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INDUCED CONVERSION OF ALUMINIUM SILICATE FIBERS INTO MULLITE AND CRISTOBALITE BY ELEVATED TEMPERATURES: A COMPARATIVE STUDY ON TWO COMMERCIAL PRODUCTS *

J. KHORAMI [1], A. LEMIEUX [1], J. DUNNIGAN [2] and D. NADEAU [1]

[1] *Laboratoire de Caractérisation de l'Amiante. Programme de recherche sur l'amiante de l'Université de Sherbrooke;* [2] *Institut de l'Amiante, Division de la recherche, Université de Sherbrooke, Sherbrooke (Québec) Canada J1K 2R1*

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ABSTRACT

Aluminium silicate fibers (ALF) are used in a variety of industrial products, including as a substitute for asbestos in insulation materials. Although many studies evaluating the thermal resistance of these compounds have been made, conflicting results were sometimes obtained on the conversion of these amorphous silicates into mullite and cristobalite. For our study, two types of ALF were selected: type I (Triton Kaowool®, Normal grade) and type II (Fiberfrax®; High Specific Area "HSA" grade). These two silicate fibers differ mainly in the percentage of impurities such as iron, titanium, sodium and potassium oxides. As observed by X-ray diffraction, differential thermal analysis and infrared spectroscopy, our results show that both types of ALF are transformed into mullite at 1016 °C and 990 °C respectively for the type I and type II fibers. With the type I ALF, when heated at 1050 °C, the quantity of mullite increased with time. No trace of cristobalite was detected even after a 4 weeks heat treatment at 1050 °C. However, for the type II ALF which are richer in oxide impurities, two conversion steps were observed: (a) as with the type I fibers, the quantity of mullite increased with time; (b) after 64 h at 1050 °C, the second crystallization step into cristobalite started and increased after the 4 weeks heat treatment. These results indicate that the level of oxide impurities can accelerate the conversion of mullite into cristobalite. Considering the known danger associated with the inhalation of cristobalite, these finding indicate that different ALF might have new biological activities when subjected to elevated temperatures for long periods of times.

INTRODUCTION

The structural changes taking place in aluminium silicate fibers (ALF) submitted to high temperatures have been recently studied [1-4]. Hence, Gaodu et al. [1] have investigated the crystallization phases of glass fibers (Kaolin composition) during a heat treatment from 400 to 1400 °C. They

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concluded that the principal crystalline phase appearing in the material was mullite, a transformation of which appeared at 1100–1200 ° C. Olds et al., [2] examined the behaviour of ALF, containing 47% alumina and small amounts of chromium oxide, heated at temperature up to 1412° C. The quantitative X-ray analysis of these fibers indicated the presence of mullite (63%) and cristobalite (37%), which corresponds to the equilibrium phase composition. Belyakova et al., [3] established that heating ALF at 1397° C leads to a monotonic increase in the amount of mullite and cristobalite; the latter appears at higher temperature and after a longer residence time. Above 1397° C, the mullite content remains constant but the cristobalite content decreases. In a fibrous clay, and above 1397° C, the mullite content decreases and vitrification begins at a lower temperature. Aluminophosphate binder retards mullitization of the fiber at 997–1397° C and increases the yield of mullite at 1397° C. More recently, Vine et al., [4], showed that after an exposure of a commercial grade of Kaowool fibers at 1150° C, the conversion to mullite was rapid and took place within hours. However, the conversion to cristobalite occurred only after a few weeks.

Therefore, the purpose of this study was to investigate the thermal behaviours of two types of commercial ALF differing mainly by their levels of impurities. Our results, obtained by X-ray powder diffraction, differential thermal analysis (DTA) and Fourier-transform infrared (FT-IR) spectroscopy will show that the rate of crystallization, as well as the conversion of mullite into cristobalite, can be related to the level of oxide impurities present in the ALF. Moreover, our study will show that the relatively pure ALF are converted principally into a stable crystalline phase of mullite, with no trace of cristobalite even after four weeks of heating at 1050° C.

EXPERIMENTAL DETAILS

Apparatus

The following analytical instruments have been used in this study:

(a) Automatic X-ray powder diffractometer with X-ray diffractometer kit (PW 1349) in combination with an X-ray generator (PW 1140); Philips Electronic Instruments, Inc.

(b) Differential thermal analyzer (DTA), model 1700, high temperature differential thermal analyzer; Perkin-Elmer Corporation.

(c) Infrared spectrometer (FT-IR), model MX-1; Nicolet Instrument Corporation.

Fibers

The two types of ALF used are listed below:

(a) Triton Kaowool®, normal grade, from Morgan GMBH, Germany.

TABLE 1

Physico-chemical characteristics of ALF [a]

Samples	Melting point (°C)	Al_2O_3 (%)	SiO_2 (%)	Fe_2O_3 (%)	TiO_2 (%)	K_2O+Na_2O (%)	Density (g cm^{-3})
Kaowool®	1760	44.8	54.4	0.05	0.04	0.03	2.56
Fiberfrax® HSA	1790	43.4	53.9	0.8	1.6	0.2	2.7

[a] According to the manufacturers' data.

(b) Fiberfrax®, HSA grade, from Carborundum Co., Niagara Falls, U.S.A. Their chemical compositions are shown in Table 1.

Heat treatment

The two samples of ALF, type I (Triton Kaowool) and type II (Fiberfrax), were exposed in a high temperature muffle furnace at 1050 °C for 3.5 h, 8 h, 64 h, 2 weeks and 4 weeks. Then, the samples were analyzed according to the analytical methods described above.

RESULTS

To determine to which extent the two types of amorphous ALF were converted to mullite and cristobalite after heating, we compared the X-ray diffraction peaks of the samples heated at various times of residence at 1050 °C (Figs. 1 and 2). The main characteristic peaks of mullite (M) and

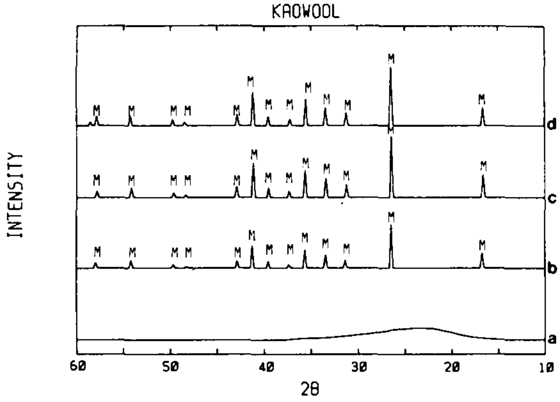

Fig. 1. Diffraction patterns of Kaowool fibers. (a) Original fibers. (b) After 3.5 h at 1050 °C. (c) After 64 h at 1050 °C. (d) After 4 weeks at 1050 °C.

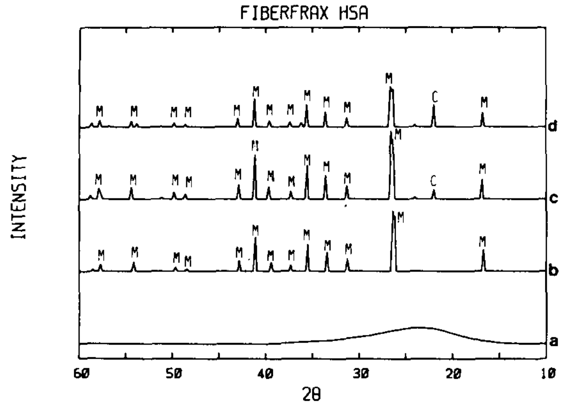

Fig. 2. Diffraction patterns of Fiberfrax. (a)–(d) as for Fig. 1.

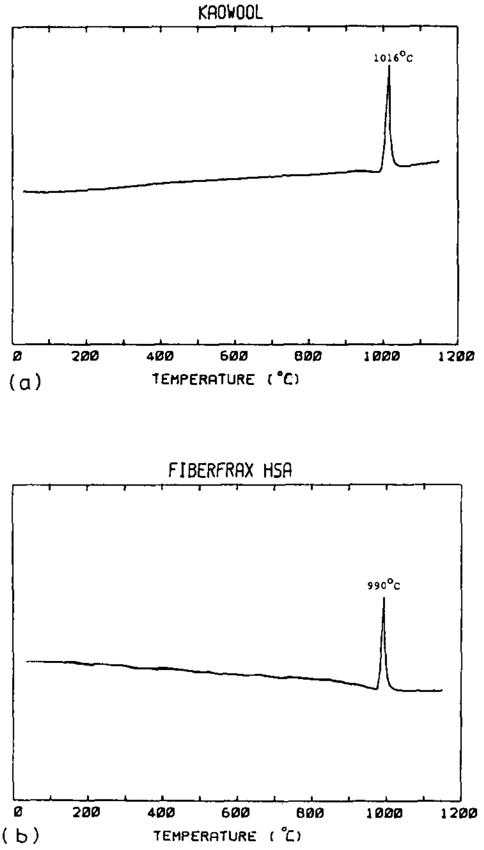

Fig. 3. Thermal curves (DTA) of Kaowool and Fiberfrax. (a) Kaowool. (b) Fiberfrax.

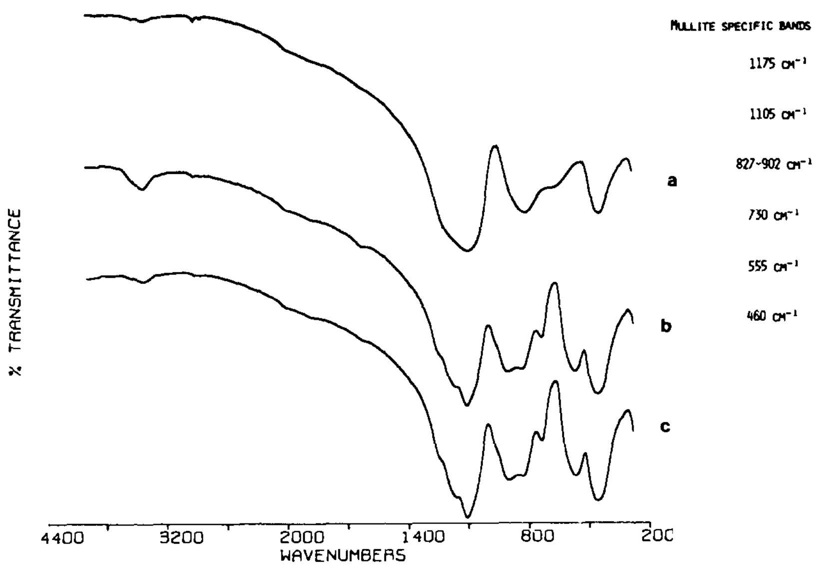

Fig. 4. Infrared spectra of Kaowool. (a) Original fibers. (b) After 2 weeks at 1050 °C. (c) After 4 weeks of 1050 °C.

cristobalite (C) are identified on these figures. As we can see from these results, both types of ALF are transformed into mullite after 3.5 h of exposure at 1050 °C. With the type I fibers (Kaowool), the quantity of mullite increases with time up to 64 h; there is no change in crystalline phase

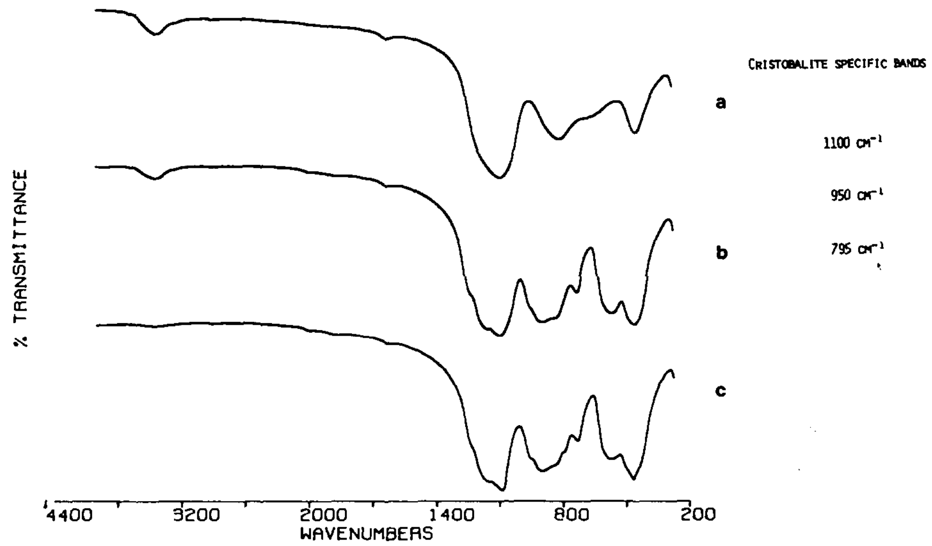

Fig. 5. Infrared spectra of Fiberfrax. (a)–(c) Have the same significance as in Fig. 4.

after 64 h of residence at 1050 ° C. However, for the type II fibers (Fiberfrax), no trace of cristobalite is observed after 3.5 h. Nevertheless, after 64 h, the characteristic peaks of cristobalite appear; their intensities increase after longer residence times at high temperature.

Figure 3 illustrates the thermal curves (DTA) of type I and type II ALF fibers. Both types of amorphous ALF have an exothermic peak due to a crystallization into mullite. However, we can observe that the maximum of the DTA peak in the case of Kaowool is displaced towards higher temperature. The temperature of conversion into mullite is 990 ° C for Fiberfrax and 1016 ° C for Kaowool.

The FT-IR spectra of type I and type II ALF fibers, before and after the heat treatment, are compared in Figs. 4 and 5. In both cases, the spectra of the untreated fibers show the presence of broad vibration bands which are characteristics of amorphous materials. However, after heating at 1050 ° C, one can observe only the presence of mullite specific bands for type I fibers: 1175 cm^{-1}, 1105 cm^{-1}, 827–902 cm^{-1}, 730 cm^{-1}, 555 cm^{-1} and 460 cm^{-1}. The FT-IR spectra of the type II fibers show the presence of mullite and cristobalite. We could identify the specific bands of cristobalite at 1100 cm^{-1}, 950 cm^{-1} and 795 cm^{-1}; one can also note that the intensities of these bands increase with the time of residence at 1050 ° C.

CONCLUSION

The results reported here show that both amorphous ALF, type I (Kaowool) and type II (Fiberfrax) are converted within a few hours to mullite. However, the temperature of conversion is higher for type I ALF. With the two types of commercial fibers studied in this work, only one step of crystallization was observed for type I. These fibers are converted principally into mullite and no trace of the cristobalite phase was detected, even after 4 weeks at 1050 ° C. Nevertheless, in the case of type II fibers (Fiberfrax), two conversion steps were observed. As with the type I fibers, type II fibers are converted first into mullite; then, after 64 h at 1050 ° C, the second crystallization step started and the quantity of cristobalite increased with the time of residence at 1050 ° C.

As judged by the chemical composition of the ALF fibers (Table I), it is believed that the highest level of iron, titanium, sodium and potassium oxides of the type II fibers (Fiberfrax) can play the role of accelerators for the conversion of mullite into cristobalite. Consequently, it is believed that the conversion of ALF into cristobalite at high temperatures can be retarded significantly by the elimination of oxide impurities. Our results are in accordance with the data of Vine et al., [4] which showed that another grade of Triton Kaowool, containing higher levels of oxide impurities than ours, could also be converted into cristobalite by high temperatures.

Finally, these results might have some biological significance since cristobalite is already well known for its lung toxicity both in vitro and in vivo [5,6].

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