の生成.

(3) 1500°C における重量の減少速度は、放物線則によく適合した. 具体的な律速段階は不明であるが、試料中の pore structure が重量減少速度に、影響をもつことが明らかとなった.

(4) 炭素管の内部には、 α - Si_3N_4 繊維と β - Si_3N_4 及び β -SiC の混合物の析出が認められた. これらは重量の減少に伴って生成した $\text{SiO}(\text{g})$ が、炭素管と以下のように反応し生成したものと考えられた.

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論文・Paper

The Composition of Mullite Like Compound Appeared in Si-Al-O-N System

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Composition of the mullite like compound (often called as X-phase in Si-Al-O-N system) were studied by the following experiments.

(1) Correspondence between the composition of raw mixture and formed compound after hot-pressing the mixture at 1700°~1820°C.

(2) Analytical results of the X-phase with E.P.M.A. and wet chemical analysis.

(3) Correspondence between X-ray diffraction data collected with a “single” crystal of the X-phase and the analytical results.

From the results of those experiments, it was concluded that the X-phase has very close composition to that proposed by L.J. Gauckler et al., $\text{Si}_4\text{Al}_4\text{O}_{11}\text{N}_2$. The atomic ratio, Al/Si was considered to be variable in a range, 1.0~1.8, but the ratio N/O was considered to be in fairly narrow range, 0.17~0.18 at about 1700°C. Typical compositional formula, $\text{Si}_5\text{Al}_7\text{O}_{18}\text{N}_3$ was proposed for the X-phase under fully occupied state.

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Si-Al-O-N 系に現れるムライト様化合物の組成

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Si-Al-O-N 系に現れるムライト様化合物(この系でしばしば X 相と呼ばれる)の組成を次の実験により検討した.

(1) 原料組成とこれを 1700°~1820°C に加圧焼結して生成した化合物との対応.

- (2) X 相の湿式化学分析及び E.P.M.A. による分析の結果.
- (3) X 相“単結晶”の X 線回折データと上記分析結果との対比.

これらの結果から, X 相は L.J. Gauckler らの提案した組成式, $\text{Si}_4\text{Al}_4\text{O}_{11}\text{N}_2$ に極めて近い組成を有することが結論された. 1700°C 付近において原子比 Al/Si は $1.0\sim 1.8$ の範囲で変わり得るものと考えられたが, 原子比 N/O は比較的狭い範囲, $0.17\sim 0.18$ に位置しているようである.

占有率 100% とした場合の代表的な組成として $\text{Si}_6\text{Al}_7\text{O}_{18}\text{N}_3$ を提案した,

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Key-words : Composition, Mullite like compound in Si-Al-O-N system

1. Introduction

The mullite like compound (often called as X-phase) appeared at about 1700°C in Si-Al-O-N system was first reported by Y. Oyama et al.¹⁾ After them, many works have been reported on the structure and the composition of this compound^{2)~6)}, but those results still leave some uncertainty. The X-phase is considered to melt at about 1720°C ^{5), 6)} and to contribute to the sintering of Si_3N_4 with Al_2O_3 additive. On the contrary, sintered articles containing the phase was reported to show low creep resistance at the temperature above 1200°C ⁷⁾.

Following descriptions relate to a results of experiments on the synthesis of the X-phase, X-phase “single” crystals and its structure and

composition.

2. Experiments and results

2.1 Preparation of X-phase specimen

Initially, raw mixtures of powder shown in **Table 1** were hot-pressed to clarify proper composition of raw mixture to prepare the X-phase sample. In the experiment, fine powder of AlN (particle size < 300 mesh) and reagent grade, Ig. loss free powder of Al_2O_3 and SiO_2 were used as raw materials. Major cation impurity detected in those powder was $0.02\text{ wt}\%$ Fe in the AlN . Oxygen introduced from AlN (ca. $1.9\text{ wt}\%$ in the AlN powder) was compensated by adjusting the Al_2O_3 addition in the mixture.

After mixing those powders under dry con-

Table 1. Relation between initial composition of raw mixture and compounds detected after hot-pressing.

Sample No.	Equivalent % of Al and O in the raw mixture		Reaction temperature ($^\circ\text{C}$)	Compounds detected by X-ray diffraction*	Ref.
	Al	O			
1	23.84	76.16	1770	$\text{SON}\sim\text{X}\gg\beta'$ with glass	
2	24.43	81.20	1770	$\text{SON}\sim\text{X}$ with glass	
3	33.73	66.27	1770	$\text{X}\sim\beta'>\text{UK}\gg\text{SON}$	
4	37.54	68.04	1770	$\text{X}>\beta'>\text{SON}>\text{UK}$	
5	40.00	80.00	1720	$\text{X}\gg\beta'>\text{UK}$	
6	42.19	76.56	1720	$\text{X}\gg\beta'>\text{UK}$	
7	42.86	78.57	1720	$\text{X}\gg\beta'>\text{UK}$	(3)
8	42.86	57.14	1720	$\text{X}>\beta'$	(2)
9	43.42	80.26	1720	$\text{X}\gg\beta'>\text{UK}$	
10	46.15	76.92	1720	$\text{X}\gg\beta'>\text{UK}$	
11	49.04	73.93	1770	$\text{X}>\text{B}'\sim\text{UK}\gg\text{SON}$	
12	49.09	83.64	1670**	$\text{X}>\text{M}\gg\beta'$ with glass	(5)
13	55.56	66.67	1720	$\text{X}>\beta'>\text{Al}_2\text{O}_3>\text{UK}$	
14	59.42	91.65	1770	$\text{X}\sim\text{M}\gg\text{UK}$ with glass	
15	60.00	80.00	1770	$\text{X}\gg\text{M}\gg\beta'\sim\text{Al}_2\text{O}_3$	(4)
16	68.06	83.66	1770	$\text{X}>\text{M}>\beta'$	
17	69.23	76.92	1720	$\text{Al}_2\text{O}_3>\text{X}>\beta'>\text{UK}$	
18	70.81	96.45	1770	$\text{M}\gg\text{X}$	
19	81.77	90.67	1770	$\text{Al}_2\text{O}_3>\text{M}>\text{X}>\beta'>\text{UK}$	
20	84.00	88.00	1720	$\text{Al}_2\text{O}_3\gg\text{X}>\beta'>\text{UK}$	

* $\text{SON}:\text{Si}_2\text{N}_2\text{O}$, $\beta':\beta\text{-Si}_3\text{N}_4$ type solid solution, M : Mullite, UK : Unknown compound

** Hot-pressing at 1720°C could not be tested as the sample was extruded out of the dies.

dition, the mixture was put in a BN coated graphite mold and rapidly heated by r.f. current up 1720~1770°C under 1 atm of nitrogen atmosphere, kept at the temperature for 1~10 min, then cooled by turning off the electric power for heating. In the heating schedule, uniaxial pressure of 100 kg/cm² was applied. Compounds detected by X-ray powder diffraction method in the recovered sample are shown in Table 1.

From the table, adequate range of equivalent% of oxygen and that of aluminum in the mixture is considered to be 40~60% and 76~80%, respectively.

2.2 Preparation of X-phase "single" crystals

From the background described above, raw mixture having a composition, Si₄Al₄O₁₁N₂³⁾ was used to prepare X-phase "single" crystals. Experiments were performed nearly the same way described in 2.1, but in present case, maximum temperature, 1820°C was adopted, sample was kept at the temperature for 20~30 min, then cooled to 1600°C at the rate of 1.5°C/min and the electric power for heating was turned off. In the heating schedule, initially uniaxial pressure of 100 kg/cm² was applied up to 1770°C (melts were formed) and after when the pressure was released.

Needle shaped colourless crystals were grown mainly in the voids in the recovered samples. An example of those crystals grown is shown in Fig. 1. X-ray diffraction data showed those samples being predominantly consisted with X-phase and most of those crystals being twinned.

2.3 Composition and structure

As the X-ray powder diffraction data of a

Fig. 1. An example of X-phase crystals grown in the cavity in the slowly cooled sample. Section paper indicates 1 mm.

Table 2. Analytical results of the X-phase sample synthesized (wt%).

Trial No.	Si*	Al*	O**	N*
1	25.61	26.76	40.96	6.67
2	25.79	26.71	41.37	6.13
3	26.06	26.93	40.75	6.26
Av.	25.82	26.80	41.03	6.35

* Wet chemical analysis⁹⁾.

** The remainder : 100-(Si+Al+N)

sample obtained by the above experiments virtually showed to consist only of the X-phase, the sample was crushed and chemically analyzed⁹⁾, and the result as shown in Table 2 was obtained. Analytical results with E.P. M.A. showed the atomic ratio, Al/Si in the crystals being larger than unity, and all of X-phase sample prepared showed the value in a range, 1.0~1.8.

X-ray diffraction data on a twinned "single" crystal recovered from the chemically analyzed specimen gave a result as shown in Table 3⁹⁾. The unit cell was consisted with 52 metal and 84 anion sites under fully occupied state.

Table 3. Structural data on the X-phase⁹⁾.

System : Triclinic ($\bar{C}1$)
Unit cell dimensions ($\text{\AA}$ and degree)
$a : 15.931, b : 11.165, c : 8.540, \alpha : 90.010, \beta : 100.289,$
$\gamma : 90.989, V_{\text{cell}} : 1494.35 \text{\AA}^3$
Atomic site in the unit cell : $M_{52}X_{84}$ being allowable under fully occupied state.

3. Discussion

3.1 Composition of X-phase

Proposed compositions for X-phase are listed in Table 4. Though, the valency balance of the present analytical result being incomplete, it shows good agreement with the composition of initial mixture prepared according to L.J. Gauckler et al., especially in the values, Al/Si and N/O. The compositional difference observed between initial mixture and synthesized specimen in the table, is considered mainly based on the evaporation of SiO and N₂ from the sample at high temperature around 1700°C, typically as follows¹⁰⁾.

The composition of X-phase initially pro-

Table 4. Proposed composition of the X-phase.

Composition	at. %				at. ratio			Ref.
	Si	Al	O	N	M/X	Al/Si	N/O	
Si ₆ Al ₆ O ₉ N ₃	20.69	20.69	31.03	27.59	0.7059	1.0000	0.8891	(1)
SiAlO ₂ N	20.00	20.00	40.00	20.00	0.6667	1.0000	0.5000	(2)
Si ₄ Al ₄ O ₁₁ N ₂	19.05	19.05	52.38	9.52	0.6154	1.0000	0.1817	(3)
Si ₃ Al ₆ O ₁₂ N ₂	13.04	26.09	52.17	8.70	0.6429	2.0000	0.1667	(4)
Si ₇ Al ₉ O ₂₃ N ₃	16.67	21.43	54.76	7.14	0.6154	1.2860	0.1304	(5)
Si ₁₂ Al ₁₈ O ₃₉ N ₃	15.58	23.38	50.65	10.39	0.6383	1.5000	0.2051	(6)
Present result*	18.65	20.15	52.01	9.19	—	1.0800	0.1770	

* Analytical results in Table 2.

posed by K.H. Jack³⁾, SiAlO₂N may be inadequate together with that proposed by Y. Oyama et al. because fairly large amounts of β-Si₃N₄ type solid solution being detected in the sample No. 8 in Table 1. Recent proposal by K.H. Jack³⁾, Si₇Al₉O₂₃N₃ may be excess in oxygen, the sample No. 12 in Table 1 showed clear presence of mullite.

On the contrary, that of G.K. Layden⁴⁾, Si₃Al₆O₁₂N₂ is considered to represent very close composition to the X-phase near the substitutional limit of Al against Si atoms, the sample No. 15 in Table 1 is mainly consisted of X-phase. Recent proposal by I.K. Naik et al.⁶⁾, Si₁₂Al₁₈O₃₉N₃ is an intermediate composition lying between that of L.J. Gauckler et al. and that of G.K. Layden.

Those results and the results from E.P.M.A. suggest the X-phase having a composition in a range of the atomic ratio Al/Si : 1.0~1.8 and that of N/O : 0.17~0.18 at about 1700°C.

3.2 Composition and structure

Result of structure determination with X-ray single crystal diffractometry showed the unit cell of X-phase is able to contain at most 52 metal and 84 anion sites⁹⁾ (according to K.H. Jack³⁾, this may correspond to Low-X). The fact suggests Si₆Al₇O₁₈N₃ being one of possible compositional formula for present X-phase crystal under fully occupied state. The atomic composition of the formula is very

close to that proposed by L.J. Gauckler et al.

Though, it was shown recently by K.H. Jack³⁾ that the X-phase showed two polymorphs, High- and Low-X, above results suggest that the phenomenon is based on the compositional difference together with the high-low or order-disorder transformations, because the compositional change during reaction depends on the reaction temperature.

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