

Microstructure Development during Sintering of Nb₂O₅-doped UO₂ pellets under H₂ and CO₂ atmospheres

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Nb₂O₅ 첨가 UO₂ pellet의 수소 분위기와 이산화탄소 분위기 소결 중 미세조직의 형성에 대한 연구

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Abstract

Microstructures of Nb₂O₅-doped UO₂ pellets have been investigated during sintering under H₂ and CO₂ atmospheres. Pellets are sintered at 1700°C in H₂ atmosphere and at 1300°C in CO₂ atmosphere for 1 to 41 hr. The addition of Nb₂O₅ causes the formation of large pores, which shrink to some extent in H₂ atmosphere but very little in CO₂. Fine pores in the Nb₂O₅-doped UO₂ pellet are almost annihilated when sintered under H₂ atmosphere but little changed under CO₂ atmosphere. The increase in grain size due to Nb₂O₅ addition is much larger in H₂ atmosphere than in CO₂. Thus the enhancement of uranium diffusion in UO₂ due to the Nb₂O₅ addition is thought to be more significant in H₂ atmosphere. Microstructures of Nb₂O₅-doped UO₂ pellets sintered in H₂ atmosphere are discussed from the viewpoint of in-reactor performance. Possible defects formation due to Nb₂O₅ addition is discussed to explain the enhancement of uranium diffusion in H₂ and CO₂ atmospheres.

요 약

Nb₂O₅가 첨가된 UO₂ 소결체의 미세조직을 수소와 이산화탄소 분위기에서 연구하였다. Pellet을 1700°C 수소분위기 그리고 1300°C 이산화탄소 분위기에서 1-41 시간 동안 소결하였다. Nb₂O₅를 첨가하면 큰 기공들이 형성되고, 이 기공들은 수소분위기에서는 어느정도 수축하지만 이산화탄소 분위기에서는 거의 소멸하지 않는다. 작은 기공들은 수소분위기에서는 거의 전부 소멸되며 이산화탄소 분위기에서는 거의 소멸하지 않는다. 그리고 결정립의 크기도 수소분위기에서 훨씬 증대한다. 따라서 Nb₂O₅ 첨가에 의한 우라늄 확산은 수소분위기에서 훨씬 증가하는 것으로 생각된다. 수소 분위기에서 소결한 Nb₂O₅ 첨가 UO₂ pellet의 미세조직을 노내성능의 관점에서 평가하였다. 우라늄 확산의 증가를 설명하기 위해서 Nb₂O₅ 첨가에 의해서 형성 가능한 결함들을 고찰하였다.

1. Introduction

UO₂ has widely been used as nuclear fuel in water reactors since it has good thermal stability and compatibility with water. Nuclear fuel performances have shown that the irradiation behavior of the UO₂ fuel pellet depends to a great extent on its microstructure [1]. In particular in-reactor densification is mainly dependent on pore size and its distribution [2, 3], and fission gas release during irradiation is influenced by grain size [4]. Pore size distribution was optimized with respect to in-reactor densification and should be controlled during the manufacturing of UO₂ fuel pellets.

The UO₂ fuel of large grain size is recognized as desirable especially in high burnup fuel since it can reduce the amount of fission gas released during irradiation [4]. With pure UO₂ powder, the large-grained fuel can be achieved under the sintering condition of higher temperature and longer time [5, 6]. Thus the addition of various elements into UO₂ has been attempted as a way to attain large-grained UO₂ pellets, without having deleterious effects on sintering temperature and time.

Effects of some additives on grain growth and densification have been widely studied. The oxides of niobium [7, 8] and titanium [9, 10] are known to increase grain size, whereas the effect of vanadium oxide are controversial; decreasing [11] or increasing [7] the grain size. The Nb₂O₅-doped UO₂ has been studied to a relatively large extent because it has the grain size of an order of magnitude larger than pure UO₂. Thermal creep [12, 13], electrical conductivity [14, 15], and defect structure [15] of Nb₂O₅-doped UO₂ have been reported. However, pore structure has little been studied although it can probably be affected by the Nb₂O₅ addition, and most of the works on Nb₂O₅-doped UO₂ have been carried out in H₂ atmosphere.

It is known that UO₂ pellets are properly sintered even at temperatures of 1100–1300°C under CO₂ atmosphere due to faster uranium diffusion [16, 17].

In an oxidizing atmosphere, predominant defects are oxygen interstitials, which can influence defects to be formed in Nb₂O₅-doped UO₂. Thus densification and grain growth in oxidizing atmosphere are expected to be different from those in reducing atmosphere.

The aim of the present work is to study effects of Nb₂O₅ addition on pore and grain structures in CO₂ and H₂ sintering atmospheres. Possible defects to be formed in both atmospheres are discussed.

2. Experimental

The UO₂ powder used in this work was produced via the ADU (Ammonium Diuranate) process. The impurities of UO₂ powder were analyzed spectroscopically, and results are listed in Table 1. The O/U ratio of UO₂ powder was 2.16, which was determined by the weight gain during the oxidation of UO₂ to U₃O₈. The 0.5mol% Nb in the form of Nb₂O₅ powder was added into UO₂ powder. Particle size distribution was measured by the laser light scattering method. The mean particle size of Nb₂O₅ powder determined by 50% volume fraction was 25.3μm, which was quite larger than that of UO₂ powder (0.9μm). The mixed powder of UO₂ and Nb₂O₅ was ball-milled for 90min, and pure UO₂ powder was also ball-milled in the same condition. The particle size is expected to be reduced by the ball-milling. In addition, the ball-milling treatment increased the O/U ratio of pure UO₂ powder from 2.16 to 2.18.

Table 1. Impurities of UO₂ Powder

| Element | Content (μg/gU) | Element | Content (μg/gU) |
|---------|-----------------|---------|-----------------|
| Al | < 10 | B | < 0.2 |
| C | 90 | Ca | < 20 |
| Cd | < 0.2 | Cr | < 10 |
| Cu | < 10 | Dy | < 0.1 |
| F | < 2 | Fe | < 50 |
| Gd | < 0.1 | Mg | < 10 |
| Mn | < 5 | Mo | < 1 |
| Ni | < 10 | Si | < 10 |
| Th | < 200 | | |

Powders were pressed to a green density of 5.30 g/cm³ with die-wall lubrication. This work includes two sintering conditions: (1) Green pellets were sintered at 1700°C for 1, 5, 9, 21 and 41 hrs under H₂ atmosphere in a box furnace whose heating element is tungsten. The chamber was evacuated and then hydrogen gas was flown. (2) sintered at 1300°C for 1, 5, 9, 21 and 41 hrs under CO₂ atmosphere in a tube furnace which are wound Super Kanthal. The interior of tube was purged with argon gas for 20min and then CO₂ gas was flown. The former sintering temperature and atmosphere is a typical manufacturing condition of UO₂ fuel pellets, while the latter sintering temperature and atmosphere is the same as the low temperature sintering (NIKUSI process) condition as described elsewhere [16]. The pellets sintered in CO₂ atmosphere were reduced at 1300°C for 1 hr in H₂.

The density of pellets was measured by the water immersion method. Pellets were longitudinally sectioned, ground and polished. In order to disclose grain boundaries, thermal etching was carried out at 1250°C for 1 h under CO₂ atmosphere for Nb₂O₅-doped UO₂ pellets and at 1300°C under CO₂ for pure UO₂, respectively. The grain size was determined by the conventional linear intercept method.

3. Results and Discussion

Fig. 1 shows the densities of pure and Nb₂O₅-doped UO₂ pellets sintered for various lengths of time under H₂ and CO₂ atmospheres. The density of the pure UO₂ pellet sintered for 1 hr in H₂ atmosphere is about 10.60 g/cm³ and increases up to 10.78 g/cm³ with sintering time. The density of Nb₂O₅-doped UO₂ pellet sintered for 1 hr in H₂ atmosphere is quite low (10.25 g/cm³) since the Nb₂O₅ particles were not completely dissolved. However, the density of Nb₂O₅-doped UO₂ pellets increases to 10.70 g/cm³ in 5 hr and remains almost constant for further sintering.

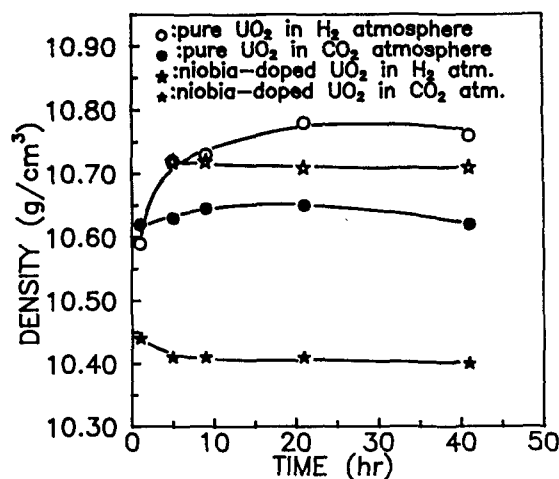


Fig. 1. Variations in Sintered Density of Pure and Nb₂O₅-doped UO₂ Pellets During Sintering at 1700°C Under H₂ and at 1300°C Under CO₂.

The density of pure UO₂ pellets sintered in CO₂ is higher by about 0.2 g/cm³ than that of the Nb₂O₅-doped UO₂ pellet sintered in the same condition. The density of pure UO₂ pellets increases slightly with time in CO₂ atmosphere, but the density of Nb₂O₅-doped UO₂ pellets decreases with time. It was found that the Nb₂O₅ addition decreased the pellet density to a larger extent in CO₂ atmosphere than in H₂.

The pore structures of Nb₂O₅-doped UO₂ pellets sintered at 1700°C in H₂ atmosphere for 1 hr and sintered at 1300°C in CO₂ are shown in Figs. 2(a) and 2(b), respectively. The pore structures of pure UO₂ pellets sintered at 1700°C in H₂ for 1 hr and sintered at 1300°C in CO₂ are shown in Figs. 2(c) and 2(d), respectively. Some large Nb₂O₅ particles were not completely dissolved in H₂ atmosphere (indicated by arrows in Fig. 2(a)). The microstructure obtained in CO₂ atmosphere does not show any evidence of such Nb₂O₅ particles (Fig. 2(b)). As the pore structures of Nb₂O₅-doped UO₂ pellets are compared to those of pure UO₂ pellets, it seems that large pores of 10 to 50 μm were formed due to Nb₂O₅

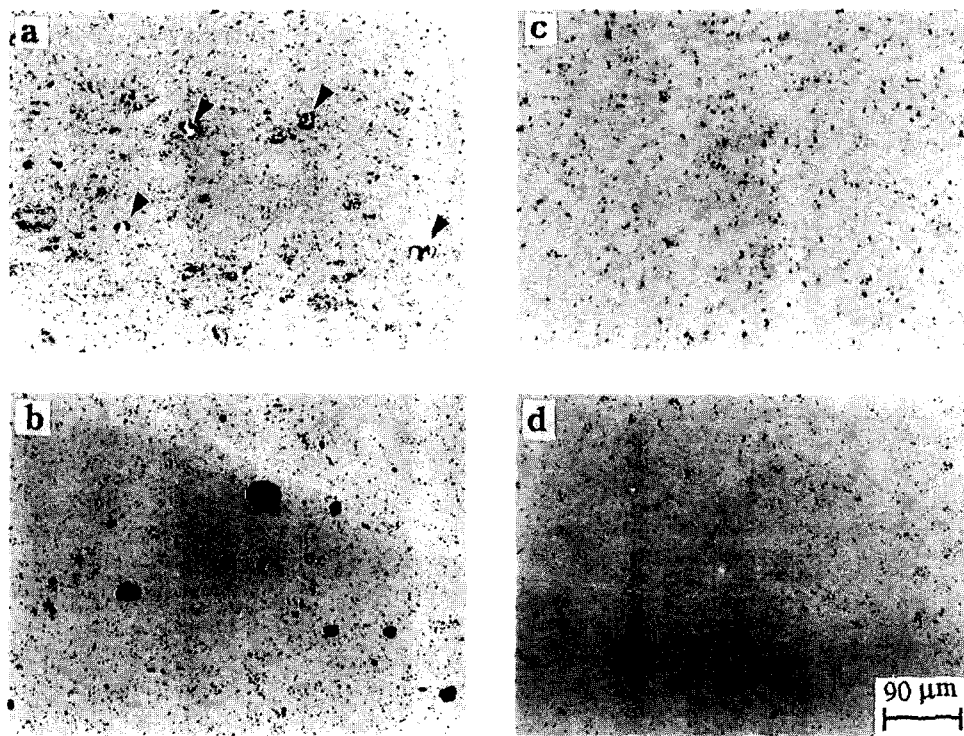


Fig. 2. Pore Structures of UO₂ Pellets Sintered for 1hr Under the Conditions; (a) Nb₂O₅-Doped, at 1700°C in H₂, (b) Nb₂O₅-Doped, at 1300°C in CO₂, (c) Pure, at 1700°C in H₂, (d) Pure, at 1300°C in CO₂. Arrows in Fig. 2(a) Indicate Nb₂O₅ Particles Which are not Completely Dissolved.

addition. Fig. 2(a) shows that periphery of large Nb₂O₅ particles were partially changed into pores. So it can be inferred that niobium ions diffuse into UO₂ lattice faster than the reverse diffusion of uranium ions, and in this connection large pores are probably formed at original sites of Nb₂O₅ particles by means of Kirkendall effect.

Figs. 3(a) and 3(b) show the pore structures of the Nb₂O₅-doped UO₂ pellets sintered at 1700°C in H₂ atmosphere for 5 and 41hr, respectively. Nb₂O₅ particles were dissolved and fine pores annihilated after 5hr. As sintering time increases, large pores seem to shrink a little in H₂ atmosphere. Figs. 3(c) and 3(d) show the pore structures of pure UO₂ pellets sintered at 1700°C in H₂ atmosphere for 5 and 41hr, respectively. As the pore structure of Nb₂O₅-doped UO₂ pellets is compared to that of

pure UO₂ pellets, the Nb₂O₅-doped UO₂ pellet has fine pores much less than pure UO₂ pellet. It is supposed that the Nb₂O₅ addition enhances significantly pore shrinkage in H₂ atmosphere and thus enhances the diffusion of cation vacancy.

Figs. 4(a) and 4(b) show pore structures of the Nb₂O₅-doped UO₂ pellets sintered at 1300°C in CO₂ atmosphere for 21 and 41hr, respectively. As sintering time elapsed, large pores shrank negligibly and fine pores also remained intact in CO₂ atmosphere. Figs. 4(c) and 4(d) show pore structures of the pure UO₂ pellets sintered at 1300°C in CO₂ atmosphere for 21 and 41hr, respectively. The pore structures of Nb₂O₅-doped and pure UO₂ pellets seem to be similar except for large pores. The Nb₂O₅ addition in CO₂ atmosphere is supposed to enhance pore shrinkage negligibly, contrasting with that in H₂ at-

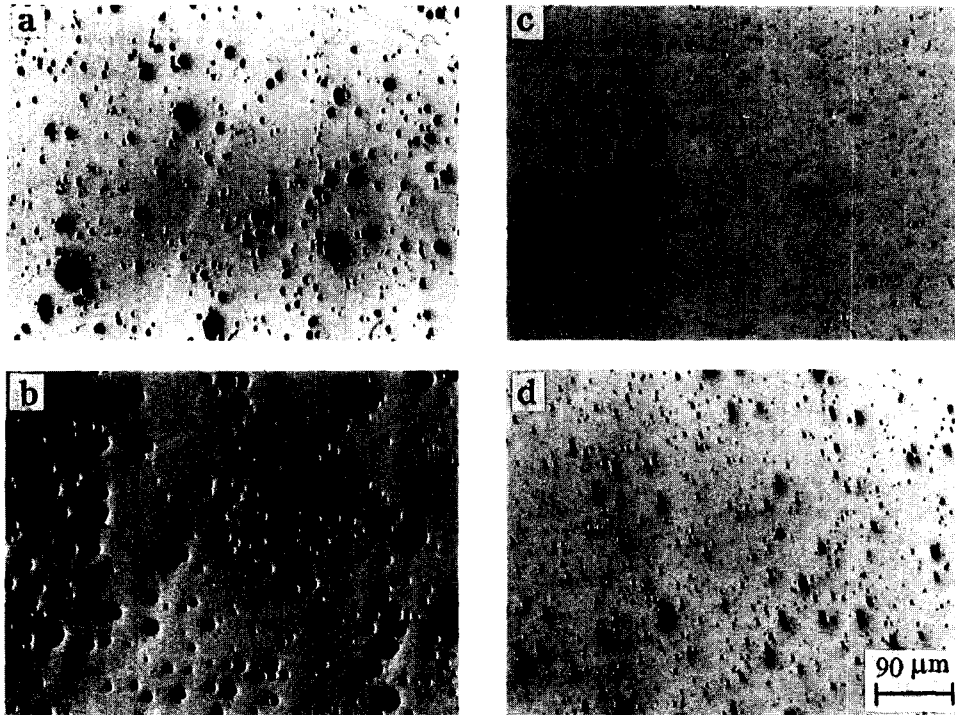


Fig. 3. Pore Structures of UO_2 Pellets Sintered at 1700°C in H_2 Under the Conditions; (a) Nb_2O_5 -doped, 5hr, (b) Nb_2O_5 -Doped, 41hr, (c) Pure, 5hr, (d) Pure, 41hr.

mosphere.

Based on the above-mentioned pore structures, we can understand the density decrease due to Nb_2O_5 addition shown in Fig. 1. The large pores formed in the Nb_2O_5 -doped UO_2 pellets are likely to be the main reason for the density decrease. The magnitude of density decrease is smaller in H_2 atmosphere than in CO_2 , since the annihilation of fine pores in the Nb_2O_5 -doped pellet sintered in H_2 atmosphere probably compensates for the density decrease which would be caused by the formation of large pores.

Table 2 lists the grain sizes of pure and Nb_2O_5 -doped UO_2 pellets sintered for various lengths of time in H_2 and CO_2 atmospheres. The Nb_2O_5 addition increases the grain size by an order of magnitude in H_2 atmosphere ($68\mu\text{m}$ in 5hr and $102\mu\text{m}$ in 41hr) but increases a little in CO_2 atmosphere. The

Table 2. Grain Sizes of the Pure and the Nb_2O_5 -doped UO_2 Pellets Sintered in H_2 and CO_2 Atmospheres

| Time (hr) | Pure UO_2 pellet | | Nb_2O_5 -doped UO_2 pellet | |
|-----------|---------------------------|--------------------|---|--------------------|
| | H_2 atm. | CO_2 atm. | H_2 atm. | CO_2 atm. |
| 1 | 4.2* | 5.6 | 4.8 | 10.3 |
| 5 | 8.4 | 6.1 | 67.9 | 13.9 |
| 9 | 10.6 | 6.5 | 75.7 | 14.0 |
| 21 | 12.3 | 7.6 | 96.5 | 15.1 |
| 41 | 15.8 | 8.3 | 102.3 | 15.1 |

*: The unit of grain size is μm .

enhancing effect of Nb_2O_5 addition on grain size has been well known in H_2 atmosphere [7] but scarcely published in CO_2 atmosphere.

Grain structures of pure UO_2 pellets sintered for 5hr in H_2 and CO_2 atmosphere are shown in Figs. 5 (a) and 5(b), respectively, and those of Nb_2O_5 -

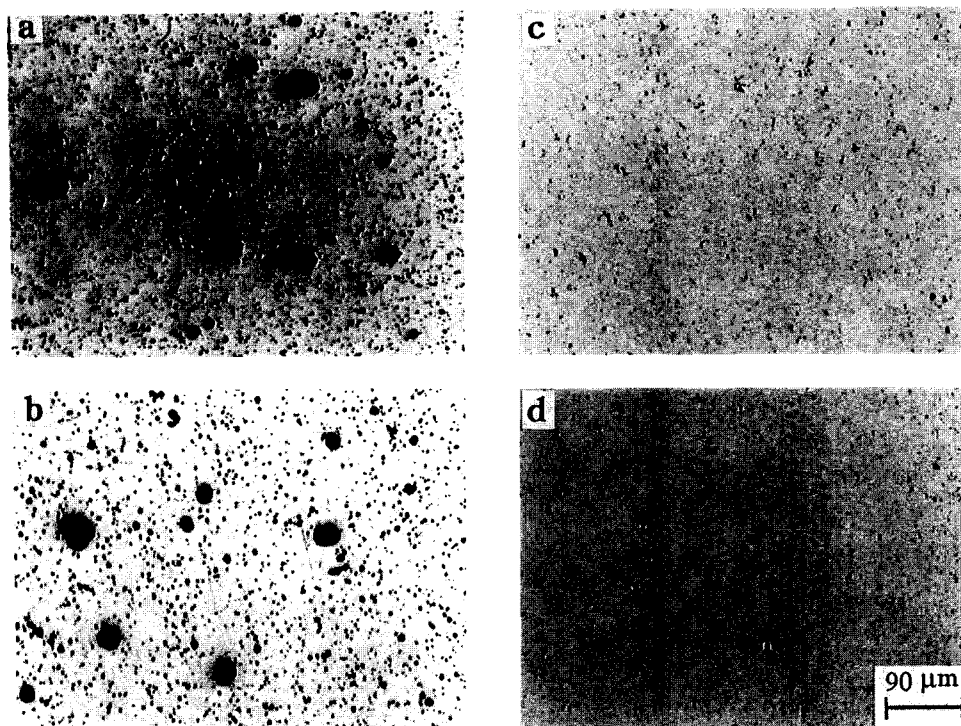


Fig. 4. Pore Structures of UO₂ Pellets Sintered at 1300°C in CO₂ Under the Conditions; (a) Nb₂O₅-doped, 21hr, (b) Nb₂O₅-Doped, 41hr, (c) Pure, 21hr, (d) Pure, 41hr.

doped UO₂ pellets in Figs. 5(c) and 5(d). A common grain structure was observed in all pellets, but it can be seen that pores separated from grain boundaries are prevalent in Fig. 5(c). Such separation indicates that grain boundaries migrated so fast that pores could not catch up with it. On the assumption that pore mobility is controlled by the evaporation and condensation [18], it can be inferred that the Nb₂O₅ addition can enhance to a great extent the uranium diffusion for grain boundary migration but enhance to a relatively negligible extent the evaporation and condensation.

It is known that pores smaller than about 1 μm are unstable to in-reactor densification [2, 3]. Thus the pore structure of Nb₂O₅-doped UO₂ pellets sintered in H₂ seems to be stable to in-reactor densification. The large grain size reduces the release of fission

gas. Moreover, intragranular pores which are to trap fission gas can decrease the amount of fission gas diffusing to a grain boundary. Consequently the intragranular pores are able to decrease the release of fission gas, differently from intergranular pores. It can tentatively be concluded that the microstructure of Nb₂O₅-doped UO₂ pellets sintered in H₂ has beneficial features with respect to in-reactor densification and fission gas release in comparison to that of pure UO₂ pellets.

Grain growth can generally be formulated as follows:

$$G^n - G_0^n = kt, \quad (1)$$

where G_0 is the initial grain size, G the grain size after the elapse of time, t the time, n and k constants. If it is assumed that initial grain size is

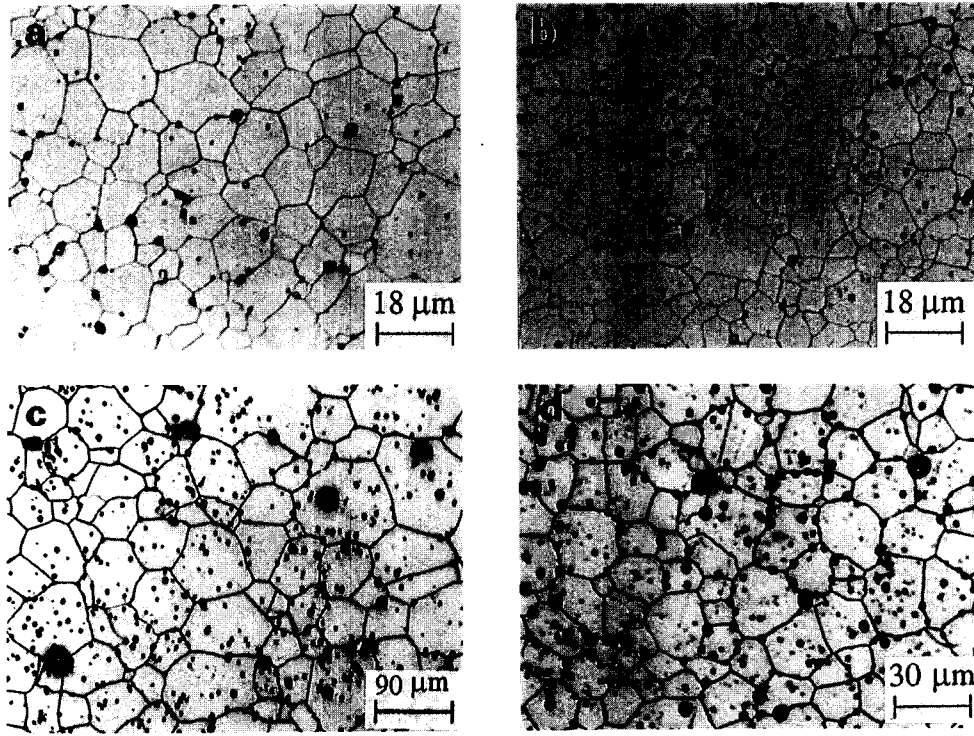


Fig. 5. Grain Structures of UO_2 Pellets; (a) Pure, Sintered at 1700°C in H_2 for 5hr, (b) Pure, Sintered at 1300°C in CO_2 for 5hr, (c) Nb_2O_5 -doped, Sintered at 1700°C in H_2 for 5hr, (d) Nb_2O_5 -doped, Sintered at 1300°C in CO_2 for 5hr.

sufficiently small compared with G , Eq. (1) can be approximated as;

$$G^n = kt. \quad (2)$$

The exponent, n , is known to be the key parameter to predict the dominant mechanism of grain growth. According to Nichols [18], when grain growth is controlled by pore mobility the exponents 3, 4, and 5 are the indicative of the mechanism of vapor transport, volume diffusion and surface diffusion, respectively.

The plots between $\log(\text{grain size})$ and $\log(\text{time})$ are shown in Fig. 6. Linear relationships are fitted, whose slopes are also included in Fig. 6. The slope,

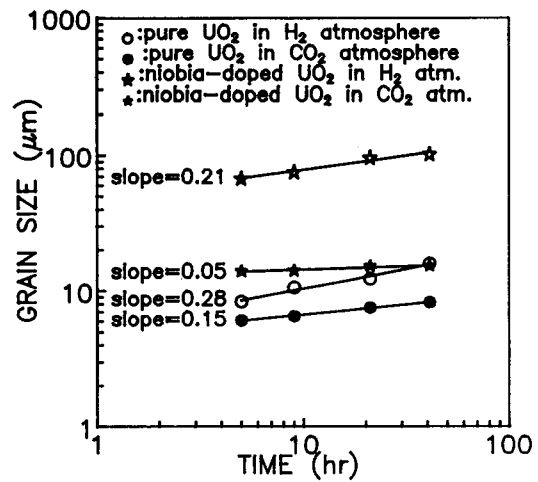


Fig. 6. Logarithmic Plot of Grain Size Versus Time.

$1/n$, of 0.28 for the pure UO₂ pellet in H₂ atmosphere is in agreement with the vapor transport ($n=3$) [18] or the volume diffusion ($n=4$) [19]. The slope of 0.21 was determined for the Nb₂O₅-doped UO₂ pellet in H₂ atmosphere. However, it should be noted that this slope is probably not resulting from the surface diffusion mechanism, because most pores are detached from grain boundaries (see Fig. 5(c)) and thus migration of grain boundaries is little controlled by pore mobility.

Main experimental results are that fine pores are annihilated and grain size is increased by the Nb₂O₅ addition, suggesting enhanced uranium diffusion. The effect of the Nb₂O₅ addition is much larger in H₂ atmosphere than in CO₂. It is generally agreed that the enhancement of uranium diffusion is attributed to the formation of defects in UO₂ lattice due to the Nb₂O₅ addition.

It is supposed that possible defects to be formed can vary in accordance with atmospheres. Nb ions are present as Nb⁴⁺ under H₂ atmosphere [10] which is the typical sintering condition of UO₂ fuel pellets. If Nb⁴⁺ ions substitute U⁴⁺ ions, any extrinsic defects shall not be formed. Consequently enhancement of uranium diffusion would not be expected, which can not explain the experimental results. Recently, interstitial penetration of Nb ion was assumed by Radford and Pope [7]. In fact, the body-centered sites in oxygen sub-lattices of the UO₂ lattice are only half-filled by uranium ions so that a number of interstitial sites are available. When Nb⁴⁺ ions enter into UO₂ lattice interstitially under H₂ atmosphere, uranium vacancies can be formed in order to maintain electrical neutrality. The increase in the concentration of uranium vacancies gives rise to the increase in uranium diffusion coefficient, being in good agreement with the results in H₂ atmosphere. Therefore, it may be concluded that Nb ions enter interstitially into UO₂ lattice under reducing atmosphere.

Nb ions exist as Nb⁵⁺ under oxidizing atmosphere where oxygen interstitials can be easily formed in UO₂ lattice. Matsui and Naito [15] showed that Nb₂O₅-doped UO₂ had higher O/M ratio under the oxygen partial pressure above 10⁻¹⁵ Pa than pure UO₂. The authors [20] proposed that Nb⁵⁺ ions entered interstitially into UO₂ lattice under CO₂ atmosphere and oxygen interstitials were formed for charge compensation. Since both Frenkel and Schottky defects are present simultaneously, the formation of oxygen interstitials should decrease the concentration of oxygen vacancies, thereby increasing the concentration of uranium vacancies through Schottky equilibrium. The increase in the concentration of uranium vacancies leads to the increase in uranium diffusion coefficient and thus enhances grain growth. This can explain the enhancement of grain growth due to Nb₂O₅ addition in CO₂ atmosphere.

4. Conclusions

Microstructure development in UO₂ pellets is influenced by Nb₂O₅ addition and a sintering atmosphere. Pores larger than 10 μm seem to be formed at original sites of Nb₂O₅ particles. Such pores shrink to some extent in H₂ atmosphere but to a negligible extent in CO₂ atmosphere. Particularly in the Nb₂O₅-doped UO₂ pellet sintered under H₂ atmosphere, fine pores are annihilated and most pores are isolated within grains. The grain size of Nb₂O₅-doped UO₂ pellet sintered in H₂ atmosphere is larger than 60 μm. It is thought that the Nb₂O₅ addition enhances uranium diffusion very much in H₂ atmosphere but a little in CO₂. It can tentatively be concluded the microstructure of the Nb₂O₅-doped UO₂ pellet sintered in H₂ atmosphere has advantages over the pure UO₂ fuel pellet from the viewpoint of in-reactor densification and fission gas release.

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