

Thermodynamic modelling of the (U, Pu, Np)O_{2±x} mixed oxide

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Abstract

To assess the phase stability of actinide oxides with a fluorite structure which has a variable composition (MO_{2±x}), thermodynamic modelling has been performed for O–Pu–U–Np quaternary systems on the basis of thermodynamic data available in the literature. Using the thermodynamic data for O–Pu, O–U and O–Np binary systems obtainable in the literature, the thermodynamic modelling for O–Pu–U–Np quaternary system was carried out by a means of CAL-culation of PHase Diagram (CALPHAD) technique. Using this model, the oxygen potentials for (Pu_{0.3}U_{0.7})O₂, (Pu_{0.3}U_{0.65}Np_{0.05})O₂ and (Pu_{0.3}U_{0.58}Np_{0.12})O₂ were calculated between 1123 K and 1973 K and compared with the experimental data. Interaction parameters required for calculation of the Gibbs free energy of the solid solution phase were estimated for O–Pu–U–Np system.

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1. Introduction

In order to meet the requirements for future nuclear systems, a fast breeder reactor (FBR) development requires a transuranium (TRU) recycling system. Utilization of plutonium as a mixed oxide (MOX: PuO₂ + UO₂) fuel would be the current most practical answer to the subject. Plutonium is formed by a neutron capture in ²³⁸U during irradiation of UO₂ in nuclear power plants. It is well known that the plutonium can

be efficiently recovered from the spent nuclear fuel in the present commercial PUREX installations. Such recovered plutonium would be reused more efficiently as a metallic fuel in the fast reactors, combining with the pyro-processing for the plutonium separation [1,2]. Therefore, there is a great possibility that plutonium plays an important role as an energy resource. However, since the fast reactor program is stopped, plutonium recovering is one of the most urgent issues at the world level for nonproliferation [3]. In the present circumstance, although Japan Nuclear Cycle Development Institute (JNC) and some groups are further developing such recycling systems in Japan, MOX fuel, particularly containing minor actinides (MA) is one of the most feasible candidates for advanced nuclear fuel recycle. JNC

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is especially planning utilization of the plutonium–uranium–neptunium MOX fuel [4].

When developing such MOX fuel containing Np, basic physical properties and sintering conditions are very important to fix for fuel design and fabrication. Although there are few informations on MOX fuel containing minor actinides, there is one report on the lattice parameter of the fluorite phase in the O–Pu–U–Np system. A lattice parameter of (U_{0.75}, Pu_{0.23}, Np_{0.02})O₂ equal to 5.4563 Å is reported in [5]. This means that the (Pu, U, Np)O_{2±x} oxide is stable with the fluorite structure. No data are available on the extent of the hyper- and hypo-stoichiometric regions in oxygen.

In the present study, thermodynamic modelling has been carried out for the O–Pu–U–Np quaternary system. In order to obtain the O–Pu–U–Np phase diagram and associated thermodynamic data, as a preliminary stage, the interaction parameters of the excess Gibbs energies of the fluorite structure FCC_C1 phase were evaluated with respect to the deviation from the ideal solution in oxygen potential. The thermodynamic modelling used in this study is based on the CALculation of PHase Diagram (CALPHAD) technique [6]. This technique enables to predict both phase behavior and thermodynamic properties in highly complex multi-component systems based on the Gibbs energy of the components. This technique has been successfully applied for such systems as O–Pu–Zr [7] and O–U–Zr [8].

2. Thermodynamic modelling

Thermodynamic modelling was performed by using the program Thermo-Calc [9]. The quantity stored in

the database for the calculation is the Gibbs energy of formation for phases, $(G - H^{\text{SER}})$ (J/mol) expressed as

$$G - H^{\text{SER}} = a + bT + cT \log_e T + dT^2 + eT^3 + fT^{-1} + \dots, \quad (1)$$

where a, b, c, d, e and f are constants. T is temperature in Kelvin. SER indicates ‘stable element reference’. It corresponds to the enthalpy of the pure elements in its stable state at $T = 298.15$ K and 1 bar. In the present calculation, Eq. (1) was applied to the pure substances and stoichiometric compounds.

Gibbs energy of a solid solution is defined as the sum of several terms:

$$G = G^{\text{ref}} + G^{\text{id}} + G^{\text{xs}}. \quad (2)$$

G^{ref} is the contribution of pure components, G^{id} is the ideal mixing contribution, known as ideal entropy of mixing, and G^{xs} is the contribution due to nonideal interactions between the components, also known as excess Gibbs free energy of mixing. G^{ref} , G^{id} and G^{xs} are generally expressed, respectively, as

$$G^{\text{ref}} = \sum_i (x_i G_i^0), \quad (3)$$

$$G^{\text{id}} = RT \sum_i (x_i \log_e x_i), \quad (4)$$

$$G^{\text{xs}} = \sum_i \sum_{j>i} x_i x_j \left\{ L_{ij}^0 + L_{ij}^1 (x_i - x_j) + L_{ij}^2 (x_i - x_j)^2 + \dots \right\}, \quad (5)$$

where x_i is the mole fraction of component ‘ i ’ and G_i^0 is the Gibbs free energy of the pure component ‘ i ’. The L_{ij}^n are interaction parameters derived from Redlich–Kister’s polynomial expression [10].

Table 1

Interactions between components which must be taken into consideration for fluorite structure (FCC_C1) phase of O–Pu–U–Np quaternary system

System	Sublattice model for FCC_C1 phase	Interaction between components which must be taken into consideration
O–Pu–U–Np	(Pu, U, Np, VA) ₁ (O, VA) ₂	(Pu) ₁ (O) ₂ –(Pu) ₁ (VA) ₂ (U) ₁ (O) ₂ –(U) ₁ (VA) ₂ (Np) ₁ (O) ₂ –(Np) ₁ (VA) ₂ (VA) ₁ (O) ₂ –(VA) ₁ (VA) ₂ (Pu) ₁ (O) ₂ –(U) ₁ (O) ₂ (Pu) ₁ (O) ₂ –(Np) ₁ (O) ₂ (Pu) ₁ (O) ₂ –(VA) ₁ (O) ₂ (U) ₁ (O) ₂ –(Np) ₁ (O) ₂ (U) ₁ (O) ₂ –(VA) ₁ (O) ₂ (Np) ₁ (O) ₂ –(VA) ₁ (O) ₂ (Pu) ₁ (VA) ₂ –(U) ₁ (VA) ₂ (Pu) ₁ (VA) ₂ –(Np) ₁ (VA) ₂ (Pu) ₁ (VA) ₂ –(VA) ₁ (VA) ₂ (U) ₁ (VA) ₂ –(Np) ₁ (VA) ₂ (U) ₁ (VA) ₂ –(VA) ₁ (VA) ₂ (Np) ₁ (VA) ₂ –(VA) ₁ (VA) ₂

Table 2

Gibbs energy parameters for fluorite structure (FCC_C1) phase of O–Pu–U–Np quaternary system used in the present modelling: the hatched six interaction parameters have been determined in the present study to evaluate the system

Gibbs energy functions	Parameters (J/mol)	Temperature range (K)	Reference
G_{PuO_2}	$= -1087288.7 + 505.66828T - 83.319199T \ln T - 5.8418 \times 10^{-3}T^2 - 2.2924167 \times 10^{-11}T^3 + 913505T^{-1}$	298 < T < 4000	[13]
G_{PuVA_2}	$= +42603.691 + 80.301382T - 18.1258T \ln T$ $= -0.02241T^2 + 33394.038 + 236.786603T - 42.4187T \ln T$ $= -0.00134493T^2 + 2.63443 \times 10^{-7}T^3 + 579325T^{-1} + 35537.844$ $+ 232.961553T - 42.248T \ln T$	298 < T < 400 400 < T < 944 944 < T < 4000	
G_{UO_2}	$= -1112055.29 + 433.851907T - 74.6514T \ln T - 0.00610305T^2$ $= +1.7213 \times 10^{-7}T^3 + 649010T^{-1} - 1707426.87 + 4369.94495T$ $- 604.679T \ln T$ $= +0.205276T^2 - 1.58314833 \times 10^{-5}T^3 + 126580500T^{-1} - 1303255.56$ $+ 1218.63701T - 167.038T \ln T$	289 < T < 1500 1500 < T < 2670 2670 < T < 4000	
G_{UVA_2}	$= +41592.266 + 130.955151T - 26.9182T \ln T + 0.00125156T^2$ $= -4.426050 \times 10^{-6}T^3 + 38568T^{-1} + 27478.2 + 292.121093T - 48.66T \ln T$	298 < T < 955 955 < T < 4000	
G_{NpO_2}	$= -1059069.6 + 469.04396T - 80.332802T \ln T - 0.0033890400T^2$ $+ 828430.00T^{-1}$	298 < T < 4000	[12]
G_{NpVA_2}	$= +50241.888 - 57.531347T + 4.0543T \ln T - 0.04127725T^2 - 402857T^{-1}$ $= -7015.112 + 664.27337T - 102.523T \ln T + 0.0284592T^2$ $- 2.483917 \times 10^{-6}T^3 + 4796910T^{-1}$ $= +37907.264 + 255.780866T - 45.3964T \ln T$	289 < T < 553 553 < T < 1799 1799 < T < 4000	
G_{VAO_2}	$= +93038.3 - 51.0061T - 22.2720T \ln T - 0.0101978T^2$ $+ 1.32369 \times 10^{-6}T^3 - 76730.0T^{-1}$ $= +86862.5 + 25.3198T - 33.6276T \ln T - 0.0011916T^2$ $+ 1.35620 \times 10^{-8}T^3 + 525810T^{-1}$ $= +72026.5 + 62.5193T - 37.9072T \ln T - 0.000850486T^2$ $+ 2.14420 \times 10^{-8}T^3 + 8766400T^{-1}$	298 < T < 1000 1000 < T < 3300 3300 < T < 4000	[13]
G_{VAVA_2}	$= +0$	298 < T < 4000	
$L_{\text{Pu:O,VA}}^0$	$= +90000 + 68T$	298 < T < 4000	
$L_{\text{Pu:O,VA}}^1$	$= -935000 - 196T$	298 < T < 4000	
$L_{\text{Pu:O,VA}}^2$	$= +787200$	298 < T < 4000	
$L_{\text{U:O,VA}}^0$	$= +88353.17 - 32.37686T$	298 < T < 4000	
$L_{\text{U:O,VA}}^1$	$= +42858.36$	298 < T < 4000	
$L_{\text{Np:O,VA}}^0$	$= +12498.8561 + 681.601745T$	298 < T < 4000	[12]
$L_{\text{Np:O,VA}}^1$	$= -17301.578 - 749.30885T$	298 < T < 4000	
$L_{\text{VA:O,VA}}^0$	$= +0$	298 < T < 4000	[13]
$L_{\text{Pu,U:O}}^0$	$= +0$	298 < T < 4000	
$L_{\text{Pu,Np:O}}^0$	$= +0$	298 < T < 4000	Present study
$L_{\text{Pu,VA:O}}^0$	$= -205000$	298 < T < 4000	[13]
$L_{\text{Pu,VA:O}}^1$	$= +0$	298 < T < 4000	
$L_{\text{Pu,VA:O}}^2$	$= +600000$	298 < T < 4000	
$L_{\text{U,Np:O}}^0$	$= +0$	298 < T < 4000	Present study
$L_{\text{U,VA:O}}^0$	$= +184216.70 + 135.94271T$	298 < T < 4000	[13]
$L_{\text{U,VA:O}}^1$	$= -1422742.46$	298 < T < 4000	
$L_{\text{U,VA:O}}^2$	$= +782551.16$	298 < T < 4000	
$L_{\text{Np,VA:O}}^0$	$= +0$	298 < T < 4000	Present study
$L_{\text{Pu,U:VA}}^0$	$= -340000$	298 < T < 4000	[13]
$L_{\text{Pu,U:VA}}^1$	$= +1189000$	298 < T < 4000	
$L_{\text{Pu,U:VA}}^2$	$= -1500000$	298 < T < 4000	
$L_{\text{Pu,Np:VA}}^0$	$= +0$	298 < T < 4000	Present study
$L_{\text{Pu,VA:VA}}^0$	$= +0$	298 < T < 4000	[13]
$L_{\text{U,Np:VA}}^0$	$= +0$	298 < T < 4000	Present study
$L_{\text{U,VA:VA}}^0$	$= +0$	298 < T < 4000	[13]
$L_{\text{Np,VA:VA}}^0$	$= +0$	298 < T < 4000	Present study

When atoms are sufficiently different in size, electro-negativity or charge, they may prefer different types of sites in a lattice. In the present study, such a preferential occupancy of the atoms in the lattice was treated by a general multi-sublattice model proposed by Sundman and Agren [11]. For example, in a simple case of a phase with a formula $(A)_1(B,C)_2$, the reference (G^{ref}), ideal (G^{id}) and excess (G^{xs}) Gibbs free energies are expressed as

$$G^{\text{ref}} = y_A^1 y_B^2 G_{AB}^0 + y_A^1 y_C^2 G_{AC}^0, \quad (6)$$

$$G^{\text{id}} = RT \{ N^2 (y_B^1 \log_e y_B^2 + y_C^2 \log_e y_C^2) \}, \quad (7)$$

$$G^{\text{xs}} = y_A^1 y_B^2 y_C^2 \left\{ L_{A:B,C}^0 + L_{A:B,C}^1 (y_B^1 - y_C^1) + L_{A:B,C}^2 (y_B^1 - y_C^1)^2 + \dots \right\}, \quad (8)$$

where y_i^s represents the site fraction of component 'i' on sublattice 's' and N^s is the total number of the site on the sublattice 's'.

3. Results and discussion

The thermodynamic modelling of the O–Pu–U–Np system was based on the data for O–Pu [7], O–U [8] and O–Np [12] binary systems.

The sublattice model used for fluorite structure (FCC_C1) phase of O–Pu–U–Np quaternary system is expressed with a formula $(\text{Pu}, \text{U}, \text{Np}, \text{VA})_1(\text{O}, \text{VA})_2$ in which VA denotes vacancy. In this system, we need to take into account nonideal interactions between the components listed in Table 1 and have to determine the interaction parameters of the excess Gibbs energies for the hatched six interactions in addition to the parameters for the O–Pu–U ternary system which have already been evaluated in our previous works [7,13]. These additional interaction parameters have been determined by an optimization using the experimentally determined oxygen potentials of Np containing MOX fuel in literature. In a first step, the modelling was performed by assuming all the additional interaction parameters for the fluorite structure phase to be 0 as shown in Table 2. Using this model, the oxygen potentials for $(\text{Pu}_{0.3}\text{U}_{0.7})\text{O}_2$, $(\text{Pu}_{0.3}\text{U}_{0.65}\text{Np}_{0.05})\text{O}_2$ and $(\text{Pu}_{0.3}\text{U}_{0.58}\text{Np}_{0.12})\text{O}_2$ were calculated between 1123 K and 1973 K in comparison with the experimental data available in [4]. In Fig. 1(a)–(c), the calculated oxygen potentials in the fluorite structure phase in the hyper- and hypo-stoichiometric region are composed with the experimental data. It can be seen that the calculated oxygen potential decreases in the hypo-stoichiometric side and increases in hyper-stoichiometric side according to an increase of Np content. Although such a tendency is not seen between each experimental value, similar trend may be seen if the number of the data is increased. However, each oxygen potential calculated using the interaction

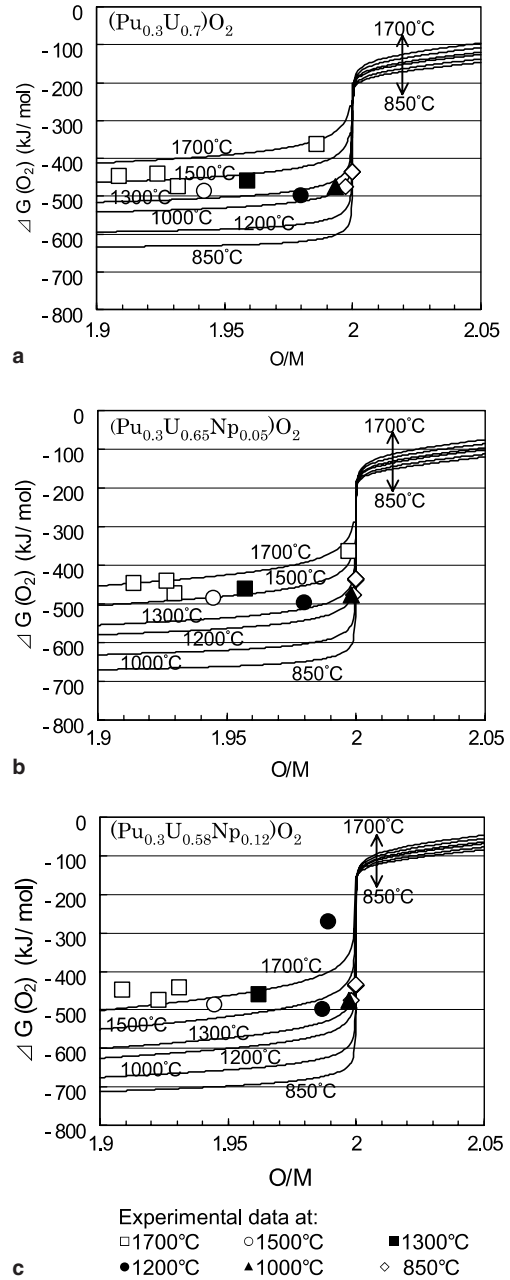


Fig. 1. Oxygen potential of fluorite structure phase in the O–Pu–U–Np quaternary phase in hyper- and hypo-stoichiometric region: (a) $(\text{Pu}_{0.3}\text{U}_{0.7})\text{O}_2$, (b) $(\text{Pu}_{0.3}\text{U}_{0.65}\text{Np}_{0.05})\text{O}_2$ and (c) $(\text{Pu}_{0.3}\text{U}_{0.58}\text{Np}_{0.12})\text{O}_2$ in comparison with experimental data [4].

parameters in Table 2 shows a relatively good agreement with the experimental ones at any temperatures without newly determining the interaction parameters. In our previous modelling for O–Pu–U ternary system [13], the oxygen potential calculated before optimizations of additional interaction parameters is quite different from

experimental one. Judging from these results, it seems that it is not necessary to optimize the new interaction parameters concerned with Np, at least, in the range of Np content calculated in this study, even if Np is newly added to the O–Pu–U ternary system, that is, the influence of existence of Np in the O–Pu–U–Np quaternary system is very small in the present work.

4. Conclusion

For the nonstoichiometric fluorite structure phase of the O–Pu–U–Np quaternary system, the thermodynamic modelling was presented. The interaction parameters of the excess Gibbs energies have been assessed and the oxygen potentials were calculated by using the evaluated parameters. The oxygen potentials both in hyper- and hypo-stoichiometric region were calculated for $(\text{Pu}_{0.3}\text{U}_{0.7})\text{O}_2$, $(\text{Pu}_{0.3}\text{U}_{0.65}\text{Np}_{0.05})\text{O}_2$ and $(\text{Pu}_{0.3}\text{U}_{0.58}\text{Np}_{0.12})\text{O}_2$ between 1123 K and 1973 K. The calculated oxygen potentials were compared with the experimental data available in the literature. Although the interaction parameters with respect to Np have been treated as 0 in this study, the computed values showed a relatively good agreement with the experimental ones. Consequently, it was found that the influence of existence of Np in the O–Pu–U–Np quaternary system is very small, at least, in

the range of Np content examined by the current study.

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