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Properties of Compacts and Pellets Made Using Bimodal-Sized UO_2 Powder

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Abstract

The powder mixture which has a bimodal size distribution, with a large mode corresponding to AUC-UO_2 powder and a small one corresponding to ADU-UO_2 powder, was prepared, pressed into compacts, and sintered at 1680℃ for 4 hours in hydrogen gas. The compact density of the powder mixture increases with increasing ADU-UO_2 content within a content of 20 wt %, since small ADU-UO_2 particles can fill interstices between large AUC-UO_2 particles. The UO_2 pellet made using the powder mixture has a lower open porosity than that made using AUC-UO_2 powder alone. The mechanism for the formation of a flake-like pore is proposed, and the decrease in open porosity may be ascribed to the decrease in the number of flake-like pores.

Key Words : UO_2 fuel, open porosity, powder mixture, flake-like pore

1. Introduction

UO_2 fuel pellets are commonly fabricated from UO_2 powder through the processes of pressing and sintering, of which conditions are influenced by the properties of UO_2 powder. The properties of UO_2 powder, in turn, are largely dependent on the manufacturing method. AUC (Ammonium Uranyl Carbonate), ADU (Ammonium DiUrante) and DC (Dry Conversion) processes have been widely used in the production of UO_2 powder from UF6.

The typical properties of AUC-UO_2 powder and ADU-UO_2 powder are summarized in Table 1 [1]. In this paper 'AUC-UO_2 powder' and 'ADU-UO_2 powder' represent the UO_2 powder manufactured by the AUC process and by the ADU process, respectively. The AUC-UO_2 powder has some different properties compared to the ADU-UO_2 powder. The AUC-UO_2 powder has a large particle size, a round particle shape, and a good flowability. Despite its large size, the AUC-UO_2 powder has a high specific surface area compared to the ADU-UO_2 powder, since its particle includes a number of very small open channels [2,3]. From the viewpoint of mass

Table 1. Typical Properties of UO_2 Powder

properties	AUC-UO_2	ADU-UO_2
specific surface area (m^2/g)	5	3
apparent density (g/cm^3)	2.3	1.41
O/U ratio	<2.15	<2.14
flow characteristics	good	bad

production, the AUC-UO_2 powder has an advantage in that it can be directly pressed into compacts, but the ADU-UO_2 powder needs a granulation process to prepare granules before being pressed. UO_2 pellets are produced by sintering UO_2 compacts at temperatures of 1700℃ to 1750℃ in hydrogen gas.

Our experiences have indicated that the UO_2 pellet made using AUC-UO_2 powder has a lower density than that made using ADU-UO_2 powder although the sintering condition is the same. This result needs some more understanding of the densification of AUC-UO_2 powder, because a rough rule-of-thumb presumes that the powder with a higher surface area has a higher sinterability and thus yields a higher pellet density. The UO_2 pellet made using AUC-UO_2 powder also has a disadvantage in that it has a high open porosity, i.e., a high fraction of the total porosity is connected to pellet surface [4]. The open porosity is known to assist for a pellet to absorb moisture from environment, so the open porosity of a pellet should be kept as low as possible [4].

Any UO_2 powder manufactured by a particular method has generally both advantages and disadvantages that are derived from its properties. Only one kind of UO_2 powder has usually been used in pellet fabrication, and the disadvantages of powder can give burdens on the next process of pellet fabrication. For example, aluminium compound came to be added to UO_2 powder in order to reduce the open porosity of the UO_2 pellet made using AUC-UO_2 powder [5]. In addition, it is difficult for the AUC-UO_2 powder to be used in the fabrication of CANDU fuel pellets because a CAUDU fuel pellet requires a higher density by an amount of about 2% TD than a LWR fuel pellet. In this regard, powder mixtures of different UO_2 powders are expected to solve problems associated with disadvantages of one kind of UO_2 powder.

The purpose of this work is to study a feasibility of fabricating UO_2 fuel pellets from the powder mixture of AUC-UO_2 and ADU-UO_2. The properties of compacts and pellets have been investigated. This paper describes the relationship between the open porosity of pellets made using powder mixture and ADU-UO_2 contents in the powder mixture, and proposes a mechanism for pore formation in the UO_2 pellet made using AUC-UO_2 powder.

2. Experimental Procedures

Two different UO_2 powders were used in this work; AUC-UO_2 powder and ADU-UO_2 powder. The particle size was measured by a laser light scattering method, and the morphology was observed by SEM. The powder mixtures of AUC-UO_2 and ADU-UO_2 were prepared with determined ratios. Two UO_2 powders were mixed together in a tumbling mixer, and a very small amount of alumina balls was put in the tumbling mixer in order to reduce the agglomeration of ADU-UO_2 powder. It was found that such alumina balls had a negligible effect on the size of each powder during the mixing.

Powder mixtures were pressed directly into compacts under pressures ranging from 2 to 3.5 ton/cm^2, and the compact density was then measured by a geometrical method. Compacts were sintered at 1680℃ for 4 hours in hydrogen gas to make a pellet. The density and open porosity of a pellet was determined by the water

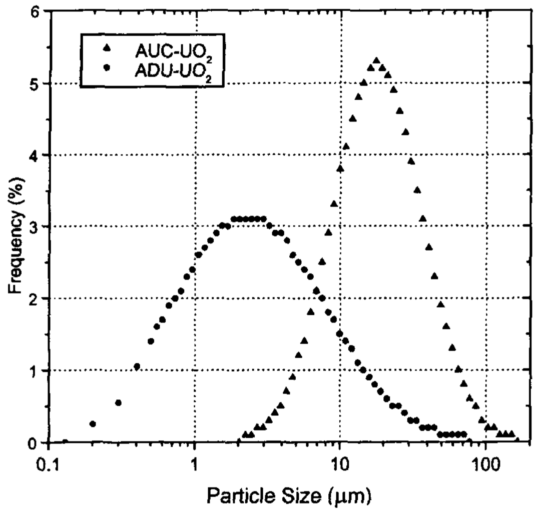

Fig. 1. Particle Size Distribution of UO_2 Powder

immersion method. In order to impregnate water in the open porosity, pellets soaked in water were evacuated for 30 minutes and then a vacuum reverted to an atmospheric pressure. The measurement error for the density and open porosity could be derived from the balance and water temperature, and the estimated error was $\pm 2\%$. Pellets were cut longitudinally, ground and polished, and then their microstructures were observed.

Pore size and pore shape were determined with the aid of the software (Image-Pro Plus) for image analysis. About 8000 pores were characterized two-dimensionally in area and perimeter for each specimen. The equivalent diameter of a pore was assumed to be pore size and was expressed as the following equation:

$$\text{Equivalent diameter} = \text{Pore size} = 2(\text{area}/\pi)^{\frac{1}{2}}.$$

The shape factor of a pore was determined by the following equation:

$$\text{Shape factor} = \frac{4\pi \times \text{area}}{(\text{perimeter})^2}$$

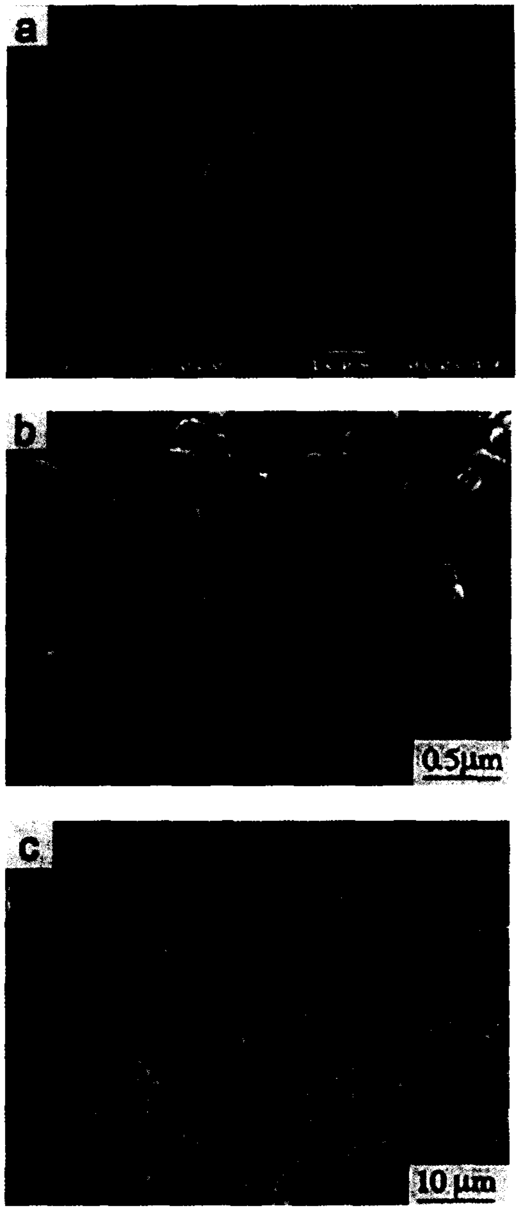

Fig. 2. Morphology of UO_2 Powder
(a) AUC-UO_2 (macroscopic), (b) AUC-UO_2 (microscopic), (c) ADU-UO_2

A perfectly round pore has a shape factor of 1, and the shape factor of a pore decreases as the shape of a pore deviates from roundness.

3. Results and Discussion

Fig. 1 shows the relationship between frequency and particle size for AUC-UO_2 and ADU-UO_2 powder. The AUC-UO_2 powder has a narrow range of distribution, but the ADU-UO_2 powder has a wide range of distribution. The modes of size distributions for AUC-UO_2 and ADU-UO_2 powder are 17.4, and 2.5 μm, respectively. It can be deduced that the powder mixture of AUC-UO_2 and ADU-UO_2 has a bimodal size distribution.

The morphology of AUC-UO_2 is shown in Figs. 2(a) and 2(b), and that of ADU-UO_2 powder in Fig. 2(c). Fig. 2(a) shows that the particle of AUC-UO_2 powder has a round shape and is not agglomerated. When examining a particle with a higher magnification, it can be noticed that a particle is composed of a number of very small crystallites (see Fig. 2(b)). According to the works [2,3], open channels of which sizes are mostly less than 0.1 μm are formed between the crystallites. In Fig. 2(c) the size of ADU-UO_2 powder appears to be larger than the real size as a result of its agglomeration. The apparent size of powder agglomerates seems to be irregular.

The compact density of the powder mixture of AUC-UO_2 and ADU-UO_2 is plotted as a function of ADU-UO_2 content in Fig. 3. It is readily seen that the compact density of AUC-UO_2 powder is higher than that of ADU-UO_2 powder. The compact density of the powder mixture varies with ADU-UO_2 content. Under the pressures of 2.4 and 2.8 t/cm^2, the compact density increases initially with increasing ADU-UO_2 content, reaches a maximum at 20 wt % ADU-UO_2 , and thereafter decreases with increasing ADU-UO_2 content. If the compact density of the powder mixture is assumed to be governed by the mean value of the two compact densities of AUC-UO_2 and ADU-UO_2 powder, the compact density can

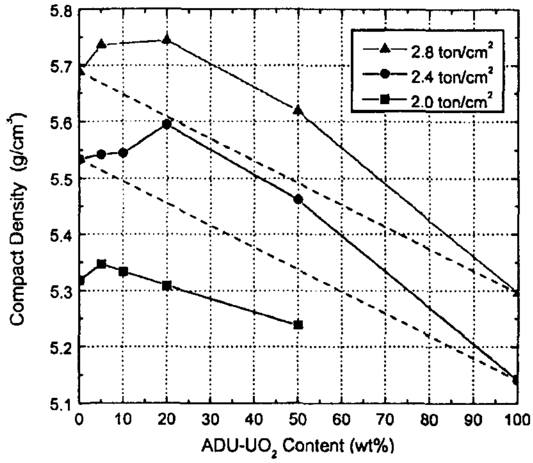

Fig. 3. Variations in Compact Density of Powder Mixtures with ADU-UO_2 Content

be calculated by the following equation:

Compact density = (compact density of AUC-UO_2) * (100 - wt% of ADU-UO_2)/100 + (compact density of ADU-UO_2) * (wt % of ADU-UO_2)/100.

The compact density according to the above equation is plotted as a straight line in Fig. 3, and the compact density calculated is lower than the compact density measured. This suggests that the compact density of powder mixtures be not determined by the mean value of the compact density of its component powder.

The powder mixture has a bimodal size distribution; one mode corresponding to the AUC-UO_2 powder and the other corresponding to the ADU-UO_2 powder. The small particles (ADU-UO_2) are expected to fill interstices between the large particles (AUC-UO_2) during the operation of pressing, so the degree of powder packing and the compact density become higher in accordance with the ADU-UO_2 content. It is found that such a filling effect of ADU-UO_2 powder on the powder packing increases with the ADU-UO_2

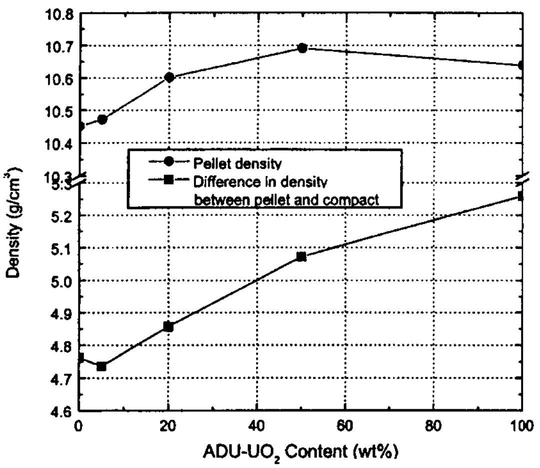

Fig. 4. Dependence of Pellet Density and Density Difference Between Pellet and Compact on ADU-UO_2 Content

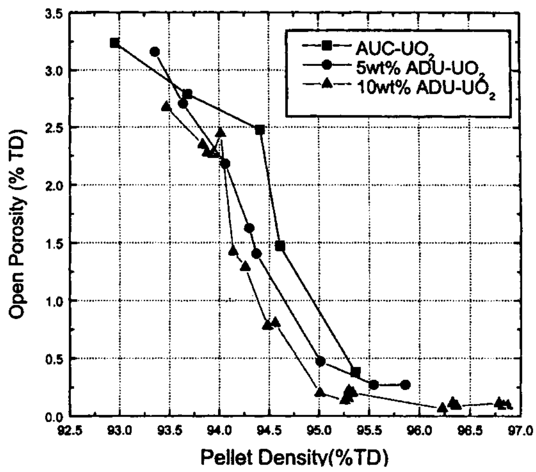

Fig. 5. Dependence of Open Porosity of Pellets on Pellet Density

content in the content range of 20 wt% for the pressing pressures of 2.4 and 2.8 t/cm^2.

Fig. 4 shows the dependences of pellet density and of density difference between pellet and compact on ADU-UO_2 content. The pellet density is lower for the AUC-UO_2 powder alone than for the ADU-UO_2 powder. The pellet density increases with increasing ADU-UO_2 content in the content range of about 50 wt%. Fig. 4 shows that the density difference between pellet and compact decreases at 5 wt% ADU-UO_2 and then linearly rises in accordance with the ADU-UO_2 content. It is generally agreed that pellet density increases with increasing compact density and/or compact densification. The difference of densities between pellet and compact may represent the extent of compact densification. It can be deduced that the increase in pellet density that occurs with the ADU-UO_2 content of less than 5 wt % is mainly ascribed to the increase in compact density. On the other hand, the increase in pellet density that occurs in the range of ADU-UO_2 content of 10 to 50 wt % may be mainly ascribed to the increase in compact densification.

Fig. 5 shows the variation of the open porosity of various UO_2 pellets made using AUC-UO_2 powder and powder mixtures. Compacts were pressed under the pressures of 2.0 to 3.5 t/cm^2 and then sintered at 1680℃ for 4 hours in hydrogen gas. The open porosity of the UO_2 pellet, which is made using AUC-UO_2 powder alone, decreases with increasing pellet density, especially enormously in the range of pellet density between 94.5 and 95 % TD. The open porosity of a pellet is reduced when the powder mixture of AUC-UO_2 and ADU-UO_2 is used.

UO_2 pellets absorb moisture through the open pores from environment during the period of handling and storage. Because the moisture of pellets may cause a hydriding failure of fuel cladding during the reactor operation, its content has to be kept as low as possible. It will be difficult to remove the moisture if the pellet has much open porosity. Since the open porosity of a pellet declines with pellet density, the open porosity is usually controlled to be below a certain value, for example, 1 % by the volume of a pellet, by increasing the pellet density. The value of

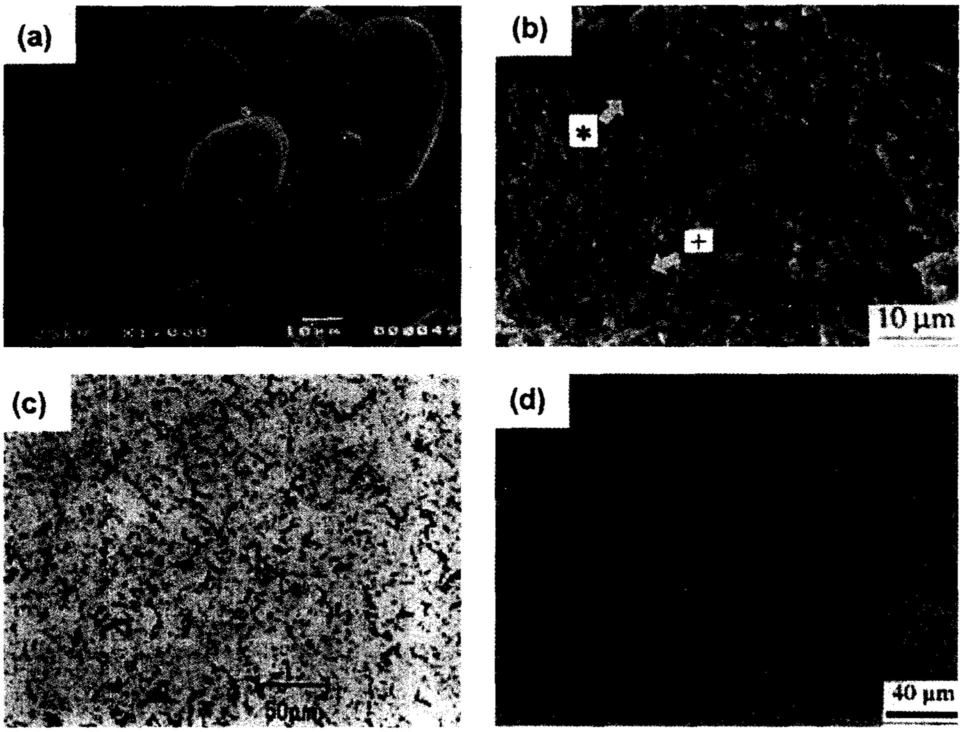

Fig. 6. Microstructures Associated with Intermediate Products in UO_2 Pellet Fabrication Using AUC-UO_2 Powder
(a) UO_2 powder, (b) compact, (c) partially sintered pellet, (d) sintered pellet
*** intact particle + deformed particle**

pellet density, above which the open porosity is lower than 1 % by volume, varies with powder types; about 95.0 % TD for the UO_2 pellet made using AUC-UO_2 powder and 94.5 % TD for the pellet made using the powder mixture. The mixing of ADU-UO_2 powder with AUC-UO_2 powder results in the reduction of open porosity, improving the pellet property.

Figs. 6(a), 6(b), 6(c), and 6(d) show the microstructure of intermediate products encountered in UO_2 pellet fabrication. Fig. 6(a) shows the typical morphology of AUC-UO_2 powder, and Fig. 6(b) shows the cross-section of a compact. Most of the AUC-UO_2 particles seems to remain almost intact in a compact, and interstices appear to be formed between particles. It can be inferred that the AUC-UO_2 particle is too strong to be broken or deformed notably during the process of pressing [6]. Figs. 6(c) and 6(d) show the microstructures of a partly sintered pellet and a final pellet, respectively. Long pore channels are present in a partly sintered pellet, and large ones of such pore channels remain as pores in a final pellet. The morphology of these pores may be a flake in three-dimension.

Figs. 7(a), 7(b), 7(c) and 7(d) show a series of schematic diagrams illustrating pore development, based on the findings in Fig. 6. Fig. 7(a) shows that there is a large interstice between particles in a compact. In the initial stage of sintering (see Fig.7(b)), individual AUC-UO_2 particles may sinter

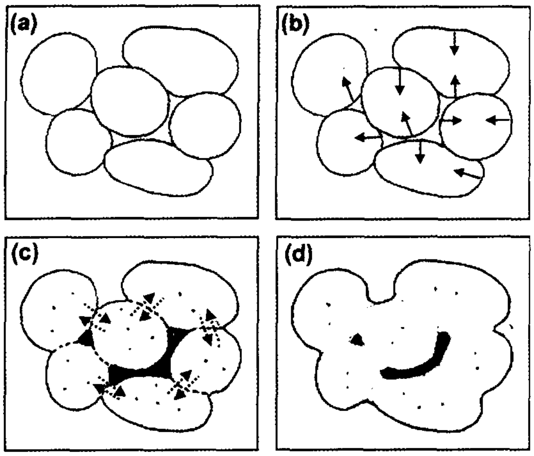

Fig. 7. A Series of Schematic Diagrams Illustrating Pore Development in the UO_2 Pellet Made of AUC-UO_2 Powder
(a) formation of an interstice between particles, (b) expansion of an interstice due to the primary self-shrinkage of particles, (c) sintering between particles, (d) formation of a flake-like pore

by themselves rather than one another since each of them has many open channels of about 0.1 ㎛-sized and these open channels are to shrink primarily. Thus particles shrink while the interstice between particles comes to expand. In the intermediate stage of sintering (see Fig.7(c)), the UO_2 particles may be sintered one another and the interstice starts to shrink. The interstice may not shrink completely because of its large size, and it becomes a flake-like pore in a pellet (see Fig. 7(d)). Therefore, it is proposed that the flake-like pore is originated from a large interstice between AUC-UO_2 particles and is formed by the primary self-shrinkage of individual AUC-UO_2 particles.

Figs. 8(a), 8(b) and 8(c) show the microstructures of UO_2 pellets made using AUC-UO_2 , mixture with 20% ADU-UO_2 , and ADU-UO_2 powders, respectively. The flake-like pores are less found in Fig. 8(b) than in Fig. 8(a), and

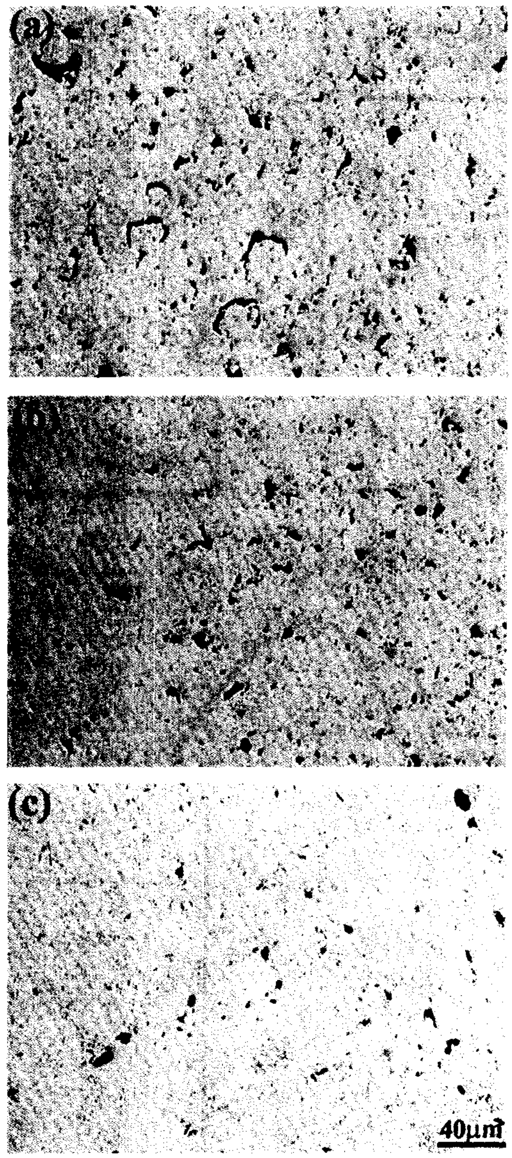

Fig. 8. Microstructures of the UO_2 Pellets Made from Various Powders
(a) AUC-UO_2 (b) powder mixture with 20 wt% ADU-UO_2 , (c) ADU-UO_2

they are scarcely found in Fig. 8(c). It can be readily seen from Fig. 8 (a) that the size of flake-like pores is large compared to that of round pores, so that it is expected that they are difficult to shrink during sintering. The formation of flake-

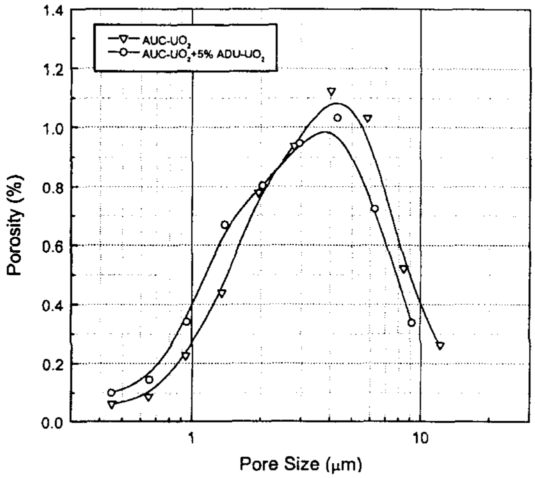

Fig. 9. Pore Size Distribution of UO_2 Pellets

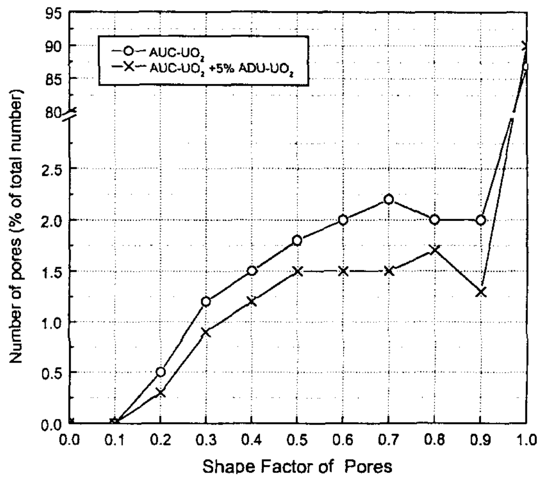

Fig. 10. Variations in the Number of Pores with Shape Factor

like pores may be the reason why the pellet made using AUC-UO_2 powder has a lower density than that made using ADU-UO_2 powder, in spite of a higher specific surface area.

Fig. 9 shows the pore size distribution for UO_2 pellets made using the AUC-UO_2 powder and the powder mixture with 5 wt % ADU-UO_2. The pores in the former pellet have a momomodal distribution, and its mode is about 4 μm. This size distribution is in good agreement with the other work [7]. It can be noticed that the pellet of AUC-UO_2 powder has a somewhat lower fraction of porosity in a range of pore size of 3 μm and has a larger fraction of porosity beyond that range than the pellet of the powder mixture with 5 wt% ADU-UO_2 .

Fig. 10 shows the relationship between the number of pores and the shape factor of pores. The pellet of AUC-UO_2 powder exhibits a larger fraction of the number of pores over shape factors of 0.2 to 0.9 than the pellet of the powder mixture with 5 wt % ADU-UO_2. The shape factors ranging from 0.2 to 0.4 are derived from the long flake-like pores such as those indicated by arrows in Fig. 6(d), and the shape factors ranging from 0.5 to 0.7 are derived from relatively short flake-like pores. Fig. 10 indicates that the flake-like pores are less formed in the pellet made from the powder mixtures. In the compact made of a powder mixtures AUC-UO_2 and ADU-UO_2 , small ADU-UO_2 particles may fill the interstices between AUC-UO_2 particles, so the interstices formed are less in number. Accordingly, relatively small quantities of flake-like pores are formed in the pellet made from the powder mixture after sintering.

Porosity consists of open and closed porosity. The open porosity of a pellet is representative of the total volume of pores connected to the pellet surface. A higher value of open porosity implies that the pores which are directly connected to the pellet surface extend longer into the interior of a pellet. Such morphology of open pores is scarcely observed in plane microstructure since it is possible that one really interconnected pore appears to be separated pores in plane microstructure. However, it is supposed that the possibility of such interconnection can be estimated from the pore shape in plane microstructure. Round pores probably have a very low possibility of the interconnection, but irregularly shaped pores such as cylinder and flake have a relatively high possibility. It can be inferred that the possibility of the interconnection between pores becomes higher as the shapes of pores deviate from roundness. It is reasonable to assume that the open porosity increases with increasing the number of interconnection between pores since the pores which are directly connected to the pellet surface can extend longer into the interior of the pellet. The pores which have low shape factor may be interconnected one another with a high possibility, providing a high open porosity for the UO_2 pellet made using AUC-UO_2 powder. Therefore, the reduction of open porosity in the UO_2 pellet made using the powder mixtures can be explained by the decrease in the number of flake-like pores.

4. Conclusions

The powder mixture composed of AUC-UO_2 and ADU-UO_2 powder has a bimodal size distribution with a large mode of 17.4 μm and a small one of 2.5 μm. The compact density of the powder mixture increases with increasing ADU-UO_2 content in the content range of 20 wt%, mainly because small particles (ADU-UO_2 powder) may fill interstices between large particles (AUC-UO_2 powder). The pellet density appears to increase mainly due to the increase in compact density in the range of 10 wt% ADU-UO_2 content and then appears to increase mainly due to the increase in compact densification in range of ADU-UO_2 content of 10 to 50 wt %.

It is proposed that a flake-like pore is formed at the interstice between AUC-UO_2 particles as a result of a primary self-shrinkage of individual AUC-UO_2 particles. In the compact of the powder mixture, small particles (ADU-UO_2) may fill the interstice between large particles (AUC-UO_2), and eventually the flake-like pores formed in a pellet are less in number.

The UO_2 pellet made using the powder mixture has a lower open porosity than that made using AUC-UO_2 powder. It is assumed that the pores which appear to be separated in plane microstructure can be really interconnected, and that the interconnection of pores increases the open porosity. The possibility of such interconnection may increase as the shapes of pores deviates from roundness. The reduction of open porosity in the pellet made using the powder mixture is mainly ascribed to the decrease in the number of flake-like pores, which have low shape factors.

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