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Sol–Gel Synthesis of Mullite Long Fibres from Water Solvent Systems

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Abstract

Mullite long fibres, which are candidates for high temperature applications were prepared by sol–gel method from various water solvent systems. They were synthesized from three water solvent systems in different combinations of raw materials as follows: (1) $Al(O^iC_3H_7)_3$*(AIP),* $Al(NO_3)_3{\cdot}9H_2O$ *(AN) and* $Si(OC_2H_5)_4$ *(TEOS); (2) Al metal,* $AlCl_36\text{-}H_2O$*(AC) and TEOS; (3) Al metal, AN and TEOS. In the methods (1) and (2), very fine* SiO_2 *aerosil powder was also used partially replacing TEOS. The prepared solutions were condensed and examined the spinnability by a hand drawing method. Dense and crack free mullite fibres were obtained by firing the fibres prepared from methods (1) and (3) up to 1100°C, whereas those prepared from method (2) were less* SiO_2 *than mullite composition and were porous after the calcining due to evaporation of residual* Cl^- *ions at high temperature. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Fibres are useful materials for ceramic composites to enhance the fracture toughness and also thermal shock resistance.[1] SiC fibres such as Nicalon®[2–4] and Sylramic[5] show excellent mechanical strength up to very high temperature under inert gas atmosphere. However, since non-oxide ceramics oxidize at high temperature in air, they are considered to degrade the excellent properties during long term use and/or cyclic use at high temperature in air due to the oxidation. It is, therefore, required to develop fibres with high mechanical strength and high oxidation resistance properties. Considering the actual use of these materials at high temperature in air, development of oxide ceramic fibres instead of non-oxide ceramic fibres is important to essentially overcome oxidation problems at high temperature. Among the various oxide ceramic fibres, alumina fibres are reported to show good mechanical properties, especially at room temperature.[6] However, they degrade the mechanical properties at high temperature. Since mullite has good properties on mechanical strength and creep resistance at high temperature among various oxide ceramics,[7] it is a good candidate for fibre material for the above purpose.

Mullite fibres were first prepared by sol–gel method using colloidal silica and alumina sol by 3M group.[8] However, the fibres contain a considerable amount of B_2O_3 as additives, the good mechanical properties at room temperature degraded at higher temperature than 1000°C. Recently, this degradation is improved by preparing the fibres without B_2O_3 and also by shifting to Al_2O_3 rich composition to form composite texture with mullite in matrix dispersing alumina grains in the grain boundaries.[9] Since the process used by 3M group is not chemically homogeneous in molecular level to form mullite, preparation of mullite fibres through better chemical process using alkoxides and various organic solvent systems has been reported by many workers[10,11] to improve chemical homogeneity of mullite fibres and also its mechanical properties at high temperature. However, since most of their processes are necessary to use special and expensive reagents, e.g. Al- and Si-alkoxides, and 3-oxobutanoatodiisopropoxyaluminium and/or to manage under a controlled atmosphere they cannot be applicable for actual manufacturing production. On the other hand Nishio and Fujiki[12] succeeded in preparing mullite fibres from water solvent system using AIP, AN and TEOS. Since mullite fibres can be prepared from water solvent

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system and an open atmosphere by this method, it is interesting to further examine synthesis of mullite fibres from different combinations of starting materials using water solvent system.

In this paper, we examined preparation of mullite fibres from various combinations of reagents dissolved in water solvent.

2 Experimental

Reagents of AN, AIP, AC and/or Al metal (Wako Pure Chemicals) were used as an Al source, and TEOS (Wako Pure Chemicals) and SiO_2 aerosil (Aerosil 200, Japan Aerosil) were used as a Si source. The fibres were prepared from three different combinations of these raw materials. The starting materials and experimental conditions of the samples are summarized in Table 1. In method (1), AN was dissolved into deionized water at room temperature with vigorously stirring for 30 min and AIP was added further stirring for 30 min. Then, TEOS was added to the solution and stirred for 24 h. When SiO_2 aerosil powder used as a part of Si source, it was added after this step. The solution was then condensed at around 90°C using a water bath and further at 110°C in an oven. After appropriate condensation of the solution, gel fibres were drawn at room temperature by a hand drawing method, i.e. immersing a thin glass rod into the solution and pulling out it slowly. The gel fibres were then dried at room temperature and further dried at various temperatures by gradually elevating the drying temperatures with holding a certain time at each temperature step by step from room temperature to 160°C. The dried fibres were heat treated in air up to 1100°C with heating rates 0·1–0·5°C min^{-1}. In method (2), AC was first dissolved into deionized water and then Al metal powder and TEOS were added with vigorously stirring. The solution was refluxed at around 90°C for 18 h and then condensed similarly with method (1). Drawing, drying and heating of fibres were also performed similarly. Method (3) was performed in a similar manner as method (2) using AN instead of AC as the raw materials.

The prepared fibres were characterized by thermogravimetric analysis/differential thermal analysis (TG/DTA), powder X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The TG/DTA was measured on Rigaku Thermoplus 8120 with a heating rate 5°C min^{-1} and sample weight about 20 mg. The XRD patterns were obtained on Rigaku Geigerflex diffractometer using monochromated Cu K_α radiation. The SEM observation was done on Hitachi S-2050 instrument at 15 kV.

3 Results and discussion

3.1 Preparation of mullite fibres

In method (1), the spinnability of solutions mainly changed depending on AIP/AN ratio as reported by Nishio and Fujiki.[12] With decreasing the AIP/AN ratio, the length of fibres becomes shorter and finally fibres can not spin in the AIP/AN $\leqq 0{\cdot}5$. The viscosity properties (shear stress versus shear rate) of these solutions condensed for 5 h were examined using a viscometer. When a solution

Table 1. Experimental conditions of mullite fibre preparation

Method	*Sample*	*Al-source (mol)*				*Si-source (mol)*		*H_2O (mol)*	*Al_2O_3/SiO_2 (mol%)*	*Spinnability*
		AN	*AIP*	*AC*	*Al*	*TEOS*	*SiO_2*			
(1)	1–1	0·30	0·30	—	—	0·20	—	12·4	60/40	Good
	1–2	0·32	0·29	—	—	0·20	—	12·9	60/40	Good
	1–3	0·34	0·26	—	—	0·20	—	13·2	60/40	Fair
	1–4	0·40	0·20	—	—	0·20	—	13·3	60/40	No
	1–5	0·12	0·24	—	—	0·11	—	8·3	62/38	Good
	1–6	0·12	0·24	—	—	0·096	0·014	8·3	62/38	Good
(2)	2–1	—	—	0·10	0·38	0·042	—	5·5	85/15	Good
	2–2	—	—	0·10	0·38	0·056	—	5·5	81/19	Good
	2–3	—	—	0·10	0·38	0·080	—	5·5	75/25	No
	2–4	—	—	0·10	0·38	0·103	—	5·5	70/30	No
	2–5	—	—	0·10	0·38	0·147	—	5·5	62/38	No
	2–6	—	—	0·10	0·38	0·054	0·006	5·5	80/20	Good
	2–7	—	—	0·10	0·38	0·072	0·008	5·5	72/25	No
	2–8	—	—	0·10	0·38	0·093	0·009	5·5	70/30	No
	2–9	—	—	0·10	0·38	0·132	0·013	5·5	62/38	No
(3)	3–1	0·08	—	—	0·30	0·116	—	5·5	62/38	No
	3–2	0·08	—	—	0·15	0·070	—	5·5	62/38	Good
	3–3	0·08	—	—	0·08	0·049	—	5·5	62/38	Fair
	3–4	0·08	—	—	0·04	0·036	—	5·5	62/38	Fair

behaves as Newtonian-type flow, the spinnability is good but it changes poorer in pseudoplastic flow and finally unspinnable in thixotropic flow. Corresponding to these change in viscosity properties, the volume of solution after condensation showes correlation to increase with lowering spinnability of the solutions. Nishio and Fujiki[12] pointed out the important role of AIP to suppress polymerization of TEOS in this system because TEOS rapidly polymerizes to form SiO_2 sol in water solvent system without AIP. It may be plausible to consider from these results that the structure of precursors in the solution is one dimensional like state in high AIP/AN ratio but changes to three dimensional like state with lowering the AIP/AN ratio. This is also compatible with the results of the volume of sol after condensation because the volume decreased largely when it was spinnable whereas the volume decreased a little when it was unspinnable. In the samples no. 1–5 and 1–6, the gel fibres with mullite composition are easily drawn as long as around 100 cm by the hand drawing method.

In method (2), fibres were prepared with changing Al_2O_3/SiO_2 ratios because this combination of raw materials was originally used in the preparation of Al_2O_3 fibres.[13] With increasing SiO_2 composition in Al_2O_3–SiO_2 fibres, fibres up to $Al_2O_3/SiO_2 = 81/19$ mol% composition are spinned but not to further SiO_2 rich composition, i.e. mullite compositions ($Al_2O_3/SiO_2 = 60/40$ mol%). Increasing the amount of TEOS may cause more rapid hydrolysis and polymerization of TEOS to form SiO_2 sol and it may form precursor with three dimensional framework structure in the solution. The fibre preparation was also performed partially replacing Si source by SiO_2 aerosil but the spinnable composition range of fibres did not change with those in the above series as listed in Table 1. The gel fibres obtained by this method (No. 2–2) are as long as around 80 cm in length.

In method (3), the fibres were prepared by replacing Al source of AC by AN. The solution (No. 3–1) was first prepared by the similar condition with the sample no. 2–5 and refluxed. However, the solution is not transparent and a part of Al metal powder remains undissolved due to low solubility of Al metal in nitrate solution. Therefore, the solutions were prepared with decreasing the amount of Al metal and refluxed. Transparent solution is prepared in the samples no. 3–2, 3–3 and 3–4. The gel fibres are drawn from these solutions but the spinnability becomes poorer with decreasing the amount of Al metal. The best spinnability in this method is obtained in the sample no. 3–2 but the length of the gel fibres spinned is shorter than those of methods (1) and (2), i.e. around 30 cm in length.

3.2 Drying and firing of mullite fibres

The TG/DTA of dried fibres (at 110°C) was measured using the pulverized samples to examine appropriate drying and firing conditions of the gel fibres (Fig. 1). The sample (No. 1–5) prepared by method (1) shows two endothermic peaks at about 150 and 350°C, and two exothermic peaks at about 410 and 980°C as shown in Fig. 1(a). Two endothermic peaks are assigned to dehydration of water whereas two exothermic peaks are assigned to decomposition of nitrates and crystallization of mullite, respectively. The weight loss up to 1300°C is around 50 mass% but it is almost completed by 400°C. The samples prepared with SiO_2 aerosil powder shows almost similar results but the temperature to complete weight loss (450°C) is slightly higher than that without SiO_2 aerosil. The sample

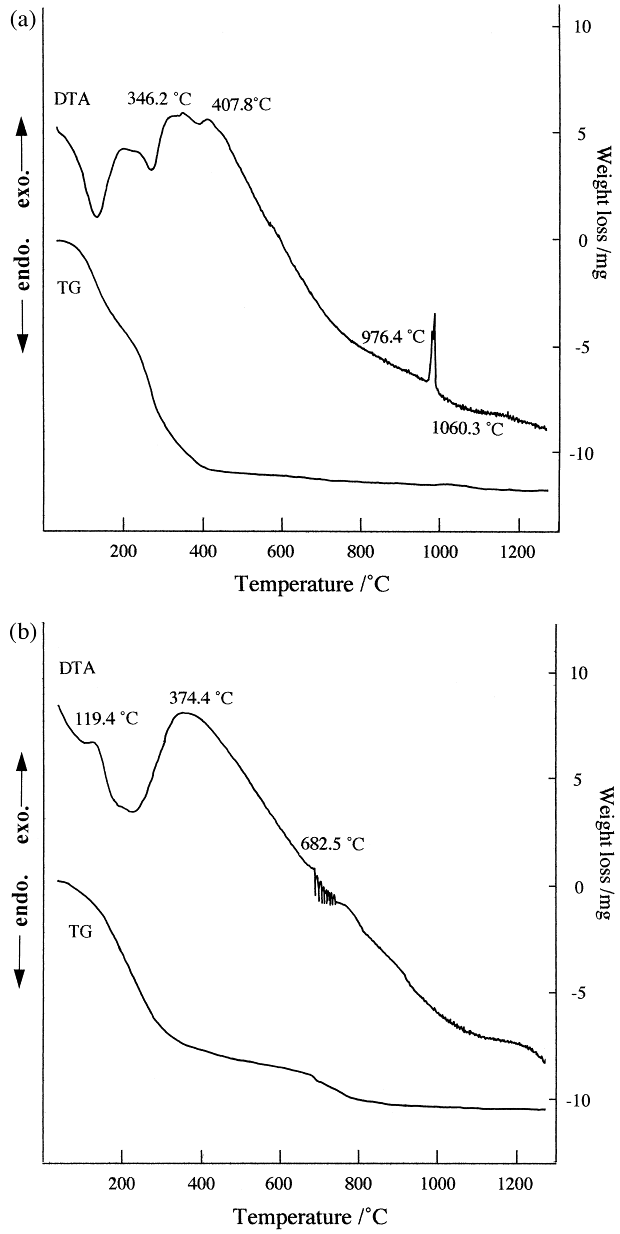

Fig. 1. DTA/TG curves of the pulverized samples of dried fibres; (a) sample no. 1–5; (b) sample no. 2-2.

(No. 2-2) prepared by method (2) shows three endothermic peaks at 120, 230 and 690°C [Fig. 1(b)]. Two endothermic peaks appeared at lower temperatures are assigned to dehydration of water while the highest one to evaporation of residual Cl^- ions and/or melting of Al metal. Therefore, the weight loss showed two step curve and continued up to around 800°C. The total amount of weight loss of this sample is also around 50 mass% and is similar level with that of method (1). The exothermic peak corresponding to crystallization of mullite is not clearly observed up to 1300°C in this sample. The mullization of this sample should be higher than 1300°C, in which temperature is similar as in the case of inhomogeneous gels reported by Colomban.[14] On the other hand, the TG/DTA of method (3) sample was similar with those of method (1) but not method (2).

The prepared gel fibres were dried by slowly elevating the drying temperatures step by step up to 160°C. Many cracks were, however, observed in all the dried fibres especially when they were thicker than 10 μm in diameter. As shown in Fig. 2, the SEM photographs of the dried thick fibres show deep lateral cracks running to the elongated direction of the fibre and circumferential cracks, which divided the cross section of fibres into two zones, outside and inside [Fig. 2(a)]. Although the fibres are dried very carefully and slowly (2–3 days), the SEM photographs suggests that the drying speed is too fast for these fibres without generating cracks during this drying stage. Two approaching methods are considered to settle this issue, i.e. (1) increasing of the pore size in the fibres to lower the stress yielded by the drying and (2) reducing the diameter of the fibres to shorter the transport distance of water vapor for evaporation. As the first approaching, we used fine SiO_2 aerosil powder in the fibre preparation to increase the pore size in the gel fibres. As the second approaching, the glass rod used for spinning of gel fibres changed to thinner diameter to reduce the diameter of gel fibres. As a result, reducing the diameter of glass rod is effective to reduce the diameter of fibres and is found to be very effective to decrease the cracks in the fibres as shown in Fig. 2(b). The cracks are further decreased by preparing the fibres using SiO_2 aerosil powder and the dried fibres prepared became almost crack free.

From the thermal analysis, the heat treatment temperatures of the dried fibres were determined to set at 900 and 1100°C, in which temperatures corresponded to before and after the crystallization of mullite. The SEM photographs of the fibres prepared by methods (1) and (2) and fired at 900°C are shown in Fig. 3. The fired fibres prepared by the method (1) are observed to be dense and crack

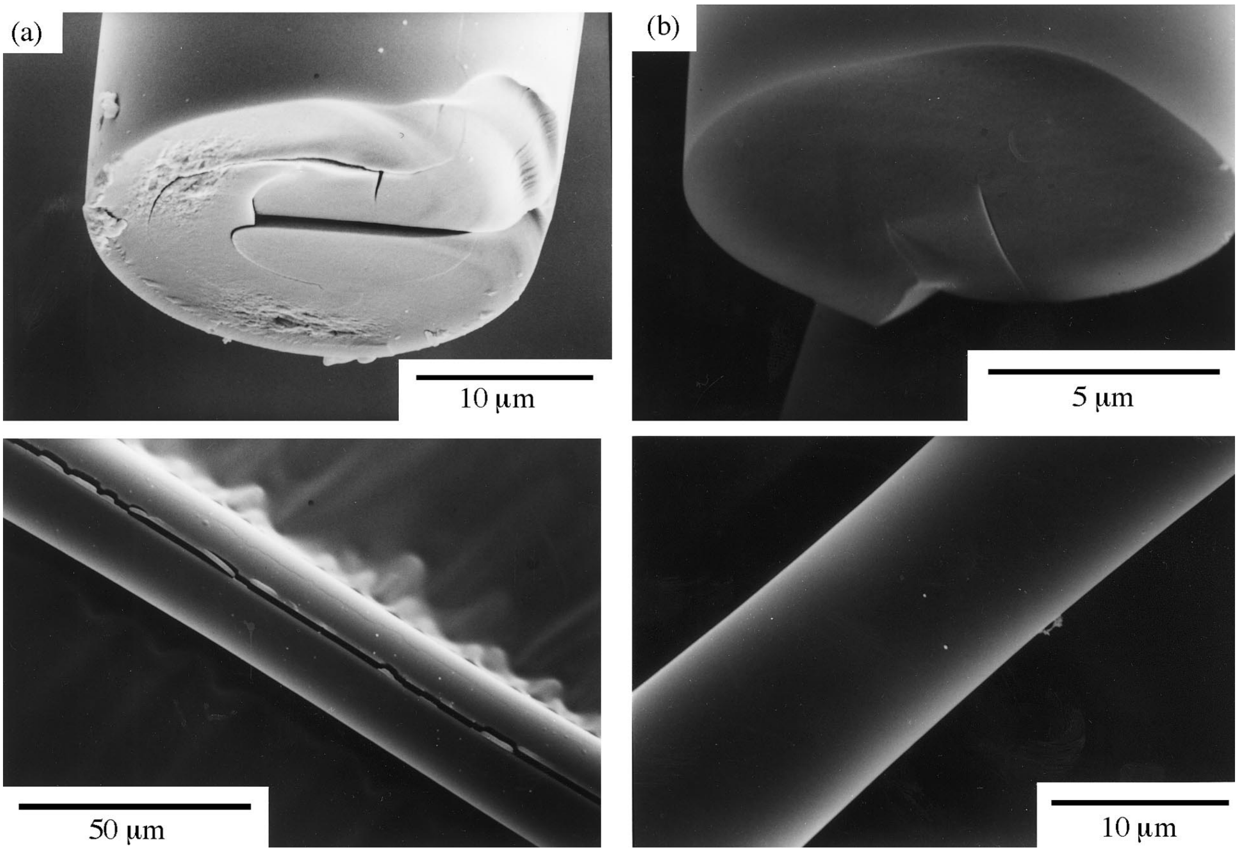

Fig. 2. SEM photographs of the dried fibres prepared by method (1) and dried at 160°C; (a) thick fibre; (b) thin fibre.

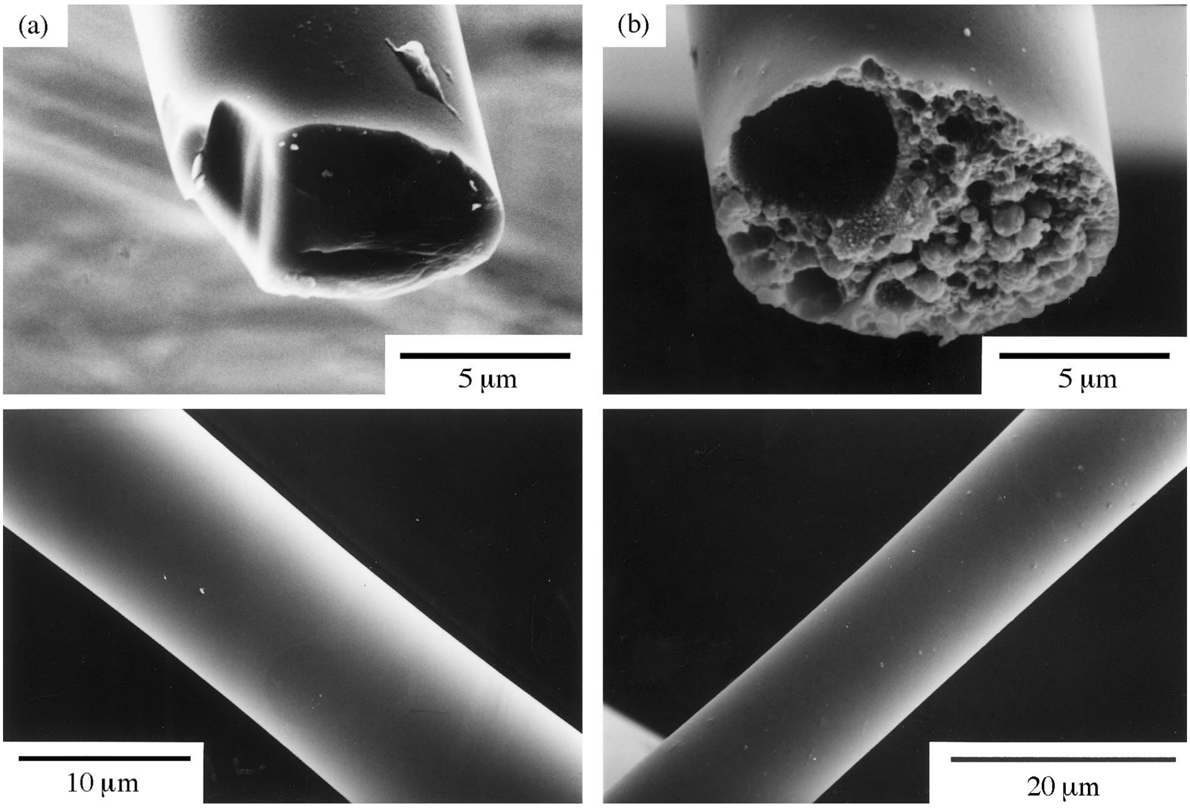

Fig. 3. SEM photographs of the calcined fibres fired at 900°C; (a) method (1); (b) method (2).

free in the SEM photographs [Fig. 3(a)]. These fibres are flexible and transparent at this stage. They can make loop around 1·5 mm in diameter. On the other hand, the fired fibres prepared by method (2) were apparently porous and included many pores in the fibres as shown in Fig. 3(b). As mentioned in the DTA curve of this sample, two reasons, i.e. evaporation of Cl^- ions and/or

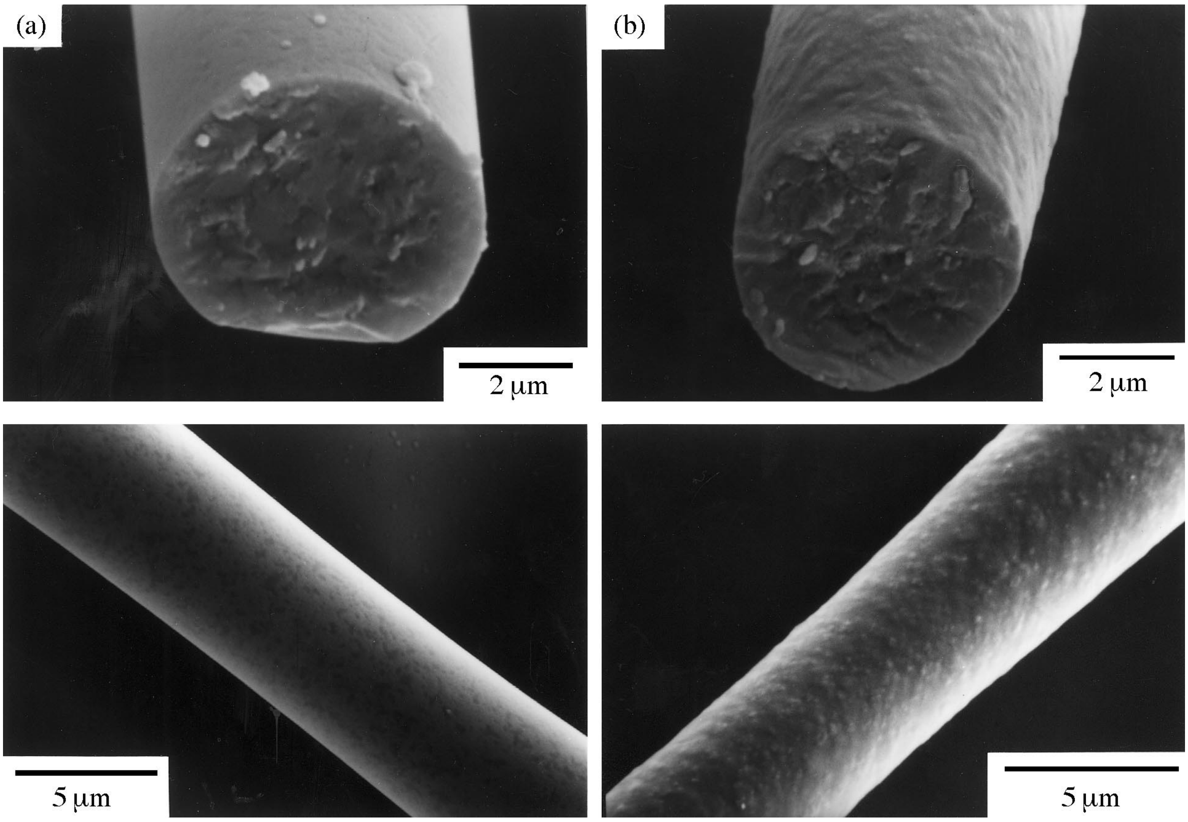

Fig. 4. SEM photographs of the mullite fibres prepared by method (1) and fired at 1100°C; (a) without sample; (b) with SiO_2 aerosil sample.

melting of residual Al metal are considered for formation of the porous fibres. Judging from the microstructure of the fibers, melting of Al metal in the fibres is unlikely to occur while evaporation of Cl^- ions is likely to occur as the reason for pores. In this fibre, since the Cl^- ions in the dried fibres evaporate at relatively high temperature [Fig. 1(b)], sintering of the fibres is considered to occur before the decomposition of Cl^- ions and the microstructure caused by bloating of Cl_2 gas is likely to be formed. It is, therefore, concluded that AC is inadequate as starting materials for the preparation of dense mullite fibres.

Figure 4 shows the SEM photographs of the mullite fibres prepared by method (1) and fired at 1100°C. Since the both fibres with and without SiO_2 aerosil crystallized to mullite by the firing, they were found to keep dense and crack free state after the mullitization. In the XRD patterns of these two samples, only mullite phase was observed in the fibres prepared without SiO_2 aerosil whereas reflections of γ-Al_2O_3 and halo by amorphous SiO_2 as well as reflections of mullite were detected in that with SiO_2 aerosil. Thus, the added SiO_2 aerosil powder did not react to form mullite by the firing at 1100°C. As apparent from Fig. 4(b), the fibres with SiO_2 aerosil are rough surface compared with those without SiO_2 aerosil and this may be corresponding to the difference of formed phases in these fibres. The fibres seem to loose flexibility after the firing at 1100°C compared with that of the fibres fired at 900°C. The decrease of flexibility of fibres may be due to the crystallization and grain growth of mullite in the fibres.

4 Conclusions

Mullite fibres were prepared by sol–gel method using water as a solvent from three different combinations of the starting materials and the following conclusions were obtained.

1. In method (1) using AN, AIP, TEOS and/or SiO_2 aerosil, the spinnability became worse with lower the AIP/AN ratio. Dense and crack free mullite fibres were obtained by firing at 1100°C when the diameter of the gel fibres was thinner than $10\,\mu m$.
2. In method (2) using AC, Al metal, TEOS and/or SiO_2 aerosil, the fibres were spinned up to around $Al_2O_3/SiO_2 = 80/20$ composition but the fibres with mullite composition ($Al_2O_3/SiO_2 = 60/40$) were not spinned. The fibres became porous by calcining due to decomposition and evaporation of residual Cl-ions in the fibres at high temperature.
3. In method (3) using AN, Al metal and TEOS, the fibres were spinned but the spinnability was poorer than those in methods (1) and (2).

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