て敏感でないものと考えられる。また、本実験で測定した3試料の Cls ピークは J.M. Thomas らの実験結果と同じように非対称を示した。しかしながら、図2に見られるようにホウ素固溶黒鉛の Cls ピークはホウ素を含まない試料1のそれと比較して、その非対称性は大きく、その半値幅は大きかった。そして、そのピーク位置はホウ素を含まない試料1の値と完全に一致した。ホウ素の固溶に伴う Cls ピークの非対称化あるいは半値幅の増大の原因として、結晶構造あるいは電子構造の変化が考えられる。すなわち、ホウ素固溶黒鉛の格子定数は表1に見られるように、ホウ素を含まない試料1のそれと異なり、また、ホウ素が黒鉛構造中に固溶すると黒鉛のフェルミ準位は低下する^{9),10)}。このような結晶あるいは電子構造の変化が Cls ピークの半値幅の増大あるいは非対称性の増加の原因となっているものと考えられる。それらを明らかにするためには、黒鉛を始めとする格子定数の異なるコークスあるいはホウ素固溶量の異なる黒鉛などの光電子スペクトルを詳細に調べる必要があらう。

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文 献

- 1) C.E. Lowell, *J. Am. Ceram. Soc.*, **50**, 142 (1967).
- 2) J.A. Turnbull, M.S. Stagg and W.T. Eeles, *Carbon*, **3**, 387 (1966).
- 3) D.E. Soule, 5th Carbon Conference, 13 (1963).
- 4) P. Wagner and J.M. Dickinson, *Carbon*, **8**, 313 (1970).
- 5) H.N. Murty, D.L. Biederman and E.A. Heintz, *Fuel*, **56**, 305 (1977).
- 6) 萩尾, 宮崎, 小林, 窯協, **87**, 416 (1979).
- 7) T.A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press (1975) p. 350.
- 8) J.M. Thomas, E.L. Evans, M. Barber and P. Swift, *Trans. Faraday Soc.*, **67**, 1875 (1971).
- 9) J. Hedman, Y. Baer, A. Berndtsson, M. Klasson, G. Leonhardt, R. Nilsson and C. Nordling, *J. Electron Spectrosc. Relat. Phenomena*, **1**, 101 (1972).
- 10) 宮崎, 小林, 菱山, 炭素材料学会第5回年会要旨集, 54 (1978).

ノート・Note

The Stability of α -sialon at High Temperatures

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α -サイアロンの高温での安定性

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Key-words : α -sialon, Stability, Thermal decomposition, N_2 pressure, Sintering

The formation of α -sialons was reported previously¹⁾. The mechanical and electrical properties of some α -sialons were also investigated^{2),3)}. But there was no thermochemical data on α -sialons, so that it is not possible to calculate the stable temperature range of α -sialons. The information on the stability of α -sialons at high temperatures is very important for the sintering and the application of α -

sialons.

Present note intends to know the stable temperature range of Y- α -sialon under 1 atm N_2 and show the condition to stabilize the sialon at high temperature, experimentally.

The general formula for α -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 α -sialon, Si and N sites in

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

N ₂ pressure (atm)	Temperature (°C)	wt. loss (%)	composition.
1	1700	8.7	α -sialon $\gg$ Y ₂ Si(Si ₂ O ₃ N ₄) $\sim \beta$ -Si ₃ N ₄
	1750	33.6	Si $\gg$ YSi ₂ $\sim$ AlN $\sim$ α -sialon $\sim$ Y ₂ Si(Si ₂ O ₃ N ₄)
	1800	35.0	Si $>$ YSi ₂ $>$ AlN $>$ α -sialon
10	1800	1.1	α -sialon $\gg$ β -Si ₃ N ₄
30	1900	2.0	α -sialon $\gg$ β -Si ₃ N ₄

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

α -Si₃N₄ structure are partly replaced by Al and O respectively as in β -sialon⁴⁾. The dissolution of M metal in α -Si₃N₄ structure was supposed to be at the interstitial sites.

An Y- α -sialon was fabricated by hot pressing the powder mixture of Si₃N₄ and (Y₂O₃ + 9 AlN) at 1700°C for 1 h under a pressure of 200 kg/cm²). The composition used in the present work was,

The sintered materials were then pulverized to the powder $< 50 \mu\text{m}$. The powder was mostly composed of Y- α -sialon ($> 95\%$). The unit cell of hexagonal Y- α -sialon was $a = 7.827 \text{ \AA}$ and $c = 5.704 \text{ \AA}$, which agreed well with that by Hampshire and co-workers¹⁾.

About 0.8 g of the α -sialon powder was heated in the temperature range 1700°~1800°C for 0.5~2 h under 1 atm N₂ 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, on the other hand, it was very large ($> 35\%$) after heating for 2 h. The results show that Y- α -sialon is stable at lower temperatures than 1700°C under 1 atm N₂.

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 Y₂Si(Si₂O₃N₄) was observed after heating at 1700° and 1750°C. This phase was formed by the reaction of Si₃N₄ with Y₂O₃⁵⁾. There was no diffraction peak of Y₂Si(Si₂O₃N₄) in the starting powder. The table suggests that the part of Y₂O₃ remained at grain boundaries as glassy phase and crystallized as Y₂Si(Si₂O₃N₄) by the heat treatments. At 1750°C and 1800°C, Si, YSi₂, and AlN were detected as reaction products. It is the most likely that gaseous products were SiO and N₂ as in the thermal decomposition of sialons⁶⁾.

The thermal decomposition of Y- α -sialon may be inferred to be,

The evaporation of SiO and N₂ from α -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 N₂. The molar ratio for SiO/N₂ in the equation (2) is about 1/7, which is smaller than that in β -sialon of 2.5 or 3⁹⁾. It means that the effect of N₂ pressure on the stability of Y- α -sialon at high temperatures is more significant than that of SiO pressure.

The stability of α -sialon was also examined at 1800° and 1900°C under 10 and 30 atm N₂, respectively. The results were added in Table 1. The table shows that α -sialon was stabilized under high N₂ pressures. The table also shows that there was no diffraction lines of AlN and

$Y_2Si(Si_2O_3N_4)$. It means that the degree of solid solubility in α -sialon was increased at high temperatures.

Present work showed that Y- α -sialon $Y_{0.6}(Si_{9.3}, Al_{2.7})(O_{0.9}, N_{15.1})$ was stable up to about 1700°C under 1 atm N_2 . Under high N_2 pressures, α -sialon was stable at higher temperatures. The stability of α -sialon was related to the pressure of ambient N_2 . The results suggest that α -sialon could be sintered at high temperatures under high N_2 pressures at which the amount of residual intergranular phase

might be decreased by its dissolution in α -sialon grains.

References

- 1) S. Hampshire, H.K. Park, D.P. Thompson and K.H. Jack, *Nature*, **274**, 880 (1978).
- 2) M. Mitomo, H. Tanaka, K. Muramatsu, N. Ii and Y. Fujii, *J. Mater. Sci.*, **15**, 2661 (1980).
- 3) M. Mitomo and Y. Uemura, *ibid.*, **16**, 552 (1981).
- 4) K.H. Jack, *ibid.*, **11**, 1135 (1976).
- 5) A. Tsuge, H. Kudo and K. Komeya, *J. Am. Ceram. Soc.*, **57**, 267 (1974).
- 6) M. Mitomo, N. Kuramoto and Y. Yajima, *Yogyo-Kyokai-Shi*, **88**, 49 (1980).

ノート・Note

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 oxyfluotetratitanate ($K_2Ti_4O_{9-x}F_{2x}$) in 1960. Those data are not considered to be precise enough¹⁾. Eastal and Udy (1972) reported the X-ray powder diffraction data and lattice parameters but did not give indices²⁾. 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 ($Tl_2Ti_4O_9$) at 800°C, but reported no X-ray powder diffraction data in 1978³⁾.

The present authors synthesized a high-quality crystals of potassium tetratitanate obtained form of the whisker-like potassium titanate "Fur-fibers" by the KDC (Kneading-Drying-Calcination) method, from which lattice parameters, indices of X-ray powder diffraction data and infrared spectra were obtained^{4)~6)}.

2. Experimental

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