Original Paper

Variations in effects of heating on the dissolution of amorphous alkaline earth silicate fibers in a simple amino acid solution

Masato Ohsawa

Research & Development Division, SAINT-GOBAIN TM K.K., Chiba (Japan)

Dissolution experiments of amorphous alkaline earth silicate (AES) fibers heat-treated in the temperature range of 110 to 1260 °C have been carried out in a glycine, a simple amino acid, solution. Results of the experiments suggest that variations in the dissolution rate of AES fibers in the glycine solution as a function of heat treatment temperature can be categorized into two types, one of which shows a peak around 700 °C, whereas the other exhibits a sharp rise up to 800 °C and then is kept constant in the temperature range over 800 °C. The AES fibers which fall into the first category are in the Mg-rich systems and are crystallized dominantly into enstatite, augite or diopside by heating at a temperature of 800 °C or over. Meanwhile, the AES fibers of the second category are in the Ca-rich systems and are crystallized dominantly into wollastonite or pseudowollastonite by heating at a temperature of 800 °C or over.

1. Introduction

Man-made vitreous fibers (MMVFs) in the form of wools are widely used in heat resistance, thermal and acoustic insulation and in other manufactured products. These MMVFs, such as glass wool, rock (stone) wool, slag wool and ceramic fibers, have similar aerodynamic properties to asbestos. Therefore, the potential for increased risk of lung cancer caused by deposition of these fibers has been pointed out [1 to 4].

In recent years, much industrial effort has gone into development of newer fibers that are more biosoluble and disappear much more rapidly from body tissues [1].

An example of the newly developed, more biosoluble fibers is amorphous alkaline earth silicate (AES) fibers [1]. AES fibers are considered to be alternative materials for ceramic fibers which are used in high temperature circumstances. A current study has shown recrystallization in AES fibers under thermal stress [5]. However, effects of thermal histories on the dissolution of AES fibers have not been investigated well enough. It has been pointed out that thermal histories can have considerable influence on the dissolution properties of glassy materials [6].

In addition, notice that dissolution in the alveolar region can be different from normal dissolution in water. It is known that amino acids and proteins in the alveolar region can dissolve respired substances [7]. The dissolution properties of various substances in amino acid solutions should be evaluated [8].

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This paper describes the effects of heating on the dissolution of Mg-rich and Ca-rich AES fibers in a glycine, a simple amino acid, solution.

2. Materials and methods

2.1 Fiber samples preparation

AES fiber samples used in this study were produced by the method shown in the previous study [9].

The chemical composition of the AES fiber samples was analyzed by a wave-length dispersion X-ray fluorescence spectrometer.

Chemical composition of the AES fiber samples is shown in table 1 (samples no. 1 to no. 13). The table displays the variations in the composition range from MgO-rich to CaO-rich AES systems including the SrO component.

The AES fiber samples were heat-treated in a laboratory drying oven or an electric furnace for the temperatures and times indicated in tables 2 and 3.

The fiber samples which were heat-treated for the temperatures and times indicated in table 3, column 1, were examined by X-ray powder diffraction (XRD) analysis at 40 kV, 30 mA with scanning speed of 2 degree/min.

2.2 Experimental procedure

Each heat-treated fiber sample was first chopped until the fiber passed through a 200 mesh (pore diameter: 0.075 mm)

Table 1. Chemical oxide composition in wt% of the AES fiber samples

sample no.	SiO_2	MgO	SrO	CaO	Fe_2O_3	Al_2O_3
1	75.2	12.8	3.8	7.9	0.1	0.1
2	61.1	4.1	0.0	34.0	0.5	0.3
3	76.6	22.6	0.0	0.4	0.1	0.2
4	77.2	19.9	2.3	0.4	0.1	0.1
5	77.3	18.6	3.3	0.3	0.1	0.4
6	76.6	17.0	5.8	0.3	0.1	0.1
7	74.8	14.0	1.3	9.6	0.2	0.1
8	74.8	11.4	5.1	8.3	0.1	0.2
9	63.7	14.6	0.0	21.2	0.1	0.2
10	73.7	9.2	5.9	10.9	0.2	0.2
11	61.8	5.9	0.0	31.4	0.2	0.6
12	63.2	1.0	6.7	28.6	0.3	0.2
13	65.2	0.0	0.0	34.6	0.1	0.1

screen. Thereafter, (1.0000 ± 0.0003) g of the chopped fiber sample was weighed into a conical beaker, and 150 ml of 2 wt% glycine solution with 5 ml of 0.05 mol/l phthalate, $C_6H_4(COOK)(COOH)$, solution was added to the beaker. The beaker with the fiber sample and the liquid was inserted into a shaking incubator bath maintained at 40 °C ± 1 K (nearly at body temperature). The shaker speed was set at 120 cycles/min and the experimental period was 50 h. After the period, the fiber sample was separated from the liquid by filtration and dried in an oven at 100 °C. The separated and dried fiber sample was weighed accurately. The calculation of weight loss of the dissolved fiber sample determined the dissolution rate of the fiber sample. It has been reported that the dissolution rate obtained by the similar method is independent of the diameters of the fibers [9].

In addition, pH of the liquid reacted with the fiber sample was determined.

The reason for the addition of the phthalate, $C_6H_4(COOK)(COOH)$, solution is the following. It is known that dissolved alkaline earth ions raise the pH of liquids [10], and the rise of pH to the range of 12 to 13 precipitates Mg ions as $Mg(OH)_2$, magnesium hydroxide, in the liquids [11]. This precipitation would cause incorrect determination of the dissolution rate of the fiber samples. The pH of the phthalate solution is approximately 4.0. Therefore, the addition of the phthalate solution is able to limit the rise of pH in the liquid and the precipitation of Mg^{2+} as $Mg(OH)_2$. It is known that phthalate solution gives very few effects on dissolution of glassy materials [12].

3. Result

3.1 X-ray diffraction analysis

Table 4 shows the phases of the heat-treated AES fiber samples no. 1 and no. 2 identified by X-ray diffraction (XRD) analysis.

The glassy states of the amorphous AES fiber samples remain unchanged in the heat treatment temperature range up to 700 °C. The AES fiber samples are crystallized partly into crystalline alkaline earth silicates such as augite (no. 1), wollastonite, pseudowollastonite and diopside (no. 2) in the temperature range of 800 °C or over, leaving an excessive silica glassy phase. Cristobalite is formed at 1260 °C, resulting from crystallization of the excessive silica glassy phase.

3.2 Variation in the dissolution rate as a function of heat treatment temperature

The dataset of the dissolution rate of the heat-treated AES fiber samples no. 1 (MgO-rich $MgO-CaO-SrO-SiO_2$ system) and no. 2 (CaO-rich $CaO-MgO-SiO_2$ system) in the glycine solution at 40 °C over 50 h and the pH of the post-reacted glycine solution is given in table 3.

All of the glycine solutions reacted with the fiber samples indicate pH less than 9.

Table 2. Molar ratio-weighted mean ionic radius of alkaline earth ions and the dissolution rate of the heat-treated AES fiber samples and pH of the post-reacted glycine solution

sample no.	r_{avg} in $\times 10^{-12}$ m	dissolution rate in µg/ml, run at 40 °C, 50 h, 120 rpm			pH of the glycine solution reacted with fiber sample		
		heat treatment in °C/h					
		110/24	700/24	1100/24	110/24	700/24	1100/24
1	78.8	290	555	45	7.4	8.4	5.1
2	94.3	84	39	510	6.4	4.9	8.2
3	66.5	45	381	29	5.3	8.0	4.4
4	68.3	148	400	14	7.1	8.1	4.4
5	69.3	161	465	19	6.4	8.0	4.6
6	71.7	258	439	71	7.7	8.1	4.8
7	77.7	265	542	39	7.7	8.3	4.6
8	80.9	142	555	52	6.2	8.4	4.7
9	82.9	252	606	71	7.4	8.6	4.9
10	84.8	277	413	45	7.3	8.1	4.6
11	92.1	39	32	439	5.1	4.9	7.9
12	99.0	129	58	806	5.9	5.0	8.6
13	99.0	155	110	613	7.0	5.7	8.3

Table 3. Heat treatment condition, dissolution rate of the heat-treated AES fiber samples no. 1 and no. 2 and pH of the post-reacted glycine solution

heat treatment in °C for 24 h	dissolution rate in µg/ml, run at 40 °C, 50 h, 120 rpm	pH of the glycine solution reacted with fiber sample
sample no. 1 ($MgO-CaO-SrO-SiO_2$):		
110	290	7.4
400	277	7.3
600	387	7.9
700	555	8.4
800	155	7.2
900	110	6.3
1000	65	5.5
1100	45	5.1
1260	19	4.8
sample no. 2 ($CaO-MgO-SiO_2$):		
110	84	6.4
200	52	5.1
300	34	4.8
400	19	4.7
500	32	4.6
600	26	4.7
700	39	4.9
800	484	8.3
900	523	8.3
1000	510	8.1
1100	510	8.2

Figure 1 shows variations, as a function of heat treatment temperature, in the dissolution rate of the AES fiber samples no. 1 (MgO-rich AES fiber sample) and no. 2 (CaO-rich AES fiber sample).

The dissolution rate of the fiber sample no. 1 rises sharply with increasing heat treatment temperature and reaches its maximum at 700 °C. Thereafter, the dissolution rate falls off up to 800 °C.

Meanwhile, the dissolution rate of the fiber sample no. 2 does not change substantially up to 700 °C. Thereafter, the dissolution rate rises sharply up to 800 °C, and then is kept constant in the temperature range over 800 °C.

Thus, figure 1 indicates that variations, as a function of heat-treatment temperature, in the dissolution rate of the AES fibers are categorized into two types, one of which

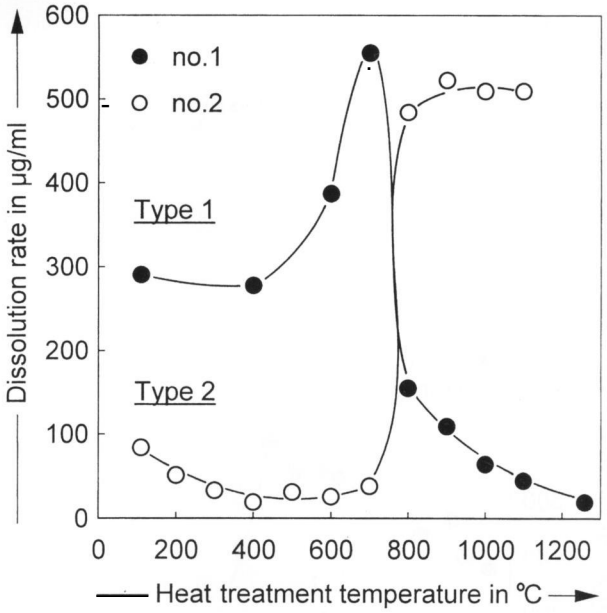

Figure 1. Variation, as a function of heat treatment temperature, in the dissolution rate of the Mg-rich AES fiber sample no. 1 (●) and the Ca-rich AES fiber sample no. 2 (○) in the glycine solution.

shows a peak around 700 °C (figure 1, type 1), and the other shows a sharp rise up to 800 °C, and then is kept constant in the temperature range above (figure 1, type 2).

3.3 Variation in the dissolution rate as a function of molar ratio-weighted mean ionic radius of alkaline earth ions

As shown in figure 1, it depends on the chemical composition of the AES fiber, especially the kind and the amount of alkaline earth ions including Mg into which type the variation in the dissolution rate of the AES fiber sample is categorized.

Thereupon, this study directs its attention to a chemical index "molar ratio-weighted mean ionic radius of alkaline earth ions" based on the composition of the AES fibers shown in the previous study [9]. The molar ratio-weighted mean ionic radius of the alkaline earth ions as glass network modifiers of the AES fiber (r_{avg}) is defined as:

Table 4. Phases of the heat-treated AES fiber samples no. 1 and no. 2 identified by X-ray diffraction analysis

sample no.	identified phase by XRD	heat treatment in °C (over 24 h)											
		110	200	300	400	500	600	700	800	900	1000	1100	1260
1	glassy phase augite cristobalite	●	●	●	●	●	●	●	●	●	●	●	●
2	glassy phase wollastonite pseudowollastonite diopside	●	●	●	●	●	●	●	●	●	●	●	

Table 5. Ionic radius of alkaline earth ions as glass network modifiers used in this study

ion	ionic radius in 10^{-12} m
Mg^{2+}	66
Ca^{2+}	99
Sr^{2+}	112

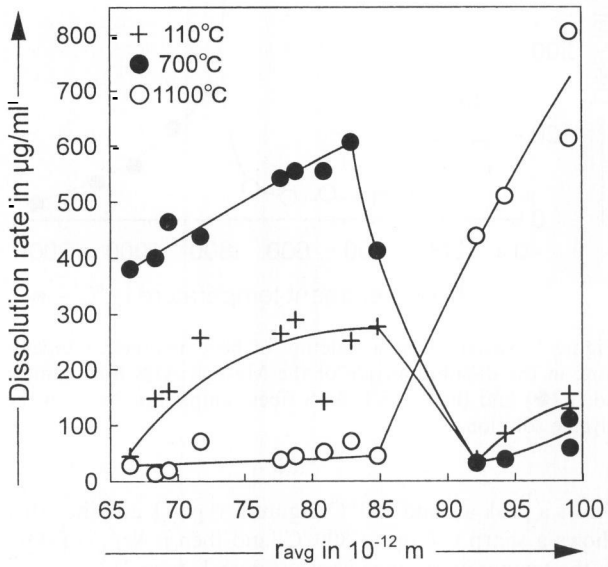

Figure 2. Variation, as a function of the molar ratio-weighted mean ionic radius of alkaline earth ions (r_{avg}), in the dissolution rate of AES fiber samples heat-treated at 110 °C (+), 700 °C (●) and 1100 °C (○) over 24 h.

$$r_{avg} = \Sigma(r_i \cdot R_iO). \quad (1)$$

Here, r_i is the ionic radius of the alkaline earth ions given in table 5 [13 and 14], R_iO is the molar ratio value normalized in order to make the sum of R_iO equal 1. This means that the parameter, the r_{avg}, is calculated by the molar ratio of alkaline earth ions only, not depending on the SiO_2 and the other impurities concentration of the AES fibers.

The dataset of the dissolution rate and the r_{avg} of the heat-treated AES fiber samples no.1 to no.13 and the pH of the post-reacted glycine solution is given in table 2.

Figure 2 shows variation, as a function of r_{avg}, in the dissolution rate of the heat-treated AES fibers at 110, 700 and 1100 °C over 24 h.

The dissolution rate of the AES fibers heat-treated at 700 °C increases gradually with increasing the r_{avg} value, and reaches its maximum around the r_{avg} of 83 pm. Thereafter, it falls off sharply down to the r_{avg} of 92 pm. The dissolution rate of the AES fibers heat-treated at 700 °C is much higher than that of the fibers heat-treated at 110 °C in the r_{avg} range of 66 to 85 pm, and is equivalent substantially to that of the fibers heat-treated at 110 °C in the r_{avg} range of 92 to 100 pm.

Meanwhile, the dissolution rate of the AES fibers heat-treated at 1100 °C over 24 h remains constant in the low

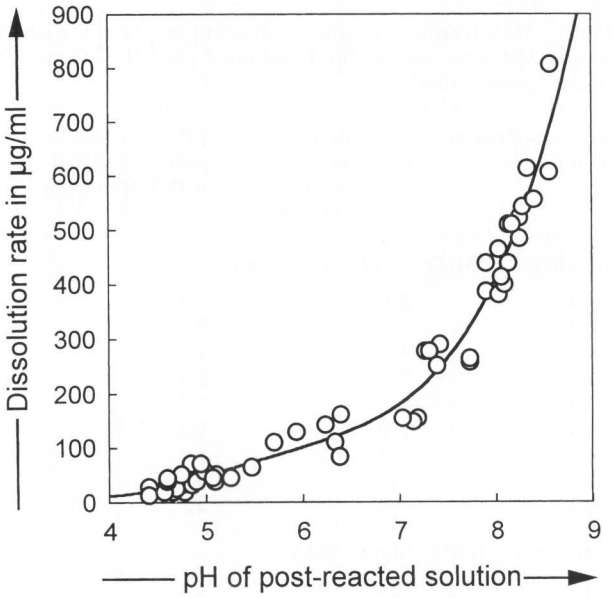

Figure 3. Variation, as a function of pH of the post-reacted glycine solution, in the dissolution rate of the AES fiber samples.

value range less than 100 µg/ml up to the r_{avg} of 85 pm. Thereafter, it rises sharply with increasing the r_{avg} in the r_{avg} range more than 92 pm. The dissolution rate of the AES fibers heat-treated at 1100 °C is less than that of the fibers heat-treated at 110 °C in the r_{avg} range from 66 to 85 pm, and is much higher than that of the fibers heat-treated at 110 °C in the r_{avg} range from 92 to 100 pm.

Figures 1 and 2 indicate the following:

a) The AES fibers which have the variation in the dissolution rate, as a function of heat treatment temperature, showing a peak around 700 °C are in the r_{avg} range from 66 to 85 pm.

b) The AES fibers which have the variation in the dissolution rate as a function of heat treatment temperature, showing a sharp rise up to 800 °C and then kept constant in the temperature range above, are in the r_{avg} range from 92 to 100 pm.

3.4 Variation in the dissolution rate as a function of pH of the post-reacted solution

Tables 2 and 3 show that pH of the solution is not kept constant throughout the dissolution of each fiber sample.

Figure 3 shows the variation, as a function of pH of the post-reacted glycine solution, in the dissolution rate of the AES fiber samples in the solution. The increase in the dissolution rate of the fiber samples is associated with increase in pH of the post-reacted solution. Especially, a sharp rise in the dissolution rate of the fiber samples is accompanied by an increase in the pH in the range above 7.

4. Discussion

Variations, as a function of heat treatment temperature, in the dissolution rate of the AES fibers in the glycine solution

have been categorized into two types, one of which has a peak around 700 °C (figure 1, type 1), and the other shows a sharp rise up to 800 °C, and is kept constant in the temperature range over 800 °C (figure 1, type 2).

The AES fibers which have the variation in the dissolution rate showing a peak around 700 °C (figure 1, type 1) have been in the r_{avg} range from 66 to 85 pm (figure 2). Meanwhile, the AES fibers which have the variation in the dissolution rate showing a sharp rise up to 800 °C and then being kept constant in the temperature range over 800 °C (figure 1, type 2), have been in the r_{avg} range of 92 to 100 pm (figure 2). Therefore, the variation type of the dissolution rate switches from type 1 to type 2 in the r_{avg} range of 85 to 92 pm. It might have been expected that the difference between the variation types merely depends on the SiO_2 concentration of the AES fibers. The fiber sample no. 1, the variation in the dissolution rate of which is the type 1, has a higher SiO_2 concentration than the fiber sample no. 2, the dissolution rate variation of which is type 2 (tables 1 and 2 and figure 1). However, the fiber sample no. 9, the variation in the dissolution rate of which is the type 1, has an SiO_2 concentration substantially equivalent to the fiber sample no. 2 of type 2 dissolution rate variation (tables 1 and 2 and figure 2). It is not likely that the variation type of the dissolution rate depends on the SiO_2 concentration of the fiber sample, at least not within the SiO_2 concentration range shown in table 1.

The r_{avg} range from 85 to 92 pm corresponds to the boundary range between diopside and wollastonite into which the AES fibers crystallize when the fibers are heated to a temperature of 800 °C or over. The r_{avg} value of the ideal composition-crystallizing diopside, $CaMgSi_2O_6$, is 83 pm, calculated by using the ionic radius shown in table 5. The r_{avg} value of the ideal composition-crystallizing wollastonite, $CaSiO_3$, is 99 pm. The central r_{avg} value between the r_{avg} of diopside and of wollastonite is calculated to be 91 pm. The central r_{avg} value (91 pm) is in the r_{avg} range for switching from the variation type 1 to type 2 (the r_{avg} range from 85 to 92 pm).

Therefore, the variation in the dissolution rate of the AES fibers in the glycine solution seems to depend on whether the amorphous AES fibers are crystallized dominantly into diopside (augite, enstatite) or wollastonite (pseudowollastonite) by heating at a temperature of 800 °C or over.

The sharp peak around 700 °C of the variation, as a function of heat-treatment temperature, of the dissolution rate of the Mg-rich AES fiber samples, the r_{avg} values of which are in the range from 66 to 85 pm (shown in figures 1 and 2), may be related to phase separation.

The heat-treated AES fiber samples have remained amorphous up to 700 °C and have been crystallized partly into crystalline alkaline earth silicates at 800 °C (table 4). Therefore, the estimation that the heat treatment around 700 °C causes phase separation is congruous with the facts that phase separation occurs before crystallization by heat treatment [15], the phase-separated microstructure is preferable for the pre-state of crystal nucleation [16] and the phase-separated phases are amorphous [17]. The possibility of the phase separation of Mg-rich AES fibers by heat treatment around 700 °C has been pointed out in the previous studies [18 and 19].

Phase separation of silicate glasses is the phenomenon that the original homogeneous glassy phase is separated into a chemically less durable phase and a silica-rich phase caused by heat treatment [20 and 21]. The formation of the chemically less durable phases, which correspond to alkaline earth-rich phases, may facilitate the dissolution of the phase separated Mg-rich AES fiber samples, the r_{avg} values of which are in the range from 66 to 85 pm (figures 1 and 2).

However, the heat treatment around 700 °C has not increased the dissolution rate of the Ca-rich AES fiber samples, the r_{avg} value of which are in the range of 92 to 100 pm (figures 1 and 2). This might be related to the difference between the phase-separated microstructure of the Ca-rich fibers and that of Mg-rich fibers. It has been shown that, when the phase-separated glass has a chemically less durable phase interconnecting with the silica-rich phase, the dissolution of the phase-separated glass can be facilitated because the chemically less durable phase is directly exposed to solutions. On the other hand, when the phase-separated glass has a dispersed chemically less durable phase embedded in the silica-rich phase, the dissolution is independent of the extent of phase separation because the silica-rich phase protects the chemically less durable phase from exposure to solutions [21].

Meanwhile, the heat treatment at 800 °C or over has given a sharp rise to the dissolution rate of the Ca-rich AES fiber samples, the r_{avg} values of which are in the range of 92 to 100 pm, although the same heat treatment has decreased the dissolution rate of the Mg-rich AES fiber samples, the r_{avg} values of which are in the range of 66 to 85 pm (figures 1 and 2). This might be related to the kind of the dominant crystalline alkaline earth silicate formed by the heat treatment. The dominant phase in the Ca-rich AES fibers heat-treated in the temperature range of 800 °C or over is wollastonite or pseudowollastonite and that in the Mg-rich AES fibers is enstatite, augite or diopside. It has been shown that increase in the ratio of diopside to wollastonite is advantageous to chemical durability in $CaO-MgO-SiO_2$ glass-ceramics [22]. Therefore, crystallized AES fibers including wollastonite or pseudowollastonite as the dominant phase are more soluble than those including enstatite, augite or diopside as the dominant phase.

It has been shown that wollastonite slurry can have a naturally high pH of 9.9 [23]. This is congruous with the result that the glycine solutions reacted with the Ca-rich AES fiber samples heat-treated in the temperature range above 800 °C, in which wollastonite or pseudowollastonite has been formed as the dominant phase, have had the increased pH (tables 2 and 3).

Also the glycine solutions reacted with the Mg-rich AES fiber samples heat-treated around 700 °C have had the increased pH (tables 2 and 3).

The increase in the dissolution rate of the AES fiber samples is accompanied by the increase in pH of the solution. Notice that the dissolution rate of the AES fiber samples in the glycine solution has risen sharply in the pH range more than 7 (figure 3). The author's previous study has also pointed out that the dissolution rate of Mg-rich AES fibers in the glycine solution rises sharply in the pH range over 7 whereas the dissolution rate in the mild phthalate solution, which does not include glycine ions, has not sharply risen [18]. Therefore, the increase of pH may acti-

vate glycine ions to facilitate the dissolution of the heat-treated AES fiber samples.

5. Conclusions

This study shows that variations in the dissolution rate of amorphous alkaline earth silicate (AES) fibers in a glycine, a simple amino acid, solution as a function of heat treatment temperature can be categorized into two types, one of which shows a peak around 700 °C, and the other shows a sharp rise up to 800 °C and then is kept constant in the temperature range above. The AES fibers which have the variation, as a function of heat treatment temperature, in the dissolution rate showing a peak around 700 °C are in the Mg-rich systems which have an r_{avg} in the range of 66 to 85 pm and can be crystallized dominantly into enstatite, augite or diopside by heating at a temperature of 800 °C or over. Meanwhile, the AES fibers which have the variation, as a function of heat treatment temperature, in the dissolution rate showing a sharp rise up to 800 °C and then kept constant, are in the Ca-rich systems which have an r_{avg} in the range of 92 to 100 pm and can be crystallized dominantly into wollastonite or pseudowollastonite by heating at a temperature of 800 °C or over. Notice that crystallized Ca-rich AES fibers can be more soluble than amorphous ones in the glycine solution.

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Contact:

Masato Ohsawa
Research & Development Center, HITEC Corporation
2-1-2-13-301 Karabe, Narita
Chiba 286-0036
Japan
E-mail: moosawa@s4.dion.ne.jp