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Study of the thermodynamic properties of (U, Ce)O_2

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Abstract

The X-ray diffraction analysis of (U, Ce)O_2 with the CeO_2 contents ranging from 0 to 20 mol% CeO_2 was performed at room temperature to obtain the variation in the lattice parameter with the CeO_2 content. Ultrasonic pulse echo measurements were also carried out to estimate the change in the mechanical properties of (U, Ce)O_2 with the CeO_2 content. The lattice parameter of (U, Ce)O_2 was found to decrease with increasing CeO_2 content. The variation in the lattice parameter with the CeO_2 content closely followed the Vegard law. The shear and longitudinal velocities in (U, Ce)O_2 were found to decrease with increasing CeO_2 content. The Young's and shear moduli, and Poisson's ratio estimated from the wave velocities decreased with the CeO_2 content. No mechanical property showed anomaly in low CeO_2 content region. © 1997 Elsevier Science B.V.

1. Introduction

Cerium is produced in nuclear fuel as one of the fission products of high yields. The knowledge of (U, Ce)O_2 is, therefore, of basic importance for investigating the irradiation behavior of uranium dioxide fuel in connection with the changes in the phase relations and in the thermodynamical and mechanical properties caused by accumulated fission lanthanoid elements. In the present study, (U, Ce)O_2 has been therefore selected, and the lattice parameter and mechanical properties were examined for (U, Ce)O_2 with low CeO_2 contents.

2. Experimental

The UO_2 and (U, Ce)O_2 sample pellets used in the present study were supplied by Nuclear Fuel Industries. The UO_2 and CeO_2 powder was mixed with binder and pore former (0–11.6 g, according to the porosity desired), and pressed in a steel die to be in the form of pellets (20 mm in diameter and 10 mm in length). The binder was burned out at 900°C for 2 h (in flowing hydrogen), and the pellets were also sintered in hydrogen at 1750°C for 4 h. The compositions of (U, Ce)O_2 were 5, 10, 15, and 20 mol% of CeO_2, and porosities were about 6%, 15%, 22% for each sample.

The X-ray diffraction analysis for the (U, Ce)O_2 samples was performed at room temperature using a diffractometer to obtain the variation in lattice parameter with the CeO_2 content. The O/M ratios of samples were not measured exactly, but samples appeared to be stoichiometric from the results of lattice parameter measurements.

Ultrasonic pulse-echo measurement was also carried out using an Echometer 1062 supplied by Nihon Matech to estimate the change in the mechanical properties of (U, Ce)O_2 with the CeO_2 content. The sample was cemented to the crystal delay line, and the other end of the delay line is bonded to the 5 MHz Leadmateriobeate transducer connected with the Echometer. The sound velocity in the sample is found from the sample length and time separation between ultrasonic echoes t obtained from the Echometer. The glue joint between transducer and delay line was Sonicoat-SHN13 [1]. Measurements were performed three times over changing the sample position, and the error in the sound velocity calculated from t was within 20 m/s.

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3. Results and discussion

The change in the lattice parameter of (U, Ce)O_2 with the CeO_2 content is shown in Fig. 1, together with the literature data [2,3]. As obvious from this figure, the lattice parameter obtained in the present study agrees well with the reported values for (U, Ce)O_2. The variation in the lattice parameter with CeO_2 content closely follows the Vegard law. The relationship between the lattice parameter a in pm and the CeO_2 content C_{CeO_2} (mol%) obtained in the present study can be written as

$$a = 547\left(1 - 1.14 \times 10^{-4} C_{CeO_2}\right).$$

Measured longitudinal and shear sound velocities of (U, Ce)O_2 were found to decrease with increasing porosities of the sample. Both the longitudinal velocity V_L and shear sound velocity V_S of the (U, Ce)O_2 with 100% theoretical density were estimated from

$$V_L = V_L^*/(1 - bP), \qquad V_S = V_S^*/(1 - cP),$$

where V_L^* and V_S^* are the sound velocities of the (U, Ce)O_2, b and c are constants and P is the porosity which is defined as $P = 1 -$ (bulk density)/(theoretical density).

For isotropic media, the shear modulus G and Young's modulus E are expressed in terms of the longitudinal sound velocities V_L and shear sound velocities V_S as

$$G = \rho V_S^2, \qquad E = G\left[\frac{3V_L^2 - 4V_S^2}{V_L^2 - V_S^2}\right],$$

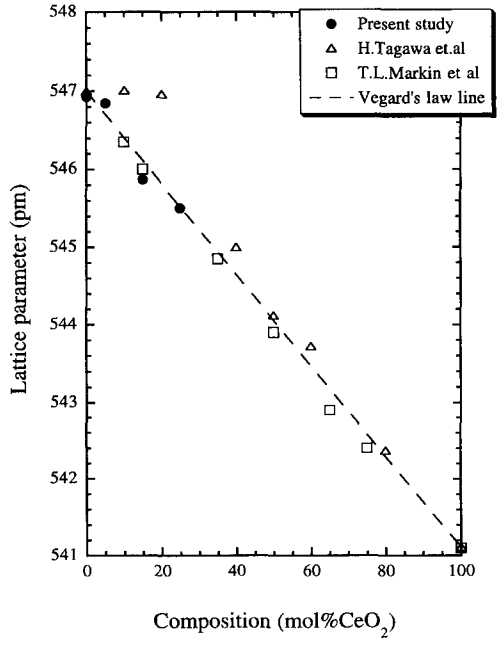

Fig. 1. Change in the lattice parameter of (U, Ce)O_2 with CeO_2 content.

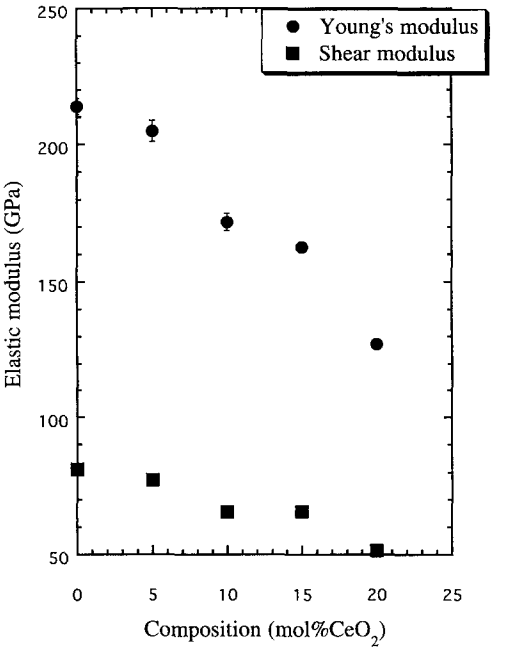

Fig. 2. Changes in the elastic moduli of (U, Ce)O_2 with CeO_2 content.

where ρ is the sample density. The Poisson's ratio υ is defined as

$$\upsilon = E/2G - 1$$

which in terms of V_L and V_S becomes

$$\upsilon = \left(V_L^2 - 2V_S^2\right)/2\left(V_L^2 - V_S^2\right).$$

The values of G, E and υ were estimated from V_S and V_L using these equations. In Figs. 2 and 3, the values of G, E and υ are shown as a function of the CeO_2 content, respectively. As can be seen from the figures, the Young and shear modulus are found to decrease with increasing CeO_2 content. In Fig. 1, the lattice parameter decreased with CeO_2 content. The mechanical properties of ceramics such as the Young and shear modulus depend on the Coulomb force between ions. Because ceramics have the ionic bond and the covalent bond, and the latter is also caused by the electrostatic attractive force. Generally, it is known that the Young and shear modulus increased with decreasing bond length. However, the Young and shear modulus of (U, Ce)O_2 decreased with decreasing lattice parameter. This may be caused by the decreasing of the bond energy with increasing CeO_2 content.

The Young modulus for UO_2 (E_0) obtained in the present study is compared in Table 1 with the reported data [4–9]. The value of E_0 in the present study is slightly smaller than the reported data. In Fig. 3, the Poisson's ratio estimated from V_S and V_L appeared to decrease with the CeO_2 content. The Poisson ratio of 5 mol% CeO_2 is a

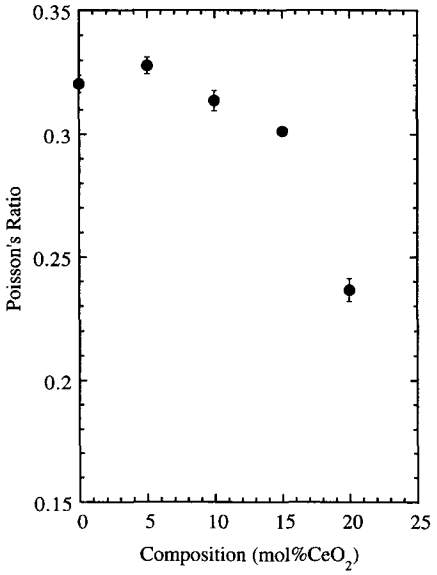

Fig. 3. Change in the Poisson's ratio of (U, Ce)O_2 with CeO_2 content.

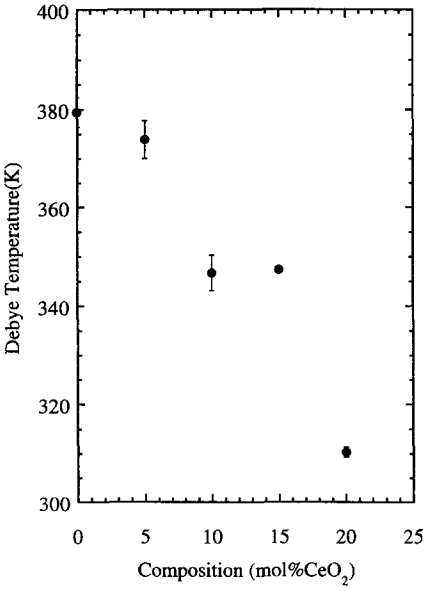

Fig. 4. Change in the Debye temperature of (U, Ce)O_2 with CeO_2 content.

few percent greater than the value of UO_2. The values of the Poisson ratio for UO_2 υ_0 ($= 0.320 \pm 0.003$) is in good agreement with the value ($\upsilon_0 = 0.319$) reported by Skelding [10].

We derived the Debye temperature Θ_D for (U, Ce)O_2 using the sound velocities of (U, Ce)O_2 with 100% theoretical density and the lattice parameters obtained in the present study to undertake qualitative consideration on the feature of potential energy in (U, Ce)O_2. The Debye temperature Θ_D is defined as

$$\Theta_D = h\upsilon_D/k,$$

where h is the Plank constant ($h = 6.62607 \times 10^{-34}$ J s) and k is the Boltzman constant ($k = 1.380658 \times 10^{-23}$ J/K). υ_D is calculated from the shear and longitudinal sound velocities:

$$\upsilon_D = \left[9N/4\pi a^3\left(1/V_L^3 + 2/V_S^3\right)\right]^{1/3},$$

where N is the number of atoms in a unit cell, and a is the lattice parameter of (U, Ce)O_2.

Table 1
Values of Young's modulus of UO_2 (E_0), obtained by least-squares fitting of linear equations

E_0 (GPa)	Authors
214.00 ± 2.9	present study
229.55	Claussen [4]
223.47	Forlano et al. [5]
217.60	Igata and Domoto [6]
223.37	Watchtman et al. [7], Padel and de Novin [8]
223.00	Marlowe and Kaznoff [9]

The Debye temperature Θ_D for UO_2 is estimated to be 379 K. There are various values of Θ_D for UO_2 obtained by other methods: the analysis of high-temperature neutron diffraction data gives $\Theta_D = 377$ K above 700 K [11], and the analysis of high-temperature X-ray diffraction data gives $\Theta_D = 370$ K [12], and they are in good agreement with the value obtained in the present study.

At room temperature, the dispersion relation of a phonon cannot be strictly described by Debye's model. But the Debye temperature appears to be an indication of the shape of the potential energy. Fig. 4 represents the variation in the Debye temperature with the CeO_2 content. The Debye temperature is found from this figure to decrease with increasing CeO_2 content. This result suggests that the potential energy of UO_2 is broader with CeO_2 addition.

In general, it is known that the Debye temperature increases as the average mass of a compound or the atom distance in a compound decreases. Although the CeO_2 addition into UO_2 yields the reduction in both the average mass and the atom distance, it decreases the Debye temperature of (U, Ce)O_2.

The lattice parameter obtained by X-ray diffraction analysis decreased with CeO_2 content, whereas both sound velocities decreased. This may be caused by the change of the potential energy bonding ions in the crystal with addition of CeO_2. Further studies are required for a sound understanding of physical properties of (U, Ce)O_2.

4. Conclusions

The X-ray diffraction analysis and ultrasonic pulse echo measurement of (U, Ce)O_2 with the CeO_2 contents

ranging from 0 to 20 mol% of CeO_2 were performed at room temperature to elucidate the change in thermodynamical and mechanical properties of UO_2 with CeO_2. The lattice parameter of (U, Ce)O_2 was found to decrease with increasing CeO_2 content. The variation in the lattice parameter with the CeO_2 content closely followed the Vegard law. The shear and longitudinal velocities in (U, Ce)O_2 were found to decrease with increasing CeO_2 content. The Young's and shear moduli, and Poisson's ratio estimated from the sound velocities decreased with the CeO_2 content. The Debye temperatures of (U, Ce)O_2 were derived from sound velocities and lattice parameters. The Debye temperature was found to decrease as the CeO_2 content increased. These results suggest that the potential energy of UO_2 is shallower and broader with CeO_2 addition.

Acknowledgements

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