

Microstructural Analysis on UO_2 and UO_2 -4wt% CeO_2 by Using Additives in Reducing and Oxidizing Atmospheres

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Abstract

The effects of dopants on the modification of microstructure of UO_2 and UO_2 -4wt% CeO_2 sintered pellets have been studied in hydrogen and CO_2/CO mixture atmospheres by using Ta_2O_5 , TiO_2 and Nb_2O_5 as sintering additives. The dopants were added as oxide powders and homogenized by attrition milling. The mixed powders were pressed, and then sintered in hydrogen at 1700°C , or in oxidizing atmosphere using controlled CO_2/CO mixtures at 1250°C .

Both density and microstructure of UO_2 are modified by the addition of dopants in reducing atmosphere. The sintered density is increased with Ta_2O_5 addition up to 0.33wt% and subsequently decreased with higher content of the additive. The effects on the densification and the grain growth are apparent with the addition of 0.24wt% Nb_2O_5 . With 0.1wt% titania and 0.6wt% Ta_2O_5 , the sintered density is decreased, but the grain size is increased.

In oxidizing atmosphere, the grain sizes for UO_2 doped with the above additives are smaller than that for pure UO_2 . The grain size of Ta or Nb-doped UO_2 is decreased with increasing CO_2/CO ratio, but that of pure UO_2 or Ti-doped UO_2 is increased. A large portion of second phases is observed in UO_2 doped with 0.1wt% TiO_2 sintered in hydrogen atmosphere, while, in CO_2/CO atmospheres, the second phases or dopant agglomerates are not observed.

For UO_2 -4wt% CeO_2 mixed oxide, the effect of additives on the grain growth is not so much as that for the pure UO_2 . This is attributed to the formation of clusters by dopant cations and Ce ions, so that the additives contribute to a lesser extent to the grain growth for the mixed oxide.

1. Introduction

It is known that the microstructure of UO_2 and UO_2 -based fuel pellets is modified by the addition of sintering additives, so that their plasticity, ability of retaining fission gas and/or fuel swelling can be improved during irradiation [1-2]. Densification of fuel pellet during reactor operation depends strongly on the porosity content, grain size and fission rate. Fine por-

es in coarse grain fuel are more stable than those in fine grain fuel during irradiation. Therefore, the fuel with controlled microstructure is expected to improve the safety margin of fuel in extended burnup stages.

In early investigations, Ti [3-7], Nb [6-8], V [9] and Mg [10] have been used as sintering additives for UO_2 . These additives result in larger grains than would have been produced by sintering pure UO_2 at the same oxygen potential, as the additives cause

enhanced uranium diffusion rates. However, the contributions of these additives are a little different among them, and the causes of the accelerated grain growth have not been clarified yet.

TiO_2 and Nb_2O_5 can be reduced in dry hydrogen atmosphere at sintering temperature, but can be present as higher valence states as the oxygen potential increases in oxidizing atmosphere. Reduction of TiO_2 occurs above $300^\circ C$ in reducing atmospheres or vacuum, and above about $800^\circ C$ in air [3], which shows the readiness in reduction of the Ti^{4+} ions to Ti^{3+} ions. Nb is also reduced from 5+ valence state and is present as Nb^{4+} in UO_2 for sintering in hydrogen atmosphere [11].

If Ti^{3+} or Nb^{3+} ions which are reduced in hydrogen enter into UO_2 lattice substitutionally during sintering, the grain size of Ti- or Nb-doped UO_2 rather decreases than pure UO_2 . The reason for the positive effects of Nb and Ti on the grain growth of UO_2 in reducing atmosphere can be interpreted if Nb^{3+} or Ti^{3+} enters into the UO_2 lattice interstitially.

Moreover, the UO_2 - TiO_2 system is a simple eutectic system which melts at about $1645^\circ C$ [7, 12]. It was suggested that the increased densification and grain growth rates of Ti-doped UO_2 are due to the effect of the liquid eutectic at the grain boundaries [3]. Arthur and Scott [12], however, have shown, by sintering above and below the eutectic temperature, that the increased densification rate is not due to the eutectic phases, though a liquid eutectic is a pre-requisite for enhanced grain growth. The main contribution of Nb_2O_5 or TiO_2 additions to the grain growth of UO_2 has not been clearly known.

In this study, the contributions of dopants on the sinterability of UO_2 and UO_2 -4wt% CeO_2 have been studied in hydrogen and CO_2/CO mixture atmospheres. TiO_2 and Nb_2O_5 have been used as sintering additives. Ta_2O_5 is selected as another candidate for sintering additive because Ta has a stable 5+ valence.

The sintering behaviors are compared between pure UO_2 and additive-doped UO_2 , in reducing and

oxidizing atmosphere, respectively. The effects of additives on the densification and grain growth of UO_2 -4wt% CeO_2 mixed oxide are also studied. The causes of the different contributions of dopants between oxidizing and reducing atmosphere are discussed in terms of defect structures.

2. Experimental

UO_2 powder used for the experiment was AUC-derived UO_2 , of which the main impurity levels are shown in Table 1. CeO_2 and the sintering additives, Ta_2O_5 , TiO_2 , and Nb_2O_5 , were added as fine oxide powders with the purity of 99.99%. The additives were doped to UO_2 at the level of 0.1wt% of oxide, and further addition of 0.24wt% for Nb_2O_5 , 0.33 and 0.6wt% for Ta_2O_5 were made. The addition of dopants to UO_2 and homogenization was made for 30minutes by attrition milling using zirconia ball media which occupy 43 vol% of mill jar volume.

The mixed powders were pressed into pellets of 10mm in diameter at 312MPa with die wall lubrication. The pellets were subsequently sintered in hydrogen at $1700^\circ C$ for 4 hrs or in oxidizing atmosphere using controlled CO_2/CO mixture at $1250^\circ C$ for 5hrs. The pellets sintered in oxidizing atmospheres were reduced in hydrogen at $1200^\circ C$ for 2 hrs. Densities of the sintered pellets were measured by

Table 1. Impurity contents of UO_2 powders

U content : 87.72%			
H_2O : 0.22%			
O/U ratio : 2.099			
Impurities (ppm U basis) :			
Al	< 10	B	< 0.2
C	60	Ca	< 20
Cd	< 0.2	Cr	< 10
Cu	< 10	Dy	< 0.1
F	2.8	Fe	< 50
Gd	< 0.1	Mg	< 10
Mn	< 5	Mo	< 1
Ni	< 10	Si	< 10
Th	< 100		

water immersion method. A pellet of each experimental variable was examined metallographically. Pore size and area fraction of the second phase were quantitatively analyzed by image analyser. Grain size was measured by a linear intercept method.

3. Results and Discussion

Both grain and pore structures of UO_2 are significantly modified by the additions of sintering additives in reducing atmosphere, as shown in Fig. 1. The

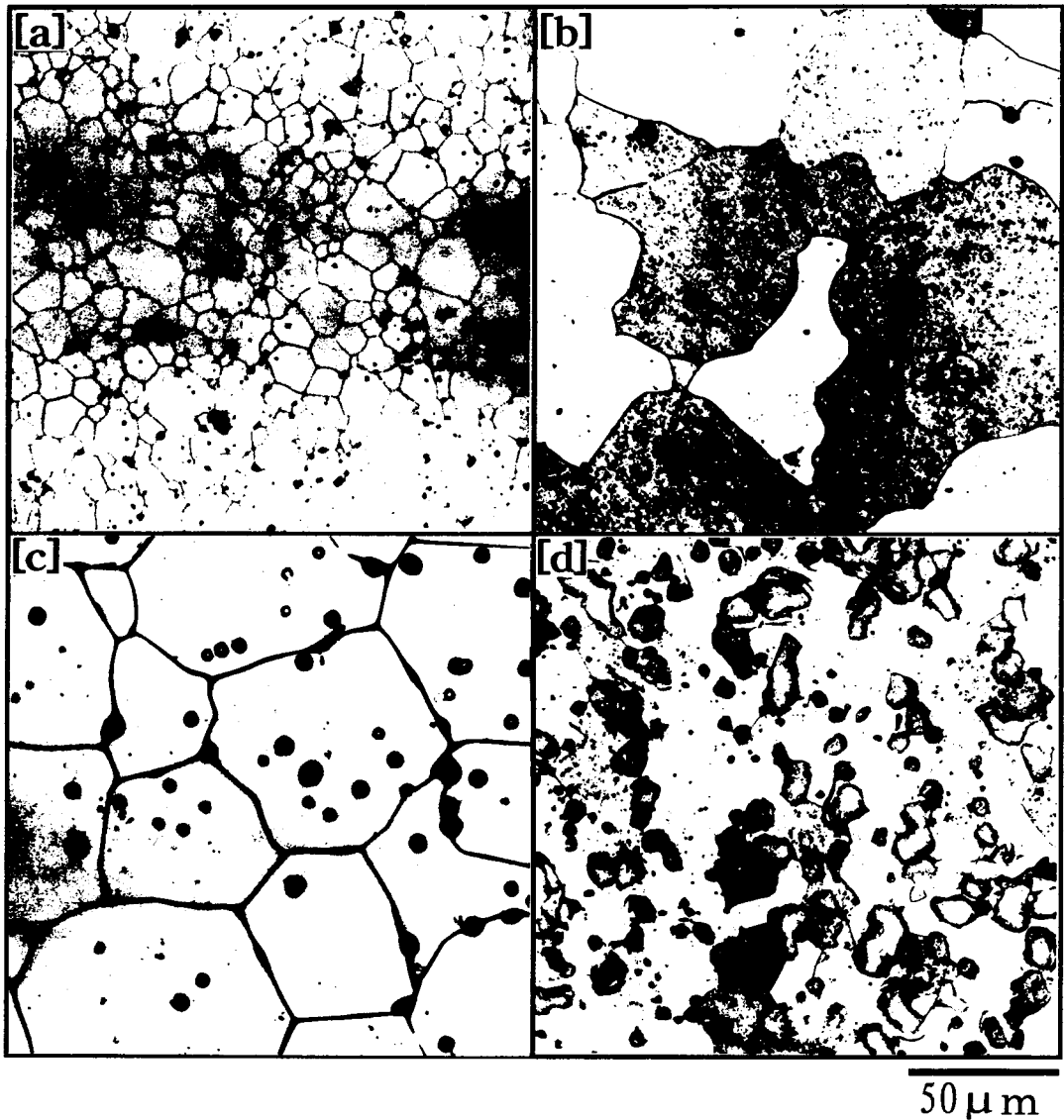


Fig. 1. Micrographs of UO_2 and additives-doped UO_2 in reducing atmosphere at 1700°C .

[a] pure UO_2 (density= $10.73\text{g}/\text{cm}^3$, G.S.= $9\mu\text{m}$)

[b] UO_2 -0.33wt% Ta_2O_5 (density= $10.82\text{g}/\text{cm}^3$, G.S.= $52\mu\text{m}$)

[c] UO_2 -0.24wt% Nb_2O_5 (density= $10.72\text{g}/\text{cm}^3$, G.S.= $49\mu\text{m}$)

[d] UO_2 -0.10wt% TiO_2 (density= $9.30\text{g}/\text{cm}^3$, G.S.= $18\mu\text{m}$)

grain size of pure UO_2 of $9\mu\text{m}$ is increased up to 18, 49 and $52\mu\text{m}$ for the additions of 0.1wt% TiO_2 , 0.24wt% Nb_2O_5 and 0.33wt% Ta_2O_5 , respectively. The sintered density is little affected by additives except for UO_2 doped with 0.1wt% TiO_2 and 0.6wt% Ta_2O_5 , for which the densities are considerably decreased. Originally hyperstoichiometric UO_{2+x} are reduced by the hydrogen to near-stoichiometry, and the sintering additive cations, Ti and Nb are expected to be reduced at the sintering temperature [3, 4, 11]. Previous studies of Ti-doped UO_2 indicated that the reduction of additive cations occurs under reducing sintering conditions [3, 4]. Sawbridge et al. [11] suggested that Nb is present as Nb^{4+} in UO_2 when sintered under dry hydrogen conditions typical of fuel fabrication conditions but can be present as Nb^{5+} as the oxygen potential increases. If Nb^{3+} or Ti^{3+} ions which are reduced in hydrogen enter UO_2 lattice substitutionally, the sinterability of Nb or Ti-doped UO_2 rather decreases than pure UO_2 . Therefore, the reason for the positive effect on the grain growth of Nb and Ti in reducing atmosphere can be interpreted when Nb^{3+} and Ta^{5+} enters the UO_2 lattice interstitially. It has been reported that both Ti and Nb ions can be accommodated readily in the large interstitial holes regardless of their valence state [6, 13]. However, the higher valent Ta^{5+} or Nb^{5+} ion is difficult to enter the UO_2 lattice because of the charge compensation. Ta^{5+} or Nb^{5+} which has higher valence than U^{4+} also imparts an effective positive charge to the UO_2 lattice regardless of the mechanism of solid solution formation.

The main reason of the grain growth of UO_2 with additive addition is due to the increase of uranium diffusivity. Once the solid solution is formed, the Ta, Nb or Ti imparts an effective positive charge to the UO_2 lattice and decreases; although the prevailing defects in UO_2 are oxygen vacancies and interstitials (anti-Frenkel type defect), both Frenkel and Schottky defects are present simultaneously and additions of Nb_2O_5 , Ta_2O_5 and TiO_2 should decrease the concentration of anion vacancies, thereby increasing the con-

centration of cation vacancies through Schottky equilibrium [6]. The increase of the uranium lattice vacancies increases its diffusion coefficient.

Fig. 2 shows the effect of Ta addition on the sinterability of UO_2 in reducing atmosphere. The sintered density and the grain size are increased with Ta content up to 0.33wt% Ta_2O_5 but subsequently decreased by higher contents of Ta. The sintered density is decreased by the addition of 0.6wt% Ta_2O_5 , but grain size is larger than that for pure UO_2 . Ta contributes positively to the sinterability of UO_2 within the solubility limit when Ta^{5+} ions form a solid solution with UO_2 . If the amount of the additive exceeds the solubility limit, the additive cations can affect negatively on the sinterability [3].

Fig. 3 shows the sintering behaviors of UO_2 and 0.1wt% additive-doped UO_2 in reducing and oxidizing atmospheres, respectively. The sintered density of doped UO_2 is nearly the same as that of pure UO_2 , except for Ti-doped UO_2 sintered in reducing atmosphere. In the case of 0.1wt% Ti-doped UO_2 , the sin-

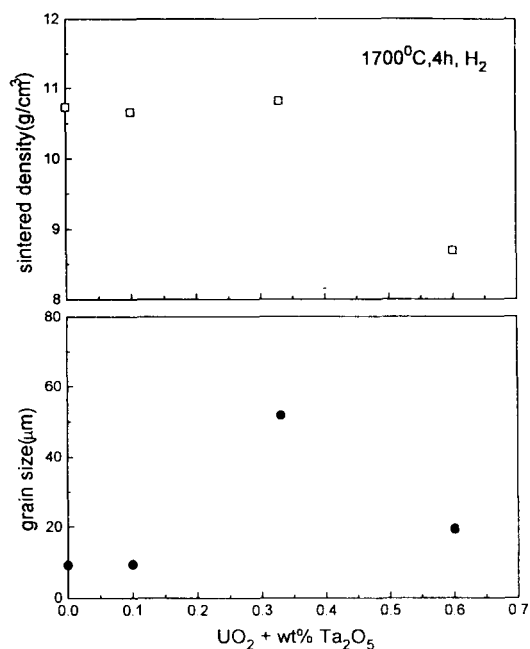


Fig. 2. Variations of sintered density and grain size with the content of Ta_2O_5 in reducing atmosphere.

tered pellets have the minimum density of 9.3g/cm^3 , but the grain size is increased up to $18\mu\text{m}$. For Ta- or Nb-doped UO_2 , both the sintered density and the grain size are nearly the same as pure UO_2 sintered in reducing atmosphere. Both the grain and the pore size for 0.1wt% Nb-doped UO_2 are larger than those for any others sintered in oxidizing atmosphere with $\text{CO}_2/\text{CO}=1/1$. The grain size of pure UO_2 and Ti-doped UO_2 is increased with increasing CO_2/CO ratio, contrary to that of Ta- and Nb-doped UO_2 which is decreased as CO_2/CO ratio increases. Pore size is slightly increased by dopant addition in hydrogen, but decreased in $\text{CO}_2/\text{CO}=80/1$.

Fig. 4 shows the microstructures of UO_2 and 0.1wt% additive-doped UO_2 sintered in oxidizing atmosphere with $\text{CO}_2/\text{CO}=1/1$ and $\text{CO}_2/\text{CO}=80/1$. The grain size for additive-doped UO_2 is smaller than that for pure UO_2 in oxidizing atmosphere. It is evi-

dent that each of the sintering additives produces a suppression in grain growth of UO_2 sintered in oxidizing atmosphere, meanwhile, in reducing atmosphere, it enhances the grain growth.

In the reducing atmosphere, it is difficult to form a complex defects in additive-doped UO_2 solid solutions because the concentration of oxygen vacancy is very low. However, in oxidizing atmospheres, the interstitial oxygen ions which have negative effective charge compensate the positive charge of dopant cations. In this case, the dopant cations can not contribute to the formation of uranium vacancies, but can make dopant-oxygen clusters, such as (Ta O_i) , (Nb O_i) and (Ti O_i) . These clusters restrict the transport of uranium ions, so that the grain size is rather decreased in oxidizing atmospheres. Microstructures in Fig. 4 also show that the grain growth for UO_2 and Ti-doped UO_2 is much enhanced as increasing CO_2/CO ratio, whereas that for Ta and Nb-doped UO_2 is inhibited. The different dependence of grain growth on CO_2/CO ratio is due to the difference in the formation of defect structure with charge compensation in each of the hyperstoichiometric solid solutions. Other factors such as the ionic size of the dopant cations and their solubility limits are also considered to play an important role. The oxygen potential of $\text{U}_{1-y}\text{Ta}_y\text{O}_{2+x}$ is lower than that of pure UO_2 [14], similar to those of $\text{U}_{1-y}\text{Ti}_y\text{O}_{2+x}$ [13] and $\text{U}_{1-y}\text{Nb}_y\text{O}_{2+x}$ [15]. The effect of aliovalent cations doped substitutionally in UO_2 on the oxygen potential is generally explained by the valence control rule. If all the titanium cations are present as Ti^{4+} ions substitutionally, no direct effect on the defect structure and on uranium diffusion is to be expected. In the case of TiO_2 , Ti ions enter into UO_2 lattice interstitially, and interstitial Ti_i ions react with interstitial oxygen to form $(\text{Ti}_i \text{O}_i)^{\bullet\bullet}$ clusters which have the positive effective charge. Therefore, the grain size of pure UO_2 and Ti-doped UO_2 can be increased as CO_2/CO ratio increases. For Nb^{5+} and Ta^{5+} , these ions enter into UO_2 lattice substitutionally in oxidizing atmosphere, since it is difficult for them to compensate the

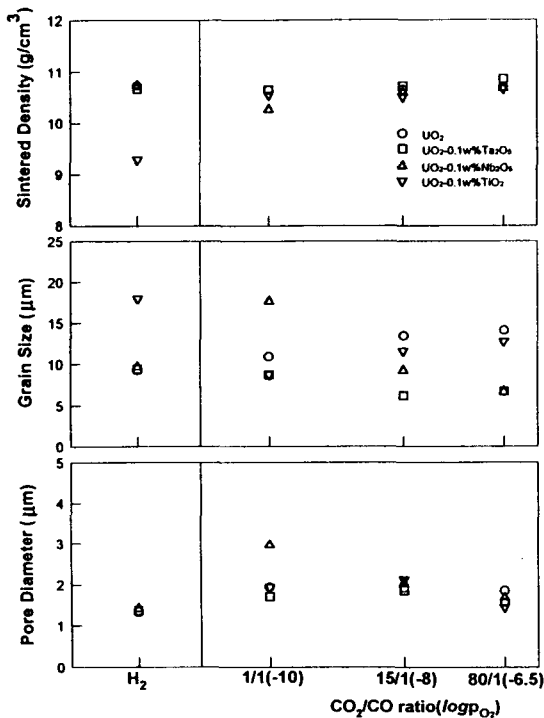
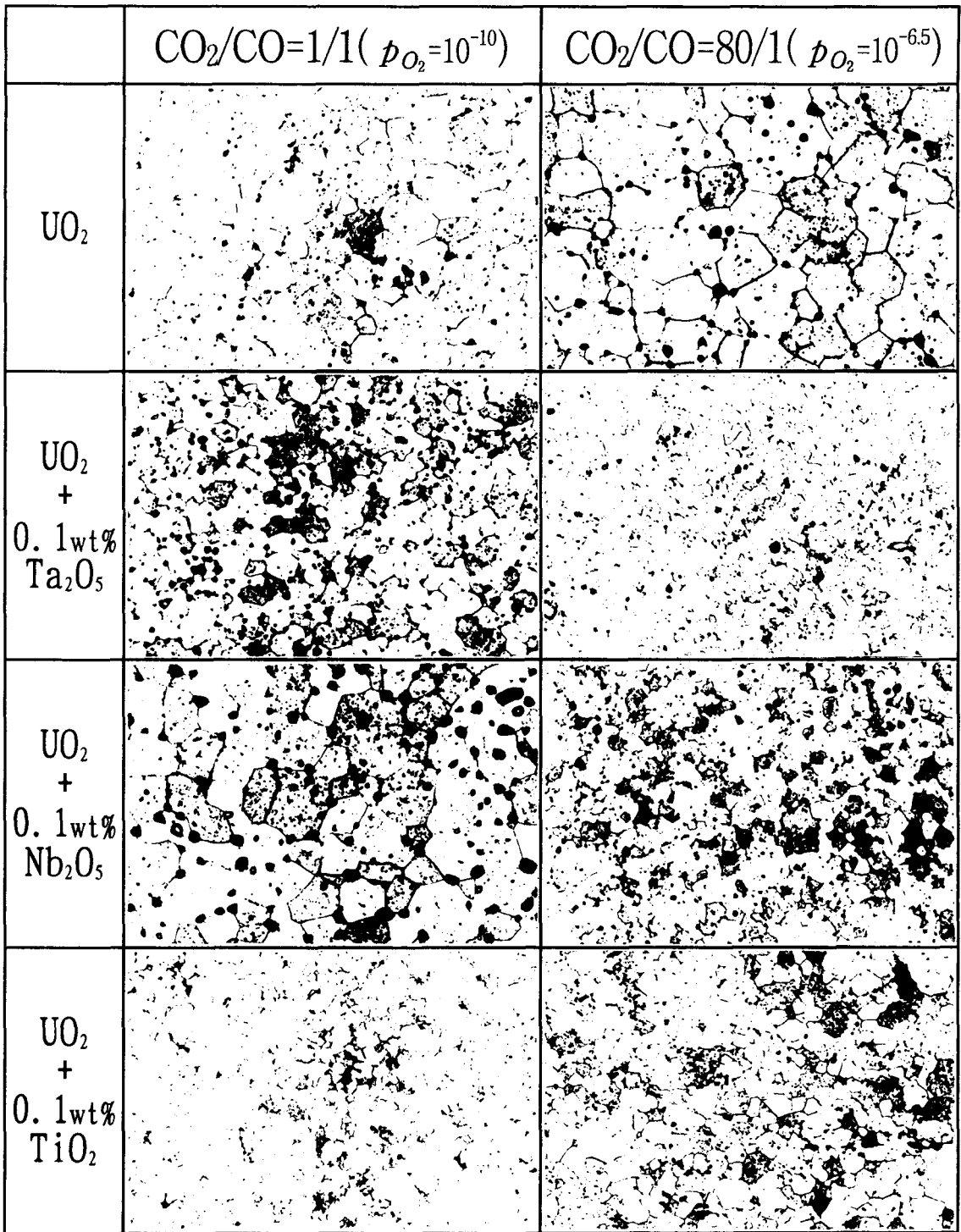


Fig. 3. Sintering behaviors of UO_2 and additives-doped UO_2 in hydrogen at 1700°C and in CO_2/CO at 1250°C , respectively.



50 μm

Fig. 4. Micrographs of UO_2 and additives-doped UO_2 sintered at $1250^\circ C$ in CO_2/CO ratio=1/1 and 80/1, respectively.

charge valence by entering interstitially [16]. The substitutional Nb and Ta ions react with interstitial oxygen ions and form clusters such as $(\text{Nb}_U \cdot \text{O}_i'')$, $(\text{Ta}_U \cdot \text{O}_i'')$ which have the negative effective charge so that the grain sizes are decreased as CO_2/CO ratio increases.

Fig. 1, [c] and Fig. 4 show that the solubility limit is affected by the sintering atmospheres. A large portion of second phase is observed in UO_2 doped with 0.1wt% TiO_2 sintered in hydrogen atmosphere at 1700°C , while none of any dopant oxides or the eutectic phases can be observed in the pellets sintered in CO_2/CO atmospheres at 1250°C . Second phases have been previously reported in the $\text{UO}_2\text{-TiO}_2$ [4, 12] and $\text{UO}_2\text{-V}_2\text{O}_5$ [9] systems. The eutectic can form only if the additive concentration exceeds the solubility limit [3].

The additive cations going into solutions require the formation of defects such as oxygen interstitials or uranium vacancies to compensate charge valence in hyperstoichiometric UO_{2+x} . Ti^{4+} has been found to be more soluble in UO_2 than the lower valence states [4]. It is probably due to the smaller radius of Ti^{4+} ion than that of Ti^{3+} , and moreover, the easier compensation of charge valence by the interstitial oxygens in oxidizing atmosphere. The Ta ion exists only in 5+ valence state and can not form non-stoichiometric compositions, however, the results are the same as Ti-doped UO_2 because of its easier charge compensation by the formation of the $(\text{Ta}_U \cdot \text{O}_i'')$ clusters. Therefore, the solubilities of both Ti and Ta are increased in hyperstoichiometric UO_{2+x} . The amount of dopants going into solid solutions at a given temperature can therefore be controlled by the oxygen potential of the sintering atmosphere.

For $\text{UO}_2\text{-4wt}\%\text{CeO}_2$ mixed oxides, the pellet sintered in H_2 at 1700°C shows the density of $10.38\text{g}/\text{cm}^3$ and the grain size of $7\mu\text{m}$. Fig. 6 shows the microstructural appearance of the mixed oxide and additives-doped mixed oxide pellets. The grain and pore morphology was not affected by the addition of Ta_2O_5 . The grain size of the mixed oxide pellet dop-

ed with Nb_2O_5 was $10\mu\text{m}$ and reached to a density of $10.29\text{g}/\text{cm}^3$.

The pellet of TiO_2 -doped $\text{UO}_2\text{-4wt}\%\text{CeO}_2$ mixed oxide reached only to a density of $9.87\text{g}/\text{cm}^3$, but shows increased grain size of $16\mu\text{m}$. The eutectic phases have also been observed in the TiO_2 -doped mixed oxide.

In the mixed oxide, Ce ions make a substitutional solid solution with UO_2 , and have negative effective charge in the solution. If each of sintering additives, Ta_2O_5 , Nb_2O_5 and TiO_2 is added to the mixed oxide, the dopant cation which has positive effective charge would react with Ce and form defect cluster, such as $(\text{Ce}_U \text{Ta}_U)^x$, $(\text{Ce}_U \text{Nb})''$ or $(\text{Ce}_U \text{Ti})''$ in reducing atmosphere at the sintering temperature. The defect cluster which has neutral or negative effective charge reduce the sinterability of the mixed oxides. Ta_2O_5 little contributes to the sinterability of the $\text{UO}_2\text{-4wt}\%\text{CeO}_2$ mixed oxide, however, for TiO_2 and Nb_2O_5 , the grain sizes are increased since their defect clusters have positive effective charges in reducing atmosphere.

4. Conclusions

Ta, Ti and Nb are effective sintering additives for UO_2 in reducing atmosphere. The sintered density and the grain size are increased with Ta content up to 0.33wt% Ta_2O_5 but subsequently decreased by higher contents of Ta. The grain size of pure UO_2 and Ti-doped UO_2 is increased with increasing CO_2/CO ratio, but those of Ta and Nb-doped UO_2 is decreased.

A large portion of second phase is observed in UO_2 doped with 0.1wt% TiO_2 sintered in hydrogen atmosphere at 1700°C , but none of any dopant oxides or the eutectic phases is found in the pellets sintered in CO_2/CO atmospheres at 1250°C . It is found that TiO_2 is more soluble in hyperstoichiometric UO_{2+x} than in stoichiometric UO_2 .

Each additive, Ta, Nb or Ti is considered to react with Ce ions and form defect clusters in $\text{UO}_2\text{-4wt}\%$

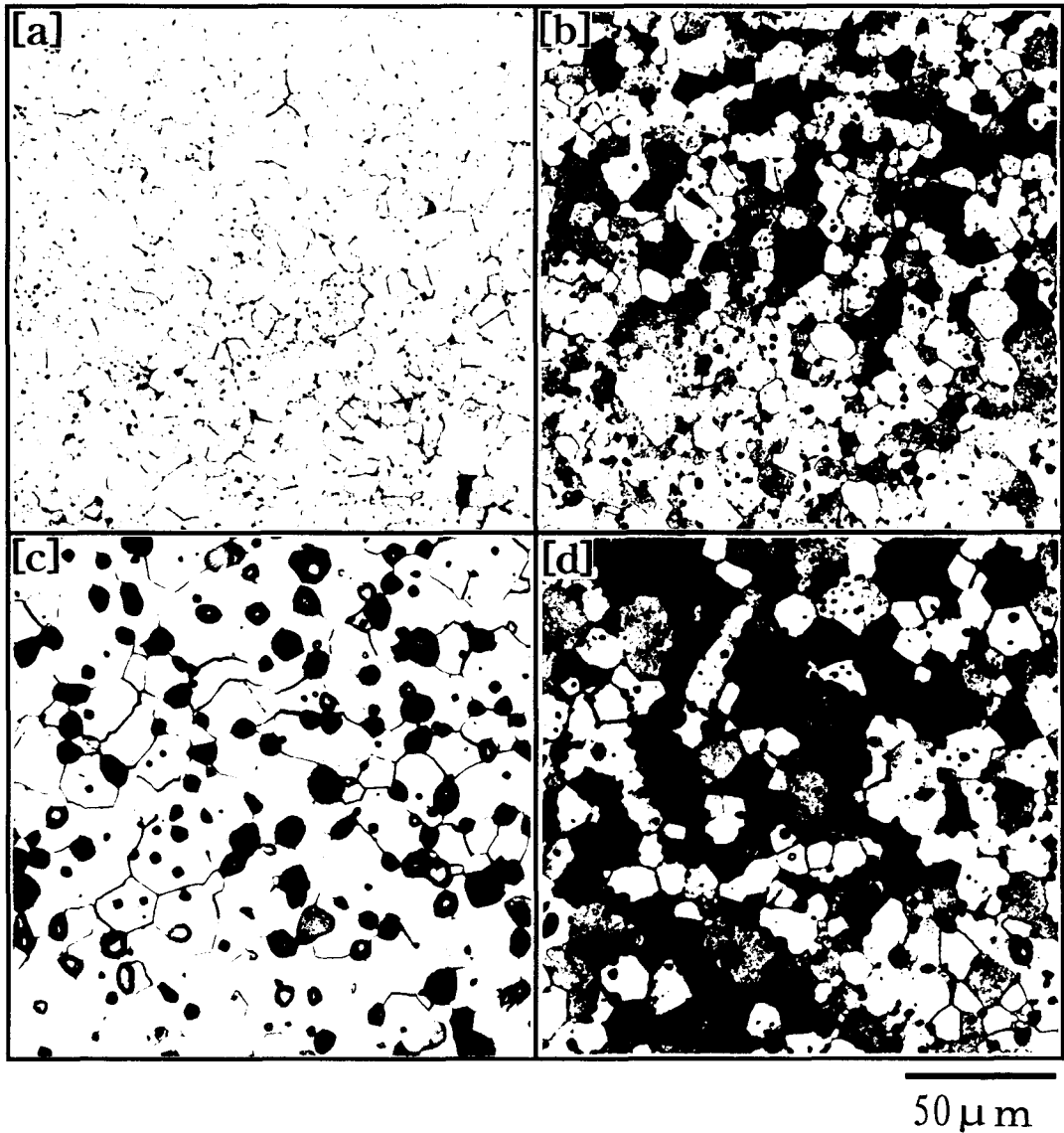


Fig. 5. Micrographs of mixed oxide pellets sintered in hydrogen at 1700°C for 4hrs;
 [a] UO_2 -4wt% CeO_2 (density=10.38g/cm², G.S.=7μm)
 [b] UO_2 -4wt% CeO_2 -0.3wt% Ta_2O_5 (density=10.42g/cm³, G.S.=7μm)
 [c] UO_2 -4wt% CeO_2 -0.1wt% TiO_2 (density=9.87g/cm³, G.S.=16μm)
 [d] UO_2 -4wt% CeO_2 -0.15wt% Nb_2O_5 (density=10.29g/cm³, G.S.=10μm)

CeO_2 mixed oxide at the sintering temperature. The grain of UO_2 -4wt% CeO_2 mixed oxide is not affected by the addition of Ta_2O_5 in reducing atmosphere. However, TiO_2 and Nb_2O_5 contribute to the grain growth of the mixed oxide since the clusters have

positive effective charges in reducing atmosphere.

References

1. J. A. Turnbull, J.Nucl. Mater. 50 (1974) 62.

2. J. C. Killeen, *J. Nucl. Mater.* 58 (1975) 39.
3. H. J. Matzke, AECL-2585, May, (1966)
4. J. B. Ainscough, F. Rigby and S. C. Osborn, *J. Nucl. Mater.* 52 (1974) 191.
5. H. J. Matzke, *J. Nucl. Mater.* 20 (1966) 328.
6. K. C. Radford and J. M. Pope, *J. Nucl. Mater.* 116 (1983) 305.
7. R. D. MacDonald, AECL-1810, April, (1963)
8. H. Assmann et al., *J. Nucl. Mater.* 98 (1981) 216.
9. I. Amato et al., *J. Nucl. Mater.* 23 (1967) 103.
10. F. Rigby, UK Patent Application, GB 2 107 691 A
11. P. T. Sawbridge, G.L. Reynolds and B. Burton, *J. Nucl. Mater.* 97 (1981) 300.
12. G. Arthur and D. Scott, *Trans. Brit. Cer. Soc.* 63 (1964) 417.
13. T. Tsuji et al., *J. Nucl. Mater.* 168 (1989) 151.
14. H. S. Kim et al., "Manufacturing Technology and Process for Reactor Fuels" JAERI Workshop, Department of Chemistry and Fuel Research, March 20-24 (1995)
15. T. Matsui and K. Naito, *J. Nucl. Mater.* 136 (1985) 59.
16. O. Toft Soerensen, *Nonstoichiometric Oxides*, Academic Press, p283, (1981)