Synthesis of Indium Tin Oxide powder by Solid-phase Reaction with Microwave heating

Department of Chemical Engineering,
Graduate School of Engineering, Hiroshima University

Kunihiro Fukui, Keiji Kanayama, Manabu Katoh,
Tetsuya Yamamoto and Hideto Yoshida

1-4-1, Kagamiyama, Higashi-Hiroshima, 739-8527, Japan

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To whom correspondence should be addressed
E-mail : kfukui@hiroshima-u.ac.jp

The name and address of the responsible author ;
Dr. Kunihiro FUKUI
Department of Chemical Engineering,
Graduate School of Engineering, Hiroshima University,
1-4-1, Kagamiyama, Higashi Hiroshima 739-8527, Japan
Tel & Fax : +81-82-424-7715
E-mail : kfukui@hiroshima-u.ac.jp

Abstract

Indium tin oxide (ITO) powder was synthesized from indium oxide and tin oxide powders by a solid-phase method using microwave heating and conventional heating methods. Microwave heating could reduce the treatment time necessary for the completion of the solid-phase reaction by 1/30. This decrease was attributed to an increase in the diffusion rate of Sn at the local heat spot in the indium oxide formed by microwave irradiation. However, microwave heating also decreased the amount of ITO produced, since the powder layer of the raw material was heated unevenly and had an uneven temperature distribution.

Therefore, a microwave heating method including a mixing process was proposed in order to diminish the uneven progress of the ITO synthesis reaction in the powder layer. This revised method could increase the conversion to ITO, which is higher than that obtained by using the conventional heating method. Hence, the electric conductivity of the powder layer obtained by the proposed method was higher than that of the commercially supplied ITO powder layer.

1. INTRODUCTION

The solid-phase reaction is a method that a product powder is acquired from several types of raw material powders by mixing and heating these raw material powders at a high temperature. This method is widely used for synthesis of ceramic powders and so on. Unfortunately, this method requires both a long reaction time and an enormous amount of energy to maintain a high temperature because the reaction rate is very low. In order to overcome these disadvantages, the use of monodispersed nanoparticles as a raw material have been investigated [1].

A microwave can heat up an object rapidly, directly, and selectively. The microwave generates heat by its interaction with the dipole and the charge of the object. Further, this microwave heating method induces a heat spot and superheat [2]. Therefore, in recent years, this microwave heating method has been widely used for synthesizing fine powder materials in a liquid phase [3, 4] and for sintering ceramic powders at a high temperature [5, 6]. The development of the yields and the reduction in the reaction time observed by using this method have been reported [7]. However, the synthesis of an ITO powder from indium oxide and tin oxide powders by a solid-phase reaction using the abovementioned microwave heating method has not yet been reported sufficiently.

In contrast, indium tin oxide, commonly called ITO, is well known as a transparent conducting oxide. An ITO thin film is indispensable in electrical and optical devices such as flat panel displays (FPDs), organic light-emitting diodes (OLEDs), solar cells, touch panels, and so on [8, 9]. An ITO thin film is commonly prepared by magnetron sputtering method with using ITO target, which is usually formed by heating a mixture of indium oxide and tin oxide powders above 1400 ˚C for more than 10 h.

Therefore, in this paper, the properties of an ITO powder prepared by using the microwave heating method are compared with those of an ITO powder prepared by using a conventional furnace heating method, and the advantages and defects of the ITO synthesis with using the microwave heating are clarified in terms of the performance of the ITO powder and the reaction rate. Further, the effects of microwave irradiation on the progress of the solid-phase reaction are investigated and the revised type microwave heating method is newly proposed in this study.

2. EXPERIMENTAL

Commercially supplied high-purity indium oxide, In_2O_3 (Nakalai Tesque) and tin oxide, SnO_2 (Sigma Aldrich) powders with mass median diameters of 9.0 μm and 0.12 μm, respectively, were used as raw materials. The mixture of In_2O_3 and SnO_2 (mass-based ratio : 10/1) was mixed completely with a pot rotator for 10 min. This mixture was set into a glass tube (inner diameter : 16.0 mm) on a glass plain dish. The mixture in the tube was tapped or pressed to an arbitrary packing fraction. In this way, a cylindrical powder layer was formed as a starting material for the synthesis of the ITO powder. The packing fraction of the powder layer made by using a tapping method was 0.13.

The schematic representation of the microwave heating equipment is given in **Fig.1(a)**. A 2.45 GHz microwave generated by a magnetron (electric power : 750 W) was introduced into a cavity via a waveguide. The cylindrical powder layer, which was set on a silica glass plate in the cavity, was irradiated and heated up by the microwave. A thermocouple shielded with a stainless pipe measured the temperature at the center of the powder layer. The temperature measured by the thermocouple was defined as the reaction temperature and was controlled by an on-off controller. As a control experiment, the starting material was heated to the same reaction temperature with a conventional electric furnace (Koito, KPD-12).

The progress of the synthesis reaction was evaluated by the electric conductivity of a product powder, because ITO has a much higher electric conductivity than In_2O_3 and SnO_2. The electric conductivity was calculated from the electric resistance. **Fig.1(b)** shows a schematic representation of the measurement apparatus. 0.5 g of the obtained product powder filled the measurement cell. The powder in the cell was pressed by two electrodes ranging from 5 MPa to 40 MPa, and its packing fraction and thickness were set at 0.45 and 0.9 mm, respectively. The electric resistance was measured by a low-resistance meter (HIOKI, 3540) using a direct-current four-terminal method. The conductivity was calculated from the resistance. The error margin of this measurement was within 10 %. The conductivity of the product powder was compared with the commercially available ITO reagent（Alfa Aesar, In_2O_3 : SnO_2

= 9 : 1）.

The particle size was measured by using a laser scattering particle size analyzer (Horiba, LA-920). The crystalline phase was identified by XRD (Rigaku, RINT-2000). The morphology was observed by SEM (JEOL, JSM-5600).

3. RESULTS AND DISCUSSIONS

Powder layers with various mass and packing fractions were prepared. These were then heated up by using microwave irradiation for 5 min. Here, the microwave was irradiated continuously, and the reaction temperature was not controlled. **Fig.2** shows the relationship between the mass of the powder layer and the electric conductivity of the product powder. In the case of all packing fractions, electric conductivity increases gradually with an increase in the mass of the powder layer. This is because the apparent specific surface area of the powder layer decreases with its mass and the heat loss is reduced. The powder layer with a lower packing fraction provides a higher conductivity to the product powder. It can be found that the effect of the packing fraction on the electric conductivity is greater than that of the mass.

The reason why the packing fraction of the powder layer affects the electric conductivity of the product powder is investigated on the basis of the temperature change of the layer while the microwave is irradiated. **Fig.3** shows the change in the temperature of the layer with a change in the microwave irradiation time. Here, the mass of the powder layer was 2.0 g constant. In the case of any packing fraction, the temperature increases up to a observed constant value very rapidly in 1 min. However, it can be observed that the temperature at the steady state increases with a decrease in the packing fraction of the powder layer. As the packing fraction of the layer increases, the opening space in the layer and the surface area decrease. Hence, the power of the microwave penetrating into the layer and the surface area that is heated by the microwave decrease. Accordingly, since a decrease in the packing fraction raises the reaction temperature, the electric conductivity of product powder, that is, the synthesis of ITO is improved. After this, the powder layer whose mass and packing fraction are 2.0 g and 0.13, respectively, was used as the starting material.

The powder layers were treated with the microwave heating and the conventional furnace heating methods at reaction temperatures of 800 ˚C and 1200 ˚C. The relationship between the treatment time and the electric conductivity of the acquired product powder is shown in **Fig.4**. In the case of 800 ˚C, though conventional heating does not result in any change in the electric conductivity, microwave heating increases the electric conductivity slightly when the treatment time is increased. It is suggested that the microwave heating method requires a lower reaction temperature than the conventional heating method in order to begin the ITO synthesis. This is attributed to the fact that the synthesis reaction is induced at the local heat spot in the powder layer; the temperature at this spot is higher than the bulk temperature. On the other hand, when the reaction temperature is set to 1200 ˚C, the electric conductivity of the product powder increases with the treatment time and maintains constant conductivity in both heating methods. While the conventional heating method takes 300 min to increase the conductivity to a constant value, the microwave heating method requires only 10 min to do so. Hence, it can be concluded that microwave heating significantly reduces the necessary treatment time for the completion of the ITO synthesis reaction. However, conventional heating results in a higher conductivity at the steady state than microwave heating. In other words, it suggests that the conversion into ITO by using the conventional heating method is higher than that by using the microwave heating method. Moreover, product powders obtained with both heating methods have a lower conductivity than the commercially available ITO reagent（Alfa Aesar, $In_2O_3 : SnO_2 = 9 : 1$）.

Powder layers that were treated at 1200 ˚C by the microwave heating method for 20 min and by the conventional furnace heating method for 15 h are shown in **Fig.5**. The powder layer obtained by using the conventional heating method has a uniform green color, which can be attributed to ITO. On the contrary, in the case of the microwave heating method, thin portion of the powder layer remains yellow; this originates from In_2O_3. This implies that microwave heating leads to an uneven temperature distribution in the powder layer; the periphery of the layer has a lower temperature than the center. It is thought that this uneven temperature distribution is held responsible for the reduction of the conversion to ITO. For this reason, microwave heating results in the lower conductivity of the product powder at the steady state as compared to conventional heating.

Therefore, in order to improve the uniformity of the ITO synthesis reaction when the microwave heating method was used, the following treatment was carried out. The starting material that was heated at 800 or 1200 ˚C for 1 min by the microwave was quenched to room temperature, and it was mixed thoroughly with the pot rotator mentioned in experimental section for 10 min. This treatment cycle was repeated. **Fig.6** shows the relationship between the treatment time and the electric conductivity of the product powder obtained by using the abovementioned treatment. Here, the treatment time given in this figure refers to the microwave heating time, and does not include the quenching time and the mixing time. It can be found that the introduction of the mixing process to the microwave heating method increases the electric conductivity of the product powder at the steady state at any reaction temperature. Moreover, the product powder obtained by using the microwave heating method at 1200 ˚C with a mixing process has higher electric conductivity than the product powder by using the conventional heating method at 1200 ˚C and a commercially available ITO reagent. Hence, it can be concluded that the microwave heating method reduces the necessary treatment time and also increases the conversion of the solid-phase reaction when the uneven temperature distribution is prevented.

Fig.7 shows the change in the mass median diameter of the product powder treated at 1200 ˚C with treatment time. Although the median diameter of the product powder that is treated with the conventional heating methods keeps almost constant, the mass median diameter of the product powder treated with the microwave heating increases with treatment time. In particular, this tendency can be observed clearly when the microwave heating method is used without the mixing process. This result implies that this method accelerates the sintering among particles. In contrast, in the case of the microwave heating method including the mixing process, the sintering among particles is not considerably enhanced since the microwave is irradiated intermittently. Sintered particles may have been broken down during the mixing process. For this reason, the change in the mass median diameter for this method is smaller than that for the method excluding the mixing process.

The enhancement in the sintering when the microwave heating is used can be observed in the SEM image of the product powder, shown in **Fig.8**. The product powder prepared by using the microwave heating method excluding the mixing process contains enormous particles with smooth surfaces. By using EPMA, we confirmed that the enormous particles are ITO particles. However, such enormous particles were not observed in the product powder prepared by using the conventional heating method. This result indicates that the ITO particles are sintered at the local heat spot induced by the microwave irradiation.

Fig.9 shows the change in the SnO_2 [220] peak intensity of the product powder with treatment time. In the case of the conventional heating method, the SnO_2 peak intensity increases with treatment time. Hence, the crystallinity of SnO_2 is developed by annealing effects since the treatment time is considerably longer than that in the case of the microwave heating method. On the other hand, in the case of the microwave heating method, the SnO_2 peak intensity decreases monotonously with treatment time and is maintained almost constant after a certain time period. This is because in the case of microwave heating, the treatment time is so short that the crystallinity of SnO_2 can not improved by the annealing effects. Moreover, it can be concluded that the solid-phase diffusion of Sn to In_2O_3 is enhanced at the heat spot since microwave heating leads to a heat spot where the temperature is higher than the reaction temperature. This, in turn, leads to the reduction of the crystallinity of SnO_2. Thus, it can be concluded that the remarkable reduction in the necessary treatment time is induced by the promotion of sintering among the ITO particles and the solid-phase diffusion of Sn to In_2O_3 at the heat spot formed by the microwave irradiation.

4. CONCLUSIONS

Effects of the microwave irradiation on the progress of the solid-phase reaction from In_2O_3 and SnO_2 powders to the ITO powder were investigated. The results obtained in this study can be summarized as follows:

1. The powder layer of raw materials having a lower packing fraction provides a higher conductivity to the product powder since the reaction temperature at the steady state increases with a decrease in the packing fraction of the powder layer.

2. Microwave heating can remarkably shorten the necessary treatment time for the electric conductivity of the product powder to attain a constant value.
3. The electric conductivity of the product powder synthesized by using the conventional heating method is higher than that of the product powder synthesized by using the microwave heating method at the same reaction temperature.
4. The product powder obtained by using the microwave heating at 1200 ˚C with a mixing process has a higher electric conductivity than the product powder obtained by using the conventional heating method at the same reaction temperature and a commercially available ITO reagent.
5. While the median diameter of the product powder treated with the conventional heating method is almost constant, the mass median diameter of the product powder treated by the microwave heating method increases with treatment time.
6. While the crystallinity of SnO_2 in the product powder treated with the conventional heating method increases with treatment time, that with the microwave heating decreases.

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Figures and Tables

Fig.1 Schematic diagram of the microwave heating reactor and the electric resistance measurement apparatus

Fig.2 Electric conductivity of the product powder layer obtained by using the microwave heating method as a function of the mass of the raw material for various packing fractions

Fig.3 Change in the temperature of the tested powder layer with the treatment time

Fig.4 Change in the electric conductivity of the product powder layer with treatment time for both the microwave heating and the conventional heating methods

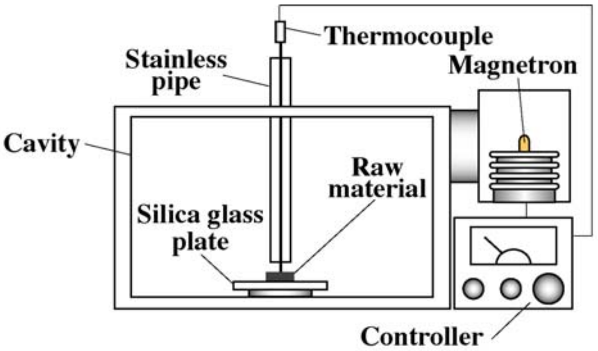
Fig.5 Appearances of the product powder layers obtained by using the microwave heating and the conventional heating methods

Fig.6 Change in the electric conductivity of the product powder layer obtained by using the microwave heating method at 800 ℃ and 1200 ℃ with the treatment time

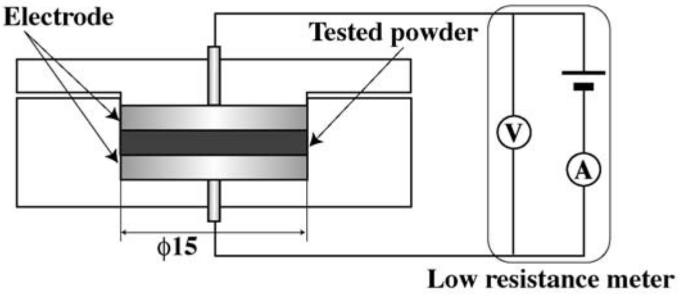
Fig.7 Change in the mass median diameter of the product powder with the treatment time for microwave heating and conventional heating

Fig.8 SEM images of the product powders obtained by using the microwave heating and the conventional heating methods

Fig.9 Change in SnO_2 [220] peak intensity of the product powder with the treatment time for microwave heating and conventional heating methods



(a) Microwave heating reacor



(b) Electric resistance measurement set-up

Fig.1 Schematic diagram of the microwave heating reactor and the electric resistance measurement apparatus

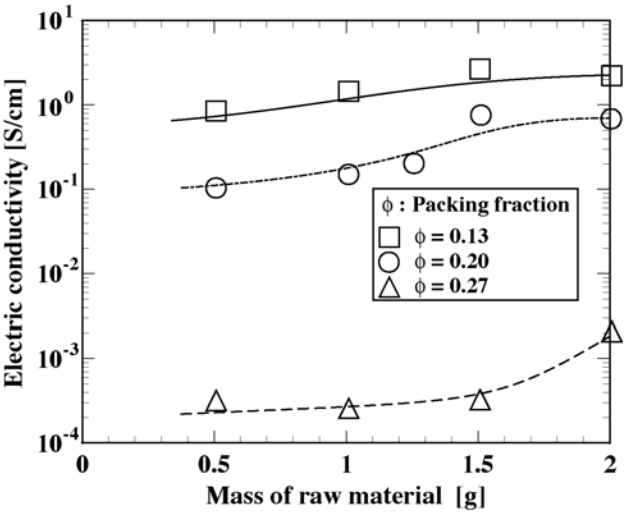


Fig.2 **Electric conductivity of the product powder layer obtained by using the microwave heating method as a function of the mass of the raw material for various packing fractions**

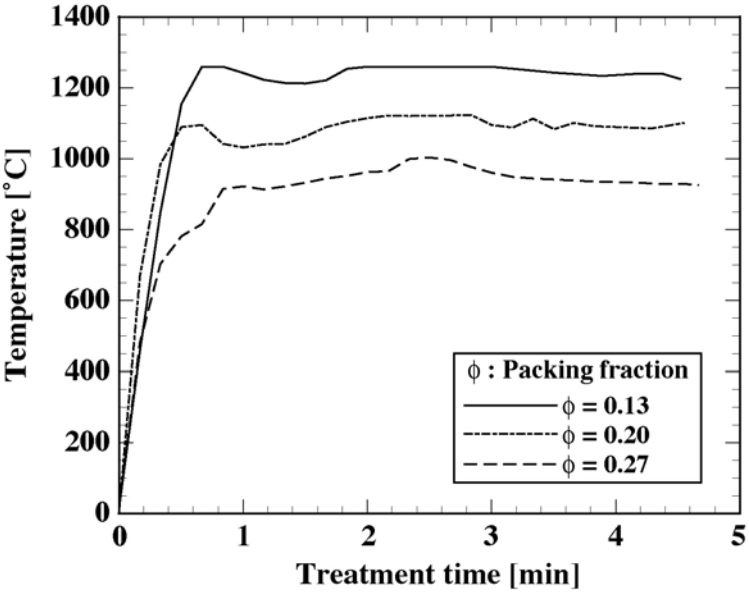


Fig.3 Change in the temperature of the tested powder layer with the treatment time

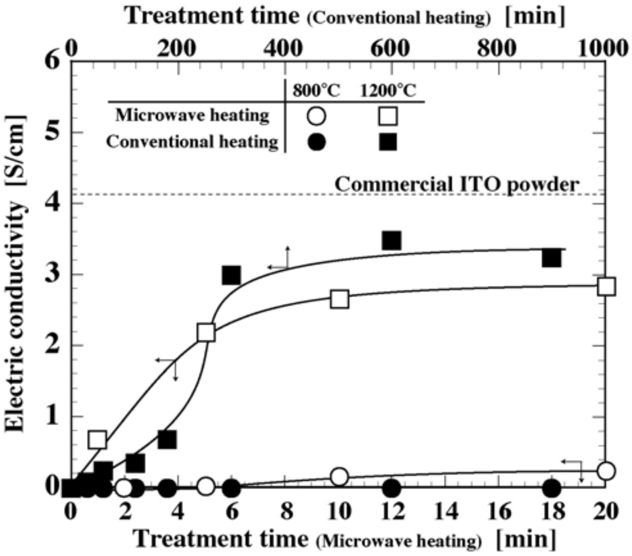
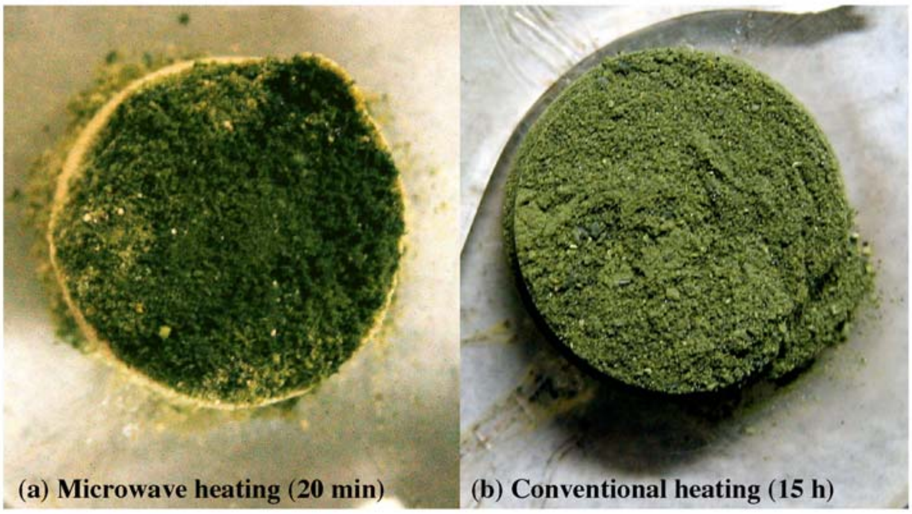


Fig.4 Change in the electric conductivity of the product powder layer with the treatment time for both the microwave heating and the conventional heating methods


(a) Microwave heating (20 min)

(b) Conventional heating (15 h)

Fig.5 Appearances of the product powder layers obtained by using the microwave heating and the conventional heating methods

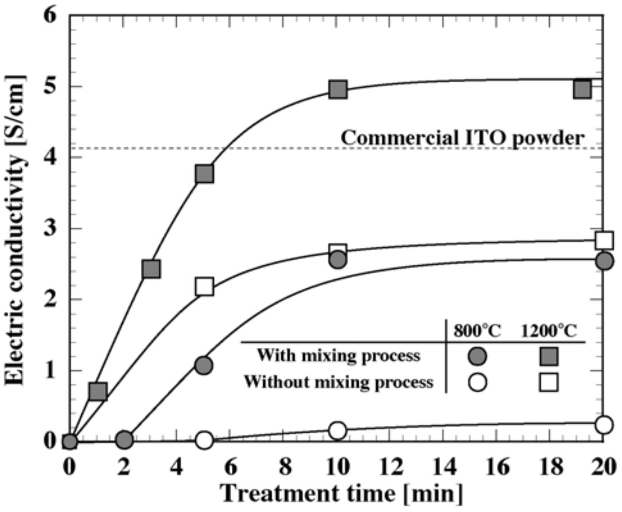


Fig.6 Change in the electric conductivity of the product powder layer obtained by using the microwave heating at 800 ˚C and1200 ˚C with the treatment time

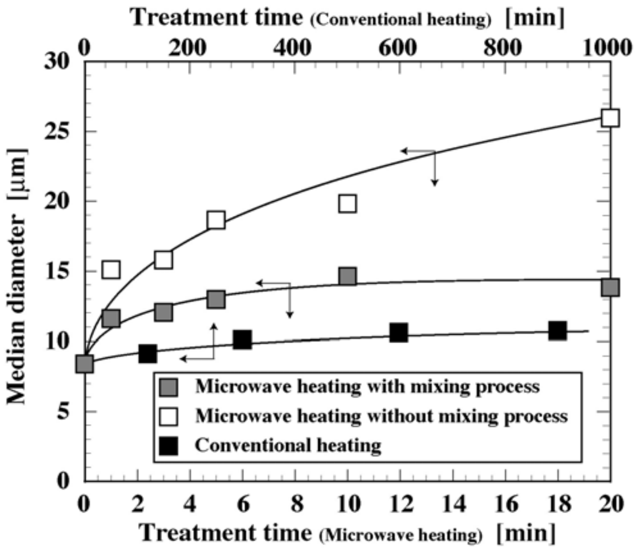
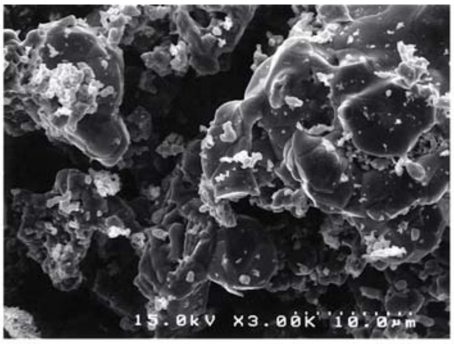
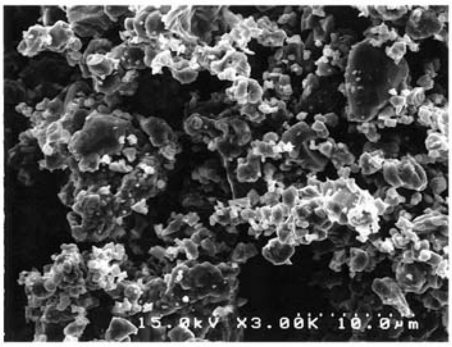


Fig.7 Change in the mass median diameter of the product powder with the treatment time for the microwave heating and the conventional heating methods



(a) Microwave heating without mixing (20 min)



(b) Conventional heating (15 h)

Fig.8 SEM images of the product powders obtained by using the microwave heating and the conventional heating methods

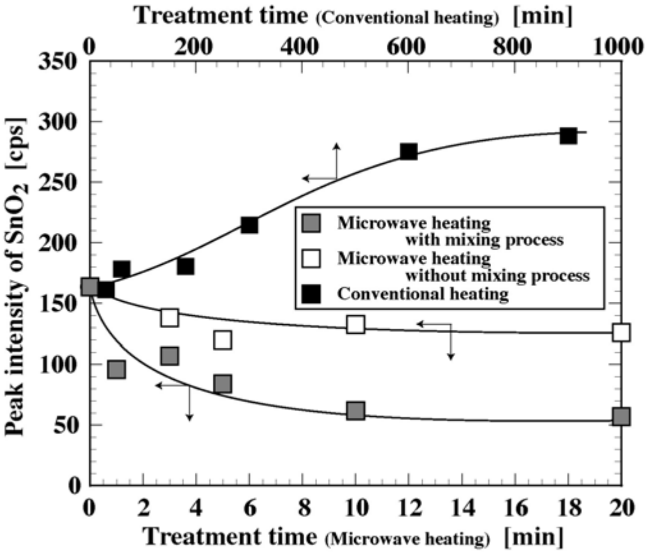


Fig.9 Change in SnO_2 [220] peak intensity of the product powder with the treatment time for the microwave heating and the conventional heating methods