CHARACTERISTICS OF FUEL PELLET WITH ADDITIVE OF Al AND Si

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Abstract

The large grain pellet is a candidate for a high burnup fuel pellet. We have investigated the large grain pellet in which Al and Si are added within the impurity limits. These additives promote the grain growth of uranium dioxide during sintering and modify the characteristics of the grain boundary. It is expected to reduce fission gas release and pellet cladding mechanical interaction. We have already confirmed that there is a slight difference in the out of pile properties of the UO_2 pellet except for creep behavior. The additive enhances the creep rate over a wide range of creep conditions.

To precisely understand the effect of additives on the fabrication conditions and properties of the pellet, we investigated a UO_2 pellet in which an excess of Al and Si is added. As for grain growth only small amount of additives is needed to cover the grain boundary of UO_2. An excess of additive does not promote further grain growth but leads to suppression of pellet densification by volatilization of the additives. So, an excess of Al and Si is not necessary to improve the microstructure of the pellet and creep behavior, while thermal expansion and diffusivity are not significantly affected by the amount of additive.

1. INTRODUCTION

Coarsening the grain of a UO_2 pellet is considered an effective method to reduce fission gas release. In order to change the microstructure of the UO_2 pellet, various methods are used such as the use of sintering aid and changing the sintering conditions [1]. It is known that some kinds of additives can promote grain growth of the UO_2 pellet during sintering. One is the matrix modification type such as TiO_2 and/or Nb_2O_5 [2.3] which enhances the diffusion in the UO_2 lattice. Another type of additive modifies the grain boundary characteristics such as silicate which forms a glassy phase in the grain boundary and promotes sintering.

In general, it is known that impurities such as silicates easily form a glassy phase. These materials are believed to form glassy phase so that an intergranular phase acts as a rapid diffusion path during the sintering. There are many proposals for the mechanisms of grain growth in the presence of a liquid phase. Also, diffusion or an interface-reaction is considered to be the rate controlling step.

We have investigated a large grain pellet in which Al and Si are added within the impurity limits [4]. The solubility of Al and Si in UO_2 is considered to be limited to a low level and this form an intergranular phase. That phase is considered to promote the grain growth of UO_2 during sintering. But the total amount of the additives is too small to determine how the additives behave in the compacts during sintering. Furthermore, it is important to understand the effect of additive content on sintering behavior and the UO_2 characteristics. In this paper, we describe the behavior of additives in case of a high concentration and the effect of additive content. The microstructure of a sintered UO_2 pellet containing various amounts of Al and Si are presented. The sintering behavior of these compacts are discussed.

2. SINTERING BEHAVIOR

In the presence of additives, which is believed to form a liquid phase such as a silicate, the sintering mechanism differs from that of the solid state shown Fig. 1. But the information for U-Al-Si-O is limited and amount of additive is not sufficient in order to understand the sintering behavior. To understand the behavior of additives during sintering, an excess of Al and Si were added to UO_2.

The ADU process powder was used as UO_2 in this study. Fig. 2 shows a schematic diagram of the manufacturing process. Al_2O_3 and SiO_2 were used as the source of Al and Si, respectively. These powders and UO_2 were mechanically blended and then formed into a pellet using a press. Sintering tests were performed in cracked NH_3 using a dilatometer or batch type furnace.

2.1 Basic behavior of additives during sintering

The sintering kinetics of UO_2 compacts containing various kinds of oxides have been investigated in a dilatometer. Each compact contains a total of 0.5wt% additives. Fig.3 shows the sintering curves of the compacts. The compact with no additives shows a higher shrinkage than the compacts with additives up to 1300°C. By increasing, temperature, the $Al_2O_3{\cdot}SiO_2$-added compact rapidly densifies at about 1400°C. It indicates that the additives inhibit densification of the UO_2 compact during the early stage of sintering and some kinds of additives such as $Al_2O_3{\cdot}SiO_2$ act as a sintering promoter near 1400°C.

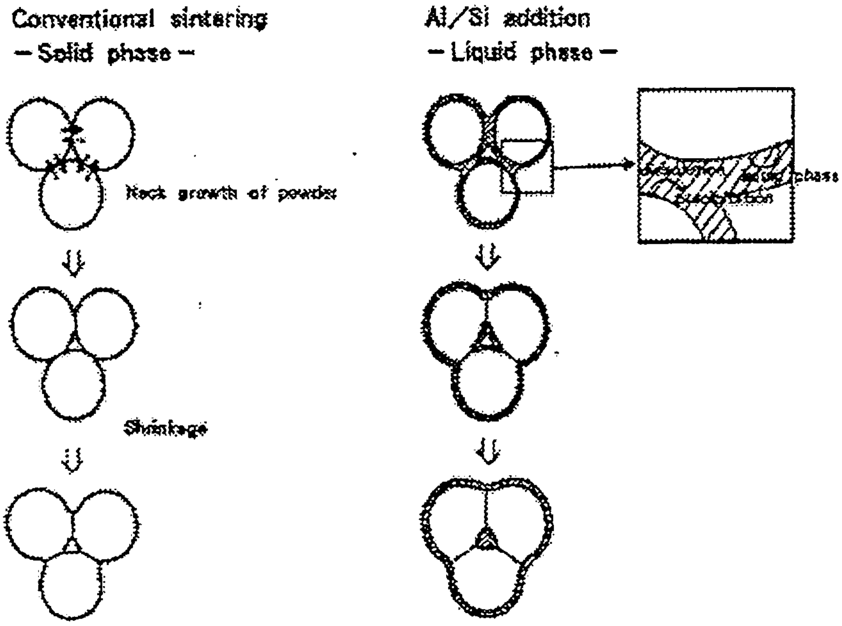

FIG. 1. Sintering behaviour in the presence of Al and Si

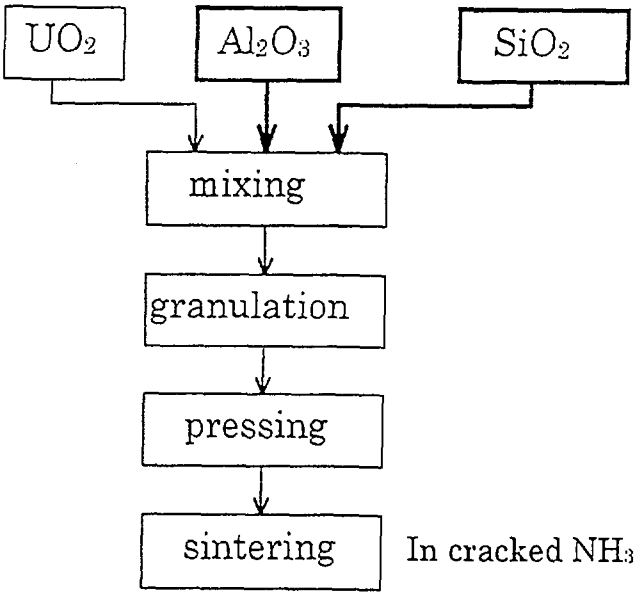

FIG. 2. Schematic diagram of manufacturing process (Al/Si added pellet)

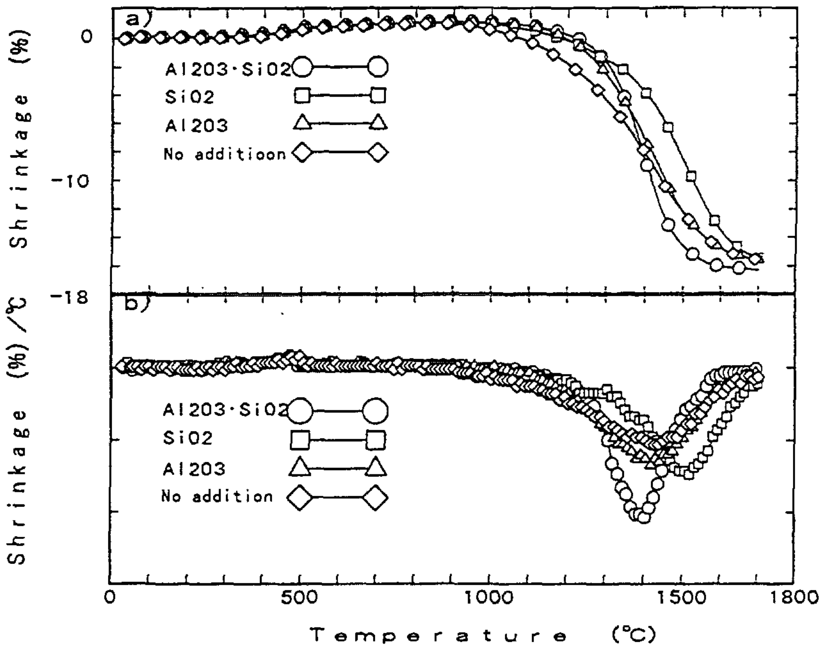

FIG. 3. Effect of additives on sintering behaviour:
a) shrinkage curve b) shrinkage rate

Fig. 4 shows SEM photographs of the polished surface of UO_2 pellets sintered for 4h. at 1500°C. Only the $Al_2O_3SiO_2$-added pellet shows an apparent grain boundary phase which forms a low dihedral angle. The dihedral angle in the sintered body of pure UO_2 is approximately 90° [5]. Strictly speaking, the dihedral angle seems to depend on the number of faces and pore size. Fig. 4 indicates the existence of the boundary phase which has a low interfacial energy with UO_2. The SEM photographs of the $Al_2O_3SiO_2$-added compacts show

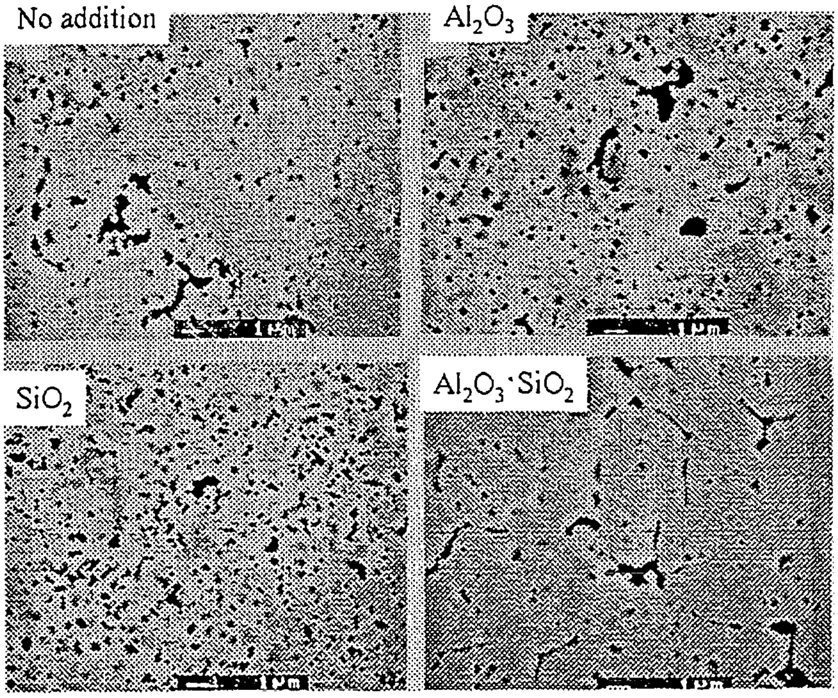

FIG. 4. SEM image of polished surface of sintered UO_2 with 0.5wt% of additives (at 1500 °C, 4h, in cracked NH_3)

that the UO_2 grain form a low dihedral angle in the range of 1400 ~ 1500 °C (Fig. 5). The intergranular phase composed of Al-Si compounds are shown in Fig.6. It is known that SiO_2 easily forms a glass phase during its coexistence with other metal oxides. The intergranular phases are believed to be the liquid phase during the sintering.

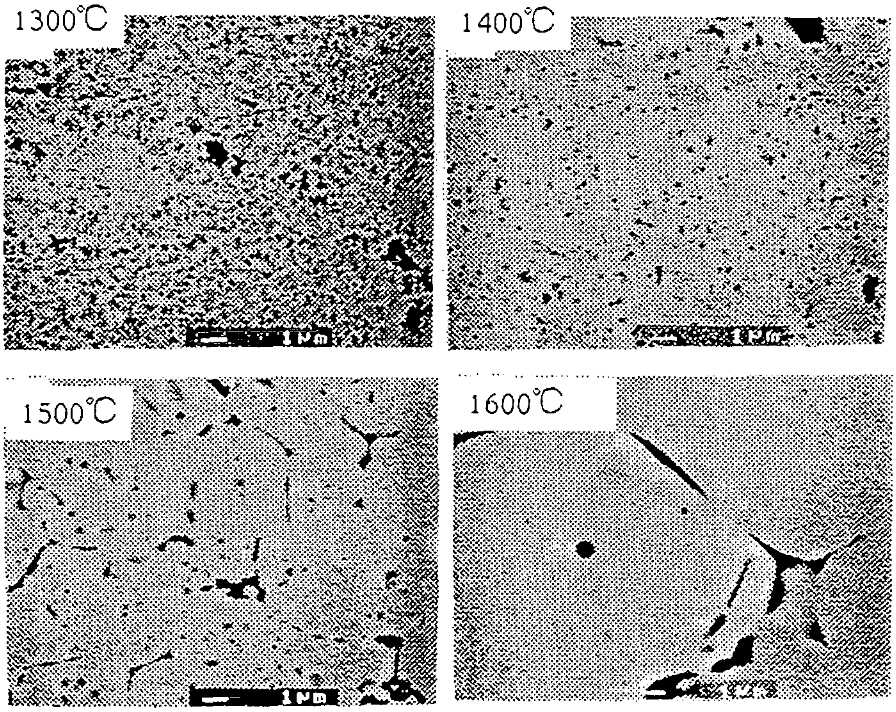

FIG. 5. SEM image of polished surface of sintered UO_2 with 0.5wt% of Al_2O_3 and SiO_2. (for 4h, in cracked NH_3, at various temperature)

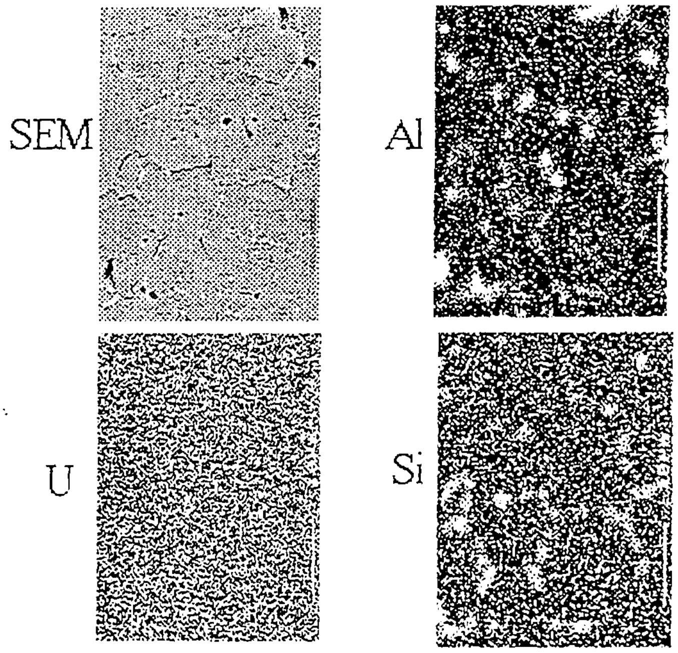

FIG. 6. *SEM image of sintered UO_2 pellet*
Polished surface of sintered UO_2 with 0.5wt% of Al_2O_3 and SiO_2. (for 4h, in cracked NH_3, at various temperature)

As for the compacts manufactured in the same lot, the weight change of the compacts during sintering were measured using thermogravimetry. Fig. 7 shows the weight change of the compact, during heating. The weight of the $Al_2O_3SiO_2$-added and $Si0_2$-added compacts gradually decrease above 1400°C while the no- added and Al_20_3-added compacts are almost stable. This suggests that volatilization of the additives from the compacts has a higher vapor pressure under this condition. Fig. 8 shows the vapor pressure over Al_20_3 and SiO_2 in the equilibrium state, which is calculated from the Gibbs free energy [6]. Each pressure shows the pressure of the gas phase having a maximum partial pressure over the metal oxide. By lowering the oxygen pressure, the partial pressure is higher over the oxide. This supports the results of the weight change of the compacts during sintering.

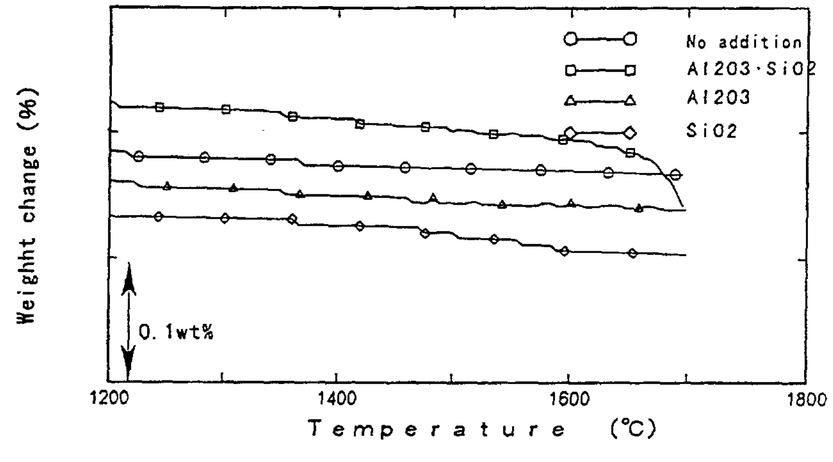

FIG. 7. *Weight change of UO_2 compacts during sintering (sintered rate of 6 °C/min in cracked NH_3)*

Above 1600°C, the rate of weight change for the $Al_2O_3SiO_2$-added compact is apparently higher than that with SiO_2. This indicates that there is a more volatile phase than SiO_2. The rapid weight loss suggests the existence of a liquid phase during sintering.

2.2 Sintering with $Al_2O_3 \cdot SiO_2$

Fig. 9 shows the effects of additive content on sintering behavior. These pellets were sintered for 4h in a batch type furnace. The higher the amount of additive, the lower the density of the pellets, because volatilization of the additives prevents the pellets from densification. This is consistent with the fact that vapor pressures from Al_2O_3 and SiO_2 oxides are quite high in a reducing atmosphere from a thermodynamically viewpoint as shown in Fig. 8. The grains of the pellet have coarsened with only a small amount of additive, but an excess of additive did not cause any further grain growth. This means that only a small amount of additives are needed for grain growth in order to cover the grain boundary of UO_2. An excess of additive leads to suppression of pellet densification by volatilization of the additives.

3. CHARACTERIZATION

UO_2 compacts with various $Al_2O_3 \cdot SiO_2$ contents were sintered for 10h at 1650°C to evaluate their thermal expansion and thermal conductivity.

Thermal expansion of the pellets were examined using differential dilatometer in cracked NH_3. Fig. 10 shows the results of the thermal expansion with additives up to O.Gwt%. It indicates that the UO_2 pellet is not significantly affected by additives. This is consistent with the summation of the theoretical expansion of each UO_2,Al_2O_3 and SiO_2 component.

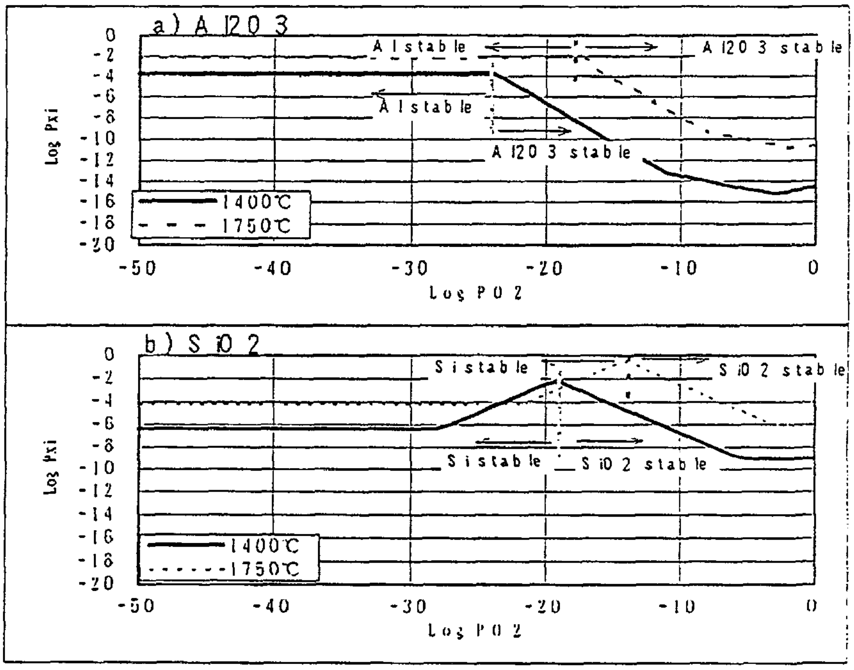

FIG. 8. Maximum vapor pressure for vapor species over oxides in atmospheres with various PO_2 at 1400 and 1750 °C

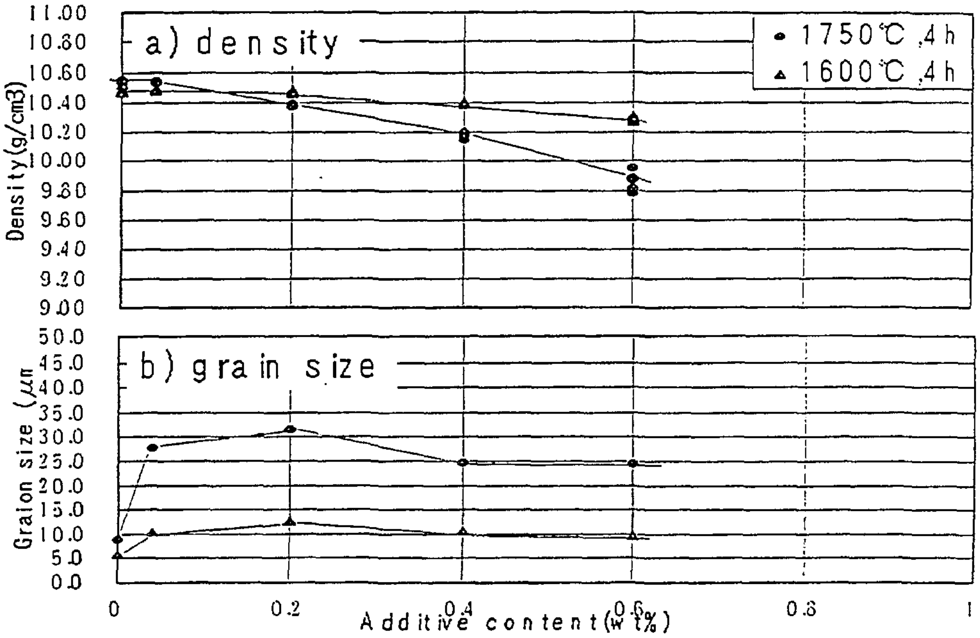

FIG. 9. Effect of additive content on sintering
Each compact is sintered for 4 hrs at prescribed temperature in cracked NH_3

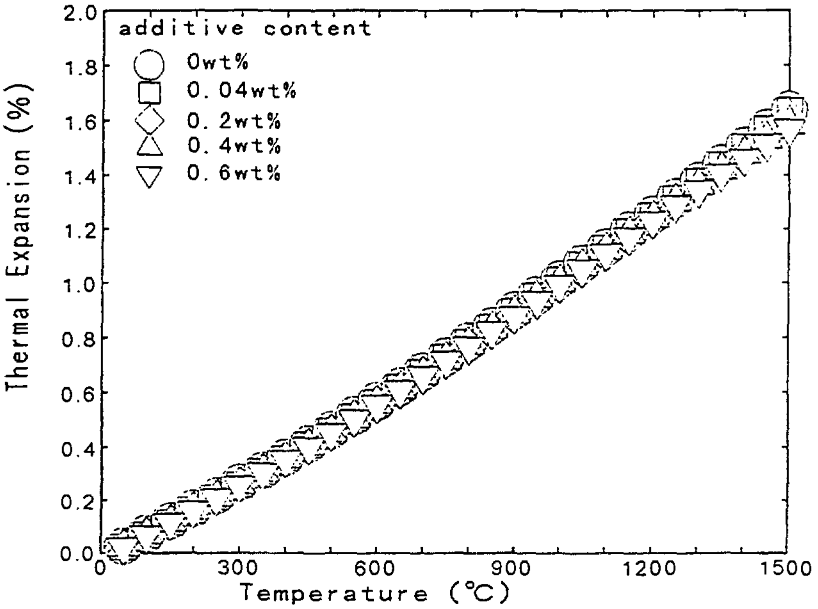

FIG. 10. Thermal expansion of UO_2 pellet containing various amount of Al_2O_3 and SiO_2

Thermal conductivity was calculated from the thermal diffusivity, specific heat and density. Thermal diffusivity was determined using the laser flash technique. In regard to specific heat and density of the pellet, published data were used. Fig. 11 shows the results that the thermal conductivity is not dependent on additives. So, thermal conductivity of the UO_2 pellet with additives within the specified impurity levels is almost the same as that for UO_2.

Fig. 12 shows the effects of additives on the high temperature creep of a UO_2 pellet in a vacuum. These pellets were all sintered for 4h at 1760°C. All the tests were carried out in a vacuum using a compressive creep apparatus under constant load. Initial stress was set to be 45Mpa. Small amounts of additives can enhance the creep rate of the UO_2 pellet. The UO_2 pellet with 50ppm Al and Si shows a higher creep rate than pure UO_2.

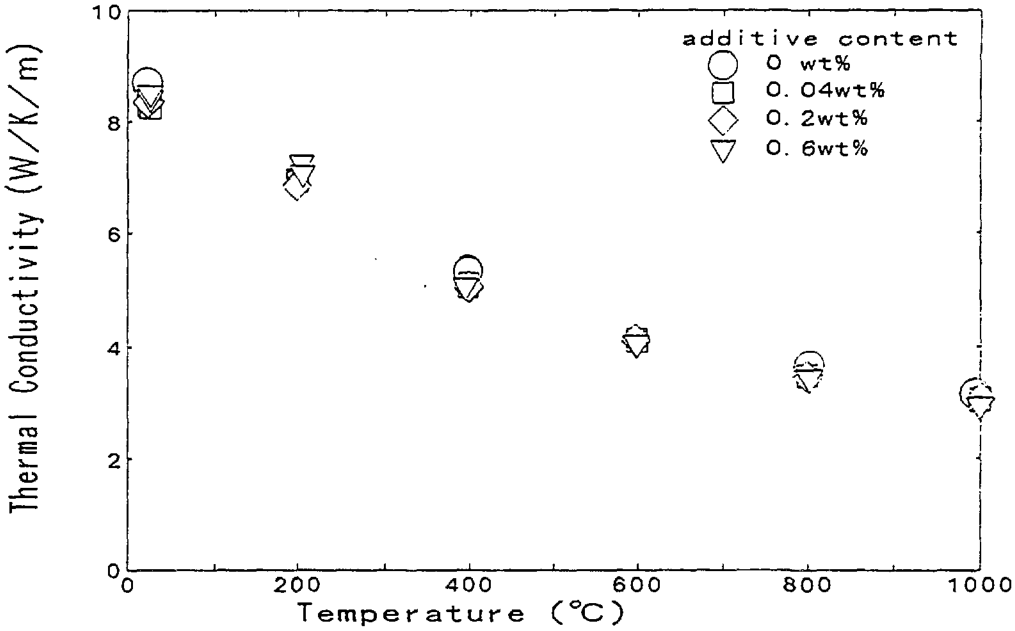

FIG. 11. Thermal conductivity of UO_2 pellet containing various amount of Al_2O_3 and SiO_2

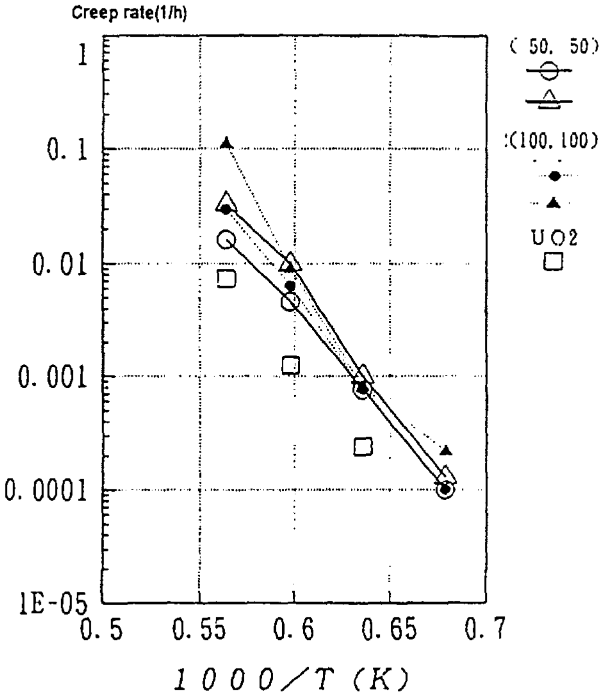

FIG. 12. Creep rate of UO_2 pellets containing Al and Si compressive creep, 45MPa

4. CONCLUSIONS

In order to understand the sintering behavior of the UO_2 compacts containing Al and Si, the compacts in which an excess of Al and Si is added have been sintered and evaluated. The microstructure having a low dihedral angle at the grain boundary intersection was observed after sintering above 1500° C. The intergranular phase rapidly volatilized above 1600°C.

From the results of the sintering tests, we confirmed that only a small amount of additives were needed to cover the grain boundary of UO_2. An excess of additive did not promote further grain growth but lead to suppression of pellet densification by volatilization of the additives.

As for the properties of the UO_2 pellet, thermal expansion and diffusivity were not sufficiently affected by the amount of additive. Also UO_2 the creep rate easily increase by the addition of small amount of Al and Si.

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DISCUSSION

(Questions are given in italics)

As a result of potential volatility of the additives under sintering conditions: Is there any evidence for this in terms of a difference in grain size between the center and surface of pellets doped with alumina silicate ?

No, the microstructure is uniform in the pellet.

Since the Al and Si is concentrated at the grain periphery, what is the influence on the melting point of the resulting fuel?

We think there is no impact on the melting point because of its low content. Our goal is low contents of Al_2O_3 and SiO_2. These contents are under 50 ppm for each element.