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Mechanical properties of $(U,Ce)O_2$

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Abstract

Ultrasonic pulse echo and Vickers hardness measurements were performed to estimate the mechanical properties of single crystal UO_2 and sintered $(U,Ce)O_2$ with various porosities. From the sound velocities obtained for single crystal UO_2 and sintered $(U,Ce)O_2$, the Young's and shear moduli and Poisson's ratio were estimated. The Young's and shear moduli and Poisson's ratio decreased with the CeO_2 content. By careful measurements with various loads, the Vickers hardness of 100% dense $(U,Ce)O_2$ (porosity 0%) was obtained. The value for 100% dense UO_2 was in good agreement with the hardness of single crystal UO_2. The Vickers hardness of $(U,Ce)O_2$ also decreased with the CeO_2 content, irrespective of porosity (0 and 14% porosity). There is a good correlation between the Young's modulus and the Vickers hardness obtained for $(U,Ce)O_2$ irrespective of porosity. The yield stress of $(U,Ce)O_2$ evaluated from both the Young's modulus and the Vickers hardness decreased with the CeO_2 content. The diagonal of the radial crack of UO_2 single crystal was also measured, and the fracture toughness K_C was estimated to be 1.1 ± 0.2 MPa $m^{1/2}$.

Keywords: Elastic modulus; Fracture toughness; $(U,Ce)O_2$; Vickers hardness; Yield stress

1. Introduction

To understand the change in the basic characteristics of uranium dioxide fuel caused by lanthanoid addition the mechanical properties of $(U,Ce)O_2$ were measured. In addition, for $(U,Ce)O_{2-x}$, the oxygen potential and the lattice parameter obtained from X-ray diffraction analysis have been reported [1,2], and such studies have revealed similar phase diagrams for $(U,Ce)O_2$ and $(U,Pu)O_2$. Therefore, studies of the mechanical properties of $(U,Ce)O_2$ would contribute to our knowledge of the properties of $(U,Pu)O_2$.

In the pellet–cladding mechanical interaction, the strength of the mixed oxide is a very important property involving the reliability and the safety of nuclear fuel elements. As the elastic modulus is a fundamental property for understanding the strength of materials, many studies have been performed on uranium dioxide [3–7]. The plastic properties of uranium dioxide such as the ultimate tensile stress, fracture strength and yield stress have also been reported [8,9]. However, there is limited information on the influence of the microstructure on the mechanical properties of the mixed oxide.

In the present study, $(U,Ce)O_2$ was therefore selected, and the mechanical properties such as Young's and the shear moduli, Poisson's ratio, Vickers hardness and yield stress were examined for $(U,Ce)O_2$ with low CeO_2 content.

2. Experimental

2.1. Sample preparation

The specimens used in the present study were single crystal UO_2 and sintered $(U,Ce)O_2$ pellets with 0, 5, 10, 15, and 20 mol% CeO_2. UO_2 and CeO_2 powders were mixed with an organic binder and starchy pore former (0–11.6 g, according to the desired porosity) and pressed in a steel die into a pellet of 20 mm diameter and 10 mm length. The binder was burned out at 1173 K for 2 h in flowing H_2/H_2O, and the pellets were also sintered at 2023 K for 4 h. The porosities were about 6, 15 and 22% for each sample, independent of the CeO_2 content. The pellet prepared without pore former had a porosity of 6%. These samples appeared to be stoichiometric judging from the lattice parameter determined by X-ray diffraction analysis.

2.2. Ultrasonic pulse echo measurement

Ultrasonic pulse echo measurement at room temperature was carried out to estimate the change in the mechanical

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properties of $(U,Ce)O_2$ with CeO_2 content. The apparatus for the measurement of the sound velocity of $(U,Ce)O_2$ was designed and constructed similar to those described in Ref. [10].

2.3. Vickers hardness measurement

The Vickers hardness measurement was performed to estimate the change in the yield stress of $(U,Ce)O_2$ with CeO_2 content. The Vickers hardness measurement was carried out using an MHT-1 Vickers hardness tester supplied by Matsuzawa Seiki Co. Ltd. Measurements were repeated 10 times a sample, and the average was calculated from the data in which the maximum and minimum values were excluded.

Generally, it is known that the Vickers hardness is affected by the load, load time, surface condition, and indent depth, and for ceramics it is affected by grain size and porosity. For example, for the case of tungsten carbide, it has been shown that, in polycrystalline samples, grain size has an important effect when it is of the same order as the indent diameter [11]. A decrease in grain size is accompanied by an increase in hardness as the dislocations generated by the indenter are blocked by the grain boundaries. It should be noted that because the grain size of the samples used in the present study was 8–10 μm for UO_2 and 3–7 μm for $(U,Ce)O_2$, the hardness of $(U,Ce)O_2$ may be measured to be slightly higher than that of UO_2. Because the hardness on the surface is affected by the grain boundaries and pores, in the present study the hardness measurements were performed under the following conditions:

(i) $P=25$ g and $T=30$ s so that the indenter is not blocked by the grain boundaries by careful measurement, and the indent diameter was 5–7 μm;
(ii) $P=1$ kg and $T=30$ s, and the indent diameter was about 60 μm and contained about seven grains and grain boundaries.

For condition (i), since the obtained value corresponds to the hardness of the grain and is not affected by the grain boundaries and pores, the measured hardness corresponds to that of $(U,Ce)O_2$ with 100% theoretical density. For condition (ii), the measured hardness is considered to be the average value of the bulk, consisting of grains, grain boundaries and pores.

3. Results and discussion

3.1. The change in the elastic properties of $(U,Ce)O_2$ with CeO_2 content

In our previous study [10], the shear modulus G and Young's modulus E of $(U,Ce)O_2$ estimated from the longitudinal velocity V_L and shear sound velocity V_S at room temperature were found to decrease with increasing porosity, and the extrapolated moduli of $(U,Ce)O_2$ with 100% theoretical density also decreased with increasing CeO_2 content.

Poisson's ratio estimated from V_S and V_L also appeared to decrease with CeO_2 content. When Poisson's ratio increases, deformation can occur more easily and the brittleness of materials decreases. Thus the reduction in Poisson's ratio caused by CeO_2 addition in UO_2 means that $(U,Ce)O_2$ is more brittle than UO_2.

3.2. Variation in the Vickers hardness of $(U,Ce)O_2$ with CeO_2 content

The Vickers hardness H_V is measured by forcing a diamond pyramid-type (with apex 136°) indenter into the surface of the specimen and is defined by

$$H_V = \frac{2p_H \sin\phi}{d^2}$$

where d is the mean diagonal length expressed in millimeters of the diamond-shaped impression made in the indented surface.

Fig. 1 shows the Vickers hardness as a function of CeO_2 content. The Vickers hardness of $(U,Ce)O_2$ also decreased with CeO_2 content, irrespective of porosity.

The Vickers hardness of UO_2 obtained by the Vickers

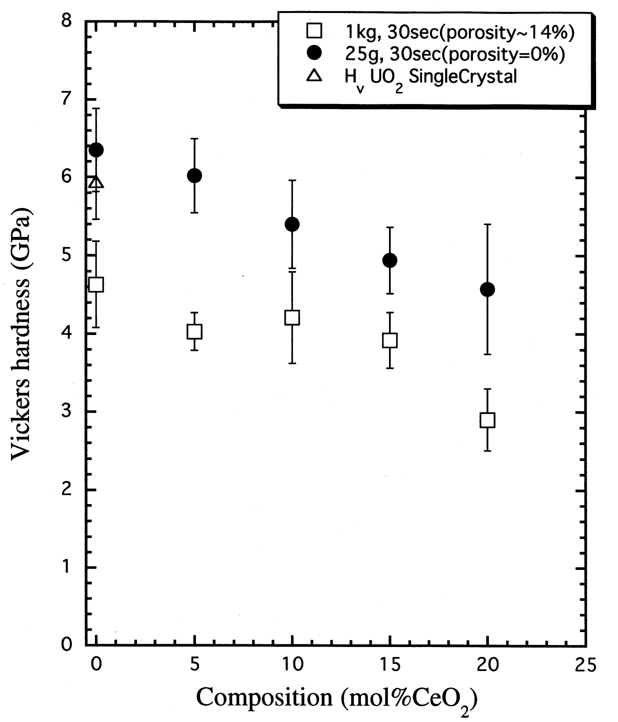

Fig. 1. Change in the Vickers hardness of $(U,Ce)O_2$ with CeO_2 content.

hardness measurement under condition (i) is 6.4±0.5 GPa, which is in good agreement with the hardness of single crystal UO_2 (5.9±0.5 GPa).

3.3. Change in the yield stress with CeO_2 content

The yield stress of ceramic materials is deduced from the results of hardness measurements. For the case of ductile materials such as metals, plastic deformation can occur and the volume pressed out by the indenter flows to the outside of the indent and piles up there. In this case, the yield stress of the indenter (p_H) is assumed to be about 2.6 times the yield stress of the material (Y) from the slip system theory [12]. By contrast, for ceramics for which it is difficult to measure the plastic deformation (the volume pressed out by the indenter cannot flow to the outside of the indent) a high stress concentration is measured as the volume is constrained by the surroundings just under the indenter. For the calculation taking into account the internal stress [13], the Vickers hardness of ceramics is approximately given by

$$\frac{p_H}{Y} = \frac{H_V}{Y \sin\phi} = 1 + \ln\left[\frac{\pi^{1/2}\cot\phi}{11(1-\nu^2)}\left(\frac{E}{Y}\right)\right] \quad \text{(for covalent bond ceramics)}$$

$$\frac{p_H}{Y} = \frac{H_V}{Y \sin\phi} = 1 + 1.2\ln\left[\frac{\pi^{1/2}\cot\phi}{8(1-\nu^2)}\left(\frac{E}{Y}\right)\right] \quad \text{(for ionic bond ceramics)}$$

In these equations, ϕ is half of the indenter apex angle (=136°), E and ν are the Young's modulus and the Poisson's ratio of the material, respectively, p_H and Y are expressed in kilograms, and H_V is the Vickers hardness of the material. For UO_2 and $(U,Ce)O_2$, the ionic bond is thought to predominant rather than the covalent bond, therefore in the present study the latter equation was used.

Fig. 2 shows the yield stress Y, calculated from the above equation, as a function of the CeO_2 content. For $(U,Ce)O_2$ (condition (i), porosity 0%), Y is found to decrease with increasing CeO_2 content, and for $(U,Ce)O_2$ (condition (ii), porosity 14%), although the yield stress of the 5 mol% CeO_2 compound is slightly lower than the value for the 10 mol% CeO_2 compound, Y is also found to decrease with increasing CeO_2 content.

Figs. 3 and 4 show the stress–strain diagrams for $(U,Ce)O_2$ (porosity 0 and 14%, respectively) obtained from the calculated Y and E. When the fracture toughness is not taken into account, with increasing CeO_2 content, $(U,Ce)O_2$ is broken at lower stress than UO_2, irrespective of porosity. Generally, as the value of the elastic strain ε at

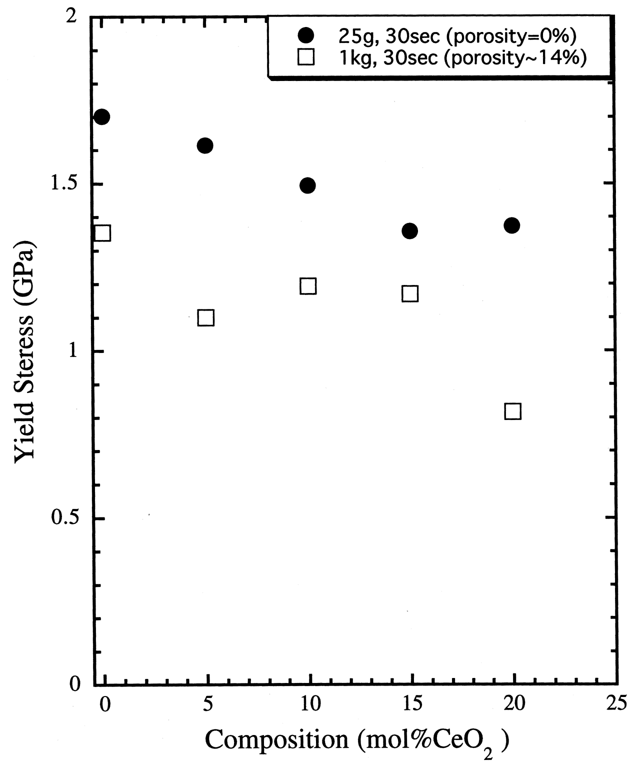

Fig. 2. Change in the yield stress of $(U,Ce)O_2$ with CeO_2 content.

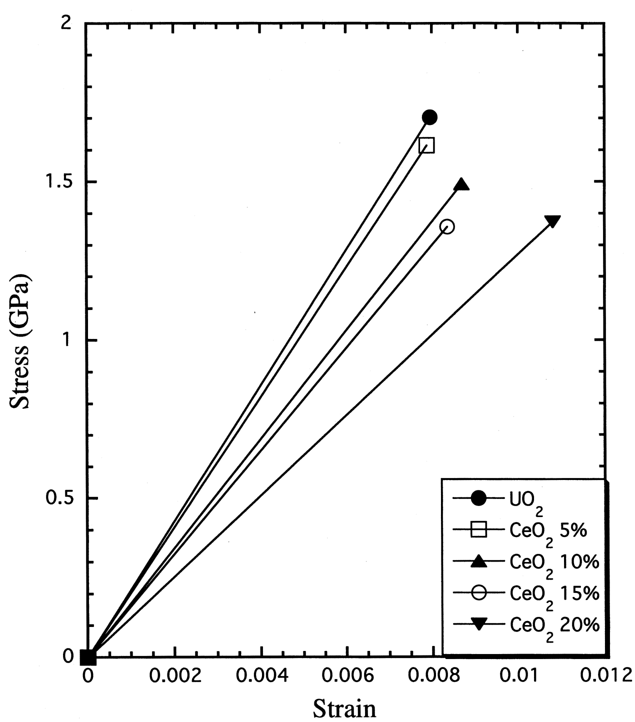

Fig. 3. The stress–strain diagram for $(U,Ce)O_2$ (porosity 0%).

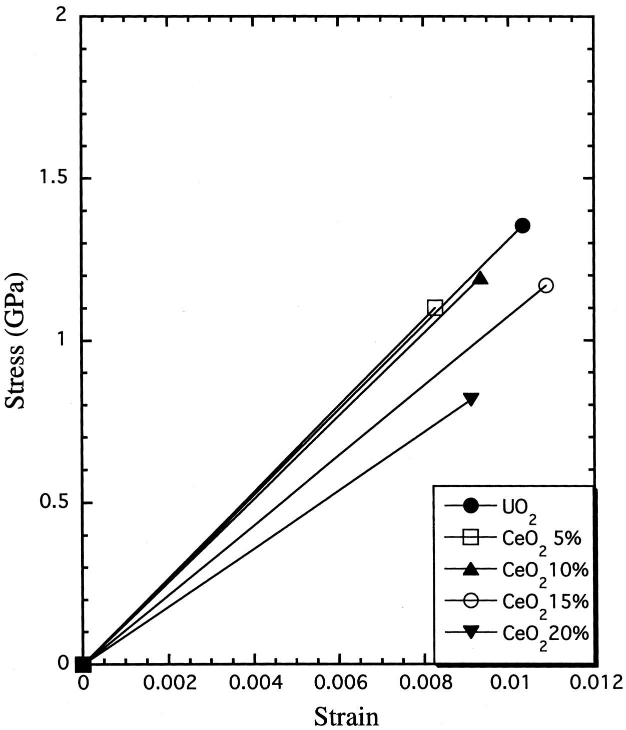

Fig. 4. The stress–strain diagram for $(U,Ce)O_2$ (porosity ~14%).

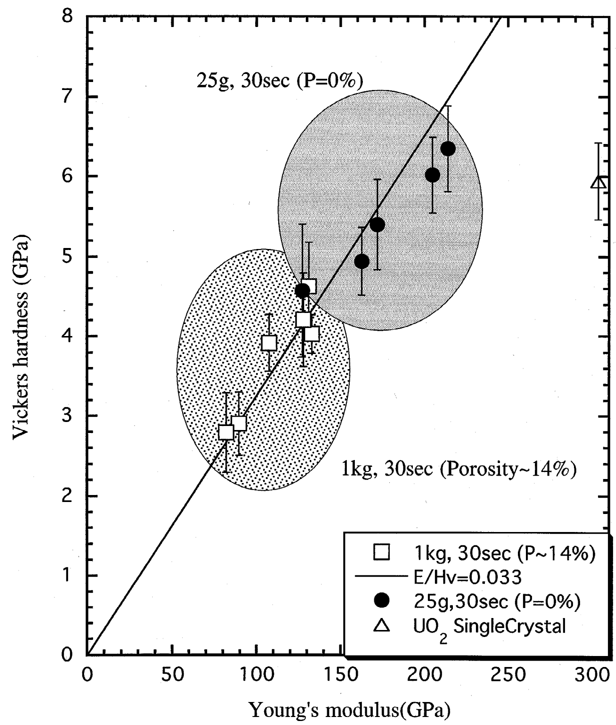

Fig. 5. Change in the Vickers hardness of $(U,Ce)O_2$ with Young's modulus.

the yield stress for ceramics is about 1%, the values of ε for $(U,Ce)O_2$ (1.2–2.5%) are reasonable.

3.4. Determination of the hardness–Young's modulus ratio and estimation of the fracture toughness of UO_2 single crystal

The Vickers hardness is plotted in Fig. 5 as a function of the Young's modulus obtained from sound velocities. In Fig. 5, the Vickers hardness of UO_2 and $(U,Ce)O_2$ is proportional to the Young's modulus, irrespective of porosity. The value of H_V/E is evaluated to be about 0.033 ± 0.002 for UO_2 and $(U,Ce)O_2$.

The fracture toughness K_C, one of the most important physical properties when considering the fracture performance of ceramics, was given by Evans and Charles [14]

$$K_C = 0.057\left(\frac{E}{H_V}\right)^{0.4} H_V a^{1/2}\left(\frac{c}{a}\right)^{-3/2}$$

where a is the half diagonal of the indent trace and c is the half diagonal of the radial crack giving the surface trace. The diagonal of the radial cracks of UO_2 single crystal was measured, and the fracture toughness K_C was estimated to be 1.1 ± 0.2 MPa m$^{1/2}$ from the Evans equation. The fracture toughness for stoichiometric UO_2 (0.91 MPa m$^{1/2}$) obtained by the Hertzian fracture test was reported by Matzke [15]. The fracture toughness K_C obtained in the present study is slightly higher than the value of Matzke, but they are in agreement in spite of the differences in the experimental methods.

4. Conclusions

The mechanical properties such as Young's and shear moduli, Poisson's ratio and Vickers hardness were obtained for $(U,Ce)O_2$ with low CeO_2 content, and the values were found to decrease with increasing CeO_2 content. There is a good correlation between the Young's modulus and the Vickers hardness obtained for $(U,Ce)O_2$ irrespective of porosity. The yield stress of $(U,Ce)O_2$ evaluated from both the Young's modulus and the Vickers hardness is found to decrease with CeO_2 content. The stress–strain diagrams for $(U,Ce)O_2$ were also evaluated from the calculated yield stress and Young's modulus and, with increasing CeO_2 content, $(U,Ce)O_2$ is found to be broken at lower stress than UO_2, irrespective of porosity. The fracture toughness K_C of UO_2 single crystal was estimated to be 1.1 ± 0.2 MPa m$^{1/2}$.

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