# RECENT STUDIES ON FUEL PROPERTIES AND IRRADIATION BEHAVIORS OF AM/NP-BEARING MOX

S. HIROOKA

Japan Atomic Energy Agency

Tokai, Japan

Email: hirooka.shun@jaea.go.jp

K. Yokoyama

Japan Atomic Energy Agency

Oarai, Japan

M. Kato

Japan Atomic Energy Agency

Oarai, Japan

**Abstract**

Recent studies on the properties of mixed oxide (MOX) fuels are summarized by focusing on the influence of MA (Am and Np) addition. A major influence regarding fuel design is the decrease in thermal conductivity accompanied by the enhancement of impurity-phonon scattering and the increase in oxygen potential. The influence of MA addition on the fuel temperature during irradiation was evaluated using a simulation code developed in the Japan Atomic Energy Agency (JAEA). The addition of 5% Am and 5% Np in MOX pellets, which are 5.42 mm in diameter, increases by ~50 K at the center of the fuel pellet at a linear heating power of 42.4 kW/m because of a decrease in thermal conductivity while the discrepancy vanishes as a larger central void is generated in MA-MOX. The results are critical in evaluating fuel performance and safety in using MA-MOX for reducing volume and toxicity of high-level radioactive wastes.

## INTRODUCTION

Various chemical form of fuels such as metals, oxides, nitrides, carbides and molten salts have been proposed for fast reactor (FR); each type has its advantages in economy and safety [1,2]. Mixed oxide (MOX) fuels with the advantages of high melting temperature and abundant experience as UO2 in light water reactors have been strong candidates for usage in FRs for reducing the volume and toxicity of high-level radioactive wastes in Japan and other countries. Challenges remain in assessing safety and performance in fuel that relies on computational simulations in a reactor with a combination of fuel properties because the MOX fuel reaches high temperatures exceeding 2000 K and the steep temperature gradient in pellets causes pore migration resulting in restructuring and redistribution of elements [3,4]. These behaviors are tightly concerned with fuel properties, such as thermal conductivity, vapor pressure, and diffusion, and the properties depend on temperature, density, and contents of the composing element. Thus, a property study with these parameters is critical in R&D of FR.

For example, the oxygen contents in MOX, which continuously varies depending on temperature and surrounding oxygen partial pressure with the valence state of cations changing, is an influential parameter on the properties [5–9]. The ratio of oxygen content and metal elements, such as uranium, plutonium, and minor actinides, is called the oxygen-to-metal (O/M) ratio. Our group has extensively investigated and quantified the influence of O/M on the MOX properties and modelled them using mechanistic models based on physical/chemical theories to describe the properties with better accuracy and extrapolation [10]. The addition of minor actinides, such as Am and Np, the target for transmutation because of their long half-lives, has been an interest for studies. As explained in the next chapter, a small amount of MAs forms a solid solution with MOX and maintains the fluoride structure [11]. For phonon behaviors, the addition of MAs in MOX enhances phonon-defect scattering, decreasing the thermal conductivity in the temperature range where the phonon conductivity is dominant [12,13].

This study summarizes property studies on MA-MOX that have been published mostly by Japan Atomic Energy Agency (JAEA). Then, fuel irradiation behaviors, focusing on the radial temperature distribution and restructuring, are analysed using a simulation code developed in JAEA using the properties, and how MA addition influences the properties and irradiation behaviors is discussed.

## Properties

### Lattice constant and thermal expansion

The chemical and physical properties of a material significantly depend on the lattice structure. UO2 and PuO2 form a fluoride structure, making a solid solution at any composition rate with a single lattice parameter [14]. X-ray diffraction studies assessed the lattice parameters of MA-MOX considering that the lattice structure around the stoichiometric composition is a single face-centered cubic (FCC) of fluoride [11]. Some studies indicate a phase separation into two FCC phases at low temperatures with higher Pu content [15,16]. Figure 1 shows that the obtained lattice parameters show a good linear relation with O/M, Pu, and MA contents and formulated them as

|  |  |
| --- | --- |
|  | (1) |

where is the lattice parameter. , , , and are the ionic radii of each species, , , and are the fraction of each species, and is .



*(a) (b) (c)*

*Fig. 1. Lattice parameter of MOX as a parameter of (a) Pu content, (b) Am/Np content and (c) O/M*

Thermal expansion of MOX with Pu contents of 0%, 30%, 50%, and 100% and O/M of 2.00, 1.99, 1.98, and 1.97 was obtained using dilatometer up to 1923 K [17–19]. Note that O/M was maintained at high temperature by controlling the oxygen partial pressure based on the oxygen potential data described in Section 2.3. Thermal expansion at the absolute temperature can be described using the following relation with the coefficients in Table 1.

|  |  |
| --- | --- |
|  | (2) |
|  | (3) |

TABLE 1. COEFFICIENTS IN EQUATION (3)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |
|  | −2.8809 | 0.0301 | −4.3954 | 0.0156 | −15.1759 | 2.5642 |
|  | 9.5024 | −0.1864 | 15.8173 | −0.0229 | 7.6258 | −7.5789 |
|  | 2.0894 | 2.9483 | −19.9227 | −1.0355 | 73.8931 | 11.6442 |
|  | 4.4096 | −1.4263 | 23.5638 | 0.0251 | −54.751 | −14.418 |

Figure 2 shows that thermal expansion slightly reflects O/M and Pu content; the thermal expansion islarger at lower O/M and Pu contents. The influence of the small amount of MA addition should be small considering that the thermal expansion of AmO2 and NpO2 is equivalent to MOX [20]. Thermal expansion obtained using a dilatometer reflect the increase in lattice parameters and the amount of defects, such as Frenkel defect, which might not be critical at the temperature range, whereas it would be predominant at higher temperatures, as is reported in CaF2 [21].

*(a) (b)*

*Fig. 2. Thermal expansion of MOX exhibiting larger trend at (a) lower Pu content and (b) lower O/M*

### Thermal conductivity

Thermal and safety performances of fuel pellets under irradiation are evaluated by calculating heat transport with thermal conductivity. Several parameters, such as temperature, composition, O/M, and density, influence the magnitude of thermal conductivity [12,13,22]. The fuel pellets are inhomogeneous regarding these parameters radially, attributed to the temperature gradient during irradiation. A laser flash method that measures thermal diffusivity is a common approach to study thermal conductivity by multiplying the thermal diffusivity, specific heat, and density. A simplified form of , a semi-empirical model to describe the phonon conduction, is used where and are impurity-scattering term analyzed using Ambegaoker’s theory [23] and phonon-phonon scattering term using by Liebfried-Schlomann’s relation [24], respectively. To include all parameters and the collection factor of density, such as Maxwell–Eucken relation [25–27], the following fitting relation for thermal conductivity was suggested [28].

|  |  |
| --- | --- |
| , | (4) |

where , in the collection factor of density, is porosity. Figure 3 shows that Am has a larger impact to decrease thermal conductivity than Np. However, the addition of a small amount of Mas (~ 10 mol%) that works as an impurity to enhance phonon-defect scattering has a relatively small impact. In contrast to adding MAs, oxygen defects that similarly enhances phonon-defect scattering have a larger impact on thermal conductivity.



*Fig. 3. Thermal conductivity of MOX with a smaller decrease by Am/Np addition and relatively a larger decrease by change of O/M*

Therefore, O/M, which is rapidly fluid along the temperature gradient during irradiation, is a decisive factor in the thermal analysis of pellets and, thus, a thermodynamic database of the relation among O/M and other factors is critical. The last term in equation (4) is incorporated to describe the increase in thermal conductivity at the high temperature region, reflecting the increase in specific heat attributed to the increase in Frenkel/electron defect concentrations. Many literatures exist for the scattered high temperature thermal conductivity. New techniques, such as laser heating [29], should lead to reliable results with persuading understanding.

### Oxygen potential

As discussed in the previous sections, the MOX properties depend significantly on O/M in the range that the fuel would experience during irradiation and the sintering process. The equilibrium state of oxygen content dissolved in MOX depends on the composition rate of Pu and MAs, temperature, and the surrounding oxygen partial pressure. The change in O/M is considered via defect reactions, generating oxygen defect and interstitial oxygen. The following relations were proposed based on the hundreds of data points obtained using the gas equilibrium method by analyzing the defect reactions to fit the experimental data with Arrhenius-type energies [9].

|  |  |
| --- | --- |
|  | (5) |
|  | (6) |
|  | (7) |
|  | (8) |
|  | (9) |

where is the oxygen partial pressure, is the gas constant and is defined as

|  |  |
| --- | --- |
|  | (10) |

Figure 4 shows the calculation results of equations (5)–(10). The increase in Pu content increases the oxygen potential, which means that O/M of MOX with higher Pu content decreases at the same oxygen potential. Equation (10) shows that the effect of MA addition to increase the oxygen potential is larger in the order of Am (2.5 larger than Pu), Pu, and Np (0.6 larger than Pu).



*Fig. 4. Oxygen potential of MA-MOX at 1000 K, 1500 K and 2000 K*

### Vapor pressure

Vaporization of actinide species in pores distributed in a fuel pellet is critical at high temperatures and along steep temperature gradients. Transporting the actinide species arises from the hotter to the colder area in a pore that lies along the temperature gradient because of the difference in vaporization and condensation rates between the areas, resulting in the migration of the pore to the hotter direction, i.e., to the center of the pellet [30]. The velocity of pore migration v can be described as

|  |  |
| --- | --- |
|  | (11) |

where is the molecular volume and is the diffusion coefficient. is described as

|  |  |
| --- | --- |
|  | (12) |

where is the number of molecules, is the vapor pressure of the actinide species, and is the Boltzmann constant. Here, the vapor pressure as a MOX property is incorporated and can be evaluated using the Rand–Marking model based on the Clausius–Clapeyron relation [31] and Gibbs energies [32–34]. Figure 5 shows the vapor pressure of the actinide species of MOX. UO2 and UO3 are the dominant vapor species and their vapor pressures are described using the following relations.

|  |  |
| --- | --- |
|  | (13) |
|  | (14) |
|  | (15) |
|  | (16) |

As such, the oxygen potential discussed in the previous section decides the vapor pressure and pore migration velocity. The fuel restructuring rate, resulting in the formation of a central pore and columnar grain, is accelerated by the inclusion of Am rather than Np because the vapor pressure of UO3 is increased, reflecting the increase of oxygen potential. Also, the increase in fuel temperature because of the decrease in thermal conductivity with MA increases the vapor pressure and, consequently, accelerates the fuel restructuring [35–36].



*(a) (b)*

*Fig. 5. (a) Temperature dependence and (b) O/M dependence of vapor pressure of (U0.7Pu0.3)O1.98 with solid lines and (U0.6Pu0.3Am0.05Np0.05)O1.98 with dashed lines*

## IRRADIATION SIMULATION

Irradiation behaviors of MOX fuel and MA-MOX fuel were computed using a simulation code “DIRAD TRANSIT” [35] developed in JAEA for calculating radial temperature distribution and restructuring based on the 1-D thermal transport and pore migration model. A previous irradiation test called B-11 [37, 38] was partly followed to simulate the irradiation behaviors of MA-MOX and MOX. Table 2 and Figure 6 show the major specifications of the fuel pellets and irradiation conditions.

TABLE 2. MAJOR SPECIFICATIONS OF FUELS AND CLADDINGS

|  |  |  |  |
| --- | --- | --- | --- |
| Pu content | 27 mol% | Cladding type | PNC1520 |
| Am content | 5 mol%, 0 mol% | Cladding outer diameter | 6.50 mm |
| Np content | 5 mol%, 0 mol% | Cladding inner diameter | 5.56 mm |
| O/M | 1.986 | Pellet-cladding gap width | 0.07 mm |
| Diameter | 5.42 mm |  |  |
| Density | 93.71 %T.D. |



*Fig. 6 Linear power history*

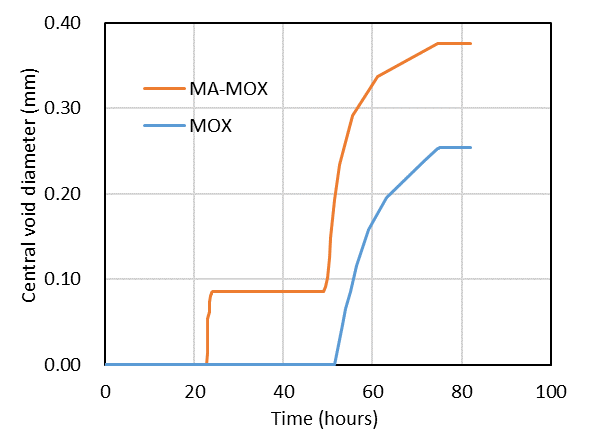
Figure 7 shows that the maximum temperature of MA-MOX is higher than that of MOX by 50 K at the first peak of 23 h. The discrepancy in the maximum temperature gradually decreases and vanishes in the second peak from 50 h to 75 h. The explanation for the first peak is considered as

* Adding MA decreases thermal conductivity, which is decisive in the difference between the peak temperatures.

Then, the second peak from 50 h to 75 h can be analysed based on the properties as;

* Adding MA decreases thermal conductivity.
* Adding MA increases the oxygen potential and vapor pressure of UO2 and UO3.
* The higher vapor pressure of UO2 and UO3 enhances the pore migration rate, forming a higher density region. The higher density increases thermal conductivity.
* These effects are offset to result in the equivalent peak temperatures.

As in the previous sections, Am is more influential in the properties than Np. The results of the central void sizes (Figure 8) indicate that MA-MOX experiences accelerated pore migration, reflecting the increase in vapor pressure. Other properties, such as the differences in thermal expansion, should be ignored in determining the temperature profiles.



*Fig. 7 Maximum fuel temperature Fig. 8 Central void dimeter*

## conclusion

Oxide–type fuels containing MAs, such as Am and Np, were considered strong candidates for FR fuels. Besides the abundant database and experiences on UO2, properties and mechanistic models to describe the properties on MA-MOX fuels were developed, enabling the numerical simulation of irradiation behaviors of the fuels. The temperature analysis performed in this study indicates that adding MA would make a small difference in fuel temperature. Am is more influential than Np in the properties and irradiation behaviors. Studies in higher rate of MAs addition and high temperature regions exceeding 2000 K must be challenged for further safety of MOX fuels and scientific interest.

ACKNOWLEDGEMENTS

The authors express their appreciation to Dr. M. Akashi for his effort in facility management and Mr. H Nakajima (NESI Inc.) for his contribution to the code development.

References

1. Sumner, T., Ghiaasiaan, S.M., “Effects of fuel type on the safety characteristics of a sodium-cooled fast reactor Part I: Background, modeling tools and pre-transient calculations”, Annals of Nuclear Energy 38 (2011) 1559-1568
2. Mignacca, B., Locatelli, G., “Economics and finance of Molten Salt Reactors”, Progress in Nuclear Energy 129 (2020) 103503
3. Ikusawa, Y., Maeda, K., Kato, M., Uno, M., “Oxide-Metal Ratio Dependence of Central Void Formation of Mixed Oxide Fuel Irradiated in Fast Reactors”, Nuclear Technology199 (2017) 83-95
4. Maeda, K., Katsuyama, K., Ikusawa, Y., Maeda, S., “Short-term irradiation behavior of low-density americium-doped uranium–plutonium mixed oxide fuels irradiated in a fast reactor”, Journal of Nuclear Materials 416 (2011) 158–165
5. Nakamichi, S., Kato, M., Tamura, T., “Influences of Am and Np on oxygen potentials of MOX fuels”, CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry, 35 (2011) 648-651
6. Komeno, A., Kato, M., Hirooka, S., Sunaoshi, T., “Oxygen potentials of PuO2-x”, Materials Research Society Symposium Proceedings, 1444 (2012) 85-89
7. Matsumoto, T., Arima, T., Inagaki, Y., Idemitsu, K., Kato, M., Morimoto, K., Sunaoshi, T., “Oxygen potential measurement of (Pu0.928Am0.072)O2–x at high temperatures”, Journal of Nuclear Science and Technology, 52 (2015) 1296-1302
8. Kato, M., Watanabe, M., Matsumoto, T., Hirooka, S., Akashi, M., “Oxygen potentials, oxygen diffusion coefficients and defect equilibria of nonstoichiometric (U,Pu)O2±x”, Journal of Nuclear Materials, 487 (2017) 424-432
9. Hirooka, S., Matsumoto, T., Kato, M., Sunaoshi, T., Uno, H., Yamada, T., “Oxygen potential measurement of (U,Pu,Am)O2±x and (U,Pu,Am,Np)O2±x”, Journal of Nuclear Materials, 542 (2020) 152424
10. Watanabe, M., Matsumoto, T., Hirooka, S., Morimoto, K., Kato, M., “Physical properties of non-stoichiometric (U,Pu)O2”, 2018 GIF Symposium Proceedings, 315-320
11. Kato, M., Konashi, K., “Lattice parameters of (U, Pu, Am, Np)O2-x”, Journal of Nuclear Materials 385 (2009) 117–121
12. Morimoto, K., Kato, M., Ogasawara, M., Kashimura, M., Abe, T., “Thermal conductivities of (U,Pu,Am)O2 solid solutions”, Journal of Alloys and Compounds 452 (2008) 54–60
13. Morimoto, K., Kato, M., Ogasawara, M., Kashimura, M., “Thermal conductivity of (U,Pu,Np)O2 solid solutions”, Journal of Nuclear Materials 389 (2009) 179–185
14. Lyon, W. L., Baily, W. E., “The solid-liquid phase diagram for the UO2-PuO2 system”, Journal of Nuclear Materials 22 (1967) 332-339
15. Komeno, A., Kato, M., Takeuchi, K., Morimoto, K., Kashimura, M, “Phase separation behaviour of (U0.7Pu0.3)O2-x (1.92<x<2.00) based fuels containing actinides and/or lanthanides”, IOP Conf. Series: Materials Science and Engineering 9 (2010) 012016
16. Belin, R.C., Strach, M., Truphemus, T., Gueneau, C., Richaud, J-C., Rogez, J., “In situ high temperature X-Ray diffraction study of the phase equilibria in the UO2ePuO2ePu2O3 system”, Journal of Nuclear Materials 465 (2015) 407-417
17. Uchida, T., Sunaoshi, T., Kato, M., Konashi, K., “Thermal Properties of UO2 by Molecular Dynamics Simulation”, Nuclear Science and Technology, 2 (2011) 598-602
18. Uchida, T., Sunaoshi, T., Konashi, K., Kato, M., “Thermal expansion of PuO2”, Journal of Nuclear Materials 452 (2014) 281–284
19. Kato, M., Ikusawa, Y., Sunaoshi, T., Nelson, A. T., McClellan, K. J., “Thermal expansion measurement of (U,Pu)O2-x in oxygen partial pressure-controlled atmosphere”, Journal of Nuclear Materials 469 (2016) 223-227
20. Sobolev, V., “Thermophysical properties of NpO2, AmO2 and CmO2”, Journal of Nuclear Materials 389 (2009) 45–51
21. Roberts, R.B., White, G.K., “Thermal expansion of fluorites at high temperatures”, J. Phys. C: Solid State Phys. 19 (1986) 7167-7172
22. Morimoto, K., Kato, M., Ogasawara, M., Kashimura, M., “Thermal conductivities of hypostoichiometric (U,Pu,Am)O2-x oxide”, Journal of Nuclear Materials 374 (2008) 378–385
23. Ambegaokar, V., “Thermal Resistance due to Isotopes at High Temperatures”, Phys. Rev. 114 (1959) 488
24. Leibfried, G., Scholmann, E., “Warmleitund in elektrische isolierenden Kristallen”, Nachrichten der Akademie der Wissenschaften in Göttingen. Akad, E., Wiss. Gottingen, Math. Phyz. Klasse 4 (1954) 71
25. Maxwell, J.C., “Treatise on Electricity and Magnetism”, vol. 1, third ed., Oxford University Press, reprinted by Dover, New York (1954)
26. Eucken, A., “Die Wärmeleitfähigkeit keramischer feuerfester Stoffe”, Forsch. Gebiete Ingenieur. B3, Forschungsheft No. 353, 1932, p.16.
27. Fricke, H., “A Mathematical Treatment of the Electric Conductivity and Capacity of Disperse Systems I. The Electric Conductivity of a Suspension of Homogeneous Spheroids”, Phys. Rev. 24 (1924) 575
28. Kato, M., Maeda, K., Ozawa, T., Kashimura, M., Kihara, Y., “Physical Properties and Irradiation Behavior Analysis of Np- and Am-Bearing MOX Fuels”, Journal of Nuclear Science and Technology 48 (2011) 646–653
29. Pavlov, T.R., Wenman, M.R., Vlahovic, L., Robba, D., Konings, R.J.M., Uffelen, P.V., Grimes, R.W., “Measurement and interpretation of the thermo-physical properties of UO2 at high temperatures: The viral effect of oxygen defects”, Acta Materialia 139 (2017) 138-154
30. De Halas, D.R., Horn, G.R., “Evolution of Uranium Dioxide Structure During Irradiation of Fuel Rods”, Journal of Nuclear Materials 8 (1963) 207 – 220
31. Rand, M.H., Marking, T.L., “Some Thermodynamic Aspects of (U,Pu)O2 Solid Solutions and Their Use as Nuclear Fuels” in Thermodynamics of Nuclear Materials, Symposium Proceedings, IAEA, Vienna (1967) 637 – 650
32. Olander, D.R., “Fundamental aspects of nuclear reactor fuel elements”, TID-26711-P1, Energy Research and Development Administration, US (1976) 155 – 160
33. Ackermann, R.J., Faircloth, R.L., Rand, M.H., “A Thermodynamic Study of the Vaporization Behavior of the Substoichiometric Plutonium Dioxide Phase ”, Journal of Physical Chemistry 70 (1966) 3698 – 3706
34. Ackermann, R.J., Faircloth, R.L., Rauh, E.G., Thorn, R.J., “The evaporation behavior of Neptunium dioxide”, Journal of Inorganic and Nuclear Chemistry 28 (1966) 111 – 118
35. Ikusawa, Y., Maeda, K., Kato, M., Uno, M., “Oxide-Metal Ratio Dependence of Central Void Formation of Mixed Oxide Fuel Irradiated in Fast Reactors”, Nuclear Technology 199 (2017) 83 – 95
36. Ikusawa, T., Hirooka, S., Uno, M., “Oxygen potential and self-irradiation effects on fuel temperature in Am-MOX”, 2018 GIF Symposium Proceedings, 321 – 327
37. K. Maeda, S. Sasaki, M. Kato, Y. Kihara, “Short-term irradiation behavior of minor actinide doped uranium plutonium mixed oxide fuels irradiated in an experimental fast reactor”, Journal of Nuclear Materials 385 (2009) 413-418
38. K. Maeda, S. Sasaki, M. Kato, Y. Kihara, “Radial redistribution of actinides in irradiated FR-MOX fuels”, Journal of Nuclear Materials 389 (2009) 78-84