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Microwave process for sintering of uranium dioxide

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Abstract

Sintering of UO_2 pellets by microwave was studied using a multi-mode-type cubic applicator (2.45 GHz). The quasi-steady-state temperature distribution in the cylindrical UO_2 pellet under microwave heating was measured. If the heating rate was as high as 20–30 K/min, local sintering occurred and a large crack was formed around the circumference of the sintered pellet. An optimum condition to have intact crack-free pellets was to heat at a rate 7 K/min up to 1550 °C and then 3 K/min to final sintering temperature. The effect of sintering temperature and time on the density and grain size of UO_2 pellets was investigated for the microwave sintering process where the heating rate was properly controlled. The results were compared with those obtained by conventional sintering method. The microwave processing produced an enhancement in both densification and grain growth. The UO_2 pellet without any cracks having more than 95% theoretical density and 5 μm grain size was obtained by the present microwave sintering in H_2 at 1600 °C for 1 h.

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1. Introduction

The pelletized fuel of uranium dioxide (UO_2) is widely used in nuclear reactors. The high density, stable pore structure and large grain size are important properties required for fuel pellet. The UO_2 pellets are generally fabricated by the conventional powder process method which consists of mixing of UO_2 powder with additive, milling, and pressing into green pellets followed by sintering [1]. In the conventional method, the sintering is incorporated with indirect heating of green pellets at about 1700 °C in a refractory-type electrical resistance furnace. This furnace, however, uses a large number of expensive heating elements and refractory materials to achieve and maintain the high temperature for a long time. Moreover, it consumes much electrical energy and time.

There has been considerable interest in microwave heating for the synthesis and processing of ceramic materials [2–5]. In contrast to the conventional resistance heating, in the case of microwave heating, the ceramic components are directly heated absorbing microwave energy. The microwave heating thus presents a potential economical sintering process with shortened processing time for the ceramic materials. This method is expected to overcome many of the shortcomings of the conventional sintering process.

Uranium oxides are known strongly to absorb microwaves. Uranium dioxide can be heated to a very high temperature by microwave irradiation [6,7]. Application of microwave heating has been progressively investigated for nuclear fuel processes such as preparation of UO_2 or UO_2-base solid solutions [8],

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oxidation or reduction of uranium oxides [9], and sintering of UO_2 [10,11].

A number of studies have been reported on the fabrication of sintered UO_2 by microwave heating. Thornton and Holaday Jr. [10] have first reported the formation of sintered pellet of UO_2 by microwave heating, where the green pellets of UO_2 loaded in alumina tube were sintered to about 95% theoretical density by employing 2.45 GHz microwave of 1.6 kW for 4 h. Recently, Subramanian et al. [11] have shown that, when the insulation box was modified, UO_2 sintered bodies of 95.5% theoretical density could be obtained even at a lower microwave power of 1 kW in a shorter sintering time less than 1 h. They used UO_2 powder as a thermal insulation material in their experiment. The design of microwave sintering furnace for mass production of nuclear fuel pellets has been suggested in the patents of SIEMENS Company [12,13]. Although these several researches showed the technical feasibility of the microwave sintering of UO_2, the detailed study on fabrication has not yet been reported.

In this work, the steady state temperature profile in UO_2 pellet under microwave heating was measured. The effect of high heating rate on the microstructure of sintered UO_2 pellet was investigated. The densification and grain growth behavior of UO_2 green pellets was studied as a function of the temperature and time of the microwave sintering. The difference of these properties between the microwave and conventional sintering was compared.

2. Experimental

The UO_2 powder used in this work was produced through the ADU process. The granulated UO_2 powder was mixed with 0.2 wt% lubricant (Zn-stearate) in a tumbling mixer for 20 min. The green pellets used for sintering experiments were obtained by pressing the mixed powder under the pressure of 3 ton/cm^2. The microwave sintering apparatus consists of a multi-mode-type cubic applicator and a power supply which can continuously change the power from 0.5 to 10 kW at a frequency of 2.45 GHz. An insulation box to prevent thermal loss was made of porous alumina tubes and boards. The UO_2 green pellets were placed in the insulation box. This assembly mounted in the applicator is shown in Fig. 1. For sufficient volumetric heating, a green pellet of about 5 g was surrounded by about 150 g sintered UO_2 pellets.

The temperature of the sintered UO_2 pellet located just below a green UO_2 pellet was measured as a reference temperature to control the microwave power (Fig. 1(a)). A hole with 4 mm diameter was drilled through the center of the sintered pellet of 10 mm diameter. The Mo-sheathed C-type thermocouple was inserted in this hole for measurement of core temperature.

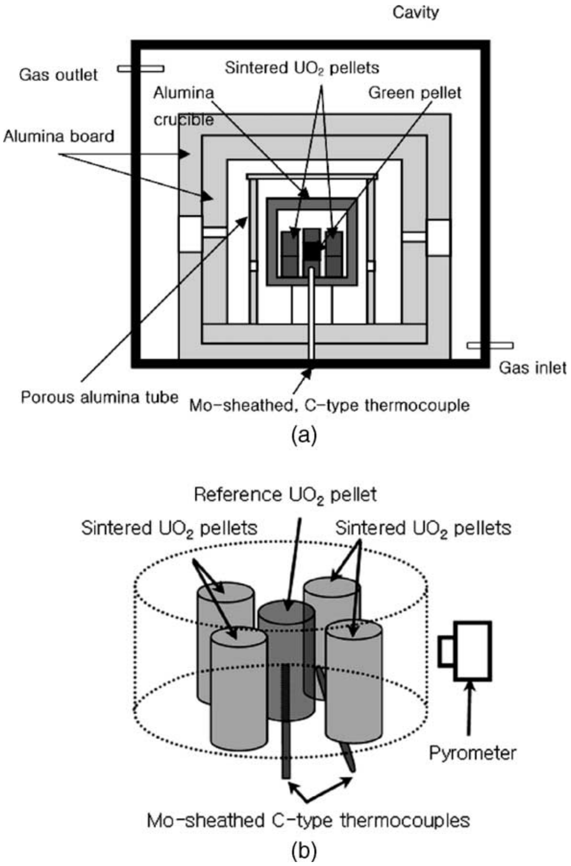

Fig. 1. (a) Schematic drawing of insulation casket in cubic metal cavity. (b) Details of pellets and thermocouples positions for measuring the core and surface temperature difference.

In a series of experiments to measure simultaneously the core and surface temperatures of the sintered reference pellet in order to investigate the temperature distribution in a quasi-steady-state, another of Mo-sheathed C-type thermocouple located in the close vicinity of the surface of the reference pellet was also used (Fig. 1(b)). The input microwave power was manually and slowly increased, and the temperature change was monitored at the core and surface of the reference pellet. Above 1200 °C an infra-red pyrometer was used to measure the surface temperature. The two color infrared thermometer (IRCON, Modline3) was focused on the circumference surface of the reference UO_2 pellet to monitor the temperature change at the surface.

The effect of microwave heating rate on sintered pellet was examined for the heating rates of 30 and 20 K/min. The appearance and microstructure of rapidly heated UO_2 pellets were investigated. The microwave heating at low heating rate was also studied, where the sample was heated at a rate of 7 K/min up to 1550 °C and subsequently the slow-down of heating rate to 3 K/min to the intended sintering temperature.

The measurement and control of the processing temperature during the microwave process was conducted using Mo-sheathed C-type thermocouple. A constant power of 0.8 kW was first applied for several minutes and then the temperature was raised with the programmed heating rate by using PID (Proportional, Integral, and Derivative) controller.

The sintering atmosphere was hydrogen. A series of sintering experiments were carried out at temperatures of 1600, 1650, 1700 and 1750 °C for 1 h. The effect of holding time was studied by changing it in a range from 0 to 4 h at 1700 °C. For comparison, sintering was made for the same green pellets by the conventional method under the same temperature and time as the present microwave processing. The density of the specimens was determined by the Archimedes method using water. The pore and grain structures of longitudinally sectioned and polished pellets were observed with an optical microscope. The grain boundary was observed after thermal etching in CO_2 gas at 1300 °C for 1 h. The grain size was determined by the linear intercept method.

3. Results and discussion

3.1. Measured difference in the core and surface temperatures of reference UO_2

Fig. 2 shows the plots of the measured surface temperatures against the core temperatures of UO_2 reference pellet during the microwave processing. The distance from surface to core was about 3 mm. In order to achieve the quasi-steady-state, input microwave power was slowly increased in a stepwise manner and the temperature variation was monitored. After the temperature increase was ceased, the next step power was applied. The microwave power increment was about 200 W per step. The maximum applied power was about 3 kW. From Fig. 2, it can be seen that the core temperature is about 50–100 °C higher than the surface temperature. The difference tends to increase with increasing temperature. The results show that the temperature difference between surface and inside of UO_2 pellet is not large, i.e. the inside temperature is not much varied along the radial direction.

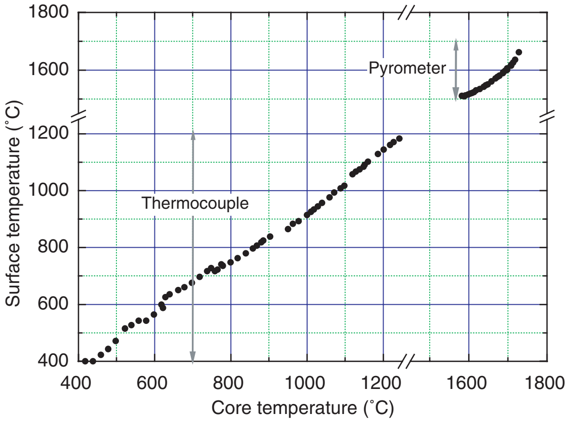

Fig. 2. Measured surface temperatures plotted against core temperatures the reference UO_2 pellet in quasi steady state heating condition.

3.2. Effect of heating rate on sintering behavior of UO_2

Fig. 3 shows the two appearances of sintered UO_2 pellets obtained by adopting rapid average heating rates of 20 and 30 K/min, respectively. The corresponding heating curves are shown in Fig. 4, where the measured temperature was the core temperature of reference UO_2 pellet. Both the sintered pellets have a large crack around the pellet circumference. The microstructures of pellets are shown in Fig. 5. It can be seen that the outer region of both pellets have higher density and larger grain size than the inner region. This fact indicates that the outer region was more intensively sintered than the inner region of pellet. Such a non-uniform microstructure seems to be caused by inhomogeneous heat generation in UO_2 pellet on high rate heating. The heat from microwave is generated larger in the thin periphery region of the pellet at elevated temperatures. If the heating rate is high, the surface temperature becomes higher than the inner temperature. The densification is started in the surface region at a certain elevated temperature, and the pellet is cracked due to the tensile stress caused by local densification in this region.

Fig. 3. UO_2 pellets sintered at high heating rates of 20 K/min (left) and 30 K/min (right).

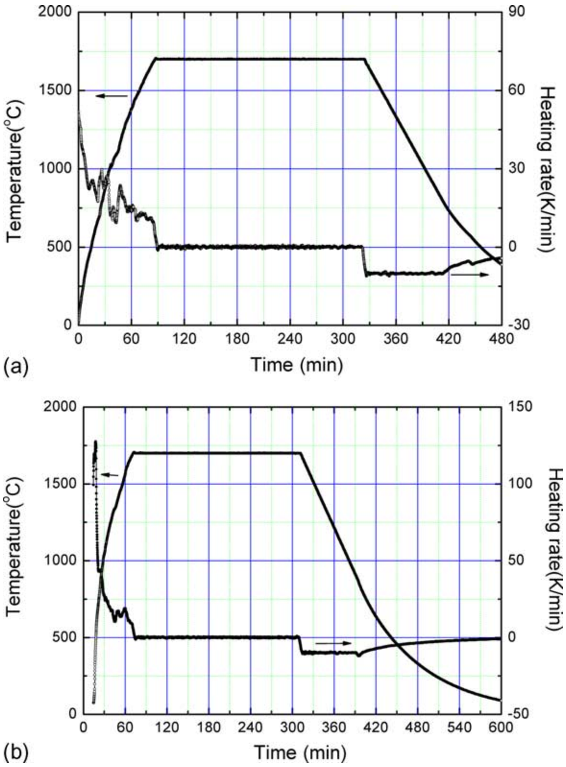

Fig. 4. Heating curves of high heating rate experiments. (a) Average heating rate, 20 K/min, (b) average heating rate, 30 K/min.

In order to prepare the crack-free UO_2 pellet without microstructure difference between surface and inside, the heating rate is required to be much lower. It was found that the intact pellets were formed by heating with a rate of 7 K/min up to 1550 °C and 3 K/min up to the final sintering temperature.

3.3. *Microwave sintering behavior of UO_2*

In Fig. 6, it is shown a photograph of UO_2 pellet sintered at 1700 °C for 4 h in microwave, together with that of a green UO_2 pellet. The intact sintered pellet without crack is shown to be obtained by the microwave sintering.

The variation of density with temperature is depicted in Fig. 7, and that with heating time in Fig. 8. These figures show the difference of the two sintering methods. It can be seen that the UO_2 pellet formed by the microwave sintering has a higher density than that formed by the conventional sintering method at the same sintering temperature and holding time. For example, the density of the microwave-sintered pellet at 1650 °C for 1 h is close to that of the pellet sintered by the conventional method at 1700 °C for 2 h.

The variation of grain size with temperature is shown in Fig. 9, and that with holding time in Fig. 10. The grain size of microwave-sintered pellets is seen to be lager than that of the sintered pellets by the conventional method at the same sintering temperature and holding

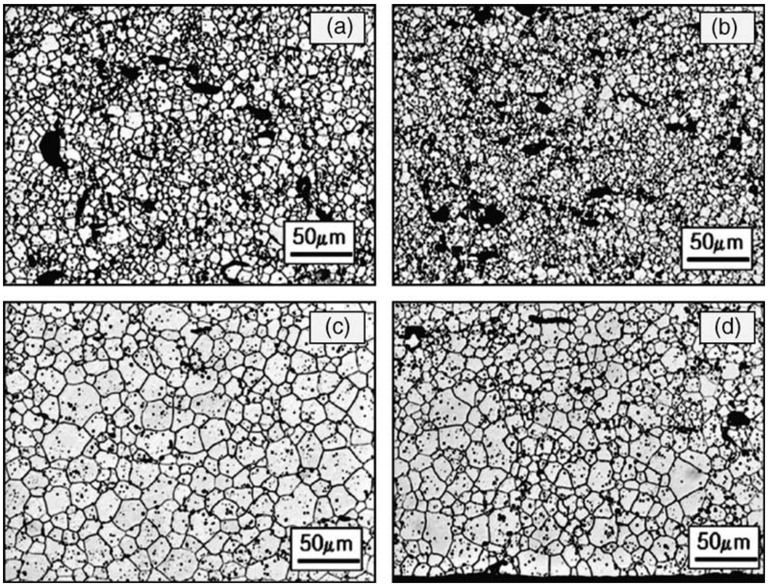

Fig. 5. Microstructure of sintered UO_2 pellets obtained by the microwave method with high heating rates. Sintering condition: 1700 °C for 4 h in H_2. (a) Inner region, 20 K/min heating rate; (b) inner region, 30 K/min heating rate; (c) outer region, 20 K/min heating rate; (d) outer region, 30 K/min heating rate.

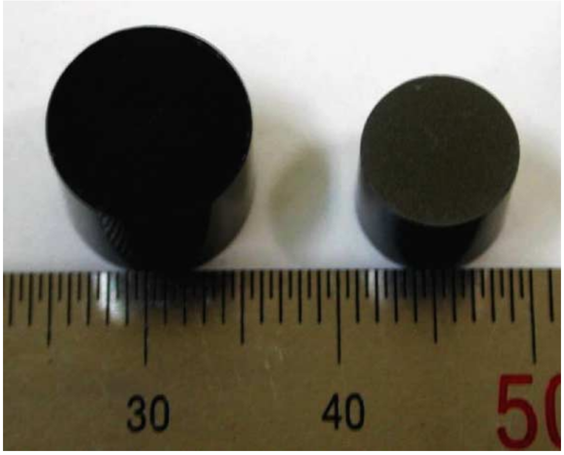

Fig. 6. Appearance of green pellet (left) and sintered UO_2 pellet (right). Sintering condition: 1700 °C for 4 h in H_2.

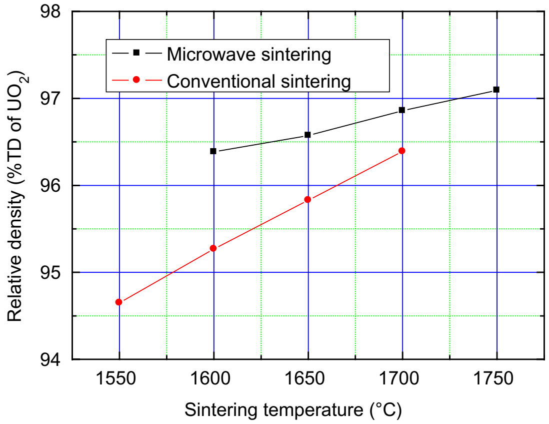

Fig. 7. Density of sintered UO_2 pellets as a function of sintering temperature. Sintering time: 1 h.

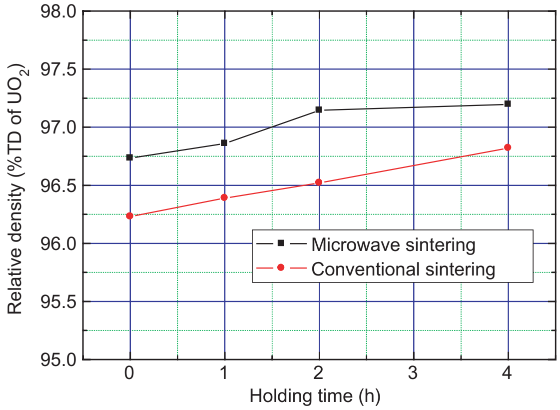

Fig. 8. Density of sintered UO_2 pellets as a function of sintering time. Sintering temperature: 1700 °C.

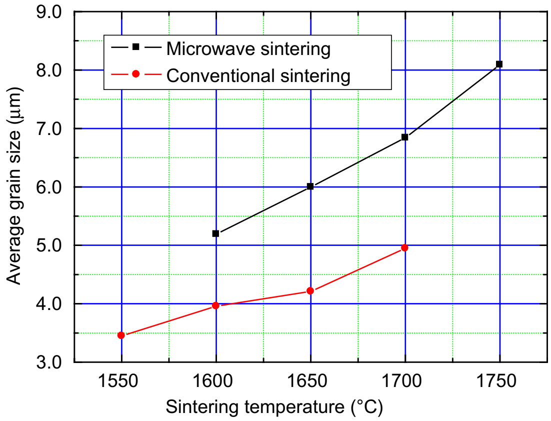

Fig. 9. Grain size of sintered UO_2 pellets as a function of sintering temperature. Sintering time: 1 h.

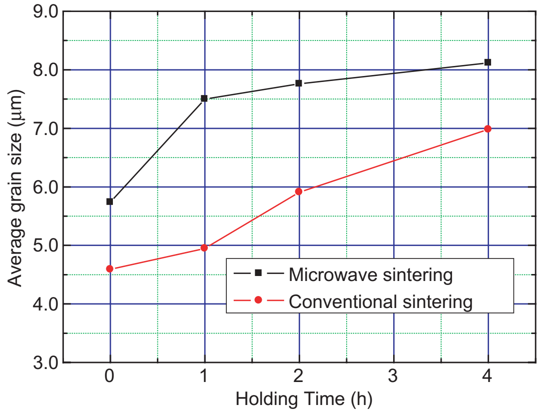

Fig. 10. Grain size of sintered UO_2 pellets as a function of sintering time. Sintering temperature: 1700 °C.

time. For example, the grain size of the microwave-sintered pellet at 1650 °C for 1 h is nearly the same as that of the conventional sintered pellet at 1700 °C for 2 h.

Figs. 11 and 12 show the typical microstructures of sintered pellets obtained by the conventional and microwave sintering methods, respectively. The sintering time at the peak temperature was 1 h. It can be seen that the pellets sintered by microwave heating have larger grain size than the pellets sintered by the conventional heating method under the same sintering conditions.

The sample density before heating is about 50% TD, which is much lower than the reference pellets (95% TD). However, since the microwave is absorbed by the molecules of UO_2, the density does not affect essentially the temperature increase. The sample pellet is surrounded by sintered pellets used for the thermal shield.

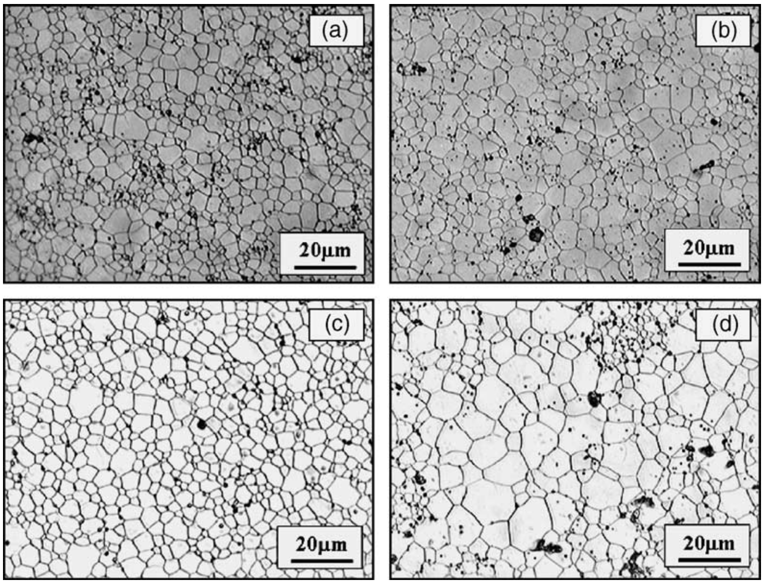

Fig. 11. Microstructure of sintered UO_2 pellets obtained by the conventional method at various temperatures. (a) 1550 °C, (b) 1600 °C, (c) 1650 °C, (d) 1700 °C. Holding time: 1 h; atmosphere: H_2.

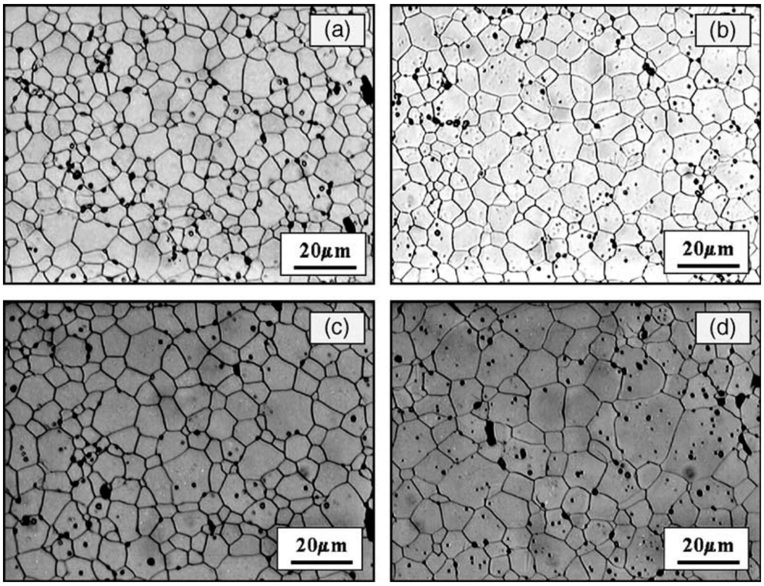

Fig. 12. Microstructure of sintered UO_2 pellets obtained by the present microwave method at various temperatures. (a) 1600 °C, (b) 1650 °C, (c) 1700 °C, (d) 1750 °C. Holding time: 1 h; atmosphere: H_2.

Thus the temperature of the sample pellet is estimated to be virtually the same as that of the reference pellets.

When the sintering and grain growth behavior of the UO_2 pellets prepared by the present microwave method is compared with that of the pellets prepared by the conventional sintering method, the microwave sintering is seen to produce the pellets of a higher density and larger grain size. As for the mechanism of enhanced sintering in the microwave process, there remain a number of unsolved points. However, several explanations for the apparent enhanced sintering, so-called ‘microwave effect’, have been proposed [14,15]. A series of recent experimental and theoretical investigations elucidate the nature of ‘non-thermal effect’ that the high-frequency electromagnetic field exerts ponderomotive forces on mobile ions in a solid, accelerating solid-state ionic diffusion [14]. Moreover, the microwave field can be concentrated at the neck region of two contacted particles, so that the ionic mass transport in the grain boundary or neck region is greatly enhanced in the microwave field [15].

The microwave heating in ceramics is closely related their dielectric properties and defect structure. In the UO_2 pellet, there are various kinds of defects with different dielectric properties. The sintering atmosphere and the addition of additives change the defect concentration and dielectric properties, which may affect the diffusion behavior of UO_2 when it is under microwave fields.

In this work, the green pellets of UO_2 of maximum 10–15 g were processed in a batch to study the basic sintering behavior. The mass production of much larger amount of pellets is considered to be possible by using improved microwave furnace replacing a part of the insulator pellets by sample pellets.

4. Conclusions

Microwave sintering process of UO_2 pellets was studied using a multi-mode-type cubic applicator which operates at a frequency of 2.45 GHz. The heating rate was found to be important for fabricating a crack-free UO_2 pellet with homogeneous microstructure. Such intact pellets were produced by microwave sintering with a slow heating rate. If the heating rate was as high as 20–30 K/min, the pellet was cracked pellet with inhomogeneous microstructure of which the density and grain size were large at the pellet surface than in the central part. The microwave sintering of UO_2 pellets can enhance the densification and grain growth compared to the conventional sintering. The UO_2 pellets having a density of 96.4% TD and a grain size of about 5 μm, which are produced by the conventional sintering method at 1700 °C for 1 h, could be produced by the present microwave sintering method at 1600 °C for 1 h.

Acknowledgements

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