

## The compressive creep behavior of (U, Ce)O<sub>2</sub>

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### Abstract

The effects of the CeO<sub>2</sub> content (3.25 and 5 wt%), density (95–98% T.D.), grain size and dopant additions (SiO<sub>2</sub>, 0.005 wt%; Li<sub>2</sub>O, 0.1 wt%) on the creep behavior of the UO<sub>2</sub>–CeO<sub>2</sub> sintered pellet have been investigated. Stress exponent,  $n$ , derived from the stress–creep rate relationship shows two values depending on the stress applied. One is  $n = 0.97$ – $2.26$  in the lower stress region, and the other is  $3.40$ – $8.90$  in the higher stress region in the experimental ranges of this study. It is noted that the former is controlled by a diffusion process, and the latter is controlled by a dislocation motion mechanism. The activation energy for the creep increased as the CeO<sub>2</sub> content increased.

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**Keywords:** UO<sub>2</sub>; Creep mechanism; CeO<sub>2</sub>; Stress exponent; Creep activation energy

### 1. Introduction

The creep properties of an oxide fuel pellet during reactor operations are very important. As a result of the interactions with the fuel cladding, a differential thermal expansion and volume change induced by fission product stresses and strains develop within the fuel pellet. These stresses and strains make the fuel element brittle and result in a crack formation or plastic deformation. In general, most plastic deformations of ceramic materials occur through a high temperature creep because they have no instantaneous deformation at a low temperature. So many studies for the creep properties of an oxide nuclear fuel pellet have been performed. Among the oxide nuclear fuels UO<sub>2</sub>, as a pure or a mixed oxide, is very widely used for reactor fuels.

In general, the creep properties of an oxide nuclear fuel are directly related to the oxygen to metal ratio (O/M), sintered density, grain size, applied stress and dopant additions. O/M refers to atoms O/(atoms Pu + atoms U). Changes in any of these variables can alter the controlling mechanism and significantly change the mechanical deformation behavior [1–7].

Most experimental data on the creep behavior of an oxide fuel can be described by the following form of the Arrhenius

equation:

$$\dot{\epsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right)$$

where  $\dot{\epsilon}$  is a creep rate,  $A$  the material parameter determined by the microstructure,  $\sigma$  the stress,  $n$  the stress exponent,  $Q$  the creep activation energy,  $R$  and  $T$  are the gas constant and absolute temperature, respectively. In the case where the  $n$  values exist in the range of 1–2 and 4–5, the creep mechanism is governed by a diffusion mechanism and a dislocation movement, respectively.

In this work, the creep behavior of (U, Ce)O<sub>2</sub> was investigated to understand the effects of the parameters (CeO<sub>2</sub> contents, sintered densities and grain sizes) as a function of the temperature and applied stress. A compression test, which was implemented under reactor operating conditions, was chosen for this investigation.

### 2. Experimental

Ex-DC depleted UO<sub>2</sub> powder with varying contents of CeO<sub>2</sub> powder (3.25 and 5 wt%) were prepared as a mixture. SiO<sub>2</sub> (0.005 wt%) and Li<sub>2</sub>O (0.1 wt%) as dopants were added into these powders. After mixing with these powders, the powder mixture was milled and homogenized by a batch-type attrition mill. The green pellets, which were compacted into a cylindrical

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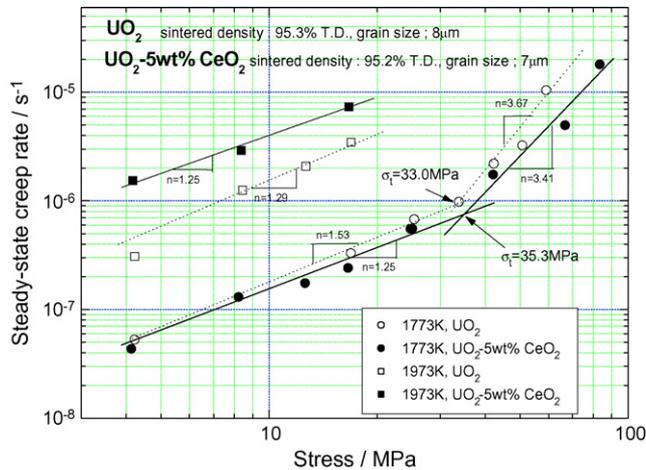


Fig. 1. The creep rate of  $\text{UO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  as a function of the stress (density;  $\sim 95\%$  T.D., grain size; 7–8  $\mu\text{m}$ ).

type from the milled powders, were sintered at the temperature of 2023 K for 4 h under a flowing hydrogen atmosphere. The size of the specimen, which is a sintered pellet, was 0.008 m (diameter) and 0.008 m (length).

The compressive creep tester (Unitherm TM 9607, Anter Corp.) is used to obtain a deformation rate of a specimen at the temperature range of 1773–1973 K and the stress range of 4–90 MPa under a flowing hydrogen atmosphere. The steady-state creep rate of a specimen,  $\dot{\epsilon}$ , was calculated from the following equation.

$$\dot{\epsilon} = \frac{(L_2 - L_1)/t}{L_1}$$

where  $L_1$  and  $L_2$  are the initial length of the specimen and the length of the specimen after time  $t$ , respectively.

### 3. Results and discussion

#### 3.1. The creep behavior of (U, Ce) $\text{O}_2$ as a function of the $\text{CeO}_2$ content

Fig. 1 shows the steady-state creep rates of both the  $\text{UO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  sintered pellets, which have a similar sintered density ( $\text{UO}_2$ ; 95.3% T.D.,  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$ ; 95.2% T.D.) and a similar grain size ( $\text{UO}_2$ ; 8  $\mu\text{m}$ ,  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$ ; 7  $\mu\text{m}$ ). As shown in the figure, both the  $\text{UO}_2$  sintered pellet and the  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  sintered pellet had a similar creep rate, however, it appeared that the creep rate of the  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  sintered pellet was higher than that of the  $\text{UO}_2$  sintered pellet at the temperature of 1973 K. It is thought that the solid solution of (U, Ce) $\text{O}_2$  plays an important role on the creep rate as a function of the temperature. And it appeared that the transition stress,  $\sigma_t$ , of the  $\text{UO}_2$  sintered pellet and the  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  sintered pellet at 1773 K are 33.0 and 35.3 MPa, respectively. At the temperature of 1773 K in the range of the stress below the transition stress ( $\sigma < \sigma_t$ ) the stress exponent,  $n$ , of  $\text{UO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  are 1.53 and 1.25, respectively, on the contrary, in the range of  $\sigma > \sigma_t$ , the  $n$  values of  $\text{UO}_2$  and  $\text{UO}_2$ -5 wt%

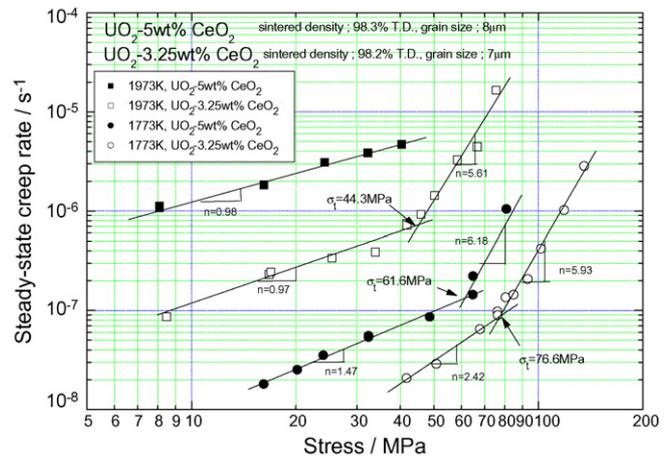


Fig. 2. The creep rate of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  as a function of the stress (density;  $\sim 98\%$  T.D., grain size; 7–8  $\mu\text{m}$ ).

$\text{CeO}_2$  are 3.67 and 3.41, respectively. However, at the temperature of 1973 K, the  $n$  values of  $\text{UO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  are 1.25 and 1.29, respectively.

Therefore, regardless of the addition contents of  $\text{CeO}_2$ , it is considered that the creep behavior of both the  $\text{UO}_2$  and the (U, Ce) $\text{O}_2$  sintered pellet in  $\sigma < \sigma_t$  and in  $\sigma > \sigma_t$  are controlled by a diffusion mechanism and a dislocation movement, respectively. Also at the temperature of 1973 K rather than 1773 K, it appeared that the creep behavior of the specimens was clearly governed by a diffusion mechanism in the higher test temperature.

Fig. 2 shows the steady-state creep rates of both the  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  sintered pellets, which have a similar sintered density ( $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$ ; 98.2% T.D.,  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$ ; 98.3% T.D.) and a similar grain size ( $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$ ; 7  $\mu\text{m}$ ,  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$ ; 8  $\mu\text{m}$ ). As shown in the figure, regardless of the creep test temperature, the specimen had a similar creep rate. And the steady-state creep rate of the specimens increased as the  $\text{CeO}_2$  addition contents increased.

It appeared that the transition stress,  $\sigma_t$  of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  at 1773 K are 76.6 and 61.6 MPa, respectively. And at 1773 K in  $\sigma < \sigma_t$ , the  $n$  values of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  are 2.42 and 1.47, respectively, on the contrary, in  $\sigma > \sigma_t$ , the  $n$  values of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  are 5.93 and 6.18, respectively. But at 1973 K in  $\sigma < \sigma_t$  ( $\sigma_t = 44.3$  MPa), the  $n$  values of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  are 0.97 and 0.98, respectively, however, in  $\sigma > \sigma_t$ , the  $n$  value of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  is 5.61. Therefore, as the addition contents of  $\text{CeO}_2$  increased the steady-state creep rate increased but the transition stress decreased. Also it is thought that the creep behaviors of the (U, Ce) $\text{O}_2$  sintered pellet in  $\sigma < \sigma_t$  and in  $\sigma > \sigma_t$  are controlled by a diffusion mechanism and a dislocation movement mechanism, respectively. And also at the temperature of 1973 K rather than 1773 K, it is considered that the creep behavior of the specimens was clearly governed by a diffusion mechanism in the higher test temperature because the  $n$  values approached 1.

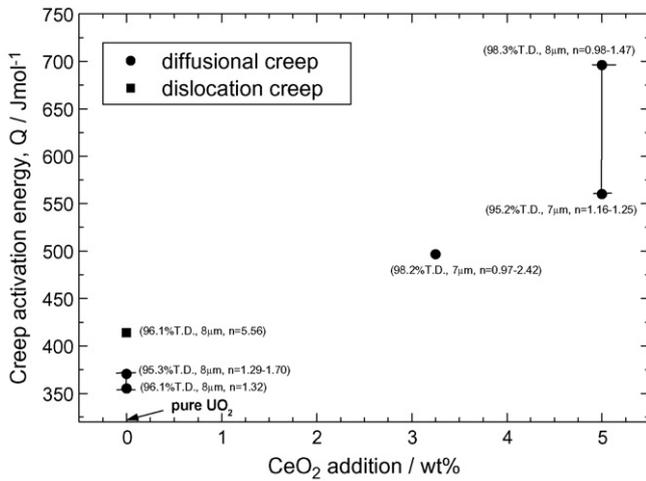


Fig. 3. The creep activation energy of (U, Ce)O<sub>2</sub> as a function of the CeO<sub>2</sub> addition content.

### 3.2. The creep activation energy of (U, Ce)O<sub>2</sub> as a function of the CeO<sub>2</sub> content

Fig. 3 shows the creep activation energies,  $Q$  as a function of the CeO<sub>2</sub> addition contents and stress exponent,  $n$ . In the case of  $n$  value is 1–2, the creep mechanism is governed by a diffusion mechanism, while in the case of  $n$  value is above 4, the creep mechanism is governed by a dislocation mechanism [1]. As shown in the figure, the creep activation energy increased with increasing addition contents of CeO<sub>2</sub> in the range of a diffusion mechanism. It is considered that the increased activation energy for creep is due to the decreased uranium diffusivity owing to the change of the stoichiometry. That is, hypo-stoichiometric CeO<sub>2-x</sub> where creep activation energies varied by a factor of 2 with increase or decrease in O/M ratio, and the creep rate increased with increasing non-stoichiometry [3]. And in the case of the UO<sub>2</sub> specimen, the creep activation energy of it in the dislocation movement mechanism appeared higher than that in the diffusion mechanism.

### 3.3. The creep behavior of (U, Ce)O<sub>2</sub> as a function of the density

Fig. 4 shows the steady-state creep rate of the UO<sub>2</sub>–5 wt% CeO<sub>2</sub> specimens with a varying sintered density (95.2 and 98.3% T.D.) as a function of the applied stress at 1773 K. As shown in the figure, under the same applied stress, as the density of the UO<sub>2</sub>–5 wt% CeO<sub>2</sub> sintered pellet increased the steady-state creep rate of it decreased but the transition stresses,  $\sigma_t$  increased. That is,  $\sigma_t$  is 35.3 and 61.6 MPa for 95.2 and 98.3% T.D., respectively. While, the  $n$  values of the densities of 95.2% T.D. and 98.3% T.D. are 1.25 and 1.47 at below  $\sigma_t$  and 3.41 and 6.18 at above  $\sigma_t$ , respectively. Therefore, as the density of the (U, Ce)O<sub>2</sub> sintered pellet decreased the creep behavior of it is clearly dominant by a diffusion mechanism in the lower stress range but it appeared by a dislocation movement in the higher stress range.

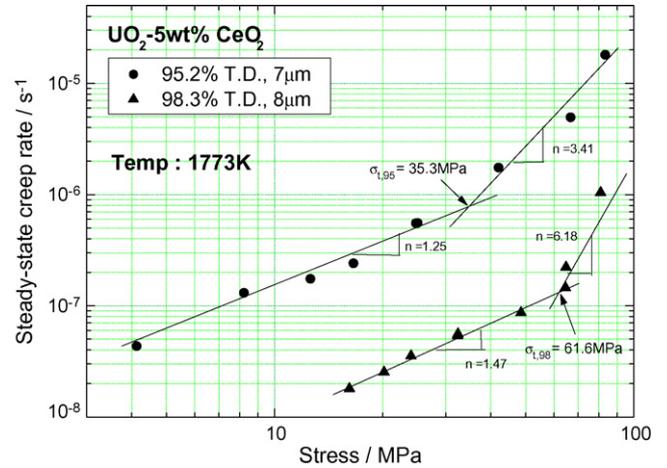


Fig. 4. The creep behavior of UO<sub>2</sub>–5 wt% CeO<sub>2</sub> of different densities.

### 3.4. The creep behavior of (U, Ce)O<sub>2</sub> as a function of the grain size

In order to investigate the effects of the grain size on the creep behavior of the (U, Ce)O<sub>2</sub> sintered pellet, 0.1 wt% of Li<sub>2</sub>O, which is a grain growth accelerator [8] was added. Fig. 5 shows the steady-state creep rates of both the UO<sub>2</sub>–3.25 wt% CeO<sub>2</sub> sintered pellet (98.2% T.D., 7 μm) and the UO<sub>2</sub>–3.25 wt% CeO<sub>2</sub>–0.1 wt% Li<sub>2</sub>O sintered pellet (95.8% T.D., 36 μm) at 1973 K. As shown in the figure, the steady-state creep rate of the sintered pellet increased as the grain size of it increased in the higher stress range.

Fig. 6 shows the steady-state creep rates  $\dot{\epsilon}$ , and the transition stress  $\sigma_t$ , of both the UO<sub>2</sub>–5 wt% CeO<sub>2</sub> sintered pellet (98.3% T.D., 8 μm) and the UO<sub>2</sub>–5 wt% CeO<sub>2</sub>–0.1 wt% Li<sub>2</sub>O sintered pellet (97.8% T.D., 30 μm) at 1773 K. As shown in figure, the transition stress decreased as the grain size increased, that is,  $\sigma_t = 61.6$  MPa for 8 μm and  $\sigma_t = 45.6$  MPa for 30 μm. And with increasing grain sizes of the specimens the steady-state creep rate decreased at below  $\sigma_t$  but the steady-state creep rate increased at above  $\sigma_t$ . These similar results appeared in the UO<sub>2</sub>–3.25 wt% CeO<sub>2</sub> sintered pellet and they agreed well with

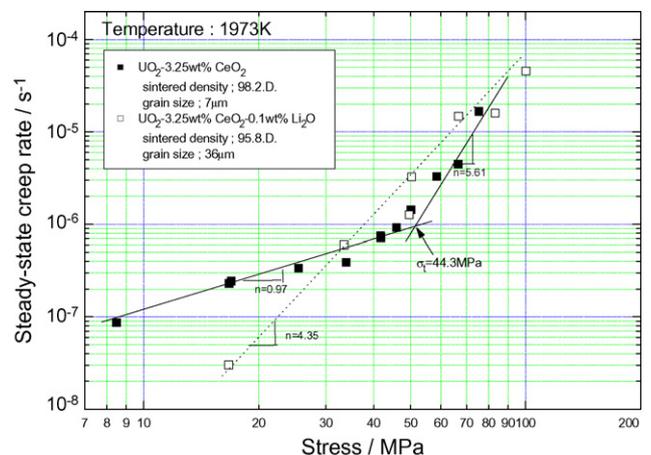


Fig. 5. The creep behavior of UO<sub>2</sub>–3.25 wt% CeO<sub>2</sub> and UO<sub>2</sub>–3.25 wt% CeO<sub>2</sub>–0.1 wt% Li<sub>2</sub>O.

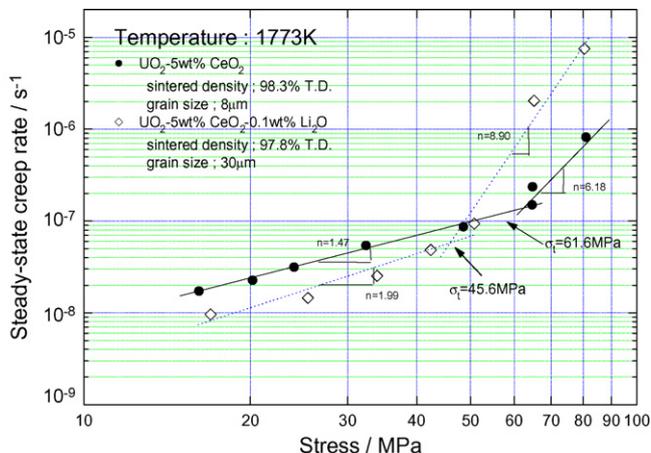


Fig. 6. The creep behavior of  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$  and  $\text{UO}_2$ -5 wt%  $\text{CeO}_2$ -0.1 wt%  $\text{Li}_2\text{O}$ .

Seltzer et al.'s results [9]. However, even though the grain size of the specimen increased the creep behavior of the specimen is controlled by a diffusion mechanism in at below  $\sigma_t$  ( $n = 1.47$  for  $8 \mu\text{m}$ ;  $n = 1.99$  for  $30 \mu\text{m}$ ) and by a dislocation movement mechanism at above  $\sigma_t$  ( $n = 6.18$  for  $8 \mu\text{m}$ ;  $n = 8.90$  for  $30 \mu\text{m}$ ).

Two types of creep behavior, which depended on the grain size, were shown. One is diffusion mechanism identified as the Nabarro–Herring creep mechanism where creep rates are linearly dependent on the stress and inversely proportional on to the square of the grain size,  $d(\dot{\epsilon} \propto d^{-2})$ . And the other is Coble creep mechanism where the creep rates are linearly dependent on the stress and inversely proportional on to the cube of the grain size ( $\dot{\epsilon} \propto d^{-3}$ ).

Fig. 7 shows the steady-state creep rate of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  as a function of the grain size. As shown in the figure, the calculated slope was about  $-1.3$ . Therefore, it is considered that the creep behavior of the  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  specimen is governed by the Nabarro–Herring creep mechanism at 16.7 MPa in the range of grain size ( $7$ – $36 \mu\text{m}$ ) of this study.

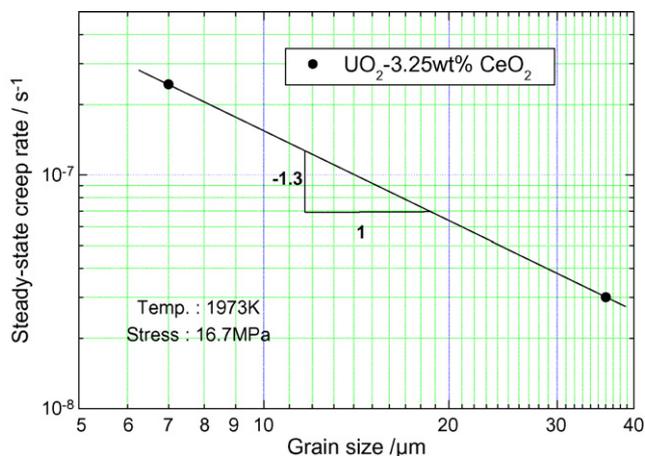


Fig. 7. Effect of grain sizes on the creep rate of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$ .

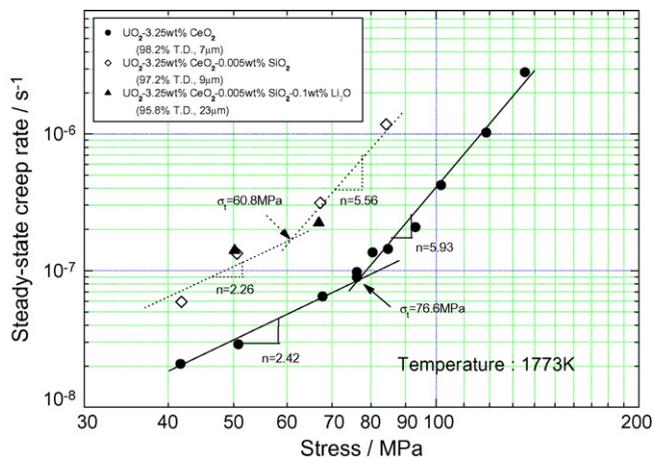


Fig. 8. The creep behavior of  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  as a function of the  $\text{SiO}_2$  addition.

### 3.5. The creep behavior of $(\text{U}, \text{Ce})\text{O}_2$ as a function of the $\text{SiO}_2$ addition

The effect of an addition amount (0.005 wt%) of  $\text{SiO}_2$  on the creep behavior of the  $(\text{U}, \text{Ce})\text{O}_2$  sintered pellet was investigated. Fig. 8 shows the steady-state creep rates  $\dot{\epsilon}$ , and the transition stress  $\sigma_t$ , of both the  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  (97.2% T.D.,  $9 \mu\text{m}$ ) and the  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$ -0.1 wt%  $\text{Li}_2\text{O}$  (95.8% T.D.,  $23 \mu\text{m}$ ) at 1973 K under a constant stress of 16.7 MPa. As shown in the figure, in the case of a  $\text{SiO}_2$  addition, the steady-state creep rate increased but the transition stress decreased, for example, 76.6 MPa for  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  and 60.8 MPa for  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$ -0.1 wt%  $\text{Li}_2\text{O}$ . The steady-state creep rate of a specimen, which has a larger grain size by a  $\text{Li}_2\text{O}$  addition, was also increased by a  $\text{SiO}_2$  addition. The creep rate of the  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$ -0.005 wt%  $\text{SiO}_2$  sintered pellet is greater than that of the  $\text{UO}_2$ -3.25 wt%  $\text{CeO}_2$  sintered pellet. This result is in good agreement with that of Armstrong and Irvine. According to Armstrong and Irvine [10],  $\text{UO}_2$  and  $\text{SiO}_2$  are mutually insoluble and hence  $\text{SiO}_2$  particles as a glassy phase, which exist mainly at the grain boundary of  $\text{UO}_2$ , cause a grain boundary sliding easily. Therefore, a  $\text{SiO}_2$  addition resulted in a increased creep rate due to the accelerated grain boundary sliding. However, it is considered that the creep behaviors of these specimens at below  $\sigma_t$  and at above  $\sigma_t$  are controlled by a diffusion mechanism ( $n = 2.26$ – $2.42$ ) and a dislocation movement ( $n = 5.56$ – $5.93$ ), respectively.

## 4. Conclusion

The effect of the  $\text{CeO}_2$  contents, density, grain size and dopant additions ( $\text{SiO}_2$  and  $\text{Li}_2\text{O}$ ) on the creep behavior of the  $(\text{U}, \text{Ce})\text{O}_2$  sintered pellet have been investigated. The conclusions are as follows:

- (1) Stress exponent,  $n$ , derived from the stress-creep rate relationship shows two values depending on the stress applied. One is  $n = 0.97$ – $2.26$  in the lower stress region, and the other is  $3.40$ – $8.90$  in the higher stress region in the experimental ranges of this study.

- (2) The creep rate of the specimen decreased with an increase of both the CeO<sub>2</sub> addition content and the sintered density. But in the case of a SiO<sub>2</sub> addition the creep rate increased.
- (3) The creep activation energy increased as the CeO<sub>2</sub> addition content increased.
- (4) The calculated slope from the creep rate in the lower stress range as a function of the grain size of UO<sub>2</sub>–3.25 wt% CeO<sub>2</sub> is about –1.3.

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