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論文・Paper

Oxidation Behavior of Hot-pressed Si_3N_4 Containing MgO

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Hot-pressed Si_3N_4 were prepared from two kinds of commercial grade Si_3N_4 with addition of MgO. Oxidation behavior of hot-pressed Si_3N_4 bodies were investigated in dry oxygen at 1200° and 1300°C, at several steps up to 30 days.

Results of the weight gain, X-ray diffraction analysis, EPMA analysis and SEM observations on the oxidized layer are discussed in relation to the mechanism of oxidation.

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MgO を添加剤として加圧焼結した Si_3N_4 の酸化挙動

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5 wt% MgO を添加剤として加圧焼結した Si_3N_4 の酸化挙動を検討した。 Si_3N_4 焼結体は AME 社とシュタルク社製の 2 種の粉末を用いて、ホットプレスにより作られた。酸化は純酸素中、1200°C と 1300°C の定温で、30 日まで行った。

酸化による増量と酸化膜の厚み測定から、酸化膜の生成量と酸化時間がほぼ放物線則に従って変化することが認められ、酸化が拡散の関与した機構で進行すると考えられた。酸化により生成する相はクリストバライト、エンスタタイト (MgSiO_3)、オケルマナイト ($\text{Ca}_2\text{MgSi}_2\text{O}_7$)、デオプサイド ($\text{CaMg}(\text{SiO}_3)_2$)、フォルスラナイト (Mg_2SiO_4) 及び若干のガラス相であり、1300°C では酸化時間が長くなると、エンスタタイトが増加した。ガラス相の生成は Na, Ca, Mg, Fe 等の不純物が酸化膜へ集積することに原因する。

酸化膜の表面形状は酸化時間とともに変化した。酸化膜内部はクリストバライト、エンスタタイト等のケイ酸マグネシウム鉱物及び若干のガラス相からなり、酸化膜表面はポーラスであるが、酸化膜内部は比較的密な層を形成した。拡散の律速は酸素の細孔内及び密な酸化層内の拡散と加圧焼結体中の不純物の酸化層への集積と考察した。

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Key-words: Silicon nitride, Magnesia, Hot-pressing, Oxidation, Oxidized layer, Cristobalite

1. Introduction

The recent studies^{1)~5)} in hot-pressed Si_3N_4 for high temperature engineering applications have prompted the need for further understanding of its oxidation behavior. Although the oxidation mechanism of hot-pressed Si_3N_4 is not well understood, it has been shown that the oxidation rates are comparatively satisfactory under the gas turbine operating conditions⁶⁾. Several studies have been reported on the oxidation of hot-pressed Si_3N_4 containing MgO. Kiehle et al.⁷⁾ studied on the high temperature chemical stability at the temperature between 600° and 1450°C, and suggested that the impurities e.g. Mg, Ca and Fe greatly lower the oxidation resistance of Si_3N_4 in air. On the other hand, Tripp and Graham⁸⁾ considered that a large increase in reaction rate above 1450°C could be caused by melting in the oxidized layer, and that the consequent increase is the rate of oxygen transport. Cubiccioti and Lau⁹⁾ reported that the oxidized layer was porous due to the bubbles on released N_2 , so the oxidized layer was not protective, and they insisted that the diffusion of Mg in the unoxidized material was the rate-controlling step in the oxidation. Singhal¹⁰⁾ summarized the oxidation results of HS-130*¹ material, and the activation energy indicated that the rate-controlling step was supposed to be the diffusion of Mg^{2+} and Ca^{2+} cations from the grain boundary glass phase through the oxidized layer. More recently, Lewis and Barnard¹¹⁾ reported the same oxidation mechanism in Si-Al-O-N ceramics. They showed that the oxidation was controlled by outward diffusion of grain boundary segregated impurities in unoxidized matrix.

The aim of this paper is to investigate the oxidation behavior of hot-pressed Si_3N_4 prepared from two kinds of commercial grade Si_3N_4 powders both containing 5 wt% MgO. Experimental conditions were in 1 atm dry

oxygen at the temperature 1200° and 1300°C, at several steps up to 30 days. The oxidation behavior was discussed on the results of weight gain measurements, X-ray diffraction analysis, scanning electron microscope (SEM) observations and electron probe X-ray microanalyser (EPMA) analysis on the oxidized layer.

2. Experimental procedure

2.1 Starting materials

The starting materials used in the present work were two kinds of commercial grade Si_3N_4 powders, i.e., AME* and Starck**. The chemical analyses of the powders are listed in Table 1. The material for the additive was MgO powder (99.99% pure; Kojundo Chemical Co., Ltd.).

2.2 Sample preparation

95 wt% Si_3N_4 (AME and Starck) and 5 wt% MgO powders were weighed. The composition powders were mixed and milled in a tungsten carbide ball mill. The contamination of tungsten carbide from the ball mill was estimated as about ~0.7 wt% from the weight change after mixing. The mixed powders were hot-pressed in a boron nitride coated graphite die at 1750°C for 1 h under the pressure of 200 kg/cm² and flowing nitrogen. After hot-pressing, the surfaces of both sides of sintered pellets (15 ϕ × 5 mm thick) were polished, and were cut into several pieces by a diamond blade. The size of specimen is about 10 × 10 × 1 mm. The surfaces of the specimens were polished using # 500, # 1000 and # 2000 silicon carbide powders successively, and then cleaned in an ultrasonic bath and rinsed thoroughly in acetone and alcohol and weighed to ± 0.00001 g by microbalance.

2.3 Oxidation

The oxidation was performed under an atmosphere of flowing dry oxygen in a high purity Al_2O_3 reaction tube. The heating temperatures were selected at 1200° and 1300°C and heating times from 1 to 30 days. A separate thin plate sample was prepared under the same conditions and used for each heating and oxidation steps. The samples placed in Al_2O_3 boats were introduced into the furnace heated at given temperature and removed after

Table 1. Chemical analysis of Si_3N_4 (wt%)*.

sample	Si	N	O	Al	Fe	Ca	Na	Mg	K
AME**	58.6	37.9	1.21	0.12	0.25	0.04	0.03	0.008	0.005
Starck***		38.65	0.42	0.10	0.03	0.01			

* manufacturer's data

** Advanced Materials Engineering CO., Ltd., England

*** Herman C. Starck, Berlin

*¹ Norton Co., Worcester, Mass.

the fixed oxidation time. Then, the error of oxidation time due to heating and cooling was neglected. The samples were reweighed after they were oxidized. The phases present in the oxidized layer were determined by X-ray diffraction patterns with $\text{Cu K}\alpha$ which had been diffracted from the oxidized surface of the specimen. The morphology of the oxidized layer was observed by SEM.

3. Results and discussion

3.1 Weight gain by oxidation

Figure 1 shows the weight gain by the oxidation of two materials as a function of the oxidation time at 1200° and 1300°C. Two materials, which differ in the starting Si_3N_4 powder, i.e., AME and Starck, show almost the same oxidation weight gain at 1200° and at 1300°C, much weight gain was measured in Starck sample compared with AME. The weight gain versus time curves approximate the classical parabolic behavior which can be represented by the equation :

$$W^2 = K_p t + C$$

where W is the weight gain, t oxidation time, K_p the parabolic rate constant, and C a constant to account for the initial reaction. The plots of square of the weight gain (W^2) as a function of time (t) for 1200° and 1300°C of the oxidation temperature are shown in Fig. 2.

Figure 2 shows that only one weight gain curve, i.e., that of Starck sample at 1300°C fits a parabolic law. Another three weight gain plots depart from the straight line in Fig. 2. The oxidation weight gain tends to decrease from the values which are expected

Fig. 1. Weight gain curves vs. oxidation time at 1200° and 1300°C.

Fig. 2. Parabolic plot of weight gain of Si_3N_4 at 1200° and 1300°C.

from the parabolic law. Transient non-parabolic behavior was observed in the samples oxidized at 1200° and 1300°C for 7 and 30 days oxidation time, the reason being not clear, and the certain changes in oxidation mechanism or unstable state may occur in the neighbourhood of that oxidation time.

Tripp and Graham⁹⁾ reported that for longer oxidation time (>100 h), the oxidation kinetics became somewhat erratic at 1450°C, and 200 h oxidation run only parabolic kinetics were measured at 1300°C. Our experimental conditions were longer oxidation time than their data, then the erratic behavior was observed at 1200° and 1300°C. The oxidation of Si_3N_4 with MgO additive could not be also explained by simple one mechanism. A possible explanation for this "erratic" behavior will be the formation of three layers structure of oxidation, which will be discussed in SEM observations. The mean thickness of the oxidized layer was also measured in the case of Starck sample at 1300°C by EPMA analysis. There are differences of impurities concentration between the oxidized layer and in the Si_3N_4 substrate. It is a typical case in which the oxidation weight gains behaved a parabolic manner. Figure 3 confirms that the weight gain by oxidation behaves in a parabolic at 1300°C. This behavior is consistent with our results of hot-pressed Si_3N_4 with 5 wt% Y_2O_3 and 2 wt% Al_2O_3 ¹³⁾.

Cubicciotti and Lau⁹⁾ reported that the oxidized layer formed during the oxidation of

Fig. 3. Mean thickness of oxidized layer of Starck sample at 1300°C in dry O_2 measured by EPMA.

hot-pressed Si_3N_4 was very porous, the pores presumably containing N_2 was formed by the oxidation, and on the basis of their weight gain measurements, the mean thickness of the oxidized layer was greater than expected. The same observation was also found in the present studies.

On the assumption that the oxidized layer is composed of a dense cristobalite mainly, the calculated thickness of the oxidized layer is approximately below one-half of the observed one. This difference indicates that the oxidized layer is not dense one. The SEM observation cleared the very porous oxidation layer near surface (see Fig. 7 and Fig. 8). The composition of the layer, oxidized at 1300°C for 30 days, consists mainly of enstatite, and cristobalite which will be shown later in X-ray diffraction analysis (see Fig. 4). If the layer consists mainly of cristobalite and enstatite, besides glassy phase and 10 vol% pores, the calculated thickness almost corresponds to the observed thickness. In the present work, the oxidation zone was found to be composed of three successive layers in terms of porosity. Namely these are stratified in the order of (a) porous layer, (b) relatively dense layer and (c) dense layer from the surface, in which the mechanism of the inward oxygen diffusion through pores or fissures may be a rate-controlling process. On the other hand, diffusion of impurities from the grain boundary glass phase through the dense oxidized layer appears to be rate-controlling step. Higher the oxidation temperature, the more glassy phase appears in grain boundary and a rapid oxidation may proceed.

3.2 Results of X-ray diffraction and EPMA analysis

Fig. 4. Relative intensities of X-ray diffraction peaks of cristobalite, enstatite, akermanite and diopside.

Fig. 5 Optical micrograph of polished cross section of Starck sample, oxidized at 1300°C for 30 days in oxygen at 1 atm pressure.

The phases formed by oxidation were cristobalite, enstatite ($MgSiO_3$), akermanite ($Ca_2MgSi_2O_7$), diopside ($CaMg(SiO_3)_2$), forsterite (Mg_2SiO_4) and glassy phase. Table 2 and Fig. 4 show the results of X-ray diffraction analysis. In Fig. 4 the relative intensities of cristobalite, enstatite, akermanite and diopside are plotted as a function of temperature and oxidation time, the solid lines and the broken lines show the results of the AME and the Starck sample, respectively. The cristobalite phase first appeared in the oxidized layer at 1200° and 1300°C. Also enstatite phase appeared at 1300°C but not observed at 1200°C. The cristobalite and enstatite tend

Table 2. Minerals detected by X-ray diffraction on the surface of oxidized sample.

1) oxidized at 1200°C

sample	time(d)	minerals detected						
		β -Silicon Nitride (β -Si ₃ N ₄)	Cristobalite (SiO ₂)	Enstatite (MgSiO ₃)	Akermanite (Mg ₂ O ₂ CaO ₂ SiO ₂)	Diopside (CaMg ₂ O ₂ SiO ₂)	Forsterite (Mg ₂ SiO ₄)	Magnesium Silicon Nitride (Mg ₂ SiN ₂)
AME	0	VS	-	-	-	-	-	Tr.
	1	VS	W	VW	VW	Tr.	Tr.	-
	3	S	W	VW	VW	Tr.	Tr.	-
	7	S	S	VW	VW	Tr.	Tr.	-
	15	M	S	VW	VW	Tr.	Tr.	-
	30	M	VS	W	W	Tr.	Tr.	-
Starck	0	VS	-	-	-	-	-	Tr.
	1	S	W	VW	VW	Tr.	Tr.	-
	3	S	M	VW	VW	Tr.	Tr.	-
	7	S	M	VW	VW	Tr.	Tr.	-
	15	M	M	VW	VW	Tr.	Tr.	-
	30	M	S	W	W	Tr.	Tr.	-

2) oxidized at 1300°C

AME	1	VS	W	W	VW	VW	Tr.	-
	3	VS	W	W	VW	VW	Tr.	-
	7	S	M	S	VW	VW	Tr.	-
	15	S	S	VS	W	VW	Tr.	-
	30	M	VS	VS	W	W	Tr.	-
	30	M	VS	VS	W	W	Tr.	-
Starck	1	VS	W	W	W	W	Tr.	-
	3	S	M	S	VS	W	Tr.	-
	7	M	M	VS	VS	W	Tr.	-
	15	M	M	VS	VS	M	Tr.	-
	30	VW	S	VS	VS	M	Tr.	-
	30	VW	S	VS	VS	M	Tr.	-

to increase remarkably when the oxidation time increase at 1300°C, whereas enstatite increased only a small amount at 1200°C. X-ray diffraction analysis showed the presence of Mg and Mg-Ca silicates and comparison of the data in Fig. 4 with the phase diagram for the system CaO-MgO-SiO₂¹²⁾ indicates that the equilibrium has not been attained at 1300°C. Judging from the phase analysis, long transient state oxidation and migration of impurities such as Na, K and Fe etc., will affect the formation and coexistence of Mg and Mg-Ca silicates. There is only an observed difference between AME and Starck samples; the formation of akermanite phase in the Starck sample, oxidized at 1300°C. The reason is not clear since Starck sample contained less Ca cation impurity compared with that of AME (see Table 1 and Fig. 4).

Figure 6 shows X-ray intensities of Mg and Fe by EPMA analysis. Microanalyses were carried out on the polished surface of cross-section on the Starck sample oxidized at 1300°C for 1, 15 and 30 days. Mg and Fe (same as Na and Ca) atoms migrate to the oxidized layer from the unoxidized Si₃N₄ substrate and they concentrate there consequently. These

impurity elements, which came from the starting material, lower the formation temperature of silicates and glass and formed the silicates and glassy phase. In the previous work, Cubicciotti and Lau⁹⁾ reported that the Mg concentration in the unoxidized Si₃N₄ substrate increased with depth in the sample, but concentration of other impurities (Na, Fe and K) did not. Therefore, Mg was diffusing out of material into the oxidized layer and was intimately involved in the rate-controlling step. Kiehle et al.⁷⁾ reported that the continuous uptake of Mg and Ca from the interface between the reacted layer and the bulk Si₃N₄ would lower the concentration of Mg and Ca at the interface. Such a concentration gradient would provide a driving force for the diffusion of Ca and Mg toward the reaction boundary from the bulk Si₃N₄. In the present work, Mg concentration of oxidation time 1, 15 and 30 days samples is almost flat and not showed any tendencies of decrease or increase except for the oxidized layer. In the oxidized layer, Mg concentration is not large at the outer surface, but they reported that the Mg concentration was very large at the outer surface, and consequently diffusion of Mg may be a

Fig. 6. Electron probe X-ray microanalysis of Mg and Fe on the cross section of Starck sample oxidized at 1300°C for 1 day, 15 days and 30 days in oxygen at 1 atm pressure.

Fig. 7. Scanning electron micrograph of cross section of AME sample, oxidized at 1300°C for 30 days in oxygen at 1 atm pressure.

rate-controlling step.

Judging from our results, the rate-controlling

step at a long oxidation period is not diffusion of Mg but inward oxygen diffusion through pores or fissures and outward diffusion of metallic impurities, we propose. Former propose for inward oxygen diffusion is consistent with the results of Tripp and Graham work of the oxidation of hot-pressed Si_3N_4 (HS-130)⁸⁾, and from the observation of our results inward oxygen diffusion through pores or fissures and outward diffusion of metallic impurities, especially liquid forming elements, appear to be the most plausible. Latter propose for outward diffusion of impurities is consistent with the results of Lewis and Bernard's work of hot-pressed Si-Al-O-N¹¹⁾. Also Singhal¹⁰⁾

proposed that impurity elements (Mg, Ca, Fe and Al etc.) which are predominantly present in grain boundary glass phase in the starting material, diffuse outwards from the grain boundaries, and the diffusion of these cations

outward from the glass phase and through the oxidized layer may be the rate-controlling process in the oxidation of hot-pressed Si_3N_4 .

3.3 SEM observations of oxidized layer

The SEM observations of oxidized layer

Fig. 8. Scanning electron micrographs of surfaces of silicon nitride containing 5 wt% magnesia specimens oxidized at 1200° and 1300°C for 1 d~30 d in oxygen at 1 atm pressure.

Fig. 9. Schematic representations of various reactions possible during oxidation of hot-pressed Si_3N_4 containing MgO.

are shown in Fig. 8. These photographs indicate that there are some morphological changes, especially in the sample made from Starck. The oxidized layer formed on the surface of the Starck sample oxidized at 1200°C , from 1 to 7 days, showed significant difference in morphology, and the "erratic" behavior of the weight gain occurred in these periods. Some morphological change would affect the "erratic" behavior of the weight gain, and at 1300°C from 3 to 7 days more rapid crystal growth occurred compared with 1 to 3 days oxidation time. The side view of the layer of AME sample oxidized at 1300°C for 30 days (Fig. 7) indicates that the oxidized layer is composed of multicomponent crystallized silicates (porous and relatively dense layer) and dense layer (see Fig. 5). The multicomponent silicates crystallized on the surface was cracked, presumably because of the 272°C phase transition in cristobalite, and for longer oxidation time,

the surface contained fissures and pores, probably caused by the outward of N_2 gas and crystal growth of silicates. Figure 9 is a schematic representation of the many possible diffusional reactions occurring in the proposed oxidation mechanism.

We assume that oxygen migrates through the surface of oxidized layer, diffusing through pores or fissures of crystallized multicomponent silicates, as O_2 and is reduced partially in the glassy phase which is predominantly present in grain boundary of silicates to O^{2-} and that the rate of oxidation is controlled by the rate of impurities diffusion out of the material into the oxidized layer and inwards oxygen diffusion through pores or fissures of relatively dense layer i.e., crystallized multicomponent silicates.

4. Summary

The oxidation of hot-pressed Si_3N_4 containing 5 wt% MgO was studied in dry flowing oxygen at 1200°C and 1300°C , at several steps up to 30 days.

The hot-pressed Si_3N_4 bodies were made from two different sources of AME and Starck powder. These two kinds of Si_3N_4 showed almost no apparent difference in oxidation behavior.

The weight gain curve of oxidation fits a parabolic one at 1300°C in Starck sample, which suggests the diffusion controlled oxidation mechanism. Some transient non-parabolic behaviors were found in weight gain measurements.

The main composition of oxidized layer were cristobalite, enstatite, akermanite, diopside, forsterite and glassy phase.

Even though it cannot be determined unambiguously with the present data, the diffusion of impurities from the unoxidized Si_3N_4 substrate through the dense oxidized layer and inward oxygen diffusion through pores or fissures of multicomponent silicates of porous and relatively dense layer may be the rate-controlling step.

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ノート・Note

Improvement of the Strength of Häüyne-Belite Cement by the Addition of Calcium Sulphates

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硫酸カルシウム類の添加によるアウイン-ベライトセメントの強度改善

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As previously reported¹⁾, supersulphated alumina-belite cements or häüyne-belite cements generally give enough strength for the practical use. However, alumina or bauxite is needed in the production, when high strength cements are desired. This is disadvantageous, since we have no bauxite resources in Japan. In previous work the author suggested that häüyne-belite cement of the mix 0.4 made from blast furnace slag, gypsum and calcium carbonate would be noteworthy for practical applications (Table 1), since this cement

required no bauxite for the burning, although the strength was rather low. If we could improve the strength a little more, especially the compressive strength in early age, this cement would be of benefit for the effective use of blast furnace slag.

Table 1. Chemical composition and mineral proportion of the cement mix 0.4. $(1/3)\text{C}_4\text{A}_3\text{S}$ was taken for molecular weight.

SiO_2	Al_2O_3	CaO	MgO	SO_3	Fe_2O_3	MnO	TiO_2	Total (wt %)
26.30	10.75	51.43	5.20	4.74	0.52	0.25	0.81	100.00
$\text{C}_4\text{A}_3\text{S}$	$\alpha'-\text{C}_2\text{S}$	CA	C $\bar{\text{S}}$ Clinker minerals — Mineralizers				C $\bar{\text{S}}$ Others	
17.8	74.2	tr.	1.2	(mole %)				2.9 3.9

Cement chemical notations are used in this paper C : CaO, A : Al_2O_3 , S : SiO_2 , $\bar{\text{S}}$: SO_3 and H : H_2O .