

Detoxification of industrial asbestos waste by low-temperature heating in a vacuum

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Industrial asbestos waste such as asbestos cement board, sprayed crocidolite and sprayed amosite was heated in a vacuum. The detoxification conditions were then established in reference to JIS A 1481:2006 and JIS K 3850-1:2006. When asbestos cement board was heated at 700°C for 1 h, detoxification of the cement board was completed. On the other hand, in the case of amphibolic asbestos waste, such as sprayed crocidolite and sprayed amosite, was heated, a phase-contrast microscope analysis was not applicable for identification of asbestos heated at more than 500°C. According to XRD analysis, crocidolite was eliminated by heating at 800°C for 3 h. Furthermore, amosite was not detected after heating at 700°C for 3 h. Finally, the grindability of heated amphibolic asbestos was investigated. When sprayed crocidolite was heated at 900°C for 3 h and then ground with a mortar for 300 s, the crushed grains had a length of less than 5 μm and an aspect ratio of 3. In addition, when sprayed amosite was heated at 1000°C for 3 h and then ground, the crushed grains had a length of less than 5 μm and an aspect ratio of 3.

Key-words : Detoxification, Asbestos, Chrysotile, Crocidolite, Amosite

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1. Introduction

Most industrial asbestos wastes, such as asbestos cement or sprayed asbestos (approximately 1,000,000 t/year), will be embedded in the ground after use. A portion of these wastes will be melted at over 1500°C using a specified furnace (this temperature treatment is recommended by the Ministry of Environment) to change a safety glass phase due to disappearance of asbestos particles. The resulting slag is mechanically hard and is of limited use for anything other than as a reinforcing material in cement or asphalt. However, the amount of the slag used effectively is very limited. In addition, a great deal of energy is needed when industrial asbestos waste is melted at over 1500°C. Therefore, recently, we have investigated the detoxification of industrial asbestos waste using low-temperature heating at approximately 1000°C and then grinding to form fine grains having an aspect ratio of less than 3.¹⁾⁻⁶⁾ Thus far, this detoxification treatment has only been performed in air. In a previous report, the thermal decomposition of amphibolic asbestos, such as crocidolite or amosite, in a vacuum was clarified with respect to the loss of hydroxyl and the reduction of FeO.⁷⁾ However, neither the changes of whole asbestos crystal structures nor their micro morphology have been investigated.

In the present study, as actual industrial asbestos wastes, asbestos cement board, sprayed crocidolite, and sprayed amosite were examined. The changes of crystal phases and micro morphology when these industrial asbestos wastes were heated in a vacuum were investigated. In addition, the grindability of heated asbestos wastes were evaluated and compared to the previous results obtained for the case of heating asbestos waste in air.¹⁾⁻⁶⁾

2. Experimental procedure

Asbestos cement board (JIS A 5423) with 10–20 mass% chrysotile and having a thickness of 5 mm was examined. The board was cut into a rectangular piece 10 × 10 × 5 mm³ for heating examination. Sprayed crocidolite and sprayed amosite, which were removed from the ceiling of a public building, were used. These sprayed amphibolic asbestos wastes were the same as the sprayed asbestos used in the previous reports with respect to detoxification of asbestos by heating in air. In addition, heating of pure chrysotile³⁾ was performed in order to clarify the thermal behavior of heating in a vacuum.

Several rectangular pieces of asbestos cement board, pure chrysotile, or approximately 0.2 g of sprayed asbestos was placed into a carbon paper box having a thickness of 0.2 mm and dimensions of 30 × 30 × 20 mm³. The carbon paper box was then placed into a carbon crucible (diameter: 60 mm, height: 80 mm). The carbon crucible containing the asbestos waste sample was placed into an electric furnace that can be sealed completely. During heating, the inside of the furnace was evacuated using an exhaust pump. The vacuum was maintained at 20 mmHg during heating. The heating and cooling rates of the electric furnace were both 10°C/min. The furnace containing the asbestos waste was heated until reaching a predetermined temperature, which was maintained for 3 h. In order to examine the change of crystal phases, after heating, the heated asbestos waste in the carbon box was analyzed by X-ray diffraction analysis (XRD: XD-D1; Shimazu Co., Ltd). The microstructures of the heated asbestos wastes after heating at various temperatures were observed using a scanning electron microscope (SEM: JEOL 5200, JEOL Co., Ltd.).

Furthermore, the grindability of the heated asbestos waste was evaluated using a Si₃N₄ mortar manually. The load

between the mortar and the pestle was maintained at approximately 2 kg, and the revolution rate of the pestle was 1–2 revolutions per second. The crushing time was 300 s. This grinding condition was the same as that used in previous detoxification reports on heating in air.^{1)–6)} Finally, industrial asbestos wastes heated at various temperatures in a vacuum were examined using a phase-contrast microscope in reference to the JIS A 1481:2006.

3. Results and discussion

3.1 Asbestos cement board with chrysotile

Generally, the chemical formula of chrysotile is given as $Mg_3Si_2O_5(OH)_4$. **Figure 1** shows XRD patterns of pure chrysotile before and after heating at 500–600°C for 3 h in a vacuum. At 550°C, diffraction peaks corresponding to chrysotile were detected. However, the diffraction peaks of chrysotile had completely disappeared after heating at 600°C for 3 h. This was thought to indicate the completion of the dehydration reaction. When the chrysotile was heated at 600°C for 3 h in air, very slight diffraction peaks corresponding to chrysotile were detected.³⁾ Therefore, heating in a vacuum is thought to accelerate the thermal decomposition of chrysotile. In an attempt to detect a small amount of chrysotile, chrysotile heated in a vacuum was evaluated by phase-contrast microscope analysis. As a result, chrysotile particles of over 0.1 mass% were detected in a sample after

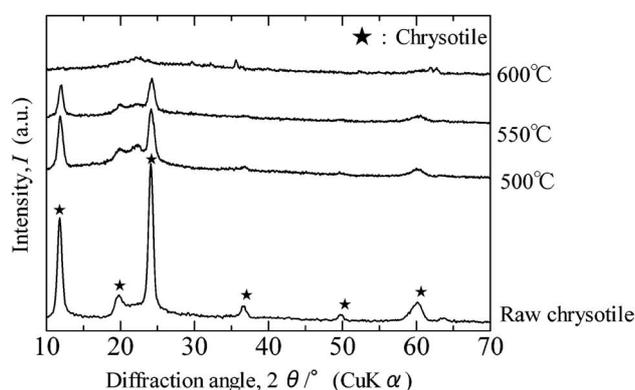


Fig. 1. XRD patterns of pure chrysotile before and after heating at 500–600°C for 3 h in a vacuum.

heating at 900°C for 3 h in a vacuum. Since most of the chrysotile was in the form of asbestos cement board, the asbestos board heated in a vacuum was analyzed using a phase-contrast microscope in reference to JIS A 1481. **Table 1** shows the counts of chrysotile particles in asbestos cement board heated at 700°C for 1, 2, and 3 h in a vacuum. In reference to JIS A 1481:2006, if more than four chrysotile particles are detected, the sample is classified as an asbestos-containing material. When the asbestos cement board was heated at 700°C for 1 h, three chrysotile particles were detected among 3000 particles in the sample. In addition, after heating at 700°C for more than 1 h, less than three per 3000 chrysotile particles were detected. Based on these results, detoxification of the asbestos cement board was completed after heating at 700°C for more than 1 h. When the same asbestos cement board was heated in air, detoxification of the asbestos cement board was completed only after heating at 800°C for more than 2 h.⁵⁾ These results indicate that the detoxification temperature in the case of heating in a vacuum was 100°C lower than in the case of heating in air.

3.2 Sprayed crocidolite

Figure 2 shows XRD patterns of sprayed crocidolite

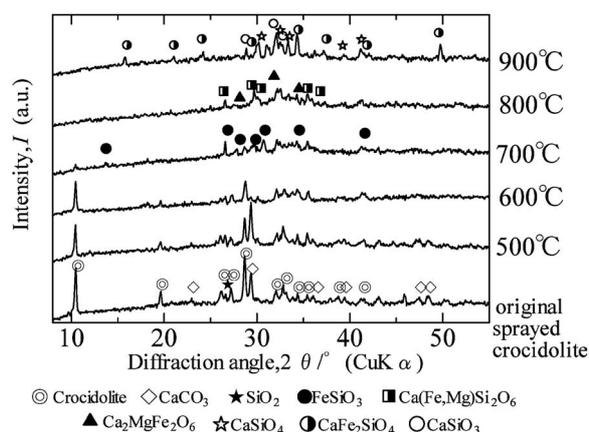


Fig. 2. XRD patterns of sprayed crocidolite before and after heating at 500–900°C for 3 h in a vacuum.

Table 1. Counts of Chrysotile Particles in Asbestos-cement Waste with Heating at 700°C for 1, 2, and 3 h in a Vacuum. (This Counting was Performed by Phase-contrast Microscope in Reference to JIS A 1481:2006.)

Temperature (°C)	Slide 1		Slide 2		Slide 3		Total	
	Chrysotile	Total	Chrysotile	Total	Chrysotile	Total	Chrysotile	Total
—		Number of		Number of		Number of		Number of
Heating time (h)		Particles		Particles		Particles		Particles
700–1	1	1,000	2	1,000	0	1,000	3	3,000
700–2	1	1,000	0	1,000	0	1,000	1	3,000
700–3	0	1,000	0	1,000	0	1,000	0	3,000

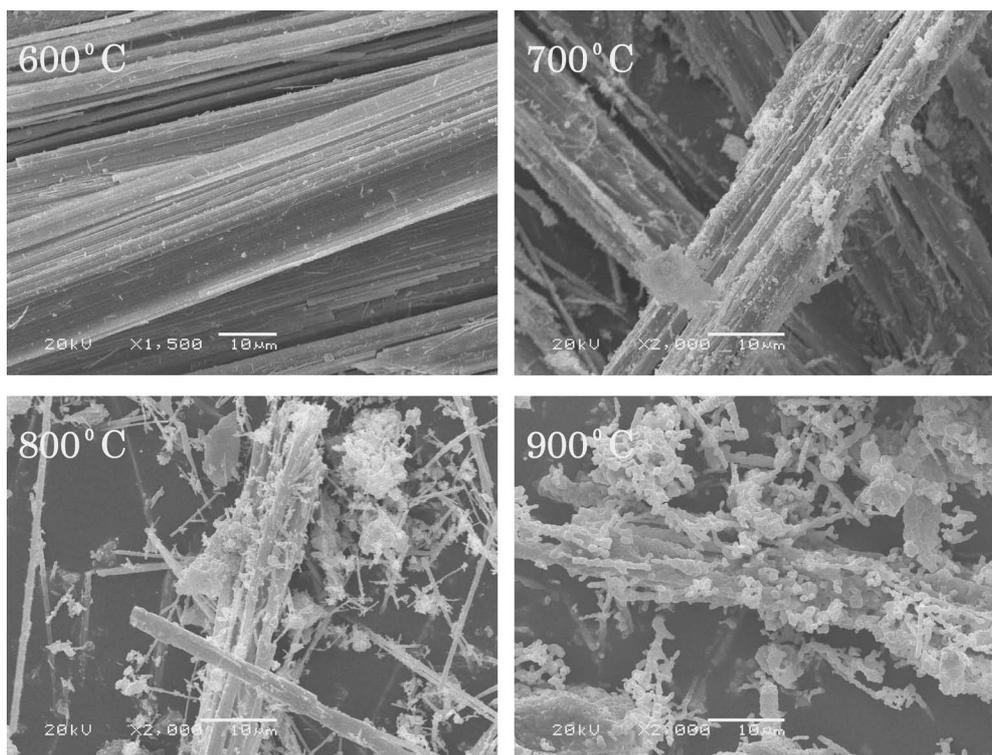


Fig. 3. SEM photographs of sprayed crocidolite after heating at 600–900°C for 3 h in a vacuum.

before and after heating at 500–900°C for 3 h in a vacuum. Diffraction peaks corresponding to crocidolite were detected up until the temperature reached 600°C. At 700°C, crocidolite was still detected, although the corresponding diffraction peaks were very weak. However, the peaks of crocidolite had completely disappeared after heating at 800°C for 3 h. This detoxification temperature is 100°C lower than that of sprayed crocidolite heated in air.⁴⁾ In other words, heating in a vacuum accelerated the thermal decomposition of crocidolite due to either the loss of hydroxyl or the reduction of FeO.⁷⁾

Furthermore, in the present study, the microstructure of sprayed crocidolite heated in a vacuum at various temperatures was investigated. **Figure 3** shows SEM photographs of sprayed crocidolite after heating at 600–900°C for 3 h in a vacuum. At 600°C, the micromorphology of the crocidolite particles was the same as that of the original crocidolite particles. After heating at 700°C, some small cracks running parallel to the elongated direction of the crocidolite particle were observed, and small grains of several microns in diameter were observed on the surface of the crocidolite particles. At 800°C, crocidolite particles of large diameter separated into small needlelike particles that extended in the elongation direction of the original needlelike particle. This morphology is thought to be caused by the evaporation of gaseous species based on the hydroxyl or reduction of FeO from inside the crocidolite particle during heating in a vacuum.⁷⁾ Furthermore, vaporization of gaseous species related to alkaline compositions was also thought to have occurred, because the chemical formula of crocidolite is described as $\text{Na}_2(\text{Fe}^{2+} > \text{Mg})_3(\text{Fe}^{3+})_2\text{Si}_8\text{O}_{22}(\text{OH})_2$, but the gaseous species related to alkaline compositions were not identified. After sprayed crocidolite was heated at 900°C, a portion of

the separated small particles was melted. This is understood by the fact that a number of small round grains, indicating the formation of a liquid phase during heating, were observed among the particles. In a previous report, no liquid phase appeared to form in sprayed crocidolite heated at 900°C in air, because no such grains were observed.⁴⁾ Thus, heating in a vacuum is thought to accelerate the thermal decomposition of crocidolite particles.

Subsequently, the grindability of sprayed crocidolite heated in a vacuum at various temperatures was investigated. **Figure 4** shows SEM photographs of sprayed crocidolite after heating at 700–900°C for 3 h in a vacuum and then grinding using a mortar for 300 s. According to the latest Japanese regulation (JIS K 3850-1:2006, Determination of airborne fibrous particles-Part 1: Optical microscopy method and scanning electron microscopy method), the asbestos grain size is defined as being over 5 µm in length and less than 3 in aspect ratio in reference to. At 700°C, needlelike grains of over 10 µm in length and 10 in aspect ratio were observed in the ground sample. With increasing heating temperature, the grain size after grinding tended to decrease, but a number of grains having an approximate length of 5 µm and an aspect ratio of 3 were observed after heating at 800°C. When sprayed crocidolite was heated at 900°C and then ground, the grindability appears to have been improved. In other words, the grain morphology of all of grains was such that the length was less than 5 µm and the aspect ratio was 3. The detoxification of sprayed crocidolite is thus thought to have been completed after heating at 900°C for 3 h in a vacuum followed by grinding.

Unfortunately, the sprayed crocidolite heated in a vacuum could not be evaluated using a phase-contrast microscope after heating at 500°C, which was also the case for sprayed

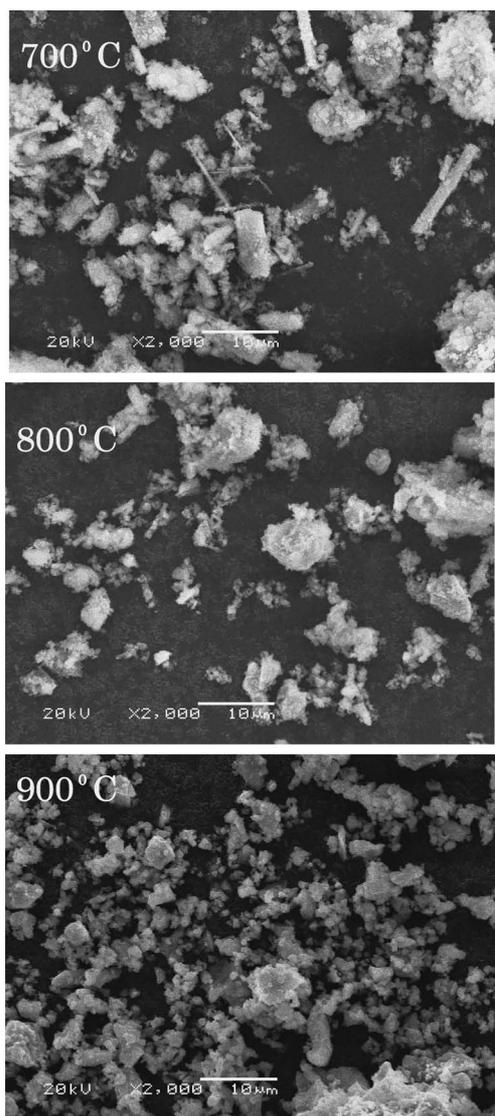


Fig. 4. SEM photographs of sprayed crocidolite after heating at 700–900°C for 3 h in a vacuum and then grinding using a mortar for 300 s.

crocidolite heated in air over 500°C.⁴⁾ It is thought that heating in a vacuum also influenced the reflective index of the crocidolite particles, due to the vaporization of some species, such as hydroxyl, or the reduction of FeO⁷⁾ or alkaline composites.

3.3 Sprayed amosite

Figure 5 shows XRD patterns of sprayed amosite before and after heating at 600–1,000°C for 3 h in a vacuum. The diffraction peaks corresponding to amosite were detected until 600°C. However, at 700°C, the diffraction peaks corresponding to amosite disappeared. When sprayed amosite was heated at 900°C for 3 h in air, the diffraction peaks corresponding to amosite had completely disappeared,⁶⁾ so that the detoxification temperature of sprayed amosite heated in a vacuum was 200°C lower than that of sprayed amosite heated in air.

Next, as in the case of sprayed crocidolite, the microstruc-

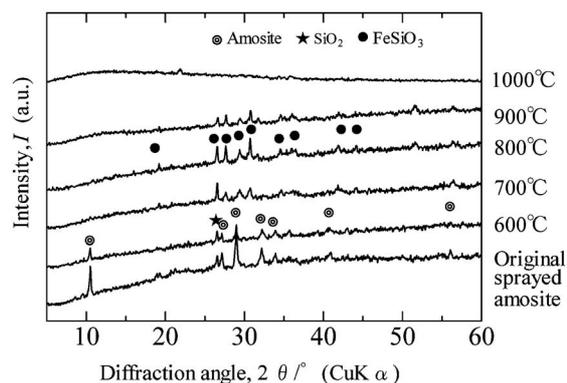


Fig. 5. XRD patterns of sprayed amosite before and after heating at 600–1000°C for 3 h in a vacuum.

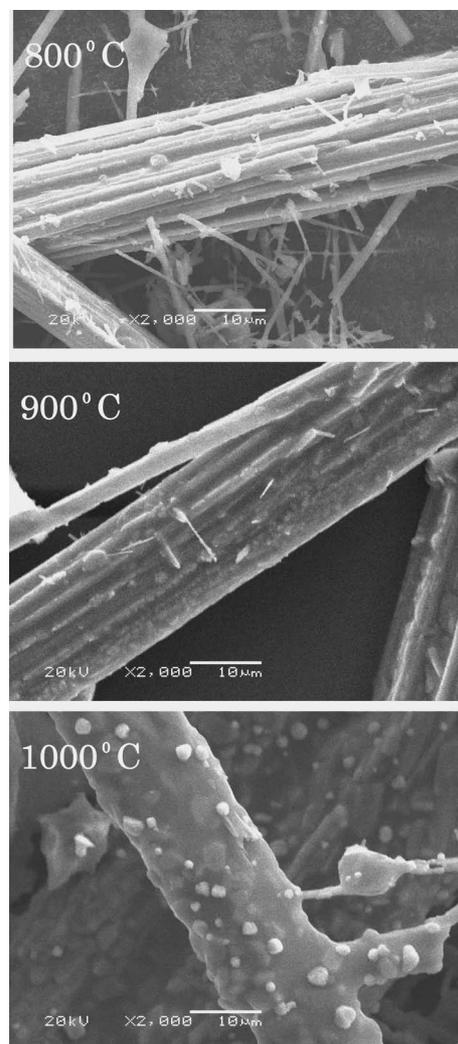


Fig. 6. SEM photographs of sprayed amosite after heating at 800–1000°C for 3 h in a vacuum.

ture of sprayed amosite heated in a vacuum was observed. Figure 6 shows SEM photographs of sprayed amosite after heating at 800–1,000°C for 3 h in a vacuum. At 800°C,

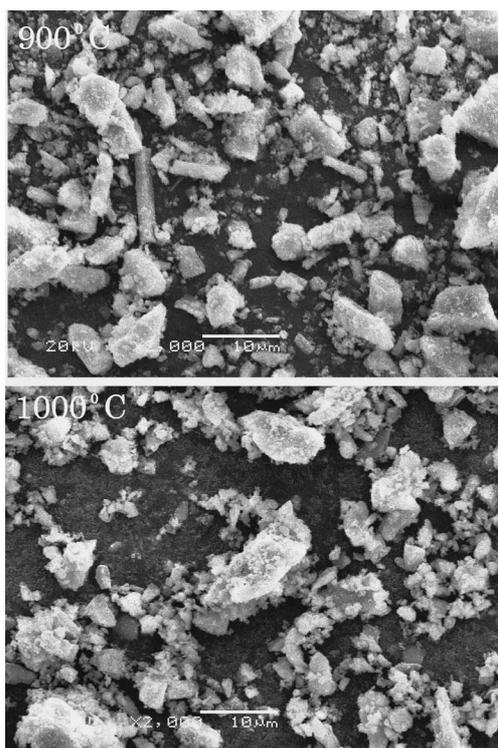


Fig. 7. SEM photographs of sprayed amosite after heating at 900 and 1000°C for 3 h in a vacuum and then grinding using a mortar for 300 s.

the surface and appearance of the amosite particles were unchanged from those of the original sprayed amosite, although the crystal structure had completely changed, as shown in Fig. 5. After heating at 900°C, stripe patterns on the surface of the amosite particles began to disappear. Finally, at 1,000°C, the stripe patterns disappeared completely. In addition, the surface of the amosite particles was not smooth and a number of round grains, indicating the formation of a liquid phase during heating, were observed on the surface of the amosite particles. However, as shown in Fig. 3, the microstructure of amosite did not change drastically, as compared to the change of micromorphology of the crocidolite particles upon heating. The content of alkaline compositions of amosite appeared to be low, as evidenced by the chemical formula, given as $(\text{Mg} < \text{Fe}^{2+})_7 \text{Si}_8\text{O}_{22}(\text{OH})_2$, so that the vaporization of related gaseous species that were thought to break down asbestos particles might not occur at high temperatures, such as 1000°C.

In addition, the grindability of the heated sprayed amosite was investigated. **Figure 7** shows SEM photographs of sprayed amosite after heating at 900°C and 1000°C for 3 h in a vacuum and then grinding using a mortar for 300 s. When sprayed amosite was heated at 1100°C in air, the grain size of amosite particles fell below 5 μm in length and had an aspect ratio of 3, which is a safe detoxification condition according to Japanese regulations. In contrast, when sprayed amosite was heated in a vacuum, the grindability was improved.

When sprayed amosite was heated at 900°C for 3 h and then ground, a number of grains over 5 μm in length and having an aspect ratio greater than 3 were observed. On the other hand, after heating at 1000°C, grains having an aspect ratio greater than 3 were not observed. Thus, detoxification of sprayed amosite was completed after heating at 1000°C for 3 h and then grinding. The detoxification temperature in the case of heating in a vacuum was 100°C lower than that of sprayed amosite heated in air.

Finally, sprayed amosite heated in a vacuum was analyzed using a phase-contrast microscope. Amosite particles were not detected after heating at 500°C. Although sprayed amosite still appeared after heating, in a vacuum, precipitation and vaporization of some species, such as hydroxyl, or reduction of FeO, also occurred⁷⁾ and the reflective index of amosite particles appeared to change.

4. Summary

Pure chrysotile, asbestos cement board with chrysotile, sprayed crocidolite, and sprayed amosite were heated in a vacuum for the purpose of detoxification in accordance with JIS A 1481:2006 and JIS K 3850-1:2006. Compared to the case of heating industrial asbestos waste in air, the detoxification temperature in a vacuum tended to decrease. When asbestos cement board was heated at 700°C for 1 h, chrysotile particles were not detected using a phase-contrast microscope. However, the phase-contrast microscope analysis was not applicable to the identification of amphibolic asbestos above 500°C. It is thought that the reflective index of amphibolic asbestos was changed after heating in a vacuum. According to the XRD analysis, crocidolite was eliminated by heating at 800°C for 3 h. Furthermore, amosite was not detected at 700°C for 3 h. Finally, when sprayed crocidolite was heated at 900°C for 3 h and then ground with a mortar for 300 s, the crushed grains were observed to have a length of less than 5 μm and an aspect ratio of 3. In addition, when sprayed amosite was heated at 1000°C for 3 h and then ground, the crushed grains had a length of less than 5 μm and an aspect ratio of 3.

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