

Preparation of fine expanded perlite

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Hollow glass microspheres named expanded perlite have been prepared from perlite, but the size is usually above 20 μm . Recently fine microspheres with low density are desired. In the conventional preparation method, it is difficult to produce fine expanded perlite with particle size under 20 μm because the water contained in finely milled perlite particle, which is the origin of foaming, is evolved during heating process. Fluidized sand-bed furnace is a useful tool to heat the fine particle rapidly. Using the rapid heat furnace fine expanded perlite with particle size under 15 μm and bulk density under 0.5 g/cm^3 is prepared successfully. Foaming conditions are discussed by water contents and foaming temperatures. Existence states of water are interpreted by temperature-programmed desorption method and FT-IR spectrum. © 1999 Kluwer Academic Publishers

1. Introduction

“Perlite” is a general term for a glassy, volcanic, rhyolitic rock, which is classified into three kinds depending on their water contents, i.e. obsidian (less than 2 mass%), perlite (2–5 mass%) and pitchstone (above 5 mass%) [1]. Perlite is known to expand up to 20 times its original volume upon heating. This is known as “expanded” perlite. The leading producer countries are Greece, Japan, Turkey and the United States. In all, twenty countries produced an estimated 1.4 million metric tons of perlite in 1992 [2].

Because of its low density, expanded perlite is used in many fields, such as ceiling tile, pipe insulation, gypsum wallboard, cryogenic insulation and filter media, etc. However, expanded hollow glass microspheres are vulnerable to shearing forces and breaks easily when mixed with resin and cement [2]. One of the methods of solving this problem is reducing their size to increase their strength [3].

In Japan, hollow glass microspheres known as Shirasuballoons have been produced from vitric volcanoclastic materials called Shirasu or Hakudo since they were first prepared by the National Industrial Research Institute of Kyushu, Japan [4]. Six companies in Japan produced 12 thousand tons of Shirasuballoons in 1992 [5]. To improve the chemical and physical properties of the conventional Shirasuballoons, we have successfully produced fine Shirasuballoons of particle sizes under 20 μm and bulk densities under 0.5 g/cm^3 using a fluidized bed furnace [5–7]. However, resources of Shirasu or Hakudo that can be used as fine Shirasuballoons are limited. Due to the greater availability of “perlite”, which is estimated to be around 800 million

tons [2], we have attempted to produce a fine particle size expanded perlite.

The origin of the foaming is water contained in the particle [1, 6]. Therefore to expand “perlite”, appropriate amount of water must remain in it at the glass softening temperature. In attempts to produce fine expanded perlite from finely milled “perlite” under a conventional method, the water is evaporated in the process of heating; therefore finely milled “perlite” can not be foamed. One of the solutions is using the rapid heating in a sand-medium fluidized bed furnace; this eliminates the water desorption until the powders reach the temperature of glass softening point. In this study, we were able to produce fine expanded perlite from pitchstone. Preparation conditions and some properties of the fine expanded perlite are presented.

2. Experimental

2.1. Preparation of raw powders

Two kinds of “perlite” are used; one is from Tensin of People’s Republic of China, and the other is from Padang of Sumatra island in Republic of Indonesia. Both materials were obtained through Showa Mining Co., Ltd. Fig. 1 shows the preparation process of raw powders that is heat treated to produce fine expanded perlite. To pulverize the raw materials into powders under the size of 15 μm , a Jet Mill (IDS-2 type: Nippon Newmatic MFG. Co., Ltd.) or a Vibration Mill (BMC-15 type: Chuo Kakohki Co., Ltd.) was used.

2.2. Heat treatment

Foaming experiments of the milled raw powders were conducted using a fluidized sand-bed furnace, whose

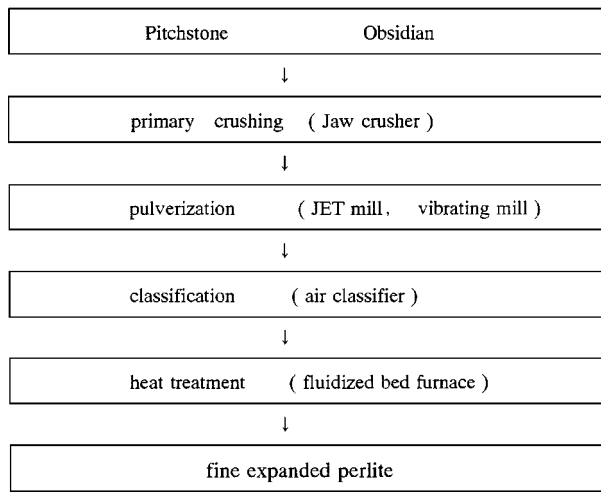


Figure 1 Schematic of preparation process of fine expanded perlite.

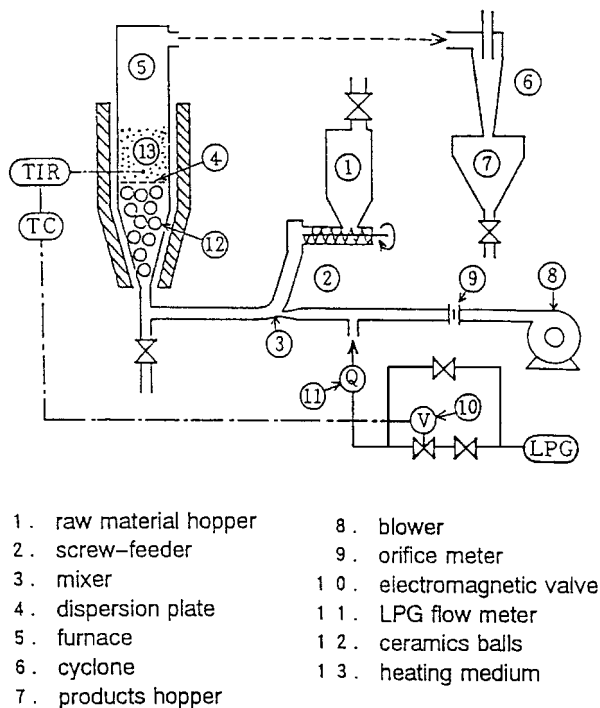


Figure 2 Schematic of a fluidized bed furnace system.

apparatus is shown in Fig. 2. As for fluid bed division, the propane gas, supplied from the lower side, is ignited and burned out on the perforated dispersion plate by the highly preheated quartz sand of approximately a diameter of 1 mm and the fluidization of the high-temperature heating medium is continuously maintained by the gas flames. The temperature of this fluid bed is controlled by the mixing ratio of propane gas to air and the feed quantity of the gases. The mixing ratio of the propane gas to air is controlled with an electromagnetic valve by monitoring the temperature of the fluidized reactor core using a thermocouple that is placed at the center of the furnace. The heating temperature ranges of 800–1200 °C is maintained within 5 °C by the automatic control system. The raw powders are supplied with the mixed gases of propane gas and air, and the powders are heated to a high temperature rapidly within 1 second. The heated powders are released with the combustion gas from the fluid bed, and they are carried to cyclone and gathered continually. In the con-

ventional preparation of expanded perlite, heating time to achieve a maximum temperature of 900–1100 °C exceeds 1 minute [4]. In this experiment, however, heating time to the maximum temperature is less than 0.06 s, which is estimated by passage time of raw gas and temperature distribution in the furnace [7]. Approximately 1 kg powder can be treated in 1 h using this furnace, which has an inside diameter of 15.24 cm.

2.3. Characterization of powders

X-ray diffraction, chemical analysis, whiteness, glass content, temperature-programmed desorption, infrared spectroscopy analysis, particle size distribution and bulk density experiments were conducted to characterize the powders.

Whiteness by Hunter (W) is calculated using following equation [8].

$$W = 100 - \{(100 - L)^2 + a^2 + b^2\}^{1/2},$$

where L is the psychometric lightness and a and b are psychometric chroma coordinates. These parameters were measured with a color-difference meter (SM-4-2 type: Suga Shikenki).

Temperature-programmed desorption measurements [9] were conducted after outgassing the powders under high vacuum (ca. 10^{-6} Pa). The evolved gases from the powders were monitored with a quadrupole mass spectrometer. Thermogravimetry measurements were also performed to examine the weight decrease in air.

The infrared spectrometry spectra were measured under a KBr dilution method using an MCT detector at 300 integrating cycles and a diffusion reflector with a single beam and by using a Fourier transformed infrared spectrophotometer (Model No. FTIR-4200, Shimadzu).

Particle size measurements were conducted using a laser diffraction particle analyzer (Helos-Rodos: Sympatec) after distributing the powders in water with an ultrasonic vibration. Bulk density was determined by tapping the powders in a cup of 100 cm³ using Powder tester (PT-E type: Hosokawa Mikuron) under the condition of tapping rate 60 times per minute and tapping frequency 200 times.

Yield of floating particles were determined as follows. The powders were distributed in water using ultrasonic vibration and separated by centrifuging the suspension at 1000 rpm for 30 min. After drying the ratio of floating powders on water were determined.

3. Results and discussion

3.1. Raw materials

Table I shows chemical composition of the milled powders. The ignition loss was determined from the weight loss after heating the powders at 1000 °C for 2 h in air. The weight loss is mainly due to water desorption from the powders as will be described later. Therefore the type of “perlite” from China (5.0 mass% water content) is classified as “pitchstone” and that from Indonesia (1.6 mass% water content) as “obsidian”. Fig. 3 shows X-ray diffraction patterns of both powders,

TABLE I Composition of the milled powders

Sample	Composition/mass%									
	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	CaO	Fe ₂ O ₃	MgO	TiO ₂	Ig.loss	Total
Pitchstone	72.23	12.30	4.72	3.75	0.62	0.93	0.10	0.12	5.05	99.82
Obsidian	73.55	12.46	4.63	3.35	0.83	0.83	0.15	0.08	1.60	97.48

TABLE II Characteristics of raw materials

Sample	Particle density		Bulk density Milled powder/ 10 ³ Kg m ⁻³	Glassy part content Milled powder/mass%	Whiteness Milled powder	Mean particle size Milled powder/ μ m
	Raw Rock/ 10 ³ Kg m ⁻³	Milled powder/ 10 ³ Kg m ⁻³				
Pitchstone	2.31	2.35	1.09	95.1	70.6	6.3
Obsidian	2.34	2.34	1.22	95.5	86.3	9.5

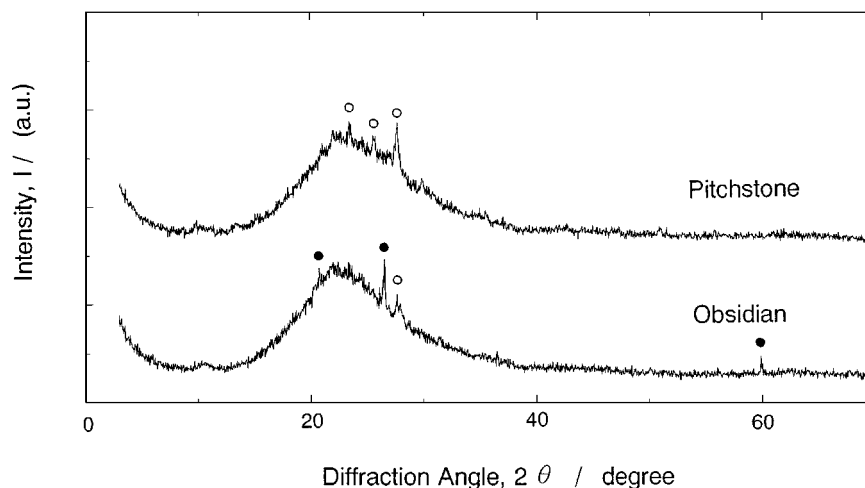


Figure 3 X-ray diffraction patterns of the milled powders. Open and closed circles denote the peak of feldspar and quartz, respectively.

which indicates that the structures of both powders are almost amorphous and that small amounts of feldspar and/or quartz exists. Table II shows characteristics of raw and milled powders. When the powders were separated into five parts using specific gravity difference of solutions, i.e. under 1.4, 1.4–1.8, 1.8–2.2, 2.2–2.4, and above 2.4, the powders with the specific gravity under 2.4 are almost glassy and the powders with the specific gravity above 2.4 are an almost crystallite mixture of feldspar and/or quartz. Therefore the glass contents of the milled powders were determined by putting the samples in a zinc bromide solution with a specific gravity of 2.4 and taking the floating component as the natural glass. It was determined that most of the milled powders consisted of glassy parts (about 95%) which is consistent with the results of the X-ray diffraction patterns.

Evolved gases from the both milled powders were almost water. Fig. 4 shows water desorption spectra of the milled powders at a constant heating rate of 5 °C/min in a vacuum. A large amount of water desorption is observed for Pitchstone. Water released from Pitchstone takes place in two temperature regions (around 280 and 600 °C). The lower water desorption in weak bonds is due to adsorbed or interlayer water, and the higher one in strong bonds is due to zeolite water, bound water or structural water [6, 10]. It is noted that water desorption from the low temperature region is small for Obsidian.

Fig. 5 shows DTG curves of the milled powders at a heating rate of 20 °C/min in air. The desorption peaks in Fig. 5 shift to higher temperatures in comparison with those in Fig. 4 due to the difference of heating rate and atmosphere, but the desorption characteristics are similar. This water desorption characteristic is very

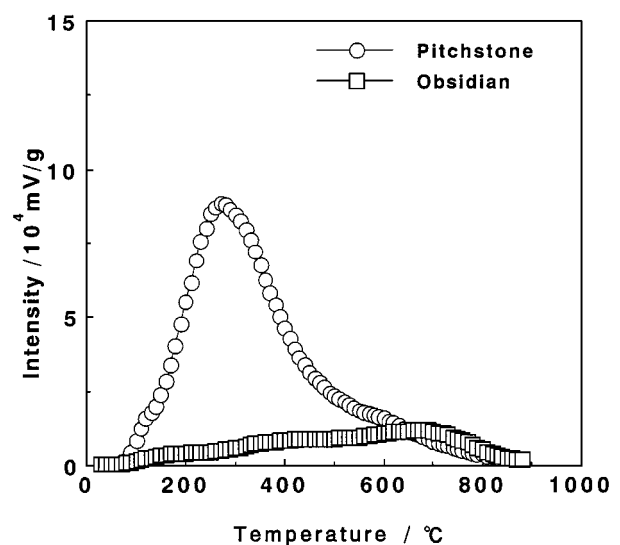


Figure 4 Water desorption spectra of the milled powders in a vacuum at a constant heating rate of 5 °C/min.

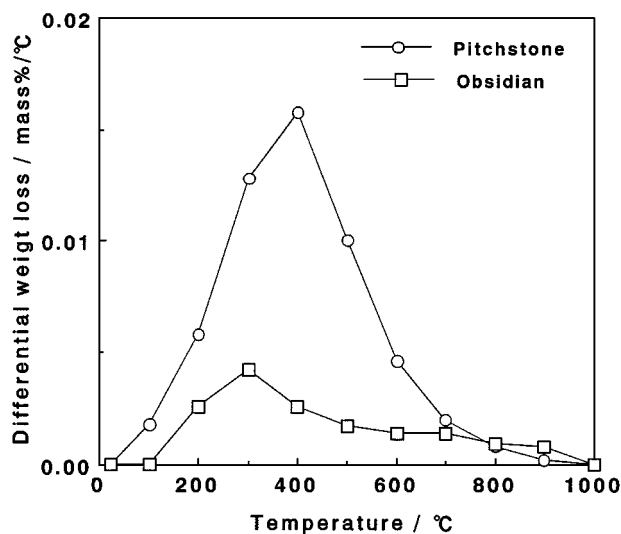


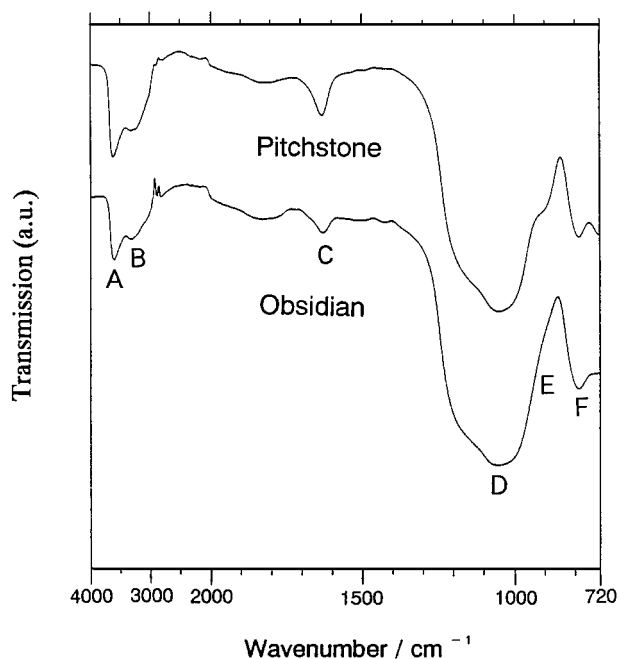
Figure 5 DTG curves of the milled powders in air at a heating rate of 20 °C/min.

important because the origin of the expansion is water remaining in the powder. The powder must contain enough water to expand until the glass softening temperature where the water is enclosed in the particle by surface softening [6, 7].

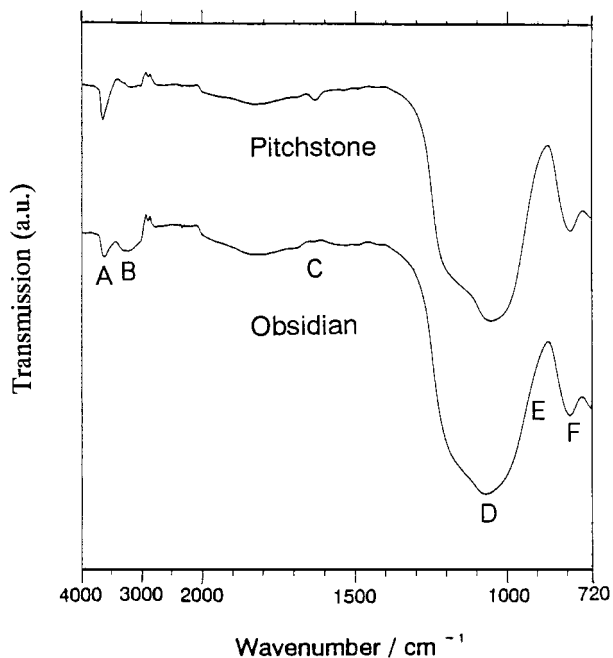
Fig. 6a shows FT-IR spectra of as-milled powders. Mainly six absorption bands are observed around at 3610 cm^{-1} (band A), 3250–3320 cm^{-1} (band B), 1630–1640 cm^{-1} (band C), 1055–1080 cm^{-1} (band D), 900 cm^{-1} (band E) and 790 cm^{-1} (band F). The band A is attributed to combination of OH stretching arising from hydrogen-bonded and free Si-OH [11]. The band B is due to molecular water of adsorbed water and interlayer water [12]. The band C is the deformation band of molecular water [13]. The bands D and F are attributed to the Si-O stretching vibrations of Si-O-Si and Si-O-Al, respectively [13]. The band E is assigned to the Si-O stretching vibration of Si-OH [14]. Here it is noted that the band E is not observed for the Obsidian. The intensities of the bands A and E are closely related to the water contents, which is also observed for the glassy volcanic materials [6]. Fig. 6b shows FT-IR spectra of the milled powders after heating at 1000 °C for 1 min. After heating, the bands of C and E disappeared, and the intensities of the bands A and B decreased.

3.2. Foaming characteristics

Fig. 7 shows bulk density of the foamed powders after heating using the fluidized bed furnace. The bulk density under 0.5 g/cm^3 is obtained in a wide temperature range for Pitchstone using the fluidized bed furnace without additional treatment on the milled powders. Minimum bulk density is seen for Pitchstone foamed at around 1080 °C. In case of Obsidian with small amount of water, however, the bulk density is high in all temperature ranges. Typical examples of particle size distributions of as-milled powders and foamed ones are shown in Fig. 8. It is seen that the Pitchstone expanded well but the Obsidian didn't. Linear expansion ratio can be calculated from the ratio of mean particle size of the milled powder to that of foamed powder. Volume



(a)



(b)

Figure 6 FT-IR spectra of (a) as-milled powders and (b) milled powders after heating at 1000 °C for 1 min.

expansion is calculated from the ratio of bulk density of the milled powder to that of the foamed powder. Fig. 9 shows linear expansion ratio and volume expansion ratio of the milled Pitchstone and Obsidian at each foaming temperature. The volume expansion involves packing errors arising from difference in the particle density and shape. However, measuring the bulk density is so simple with slight variations due to the type of measurement device used that the bulk densities can be conveniently used in estimating the expansion rate.

Fig. 10 summarizes the relationship between particle size and bulk density after foaming treatment. Fine expanded perlite with particle size under 15 μm and bulk density under 0.5 g/cm^3 was successfully prepared

by heating rapidly the milled Pitchstone. As for Obsidian, enough expansion is not observed mainly because of the lack of water in it. A hydrothermic reaction treatment is one method to increase the water content in obsidian [15].

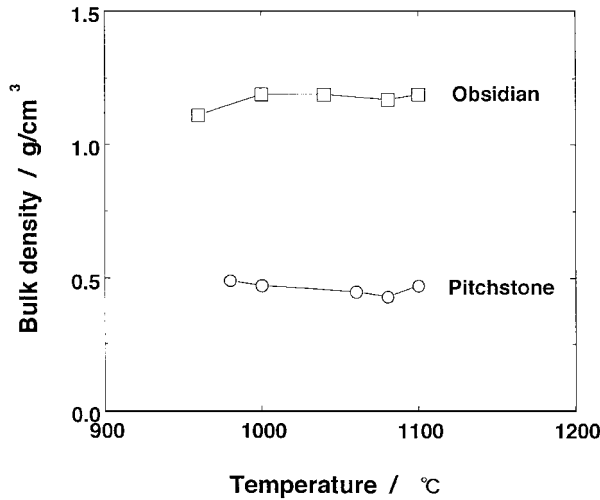


Figure 7 Relationship between bulk density and foaming temperature of foamed powders.

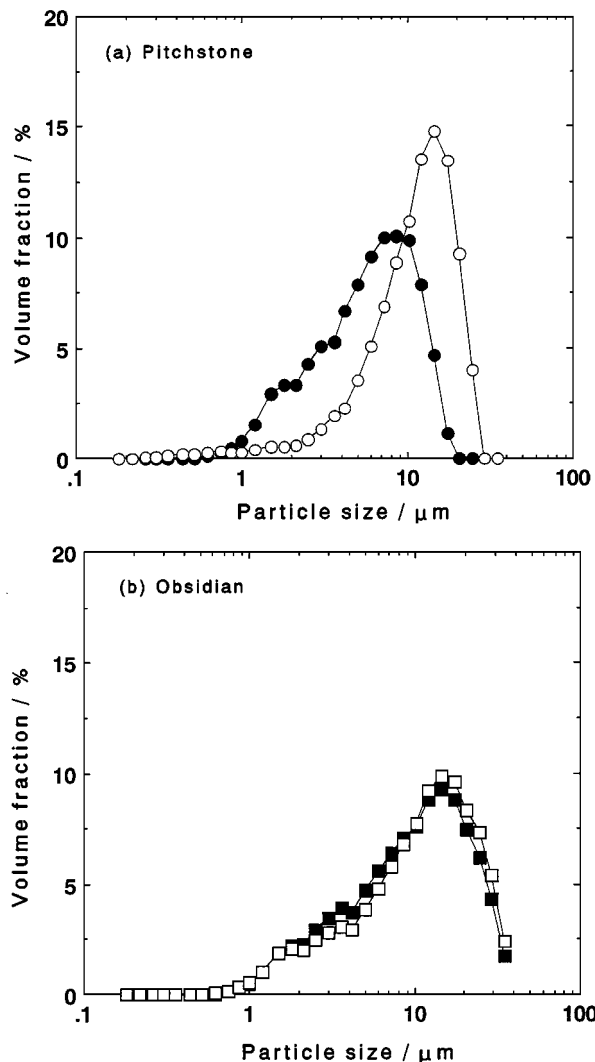


Figure 8 Particle size distribution of the as-milled powders (closed marks) and foamed powders (open marks). (a) Pitchstone, (b) Obsidian.

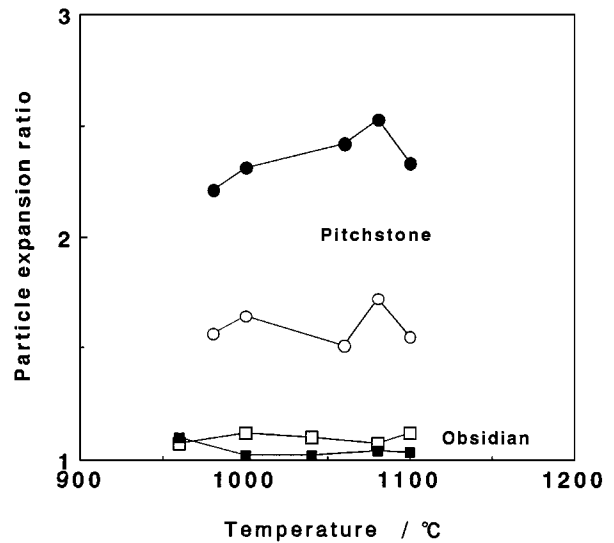


Figure 9 Linear expansion ratio and volume expansion ratio at each foaming temperature.

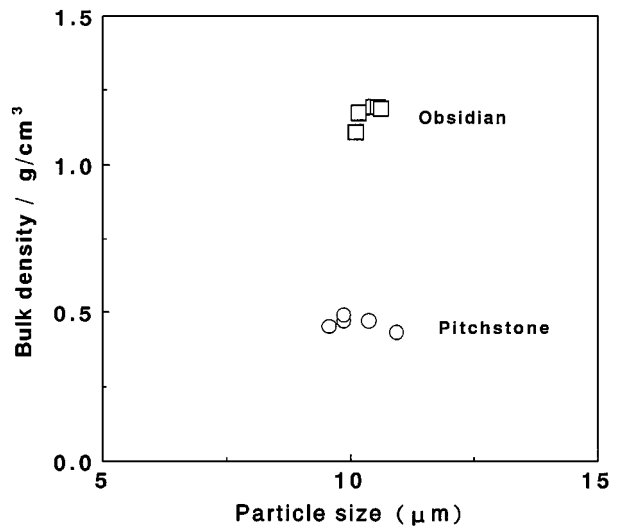


Figure 10 Relationship between bulk density and mean particle size of expanded perlite.

3.3. Characterization of fine expanded perlite

Table III summarizes mean particle size, bulk density, yield of floating particles, whiteness by Hunter, and ignition loss of the produced expanded perlite.

Fig. 11 shows X-ray diffraction patterns of the samples after heating. The structures of the milled powder (Fig. 3) remain unaltered with heating. Fig. 12 shows FT-IR spectra of fine expanded perlite. The absorption bands A, B and C are observed, which indicates that the water was not completely evolved from the powders

TABLE III Characteristics of fine expanded perlite

	Pitchstone	Obsidian
Mean particle size/ μm	9.6~10.9	10.6~11.7
Bulk density/ 10^3 Kg m^{-3}	0.43~0.49	1.11~1.19
Bulk specific gravity/ $10^{-3} \text{ m}^3 \text{ Kg}^{-1}$	2.03~2.31	0.84~0.90
Yield of floating particles in water/mass%	6.68~11.3	0.11~0.67
Whiteness by Hunter	87.6~90.1	85.7~86.1
Ig.loss/mass%	1.74	0.40

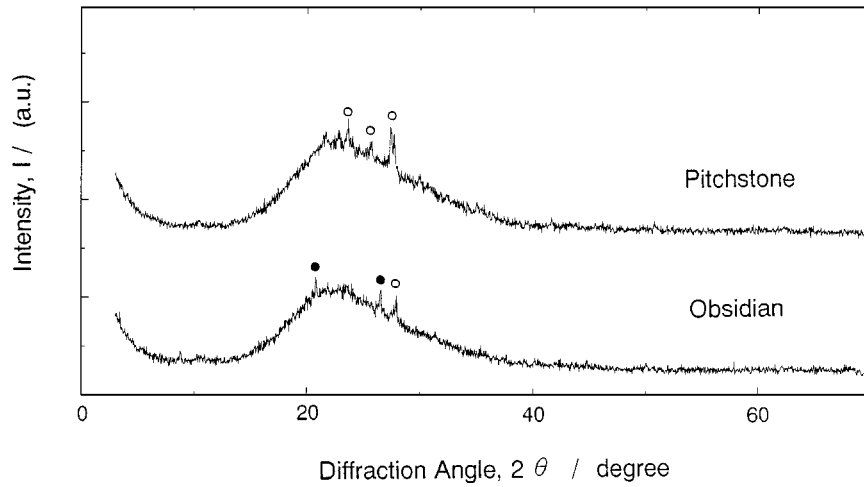


Figure 11 X-ray diffraction patterns of fine expanded perlite. Open and closed circles denote the peak of feldspar and quartz, respectively.

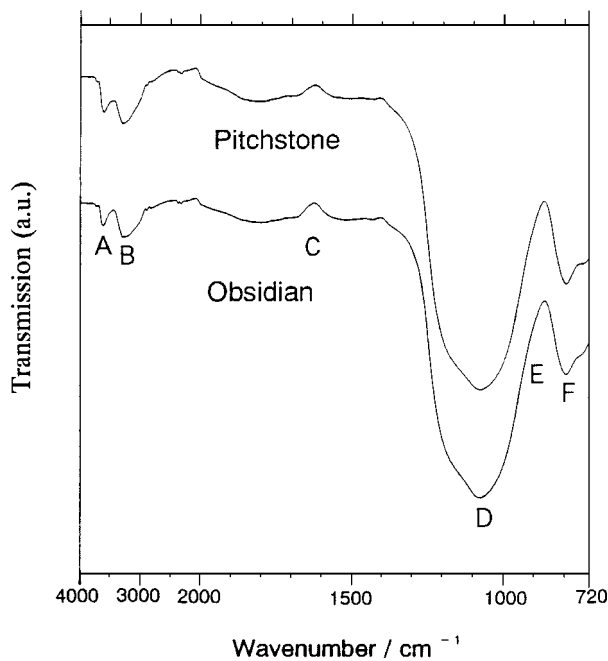


Figure 12 FT-IR spectra of fine expanded perlite.

during foaming treatment. The chemisorbed and inter-layer water may remain in the powder because the retention time of the powder at maximum temperature is very short (less than 1 min) and the chemisorbed water is not evolved completely even after heating at 1000 °C for 1 min as is seen in Fig. 6b. These are main reason why the ignition loss of the expanded perlite is relatively large. Moreover, additional water might be absorbed into the powders from the humid atmosphere in the furnace at higher temperatures [16].

Figs 13 and 14 show SEM micrographs of floating particles and settling particles in water, respectively. The floating particles are closed spheres and almost particles settled are also spherical. The settled particles of expanded Pitchstone are comparable in size to the floating ones and show signs of foaming, but those of Obsidian are almost similar in morphology to the raw milled powders. Fig. 15 shows relationship between the diameters and shell thicknesses of the fine expanded perlite. The mean diameter and mean shell thickness of Obsidian measured on SEM photographs were $11.10 \pm 3.48 \mu\text{m}$ and $0.50 \pm 0.27 \mu\text{m}$, and those of Pitchstone were $10.74 \pm 3.95 \mu\text{m}$ and

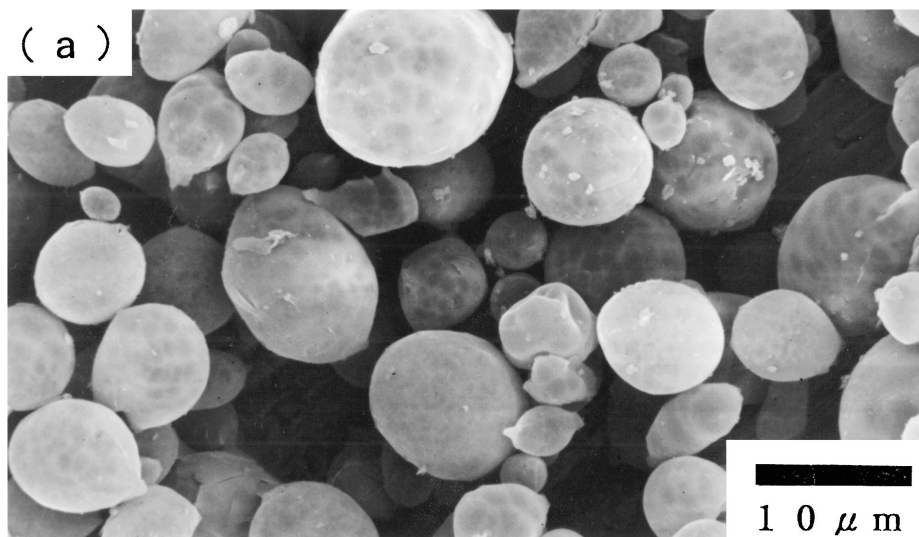


Figure 13 SEM micrographs of floating particles of expanded perlite. (a) Pitchstone, (b) Obsidian. (Continued).

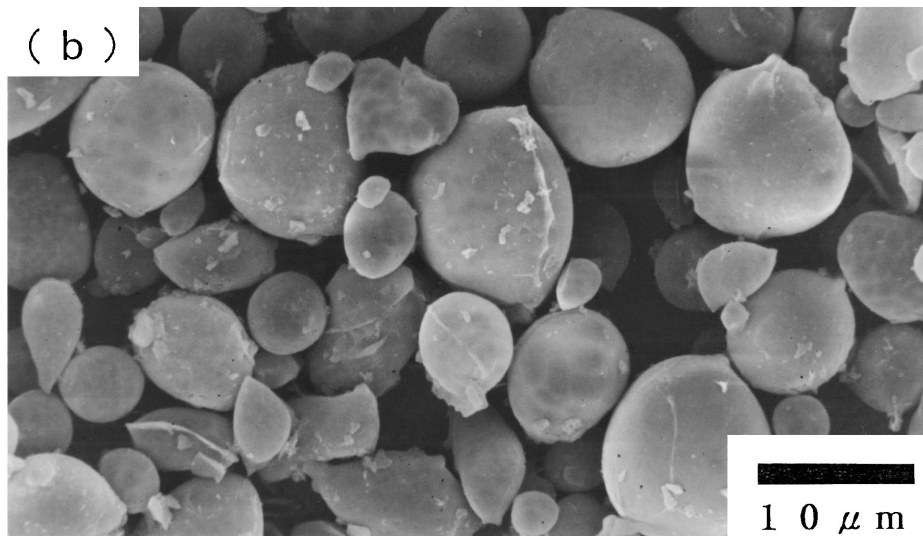


Figure 13 (Continued)

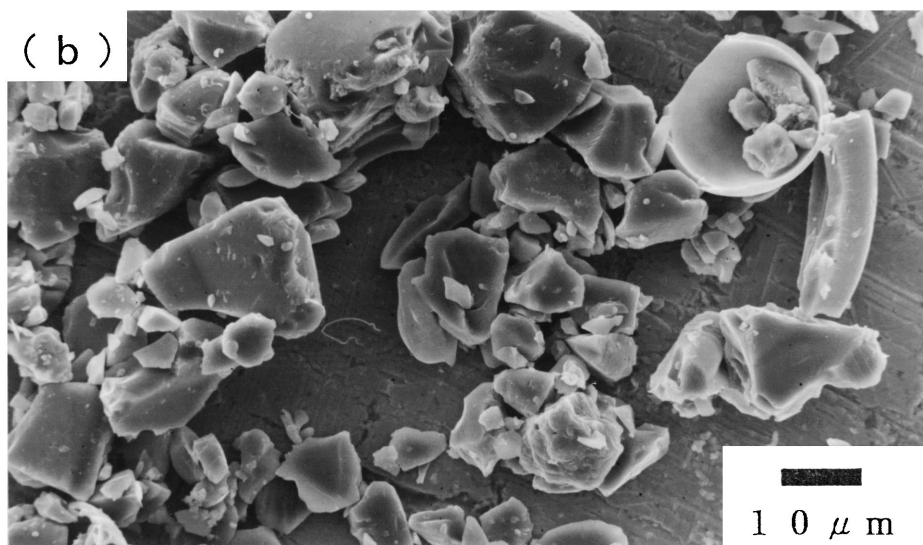
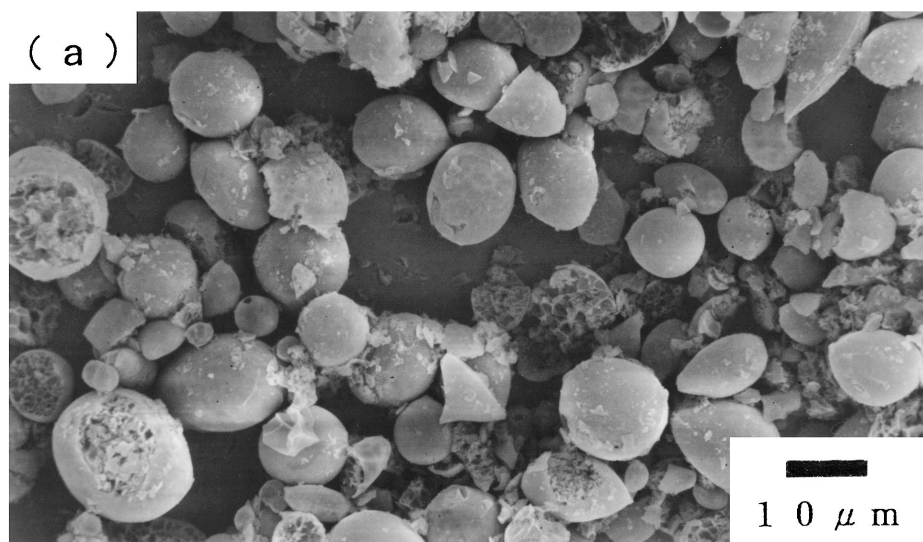


Figure 14 SEM micrographs of settling particles of expanded perlite. (a) Pitchstone, (b) Obsidian.

$0.20 \pm 0.07 \mu\text{m}$, respectively. We have reported that the shell thickness of fine Shirasuballoons is closely related to the water content of the milled powders of vitric volcanoclastic materials [6]. Similar results are observed for “perlite”. This is interpreted that the viscosity of glass decreases with water content and permits

expanded balloons to be produced, if sufficient water remains at the temperature of the glass softening.

Whiteness is an important value for application of the fine expanded perlite in special paints, adhesives, detergents, cosmetics and so on. Fig. 16 shows whiteness of the present fine expanded perlite and previously

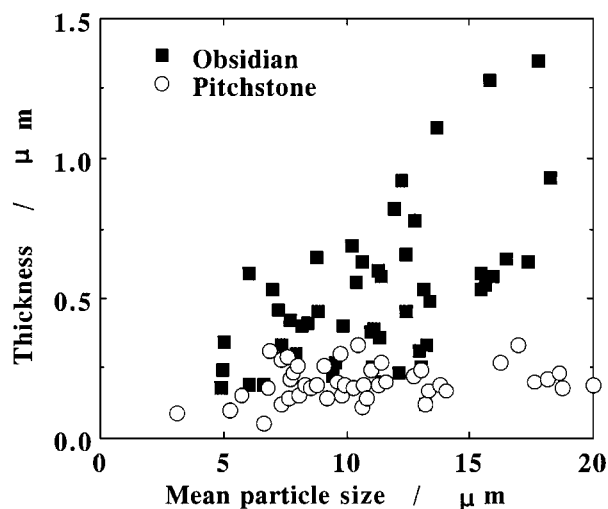


Figure 15 Relationship between shell thickness and particle size of expanded perlite.

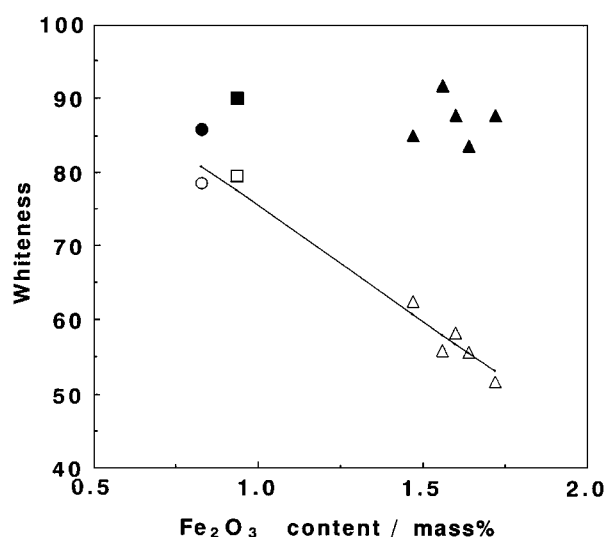


Figure 16 Whiteness of fine expanded perlite (square: Obsidian, circle: Pitchstone) and fine Shirasuballoons (triangle) as a function of Fe contents. Open marks: as-foamed particles, closed marks: foamed particles after heating at 1000 °C for 2 h in air.

reported fine Shirasuballoons as a function of Fe contents, where open marks denote the data of as-expanded balloons and closed marks denote the data after heating at 1000 °C for 2 h in air. Although the Fe content in Fig. 16 is expressed as Fe_2O_3 for the sake of convenience, the oxidation states of Fe ion in the samples are different on their heating conditions. Mössbauer spectra showed that in case of the annealed samples almost Fe existed as Fe^{3+} but that in case of the as-expanded samples about 30–40% Fe existed as Fe^{2+} ion [17]. Therefore the decrease in the Whiteness after the annealing is due to the oxidation of the Fe^{2+} ion. Linear relationship is seen between the Whiteness of the balloons after the annealing and the Fe_2O_3 content. However, the Whiteness of the as-expanded ones is high and independent on Fe content because the foaming is conducted in a reduced atmosphere.

4. Conclusions

(1) Fine expanded perlite with particle size under 15 μm and bulk density under 0.5 g/cm^3 were prepared by heating rapidly milled Pitchstone, which contains enough

water (approximately 5.05 wt %), using a fluidized bed furnace. As for Obsidian, enough expansion was not observed mainly because of the lack of water in it (approximately 1.6%).

(2) TPD experiment shows that most of the evolved gas from the raw materials was water and that at least two water desorption peaks existed. FT-IR spectra of Pitchstone and Obsidian, related to the existence of water in the raw materials, showed a peak A at around 3610 cm^{-1} assigned to the OH group of Si-OH, a peak B around $3250\text{--}3320\text{ cm}^{-1}$ assigned to water molecule vibration in the adsorbed and layer water, and a peak C around $1630\text{--}1640\text{ cm}^{-1}$ arising from deformation vibration of H_2O molecules. The Pitchstone also showed a peak E at 900 cm^{-1} due to the Si-O stretching of the Si-OH group. Heating at 1000 °C extinguished the peaks C and E, and caused peaks A and B to decline.

(3) The shell thickness of fine expanded perlite is closely related to the water content of the milled raw powders. Thin shell balloons are obtained from higher water content raw materials.

(4) Linear relationship is seen between the Whiteness of the balloons after the annealing and the Fe_2O_3 content. The Whiteness of the as-expanded ones is high and independent on Fe content because the foaming is conducted in a reduced atmosphere.

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