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Oxidation and reduction behaviors of a prototypic MgO-PuO_{2-x} inert matrix fuel

Shuhei Miwa*, Masahiko Osaka

Oarai Research and Development Center, Japan Atomic Energy Agency, 4002 Narita-cho, Oarai-machi, Higashiibaraki-gun, Ibaraki, 311-1393, Japan

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ABSTRACT

Oxidation and reduction behaviors of prototypic MgO-based inert matrix fuels (IMFs) containing PuO_{2-x} were experimentally investigated by means of thermogravimetry. The oxidation and reduction kinetics of the MgO-PuO_{2-x} specimen were determined. The oxidation and reduction rates of the MgO-PuO_{2-x} were found to be low compared with those of PuO_{2-x}. It is note that the changes in O/Pu ratios of MgO-PuO_{2-x} from stoichiometry were smaller than those of PuO_{2-x} at high oxygen partial pressure.

1. Introduction

Inert matrix fuels (IMFs) are a composite of actinide phase and an inert matrix that are being considered as an option for the rapid incineration of actinides in a future fast reactor cycle system and an accelerator driven sub-critical system [1–5]. Magnesium oxide (MgO)-based IMF, which is one of the promising candidates, is the subject of this study. MgO has been selected due to its high manufacturability, chemical and physical stability, high melting temperature, and high thermal conductivity. Americium oxide (AmO_{2-x}) and plutonium and americium mixed oxide ($(Pu,Am)O_{2-x}$) are considered as actinide oxide phases for the MgO matrix [1–5]. The development of prototypic MgO-based IMFs containing actinides is now underway [1,2,6–10].

The oxygen-to-metal (O/M) ratio of nuclear oxide fuel, e.g. $UO_{2\pm x}$, PuO_{2-x}, $(U,Pu)O_{2-x}$, is a very important parameter because it significantly affects various fuel properties, oxygen potentials [11–16], thermophysical properties [17–19] and sintering behaviors [20,21]. Therefore, the O/M ratio of oxide fuels should be accurately evaluated with their changing behaviors, i.e. oxidation and reduction behaviors, as a function of O/M ratio. Although the situation is similar with IMFs, there is little data on MgO-based IMFs, i.e. the composite media of MgO and actinide oxide. In this study, therefore, the oxidation and reduction behaviors of a prototypic MgO-based IMF containing PuO_2 (hereafter, MgO-PuO_{2-x}) were experimentally investigated by means of thermogravimetry. Results were compared with those for PuO_{2-x} specimen which was prepared for reference and discussed from the viewpoint of the effects of the MgO matrix on the oxidation and reduction behaviors of PuO_{2-x} in MgO-PuO_{2-x}.

2. Experimental

2.1. Specimen preparation

A dense disk-shaped MgO-PuO_{2-x} (size of PuO_{2-x} phase was below ϕ10 μm) specimen was prepared by a powder metallurgy method. Table 1 shows the fundamental specifications of the raw powders. Raw PuO_2 and MgO (Ube Material Co., Ltd.) powders were weighed to obtain a composition of 15 vol% of PuO_2 and 85 vol% of MgO. These powders were mixed by pestle in an agate mortar in acetone medium for 15 min. The mixed powders were compacted at 200 MPa for 2 min. Sintering was carried out at 1873 K for 3 h in air atmosphere. A sintered PuO_2 disk specimen was also prepared for reference by the same procedure. Table 2 shows the characteristics of PuO_2 and MgO-PuO_{2-x} specimens for thermogravimetric analysis (TGA). The sintered density of PuO_2 was calculated to be approximately 81% of theoretical density (%TD), and that of MgO-PuO_{2-x} specimen was approximately 90 %TD. Calculations of the

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* Corresponding author.
E-mail address: miwa.shuhei@jaea.go.jp (S. Miwa).

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Table 1
Fundamental specifications of raw powders.

	PuO_2	MgO[a]
Metal impurities (ppm)	<1065	<113
Composition	$(Pu_{0.98}U_{0.02})O_2$	MgO
Particle radius (μm)	<0.2	0.1
Specific surface area (m^2/g)	7.3	12.5

[a] Ube Material Industry Co. Ltd., 1000 A.

Table 2
Characteristics of PuO_{2-x} and MgO-PuO_{2-x} specimens for TGA.

	PuO_{2-x}	MgO-PuO_{2-x}
Volume (weight) fraction of PuO_{2-x}	–	0.15 (0.37)
Diameter (mm)	5.2	5.1
Height (mm)	1.0	1.3
Density (g/cm^3)	9.42	
(80.8 %TD)	4.34	
(89.7 %TD)		

theoretical density assumed that the PuO_2 did not form a solid solution with MgO like as the case of authors' previous studies on the MgO-$(Pu,Am)O_{2-x}$ specimen [9,10], which have shown no experimental evidences of the solid solution formation by an X-ray diffraction analysis.

2.2. Oxidation and reduction kinetics measurement

Oxidation and reduction kinetics of PuO_{2-x} and MgO-PuO_{2-x} were measured by means of TGA. TGA was carried out at 1273 K, 1373 K and 1473 K, using a Rigaku model TG-8120 connected to a gas supply system. PuO_{2-x} and MgO-PuO_{2-x} specimens were loaded into an alumina capsule and placed in the TGA apparatus. Oxygen partial pressure was adjusted in the range from 10^{-20} to 10^{-12} MPa at a constant temperature. The adjustment was effected by changing the ratio of H_2O/H_2 in slowly flowing mixed gases (265 cm^3/min). Equilibrium oxygen partial pressure was measured using a stabilized zirconia oxygen sensor. The oxygen sensor was calibrated prior to TGA using the oxidation and reduction of pure chromium metal and a standard gas containing a known amount of oxygen.

The oxygen partial pressure in the atmosphere was changed and it achieved equilibrium rapidly, in less than 10 min. Microgram-order weight changes in the specimen occurring after change in oxygen partial pressure were continuously monitored during several hundred min. Continuous weight changes with time were used for evaluation of oxidation and reduction kinetics.

O/M ratios of MgO-PuO_{2-x} were calculated from weight changes relative to stoichiometry, which should be obtained by heat-treatment at approximately −300 kJ/mol based on previous results for PuO_{2-x} oxygen potential [15]. Because MgO doesn't have non-stoichiometry and is reduced to Mg only at approximately 10^{-32} MPa at 1473 K [22], the changes in O/Mg ratio in MgO would be extremely low and, therefore, negligible in this condition. In addition, since the solid solution formation in the PuO_2-MgO system was quite limited [23], weight change of the specimen can be regarded as that of the O/Pu ratio change in MgO-PuO_{2-x}.

3. Results and discussions

Fig. 1 shows the O/Pu ratio changes in the reduction processes of PuO_{2-x} and MgO-PuO_{2-x} at 1373 K from stoichiometry to the O/Pu ratio of 1.991. Whereas the reduction of PuO_{2-x} was completed in approximately 200 min, that of PuO_{2-x} in MgO-PuO_{2-x} was continuing at 200 min. The reduction rate of PuO_{2-x} in MgO-PuO_{2-x} was lower than that of PuO_{2-x}. Fig. 2 shows the O/Pu ratio changes in the oxidation process of PuO_{2-x} and MgO-PuO_{2-x} at 1473 K from O/Pu of 1.975 to the stoichiometry. The oxidation rates of both PuO_{2-x} and PuO_{2-x} in MgO-PuO_{2-x} were higher than their respective reduction rates at the same temperature. Whereas the oxidation of PuO_{2-x} was completed in approximately 20 min, completion of PuO_{2-x} oxidation in MgO-PuO_{2-x} required approximately 120 min. The oxidation rate of PuO_{2-x} in MgO-PuO_{2-x} was lower than that of PuO_{2-x}.

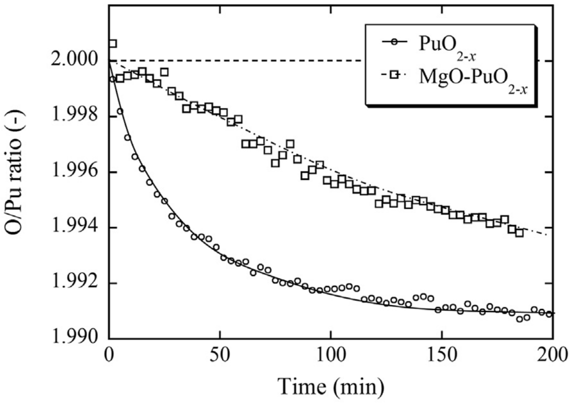

Fig. 1. The O/Pu ratio changes in the reduction process of PuO_{2-x} and MgO-PuO_{2-x} at 1373 K.

These lower oxidation and reduction rates of MgO-PuO_{2-x} can be caused by the effects of MgO matrix. The mechanisms of oxidation and reduction of actinide oxides such as $UO_{2\pm x}$ [24,25], PuO_{2-x} [26] and $(U,Pu)O_{2-x}$ [27] have been investigated, and the mechanisms of O/M ratio changes in $(U,Pu)O_{2-x}$ in the oxidation and reduction processes are found to be distinctly different [27]. The oxidation and reduction processes would be dominated, respectively, by a zero-order reaction such as one on the surface and oxygen chemical diffusion according to [27]. Since the crystal structure and the oxidation and reduction species are the same in both PuO_{2-x} and $(U,Pu)O_{2-x}$, the mechanisms of O/Pu ratio changes in PuO_{2-x} should be the same as those in $(U,Pu)O_{2-x}$ [27]. Fig. 3 shows the cross-sectional image of a prototypic MgO-PuO_{2-x} specimen with higher PuO_{2-x} content (24 vol%) than the present specimen (15 vol%) prepared by the same procedure. It is seen that the PuO_{2-x} phase is isolated, namely PuO_{2-x} phase is surrounded by the MgO phase. The present specimen should have the same isolated PuO_{2-x} phase

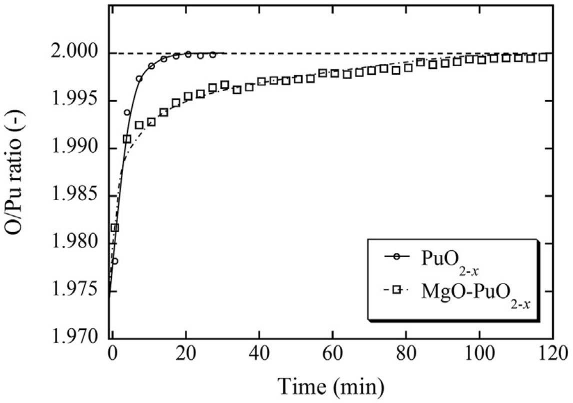

Fig. 2. The O/Pu ratio changes in the oxidation process of PuO_{2-x} and MgO-PuO_{2-x} at 1473 K.