

## Oxygen potential of $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$

Masahiko Osaka <sup>a,\*</sup>, Ken Kurosaki <sup>b</sup>, Shinsuke Yamanaka <sup>b</sup>

<sup>a</sup> *Japan Atomic Energy Agency, Narita-cho 4002, Oarai-machi, Higashi-ibaraki-gun, Ibaraki 311-1393, Japan*

<sup>b</sup> *Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita-shi, Osaka 565-0871, Japan*

Received 12 January 2006; accepted 17 May 2006

### Abstract

Oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  were measured by thermogravimetric analysis with  $\text{H}_2\text{O}/\text{H}_2$  gas equilibrium and dilute  $\text{O}_2$  gas at 1123 K, 1273 K and 1423 K. The oxygen potentials were extremely high from stoichiometry to  $\text{O}/\text{M} = 1.99$  and were somewhat lower than those of  $\text{AmO}_{2-x}$  near stoichiometry. On the other hand, those below  $\text{O}/\text{M} = 1.96$  were much lower than those of  $\text{AmO}_{2-x}$ . Valence state changes of Am and Pu in the oxide were assumed, and experimentally determined data were examined using the slope of the plot of oxygen partial pressure versus deviation from stoichiometry, the oxygen potential as a function of mean valence state of metal, activity coefficient of  $\text{AmO}_{2-x}$  and the partial molar enthalpy and entropy of oxygen. It was concluded through these examinations that aspects of the oxygen potential of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  could be interpreted by the present assumption and that several interactions between Am and Pu could exist.

© 2006 Elsevier B.V. All rights reserved.

PACS: 28.41.Bm

### 1. Introduction

Oxygen potential is an important property for oxide nuclear fuels. It has direct effects on oxidation of the cladding material during irradiation in the reactor, which may eventually lead to cladding failure. Furthermore, it is closely related to various aspects of the fuel behavior. This quantity is defined by using equilibrium partial pressures of oxygen over the oxides as given in the following equation:

$$\Delta\bar{G}_{\text{O}_2} = RT \ln p_{\text{O}_2}^* \quad (1)$$

where  $\Delta\bar{G}_{\text{O}_2}$  is the oxygen potential,  $R$  is the gas constant,  $T$  is the temperature and  $p_{\text{O}_2}^*$  is the oxygen partial pressure, which is derived from the ratio of oxygen partial pressure to its standard state, 0.101 MPa. The oxygen potential is a function of temperature and oxygen to metal (O/M) ratio of the oxide. As the fluorite structure with a wide range of oxygen non-stoichiometries, e.g.,  $\text{UO}_{2+x}$ ,  $(\text{U,Pu})\text{O}_{2\pm x}$ , represents the nuclear fuel form, it is important to know the oxygen potential as a function of the temperature and O/M ratio. This function is well established by many experimental and theoretical studies for  $\text{UO}_{2+x}$  [1,2],  $(\text{U,Pu})\text{O}_{2\pm x}$

\* Corresponding author. Tel.: +81 29 267 4141; fax: +81 29 266 0016.

E-mail address: [ohsaka.masahiko@jaea.go.jp](mailto:ohsaka.masahiko@jaea.go.jp) (M. Osaka).

[3], and rare earth-doped  $\text{UO}_2$  [4] as surrogate for irradiated fuels.

Recently, minor actinides (MAs), especially americium (Am), have become of special concern for the establishment of a future nuclear fuel cycle that is compatible with requirements for a reduced environmental burden and sustainable energy supply [5]. Americium has high and lasting radiotoxicity that can cause problems especially in view of the long term safety issues for the final disposal of radioactive waste. It is, therefore, better to recycle Am into a reactor and to transmute it into stable or less-toxic nuclides. Since Am-containing oxides are considered a promising transmutation device [6,7], their oxygen potentials are indispensable data for safe irradiation in a reactor. Among them,  $(\text{Pu},\text{Am})\text{O}_{2-x}$  is a candidate form for the Am-containing oxide for both fast reactors [8] and accelerator driven sub-critical systems [9].

Some data have been published for the oxygen potentials of Am-containing oxides. Chikalla and Eyring [10] have measured the oxygen potentials of  $\text{AmO}_{2-x}$  at temperatures ranging from 1139 K to 1445 K. The oxygen potentials of  $\text{AmO}_{2-x}$  were extremely high compared with those of standard nuclear fuels such as  $(\text{U},\text{Pu})\text{O}_{2-x}$ . Bartscher and Sari [11] measured the oxygen potentials of  $(\text{U}_{0.5}\text{Am}_{0.5})\text{O}_{2\pm x}$ . The oxygen potentials of  $(\text{U}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$  were greatly reduced compared with those of  $\text{AmO}_{2-x}$ , but were still much higher than those of standard fuels. It was also found that the oxygen potentials of  $(\text{U},\text{Pu})\text{O}_{2-x}$  doped with a low content of Am,  $(\text{U}_{0.685}\text{Pu}_{0.270}\text{Am}_{0.045})\text{O}_{2-x}$ , had higher oxygen potentials than those of  $(\text{U},\text{Pu})\text{O}_{2-x}$ , although they were somewhat lower than those of  $(\text{U}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$  [12]. However, there are no data for the oxygen potentials of  $(\text{Pu},\text{Am})\text{O}_{2-x}$ . One important purpose of the present study is, therefore, experimental determination of the oxygen potentials for  $(\text{Pu},\text{Am})\text{O}_{2-x}$ .

In addition to the above mentioned motivation, there is another significance in determination of the oxygen potentials of  $(\text{Pu},\text{Am})\text{O}_{2-x}$ . There are mainly two reasons for such high oxygen potentials of Am-containing oxides. One is caused by the extremely high oxygen potential of  $\text{AmO}_{2-x}$  itself, which is derived from unstableness of tetravalent Am [13]. The other is caused by interactions between U and Am in the case of U-containing oxides, which results in a higher valence state of U by a compensation of electrical neutrality in the oxide; i.e., U is oxidized from a tetravalent to a pentavalent state since Am

is likely to be trivalent in the fluorite structure unless the oxygen potential is not as high as those of  $\text{AmO}_{2-x}$  [14]. This cause can also be applied to the Pu-containing oxide case, namely  $(\text{U},\text{Pu},\text{Am})\text{O}_{2-x}$  [15,16], which means that such an interaction between U and Am predominates and interactions between Pu and Am can be neglected owing to their small effects compared with those between U and Am. However, interactions between Pu and Am become important in non U-containing oxides, like the present case. Also basic knowledge for such interactions are useful to construct an analytical model that can provide a reliable prediction of the oxygen potentials of  $(\text{U},\text{Pu},\text{Am})\text{O}_{2-x}$ . Actually, in a chemical thermodynamic representation of  $(\text{U},\text{Pu},\text{Am})\text{O}_{2-x}$  by the present authors [16], a small discrepancy was seen between experimental and analytical oxygen potentials at specific O/M ratio where interactions between Pu and Am become important. Additionally, some stabilization effects of tetravalent Am by tetravalent Pu are expected as a consequence of such interactions, like the stabilized tetravalent Pu in  $\text{ThO}_2$  or  $\text{UO}_2$  [17]; such effects lead to reduction of the oxygen potentials of  $\text{PuO}_{2-x}$ .

In this study, a mixed oxide  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  was prepared and its oxygen potentials were measured by thermogravimetric analysis (TGA) with  $\text{H}_2\text{O}/\text{H}_2$  gas equilibrium and dilute  $\text{O}_2$  gas. The temperatures ranged from 1123 K to 1423 K, and measured deviations from stoichiometry,  $x$ , ranged from 0 to 0.09. Results were compared with those of related oxides and discussed in views of valence state changes of Pu and Am in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  to understand interactions between Pu and Am.

## 2. Experimental

A  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  mixed oxide pellet was prepared by a conventional powder metallurgical route; i.e., ball-milling of powder, uniaxial pressing into a pellet, and sintering in Ar containing 5%  $\text{H}_2$  for 3 h at 1973 K. An appropriate amount of moisture was added to the sintering gas so as to adjust the oxygen potential to about  $-400$  kJ/mol. This was done by passing the gas through water. Americium in the powder was derived from beta-decay of  $^{241}\text{Pu}$  during storage. The powder was heat treated in Ar containing 5%  $\text{H}_2$  at 1073 K prior to the pellet preparation procedure. There were neither visible cracks nor any failures in the sintered body. The sintered pellet was then heat treated in air at 1073 K to adjust to the stoichiometry,  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_2$ . The stoichio-

metry should be obtained with this heat treatment condition, since this condition is the same as for stoichiometric  $\text{AmO}_2$  preparation and further since  $\text{PuO}_{2-x}$  has a much smaller oxygen potential than  $\text{AmO}_{2-x}$  does [10,17]. Actually, as shown later, this condition was proved to be reasonable because the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  are lower than those of  $\text{AmO}_{2-x}$  throughout the whole measured range of non-stoichiometry. X-ray diffraction patterns with  $\text{Cu K}\alpha$  radiation of the stoichiometric oxide showed a single phase fluorite structure. The lattice parameter was determined from the X-ray diffraction angles as 0.5393 nm, which is close to that calculated by Vegard's law, 0.5394 nm. After crushing the pellet, about 150 mg of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  specimen was subjected to TGA.

The TGA was carried out at 1123 K, 1273 K and 1423 K, using a Rigaku model TG-8120 connected with a gas supply system. A  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  specimen was loaded into an alumina capsule and placed in the TGA apparatus. For reference, an alpha-alumina sample was loaded into another alumina capsule and also placed in the apparatus. Oxygen partial pressure was adjusted in the region from  $10^{-21}$  to  $10^{-2}$  MPa at a constant temperature. The adjustment was done by changing the ratio of  $\text{H}_2\text{O}/\text{H}_2$  and dilution ratio of  $\text{O}_2$  in slowly flowing mixed gas for the ranges of  $10^{-21}$  to  $10^{-12}$  MPa and  $10^{-12}$  to  $10^{-2}$  MPa, respectively. The oxygen partial pressure was measured with a stabilized zirconia oxygen probe. Microgram order weight changes in the specimen were continuously monitored while changing the oxygen partial pressure at the pre-determined temperature step by step. The oxygen potentials were calculated by using Eq. (1). The O/M ratios at various oxygen partial pressures and temperatures were calculated from the weight changes relative to the stoichiometry,  $\text{O}/\text{M} = 2$ . Estimated errors of the oxygen potential and O/M ratio were  $\pm 10$  kJ/mol and  $\pm 0.002$ , respectively.

### 3. Results

Fig. 1 shows measured oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  as a function of O/M ratio at 1123 K, 1273 K and 1423 K. The oxygen potentials are very high and decrease monotonically with decrease of O/M ratio from 2.00 to 1.99; i.e., ranging from  $-20$  kJ/mol at  $\text{O}/\text{M} = 2.000$  to  $-257$  kJ/mol at  $\text{O}/\text{M} = 1.991$  at 1273 K, from  $-45$  kJ/mol at  $\text{O}/\text{M} = 1.999$  to  $-165$  kJ/mol at  $\text{O}/\text{M} = 1.992$  at 1423 K. Decreases of the oxygen potentials are very small

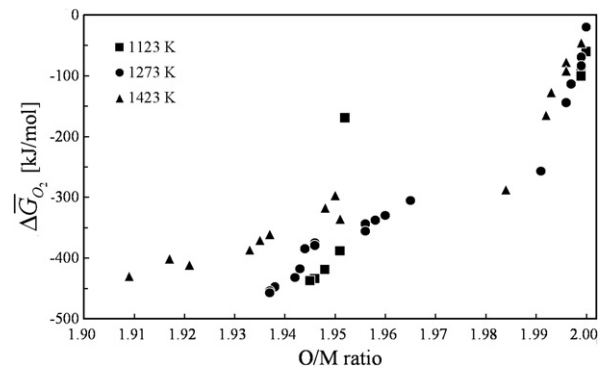


Fig. 1. Oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  as a function of O/M ratio at 1123 K, 1273 K and 1423 K.

which occur with the decrease of O/M ratio from 1.99 to 1.96 at 1273 K and 1423 K. On the other hand, the oxygen potential at 1123 K decreases steeply around  $\text{O}/\text{M} = 2$ , then hardly decreases from this O/M ratio until  $\text{O}/\text{M} = 1.952$ , at which it decreases sharply again. This may be caused by formation of a two-phase region at 1123 K. One possible form for this two-phase region is that reported by Donnet et al. [18] for  $(\text{Pu}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$ , which consists of fluorite and cubic structures. Below O/M ratio of about 1.96, the oxygen potentials decrease steadily with decrease of O/M ratio for all temperatures. Their decrease rates with decrease of O/M ratios are smaller than those near  $\text{O}/\text{M} = 2$ .

Fig. 2 compares the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  with those of related dioxides at or around 1273 K. Above  $\text{O}/\text{M} = 1.96$ , the oxygen potentials are the highest for  $\text{AmO}_{2-x}$ , then  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ , followed by  $(\text{U}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$ ,  $(\text{U}_{0.685}\text{Pu}_{0.270}\text{Am}_{0.045})\text{O}_{2-x}$ ,  $\text{PuO}_{2-x}$  [19], and finally  $(\text{U}_{0.6}\text{Pu}_{0.4})\text{O}_{2-x}$  [19]. Of special note is that the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  are higher than those having higher Am content,  $(\text{U}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$ . They are instead comparable to those of  $\text{AmO}_{2-x}$  around  $\text{O}/\text{M} = 2$ . This indicates different causes of high oxygen potentials between  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  and  $(\text{U}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$ , as mentioned later; in brief, the high oxygen potential of  $\text{AmO}_{2-x}$  is the main cause for the former, while pentavalent U due to a compensation of electric neutrality for the latter [14]. Below  $\text{O}/\text{M} = 1.96$ , the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  are still much higher than those of  $(\text{U}_{0.685}\text{Pu}_{0.270}\text{Am}_{0.045})\text{O}_{2-x}$ ,  $\text{PuO}_{2-x}$  and  $(\text{U}_{0.6}\text{Pu}_{0.4})\text{O}_{2-x}$ . However, if the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  below  $\text{O}/\text{M} = 1.96$  are compared with those of  $(\text{U}_{0.685}\text{Pu}_{0.270}\text{Am}_{0.045})\text{O}_{2-x}$ ,

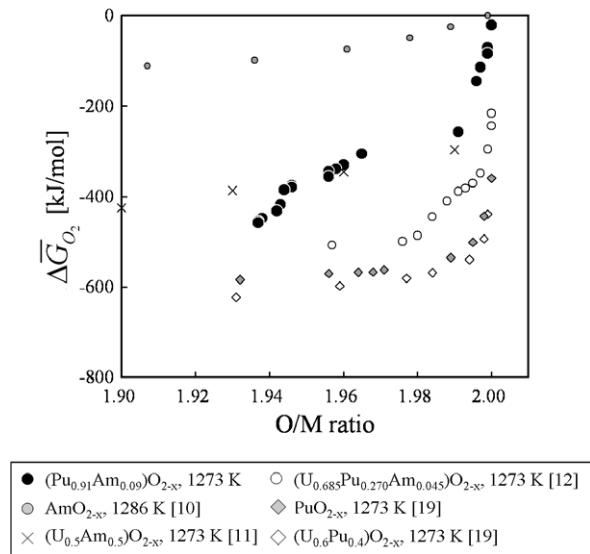


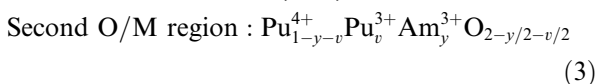
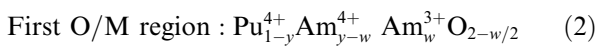
Fig. 2. Comparison of oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  with those of related non-stoichiometric dioxides at or around 1273 K.

$\text{PuO}_{2-x}$  and  $(\text{U}_{0.6}\text{Pu}_{0.4})\text{O}_{2-x}$  near  $\text{O}/\text{M} = 2$ , the differences between them are small. This result can, as discussed in the next section, be interpreted by considering the predominant effect of Pu in this O/M region for  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ .

From the viewpoint of irradiation behavior, use of the present oxide as an alternative for the standard fuel such as  $(\text{U},\text{Pu})\text{O}_{2-x}$  is not suitable unless O/M ratio is low enough to give a comparable oxygen potential to that of  $(\text{U},\text{Pu})\text{O}_{2-x}$ , namely around  $-600$  kJ/mol.

#### 4. Discussion

In this section, aspects of the oxygen potentials for  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  are discussed based on the following assumption: when the O/M ratio decreases from stoichiometry, Am is reduced first from a tetravalent to a trivalent state, then after all the Am is reduced, Pu is similarly reduced. This assumption gives two O/M regions which have different compositions of metal ions, expressed as the following formulae.



Here  $y$  is atomic fraction of Am in  $(\text{Pu},\text{Am})\text{O}_{2-x}$ . For  $y = 0.09$ , the boundary O/M ratio between

the two regions is  $2-y/2 = 1.955$ . Regarding the appropriateness of the above assumption, the following can be considered. Both  $\text{AmO}_{2-x}$  and  $\text{PuO}_{2-x}$  have substoichiometry owing to their varying valence states in the oxide, namely trivalent and tetravalent. Since  $\text{AmO}_{2-x}$  has a much higher oxygen potential than that of  $\text{PuO}_{2-x}$  mainly owing to unstableness of tetravalent Am [13], it can be regarded that tetravalent Am is more easily reduced to trivalent Am than Pu is in the oxide. Actually, the O/M ratio of  $\text{AmO}_{2-x}$  is 1.5, which means all the Am is trivalent, at the oxygen potential of about  $-400$  kJ/mol at 1273 K [13], while the O/M ratio of  $\text{PuO}_{2-x}$  is almost 2 at this oxygen potential, which means all the Pu remains in the tetravalent state.

Aspects of oxygen potentials for  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  as seen in the previous section are discussed individually for each O/M region based on the above assumption. For this purpose, the slope  $n$  of  $\ln(p_{\text{O}_2}^*)$  versus  $\ln(x)$ , oxygen potential as a function of mean valence of metal, activity coefficient of  $\text{AmO}_{2-x}$  in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  and the partial molar enthalpy  $\Delta\bar{H}_{\text{O}_2}$  and entropy  $\Delta\bar{S}_{\text{O}_2}$  of oxygen are evaluated. The slope  $n$  gives information about the predominant defect structure; i.e., what kind of defect structure is predominant in a specific O/M region can be predicted from the slope [20]. Several relationships have been identified between the oxygen potential and the mean valence state of a specific metal. For example, the oxygen potential of  $(\text{U},\text{Pu})\text{O}_{2-x}$  is expressed as a function of a mean Pu valence regardless of Pu content [21]. The mean valence of metal is, thus, a useful index to see effects of the predominant metal which affects the oxygen potential in a specific O/M region. The partial molar enthalpy and entropy can give a variety of information such as temperature dependence of the oxygen potential, defect structure change and so on.

##### 4.1. First O/M region above $\text{O}/\text{M} = 1.955$

Fig. 3 shows the slopes  $n$  of  $\ln(p_{\text{O}_2}^*)$  versus  $\ln(x)$  of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ . The slopes from  $\ln(x) = -8$  to  $-5$  are 3.5 at 1273 K and 3.1 at 1423 K. The slope in this range of  $x$  at 1123 K could not be obtained due to insufficient data points caused by the possible formation of two-phase region, as mentioned in the previous section. In this range of  $x$ , substantial deviation from stoichiometry  $z = 0$  to 0.08 of  $\text{AmO}_{2-z}$  in  $(\text{Pu}_{1-y}\text{Am}_y)\text{O}_{2-x}$  can be obtained by using the relationship  $z = x/y$  according to the

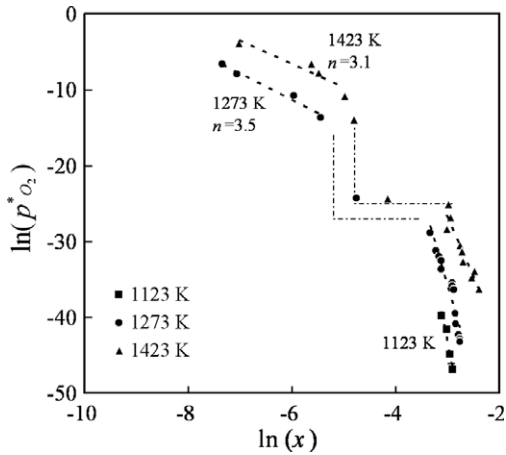


Fig. 3. Slopes of oxygen partial pressure versus deviation from stoichiometry in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ .

assumption. The slopes of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  in this substantial range of  $z$  are almost the same as those of pure  $\text{AmO}_{2-x}$  with  $x = 0$  to 0.08, namely 2.7 at 1286 K and 3.3 at 1397 K [10], when both experimental and analytical related errors are considered. Note that the same slopes are given if substantial deviation from stoichiometry  $z$  of  $\text{AmO}_{2-z}$  in  $(\text{Pu}_{1-y}\text{Am}_y)\text{O}_{2-x}$  (where  $x = yz$ ) is taken as the variable instead of  $x$  for  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ . This relation is expressed as follows:  $\ln(x) = \ln(yz) = C + \ln(z)$  with a constant  $C = \ln(y)$ , which means  $\ln(p_{\text{O}_2}^*) \propto \ln(z)$  with the same slope  $n$  as for the case of  $\ln(p_{\text{O}_2}^*) \propto \ln(x)$ . Thus, it can be considered that the predominant defect structures have not changed significantly in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  from those in  $\text{AmO}_{2-x}$  for this O/M range. Regarding the slope changes of  $\ln(x)$  from  $-5$  to  $-3$ , the slopes are infinity at about  $\ln(x) = -5$  followed by zero until  $\ln(x) = -3$ , at both 1273 K and 1423 K. Although data points at this O/M range are limited and further investigations are needed, this tendency implies formation of a two-phase region, as was seen at 1123 K.

Fig. 4 compares the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  as a function of the mean Am valence at 1273 K and 1423 K with those of roughly corresponding temperatures for  $\text{AmO}_{2-x}$  (1286 K and 1397 K) [10]. The oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  are somewhat smaller than those of  $\text{AmO}_{2-x}$  above the mean Am valence of 3.8 at the roughly corresponding temperatures. This reduction is much smaller than the difference in the oxygen potential of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  from that of

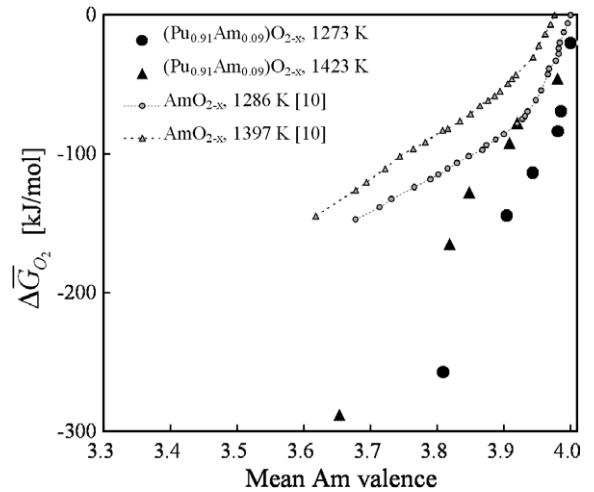
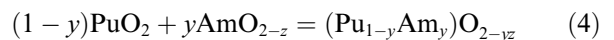


Fig. 4. Oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  and  $\text{AmO}_{2-x}$  as a function of mean Am valence above O/M = 1.955.

$\text{PuO}_{2-x}$  as shown in Fig. 2. From this fact, together with the absence of significant changes in the defect structures, effects of  $\text{AmO}_{2-x}$  on the oxygen potential should predominate in this O/M region, which confirms the appropriateness of the present assumption.

Regarding the reduction of oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  compared with those of  $\text{AmO}_{2-x}$ , since the defect structures have not changed significantly in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  from those in  $\text{AmO}_{2-x}$ , formations of the defects derived from trivalent Am should, as a consequence, be suppressed compared with those in  $\text{AmO}_{2-x}$  at a same oxygen potential. One possible reason for this is suppression of reduction of tetravalent Am to its trivalent state by surrounding tetravalent Pu. In other words, tetravalent Am has been stabilized by surrounding tetravalent Pu. This may be caused by the smaller difference in ionic radii between them, 0.001 nm [22]. Similar effects about Pu were observed for the systems of  $(\text{U},\text{Pu})\text{O}_{2-x}$  and  $(\text{Th},\text{Pu})\text{O}_{2-x}$  [17].

In order to see this stabilization effect quantitatively, activity coefficients of  $\text{AmO}_{2-x}$  in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  are calculated assuming the following chemical reaction.



In this case,  $\text{AmO}_{2-x}$  is a solute that is dissolved into the solvent  $\text{PuO}_2$  to form a pseudo-binary solid solution  $(\text{Pu},\text{Am})\text{O}_{2-x}$ . The activity coefficient of solute is expressed as the following equation [17]:

$$RT \ln \gamma_{\text{AmO}_{2-z}} = \frac{1}{2y} \int_0^{yz} \Delta \overline{G}_{\text{O}_2}[(\text{Pu}, \text{Am})\text{O}_{2-yz}] d(yz) + \frac{1}{2} \int_z^0 \Delta \overline{G}_{\text{O}_2}[\text{AmO}_{2-z}] dz. \quad (5)$$

For  $\Delta \overline{G}_{\text{O}_2}[\text{AmO}_{2-z}]$ , values evaluated by a chemical thermodynamic model are used [23]. The integrals are evaluated by a graphical integration of the presently determined oxygen potentials for  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ .

Fig. 5 compares activity coefficients of  $\text{AmO}_{2-x}$  in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  at 1273 K and 1423 K with those of  $\text{PuO}_{2-x}$  in  $(\text{U}_{0.75}\text{Pu}_{0.25})\text{O}_{2-x}$  and  $(\text{Th}_{0.75}\text{Pu}_{0.25})\text{O}_{2-x}$  at 1273 K [17]. In this case,  $\text{AmO}_{2-x}$  and  $\text{PuO}_{2-x}$  are considered solute species with the solvents of  $\text{PuO}_2$  and  $\text{UO}_2$  or  $\text{ThO}_2$ , and they form pseudo-binary solid solutions of  $(\text{Pu}, \text{Am})\text{O}_{2-x}$  and  $(\text{U}, \text{Pu})\text{O}_{2-x}$  or  $(\text{Th}, \text{Pu})\text{O}_{2-x}$ , respectively. The stabilization effects of tetravalent solutes can be considered larger when the activity coefficients are larger, which also means larger deviation from ideality. It is seen in the figure that the activity coefficients of  $\text{AmO}_{2-x}$  in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  at 1273 K and 1423 K increase rapidly with decrease of the mean Am valence. These trends are similar to those in  $(\text{U}_{0.75}\text{Pu}_{0.25})\text{O}_{2-x}$  and  $(\text{Th}_{0.75}\text{Pu}_{0.25})\text{O}_{2-x}$  [17], which indicates that there are similar stabilization effects for all of them. The activity coefficients of  $\text{AmO}_{2-x}$  in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  are larger than those of  $\text{PuO}_{2-x}$  in both  $(\text{Th}_{0.75}\text{Pu}_{0.25})\text{O}_{2-x}$  and  $(\text{U}_{0.75}\text{Pu}_{0.25})\text{O}_{2-x}$ . There may be complicated reasons for these

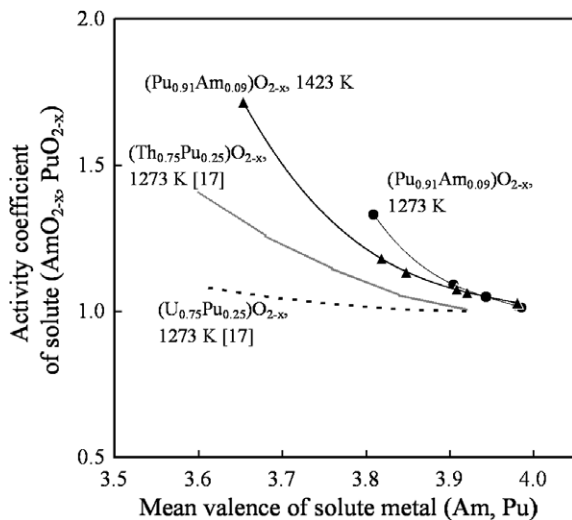


Fig. 5. Activity coefficients of  $\text{AmO}_{2-x}$  and  $\text{PuO}_{2-x}$  in their mixed oxides.

differences in the activity coefficient; e.g., the differences of ionic radii between solute and solvent, stability of tetravalent metals in the solvents and so on.

#### 4.2. Second O/M region below $O/M = 1.955$

In the second O/M region ( $O/M < 1.955$ ), reduction of tetravalent Pu to its trivalent state with the constant valence state of trivalent Am causes decrease of O/M ratio according to the assumption. Hence, the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  in the second O/M region are compared with those of  $\text{PuO}_{2-x}$  as a function of the mean Pu valence, as shown in Fig. 6. The oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  at 1273 K and 1423 K are somewhat higher than those of  $\text{PuO}_{2-x}$  at 1273 K and 1473 K [19,24], respectively. As there are no experimental data for  $\text{PuO}_{2-x}$  at 1423 K, those at 1473 K are used for the comparison. On considering this result along with the fact that  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  oxygen potentials are much lower than those of  $\text{AmO}_{2-x}$  in this O/M region as seen in Fig. 2, it can be said again that the assumption is reasonable. Concerning the small increases of the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  as shown in Fig. 6, it is considered that the oxygen potentials of  $\text{PuO}_{2-x}$  are increased by the addition of trivalent Am in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  as a consequence of interactions

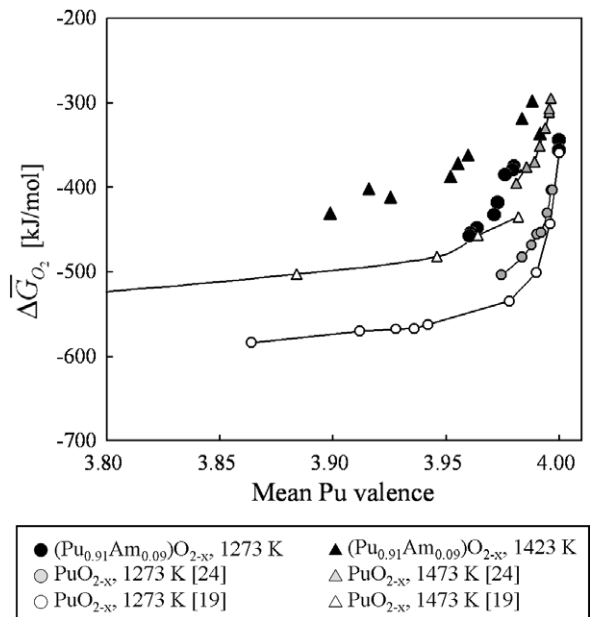


Fig. 6. Oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  and  $\text{PuO}_{2-x}$  as a function of mean Pu valence below  $O/M = 1.955$ .

between tetravalent Pu and trivalent Am. This increment of the oxygen potentials may relate to  $\text{Am}_2\text{O}_3$  effects, whose oxygen potentials are close to those of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  in the second O/M region, i.e., about  $-430$  kJ/mol at 1273 K [13]. Similar effects are seen in  $(\text{U,Pu,Am})\text{O}_{2-x}$  at low O/M ratios, where trivalent Am and tetravalent Pu are the main influences on the oxygen potential [16].

In order to see the aspects of oxygen potential in this O/M region from another viewpoint, the partial molar enthalpy and entropy of oxygen are calculated by using the following thermodynamic relationships:

$$\Delta\bar{H}_{\text{O}_2} = \Delta\bar{G}_{\text{O}_2} + T\Delta\bar{S}_{\text{O}_2}, \quad (6)$$

$$\Delta\bar{S}_{\text{O}_2} = -\frac{\partial\Delta\bar{G}_{\text{O}_2}}{\partial T}. \quad (7)$$

Here  $\Delta\bar{H}_{\text{O}_2}$  and  $\Delta\bar{S}_{\text{O}_2}$  are the partial molar enthalpy and entropy of oxygen, respectively. The oxygen potential values used in these calculations are taken from those calculated from fitting isotherms as shown in Fig. 3. The changes of partial molar enthalpy and entropy of oxygen as a function of the mean Pu valence, together with those of  $\text{PuO}_{2-x}$  [17,24], are shown in Fig. 7. It is seen that both the partial molar enthalpy and entropy of oxygen in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  are larger than those in  $\text{PuO}_{2-x}$ .

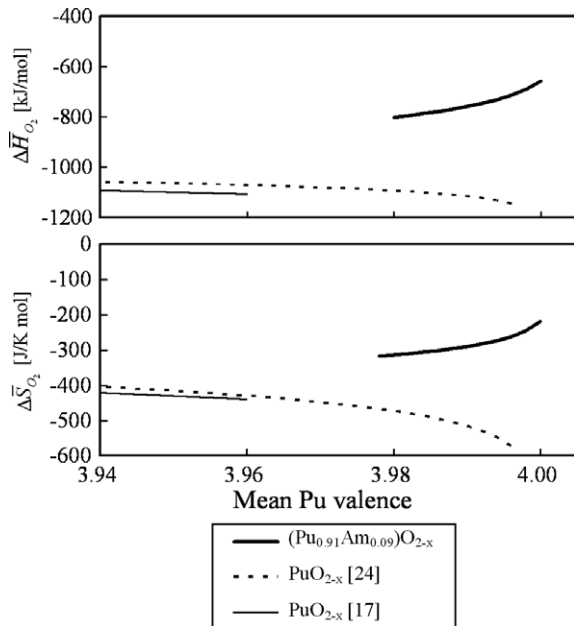


Fig. 7. Partial molar enthalpy and entropy of oxygen for  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  as a function of mean Pu valence below O/M = 1.955.

Such a relation in the partial molar enthalpy and entropy of oxygen at the substoichiometric region between solute and solution, namely  $\text{AmO}_{2-x}$  as a solute and  $(\text{Pu,Am})\text{O}_{2-x}$  as a solution, can be seen in other cases; e.g.,  $\text{PuO}_{2-x}$  as a solute and  $(\text{U,Pu})\text{O}_{2-x}$ , as a solution [25]. It is also seen that differences for both partial molar enthalpy and entropy of oxygen between  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  and  $\text{PuO}_{2-x}$  increase with increase of the mean Pu valence. This may be caused by a different aspect of the defect structure change between  $(\text{Pu,Am})\text{O}_{2-x}$  and  $\text{PuO}_{2-x}$  along with the mean Pu valence.

## 5. Conclusion

Oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  were measured by thermogravimetric analysis with  $\text{H}_2\text{O}/\text{H}_2$  gas equilibrium and dilute  $\text{O}_2$  gas at 1123 K, 1273 K and 1423 K. Experimentally determined data were discussed based on the assumption for valence state changes of Am and Pu in the oxide; i.e., when the O/M ratio decreases from stoichiometry, Am is reduced first from a tetravalent to a trivalent state, then after all Am is reduced, Pu is reduced similarly.

The changes of oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  with O/M ratio showed different aspects according to the O/M ratio and temperature. In particular, oxygen potentials from stoichiometry to O/M = 1.99 were extremely high and almost comparable to those of  $\text{AmO}_{2-x}$  near stoichiometry. However, a small decrease of the oxygen potential of  $\text{AmO}_{2-x}$  in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  was seen, which was attributed to a stabilization effect of tetravalent Am by tetravalent Pu, as an interaction between Pu and Am. Below O/M = 1.955, the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  were higher than those of  $\text{PuO}_{2-x}$ . Comparison of the oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  with  $\text{PuO}_{2-x}$  as a function of the mean Pu valence gave several insights into such behaviors as possible interactions between tetravalent Pu and trivalent Am. This was also supported by the different trend of the partial molar enthalpy and entropy of oxygen as a function of the mean Pu valence between  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  and  $\text{PuO}_{2-x}$ . Finally, it was concluded that aspects of oxygen potentials of  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$  could be interpreted based on the present assumption and that several interactions between Pu and Am, which would have caused the differences of the oxygen potentials of  $\text{PuO}_{2-x}$  and  $\text{AmO}_{2-x}$  from those in  $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$ , could exist.

## Acknowledgements

The authors are grateful to Dr N. Nakae, Mr T. Asaga, Mr K. Tanaka and Mr H. Yoshimochi of Japan Atomic Energy Agency (JAEA) for their encouragement and support of this study. The authors also thank Mr S. Miwa, Mr K. Mondo and Mr Y. Ishi of JAEA, Mr T. Ishida of Nuclear Technology and Engineering Corporation and Mr T. Seki of Inspection Development Corporation for help in the experiments.

## References

- [1] D. Labroche, O. Dugne, C. Chatillon, *J. Nucl. Mater.* 312 (2003) 21.
- [2] T.B. Lindemer, T.M. Besmann, *J. Nucl. Mater.* 130 (1985) 473.
- [3] T.M. Besmann, T.B. Lindemer, *J. Nucl. Mater.* 130 (1985) 489.
- [4] T.B. Lindemer, J. Brynstad, *J. Am. Ceram. Soc.* 69 (1986) 867.
- [5] K. Aizawa, *Prog. Nucl. Energy* 40 (2002) 349.
- [6] N. Chauvin, R.J.M. Konings, H.J. Matzke, *J. Nucl. Mater.* 274 (1999) 105.
- [7] H. Yoshimochi, M. Nemoto, S. Koyama, T. Namekawa, *J. Nucl. Sci. Technol.* 41 (2004) 850.
- [8] M. Osaka, H. Serizawa, M. Kato, et al., in: *Proceedings of the International Conference GLOBAL2005*, October 9–13, 2005, Tsukuba, Japan, Paper No. 240.
- [9] J. Wallenius, *J. Nucl. Mater.* 320 (2003) 142.
- [10] T.D. Chikalla, L. Eyring, *J. Inorg. Nucl. Chem.* 29 (1967) 2281.
- [11] W. Bartscher, C. Sari, *J. Nucl. Mater.* 118 (1983) 220.
- [12] M. Osaka, I. Sato, T. Namekawa, K. Kurosaki, S. Yamanaka, *J. Alloys Comp.* 397 (2005) 110.
- [13] S. Casalta, H.J. Matzke, C. Prunier, *Proceedings of the International Conference GLOBAL95*, September 11–14, 1995, Versailles, France.
- [14] K. Mayer, B. Kanellakopoulos, J. Naegele, L. Koch, *J. Alloys Comp.* 213/214 (1994) 456.
- [15] M. Osaka, S. Miwa, H. Yoshimochi, K. Tanaka, K. Kurosaki, S. Yamanaka, *Int. Conf. ACTINIDES2005*, July 4–8, 2005, Manchester, UK.
- [16] M. Osaka, K. Kurosaki, S. Yamanak, *J. Alloys Comp.*, in press.
- [17] R.E. Woodley, *J. Nucl. Mater.* 96 (1981) 5.
- [18] L. Donnet, F. Jorion, N. Drin, S.L. Hayes, J.R. Kennedy, K. Pasamehmetoglu, S.L. Voit, D. Haas, A. Fernandez, in: *Proceedings of the International Conference GLOBAL2005*, October 9–13, 2005, Tsukuba, Japan, Paper No. 258.A.
- [19] R.E. Woodley, HEDL-SA-1830, Hanford Engineering Development Laboratory report, 1979.
- [20] O.T. Sorensen, *Thermodynamics and defect structure of nonstoichiometric oxides*, in: *Nonstoichiometric Oxides*, Academic Press Inc, New York, 1981, p. 1.
- [21] M.H. Rand, T.L. Markin, in: *Proceedings of the Symposium on Thermodynamics of Nuclear Materials 1967*, International Atomic Energy Agency, Vienna, Austria, 1967, p. 637.
- [22] R.D. Shannon, C.T. Prewitt, *Acta Cryst.* B25 (1968) 925.
- [23] C. Thiriet, R.J.M. Konings, *J. Nucl. Mater.* 320 (2003) 292.
- [24] G.C. Swanson, LA-6083-T, Los Alamos National Laboratory report, 1975.
- [25] K. Une, M. Oguma, *J. Nucl. Mater.* 118 (1983) 189.