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ScienceDirect

Journal of Nuclear Materials 373 (2008) 39–43

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Calorimetric determination of energetics of solid solutions of UO_{2+x} with CaO and Y_2O_3

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Received 30 January 2007; accepted 26 March 2007

Abstract

Quantitative study of thermodynamic properties of solid solutions of UO_{2+x} with divalent and trivalent oxides is important for predicting the behavior of oxide fuel. Although early literature work measured vapor pressure in some of these solid solutions, direct calorimetric measurements of enthalpies of formation have been hampered by the refractory nature of such oxides. First measurements of the enthalpies of formation in the systems UO_{2+x}–CaO and UO_{2+x}–$YO_{1.5}$, obtained by high-temperature oxide melt solution calorimetry, are reported. Both systems show significantly negative (exothermic) heats of formation from binary oxides (UO_2, plus O_2 and CaO or $YO_{1.5}$, as well as from UO_2 plus UO_3 and CaO or $YO_{1.5}$), consistent with reported free energy measurements in the urania–yttria system. The energetic contributions of oxygen content (oxidation of U^{4+}) and of charge balanced ionic substitution as well as defect clustering are discussed. Behavior of urania–yttria is compared to that of corresponding systems in which the tetravalent ion is Ce, Zr, or Hf. The substantial additional stability in the solid solutions compared to pure UO_{2+x} may retard, in both thermodynamic and kinetic sense, the oxidation and leaching of spent fuel to form aqueous U^{6+} and solid uranyl phases.

1. Introduction

Doping urania, UO_2, with different di- [1,2], tri- [3–8] and tetravalent [9–11] metals has attracted interest primarily in the context of improving the performance and stability of UO_2 in nuclear applications [5,12] and in reactor accident scenarios. More than 30 different elements are produced by fission during the lifetime of fuel rods. These largely remain within the UO_2 matrix and influence its physical and chemical properties. Understanding the systematics of defect chemistry in doped fluorite structures and energetics of these materials in a variety of systems forms the microscopic basis for tailoring materials with optimized properties. Recent calorimetric studies in this laboratory of other fluorite-structured systems such as yttria-doped zirconia, hafnia and ceria based systems [13–17] provide such understanding, and the urania-based systems are also of interest in further developing systematics in terms of defect chemistry.

Direct calorimetric measurements of enthalpies of formation have been hampered by the refractory nature of such oxides. Thermodynamic investigations of UO_{2+x}-based solid solutions were restricted to obtaining partial molar free energies as a function of concentration of the dopant by measuring oxygen potential [18,19] or by measuring vapor pressure [20]. Though these methods provide useful free energy data, their deconvolution into enthalpy and entropy terms is more uncertain. We present the first direct measurements by high-temperature oxide melt solution calorimetry of the enthalpy of formation in the systems UO_{2+x}–CaO and UO_{2+x}–$YO_{1.5}$.

2. Experimental methods

Synthesis, characterization, structure and lattice parameters of the UO_{2+x}–CaO and UO_{2+x}–$YO_{1.5}$ samples were

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doi:10.1016/j.jnucmat.2007.03.269

described in previous work [1]. Chemical compositions of pelletized samples were analyzed prior to calorimetry by microprobe analysis using a Cameca SX 100 instrument operated at 15 kV with 10 nA probe current. O Kα, Ca Kα, U Mα and Y Lα lines were used for analysis using PC2, LPET and TAP analytical crystals, and UO_2, $CaMoO_4$, $CaWO_4$ and synthetic garnet $Y_3Al_5O_{12}$ as primary standards. Content of U^{4+} and U^{6+} was recalculated from the total oxygen content.

For the determination of enthalpies of formation, a custom-built Tian–Calvet high-temperature microcalorimeter was used [21,22]. Pellets were dropped into a Pt crucible containing a melt of composition $3Na_2O \cdot 4MoO_3$ at 703 °C. The reaction tube was flushed (40 ml/min) and the solvent was bubbled (5–7 ml/min) by oxygen to provide stirring, prevent local saturation, speed the dissolution, and maintain an oxidizing atmosphere. The methodology is similar to that used previously for uranium containing pyrochlore [23]. Under these conditions, all uranium is reproducibly oxidized to the hexavalent state (equivalent to dissolved UO_3) in the sodium molybdate solvent [23].

3. Results

Microprobe analysis (Table 1) shows that UO_2 in the samples is partially oxidized. Solid solution compositions show oxygen contents higher than two moles of oxygen per mole of cations for lower dopant concentrations, but show oxygen deficiency at higher dopant concentrations ($Ca/(Ca+U) = 0.35$ and $Y/(Y+U) = 0.66$). Rietveld analysis of the powder X-ray diffraction data showed that all samples have the cubic fluorite structure [1]. Results of high-temperature oxide melt solution calorimetry are given in Table 2. Reference data and calorimetric cycles for calculation of enthalpies of formations are given in Table 3.

For solid solutions formed from constituent oxides (according to analyzed stoichiometry) no oxidation involved, the formation reaction is:

$$mUO_2 + nUO_3 + (1-m-n) \cdot MO_z = U_{m+n}M_{1-m-n}O_{2m+3n+(1-m-n)z}. \quad (1)$$

All heats of formation according to reaction (1) are significantly exothermic (Table 2 and Fig. 1(a)) and become more exothermic with increasing doping for the samples studied. Despite varying oxygen contents, the values in the yttria-doped system (where enough samples were available) fall on a smooth trend. Indeed the most energetically stable solid solutions are those with negative values of x in $U_{1-y}M_yO_{2+x}$, namely solid solutions with calcium concentration equal to 0.35 and yttrium concentration equal to 0.66, corresponding to an oxygen vacancy, rather than an oxygen interstitial, regime.

We also report enthalpies of formation relative to UO_2, O_2 and CaO or $YO_{1.5}$. Thus, for solid solutions formed from UO_2, CaO or $YO_{1.5}$, plus O_2:

$$(m+n) \cdot UO_2 + 0.5n \cdot O_2 + (1-m-n) \cdot MO_z = U_{m+n}M_{1-m-n}O_{2m+3n+(1-m-n)z}. \quad (2)$$

The enthalpies of formation (Table 2) are more exothermic for reaction (2) than for reaction (1) as a direct consequence of the exothermic oxidation enthalpy of UO_2 to UO_3.

The enthalpies of formation from the elements are given by

$$(m+n) \cdot U + 0.5 \cdot \{2m + 3n + z(1-m-n)\} \cdot O_2 + (1-m-n) \cdot M = U_{m+n}M_{1-m-n}O_{2m+3n+(1-m-n)z}. \quad (3)$$

Their values (Table 2) are recommended as standard enthalpies of formation for the given stoichiometry (metal ratio and oxygen content).

Table 1
Results of microprobe analysis, wt%

	O	U	M	Total	Formula
UO_2–CaO	13.6 ± 0.4(10)[a]	84.9 ± 1.2(10)	2.5 ± 0.7(10)	100.93 ± 0.04(10)	$U_{0.861\pm0.006}Ca_{0.14\pm0.02}O_{2.05\pm0.04}$ or $(UO_2)_{0.67\pm0.02}(UO_3)_{0.19\pm0.02}(CaO)_{0.14\pm0.02}$ or $(UO_{2.22})_{0.861\pm0.0062}(CaO)_{0.14\pm0.02}$
	15.7 ± 1.1(15)	79.2 ± 1.0(15)	7.1 ± 0.6(15)	102.1 ± 1.0(15)	$U_{0.651\pm0.008}Ca_{0.349\pm0.008}\ O_{1.92\pm0.05}$ or $(UO_2)_{0.38}(UO_3)_{0.27}(CaO)_{0.35}$ or $(UO_{2.42})_{0.65\pm0.01}(CaO)_{0.35\pm0.01}$
UO_2–$YO_{1.5}$	16.5 ± 0.8(10)	46.9 ± 4.0(10)	34.6 ± 3.6(10)	97.4 ± 1.1(10)	$U_{0.34\pm0.03}Y_{0.66\pm0.07}\ O_{1.78\pm0.08}$ or $(UO_2)_{0.23}(UO_3)_{0.11}(YO_{1.5})_{0.66}$ or $(UO_{2.32})_{0.34\pm0.03}(YO_{1.5})_{0.66\pm0.07}$
	16.9 ± 1.3(10)	60.6 ± 1.5 (10)	22.2 ± 0.6(10)	99.8 ± 0.9(10)	$U_{0.50\pm0.01}Y_{0.50\pm0.01}O_{2.10\pm0.01}$ or $(UO_2)_{0.15}(UO_3)_{0.35}(YO_{1.5})_{0.50}$ or $(UO_{2.70})_{0.50\pm0.02}(YO_{1.5})_{0.50\pm0.01}$
	15.3 ± 1.7(12)	72.3 ± 2.5(12)	12.5 ± 1.4(12)	100.1 ± 0.8(10)	$U_{0.68\pm0.02}Y_{0.32\pm0.04}O_{2.13\pm0.07}$ or $(UO_2)_{0.39}(UO_3)_{0.29}(YO_{1.5})_{0.32}$ or $(UO_{2.43})_{0.68\pm0.03}(YO_{1.5})_{0.32\pm0.04}$

[a] Number in brackets reflects the number of measurements.

Table 2
Enthalpies of drop solution (into sodium molybdate, $3Na_2O \cdot 4MoO_3$) at 703 °C and enthalpy of formation of solid solutions from oxides and from elements

	Enthalpy of drop solution	$\Delta H^0_{f\,ox}$, reaction (1)	$\Delta H^0_{f\,ox}$, reaction (2)	ΔH^0_f, reaction (3)
$(UO_2)_{0.67}(UO_3)_{0.19}(CaO)_{0.14}$	−99.5 ± 1.4 (8)	−2.8 ± 2.5	−28.4 ± 2.4	−1051.1 ± 3.0
$(UO_2)_{0.38}(UO_3)_{0.27}(CaO)_{0.35}$	−26.3 ± 1.1 (9)	−54.7 ± 2.2	−91.1 ± 2.4	−1019.6 ± 2.4
$(UO_2)_{0.23}(UO_3)_{0.11}(YO_{1.5})_{0.66}$	−4.5 ± 1.9 (12)	−66.7 ± 2.5	−80.5 ± 2.5	−1078.9 ± 3.2
$(UO_2)_{0.15}(UO_3)_{0.35}(YO_{1.5})_{0.50}$	−15.2 ± 1.3 (9)	−32.1 ± 2.2	−79.4 ± 2.2	−1099.8 ± 2.7
$(UO_2)_{0.39}(UO_3)_{0.29}(YO_{1.5})_{0.32}$	−55.3 ± 1.2 (9)	−14.5 ± 3.2	−53.7 ± 3.3	−1097.5 ± 3.6

All data are in kJ/mol.

Table 3
Thermodynamic cycle, heat of the reactions and calculated enthalpies of formation from oxides

Reaction	Enthalpy of the reaction (kJ/mol)
$(UO_2)_m(UO_3)_n(MO_z)_{1-m-n,\,xl\,25\,°C} + 0.5m \cdot O_{2\,g,\,703\,°C} = (m+n)UO_{3\,sln,\,703\,°C} + (1-m-n) \cdot MO_{z\,sln,\,703\,°C}$	$\Delta H_1 = \Delta H_{ds[(UO_2)x(UO_3)y(MO_z)1-x-y]}$
$MO_{z\,xl,\,25\,°C} = MO_{z,\,sln,\,703\,°C}$	$\Delta H_2 = \Delta H_{ds(MO_z)} = -90.7 \pm 1.7(CaO)$ [23] $\Delta H_2 = \Delta H_{ds(MO_z)} = -60.4 \pm 0.9(YO_{1.5})$ [16]
$UO_{2\,xl,\,25\,°C} + 0.5 \cdot O_{2\,g,\,703\,°C} = UO_{3\,sln,\,703\,°C}$	$\Delta H_3 = \Delta H_{ds(UO_2)} = -136.4 \pm 2.3$ [23]
$UO_{3\,xl,\,25\,°C} = UO_{3\,sln,\,703\,°C}$	$\Delta H_4 = \Delta H_{ds(UO_3)} = 9.5 \pm 1.5$ [23]
$O_{2\,g,\,25\,°C} = O_{2\,g,\,703\,°C}$	$\Delta H_5 =$ Heat content $= 21.8$ [30]
$UO_{2\,xl,\,25\,°C} + 0.5 \cdot O_{2\,g,\,25\,°C} = UO_{3\,xl,\,25\,°C}$	$\Delta H_6 = \Delta H_{oxidation,\,25\,°C} = -138.9 \pm 1.3$ [30]
$mUO_{2\,xl,\,25\,°C} + nUO_{3\,xl,\,25\,°C} + (1-m-n) \cdot MO_{z\,xl,\,25\,°C} = (UO_2)_m(UO_3)_n(MO_z)_{1-m-n,\,xl,\,25\,°C}$	$\Delta H_7 = \Delta H^0_{f\,ox}$
$(m+n) \cdot UO_2 + 0.5n \cdot O_2 + (1-m-n) \cdot MO_{z\,xl,\,25\,°C} = (UO_2)_m(UO_3)_n(MO_z)_{1-m-n,\,xl,\,25\,°C}$	$\Delta H_8 = \Delta H^0_{f\,ox+oxygen}$
$M_{xl,\,25\,°C} + 0.5O_{2\,xl,\,25\,°C} = MO_{z\,xl,\,25\,°C}$	$\Delta H_9 = \Delta H^0_{f(MO_z)} = -635.1 \pm 0.9$ [30] (CaO) $\Delta H_9 = \Delta H^0_{f(MO_z)} = -953.2 \pm 2.1$ [31] $(YO_{1.5})$
$U_{xl,\,25\,°C} + O_{2\,xl,\,25\,°C} = UO_{2\,xl,\,25\,°C}$	$\Delta H_{10} = \Delta H^0_{f(UO_2)} = -1084.9 \pm 1.0$ [30]
$U_{xl,\,25\,°C} + 1.5O_{2\,xl,\,25\,°C} = UO_{3\,xl,\,25\,°C}$	$\Delta H_{11} = \Delta H^0_{f(UO_3)} = -1223.8$ [32]
$(m+n) \cdot U + 0.5 \cdot \{2m + 3n + z(1-m-n)\} \cdot O_2 + (1-m-n) \cdot M = (UO_2)_m(UO_3)_n(MO_z)_{1-m-n,\,xl,\,25\,°C}$	$\Delta H_{12} = \Delta H^0_{f,el}$
$\Delta H_7 = \Delta H^0_{f\,ox} = -\Delta H_1 + (1-m-n) \cdot \Delta H_2 + m \cdot \Delta H_3 + n \cdot \Delta H_4$	
$\Delta H_8 = \Delta H^0_{f\,ox+oxygen} = -\Delta H_1 + (1-m-n) \cdot \Delta H_2 + (m+n) \cdot \Delta H_3 + 0.5n \cdot \Delta H_5$	
$\Delta H_{12} = \Delta H^0_{f,el} = \Delta H_7 + (1-m-n) \cdot \Delta H_9 + m \cdot \Delta H_{10} + n \cdot \Delta H_{11}$	

All values are in kJ/mol.

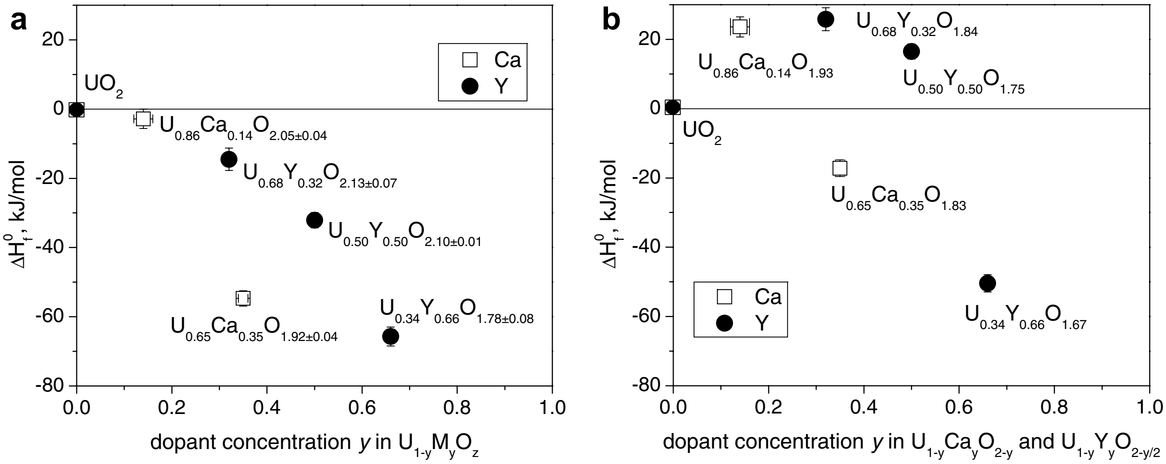

Fig. 1. (a) Enthalpies of formation from oxides (UO_2, UO_3 and CaO or $YO_{1.5}$) of samples with as-synthesized oxygen contents (shown in figure). (b) Enthalpies of formation of modeled fully reduced (all uranium tetravalent) UO_2–CaO and UO_2–$YO_{1.5}$ solid solutions relative to UO_2 and CaO or $YO_{1.5}$. The correction for the effect of oxidation was made assuming that oxidation of U^{4+} to U^{6+} in the solid solution matrix has the same enthalpy as oxidation of UO_2 to UO_3.

4. Discussion

The directly measured enthalpies of formation from binary oxides (UO_2, plus O_2 and CaO or $YO_{1.5}$ as well as from UO_2 plus UO_3 and CaO or $YO_{1.5}$) are strongly negative. A large negative deviation from Raoult's Law was observed earlier [20] for $U_{0.25}Y_{0.75}O_{2-x}$. The interaction parameter Ω, which one would get applying a regular solution model for the relationship between activity coefficient and interaction parameter, $\Omega = RT\ln\gamma_i/(1-x_i)^2$, is very negative (−174.2 kJ/mol) for $\gamma_{UO_2} = 2.52 \times 10^{-3}$ at 1300 °C at $x_{UO_2} = 0.33$ [20]. This corresponds to an enthalpy of mixing of $\Delta H_{mix} = x \cdot (1-x) \cdot \Omega$ to be equal to −38 kJ/mol. The heat of formation of $U_{0.34\pm0.03}Y_{0.66\pm0.07}O_{1.78\pm0.08}$ from the corresponding mixture of UO_2, UO_3 and $YO_{1.5}$ is −66.7 ± 2.5 kJ/mol. These values both clearly show large stabilization in the solid solution. However, there are a number of problems with applying the above calculation. (1) The activity measurements did not take into account the deviation from stoichiometry but seemed to treat the solid solution as the binary UO_2–$YO_{1.5}$ system. With such large negative deviations from ideality, it is clear that the regular solution formalism, which assumes random entropy of mixing, is not applicable. This point has been discussed previously in the context of yttria-stabilized zirconia [15] and indeed was already noted in the early work on urania systems [20]. Rather, the oxidation of uranium and formation of complex defect clusters dominate the system and are responsible for the large stabilization. A similar large decrease of activity of UO_2 in solid solution with another trivalent dopant was observed in early work [5] for high concentrations of La_2O_3. In general, we conclude that the interaction energies between UO_{2+x} and trivalent dopants such as yttria or rare earth oxides are strongly negative.

Although several statistical models of the defect structure of pure [24,25] and doped [18,26] UO_{2+x} have been discussed, 'none of these reports interpreted the thermodynamic data satisfactorily' [26]. According to one model of UO_{2+x} defects, when dopants, Y^{3+} and Ca^{2+}, are introduced, they occupy the lattice sites with −1 and −2 charge defects respectively and are assumed to interact electrostatically with U^{5+} which have +1 charged defect forming $(Y^{3+}U^{5+})$ and $(Ca^{2+}U^{5+})^-$ complexes [18]. The ratio of the concentrations of these complexes and free remaining U^{5+} defects depend on the value of x in the solid solution $U_{1-y}M_yO_{2+x}$. However it is not clear why U^{5+} and not U^{6+} was chosen as the dominant oxidized species, given the absence of any pentavalent uranium oxides in the solid state.

Although the new calorimetric data cannot be used to propose or distinguish various defect models directly, the enthalpies of formation can be analyzed further to separate, to first order, the effects of oxidation from those of cation substitution of Ca^{2+} or Y^{3+} for U^{4+}. The oxidation of U^{4+} to U^{6+}, as evidenced in its binary oxides, is very exothermic. $\Delta H^0 = -138.9$ kJ/mol at room temperature for the reaction

$$UO_2(\text{solid}) + 0.5O_2(\text{gas}) = UO_3(\text{solid}). \quad (4)$$

As a first approximation we assume that the same energetics apply for the oxidation in the solid solutions. This is a reasonable assumption because the enthalpy of oxidation is so large in magnitude that it is expected to be affected to only a small extent, perhaps 10–20%, by variations in local environment and defect clustering. Similar arguments have been made successfully for analyzing the energetics of iron, manganese and cobalt oxidation reactions in spinels [27,28] and for copper oxidation reactions in Sr and Ba doped La_2CuO_4 [29]. The oxidation reaction in Ca and Y doped UO_2 can then be written as

$$\begin{aligned} &U^{4+}(\text{in solid solution}) + 1/2O_2(\text{gas}) \\ &\quad = U^{6+}(\text{in solid solution}) + O^{2-}(\text{in solid solution}). \quad (5) \end{aligned}$$

and associated with a $\Delta H^0 = -138.9$ kJ/mol. Here the U^{6+} is just a formal oxidation state, if the electron holes are distributed over two uranium atoms, the formal oxidation state would be 5+. Similarly the oxide ion may reside in a normal oxygen lattice site or interstitially. That is, the above equation is meant to account for mass and charge balance and energetics, not for detailed defect speciation. Under this assumption of oxidation energetics, we can correct the measured heats of mixing to calculate values which would apply to a hypothetical solid solution containing no oxidized uranium, that is, one in which the charge coupled substitution is

$$U^{4+} = Y^{3+} + 0.5 \text{ oxygen vacancy} \quad (6a)$$

or

$$U^{4+} = Ca^{2+} + \text{oxygen vacancy}. \quad (6b)$$

These substitutions are analogous to those in the fluorite oxides of interest as solid electrolytes, namely stabilized zirconia, hafnia, or ceria, in which the tetravalent cation does not change oxidation state. The formation reaction not involving oxidation is then

$$(1-x) \cdot UO_2 + x \cdot CaO = U_{1-x}Ca_xO_{2-x} \quad (7a)$$

or

$$(1-x) \cdot UO_2 + x \cdot YO_{1.5} = U_{1-x}Ca_xO_{2-x/2}. \quad (7b)$$

The calculated enthalpies of these reactions are shown in Fig. 1(b). They are moderately positive (endothermic) for smaller doping levels, becoming negative (exothermic) for the most highly doped samples. The positive heats of mixing are similar to, though somewhat larger than, those seen in the ceria–yttria system [14]. Earlier studies discussed the different energetic behavior of the ceria–yttria system from the zirconia–yttria and hafnia–yttria systems [13,14]. The large exothermic heats of formation, seen in the later two systems and absent in the former, were attributed to the transfer of oxygen vacancies from the environment of the yttrium to that of the tetravalent ion, rendering Zr and Hf seven-coordinate. Such redistribution is favored by small size of the tetravalent ion and is not expected for cerium. Since U^{4+} is even larger than Ce^{4+}, the vacancies are also expected to remain near the yttrium, and heats of mixing related to size difference of dopant and matrix ions are expected to be larger in the uranium than in the cerium systems. This is indeed seen for lower dopant concentrations (Fig. 1(b)), but at the highest concentrations, negative heats of formation are seen. Thermochemistry of yttria-doped ceria at these high concentrations of dopant has not been determined, thus the comparison of the thermodynamics of cerium and uranium systems at these concentrations is not possible. The observed exothermic enthalpies at high dopant level in urania system may indicate formation of more complex defect clusters in the parent oxidized material, rendering it more stable, so that the enthalpies corrected for oxidation still show this additional stabilizing contribution. It is interesting that the two compositions showing this effect are initially in the oxygen deficiency regime (less than two moles of oxygen per mole of cations), while those showing calculated positive heats of formation of unoxidized materials all start out in the oxygen excess regime. Thus a change in defect mechanism from oxygen interstitial to oxygen vacancy, and the formation of appropriate clusters to accommodate this difference, may be related to the change in energetics. A more detailed study probing the effect of oxygen content at constant dopant concentration would be needed to investigate this further.

The direct calorimetric measurement of heats of formation clearly corroborates the negative deviations from ideality and the small activity coefficients for UO_2 in the solid solutions. This added stabilization in the solid solutions, substantially lowering the activity of UO_2, is predicted to affect the thermodynamics of oxidation of the spent fuel to U^{6+} species in aqueous solution and to eventual uranyl oxides and silicates. For example, the activity of UO_2 for 20 mol% doping with fission products would be lowered not to 0.8 (as calculated for an ideal solution) but rather to about 0.01, if the activity coefficients implied by both the vapor pressure and calorimetric data are correct. This would then raise the oxygen fugacity needed for oxidation by about two orders of magnitude. Furthermore, the kinetics of oxidation may also be slowed by the lower driving force for oxidation. In addition the dopants may form their own surface precipitate phases, e.g. rare earth phosphate or silicate phases. Both the thermodynamic and possible kinetic effects need to be considered in models of the corrosion behavior of spent fuel, which is a multicomponent solid solution, in reactor, storage and repository environments.

5. Conclusions

This work presents the first direct measurements by high-temperature oxide melt solution calorimetry of the enthalpy of formation in the systems UO_{2+x}–CaO and UO_{2+x}–$YO_{1.5}$. Solid solutions of urania–calcia with calcium concentration 0.14 and 0.35 and urania–yttria with yttrium concentration 0.32–0.66 are found to be significantly more stable than the mechanical mixture of their constituent binary oxides, UO_2, UO_3 and metal oxide, CaO or Y_2O_3. This stabilization is related to the oxidation of uranium and the likely formation of complex defect clusters. Recommended values of the standard enthalpies of formation from the elements are given for several compositions in UO_{2+x}–CaO and UO_{2+x}–$YO_{1.5}$ solid solutions. The substantially lowered activity of UO_2 in these solid solutions will hinder, in both a thermodynamic and possibly a kinetic sense, its oxidation to aqueous U^{6+} species which eventually form solid uranyl phases in the environment.

Acknowledgments

We thank Sarah Roeske for help with the microprobe analyses. This work was supported by the Department of Energy (Grant DE FG02-03ER46053).

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