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Grain size control of UO_2 pellets by adding heat-treated U_3O_8 particles to UO_2 powder

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Abstract

A method of controlling the grain size of UO_2 pellets was investigated by adding heat-treated U_3O_8 particles to UO_2 powder. The recycled U_3O_8 powder, which was made by oxidizing defective UO_2 pellets in air, was heat-treated at 1200–1500 °C in air and then divided into individual crystals. The U_3O_8 seed – product – consists of one or several crystals. The U_3O_8 seed was added to UO_2 powder, and the powder mixture was pressed and then sintered at 1700 °C in hydrogen gas. The grain size of seeded UO_2 pellets is dependent on the amount and size of the U_3O_8 seed. A seeded UO_2 pellet can have a grain size of 14 μm, while a conventional UO_2 pellet has a grain size of 8 μm. A mechanism for grain growth in seeded UO_2 is proposed and discussed.

1. Introduction

Uranium dioxide (UO_2) fuel pellets are widely used as nuclear fuel in light water reactors, and they are manufactured according to the following process [1]: UO_2 powder is mixed with lubricants and then pre-pressed into slugs, which are broken up into granules. Green pellets formed by pressing granules are sintered at about 1700–1780 °C in hydrogen-containing gas. Sintered UO_2 pellets are ground to meet the pellet diameter, and final UO_2 pellets are loaded into a cladding tube to fabricate a fuel rod.

In the above manufacturing process, defective UO_2 pellets which do not meet the fuel specifications of density and diameter may be produced. Defective UO_2 pellets should be reused in manufacturing new UO_2 pellets. It is a common recycling method that defective UO_2 pellets are oxidized in air at about 400 °C to make U_3O_8 powder and then added to UO_2 powder [1]. The mixture of UO_2 and U_3O_8 powders can be pressed and sintered in the same way as single UO_2 powder.

Because the recycled U_3O_8 powder has very low sintering activity compared to the UO_2 powder, it tends to decrease the density of UO_2 pellets. Other pellet properties such as grain size and open porosity are a little degraded by the addition of the U_3O_8 powder. So the amount of the recycled U_3O_8 powder is generally not higher than 10 wt% in UO_2 powder. However, the U_3O_8 powder has an advantage of improving the strength of green pellets, so its addition reduces the chipping of green pellets during handling and the end-capping of sintered pellets.

There has been a series of work to deal with the heat-treatments of the recycled U_3O_8 powder in order to improve its sintering activity [2]. The U_3O_8 powder is reduced to UO_2 powder, which is then further oxidized and reduced several times. The heat-treatment temperatures are kept as low as possible – below about 400 °C – not to decrease the specific surface area. The final recycled powder has a relatively high sintering activity.

Recently, Song and co-workers [3,4] have reported that a large amount of the recycled U_3O_8 powder can be directly reused without a density drop in sintering UO_2 pellets. They used the sintering additives such as Nb_2O_5

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and TiO_2 to enhance the sintered density of green pellets of UO_2 and U_3O_8 powders.

This paper mainly deals with high-temperature heat-treatments of the recycled U_3O_8 powder and mechanical treatments. This paper also describes the property of UO_2 pellets fabricated by adding the heat-treated U_3O_8 particles to UO_2 powder. It is found that the grain size of UO_2 pellets is significantly increased by the addition of the treated U_3O_8 particles. A mechanism associated with the grain growth is proposed, and a role of the heat-treated U_3O_8 particles is discussed.

2. Experimental

U_3O_8 powder was prepared by heating defective UO_2 pellets in air at 400 °C for 4 h and then by passing through a 200 mesh sieve to remove large agglomerates. During the oxidation defective UO_2 pellets were spontaneously pulverized to U_3O_8 powder because the lattice volume of U_3O_8 is about 30% larger than that of UO_2. The U_3O_8 powder was examined in size and morphology by the laser scattering method and scanning electron microscopy, respectively. This U_3O_8 powder has an average size of 7.5 μm and a BET surface area of 0.5 m^2/g.

The U_3O_8 powder was put in a tray and then heat-treated for 4 h in air at 1000–1500 °C. It was found that the heat-treatments made a crystallite (crystal) growth and additionally made U_3O_8 particles bond together. Heat-treated U_3O_8 particles lost very much their sintering activity, needing a size reduction for reuse in sintering new UO_2 pellets. Heat-treated U_3O_8 particles were mechanically divided to smaller sized particles. A heat-treated particle consisted of many crystals, so the dividing actually means a decrease in the number of crystals per particle. The dividing operation was tried to get particles that contain a minimum number of crystals. Various types of heat-treated and divided U_3O_8 particles were produced, and these are referred to as 'U_3O_8 seeds' in this paper.

Various quantities of U_3O_8 seeds were added to the UO_2 powder, which was produced through the ammonium diuranate (ADU) process. Pore former (azodicarbonamide) and lubricant (zinc stearate) were also added, and powder mixtures were mixed with a tumbling mixer. The powder mixture was granulated and then pressed into green pellets at 300 MPa. The green pellets were sintered at 1700 °C for 4 h in flowing hydrogen gas.

The sintered density of UO_2 pellets was measured by the water immersion method. The pellets were sectioned axially, ground and polished. The polished pellets were thermally etched at 1250 °C in carbon dioxide gas in order to examine grain boundaries. The grain size was determined by the linear intercept method. The pore size distribution was analyzed quantitatively with the software Image Pro. About 10 000 pores were counted for each specimen, and every pore was characterized two-dimensionally in its area. The pore size was assumed to be the same as the equivalent diameter of a pore, which was defined by the equation

$$\text{Equivalent diameter} = 2\sqrt{(\text{area}/\pi)}.$$

The UO_2 pellets were resinterd at 1700 °C for 24 h in hydrogen gas. The density increment was determined by measuring densities before and after the resintering test.

3. Results

3.1. Preparation of U_3O_8 seeds

Fig. 1 shows the SEM morphology of the U_3O_8 powder. The powder is angular in shape and many cracks develop on the surface. The oxidation of UO_2 to U_3O_8 involves so large stress build-up that bulky UO_2 pellets are converted to fine U_3O_8 powder which has many cracks. This U_3O_8 powder has a size distribution ranging from 1 to 50 μm (see Fig. 2). The average size determined by the largest volume frequency is around 7.5 μm.

When the U_3O_8 powder was heat-treated at 1200–1500 °C for 4 h in air, the crystals constituting a U_3O_8 particle increased in size remarkably with temperature. The crystals had a polyhedron shape and seemed to be bonded with each other only through a neck or several faces. These U_3O_8 particles were divided into individual crystals, and the products (U_3O_8 seed A to D) are shown in Fig. 3(a)–(d). The U_3O_8 seeds A, B, C and D are derived from the U_3O_8 particles which were heat-treated at 1200, 1300, 1400 and 1500 °C, respectively. The division mainly occurred between crystals, so the U_3O_8 seeds consist of one or several crystals. One exception is the U_3O_8 seed in Fig. 3(a); the seed A consists of many crystals because the crystals were so strongly bonded that they were difficult to divide. The average sizes of the

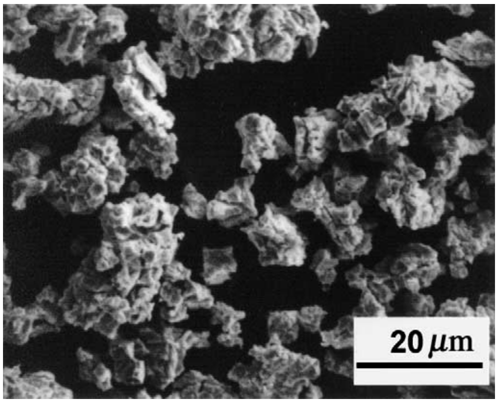

Fig. 1. SEM morphology of U_3O_8 powder.

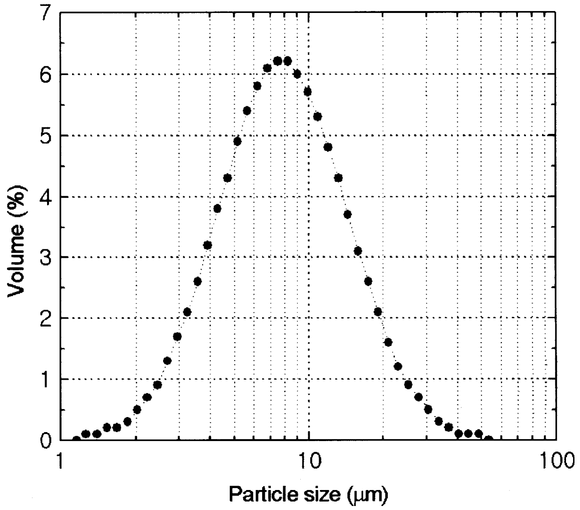

Fig. 2. Size distribution of U_3O_8 powder.

U_3O_8 seeds A, B, C and D are 8.0, 8.2, 16.5 and 28.0 μm, respectively.

In addition, U_3O_8 seeds having a variety of sizes are prepared by dividing the 1300 °C heat-treated U_3O_8 particles into various sized seeds. The average sizes of these U_3O_8 seeds are 3.1, 4.2, 5.2 7.2, and 11.6 μm, and these seeds are referred to as the 'seed E' to 'I', respectively. Fig. 4 shows the size distributions of the U_3O_8 seed E to I. Each U_3O_8 seed has a wide range of size distribution, with the average size placed at the center of the range. It can be inferred from Fig. 3(b) that the one crystal size is about 8 μm after the heat-treatment at 1300 °C, and this crystal size might be used as a criterion to determine how much portion of each U_3O_8 seed consists of one crystal. If one crystal size – 8 μm – is included in a size distribution range of a certain type of U_3O_8 seed, a portion smaller than this size might consist of one crystal but the remaining might consist of polycrystals. Fig. 4 indicates that each of the U_3O_8 seeds E to

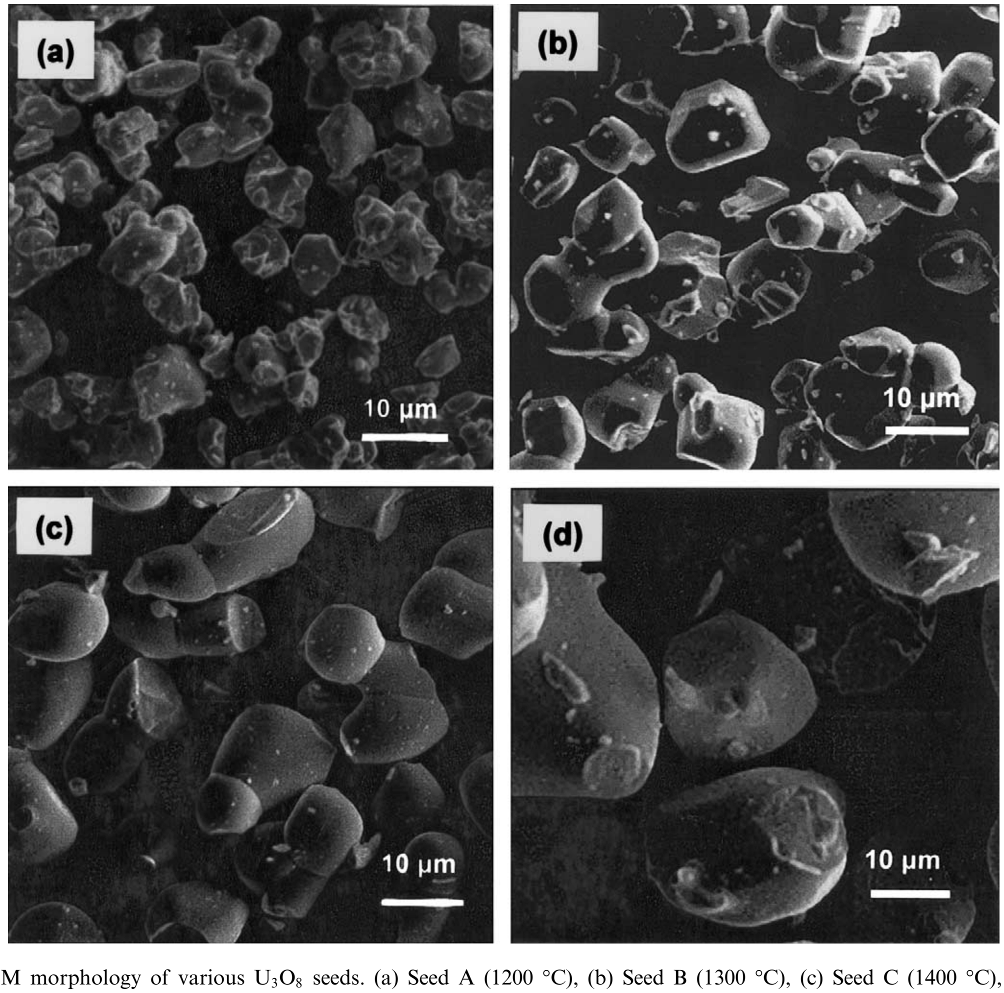

Fig. 3. SEM morphology of various U_3O_8 seeds. (a) Seed A (1200 °C), (b) Seed B (1300 °C), (c) Seed C (1400 °C), (d) Seed D (1500 °C).

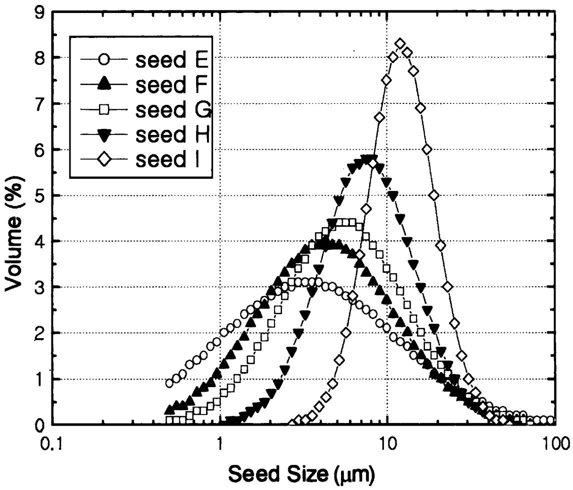

Fig. 4. Size distribution of U_3O_8 seed E to seed I.

I consists of both one crystal and poly-crystals, but the portion of one crystal increases with decreasing the average size of U_3O_8 seeds.

3.2. *Effects of U_3O_8 seeds on UO_2 pellet properties*

The U_3O_8 seeds (seed A, B, C, and D) are added in a quantity of 6 wt% to the UO_2 powder, and then sintered at 1700 °C for 4 h in hydrogen gas. The additions of the seeds A and B lead to an increase in grain size; 9.6 µm for the seed A and 12.0 µm for the seed B. Conventional UO_2 pellets produced in the same sintering condition without U_3O_8 seeds have a grain size of 8.0 µm. The seeds C and D do not increase the grain size. The UO_2 pellets to which the seeds B and C were added have the microstructures shown in Fig. 5(a) and (b), respectively. It can be seen that the microstructure is normal in Fig. 5(a) but abnormal in Fig. 5(b). Large and flake-like pores are formed on some grain boundaries in Fig. 5(b). These flake-like pores might be obstacles to grain boundary migration, so grain growth can be impeded. Of the four types of seeds, the seed B heat-treated at 1300 °C is most effective in increasing the grain size of UO_2 pellets.

The U_3O_8 seeds E to H, which were also heat-treated at 1300 °C and then divided into various sizes, were added in a quantity of 4 wt% and sintered at 1700 °C for 4 h in hydrogen gas. The relation between the grain size

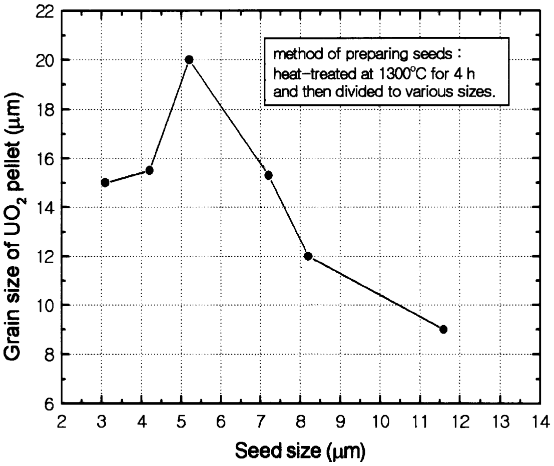

Fig. 6. Relation between the grain size of UO_2 pellets and seed size.

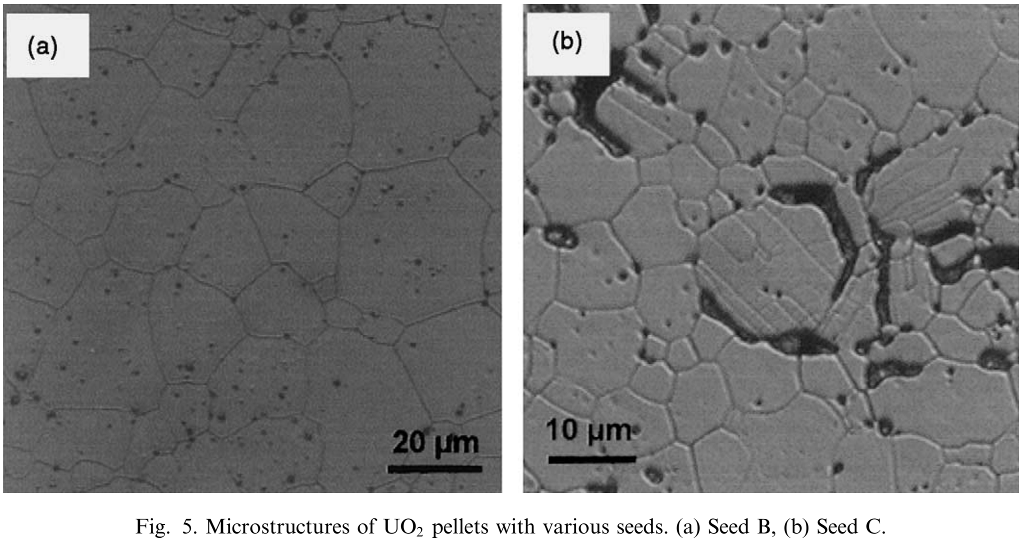

Fig. 5. Microstructures of UO_2 pellets with various seeds. (a) Seed B, (b) Seed C.

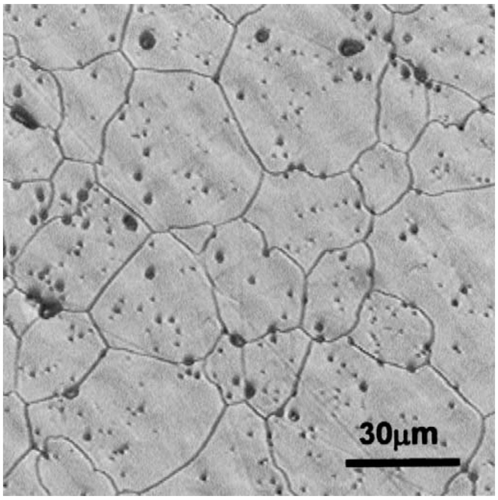

Fig. 7. Microstructure of the UO_2 pellet with seed G.

of UO_2 pellets and the U_3O_8 seed size – seeds E, F, G, H, B, I – is plotted in Fig. 6. The grain size increases gradually with the seed size and then reaches a maximum of 20 μm at the seed size of about 5 μm (seed G). The grain size tends to decline for the seeds larger than 5 μm. There is an optimum average size for seeds to enhance grain growth during the sintering of UO_2 pellets.

Fig. 7 shows the microstructure of the seeded UO_2 pellet with seed G. Fig. 7 indicates that many pores are isolated from the grain boundary, implying that grain boundary migration is so fast that pores hardly moved together with the boundary.

The relation between sintered density and seed content is plotted for the seeds E to I and for the untreated U_3O_8 powder in Fig. 8. The density of UO_2 pellets decreases linearly with the content of the U_3O_8 seeds and there are small variations in the decreasing rate depending on the seeds. The decreasing rate is about 1% TD per 8 wt% seed, and the decreasing rates for the U_3O_8 seeds are nearly the same as that for the untreated U_3O_8 powder.

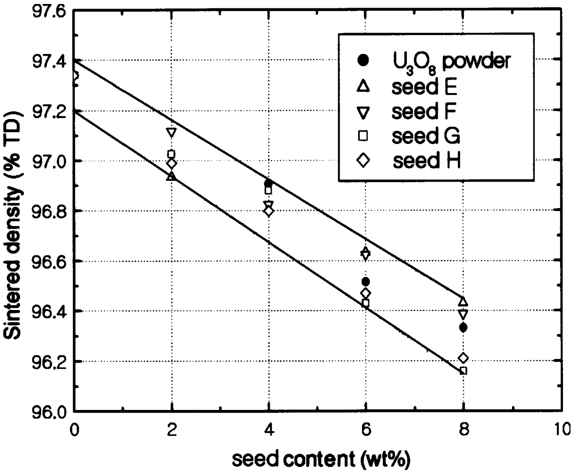

Fig. 8. Dependence of sintered density on seed content for various seeds.

Table 1
The grain size of UO_2 pellets for a variety of seed content

Seed content	0%	2%	3%	4%	6%
Grain size of UO_2 pellets (μm)	8.0	11.1	13.8	20	15.8

The grain size of seeded UO_2 pellets is influenced by the seed content. A relation between the grain size and the content of the seed G is shown in Table 1. The grain size of UO_2 pellets increases with the seed content up to 4 wt% and then decreases. Therefore, there is an optimum seed content to get a maximum grain size.

Pore former are usually used in UO_2 pellet fabrication. The seeded UO_2 pellet was fabricated by adding 0.3 wt% of pore former (azodicarbonamide) and 4 wt% of the seed G. For comparison, the conventional UO_2 pellet was fabricated by adding the same pore former. The microstructures of the conventional UO_2 pellet and the seeded UO_2 pellet are shown in Fig. 9(a) and (b), respectively. The grain size of the conventional UO_2 is 8 μm, independent of pore former. But the grain size of seeded UO_2 is decreased by the pore former: 14 μm with pore former and 20 μm without pore former. Large round pores derived from pore former might impede grain growth in seeded UO_2 pellets.

The pore size distribution is shown in Fig. 10 for the UO_2 pellets which have the microstructure shown in Fig. 9(a) and (b). The two pellets have nearly the same pore size distribution. The size distribution curve has two modes; one is between 1 and 2 μm and another is around 9 μm. The latter mode is due to the pore former.

The resintering test was performed at 1700 °C for 24 h in hydrogen gas. The density increment after the resintering test is 0.51 g/cm^3 for the conventional UO_2 pellet and 0.35 g/cm^3 for the seeded UO_2 pellet. The large pores derived from the pore former remain unaffected in both pellets, but small pores are annihilated to a larger extent in the conventional pellet than in the seeded UO_2 pellet. Densification (pore shrinkage) during the resintering test occurs through vacancy diffusion from pores to the grain boundaries. Because a larger grain size involves a longer diffusion length, the seeded UO_2 gets a smaller density increment during resintering than the conventional UO_2 pellet.

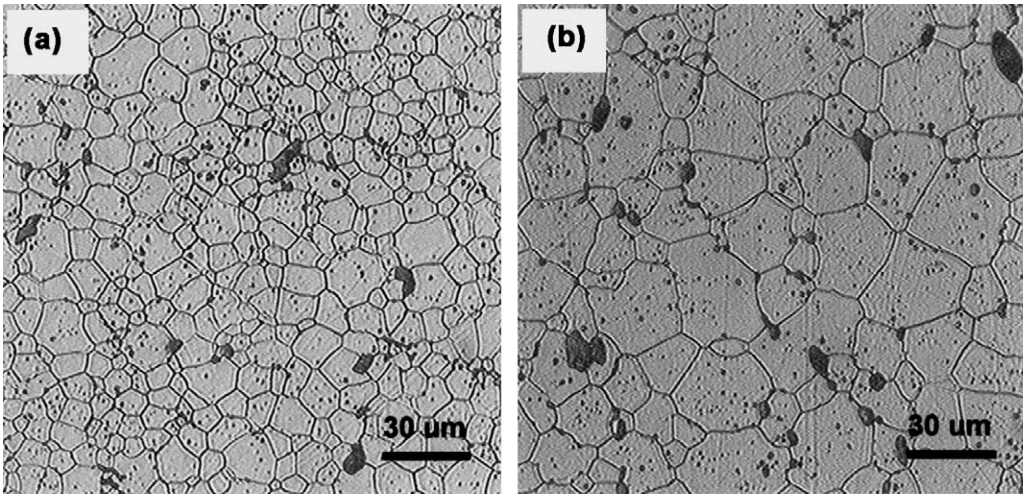

Fig. 9. Microstructures of conventional and seeded UO_2 pellets. (a) Conventional, (b) Seeded.

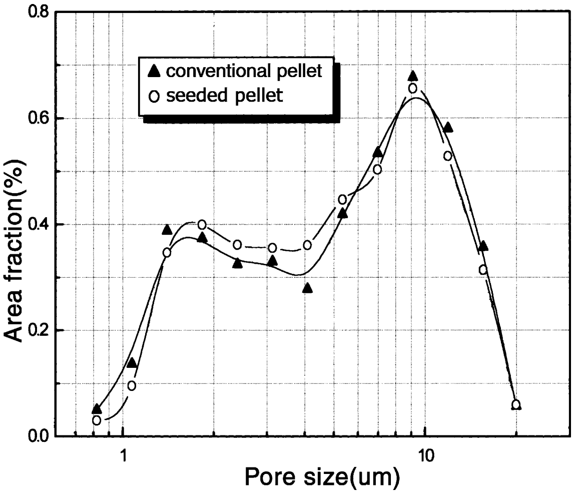

Fig. 10. Pore size distribution for conventional and seeded UO_2 pellets.

4. Discussion

The addition of U_3O_8 powder or seeds to UO_2 powder increases the O/U ratio of the green pellet. Uranium diffusion becomes faster with increasing O/U ratio [5], and thus densification and grain growth can be accelerated during the sintering of uranium oxides [6,7]. This effect of higher O/U ratio appears noticeably only in gas atmospheres that keep over-stoichiometric states at elevated temperatures – at least 1000 °C – during sintering. In hydrogen gas, however, the U_3O_8 powder contained in the green pellet reduces to UO_2 at about 600 °C during heating [8], and the produced steam is probably removed by the flowing hydrogen gas before reaching elevated temperatures. The addition of U_3O_8 to UO_2 powder is not likely to lead to an increase in O/U ratio at elevated temperature by hydrogen sintering, and it actually does not increase the sintered density and grain size of UO_2 pellets [1,4]. Therefore, the effect of U_3O_8 seed on grain growth is hardly associated with the change in O/U ratio of a green pellet.

Recently, Wood and Perkins [9] have reported that the addition of UO_2 seeds to UO_2 powder leads to large-grained UO_2 pellets by hydrogen sintering. Two types of UO_2 seeds – below 37 μm and between 37 and 53 μm – were prepared by crushing UO_2 pellets. They have mentioned that a UO_2 seed can act as a promoter for grain growth, without more detailed discussion.

In this work, the U_3O_8 seed leads to an increase in grain size but a decrease in sintered density during sintering in hydrogen gas (see Fig. 8 and Table 1). This result implies that the U_3O_8 seed does not increase transport rates such as uranium diffusion that can enhance both grain growth and densification. The U_3O_8 seed is likely to affect two types of material properties; one is unfavorable to densification and the other is favorable to grain growth. Regarding densification, the U_3O_8 seed has a very low surface area (sintering activity) compared to UO_2 powder, so it can bring a decrease in sintered density. Regarding grain growth, a role of the U_3O_8 seed can be understood in terms of the following mechanism.

A seeded green pellet consists of UO_2 particles, and additionally, a small amount of U_3O_8 seeds is uniformly dispersed in it. When this green pellet is heated in hydrogen gas, U_3O_8 seeds reduce to UO_2 seeds at about 600 °C and then the sintering between UO_2 and UO_2 particles occurs preferentially because of the high sintering activity. The sintering between a seed and its

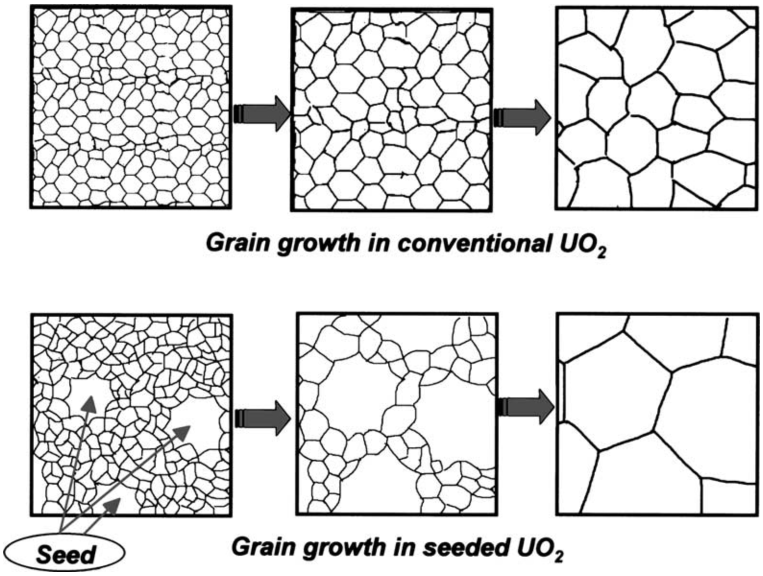

Fig. 11. Schematic diagram showing differences in grain growth between conventional and seeded UO_2 pellets during sintering.

surrounding UO_2 particles might start after the sintering between UO_2 and UO_2 particles progresses considerably. A partially sintered pellet might consist of both fine-grained matrix derived from UO_2 particles and large seed-grains imbedded in the fine grains. This microstructure is schematically shown in Fig. 11, together with a partially sintered UO_2 pellet without seeds.

According to Hillert [10], if a grain is larger than 1.8 times the average grain, it will grow abnormally at the expense of the surrounding grains. His theoretical prediction does not consider any material-dependent properties but grain boundary tension due to grain size difference. In Fig. 11, a balance of boundary tension between a large seed-grain and a fine-grain makes the grain boundary be curved toward the center of the seed-grain. This boundary can migrate rapidly into fine grains, and thus the seed-grain can grow fast by consuming the surrounding fine grains. The seed-grain can grow rapidly until it meet the neighboring seed grains which are also growing rapidly. If seeds are dispersed uniformly, the whole microstructure will have large and uniform grains. The seed can act as a site for fast grain growth.

The proposed mechanism for grain growth in seeded UO_2 can explain the experimental results about the relation between the grain size of UO_2 pellets and seed size. The size difference between a seed-grain and fine matrix-grains increases with increasing seed size. The larger this size difference, the more curved the boundary between a seed-grain and surrounding fine grains. Thus a growth rate of a seed-grain might accelerate in accordance with the seed size, and eventually, the grain size of seeded UO_2 pellets increases with the seed size. However, it is found that the flake-like pores are formed when the seed size is too large. These flake-like pores can act as obstacles to fast growth of seed grains. Therefore, there is an optimum seed size for the largest grain size.

The amount of seeds determines the number of sites for activating the fast grain growth. In principle, a seed-grain can grow up to the spacing between sites. If the sites are too many, the corresponding short distance between sites will produce small grains. If the sites are few, an inhomogeneous microstructure will be produced; some grains are very large but others are small. Therefore, a large and uniform grain size is achieved at an optimum content of seeds.

The formation of flake-like pores might be associated with both the reduction of U_3O_8 to UO_2 and low sintering activity of U_3O_8 seed. The U_3O_8 seed reduces to UO_2 during heating in a reducing gas, with its volume shrinking by about 30%. This reaction might produce a gap between a seed and its surrounding UO_2 particles in a green pellet. In addition, the preferential sintering between surrounding UO_2 particles expands a gap. A large U_3O_8 seed might provide a large gap, compared to a small seed. A small gap can shrink for the next period of sintering, but a large gap might remain or grow to be a flake-like pore.

5. Conclusions

The grain size of UO_2 pellets significantly increases when U_3O_8 seeds are added to UO_2 powder and then pressed and sintered at 1700 °C in hydrogen gas. The U_3O_8 seed which consists of one or several crystals is made by heat-treating the recycled U_3O_8 powder at 1300 °C and by dividing into individual crystals. The grain size of seeded UO_2 pellets is significantly dependent on the amount and size of the U_3O_8 seed. The largest grain size was achieved when the about 5 μm-sized seed was added in a quantity of 4 wt%. The grain size of seeded UO_2 pellets is 14 μm in the presence of pore former, while the grain size of conventional UO_2 pellets is 8 μm. The seeded UO_2 pellet is thermally more stable than the conventional UO_2 pellet because of the large grain size.

It is proposed that the U_3O_8 seed acts as a promoter for grain growth. If a green pellet, which consists of the matrix of UO_2 particles and a small amount of U_3O_8 seeds, is heated in hydrogen gas during sintering, a partially sintered UO_2 pellet might be obtained that large seed grains are uniformly imbedded in the fine-grained UO_2 matrix. For further sintering a big difference in size between a large seed-grain and surrounding fine grains makes the seed-grain grow rapidly by consuming the surrounding fine grains until it meets the neighboring seed grains which are also growing fast.

The above mechanism can explain well the experimental results about the effects of seed size and seed content on the grain size of seeded UO_2 pellets. Therefore, it can be concluded that the U_3O_8 seed activates fast grain growth during the sintering of UO_2.

Acknowledgements

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