

Effect of TiO₂ on Sintering Behavior of Mixed UO₂ and U₃O₈ Powder Compacts

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Abstract

The effect of TiO₂ on the sintering behavior of mixed UO₂-U₃O₈ powder compacts has been investigated using the U₃O₈ powder made by oxidation of defective UO₂ pellets. Without TiO₂, UO₂ pellet density is inversely proportional to U₃O₈ content and is below 94 %TD in the U₃O₈ range above 15 wt%. Using more than 0.1 wt % TiO₂, however, the density decreases slightly with U₃O₈ content and thus is higher than about 94 % TD in the whole range of U₃O₈ content. The grain sizes of UO₂ pellets with more than 0.1 wt % TiO₂ are larger than about 30 μm. Therefore, the U₃O₈ powder can be reused without any restriction on its amount in UO₂ pellet fabrication by sintering the mixed UO₂-U₃O₈ compact with the aid of TiO₂. Mechanisms for densification and grain growth are proposed and discussed, based on a dilatometry study and an examination of microstructure.

Key Words : Key Words : UO₂ fuel, sintering, U₃O₈ recycle, TiO₂ additive

1. Introduction

The uranium dioxide (UO₂) pellet which has been widely used as a nuclear fuel is manufactured from UO₂ powder by mixing, pressing and sintering. In the manufacturing process, defective UO₂ pellets which do not meet the fuel specifications of density and diameter may be produced. Because defective UO₂ pellets contain expensive enriched uranium, they should be recycled in the manufacture of new UO₂ pellets. A common recycling method is

as follows [1]. Defective UO₂ pellets are oxidized to U₃O₈ powder, which is then mixed with UO₂ powder. The powder mixture of UO₂ and U₃O₈ is pressed and sintered in the same way as the UO₂ powder.

The above recycling method, however, has a problem in that the UO₂-U₃O₈ powder mixture is less sinterable than the UO₂ powder alone. Generally, a content of U₃O₈ powder only up to about 15 wt % is allowed since a larger content of U₃O₈ powder makes a deviation from the acceptable density required by fuel specification.

If many defective UO_2 pellets happen to be made, it will take a long time for them to be recycled. Moreover, the remaining defective pellets will have to be stored for a very long time, if new UO_2 pellets of which U^{235} enrichment is different from that of defective pellets are fabricated before all the defective pellets are recycled. So it is necessary to fabricate UO_2 pellets from the powder mixture with higher U_3O_8 contents.

The effect of TiO_2 addition on the sintering behavior of UO_2 powder compacts has been studied [2,3,4], especially from a grain growth point of view. It is well known that TiO_2 increases grain size very much in UO_2 . Ainscough et al. [2] reported that TiO_2 addition enhanced the densification of UO_2 compacts, and Radford and Pope [4] showed that TiO_2 addition had an enhancing effect on the densification of UO_2 compacts at low temperatures but had a negligible effect on the final density. The effect of TiO_2 addition on the sintering behavior of mixed UO_2 - U_3O_8 powder compacts 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 TiO_2 addition on the densification and grain growth of mixed UO_2 - U_3O_8 powder compacts. The paper also describes the pellet microstructure developed by the TiO_2 addition.

2. Experimental Procedures

The UO_2 powder used in this work was produced through the AUC (Ammonium Uranyl Carbonate) process [5]. U_3O_8 powder was prepared by oxidizing defective UO_2 pellets in flowing air at 400°C for 3 hours. The particle size distribution of UO_2 and U_3O_8 powder was measured by a laser light scattering method, and

their morphology was observed by scanning electron microscopy. The specific surface area of UO_2 and U_3O_8 powder was measured by BET method.

The UO_2 powder was mixed with the U_3O_8 powder in a tumbling mixer together with TiO_2 powder. The powder mixtures had U_3O_8 contents of 10, 20, 30, 40, 60, 80, and 100 wt %, and TiO_2 concentrations were 0.05, 0.1, and 0.2 wt %, respectively. Powder mixtures were pressed under the pressure of 3 ton/cm^2 with die-wall lubrication into compacts, which had a density of about 5.75 g/cm^3 . Powder compacts were heated to 700°C in hydrogen gas and then held for 1 hour to eliminate lubricant. Subsequently, they were heated to 1680°C and held for 4 hours prior to furnace cooling. Hydrogen gas had a dew point of -30°C , so the ratio of water vapor to hydrogen gas was 5×10^{-4} . The densification rate of the powder compact composed of 60 wt % UO_2 and 40 wt % U_3O_8 was measured with a dilatometer (Netzsch) under the same heating rate and gas atmosphere as those in the above-mentioned sintering condition.

Pellet density was determined by the water immersion method, and pellets were sectioned longitudinally and polished. To observe the grain boundary, thermal etching was carried out at 1250°C for 1 hour in CO_2 gas, and the grain size was determined by a linear intercept method. The second phase formed in the TiO_2 -doped UO_2 pellet was quantitatively analyzed by electron probe micro analysis.

3. Results and Discussion

3.1. Effect of TiO_2 on Densification Behavior

The particle size distribution of UO_2 and U_3O_8

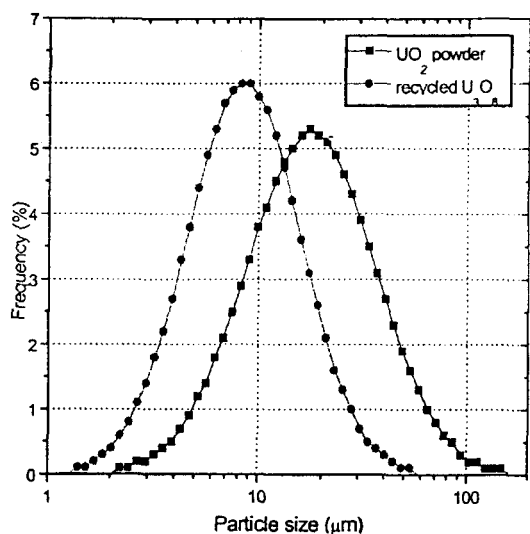


Fig. 1. Particle Size Distribution of UO_2 and U_3O_8 Powder

powder is shown in Fig. 1. Both powders have a mono-modal distribution, and the mode which occurs with the greatest frequency is $17 \mu\text{m}$ for UO_2 powder and $8 \mu\text{m}$ for U_3O_8 powder. 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 large stress involved in the oxidation of UO_2 to U_3O_8 . It has been known that the particle size of U_3O_8 powder is mainly dependent on the oxidation temperature [6]. As the oxidation temperature increases, the stress involved in the oxidation is so relieved that cracks are less developed in a pellet and the particle size of U_3O_8 powder increases. Moreover, UO_2 pellets cannot be pulverized above a temperature of about 900°C because of the formation of a crack-free U_3O_8 layer [7]. In order to make fine U_3O_8 powder, it is important to perform the oxidation of UO_2 pellets at a temperature as low as possible [6].

Figs. 2(a) and 2(b) show the morphology of

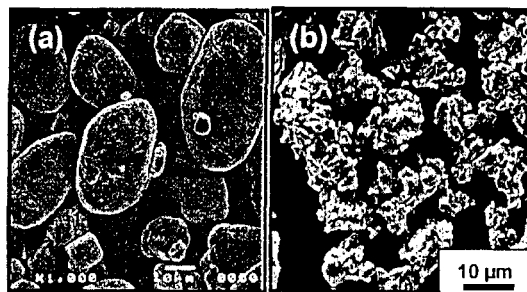


Fig. 2. Micrographs Showing the Morphology of (a) UO_2 and (b) U_3O_8

UO_2 and U_3O_8 powder, respectively. Each UO_2 particle has a round shape and a smooth surface, so the UO_2 powder is well flowing. However, each U_3O_8 particle has an angular shape and also has many cracks that were formed during the oxidation, so the U_3O_8 powder is not well flowing. The specific surface areas of UO_2 powder and U_3O_8 powder are $5 \text{ m}^2/\text{g}$ 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 reduced UO_2 powder, which can be made by reducing the U_3O_8 powder, has a specific surface area of $0.36 \text{ m}^2/\text{g}$.

The U_3O_8 fraction in the mixed UO_2 - U_3O_8 compact is reduced to UO_2 during sintering. According to the work on the kinetics of U_3O_8 reduction [8], U_3O_8 was reduced to UO_2 between 500°C and 600°C in H_2 gas for less than 1 hour. Since the densification of mixed UO_2 - U_3O_8 compacts starts at about 800°C (see Fig. 5), it is reasonable to suppose that the U_3O_8 powder in a powder compact is reduced to UO_2 powder before significant densification during the sintering in hydrogen. 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 variation of UO_2 pellet density as a function of TiO_2 concentration for

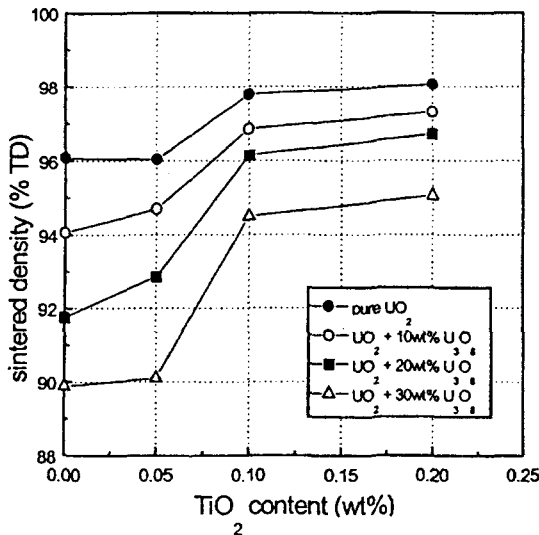


Fig. 3. Variation of UO₂ Pellet Density with TiO₂ Content

various U₃O₈ contents. In the UO₂ powder compact (without U₃O₈ content), the density is negligibly affected in the concentration range of 0.05 wt % TiO₂, increases to the extent of about 2 % TD at 0.1 wt% TiO₂, and thereafter remains almost constant. Such a correlation between density and TiO₂ concentration is readily found in the other compacts with various U₃O₈ contents, with the density a little decreased. These relations imply that the densification of mixed UO₂-U₃O₈ compacts can be enhanced by the same amount of TiO₂ concentration as that of the UO₂ compact. It can be noticed that more than 0.1 wt % TiO₂ is needed to promote the densification of mixed UO₂-U₃O₈ compacts.

Fig. 4 shows the variation of UO₂ pellet density as a function of U₃O₈ content. Without TiO₂ addition, the density decreases linearly with U₃O₈ content, and the decreasing rate is about 2 % theoretical density (TD) per 10 wt % U₃O₈. This decrease in density can be ascribed to the low specific surface area of U₃O₈ powder. With

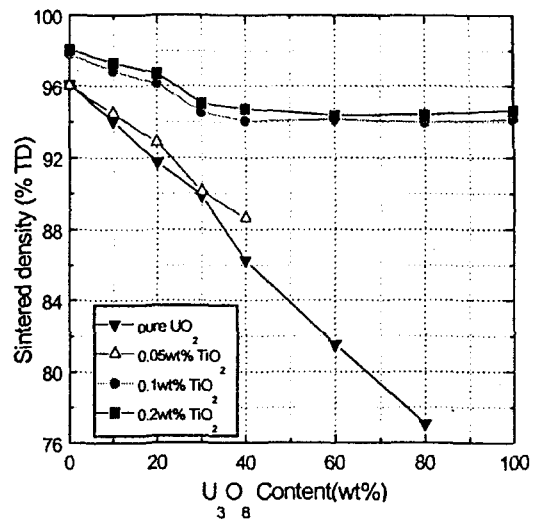


Fig. 4. Variation of UO₂ Pellet Density with U₃O₈ Content

0.05 wt % TiO₂, the dependence of density on the U₃O₈ content is similar to that without TiO₂. With 0.1 wt % and 0.2 wt % TiO₂, the density decreases with U₃O₈ content only in the U₃O₈ range of 40 wt % and remains almost constant beyond that U₃O₈ range. The density is about 94 % TD even at 100 wt % U₃O₈. The fuel specification requires the pellet density to be between 93.5 %TD and 96.5 %TD [1], so with more than 0.1 wt % TiO₂, the density is in the acceptable range under any U₃O₈ content in the mixed UO₂-U₃O₈ compact.

Fig. 4 also shows that the density difference between 'the pellet without TiO₂' and 'the pellet with 0.1 wt % TiO₂' becomes larger as the U₃O₈ content increases. The UO₂ compact is intrinsically sinterable enough to get a pellet density of about 96 %TD so it attains only a small amount of further densification by means of the TiO₂ addition. However, the sinterability of mixed UO₂-U₃O₈ powder compacts decreases with U₃O₈ content, and the amount of further

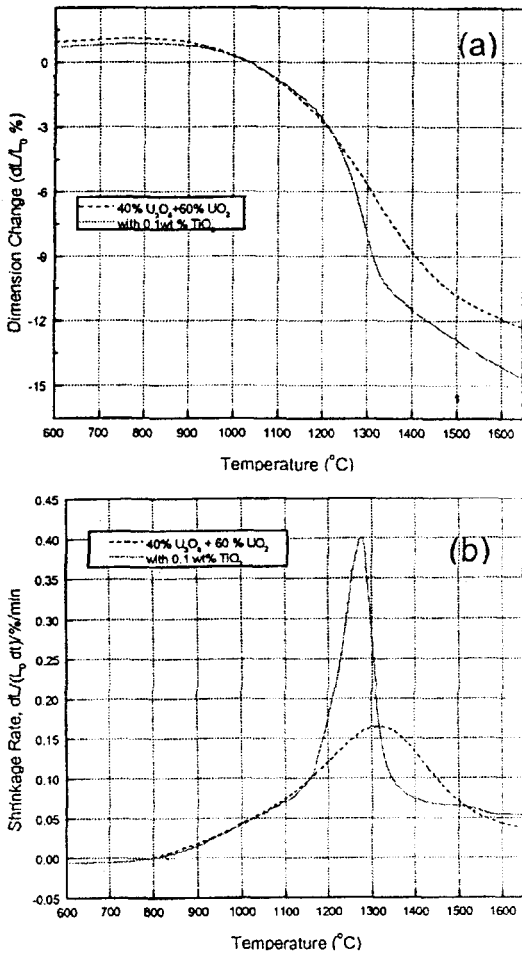


Fig. 5. Shrinkage of the Mixed 60 wt % UO₂-40 wt % U₃O₈ Compact;
(a) Shrinkage Change, (b) Shrinkage Rate

densification due to the TiO₂ addition increases with the U₃O₈ content. Therefore, it can be concluded that the amount of further densification which can be got by the addition of TiO₂ appears to increase as the sinterability of a powder compact decreases.

Fig. 5(a) shows the densification (shrinkage, L/L₀) of the mixed 60 wt % UO₂-40 wt % U₃O₈ compact as a function of temperature. The compacts with and without TiO₂ start to densify at about 800°C, and undergo similar

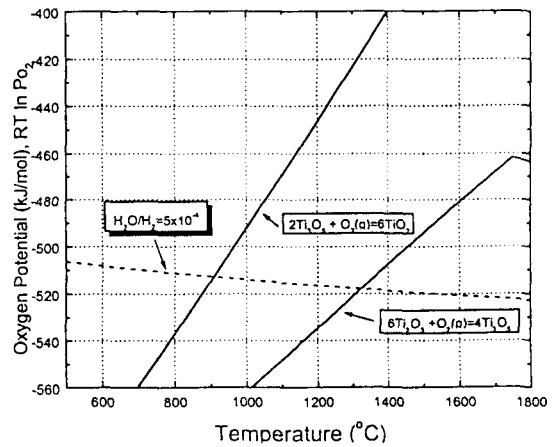


Fig. 6. Oxygen Potentials of Titanium Oxides and Hydrogen Gas with Moisture as a Function of Temperature

densification up to about 1200°C. However, the compact with TiO₂ densifies to a larger extent above 1200°C than the compact without TiO₂. The densification difference between the two compacts, which is made during heating to about 1350°C, seems to remain almost constant even at higher temperatures. This densification difference suggests that TiO₂ addition enhances the densification of the mixed UO₂-U₃O₈ compact mainly in the intermediate sintering stage.

Fig. 5(b) shows the densification (shrinkage) rates as a function of temperature. It can be readily seen that the compact with TiO₂ densifies with a high rate in a short range of temperature, but the compact without TiO₂ densifies with a low rate in a broad range of temperature. The two densification rates increase gradually with temperature and are equivalent up to 1150°C, but they become greatly different from each other above 1150°C. The compact with TiO₂ densifies more rapidly between 1150 and 1300°C than the compact without TiO₂. Therefore, the added TiO₂ seems

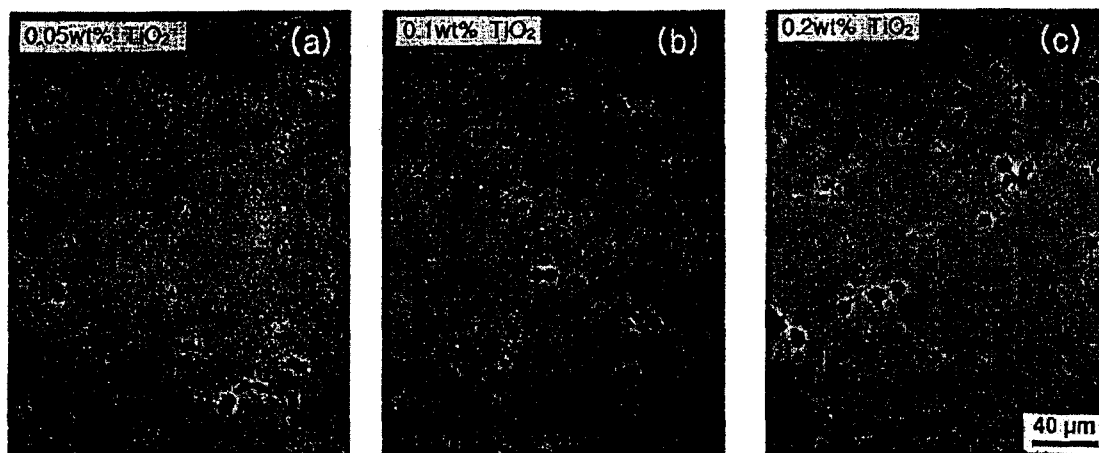


Fig. 7. Microstructures of UO_2 Pellets with TiO_2 Additions; (a) 0.05 wt%, (b) 0.1 wt%, (c) 0.2 wt% TiO_2 .

to be working in the above temperature range.

The oxygen potentials of titanium oxides and hydrogen gas with a dew point of -30°C are calculated with the HSC software [9], and the results are shown as a function of temperature in Fig. 6. A stable form of titanium oxide is dependent on temperature under hydrogen gas. TiO_2 is stable below 900°C , and Ti_3O_5 between 900 and 1300°C , and Ti_2O_3 above 1300°C . Since the mixed $\text{UO}_2\text{-U}_3\text{O}_8$ compact with TiO_2 densifies with a higher densification rate between 1150 and 1300°C than the compact without TiO_2 (see Fig. 5(b)), it is reasonable to suppose that the influential titanium oxide is mainly Ti_3O_5 . The above temperature range is much below the $\text{UO}_2\text{-TiO}_2$ eutectic melting point ($1600^\circ\text{C} - 1620^\circ\text{C}$) [2], so liquid phase sintering is not related with the enhancement of a densification rate.

Ti_3O_5 may be an oxide compound in which a titanium ion has valences of 3+ and 4+. If a titanium ion with a valence of 3+ is dissolved substitutionally in UO_2 , only the oxygen vacancy may be newly formed so that the increases in uranium diffusion is not expected. If titanium

ions with valences of 3+ and 4+ are dissolved interstitially in UO_2 , uranium vacancy may be newly formed so that densification is expected to be enhanced as a result of the increase in uranium diffusion. It can be proposed that Ti_3O_5 is dissolved interstitially in UO_2 to accelerate a densification rate.

3.2. Effect of TiO_2 on Microstructure

Figs. 7(a), 7(b) and 7(c) show the microstructures of the UO_2 pellets made of the UO_2 compacts with 0.05 wt %, 0.1 wt %, and 0.2 wt% TiO_2 , respectively. It can be readily seen that pores decrease substantially in number as the TiO_2 concentration changes from 0.05 wt % to 0.1 wt %. The pore structure of the pellet with 0.1 wt % TiO_2 seems to be similar to that with 0.2 wt% TiO_2 .

Figs. 8(a), 8(b), 8(c) and 8(d) show the microstructures of the 0.1 wt % TiO_2 -doped UO_2 pellets made from UO_2 , 80 wt % $\text{UO}_2\text{-}20$ wt % U_3O_8 , 40 wt % $\text{UO}_2\text{-}60$ wt% U_3O_8 , and U_3O_8 compacts, respectively. It can be seen that the pores increase in number significantly with the

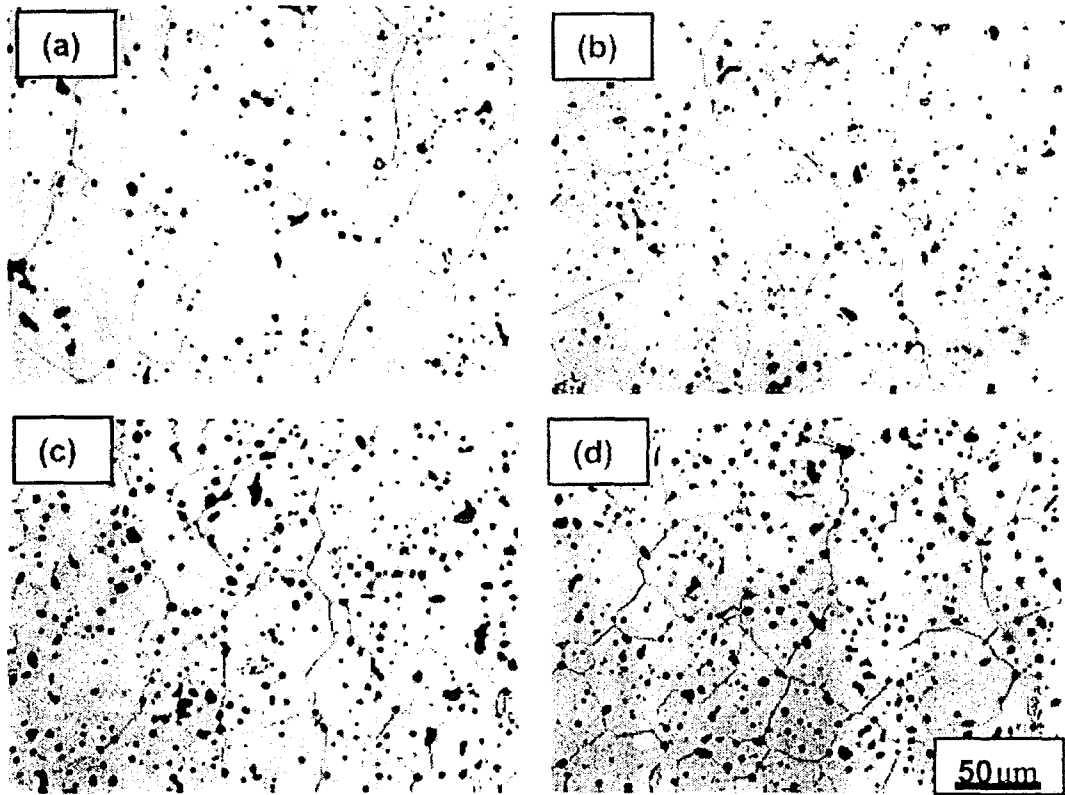


Fig. 8. Microstructures of 0.1 wt % TiO₂-doped UO₂ Pellets Made from the Compacts Comprising (a) UO₂, (b) 80 wt% UO₂-20 wt% U₃O₈, (c) 40 wt% UO₂-60 wt % U₃O₈, (d) U₃O₈

Table 1. Compositions of Matrix and a Second Phase in the 0.1 wt % TiO₂-doped UO₂ Pellet

Elements	matrix (atomic %)	second phase (atomic %)
U	31.445	21.830
Ti	0.134	9.837
O	68.422	68.331

U₃O₈ content in the U₃O₈ range of 60 wt %. However, pores increase slightly with the U₃O₈ content beyond 60 wt% U₃O₈.

Figs. 9(a) and 9(b) show the second phase found in the UO₂ pellet with 0.1 wt% TiO₂. Fig. 9(a) shows that a second phase having a very

small dihedral angle is precipitated on the grain boundary, suggesting that the second phase was once a liquid phase during sintering. The formation of a liquid phase was previously reported by Ainscough et al. [2]. The profile of titanium concentration across the second phase shows that the second phase has a higher titanium concentration than the matrix (see Fig. 9(b)). The quantitative analysis of titanium, uranium and oxygen was performed by EPMA, and the results are shown in Table 1. The matrix has a titanium concentration of 0.134 atomic %, which is equivalent to 0.125 wt % TiO₂ addition. The dissolved titanium can be derived from Ti₃O₅ in the temperature range between 900°C

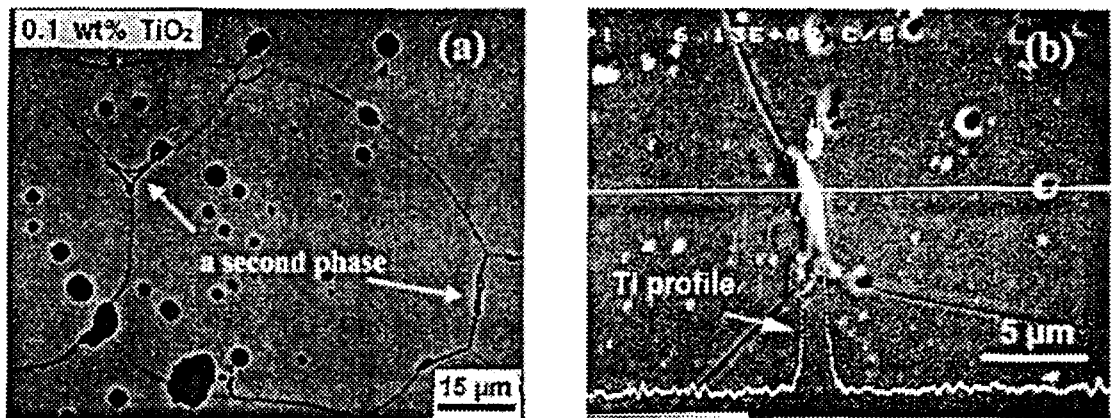


Fig. 9. Micrographs Showing the Second Phase Formed on the Grain Boundary

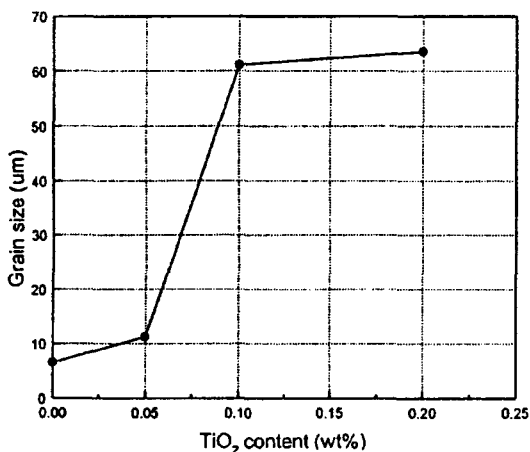


Fig. 10. Variation of the Grain Size of UO₂ Pellets with TiO₂ Content

and 1300°C, and from Ti₂O₃ above 1300°C, as shown in Fig. 6.

Fig. 10 shows the effect of TiO₂ addition on the grain size of the UO₂ pellet made from the UO₂ compact. The grain size is slightly increased by the addition of 0.05 wt % TiO₂ but is enormously increased up to about 60 μm by the addition of 0.1 wt % TiO₂. Fig. 11 shows the grain sizes of UO₂ pellets made from (UO₂ - U₃O₈) compacts with 0.1 and 0.2 wt % TiO₂.

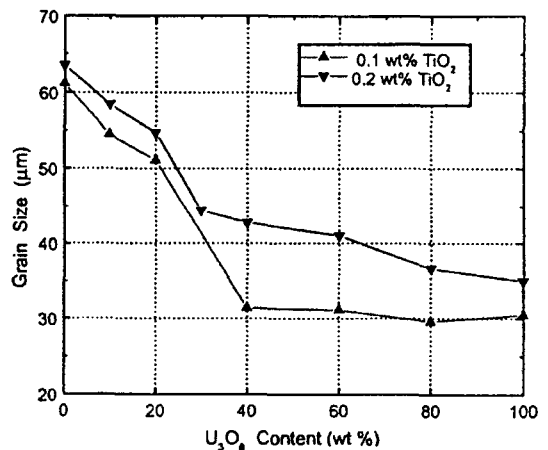


Fig. 11. Variation of the Grain Size of UO₂ Pellets with U₃O₈ Content.

The dependence of grain size on U₃O₈ content shows two different behaviors according to the U₃O₈ content. In the range of about 40 wt % U₃O₈, the grain size decreases significantly with U₃O₈ content, but in the range of above 40 wt % U₃O₈, it decreases slightly. Such decreasing behavior is probably attributed to the change in pore number in the respective range. Fig. 8 implies that pores increase in number significantly with U₃O₈ content in the range of

low U₃O₈ contents but increase slightly with U₃O₈ content in the range of high U₃O₈ contents. An increase in the pore number can yield a small grain size since grain growth in UO₂ is retarded by pores [10,11].

A powder compact is subject to densification rather than grain growth before a final sintering stage during sintering. A final sintering stage begins with the closure of open pore channels, and it is known that a powder compact is densified to at least 90 % TD to reach a final sintering stage. Fig. 5(a) suggests that the compact with TiO₂ densifies to 90 % TD above the temperature of about 1500°C, so the role of TiO₂ addition in grain growth could be negligible below 1500°C. Accordingly, the dissolved Ti₃O₅, which mainly enhances the densification of a compact between 1150 and 1300°C, is not likely to influence grain growth. It is found that a liquid phase is formed on the grain boundary during sintering. The increase in grain size may be ascribed to the presence of a liquid phase, since material transport can be substantially enhanced through the liquid phase.

4. Conclusions

TiO₂ is added to the powder mixture of UO₂ and U₃O₈, and the powder mixture is then pressed and sintered to fabricate UO₂ pellets. Without TiO₂, the UO₂ pellet density decreases very much with U₃O₈ content so that it becomes lower than 94 % TD for more than 15 wt% U₃O₈. However, with more than 0.1 wt % TiO₂, the density decreases slightly with U₃O₈ content in the U₃O₈ range of 40 wt% and then does not decrease any more. So the density is higher than 94 % TD in the whole range of U₃O₈ content. The amount of densification which can be got by TiO₂ addition appears to increase as the sinterability of powder compacts decreases. The

addition of TiO₂ enhances the densification of a mixed UO₂-U₃O₈ compact between 1150°C and 1300°C, so it is proposed that Ti₃O₅ is interstitially dissolved in UO₂ to accelerate the densification rate. The grain size is enormously increased by the addition of more than 0.1 wt % TiO₂, mainly because a liquid phase is formed on the grain boundary during the sintering.

Acknowledgement

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