Dysprosia Doped Uranium Dioxide Fuel and the λ-Transition

M. Kleczek, K. Shaheen, M. J. Welland, B.J. Lewis, W.T. Thompson

Royal Military College, Ontario, Canada

Many ionic biatomic crystals with fluorite structures, including UO_2 exhibit an order-disorder transition into a superionic state at a temperature near 85% of the absolute melting temperature. This work focuses on the effect of dysprosia doping on this transition, known as the λ-transition, in UO_2. The high-temperature behaviour of Dy_2O_3-doped UO_2 is of interest since doped fuel has been proposed as a possible advancement of the CANDU fuel design. Specifically, this Low-Void Reactivity Fuel makes use of the relatively high neutron capture cross section of dysprosium to control the neutron flux characteristics in the core, reducing the magnitude of the positive void coefficient for increased reactor safety. There is therefore a need to better understand the physical chemistry of UO_2-Dy_2O_3 in general, and in particular the high-temperature behaviour as may occur during reactor operation.

As a fluorite crystal, UO_2 exhibits a λ-transition where, at sufficiently high temperatures, the oxygen sublattice becomes almost completely disordered with a large fraction of the oxygen anions occupying randomly regular or interstitial positions. The less stable oxygen sublattice is predicted to display higher in-solid mobility into the more stable uranium sublattice [2]. This transition is confirmed by an increase in heat capacity as a function of temperature, with a characteristic lambda-shaped heat capacity curve [3]. The occurrence of this transition is most likely due to the availability of large octahedral lattice voids; a characteristic of the fluorite structure. Neutron diffraction data confirms that the UO_2 forms a very high concentration of oxygen defects at high temperatures [4].

It is speculated that the transition temperature, 2670 K for pure UO_2 [5], may decrease with an increase in concentration of dysprosia in the fuel. This may be observable through neutron diffraction studies at very high temperatures. Preliminary work was conducted on the UO_2-Dy_2O_3 system in order to prepare for investigations at the very high temperatures required to observe this effect. As a foundation for this work, high-temperature X-ray diffraction was used to study the thermal behavior and lattice constants of analogous fluorite crystals such as CaF_2.

Neutron diffraction measurements were conducted at Chalk River Laboratories on UO_2 + 15% Dy to identify patterns up to the maximum attainable temperature. As seen in Figure 1, no major change in crystal structure patterns was seen between 308 K and 1803 K, except for a downshift of peaks and decrease in peak height at a higher temperature, which is to be expected. From this data, the thermal expansion coefficient can be determined and later applied towards fuel modeling and development. The λ-transition temperature of approximately 2670 K was not achieved.

In view of the abandonment of LVRF fuel by Bruce Power, recently announced, no further diffraction work at CRL is planned.

References

[1] J.R. Lamarsh & A.J. Baratta, "Introduction to Nuclear Engineering – Third Edition", Prentice Hall, New Jersey, 2001.

[2] E. Yakub, C. Ronchi, D. Staicu, "Molecular dyamics simulation of premelting and melting phase transitions in stoichiometric uranium dioxide", J. Chem. Phys. 127 (2007).

[3] C. Ronchi and G.J. Hyland, "Analysis of Recent Measurements of the Heat Capacity of Uranium Dioxide", Journal of Alloys and Compounds, Vol. 213/214, (1994) 159-168.

[4] M.T. Hutchings, "High-temperature Studies of UO2 and ThO2 using Neutron Scattering Techniques", J. Chem. Soc. Farady Trans. II 83 (1987) 1083.

[5] Hj. Matzke, "Diffusion in Ceramic Oxide Systems", Vol. 17, ed. I. J. Hastings, The American Ceramic Society, (1986).

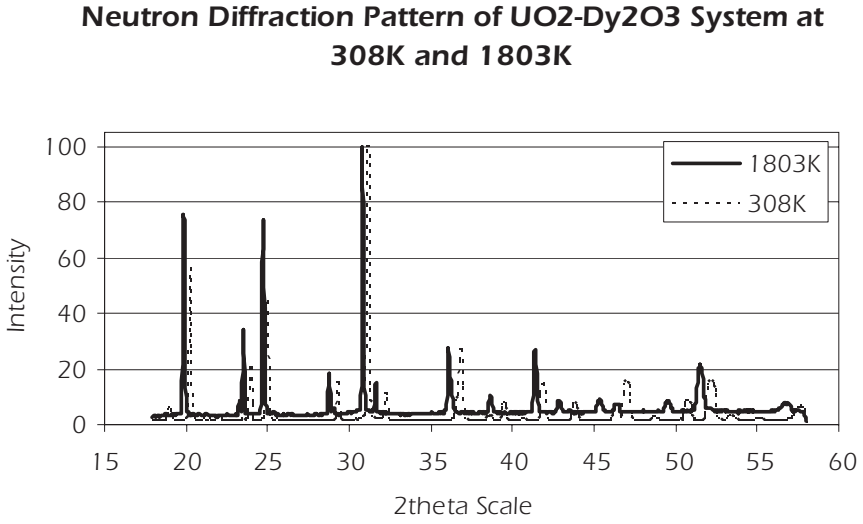

Fig 1. Neutron diffraction pattern of UO_2 + 15% Dy at 308 K and 1803 K.