# 2–6 Controlling Oxygen Content of U–Pu Mixed Oxide Fuel

## — Oxygen Potential Measurement and Application to Fuel Technologies —

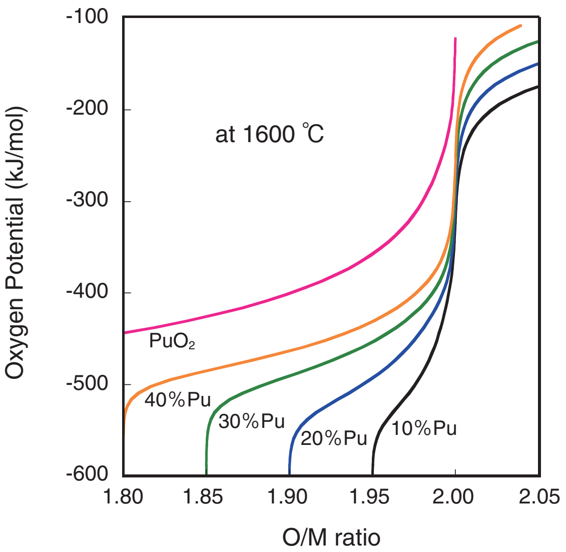


**Fig.2-13 Oxygen potential of MOX at 1600 °C as functions of O/M ratio and Pu content**
The O/M ratio decreases with decreasing oxygen potential and increasing Pu content. The O/M ratio can be controlled by controlling the oxygen potential and temperature.

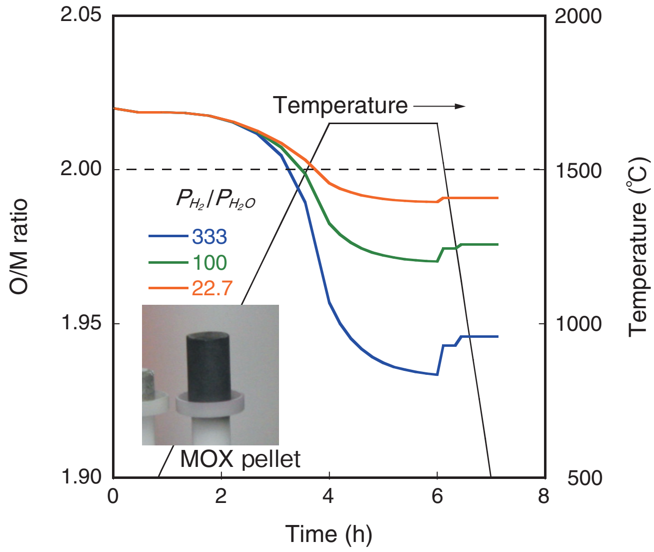


**Fig.2-14 O/M change of $(U_{0.7}Pu_{0.3})O_{2-x}$ during heat treatment**
The O/M ratio of MOX changes with $P_{H_2}/P_{H_2O}$ ratio. The O/M ratio reaches 1.94 at 1650 °C in atmosphere with $P_{H_2}/P_{H_2O}$ = 333. Photograph shows MOX pellet set in the measurement system.

Uranium–plutonium mixed oxide (MOX) has been used as a fuel for sodium-cooled fast reactors; it has a fluorite structure with an oxygen-to-metal (O/M) ratio of 2.00. $UO_2$ can take extra oxygen and exist in a hyper-stoichiometric composition with a range of O/M > 2.00. Pu atoms are substituted for U atoms, and a MOX solid solution is formed. On the other hand, MOX can exist in a hypo-stoichiometric region of O/M < 2.00 by forming oxygen vacancies. Changes in the O/M ratio significantly affect various properties of MOX, such as the thermal conductivity. Therefore, it is important to control the O/M ratio to develop fuel technologies.

It is necessary to know the relationship among the O/M ratio, temperature, and oxygen potential to develop O/M control techniques. In this work, the oxygen potential ($\Delta G_{O_2}$) of MOX was measured by the gas equilibrium method. The oxygen potential is a quantity used in thermodynamics to describe the oxygen chemical stability in MOX and can be obtained using eq.(1).

$$\Delta G_{O_2} = RT \ln P_{O_2} , \quad \cdots\cdots (1)$$

where $R$ is the gas constant. A gas mixture of $Ar/H_2$ to add moisture was used for oxygen potential control. In this gas system, the oxygen potential is determined by the reaction $H_2O \Leftrightarrow H_2 + 1/2O_2$ and controlled by adjusting the $P_{H_2}/P_{H_2O}$ ratio. Many data (more than 1000 points) were obtained and evaluated, and an equation representing the oxygen potential was derived as a function of the O/M ratio, temperature, and Pu content. On the basis of this equation, a technique for evaluating the O/M ratio was developed.

Fig.2-13 shows the relationship between the oxygen potential and the O/M ratio at 1600 °C. The oxygen potential increases with increasing Pu content. This technology for evaluating the oxygen potential has been applied to the fuel pellet fabrication process and irradiation behavior analysis. The O/M change in $(U_{0.7}Pu_{0.3})O_{2-x}$ during heat treatment is plotted as a function of the $P_{H_2}/P_{H_2O}$ ratio in Fig.2-14. The figure shows that the $P_{H_2}/P_{H_2O}$ ratio affects the variation in O/M. Further, the chemical stability of fission products inside irradiated pellets can be evaluated using this technology.

**Reference**

Kato, M., Oxygen Potentials and Defect Chemistry in Nonstoichiometric $(U,Pu)O_2$, Stoichiometry and Materials Science–When Numbers Matter, 2012, p.203–218.