

STUDY ON HIGHLY VERSATILE ADSORPTION KINETICS MODEL

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論 文 名 : A study on the structural, thermal, and mechanical properties of $U_{1-y}Ln_yO_{2-x}$ and $Ce_{1-y}Ln_yO_{2-x}$ ($Ln = Gd, Er$) solid solutions
($U_{1-y}Ln_yO_{2-x}$ 及び $Ce_{1-y}Ln_yO_{2-x}$ ($Ln = Gd, Er$) 固溶体の結晶構造、熱物性、機械物性に関する研究)

区 分 : 甲

論 文 内 容 の 要 旨

Burnable poison fuels, such as $UO_2-GdO_{1.5}$ are widely used in light-water reactors (LWRs), especially in pressurized water reactors. $UO_2-ErO_{1.5}$ is also a burnable absorber for LWRs. LWRs use $GdO_{1.5}$ or $ErO_{1.5}$ dispersed in UO_2 fuel pellets in several fuel rods in each fuel assembly. These burnable poisons help to control the initial reactivity and to spread the distribution of core power by keeping the power distribution uniform throughout the core life. In addition, they help to increase fuel burnup, to prolong the refueling cycle length, to reduce the number of control rods, and thereby to decrease the operating costs of the nuclear reactors. Moreover, burnable poisons decrease the necessary boron concentration in 1st cooling water for the chemical shim. However, the safety margin must be considered for using burnable poison fuel in nuclear reactors because $GdO_{1.5}$ - and $ErO_{1.5}$ -doped UO_2 have lower melting points and thermal conductivities than pure UO_2 . Especially, lowering the thermal conductivity causes an increase in the center temperature of the fuel pellet and results in fission gas release, irradiation swelling, and other problems during reactor operation. In addition, the $LnO_{1.5}$ ($Ln = Gd, Er$) doping leads to the degradation in elastic moduli and Debye temperature of $UO_2-LnO_{1.5}$. The change in the crystal structure due to the dopant Ln^{3+} has the largest effect on these thermal and mechanical properties. However, the literature data on the atomic-scale structure of $UO_2-LnO_{1.5}$ are limited. Furthermore, although the thermal properties of $UO_2-LnO_{1.5}$ have been extensively studied, there are some differences in the literature data. Therefore, the structural, thermal, and mechanical properties of $UO_2-LnO_{1.5}$ must be experimentally evaluated and also confirmed by simulations.

In this study, the structural, thermal, and mechanical properties were evaluated for $U_{1-y}Ln_yO_{2-x}$ and $Ce_{1-y}Ln_yO_{2-x}$ ($y = 0-0.4$) solid solution samples by using both experimental and theoretical simulation methods. Here, with the similarity in crystal structures of $UO_2-GdO_{1.5}$ and $CeO_2-GdO_{1.5}$, CeO_2 was used as a surrogate material for UO_2 to measure the sound velocities in $CeO_2-GdO_{1.5}$ samples. The whole thesis is organized into eight chapters, as follows:

Chapter 1 introduces the fundamental concepts and the background of burnable poison fuel with nuclear fuel performance.

Chapter 2 provides the phase relation of $UO_2-LnO_{1.5}$ and $CeO_2-LnO_{1.5}$ solid solutions. In addition, it explains the details about the methodology used in different sample preparations. Then, the sintered sample characteristics are also provided.

Chapter 3 provides an evaluation of the structural properties of $UO_2-LnO_{1.5}$ and $CeO_2-LnO_{1.5}$ samples by X-ray diffraction, Raman spectroscopy, and X-ray absorption fine structure (XAFS). The results are: the

lattice parameters of $\text{UO}_2\text{-LnO}_{1.5}$ decreased as the $\text{LnO}_{1.5}$ content increased to 40 mol %. The $\text{UO}_2\text{-LnO}_{1.5}$ samples sintered in Ar-10% H_2 had a slightly larger lattice size than those sintered in Ar. Since the lattice parameter of $\text{UO}_2\text{-LnO}_{1.5}$ decreases as the O/M ratio increases, this observation indicated that the sample sintered under more reducing conditions with Ar-10% H_2 had a smaller O/M ratio than that sintered in Ar. However, the lattice parameters of $\text{UO}_2\text{-LnO}_{1.5}$ sintered under both conditions were close and they were also close to that of stoichiometric $(\text{U,Ln})\text{O}_{2.00}$. When Ln^{3+} ions are substituted for U^{4+} ions in the host cation sites, either oxygen vacancies (V_O) are created or some of the U^{4+} are oxidized to U^{5+} or U^{6+} ions to maintain electrical neutrality. It was confirmed by XAFS that the oxidation state of U in the $\text{UO}_2\text{-LnO}_{1.5}$ was not solely tetravalent U^{4+} , partly oxidized to U^{5+} . A similar observation was obtained by Raman spectroscopy. The U–O and Ln–O interatomic distances decreased slightly with increasing $\text{LnO}_{1.5}$ content. The presence of U^{5+} , which has a smaller ionic radius than that of U^{4+} , therefore, resulted in the reduction in the lattice parameter of $\text{UO}_2\text{-LnO}_{1.5}$. For $\text{CeO}_2\text{-LnO}_{1.5}$ sintered in air, the lattice size of $\text{CeO}_2\text{-GdO}_{1.5}$ increased with increasing $\text{GdO}_{1.5}$ content, whereas that of $\text{CeO}_2\text{-ErO}_{1.5}$ decreased as the $\text{ErO}_{1.5}$ content increased. XAFS showed that Ce retained the Ce^{4+} cation, and both Ce–O and Ln–O interatomic distances decreased with increasing $\text{LnO}_{1.5}$ content. Therefore, the ionic radii of cations and V_O were supposed to determine the lattice sizes of these samples. Based on MD (molecular dynamics) simulation results of the lattice parameters, it is supposed that Ln^{3+} ions and V_O are not randomly distributed on cation and anion sites, respectively, but defect clusters, e.g., $\text{Ln}^{3+}\text{-V}_\text{O}\text{-Ln}^{3+}$, formed in $\text{CeO}_2\text{-LnO}_{1.5}$ samples. Thus, MD analyses well explained the increase and decrease in lattice parameters of $\text{CeO}_2\text{-GdO}_{1.5}$ and $\text{CeO}_2\text{-ErO}_{1.5}$, respectively, with an increase of Ln^{3+} content at the atomic scale.

Chapter 4 introduces the use of the laser flash analysis technique to simultaneously measure the heat capacities, thermal diffusivities, and thermal conductivities of $\text{UO}_2\text{-LnO}_{1.5}$ and $\text{CeO}_2\text{-LnO}_{1.5}$ samples. The results showed that the thermal conductivities of $\text{UO}_2\text{-LnO}_{1.5}$ and $\text{CeO}_2\text{-LnO}_{1.5}$ decreased with temperature up to 1700 K and they also decreased as $\text{LnO}_{1.5}$ content increased up to 40 mol %. Thermal conductivities of the samples were supposed to be mostly determined by phonon mean free path, which decreases due to the Umklapp processes at high temperatures, and due to the increase of phonon scattering caused by the increase of dopant Ln and oxygen vacancies at low temperatures.

Chapter 5 gives the sound velocity measurements of $\text{CeO}_2\text{-GdO}_{1.5}$ samples by the ultrasonic pulse-echo method. Then, the mechanical properties such as the elastic moduli and Debye temperature of $\text{CeO}_2\text{-GdO}_{1.5}$ samples, which were estimated from the longitudinal and transverse sound velocities, are discussed in detail. In addition, because of the lack of experimental data of $\text{UO}_2\text{-LnO}_{1.5}$ samples in this study, the data on mechanical properties of $\text{UO}_2\text{-LnO}_{1.5}$ were widely investigated in the literature. The results are: $\text{LnO}_{1.5}$ doping into CeO_2 or UO_2 decreased the sound velocities in both samples and thereby reduced their elastic moduli and Debye temperature.

Chapter 6 introduces the MD simulation method and results. The results showed that the lattice parameter, the thermal conductivity, and the bulk modulus of $\text{CeO}_2\text{-LnO}_{1.5}$ samples calculated by MD agreed well with those of experimental values.

Chapter 7 provides a comparison of the thermal and mechanical properties between $\text{UO}_2\text{-LnO}_{1.5}$ and $\text{CeO}_2\text{-LnO}_{1.5}$ samples. The results are: the effect of $\text{LnO}_{1.5}$ doping on the $\text{UO}_2\text{-LnO}_{1.5}$ system was comparable to that effect on $\text{CeO}_2\text{-LnO}_{1.5}$ system, which means these properties of both samples decreased as the $\text{LnO}_{1.5}$ content increased.

Finally, chapter 8 provides concisely the results and findings from this study, has the discussion and conclusions, and provides the potential improvements in detail for each research item.

〔作成要領〕

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