

Phase behavior of PuO_{2-x} with addition of 9% Am

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Abstract

An experimental investigation on the phase relation of PuO_{2-x} with addition of 9% americium (Am) was carried out by means of X-ray diffraction analysis, ceramography and differential thermal analysis. Solid solutions of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ with different O/M ratios ranging from 1.90 to 2.00 were prepared. The phase transition temperatures of single phase to two phases at high temperatures were slightly lower than those of AmO_{2-x} . The phase relation of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ seemed to have different trends which appeared above and below a certain O/M ratio. Consideration of the valence states of Pu and Am in the solid solution could lead to a reasonable interpretation for the phase relation.
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1. Introduction

Transmutations of minor actinides (MAs) in either a fast reactor and/or an accelerator driven sub-critical system (ADS) are currently considered one of the promising options for future nuclear cycle technology, which is essential to a reduced environmental burden and a sustainable energy supply. The Japan Atomic Energy Agency (JAEA) is promoting R&D programs for future nuclear cycle technology based on fast reactors [1]. Development of the mixed oxide (MOX) fuel and a target containing MAs, which are considered to be promising candidates for future fast reactors, is underway [1,2]. The target is composed of MA oxides and non-radioactive inert materials such as MgO [2] to enhance mainly thermal performance.

Among the MAs, americium (Am) is of special concern, especially from the viewpoint of long-term safety issues for the final disposal of radioactive waste. It is, therefore, better to recycle Am into the reactor and to transmute it into stable or less radiotoxic nuclides. Since Am-doped plutonium (Pu) oxide, $(\text{Pu,Am})\text{O}_{2-x}$, is considered a candidate form of MA-

including oxides of the target for both fast reactors [2] and the ADS [3], its phase relation should be evaluated as a fundamental property.

Some data have been published for the phase relation of PuO_{2-x} and AmO_{2-x} . Chikalla and Eyring [4] investigated the phase relation in the AmO_{2-x} system between $1.5 < \text{O/M} < 2.0$ by using X-ray diffraction (XRD) measurements. They found that AmO_{2-x} had a fluorite structure and cubic, hexagonal and monoclinic sesquioxide Am_2O_3 phases like those of PuO_{2-x} and lanthanide oxide systems. Chikalla et al. [5] investigated the phase relation of the Pu–O system by measuring thermal expansion, lattice parameters and electrical resistivity. They found that there was a two-phase solid miscibility gap with a boundary of about 650 °C for O/Pu ratios between 1.70 and 1.98. Sari and Zamorani [6] measured the phase transition behavior of AmO_{2-x} by differential thermal analysis (DTA). They found that while the profile of the phase diagram for the Am–O system was similar to that of the Pu–O system, phase transition temperatures from the single phase to two phases of the Am–O system were higher than those corresponding to the Pu–O system.

In the study of the solid solution of PuO_{2-x} and AmO_{2-x} , $(\text{Pu,Am})\text{O}_{2-x}$, it is suggested that higher oxygen potential of $(\text{Pu,Am})\text{O}_{2-x}$ compared to PuO_{2-x} is attributable to the instability of tetravalent Am [7]. In addition, although it is also suggested

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Table 1
Heat treatment conditions and resultant O/M ratios of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ samples

Temperature [°C]	$\Delta\bar{G}_{\text{O}_2}$ [kJ/mol]	O/M ratio
800	0	2.00
1000	−425	1.94
1150	−417	1.92
1000	−482	1.90

that tetravalent Am is stabilized by tetravalent Pu [7,8], there are no data on this effect for such a phase relation of $(\text{Pu},\text{Am})\text{O}_{2-x}$.

In this study, therefore, an experimental investigation on the phase relation of $(\text{Pu},\text{Am})\text{O}_{2-x}$ was carried out at temperature to 1150 °C and an O/M ratio range from 1.90 to 2.00. Focus was placed on the effects of Am addition to PuO_{2-x} on the phase relation. Results on phase relation were discussed in terms of the valence states of Am and Pu in the solid solution.

2. Experimental

The $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ solid solutions were prepared via a conventional powder metallurgical route; i.e., ball-milling of $(^{241}\text{Am}_{0.09}\text{Pu}_{0.91})\text{O}_{2-x}$ powder in which ^{241}Am was generated by β -decay of ^{241}Pu , uni-axial pressing into pellets, followed by sintering in moisture-added Ar containing 5% H_2 for 13 h at 1500 °C. The oxygen potential in the sintering atmosphere at 1500 °C was about −400 kJ/mol. The O/M ratio of as-sintered pellets was about 1.93.

The sintered pellets were then heat-treated in air at 800 °C to adjust to the stoichiometry, $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_2$. This heat treatment condition was reasonable because stoichiometric AmO_2 , for which the oxygen potential is extremely high, has been reported to be obtained under this condition [9]. The stoichiometric $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_2$ was then annealed under a moisture-added Ar/ H_2 atmosphere at different oxygen potential to adjust the O/M ratio from 1.90 to 2.00. The O/M ratios at various oxygen potentials were calculated from the weight change relative to the stoichiometry. The conditions of heat treatment are summarized in Table 1. X-ray diffraction analysis and ceramography observations were carried out for annealed samples having different O/M ratios at room temperature. Phase transition temperatures of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ were investigated by differential thermal analysis (DTA) for $1.92 < \text{O/M} < 2.00$ by both increasing and lowering the temperature at constant O/M ratios.

3. Results and discussion

XRD patterns for stoichiometric $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2.00}$ showed a single phase fluorite structure. The lattice parameter of stoichiometric $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2.00}$ was determined to be 0.5397 nm, which agreed with that calculated by using Vegard's law (0.5394 nm), in which $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2.00}$ was assumed as an ideal solid solution of $\text{PuO}_{2.00}$ and $\text{AmO}_{2.00}$. This agreement of the value indicates the formation of the solid solution. Fig. 1 reproduces a ceramographic image of stoichiometric $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2.00}$ showing its microstructure. While there were many large pores which were left in the matrixes and grain boundaries owing to the high heating rate in the sintering process, the microstructure of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2.00}$ seemed to be homogeneous, i.e. isotropic grain growth, and there were no precipitates and no phase separation.

XRD peaks for $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{1.94}$ and $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{1.92}$ that were annealed above 1000 °C also showed peaks which were derived from a single phase fluorite structure. The lat-

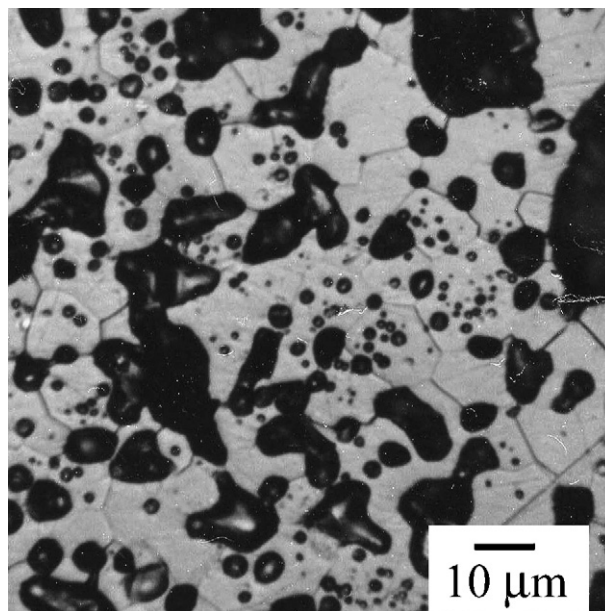


Fig. 1. Ceramographic image of as-etched stoichiometric $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2.00}$.

tice parameters of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{1.94}$ and $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{1.92}$ were 0.5411 and 0.5413 nm, respectively. Fig. 2 shows the lattice parameter dependence of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ on O/M ratio. The lattice parameter increased monotonically with the decrease of O/M ratio. From these results, $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ was judged to form a single phase fluorite structure above 1000 °C for O/M ratios from 1.92 to 2.00.

On the other hand, the $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{1.90}$ that was annealed at 1000 °C was a mixture of two-phase fluorite structures (γ_1 and γ_2). Fig. 3 reproduces a ceramographic image of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{1.90}$ showing its microstructure. Notably, $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{1.90}$ showed phase separation; there were different phases from the matrix in the vicinity of the grain boundary.

Fig. 4 shows peak locations observed in the DTA plotted on the phase diagram of the temperature versus O/M ratio for $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$. There were small DTA peaks on increasing and lowering temperatures. It was seen that there were phase transition temperatures of about 950 °C throughout the range of investigated O/M ratios, $1.92 < \text{O/M} < 1.995$. For the inves-

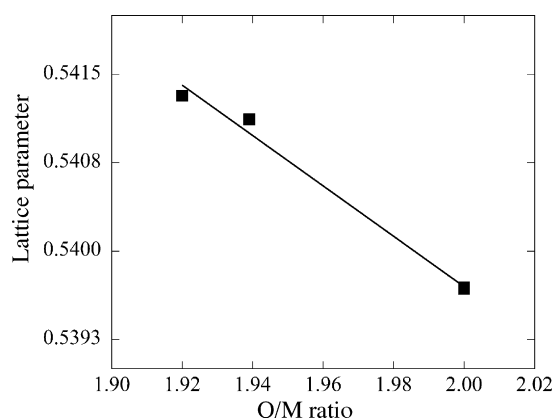


Fig. 2. Dependence of lattice parameters of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ on O/M ratio, calculated by weight change relative to stoichiometry.

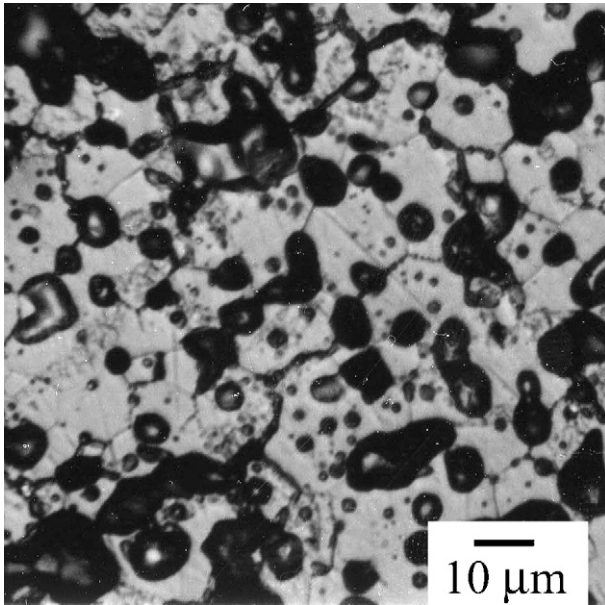


Fig. 3. Ceromographic image of as-etched substoichiometric $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$.

igated O/M ratios, the structure of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ was considered to be a single phase fluorite structure above 950°C , and there was a two-phase region ($\gamma_1 + \gamma_2$) below 950°C in these O/M ratio ranges, which was determined by XRD. There were also indications of a phase transition at about 300°C throughout the range of investigated O/M ratios. In this temperature, the phase transition from high temperature bcc to low temperature bcc ($C \rightarrow C'$) might take place for $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ analogous to Pu–O and Am–O systems [4–6]. In addition, there were also indications of phase transitions at about 630°C below an O/M ratio of 1.96. However, the DTA peaks at about 630°C were so small that they could not be due to a stable phase transition. One possible cause was those from quasi-stable phase transition.

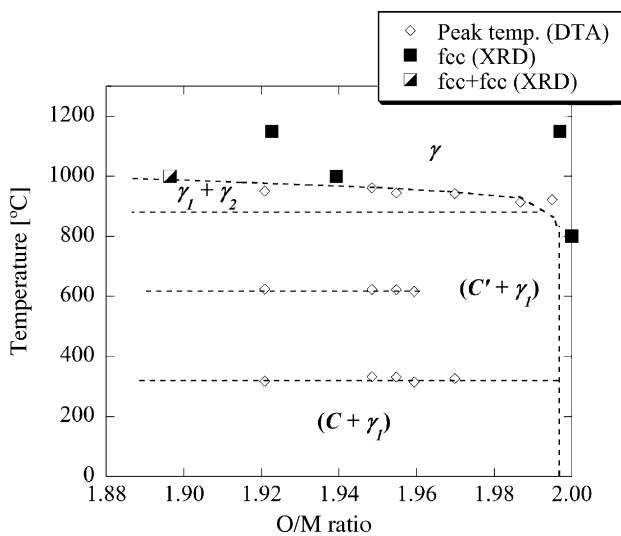


Fig. 4. Phase diagram of substoichiometric $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$. γ , γ_1 , $\gamma_2 = \text{fcc}$ $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$. C' , high temperature bcc $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_3$. C , low temperature bcc $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_3$.

The transition temperature of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ from single phase to two phase ($\gamma \rightarrow \gamma_1 + \gamma_2$; about 950°C) was higher than that of the Pu–O system (about 650°C) [5]. This transition temperature of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ corresponded roughly to the transition temperature of the Am–O system (about 1050°C) [6], rather than the Pu–O system [5]. Morimoto et al. [10] investigated the phase transition temperature of a single fluorite phase to a two-phase fluorite for $(\text{Pu}_{0.94}\text{Am}_{0.06})\text{O}_{2-x}$. They found that the phase transition temperature was higher than that for PuO_{2-x} [5,6]. From their results and this study, the phase transition temperature of single fluorite phase to two-phase fluorite ($\gamma \rightarrow \gamma_1 + \gamma_2$) in $(\text{Pu},\text{Am})\text{O}_{2-x}$ increased with increase of Am content.

The phase relation of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ seemed to have different trends which appeared above and below an O/M ratio of 1.96. To discuss this point, the following hypothesis was adopted: i.e., Am was reduced prior to Pu in $(\text{Pu},\text{Am})\text{O}_{2-x}$ when the deficiencies from stoichiometry increased. In this hypothesis, the boundary O/M ratio, at which all Am was trivalent, was 1.955 for $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$. This O/M ratio is close to the ratio that divides the different phases mentioned above. According to this hypothesis, all Pu are tetravalent above the boundary O/M ratio with Am valence varying from tetravalent to trivalent, while all Am are trivalent below the boundary O/M ratio with Pu valence varying from tetravalent to trivalent.

Above the boundary O/M ratio, the peak temperatures of DTA were observed at about 950 and 300°C . Notably, these corresponded roughly to the Am–O system, about 1050 and 300°C [6], respectively. Osaka et al. [7] investigated the oxygen potential of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ and found from the slope n of the plot $\log(p_{\text{O}_2})$ versus $\log(x)$ of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ that the predominant defect structures in $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ had not changed significantly from those in AmO_{2-x} above the boundary O/M ratio. This behavior supported the present results. These results suggested that the Am–O system was dominant in the phases of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ above the boundary O/M ratio.

Below the boundary O/M ratio, the DTA peaks which were thought to be derived from quasi-stable phase transition were observed at about 630°C , in addition to 950 and 300°C . This temperature was close to that for the phase transition of the Pu–O system from single fluorite phase structure to two-phase fluorite ($\gamma \rightarrow \gamma_1 + \gamma_2$), about 650°C [5]. In the hypothesis mentioned above, substoichiometry below the boundary O/M ratio resulted in the reduction of tetravalent Pu to its trivalent state. Although further investigation is needed, the quasi-stable phase transition at about 630°C below the boundary O/M ratio may be attributed to Pu effect.

4. Conclusion

An experimental investigation on the phase relation of PuO_{2-x} with addition of 9% americium (Am) was carried out by means of XRD analysis, ceramography and DTA. Solid solutions of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ having different O/M ratios ranging from 1.90 to 2.00 were prepared.

The phase transition temperatures of single phase fluorite structure to two phases fluorite structure at high temperatures

were slightly lower than those of AmO_{2-x} . The phase relation of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ seemed to have different trends which appeared above and below a certain O/M ratio. Consideration of the valence states of Pu and Am in the solid solution could lead to a reasonable interpretation for the different trends of phase relation. Finally, it was concluded that the effect of Am addition to PuO_{2-x} on the phase relation was to increase the miscibility gap temperature and to lead to different trends of the phase relation according to valence states of Pu and Am.

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