

Effects of Nb₂O₅ and Oxygen Potential on Sintering Behavior of UO₂ Fuel Pellets

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(Received December 18, 1998)

Abstract

The effects of Nb₂O₅ and oxygen potential on the densification and grain growth of UO₂ fuel have been investigated. 0.3 wt% Nb₂O₅-doped UO₂ fuel pellets were sintered at 1700°C for 4 hours in sintering atmospheres which have various ratios of H₂O to H₂ gas. Compared with those of undoped UO₂ pellets, the sintered density and grain size of the 0.3 wt% Nb₂O₅-doped UO₂ pellet increase under the H₂O/H₂ gas ratio of 5.0×10^{-3} to 1.0×10^{-2} and under the H₂O/H₂ gas ratio of 5.0×10^{-3} to 1.5×10^{-2} , respectively. The sintering of UO₂ fuel pellets containing 0.1 wt% to 0.5 wt% Nb₂O₅ was carried out at 1680°C for 4 hours. The enhancing effect of Nb₂O₅ on the sintered density and grain size becomes larger as the Nb₂O₅ content increases. The solubility limit of Nb₂O₅ in UO₂ seems to be between 0.3 wt% and 0.5 wt%, and beyond the solubility limit the second phase whose composition corresponds near to Nb₂UO₆ is precipitated on grain boundary. The enhancement of densification and grain growth in UO₂ is attributed to the increased concentration of a uranium vacancy which is formed by the interstitial Nb⁴⁺ ion in the UO₂ lattice.

Key Words : UO₂ fuel, sintering, Nb₂O₅-doped UO₂, oxygen potential

1. Introduction

Uranium dioxide fuel with large grains has been expected to reduce the amount of fission gas released during irradiation and thus has been recognized as desirable at high burnup [1]. Various methods to achieve large grains are available; additives, higher sintering temperature, longer sintering time, or oxidizing atmosphere. Of the above methods the use of additives has a

small effect on the universal sintering technology that UO₂ pellets are sintered in a reducing atmosphere at the temperatures between 1650°C to 1750°C.

The effect of additives on the sintering behavior of UO₂ fuel pellets has been much investigated. The additives such as Nb₂O₅, TiO₂, MgO, SiO₂, Li₂O, and Cr₂O₃ have been known to promote grain growth [2]. In particular Nb₂O₅ has been studied, since it can enhance not only

grain growth but creep rate [3]. It has been known that Nb₂O₅ facilitates material transport in UO₂ by means of the generation of uranium vacancies. However, it was found that Nb₂O₅ acted as a grain growth promoter in wet hydrogen sintering but not in dry hydrogen sintering [4]. So it is necessary to understand in a quantitative way the effect of sintering atmospheres on the sintering behavior of the Nb₂O₅-doped UO₂ fuel pellet. Moreover, it is little known how Nb₂O₅ in excess of the solubility limit acts during the sintering as the Nb₂O₅-doped fuel has been studied mostly in the range of the solubility limit.

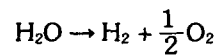
This paper describes the effects of oxygen potential and Nb₂O₅ content on the sintering behavior of Nb₂O₅-doped UO₂ fuel pellets, and defects formed by the addition of Nb₂O₅ are discussed in terms of the oxidation states of niobium ions. In particular the solubility limit of Nb₂O₅ and the related precipitate are analyzed.

2. Experimental Procedures

The UO₂ powder used in this work was produced through the AUC (Ammonium Uranyl Carbonate) process [5]. The UO₂ powder was mixed with the predetermined amount of Nb₂O₅ powder for 2 hours in a tumbling mixer (Turbula). The Nb₂O₅ contents were 0.1 wt%, 0.2 wt%, 0.3 wt% and 0.5 wt%. The sizes of UO₂ and Nb₂O₅ powder measured by laser light scattering method were 16 μm and 25 μm, respectively.

The mixed powder was pressed under 3 ton/cm² with die-wall lubrication into compacts, which had the density of 5.7 g/cm³. The powder compact was heated to 700°C and then held for 1 hour. Subsequently, it was heated to 1700°C, at which it was held for 4 hours prior to cooling. In order to closely examine the effect

of oxygen potential the mixed gases of hydrogen (H₂) and water vapor (H₂O) were used as sintering atmospheres. A measured dew point of the hydrogen gas was -30°C, and thus the ratio of H₂O to H₂ gas corresponded to 5.0 × 10⁻⁴. The hydrogen gas passed the water bath whose temperature was set in the range between 5°C and 18°C, so the ratios of H₂O to H₂ gases were controlled in the range between 2.5 × 10⁻³ and 2.0 × 10⁻². The mixture of hydrogen and water vapor constituting a sintering atmosphere reacts in thermodynamic equilibrium at elevated temperatures as follows :



The resultant composition of these gases is determined by the equilibrium constant, which is a function of the temperature of gas. The oxygen potentials of sintering atmospheres were calculated by SOLGASMIX program [6].

Another set of sintering was carried out at 1680°C for 4 hours under the mixed gas of hydrogen and carbon dioxide, in which the ratio of CO₂ to H₂ gas was 0.01. According to the results of SOLGASMIX program [6], the oxygen potential of the mixed gas was the same as that of the mixed H₂O and H₂ gas with the ratio of H₂O/H₂ = 0.01. In addition, pure UO₂ powder was pressed and sintered to make undoped UO₂ pellets.

Sintered density was determined by water immersion method, and sintered pellets were sectioned longitudinally and polished. In order to observe grain boundary thermal etching was carried out at 1200°C for 1 hour in carbon dioxide atmosphere, and grain size was determined by a linear intercept method. Precipitates formed in the 0.5 wt% Nb₂O₅-doped UO₂ were quantitatively analyzed by electron probe micro analysis (EPMA).

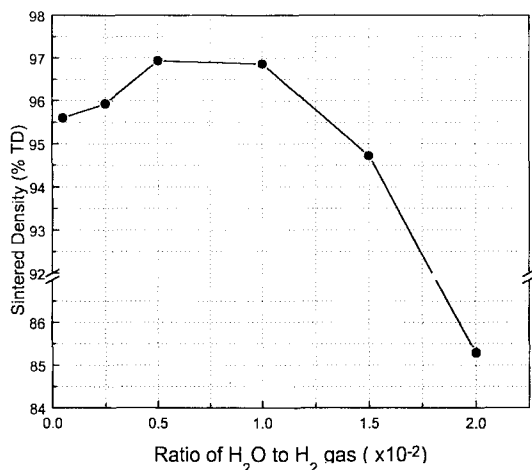


Fig. 1. Dependence of Density of the 0.3 wt% Nb_2O_5 -doped UO_2 Pellet on the Ratio of H_2O to H_2 Gas in a Sintering Atmosphere.

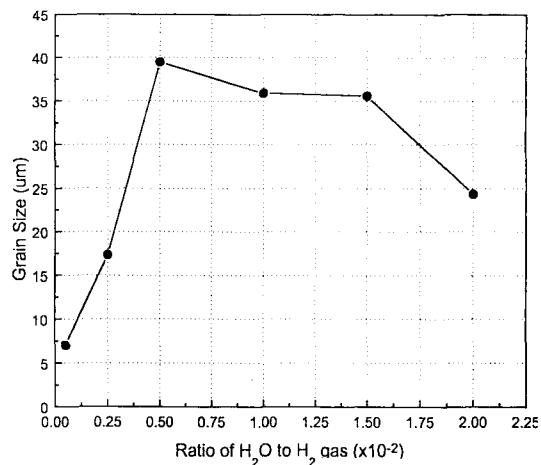


Fig. 2. Dependence of Grain Size of the 0.3 wt% Nb_2O_5 -doped UO_2 Pellet on the Ratio of H_2O to H_2 Gas in a Sintering Atmosphere.

3. Results and Discussion

3.1. Effect of Oxygen Potential on Density and Grain Size

Fig. 1 shows the sintered density of the 0.3 wt% Nb_2O_5 -doped UO_2 pellet as a function of the ratio of H_2O to H_2 gas in the sintering atmosphere. The ratio of H_2O to H_2 gas will be named as 'the gas ratio' in the following part of this paper. The density increases up to about 97 %TD as the gas ratio increases to 5.0×10^{-3} , and then it has a maximum value under the gas ratios between 5.0×10^{-3} and 1.0×10^{-2} . Above the gas ratio of 1.0×10^{-2} the sintered density decreases substantially with the gas ratio.

Fig. 2 shows the grain size of the 0.3 wt% Nb_2O_5 -doped UO_2 pellet as a function of the ratio of H_2O to H_2 gas in the sintering atmosphere. The grain size increases up to about 40 μm as the gas ratio increases up to 5.0×10^{-3} , and then it seems to remain more or less constant under the gas

ratios between 5.0×10^{-3} and 1.5×10^{-2} . The grain size becomes smaller under the gas ratio of 2.0×10^{-2} .

Fig. 3(a) and 3(b) show the microstructures of the 0.3 wt% Nb_2O_5 -doped UO_2 pellet sintered under the gas ratio of 5.0×10^{-4} and 2.0×10^{-2} , respectively. Fig. 3(a) shows that large particles of niobium oxide remain undissolved while small particles are dissolved, which suggests that the negligible effect of the Nb_2O_5 addition on the density and grain size is mainly due to such partial dissolution of niobium oxide. It is supposed that there exists a threshold of the gas ratio for the complete dissolution of niobium oxide, and Fig. 2 indicates that the threshold is probably about 5.0×10^{-3} . Fig. 3(b) shows that many large pores are formed, and thus it is supposed that such pore formation gives rise to the density decrease under the gas ratio of 2.0×10^{-2} (see Fig. 1).

Figs. 1 and 2 indicate that the variation in the gas ratio has a large effect on the densification and grain growth of the 0.3 wt% Nb_2O_5 -doped UO_2

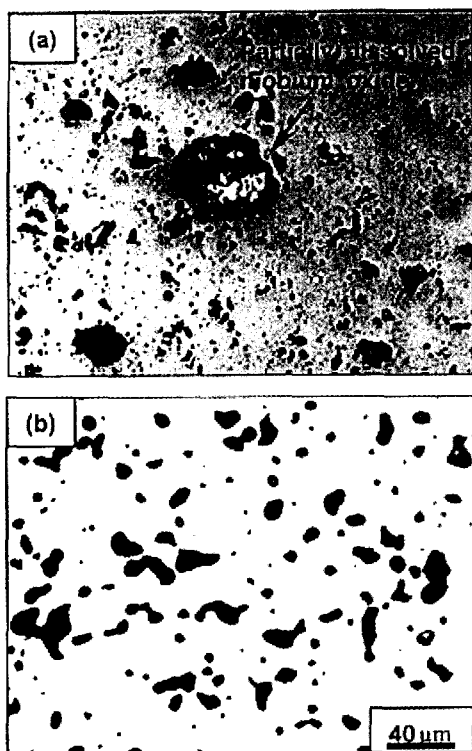


Fig. 3. Microstructures of 0.3 wt% Nb₂O₅-Doped UO₂ Pellets Sintered in Sintering Atmospheres with Various Gas Ratios of H₂O to H₂.

(a) 0.05×10^{-2} , (b) 2.0×10^{-2}

pellet, and the gas ratio also determines whether niobium oxide is fully dissolved in UO₂, or not. Consequently it is supposed that the oxidation state of niobium in the niobium oxide varies according to the gas ratio and resultantly the solubility of niobium oxide is influenced.

Fig. 4 shows the oxygen potentials ($RT \ln P_{O_2}$) of the sintering atmospheres used in this work as well as the oxygen potentials of niobium oxides as a function of temperature. It can be noticed that a stable form of niobium oxides changes in accordance with temperature even under a fixed gas ratio. When the gas ratio is 5.0×10^{-4} , a

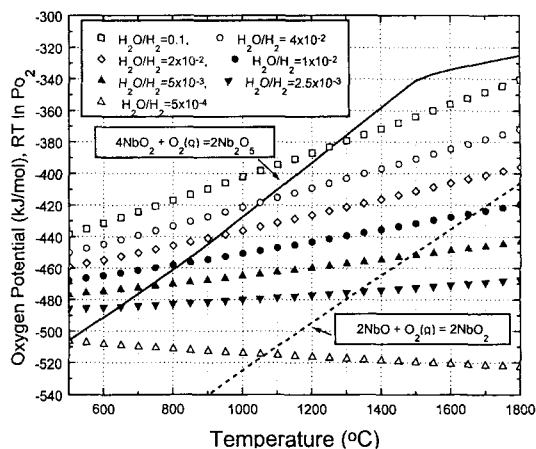


Fig. 4. Oxygen Potentials of Niobium Oxides and Various Mixed Gas as a Function of Temperature.

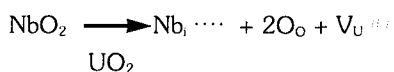
stable niobium oxide is Nb₂O₅ below 500°C, NbO₂ in the temperature range between 500°C and 1050°C, and NbO above 1050°C, which indicates that NbO is mainly operative during the sintering. It follows that the partially dissolved niobium oxide is NbO. However, when the gas ratio is 5.0×10^{-3} , a stable niobium oxide is Nb₂O₅ below about 750°C, NbO₂ in the temperature range between about 750°C and about 1500°C, and NbO above about 1500°C, which implies that not only NbO but NbO₂ can be operative during the sintering. Consequently the complete dissolution of niobium oxide under this gas ratio suggests that the added Nb₂O₅ is reduced to the NbO₂, which is totally dissolved in UO₂ at temperatures lower than about 1500°C.

Even though NbO₂ is acting at a lower temperature than NbO, it can be dissolved in UO₂ more than NbO since the size of a Nb⁴⁺ ion (0.83 Å) is smaller than that of a Nb²⁺ ion (0.85 Å) [7]. It is supposed that the partial dissolution of niobium oxide is attributed to the reduction of NbO₂ to NbO before the complete dissolution of

NbO₂. Concludingly the NbO₂ of niobium oxides is effectively dissolved in UO₂, and it has to be maintained up to at least about 1500°C for its complete dissolution.

This work does not cover the higher oxygen potentials where Nb₂O₅ is stable. According to the published works [4,8], Nb₂O₅ was fully dissolved in UO₂ at 1300°C under CO₂ gas which kept the Nb₂O₅ stable. Therefore it is supposed that Nb₂O₅ is dissolved in UO₂ more easily than NbO₂.

The substitution of the Nb⁴⁺ ion for the U⁴⁺ ion does not cause the creation of any extrinsic defects in UO₂, and thus the enhancement in densification and grain growth can not be understood. Alternatively, it is assumed that the Nb⁴⁺ ion enters interstitially the UO₂ lattice, and resultantly a uranium vacancy may be formed. This reaction can be described by the following equation:



An increase in concentration of the uranium vacancy gives rise to an increase in uranium diffusion, explaining the enhancement in densification and grain growth. There is probably enough room for the interstitial penetration of Nb⁴⁺ ions in the UO₂ lattice since the body-centered sites in oxygen sublattice are only half-filled. This type of defects was previously proposed with simple discussion by Radford and Pope [9].

The grain size of the 0.3 wt% Nb₂O₅-doped UO₂ pellet is nearly independent of the oxygen potential in the range of the gas ratio between 5.0×10^{-3} and 1.5×10^{-2} in this work, but Harada [10] reported that it increased with oxygen potential. In Harada's experiments the oxygen potential was controlled by the mixed gases of CO₂ and H₂ and ranged from -357 kJ/mole to -236 kJ/mole at 1400°C, so it can be predicted that a stable form

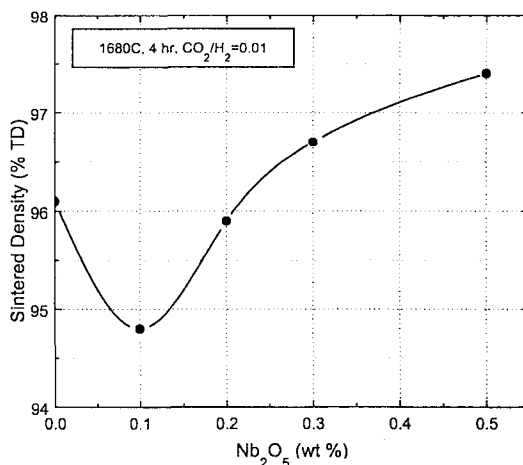


Fig. 5. Density of the Nb₂O₅-doped UO₂ Pellet as a Function of Nb₂O₅ Content.

of niobium oxide was Nb₂O₅ (see Fig. 4). Therefore it is reasonable to suppose that the dependence of grain growth on oxygen potential may be influenced by the type of niobium oxide dissolved in UO₂.

Fig. 5 shows the density of Nb₂O₅-doped UO₂ pellets as a function of Nb₂O₅ content. Those pellets were sintered at 1680°C for 4 hours in the mixed CO₂ and H₂ gas of which the ratio was 0.01 (CO₂/H₂= 1×10^{-2}). The sintered density decreases at 0.1 wt% Nb₂O₅ and thereafter increases gradually with the Nb₂O₅ content. Considering faster uranium diffusion in the Nb₂O₅-doped UO₂, the density drop at 0.1 wt% Nb₂O₅ implies that other factors which can decrease the density counteract the faster uranium diffusion. A similar density drop was reported in the other works [9].

3.2. Effect of Niobium Oxide Content on Microstructure

Pore structures of undoped UO₂ and Nb₂O₅-doped UO₂ pellets are shown in Fig. 6(a) to Fig.

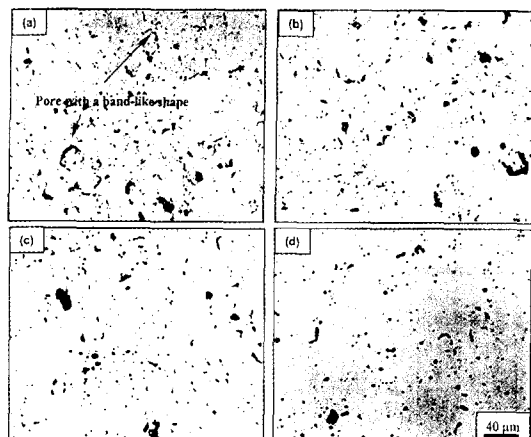


Fig. 6. Pore Structures of Undoped and Nb_2O_5 -doped UO_2 Pellets.

(a) undoped, (b) 0.1 wt% Nb_2O_5
(c) 0.2 wt% Nb_2O_5 , (d) 0.3 wt% Nb_2O_5

6(d). It can be readily seen from Fig. 6(a) that the undoped UO_2 pellet has two kinds of pores; large pores with a band-like shape and small pores with a round shape. This pore structure, more specifically the band-like pore, seems to be characteristic of the UO_2 pellet made of the AUC- UO_2 powder. Fig. 6(b) shows that both band-like pores and round pores still remain in the 0.1 wt% Nb_2O_5 -doped UO_2 pellet, suggesting that the 0.1 wt% Nb_2O_5 content is not sufficient to enhance uranium diffusion to such an extent that these pores shrink considerably. In addition, a big and round pore is newly observed. That pore is believed to be formed at the original site of niobium oxide, because Nb ions enter interstitially the surrounding UO_2 lattice, leaving the big and round pore [4]. It is thought that the big and round pore causes the density drop at 0.1 wt% Nb_2O_5 . Fig. 6(c) shows that the band-like pore shrinks considerably and the round pore of small size decreases in its number in the 0.2 wt% Nb_2O_5 -doped UO_2 pellet. Fig. 6(d) shows that the band-

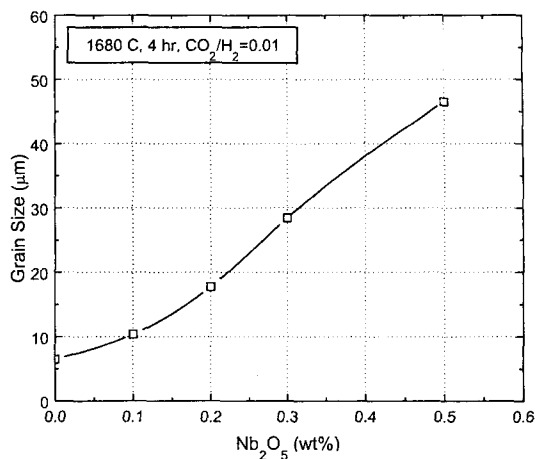


Fig. 7. Grain Size of Nb_2O_5 -doped UO_2 Fuel Pellet as a Function of Nb_2O_5 Content.

like pore almost shrinks and the round pore which is smaller than about $2 \mu\text{m}$ is annihilated in the 0.3 wt% Nb_2O_5 -doped UO_2 pellet. Therefore it is evident from Fig. 6 that pore shrinkage becomes more enhanced as the Nb_2O_5 content increases. The enhancement of pore shrinkage in UO_2 can be understood in terms of the enhancement of uranium diffusion, which in turn is attributed to the formation of a uranium vacancy in UO_2 due to the interstitial Nb^{4+} ion.

Fig. 7 shows the grain sizes of Nb_2O_5 -doped UO_2 pellets as a function of Nb_2O_5 content. The grain size increases linearly up to about $45 \mu\text{m}$ as the Nb_2O_5 content increases up to 0.5 wt%. It is thought that grain growth is promoted primarily by the enhancement in uranium diffusion due to the interstitial Nb^{4+} ion. According to the works on the grain growth in UO_2 [4,11], the movement of grain boundary is hindered by pores, so it is supposed that the decrease in pore number, as seen in Fig. 6, partly contributes to the increase in grain size.

Figs. 8(a) and 8(b) show grain structures of the Nb_2O_5 -doped UO_2 pellets in which the Nb_2O_5

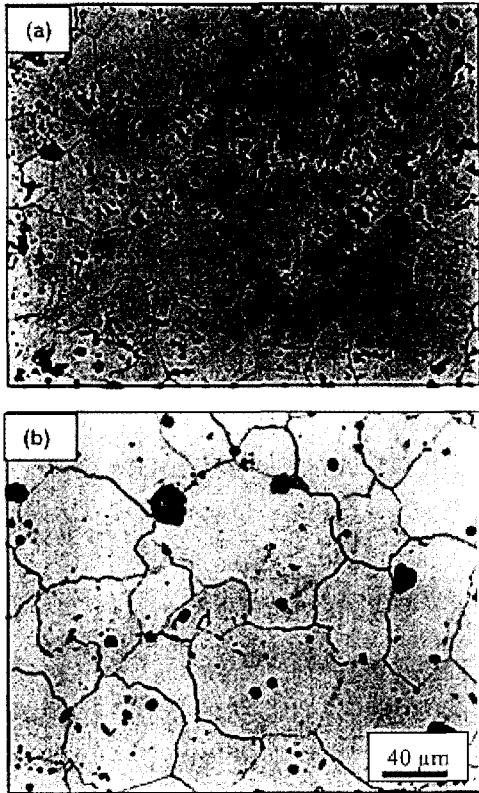


Fig. 8. Grain Structures of Nb_2O_5 -doped UO_2 Pellets.
(a) 0.3 wt% Nb_2O_5 , (b) 0.5 wt% Nb_2O_5

contents are 0.3 wt% and 0.5 wt%, respectively. Most pores are detached from the grain boundary, but large pores of several tens of microns are located on grain corners. It can be readily seen that a grain shape is regular in Fig. 8(a) but is irregular in Fig. 8(b). Such irregular grains are shown with a higher magnification in Fig. 9, in which precipitates are found on the grain boundary. The grain boundary seems to have abruptly changing curvatures around the location of the precipitate, implying that the precipitate sticks to and anchors the grain boundary so strongly that the moving grain boundary hardly escapes. It is suggested that the irregular grain

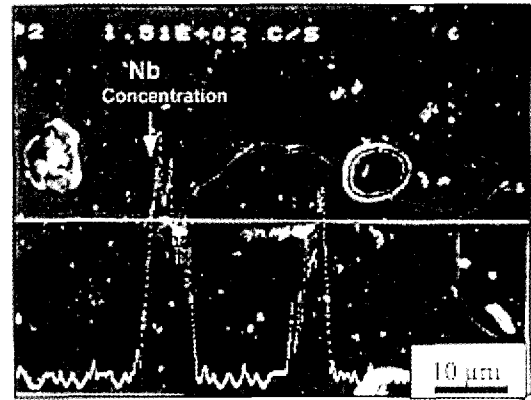


Fig. 9. SEM Micrograph Showing Precipitates in the 0.5 wt% Nb_2O_5 -doped UO_2 Pellet. The Profile of Niobium Concentration is Obtained Along the White Straight Line.

shape in the 0.5 wt% Nb_2O_5 -doped UO_2 pellet may be caused by the precipitate on the grain boundary.

The profile of Nb concentration across the precipitate shown in Fig. 9 indicates that the precipitate has a higher Nb concentration than the surrounding matrix. The quantitative analysis of niobium, uranium and oxygen on both the matrix and the precipitate was performed with EPMA and the results are shown in Table 1. Niobium concentrations of the matrix and the precipitate are 0.22 % and 20.89 % by atom, respectively. The composition of the precipitate in Table 1 indicates that it is an oxide compound like Nb_2UO_6 .

An estimation of the solubility limit of niobium oxide can be made from the results. The niobium concentration in the matrix (0.22 at %), which is equivalent to 0.33 wt% Nb_2O_5 , is probably below the solubility limit at the sintering temperature because it may be decreased during the cooling period from the sintering temperature. On the other hand, from the results that the precipitate

Table 1. The Compositions of Matrix and Precipitate in 0.5 wt% Nb₂O₅-doped UO₂

matrix (at %)	precipitate (at %)
U : 32.74	U : 11.024
Nb : 0.22	Nb : 20.886
O : 67.04	O : 68.091

hinders the migration of the grain boundary, it can be inferred that the precipitate is formed at the sintering temperature, and thus the solubility limit is less than 0.5 wt% Nb₂O₅. The dependences of density and grain size on the Nb₂O₅ content in Figs. 5 and 7 show that densification and grain growth are progressively enhanced in the range of 0.3 wt% to 0.5 wt%, suggesting that the solubility limit may be slightly below 0.5 wt%. Harada [10] determined the solubility limit of Nb₂O₅ to be 0.5 wt% using lattice parameter variation. His work, however, also included the uncertainty derived from the solubility change during the cooling period. The solubility limit which can be estimated from this work seems to be between 0.3 wt% and 0.5 wt% Nb₂O₅.

4. Conclusions

- 1) Compared with those of the undoped UO₂ pellet, both densification and grain growth are enhanced in the 0.3 wt% Nb₂O₅-doped UO₂ pellets sintered at 1700°C under the gas atmospheres which have the H₂O to H₂ gas ratios of about 5.0×10^{-3} to 1.0×10^{-2} . Such enhancement is attributed to the increased concentration of a uranium vacancy which is formed by the interstitial Nb⁴⁺ ion in UO₂ lattice. The sintered density and grain size are nearly independent of the oxygen potential in the range of the above gas ratios.
- 2) The enhancing effect of Nb₂O₅ on the sintered

density and grain size becomes larger as the Nb₂O₅ content increases up to 0.5 wt%. The solubility limit of Nb₂O₅ in UO₂ seems to be between 0.3 wt% and 0.5 wt%, and beyond the solubility limit the second phase whose composition corresponds nearly to Nb₂UO₆ is precipitated on the grain boundary.

Acknowledgements

This work has been carried out under the Nuclear R&D Program supported by MOST.

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