Surface Modification of Alumina Fibers with Si- and Al-Alkoxides and Their Thermal Behavior

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Si- 及び Al-アルコキシドによるアルミナ繊維の表面化学修飾と加熱変化

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Chemical coating on polycrystalline alumina fibers with smooth surface was carried out using a sol obtained by the hydrolysis of Al-*sec*-tributoxide (TBOA) or Si-tetraethoxide (TEOS) in ethanol. Partial deposition of TBOA-derived granules or the entire deposition of TEOS-derived thin film could be observed on the fiber. The former showed no change in appearance when heated at temperatures lower than 1400°C, and exhibited integration with the original fiber above that temperature. It was also noted that the thin film in the latter was thermally stable, keeping the smooth surface below 1400°C, while geometrical patterns evolved on the naked surface of the original fiber at the same temperature. The film thickness was estimated to be 3 nm after being dried at 90°C.

[Received January 20, 1998; Accepted May 19, 1998]

Key-words : Surface modification, Al₂O₃ fiber, Heat-resistance, Alkoxide, XPS

1. Introduction

Polycrystalline alumina fibers are useful as thermal-insulating materials, shaped into blocks, sheets or linings, and as the reinforcing materials in plastics or inorganic refractories.¹⁾⁻⁷⁾ In 1980's, the heat resistance temperature of alumina fibers was increased by reducing the amount of the spinning aids.^{8),9)} They became durable for a long period of time at a high temperature of 1300°C, which was much higher than the heat resistance temperature (ca. 800°C) of Al₂O₃-SiO₂-based glass fibers. However, the fiber-like appearance was difficult to be retained at temperatures above 1300°C because of the overgrowth of the constituent crystal grains. One of the practical ways to increase the heat-resistance temperature is to introduce materials of higher heat-resistance into the fibers.¹⁰⁾

As a simple alternative way, the surface coating on the fibers may be effective to suppress the flow-out of the liquid phase ingredients from the grain boundaries and the overgrowth of the crystal grains. The coatings as small as 0.1 μm in thickness can be fabricated from gaseous or liquid phase by several ways such as CVD, sol-gel, etc.

In this report, the surface coating on polycrystalline alumina fibers was attempted for the improvement of high temperature strength and surface chemical properties through a sol-gel method using Al-*sec*-tributoxide (TBOA) or Si-tetraethoxide (TEOS). The morphology and chemical states of their surfaces were studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

Alumina fibers (average diameter 2.4 μm and average length 2.0 mm) were provided by Denki Kagaku Kogyo K.K., chemical and crystallographic compositions of which are summarized in Tables 1 and 2. The 'others' in Table 2

possibly contains spinel type alumina (γ-, δ- and η-Al₂O₃), θ-Al₂O₃ and Al from the consideration that the fibers were manufactured by means of 'precursor technique.'¹¹⁾ The existence of θ-alumina phase was confirmed by our X-ray diffraction measurement. As-received alumina fibers were dried at 90°C for 2h before being coated. Alkoxide treatments of the fibers were carried out with TBOA (Al (-O-*sec*-C₄H₉)₃, Kanto Chemicals, reagent grade) and TEOS (Si (-O-C₂H₅)₄, Shin Etsu Silicone Chemicals, LS-2430), as shown in Fig. 1. Alumina fibers were soaked into ethanol solution containing TBOA or TEOS, and then the solution was stirred for 5h after adding a small amount of water. The fibers were separated by sedimentation, dried successively at room temperature and 90°C for 12h, and then heat-treated successively at 500, 1100, 1400 and 1500°C for 2h.

The surface of the fibers was observed by SEM (JEOL, JSM-6300F), and the composition and chemical state analysis of the fibers was carried out by XPS (Shimadzu, ESCA-K1). The Al/(Al+Si) ratio was determined from the ratio of Al2s and Si2p peak areas after being corrected conventionally with their relative cross sections of photoionization, 0.72 and 0.87, respectively.¹²⁾

3. Results

3.1 SEM observation

Figure 2 shows the SEM photographs of the fibers treated with the alkoxides, together with the original fiber. Granular materials were observed on the surface of the fiber treated with TBOA (Fig. 2(b)), while a thin film was formed on the fiber treated with TEOS (Fig. 2(c)). The surface morphologies of all these fibers kept almost unchanged under the heat-treatment below 1100°C. Figure 3 shows the surface morphologies of the fibers heated at 1400°C. On the surface of the original fiber heated at 1400°C, geometrical patterns of 0.5-1.0 μm in width and 1.0-5.0 μm in length can be observed (Fig. 3(a)), which leads to the loss of the surface smoothness of the as-received original fiber shown in Fig. 2(a). On the other hand, the crops-up of the patterns on the TBOA- and TEOS-treated fibers were not clear (Figs. 3(b) and (c)). The peculiar pat-

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Table 1. Chemical Composition of the Alumina Fiber, B97N5

Constituent	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Ig-loss
Quantity / mass%	96.3±0.6	3.5±0.5	≤ 0.2	≤ 0.3

Table 2. Crystallographic Composition of the Alumina Fiber, B97N5

Constituent	α -Alumina	Mullite	Others
Quantity / mass%	50 - 59	≤ 12	—

Fig. 1. Flow diagram of sample preparation.

terns cropped up, however, on the surfaces of all the fibers by heating at 1500°C, as shown in Fig. 4.

3.2 XPS analysis

Figure 5 shows the Al2s and Si2p XPS peak profiles observed for the surfaces of the fibers after being dried at 90°C. On the original fiber, an intensive Al2s peak and a weak Si2p peak were observed (Fig. 5(a)). On the TBOA-treated fiber, the Si2p peak almost disappeared and the intensity of the Al2p peak increased relatively (Fig. 5(b)). On the TEOS-treated fiber, on the other hand, the weak Al2s peak and the intensive Si2p peak appeared (Fig. 5(c)). As summarized in Table 3, the calculated atomic ratios, Al/(Al+Si), of the surfaces of the original, the TBOA-treated, and the TEOS-treated fibers were 0.60, 1.00 and 0.34, respectively. The Al/(Al+Si) ratios of the original fiber and the TEOS-treated fiber remarkably changed with increasing heating temperature (Fig. 6). On the original fiber, it increased to 0.86 at 500°C. On the TEOS-treated fiber, it kept 0.34 until 500°C, and then increased to 0.73 at 1400°C. After being heated at 1400°C, the Al content of the surface of the TEOS-treated fiber was a little lower than those of the original and the TBOA-treated fibers.

The Al2p peak profile of the surface of the TBOA-treated

Fig. 2. SEM photographs of (a) original, (b) TBOA-treated and (c) TEOS-treated alumina fibers, after being heated at 90°C.

Fig. 3. SEM photographs of (a) original, (b) TBOA-treated and (c) TEOS-treated alumina fibers, after being heated at 1400°C.

Fig. 4. SEM photographs of (a) original, (b) TBOA-treated and (c) TEOS-treated alumina fibers, after being heated at 1500°C.

Fig. 5. XPS peak profiles of (a) original, (b) TBOA-treated and (c) TEOS-treated alumina fibers, after being dried at 90°C.

fiber dried at 90°C could be deconvoluted into four Gaussian curves (Fig. 7). The peak ① (75.1 eV) was assigned to mullite phase, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The peak ② (74.4 eV) was assigned to both spinel phase of γ -, δ - or η - Al_2O_3 and boehmite, $\text{AlO}(\text{OH})$. The peak ③ (73.9 eV) was assigned to α - Al_2O_3 , the major constituent of the fiber, and the peak ④ (72.9 eV) was assigned to aluminum, $\text{Al}^{0,13}$. The θ -alumina phase might be positioned at the binding energy between the peak ② and the peak ③, however, an additional new peak did not appear in that energy range. As shown in Fig. 8, the α -alumina fraction of all the fibers decreased first and increased finally with increasing heating temperature. The boehmite and spinel fractions increased first and decreased finally, the changes of which were in-

Fig. 6. Relationship between the atomic ratios, $\text{Al}/(\text{Al}+\text{Si})$, in the fiber surface estimated from the XPS results and the heating temperature.

Fig. 7. Deconvoluted $\text{Al}2p$ binding energy spectrum of TBOA-treated fiber, after being dried at 90°C.

Table 3. Peak Intensities and Calculated $\text{Al}/(\text{Al}+\text{Si})$ Ratios Obtained from the XPS Spectra in Fig. 5

Specimen	Peak intensity / $\text{eV} \cdot \text{cps}$		$\text{Al}/(\text{Al}+\text{Si})$ / %
	$\text{Al}2s$	$\text{Si}2p$	
Original	347	171	60
TBOA-treated	646	N.D.	100
TEOS-treated	179	521	34

Fig. 8. Changes in area percentage of component peaks in Al₂p profiles of the fibers with the heating temperature. The symbols, ◆, ▼, ●, and ▲ denote peak ① (mullite), peak ② (boehmite and spinel type alumina), peak ③ (α -Alumina), and peak ④ (Aluminum).

verse to those of α -alumina. The mullite fraction of all the fibers increased gradually with the temperature. The aluminum fraction decreased from 90 to 500°C of the original fiber (Fig. 8(a)), on the other hand, those of TBOA- and TEOS-treated fibers decreased from 500 to 1500°C. Variation of the aluminum fractions was the most significant in the original fiber, and was the least in the TEOS-treated fiber.

Deconvolution of Si₂p profiles of the fibers into the Gaussian curves corresponding to silica, mullite and others was impossible because of the closeness of their binding energies (≤ 0.3 eV).

4. Discussion

4.1 Surface morphology

After the alkoxide treatment, granular materials and thin films were formed on the surfaces of the TBOA- (Fig. 2(b)) and TEOS-treated (Fig. 2(c)) fibers, respectively. The difference of these morphologies was probably originated from the difference of the hydrolysis rates of the starting alkoxides.¹³ The hydrolysis of TBOA must have proceeded faster than that of TEOS; hydrolyzed TBOA molecules were rapidly condensed to deposit on the surface of the fiber as granules, while TEOS molecules with relatively low hydrolysis rate tended to spread on the entire surface of the fiber before they grew up to bulky products. Also, a TBOA-derived film might be deposited to coexist with the granular materials because the Si atoms contained in the original fiber were hardly detected by XPS in the TBOA-treated one because of the shielding effect of the thin film, as shown in Fig. 5(b).

The surface geometrical patterns on the original fiber after heat-treated at 1400°C (Fig. 3(a)) could be due to the densification of spinel and mullite phases in the α -Al₂O₃ grain boundaries. On the other hand, the TBOA- and TEOS-derived materials could suppress the formation of spinel phase, showing effective retardation of the crop-up of the patterns (Figs. 3(b) and (c)). These effect of the alkox-

ide treatment diminished after heated at 1500°C, causing the rapid growth of the α -Al₂O₃ grains on all the fibers (Fig. 4). The changes of the phase and the structure will be discussed in Section 4.3.

4.2 Surface composition

A number of Si atoms, which are thought to be a major element in the spinning aid, were contained in the surface of the original fiber (Fig. 5(a)). The Al/(Al+Si) atomic ratio of the surface obtained by the XPS measurement was 0.60 (Table 3), which is much lower than 0.97 of the original fiber calculated from Table 1. The Al/(Al+Si) atomic ratios of the TBOA and TEOS-treated fiber surfaces were higher and lower, respectively, than that of the original fiber surface; these results assert that the granules and the thin film on each fiber were derived from TBOA and TEOS, respectively. The Al/(Al+Si) ratio, in which Al was detected by going through the TEOS-derived thin film on the surface, was 0.34. Also, the film thickness was estimated possibly to be about 3 nm based on the mean free path of Al₂s electrons of about 5 nm.¹⁵⁾

The Al₂p XPS profile showed that mullite, boehmite, spinel type alumina, α -alumina, and aluminum existed on the surface of the dried TBOA-treated fiber. α -alumina is the major constituent, and mullite, spinel and aluminum are the minor constituents of the fiber itself. Although, boehmite existed in the products condensed from TBOA, its content was not clear because the same peak can also be assigned to spinel phase (the peak ②).

4.3 Phase and structure changes

Since crystallographic approach by means of X-ray diffraction measurement could not be applied to the surface layer of the fibers, the phase and structure changes of the fiber is discussed here from the results of XPS analysis (Figs. 6 and 8) and SEM observations (Figs. 2, 3 and 4).

Figure 9 illustrates the change of the cross sectional view of the surface of the original fiber during the heating process. In the as-received sample and in the sample heated at 90°C (Fig. 9(a)), Si atoms preferably existed near the surface in an oxidized form compared with aluminum atoms (Al³⁺) far from the surface. The aluminum atoms were originated from part of the 'precursors' which had not been able to react with enough number of oxygen atoms at the heat treatment step in the fiber manufacturing. As heated at 500°C (Fig. 9(b)), the localization of SiO₂ and aluminum atoms was forced to be dispersed by thermal energy, that is, SiO₂ diffused toward the inside and Al toward the surface of the fiber. This diffusion caused the increase in the Al/(Al+Si) ratio on the surface. The aluminum atoms that had arrived near the surface between the existing α -alumina or mullite grains were oxidized to form the spinel type alumina. This change brought the decrease in the aluminum fraction, the increase in the spinel fraction and apparent decrease in the α -alumina fraction. When heated up to 1100°C (Fig. 9(c)), the diffusion and oxidization of the aluminum atoms proceeded further and part of the spinel reacted with the silicon oxide to form mullite. At 1400°C (Fig. 9(d)), the spinel and mullite crystallites increased in number at the surface grain boundaries and contracted with densification, resulting in the crop-up of the geometrical patterns. When further heated at 1500°C (Fig. 9(e)), the spinel changed to α -alumina on the existing α -alumina grains, resulting in the rapid growth of the grains. With these changes, the decrease of the spinel fraction and the increase of the α -alumina fraction were observed.

For the TBOA- and TEOS-treated fibers, only a small number of the aluminum atoms near the fiber surface were oxidized to form spinel from 500 to 1400°C, since most of oxygen atoms near the surface were consumed for oxidization of the alkoxide-derived materials deposited on the surface

Fig. 9. Schematic diagrams of the cross sections near the fiber surfaces.

and then they were blocked up by the resultant oxide materials. Therefore, the changes in the aluminum and spinel fractions of the TBOA- and TEOS-treated fibers were less than that of the original fiber, as shown in Fig. 8. The change of TEOS-treated fiber was the least because of the maximum oxygen blocking effect of the thin film covering the whole fiber surface. The retardation of spinel formation led to the suppression of the crop-up of the geometrical patterns. The effect of the TEOS-treatment to retard the

reactions such as the spinel and/or mullite formation will be useful to suppress the deterioration of the mechanical properties.

5. Summary

The surface of polycrystalline alumina fibers was modified through the hydrolysis of Al-tributoxide (TBOA) or Si-tetraethoxide (TEOS). The former gave the partial deposition of granular materials, and the latter the entire coating of a thin film. Both of them could reduce the deterioration of the appearance of the fiber after being heated at 1400°C, while the geometrical patterns on the original fiber cropped up at that temperature. Particularly, the thin film on the TEOS-treated fiber which was thermally stable suppressed the outward diffusion of the inner amorphous Al species to hold the smoothness of the surface up to 1400°C. The thickness of the film was estimated to be 3 nm after being dried at 90°C. This thermal stability decreased at 1500°C; that is, the patterns on the surface of the fiber cropped up.

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