than 6.0×10^{-1} atm at 1800°C. And it does not decomposed to 15 R-sialon when the SiO pressure is higher

Fig. 2. The SiO pressure for single-phase β -sialon with $z \approx 2$ at 1800°C.

than 3.9×10^{-1} atm. The SiO vapor pressure region for the single-phase β -sialon with $z=2$ was estimated to be from 6.0×10^{-1} to 3.9×10^{-1} atm at 1800°C neglecting the difference in free energies of two β -sialons with little difference in z values. The pressure of SiO for the stable β -sialon is shown in Fig. 2 as the function of (Si, Al)/(O, N).

3.4 Reaction sintering of β -sialon

An important problem on the reaction sintering of β -sialon by heating powder mixture of Si_3N_4 - Al_2O_3 - AlN or Si_3N_4 - SiO_2 - AlN is how to prevent the weight loss due to the thermal decomposition during sintering. When the weight loss occurs, the composition deviates from β -sialon toward AlN - Si_3N_4 axis as already shown, thus results in incomplete shrinkage due to lack in sinterability¹⁵⁾. To get a high density material, the composition must be rich in oxide over β -sialon, and this results in the formation of sintered material with large amount of intergranular X-sialon or glassy phase which degrades high temperature properties very much. The conclusion deduced from the present study is that the compact must be sintered under the sufficient SiO vapor pressure in order to obtain high density β -sialon with smaller amount of intergranular phase.

The reaction sintering of β -sialon was reported to be successfully performed by heating the compact packed with Si_3N_4 powder⁶⁾ or powder mixture with same composition as the specimen compact⁹⁾. But the compact composed of Si_3N_4 , Al_2O_3 and AlN , which

Table 2. The effect of kind of packing powder on the weight loss during sintering of β -sialon and the density of material.

Packing powder (wt %)	weight loss (wt %)	density of sintered sialon (g/cm ³)
Si ₃ N ₄	14.2	1.72
Si ₃ N ₄ + Al ₂ O ₃ + AlN* (66) (24) (10)	7.3	2.11
Si ₃ N ₄ + SiO ₂ (70) (30)	0.4	2.96

* corresponds to sialon with $z=2$.

were mixed to form sialon with $z=2$, showed appreciable weight loss after heating in Si₃N₄ or powder mixture with the same composition at 1800°C for 1 h as shown in **Table 2**. The packing of the compact with the equi-molar mixture of Si₃N₄ and SiO₂, on the other hand, could prevent weight loss and form high density β -sialon.

The difficulty to prevent the thermal decomposition of sialon by packing the compact with Si₃N₄ only could be well understood by the absence of SiO around the compact.

The formation of SiO vapor in the powder mixture with a same composition as a sialon with $z=2$ was not good enough for reaction sintering, because the equilibrium SiO pressure is to be 3.9×10^{-1} atm at 1800°C due to the formation of 15 R-sialon by the thermal decomposition of β -sialon formed.

The successful sintering by packing the compact with the powder mixture of Si₃N₄ and SiO₂ is associated with the formation of Si₂N₂O at the surface of and around the compact, and it was confirmed by X-ray diffraction studies. That is,

The thermal decomposition of Si₂N₂O produces SiO by a reaction,

The equilibrium partial pressure of SiO on Si₂N₂O under total pressure of 1 atm was calculated as 4.8×10^{-1} atm at 1800°C. The value is in the stable region of β -sialon as shown in Fig. 2. Under sufficient SiO pressure on the compact, the weight loss due to the thermal decomposition of β -sialon during heating at 1800°C was very small as shown in Table 2, so that the compact was sintered without the shift in composition. The present

method does not necessitate the shift to the oxide-rich composition with respect to β -sialon by oxidizing the starting powder¹⁶⁾.

The fabrication of high density β -sialon by heating the compact packed in Si₃N₄ or same composition might be associated with small shift in composition of the compact to oxide corner in Si₃N₄-SiO₂-Al₂O₃-AlN phase diagram. The addition of more than 4 wt% of alumina to β -sialon composition made possible to be sintered to high density without supplying sufficient SiO pressure.

The present method to heat the compact in Si₃N₄ and SiO₂ mixture enabled the sintering of β -sialon with improved mechanical properties¹⁵⁾.

4. Summary

(1) The thermal decomposition reaction of two-phase sialon containing both β -sialon with $z=2.3$ and X-phase and single-phase β -sialon with $z=2$ was studied by heating the specimen at 1800°C under 1 atm N₂.

(2) Two-phase sialon decomposed thermally to β -sialon, SiO and N₂. Single-phase sialon decomposed to 15 R-sialon, SiO and N₂.

(3) The region of SiO pressure for the stable single-phase β -sialon with $z=2$ was calculated to be in the range from 6.0×10^{-1} to 3.9×10^{-1} atm at 1800°C.

(4) The reaction sintering of β -sialon from powder mixture of Si₃N₄, Al₂O₃ and AlN was successfully performed when the compact was packed with powder mixture of Si₃N₄ and SiO₂. The prevention of thermal decomposition of β -sialon during sintering is attributed to the formation of Si₂N₂O and resulting SiO pressure of 4.8×10^{-1} atm at 1800°C. The presence of sufficient vapor pressure of SiO on the compact enabled the fabrication of high density β -sialon with small amount of intergranular phase.

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実験・技術・調査報告・Report

下水汚泥焼却灰からの人工軽量骨材の製造

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下水汚泥焼却灰に膨張性ケツ岩を添加して、人工軽量骨材原料としての可能性を検討した。

下水汚泥焼却灰は単味では発泡膨張しないが、焼却灰に膨張性ケツ岩を 20% 以上添加して、造粒し、焼成温度 1140°, 1150°C の 2 水準で実験した結果、添加物の増加とともに絶乾比重が小さくなり、造粒も容易になる。しかし、添加物の量が 20% 以下の場合は造粒物の十分な強度が得られない。

そこで、バッチ型ロータリーキルンで膨張性ケツ岩を 20% 添加し、造粒、乾燥後、焼成温度 1160°C、焼成保持時間 30 分で焼成した結果、絶乾比重 1.05、吸水率 4.1% で、この粗骨材を使用したコンクリートの圧縮強度は、水/セメント比 (W/C) 40% で、材令 28 日の場合に 352 kg/cm² で、市販品を使用した場合と同程度の強度があり、人工軽量骨材原料としての可能性を得た。

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Production of Lightweight Aggregate from Cindere Sludge of Urban Sewage

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Expanded aggregates were experimentally produced from cindere sludge of urban sewage.

The cindere sludge itself was not a suitable material for this purpose, but with the aid of over 20% expanded shale it was proved to be possible. When the amount of shale was less than 20%, the pelletizing was very difficult and the expansion property was worse. The experimental results suggested that the pellets had to be fired at 1160°C for 30 min.

The specifications of lightweight aggregate produced by a test rotary kiln were as follows:

(1) the specific gravity was 1.05, (2) the 24 h water absorption was 4.1%, (3) the 28 day compressive strength of the concrete was 352 kg/cm².

According to those results, the aggregate produced was acceptable for use in structural concrete.

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