



Sintering of mixed UO_2 and U_3O_8 powder compacts

Kun Woo Song*, Keon Sik Kim, Young Min Kim, Youn Ho Jung

Advanced LWR Fuel Development, Korea Atomic Energy Research Institute, P.O. Box 105, Yusong, Taejeon 305-600, South Korea

Received 8 June 1999; accepted 11 August 1999

Abstract

U_3O_8 powder made by oxidation of defective UO_2 pellets was mixed with UO_2 powder, and Nb_2O_5 was then added. Powder mixtures including various U_3O_8 contents were pressed into compacts and sintered at 1680°C in a reducing atmosphere. Without Nb_2O_5 addition, the U_3O_8 content of a mixed UO_2 – U_3O_8 compact is allowed only within about 15 wt%, since higher U_3O_8 contents make the UO_2 pellet density unacceptable. Using more than 0.3 wt% Nb_2O_5 , however, the UO_2 pellet density is higher than 94% TD under any U_3O_8 content of the mixed compact. The grain size of the UO_2 pellets increases with the Nb_2O_5 content of the mixed compact but is not influenced by the U_3O_8 content. Therefore, the U_3O_8 powder can be reused without any limit in the UO_2 pellet fabrication by sintering with Nb_2O_5 . It is supposed that NbO_2 , a reduced product of Nb_2O_5 , is dissolved in UO_2 to form uranium vacancies. The enhancement of densification and grain growth may be attributed to the increase of the uranium vacancy concentration. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Uranium dioxide (UO_2) fuel pellets 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. The powder compacts formed by pressing granules are sintered at about 1700°C in a reducing atmosphere. When UO_2 powder which has a good flowing ability is used, the granulation process to prepare granules is not needed. 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, a defective UO_2 pellet which does not meet the fuel specifications of density and diameter may be produced. Because defective UO_2 pellets contain expensive enriched uranium, it is economical for them to be recycled for the manufacture of new UO_2 pellets. It is a common recycling method that U_3O_8 powder is produced by oxidizing

defective UO_2 pellets and is then mixed with UO_2 powder. The powder mixture of UO_2 and U_3O_8 is pressed and sintered to fabricate UO_2 pellets in the same way as the UO_2 powder.

The above recycling method, however, has a problem in that the U_3O_8 content of the UO_2 – U_3O_8 powder mixture is limited since it is much less sinterable than UO_2 powder alone. If many defective UO_2 pellets happen to be made, they will have to be stored for a long time before reuse because of the limited U_3O_8 content. So it is necessary to fabricate UO_2 pellets using the powder mixture with higher U_3O_8 contents.

It is known that the sinterability of U_3O_8 powder, which is the oxidized product of UO_2 pellets, is enhanced by additional thermal treatments [2,3]. The U_3O_8 powder is reduced to UO_2 powder, which is then further oxidized and reduced about three times. The final UO_2 powder becomes sinterable enough to get a high density, because its specific surface area is increased and its particle size is decreased through repeated oxidation and reduction. However, the above method needs a fluidized bed for the powder treatments and involves a complicated process control, so it is difficult for the method to be used in the manufacturing process of UO_2 pellets.

* Corresponding author. Tel.: +82-42 868 2579; fax: +82-42 868 2403.

E-mail address: kwsong@naum.kaeri.re.kr (K.W. Song).

The effect of Nb_2O_5 on the sintering behavior of UO_2 has been studied in detail [4–6], especially from the viewpoint of grain growth. It is known that Nb_2O_5 increases the grain size very much but has little effect on the sintered density. According to the work of Radford and Pope [4], Nb_2O_5 has an enhancing effect on the densification of UO_2 compacts at low temperatures but has a negligible effect on the final density. However, the effect of Nb_2O_5 on the sintering behavior of the powder mixture of UO_2 and U_3O_8 has not been studied until now.

The purpose of this work is to fabricate UO_2 pellets reusing more U_3O_8 powder than by the conventional method. This paper mainly studies the effect of Nb_2O_5 on the densification of mixed UO_2 – U_3O_8 powder compacts and also describes the microstructure formed by the Nb_2O_5 addition.

2. Experimental

UO_2 powder used in this work was produced through the AUC (Ammonium Uranyl Carbonate) process [7]. U_3O_8 powder was prepared by heating defective UO_2 pellets in flowing air at 400°C for 3 h. The orthorhombic U_3O_8 phase has an about 30% larger lattice volume than the cubic UO_2 phase, so UO_2 pellets are spontaneously pulverized by the stress involved in the oxidation of UO_2 to U_3O_8 . The particle size of UO_2 and U_3O_8 powder was measured by a laser light scattering method, and the morphology of both powders was observed by scanning electron microscopy.

UO_2 powder was mixed with U_3O_8 powder in a tumbling mixer together with Nb_2O_5 powder. The mixtures had U_3O_8 contents of 10, 20, 30, 40, 60, 80 and 100 wt% and also had Nb_2O_5 contents of 0.1, 0.2, 0.3 and 0.5 wt%, respectively. Powder mixtures were pressed under the pressure of about 300 MPa into compacts, which had a density of about 5.75 g/cm^3 . Powder compacts were heated to 1680°C in a reducing atmosphere and then held for 4 h prior to furnace cooling. In order to analyze the relationship between temperature and the Nb_2O_5 effect on densification, the shrinkage rates of the compacts with and without 0.3 wt% Nb_2O_5 were measured with a dilatometer.

The sintering gas atmosphere was determined by preliminary experiments. It was observed that the added Nb_2O_5 particles were insignificantly dissolved in the UO_2 pellets sintered in hydrogen (H_2) gas, whose dew point was -30°C . When a small amount of carbon dioxide (CO_2) gas was added to the hydrogen gas, it was observed that the added Nb_2O_5 was completely dissolved. Some sintering experiments using various amounts of CO_2 indicated that the UO_2 pellet had a maximum density under the condition that the ratio of CO_2 to H_2 gas was 1×10^{-2} . Therefore, this mixed gas

was used as the sintering atmosphere. The effect of the oxygen potential on the dissolution of the added Nb_2O_5 in UO_2 has been described elsewhere [8].

The UO_2 pellet density was determined by the water immersion method, and the pellets were sectioned longitudinally and polished. In order to observe grain boundaries, thermal etching was carried out at 1200°C for 1 h in CO_2 gas, and the grain size was determined by a linear intercept method. The second phase formed in Nb_2O_5 -doped UO_2 pellets was quantitatively analyzed by X-ray microanalysis.

3. Results and discussion

The particle size distribution of the UO_2 and U_3O_8 powders is shown in Fig. 1. Both powders have a monomodal distribution, and the mode values of the UO_2 and U_3O_8 powders are 17 and $8 \mu\text{m}$, respectively. The particle size of the U_3O_8 powder is known to be dependent on the oxidation temperature [9]. As this temperature increases, the stress involved in the oxidation is so relieved that the related pellet pulverization is significantly suppressed and the particle size of U_3O_8 becomes larger. Moreover, UO_2 pellets cannot be pulverized above a temperature of about 900°C because of the formation of crack-free and columnar U_3O_8 grains [10]. In order to make fine U_3O_8 powder, it is important to perform the oxidation in the temperature range between 350°C and 500°C .

Fig. 2(a) and (b) show the morphology of UO_2 and U_3O_8 powders, respectively. The UO_2 particle has a round shape and a smooth surface, so the UO_2 powder is well flowing. However, the U_3O_8 particle has an angular shape and also has cracks that were formed during the oxidation, so the U_3O_8 powder is much less flowing.

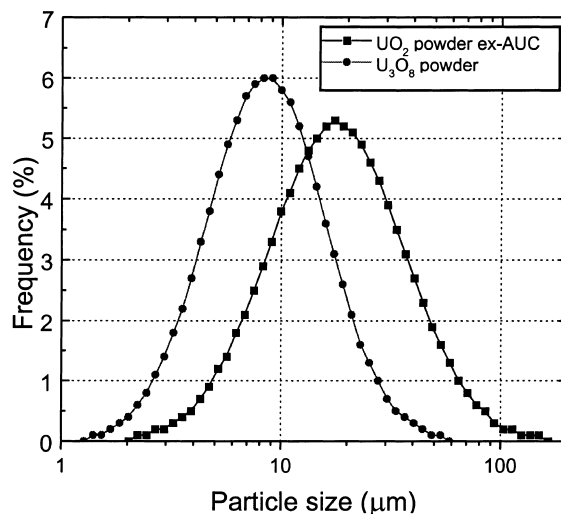


Fig. 1. Particle size distribution of UO_2 and U_3O_8 powders.

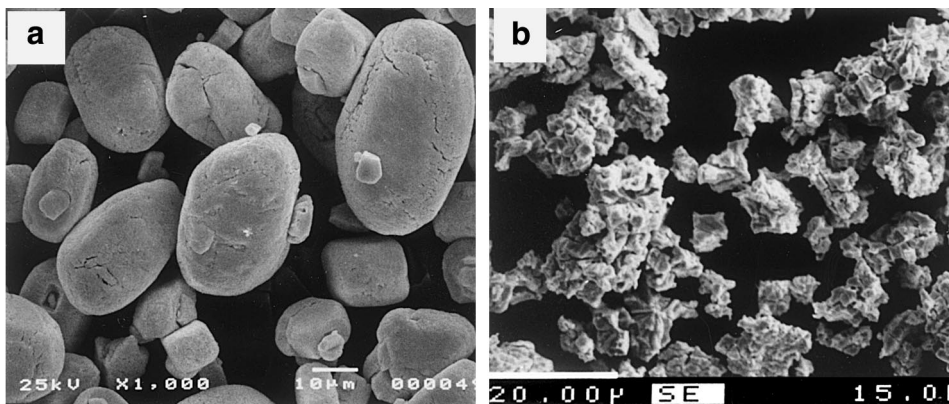


Fig. 2. Morphology of (a) the UO_2 and (b) the U_3O_8 powder.

The specific surface areas of the UO_2 and U_3O_8 powders are 5 and $0.5 \text{ m}^2/\text{g}$, respectively, suggesting that the sinterability of U_3O_8 powder is much lower than that of UO_2 powder.

The U_3O_8 fraction in the mixed UO_2 – U_3O_8 compact is naturally reduced to UO_2 during sintering. According to the work on the kinetics of U_3O_8 reduction [11], U_3O_8 was reduced to UO_2 between 500°C and 600°C in hydrogen gas for less than 1 h. Since the densification of mixed UO_2 – U_3O_8 compacts starts at about 800°C , it is reasonable to suppose that U_3O_8 in the mixed compact is reduced to UO_2 before densification during the sintering. Therefore, from the viewpoint of densification, the mixed UO_2 – U_3O_8 compact can be regarded as a poorly sinterable UO_2 compact.

Fig. 3 shows the relationship between the UO_2 pellet density and Nb_2O_5 content. The sintered density of the UO_2 powder compact (without U_3O_8 content) decreases at 0.1 wt% Nb_2O_5 and thereafter increases significantly with Nb_2O_5 content. Such a relationship between pellet density and Nb_2O_5 content is readily found in the other compacts including various U_3O_8 contents. These relationships imply that the densification of mixed UO_2 – U_3O_8 compacts can be enhanced by nearly the same amount of Nb_2O_5 as the densification of the UO_2 compact, even though the sinterability of the mixed UO_2 – U_3O_8 powder is lower than that of UO_2 powder.

Fig. 4 shows the UO_2 pellet density as a function of the U_3O_8 content. Without Nb_2O_5 addition, the density decreases linearly with the U_3O_8 content and the decreasing rate is about 2% of the theoretical density (TD) per 10 wt% U_3O_8 . Such a decrease in density is mainly due to the fact that the specific surface area of the U_3O_8 powder is much lower than that of the UO_2 powder. The fuel specification requires the UO_2 pellet density to be in the range between 93.5% and 96.5% TD [1], so the U_3O_8 content is limited within about 15 wt% of the mixed compact. With 0.2 wt% Nb_2O_5 , the density also decreases with U_3O_8 content but the decreasing rate is

significantly reduced. With 0.3 and 0.5 wt% Nb_2O_5 , the pellet density decreases very slightly with U_3O_8 content and thus it is higher than about 94% TD even at a U_3O_8 content of 100 wt%. Consequently, the pellet density is increased up to the acceptable range under any U_3O_8 content by the addition of more than 0.3 wt% Nb_2O_5 .

It can be seen from Fig. 4 that the density difference between ‘without Nb_2O_5 ’ and ‘with 0.3 wt% Nb_2O_5 ’ becomes larger as the U_3O_8 content increases. The UO_2 compact is intrinsically sinterable enough to get a pellet density of about 96% TD, and it attains only a small amount of further densification by means of the Nb_2O_5 addition. The sinterability of the mixed UO_2 – U_3O_8 compact decreases with the U_3O_8 content, and the amount of further densification due to the Nb_2O_5 addition increases with the U_3O_8 content. Therefore, the densifying ability of Nb_2O_5 appears to increase as the sinterability of the mixed UO_2 – U_3O_8 powder compact decreases.

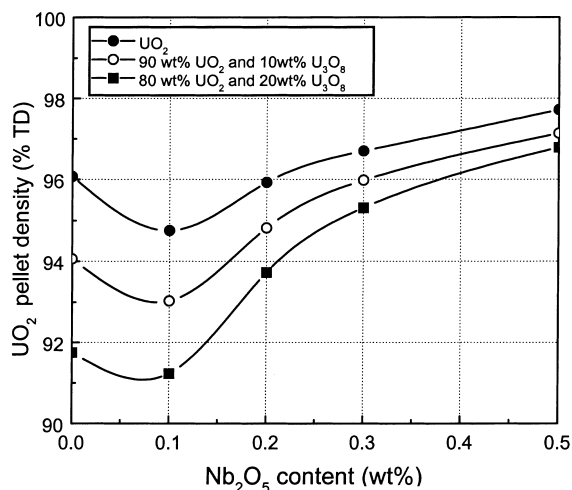


Fig. 3. UO_2 pellet density as a function of the Nb_2O_5 content.

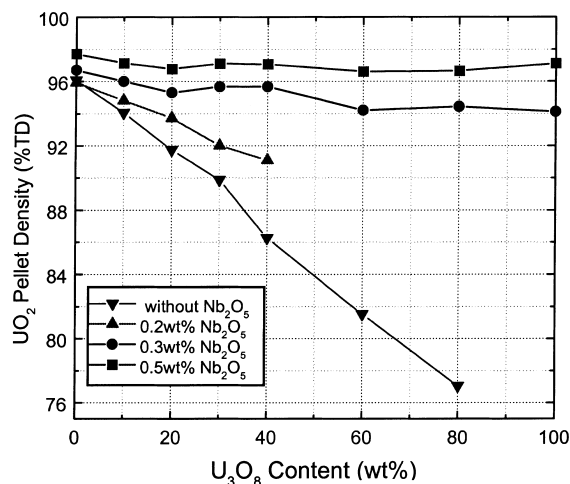


Fig. 4. UO₂ pellet density as a function of the U₃O₈ content for various Nb₂O₅ contents.

Fig. 5(a) shows the densification (shrinkage, $\Delta L/L_0$) of the compact comprising 60 wt% UO₂ and 40 wt% U₃O₈ as a function of temperature. The compacts with and without Nb₂O₅ start to densify at about 800°C, but the compact with Nb₂O₅ densifies to a larger extent above 800°C than the compact without Nb₂O₅. As the temperature increases up to about 1300°C, the densification difference between both compacts becomes larger. However, the densification difference does not become larger any more above 1300°C. Such variation in the densification curves indicates that the Nb₂O₅ addition enhances the densification of the mixed UO₂–U₃O₈ compact mainly at temperatures below about 1300°C.

Fig. 5(b) shows the densification rates (shrinkage rates) as a function of temperature. The rates of both compacts start to increase at about 800°C, but the compact with Nb₂O₅ densifies much more rapidly between 1200°C and 1300°C than the compact without Nb₂O₅. Therefore, the added Nb₂O₅ aids densification mainly in the upper temperature range.

The oxygen potentials of Nb₂O₅, NbO₂, NbO, and sintering gas are calculated with the HSC software [12] which is a tool for calculating chemical reaction equations and equilibrium compositions. The results are shown as a function of temperature in Fig. 6. It can be noticed that the stable form of niobium oxides changes in accordance with temperature under a fixed gas atmosphere. Under hydrogen gas with a dew point of –30°C ($H_2O/H_2 = 5 \times 10^{-4}$), the stable niobium oxide is Nb₂O₅ below 500°C, NbO₂ between 500°C and 1050°C, and NbO above 1050°C. It is found that the niobium oxide is insignificantly dissolved in this atmosphere, so it is supposed that NbO is hardly dissolved in UO₂. When the gas mixture of CO₂ and H₂ ($CO_2/H_2 = 1 \times 10^{-2}$) is used as a sintering atmosphere,

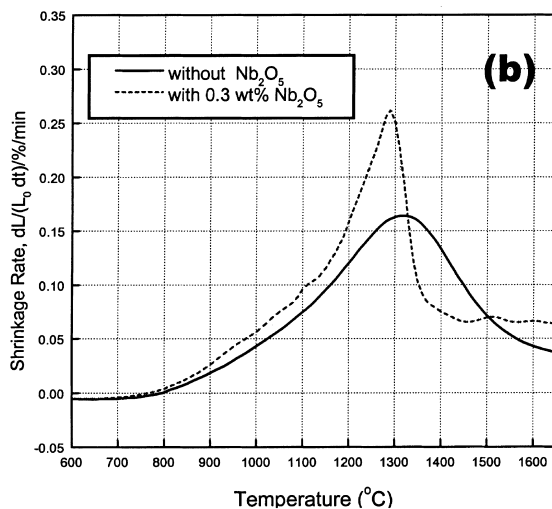
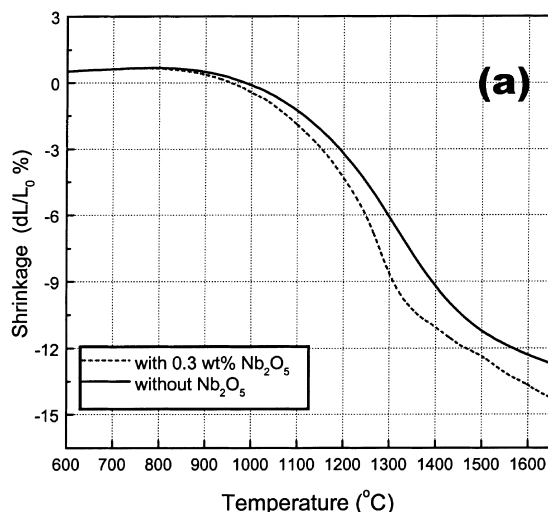


Fig. 5. Shrinkage of mixed UO₂–U₃O₈ compacts with and without Nb₂O₅: (a) shrinkage change; (b) shrinkage rate.

the stable niobium oxide is Nb₂O₅ below 820°C, NbO₂ between 820°C and 1650°C, and NbO above about 1650°C. It is found that niobium oxide is completely dissolved in this atmosphere, so it can be inferred that NbO₂ is the dissolved niobium oxide.

The dissolution of Nb₂O₅ in UO₂ has been proposed and discussed [4–6]. It is known that the entrance of Nb₂O₅ gives rise to the formation of oxygen interstitials and uranium vacancies, which can enhance uranium diffusion. However, Nb₂O₅ is stable only up to 820°C in the gas mixture of CO₂ and H₂ ($CO_2/H_2 = 0.01$), and it is supposed that this temperature is not so high to dissolve significantly Nb₂O₅ in UO₂. If the oxygen potential becomes higher than that of this work, Nb₂O₅ may be stable up to a higher temperature and thus it may be dissolved significantly. It is reasonable to suppose that

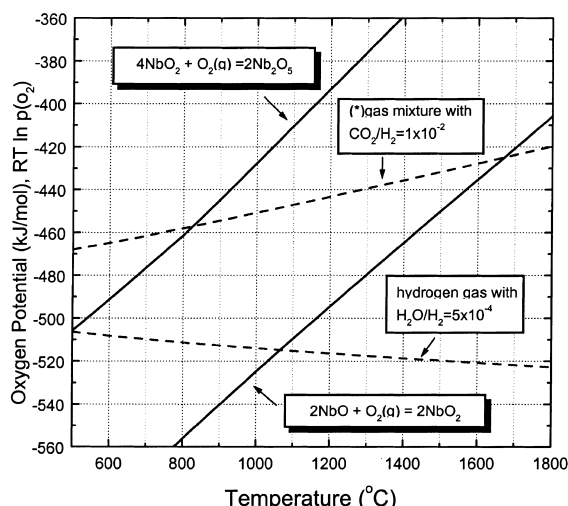
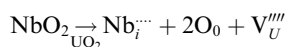


Fig. 6. Oxygen potentials of niobium oxides and of sintering gas as a function of temperature.

the oxygen potential plays an important role in determining which form of niobium oxides is dissolved. Fig. 5(b) shows that the mixed $\text{UO}_2\text{--U}_3\text{O}_8$ compact with Nb_2O_5 densifies much more rapidly between 1200°C and 1300°C, and Fig. 6 shows that the stable niobium oxide is NbO_2 in the above temperature range under the gas mixture of CO_2 and H_2 . Therefore, it can be concluded that the enhancement in densification of the mixed $\text{UO}_2\text{--U}_3\text{O}_8$ compact is mainly attributed to the dissolved NbO_2 during sintering.

NbO_2 can be dissolved in UO_2 either substitutionally or interstitially. The substitution of a Nb^{4+} ion for a U^{4+} ion cannot make any defect in the UO_2 lattice, so the enhancement in densification is not likely to be achieved. Alternatively, it is assumed that a Nb^{4+} ion enters interstitially into the UO_2 lattice to make a uranium va-

cancy. This reaction can be described by the following equation:



There may be enough space for the interstitial Nb^{4+} ions in the UO_2 lattice since the body-centered sites in the oxygen sublattice are only half-filled. Radford and Pope [4] also proposed that the Nb^{4+} ion enters interstitially the UO_2 lattice.

As discussed earlier, the mixed $\text{UO}_2\text{--U}_3\text{O}_8$ compact changes into a poorly sinterable UO_2 compact prior to densification. The densification of UO_2 compacts needs the shrinkage of pores, which in turn needs uranium diffusion. An increase in concentration of the uranium vacancies gives rise to an acceleration of uranium diffusion. Therefore, the enhancement in densification of the mixed $\text{UO}_2\text{--U}_3\text{O}_8$ compact is mainly due to the increase in concentration of the uranium vacancies, which are formed by NbO_2 dissolution.

Fig. 7(a)–(c) show the microstructures of 0.3 wt% Nb_2O_5 -doped UO_2 pellets made from the compacts comprising UO_2 , 70 wt% $\text{UO}_2\text{--}30$ wt% U_3O_8 , and 20 wt% $\text{UO}_2\text{--}80$ wt% U_3O_8 , respectively. As the U_3O_8 content changes from zero to 30 wt%, the number density of pores appears to be remarkably increased. However, the number density does not appear to increase further under a U_3O_8 content of more than 30 wt%. Such dependence of the number density of pores on the U_3O_8 content is related with the dependence of pellet density on the U_3O_8 content, which is shown in Fig. 4.

It is found that a second phase is formed on the grain boundaries in the 0.5 wt% Nb_2O_5 -doped UO_2 pellet (see Fig. 8). The niobium concentration profile across the second phase indicates that this phase has a higher niobium concentration than the matrix. The quantitative analysis of uranium, niobium and oxygen was per-

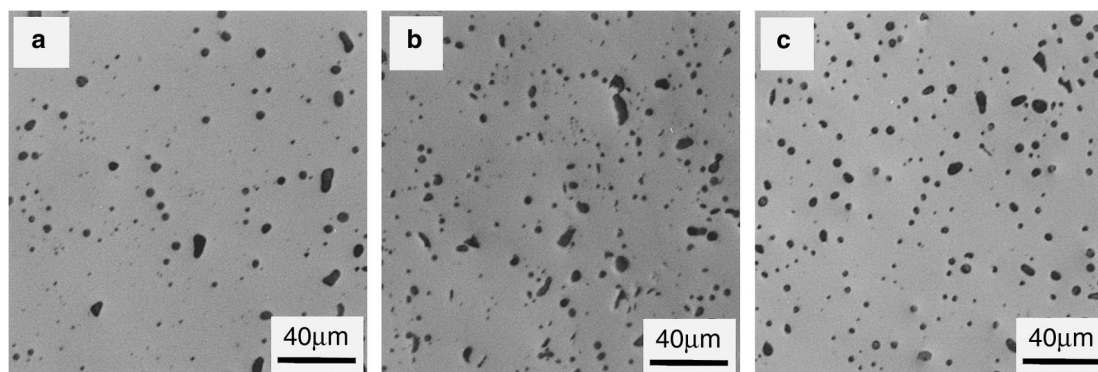


Fig. 7. Microstructures of 0.3 wt% Nb_2O_5 -doped UO_2 pellets made from the compacts comprising: (a) UO_2 ; (b) 70 wt% $\text{UO}_2\text{--}30$ wt% of U_3O_8 and (c) 20 wt% $\text{UO}_2\text{--}80$ wt% U_3O_8 .

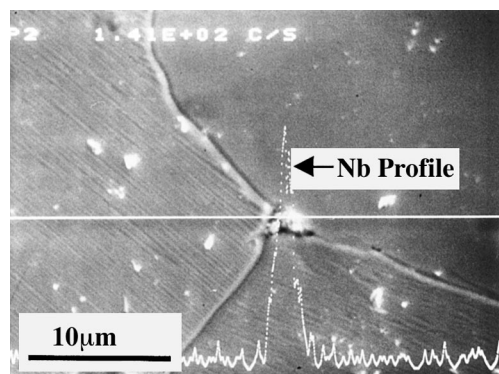


Fig. 8. SEM micrograph showing a second phase with higher Nb concentration.

formed by X-ray microanalysis, and the results suggest that the second phase may be an oxide compound whose composition corresponds to near Nb_2UO_6 .

Fig. 9 shows the grain size of UO_2 pellets made from UO_2 compacts as a function of the Nb_2O_5 content. The grain size increases linearly with the Nb_2O_5 content, so it reaches about 45 μm at 0.5 wt% Nb_2O_5 . The experimental results [4–6] have shown that Nb_2O_5 additions increased the grain size of UO_2 pellets and have explained that grain growth was enhanced by the formation of defects. As discussed earlier, the dissolution of NbO_2 may form a uranium vacancy and enhance the uranium diffusion, so grain growth may be promoted. Fig. 10 shows the grain size of UO_2 pellets as a function of the U_3O_8 content. The grain size appears almost independent of the U_3O_8 content. Therefore, the grain size of the UO_2 pellet which is made from the mixed UO_2 –

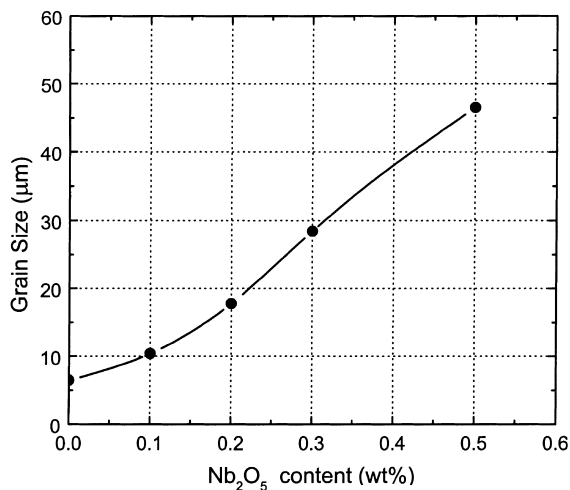


Fig. 9. Grain size of the UO_2 pellets made of UO_2 compacts as a function of the Nb_2O_5 content.

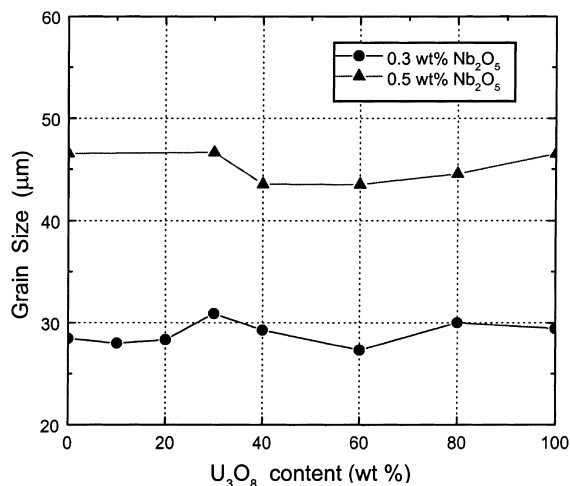


Fig. 10. Dependence of the grain size of UO_2 pellets on the U_3O_8 content

U_3O_8 compact is determined by the Nb_2O_5 content rather than by the U_3O_8 content.

4. Conclusions

The mixed UO_2 and U_3O_8 powders with and without Nb_2O_5 additions were pressed into compacts and then sintered in a reducing atmosphere to fabricate UO_2 pellets. The following conclusions can be drawn:

1. Without Nb_2O_5 , the UO_2 pellet density decreases linearly so far with the U_3O_8 content that it becomes lower than 93.5% TD above 15 wt% U_3O_8 . Using more than 0.3 wt% Nb_2O_5 , however, the UO_2 pellet density decreases very slightly with the U_3O_8 content and thus it is higher than about 94% TD even at 100 wt% U_3O_8 . The densifying ability of Nb_2O_5 appears to increase as the sinterability of the mixed UO_2 and U_3O_8 powders decreases. It is found that the added Nb_2O_5 has an enhancing effect on the densification of the mixed UO_2 – U_3O_8 compact mainly in the temperature range between 1200°C and 1300°C.
2. The grain size of the UO_2 pellets increases with the Nb_2O_5 content but it is not influenced by the U_3O_8 content. A second phase whose composition corresponds nearly to Nb_2UO_6 is formed in the 0.5 wt% Nb_2O_5 -doped UO_2 pellet.
3. The added Nb_2O_5 is reduced to NbO_2 and is then dissolved in UO_2 during sintering. It is proposed that the Nb^{4+} ions enter interstitially the UO_2 lattice to make uranium vacancies. The enhancement of densification and grain growth in the mixed UO_2 – U_3O_8 compact may be attributed to the increase in concentration of the uranium vacancies.

Acknowledgements

This work has been carried out under the Nuclear R and D Program supported by the Korean Ministry of Science and Technology.

References

- [1] H. Assmann, H. Bairiot, Process and product control of oxide powder and pellets for reactor fuel application, in: Guidebook on Quality Control of Water Reactor Fuel, Tech. Report Series No. 221, IAEA, Vienna, 1983.
- [2] G.E. Brand, E.W. Murbach, Pyrochemical reprocessing of UO_2 by AIROX, NAA-SR-11389, 1965.
- [3] R.C. Hoyt, L.F. Grantham, R.G. Clark, P.W. Twinchell, AIROX Dry Reprocessing of uranium oxide fuels, ESG-DOE-13276, 1979.
- [4] K.C. Radford, J.M. Pope, J. Nucl. Mater. 116 (1983) 305.
- [5] K.W. Song, S.H. Kim, B.G. Kim, Y.W. Lee, M.S. Yang, H.S. Park, J. Korean Nucl. Soc. 26 (1994) 484.
- [6] Y. Harada, J. Nucl. Mater. 238 (1997) 237.
- [7] E. Brandau, W. Doerr, Trans. Am. Nucl. Soc. 31 (1979) 148.
- [8] K.W. Song, K.S. Kim, K.W. Kang, Y.H. Jung, J. Korean Nucl. Soc. 31 (1999) 334.
- [9] M. Iwasaki, T. Sakurai, N. Ishikawa, Y. Kobayashi, J. Nucl. Sci. Tech. 5 (1968) 652.
- [10] K.W. Song, M.S. Yang, J. Nucl. Mater. 209 (1994) 270.
- [11] A.H. Le Page, A.G. Fane, J. Inorg. Nucl. Chem. 36 (1974) 87.
- [12] Outokumpu Research, HSC Chemistry for Windows, 1994.