Aluminium – Oxygen – Plutonium

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Introduction

Partitioning and transmutation is considered to be a complementary option in the management of waste from nuclear power generation. In this process, the radionuclides are separated from the spent fuel, followed by fission or transmutations in reactors or accelerators. As the long-term radiotoxicity of the fission products is much less than that of the actinide after about 250 years, a substantial reduction of the waste can be achieved. Plutonium is one of the actinides formed by neutron capture in ^{238}U during irradiation of UO_2 in nuclear power plants. Efficient partitioning of plutonium from the spent fuel has already been realized in present commercial PUREX (plutonium reprocessing and extraction) installations. For the fabrication of fuels for transmutation, two ways are considered: homogeneous mixing in fresh MOx (mixed oxide) fuel, and heterogeneous dispersion in an inert support material [1997Zha]. Aluminium oxide Al_2O_3 is an appropriate candidate inert matrix material for heterogeneous transmutation based on an evaluation of some its physico-chemical and neutronic properties. Among these properties, the melting behavior is extremely important. An inert-matrix fuel should have a high melting temperature to avoid melting the fuel during power ramps. In general, knowledge of the phase equilibria of fuels consisting of plutonium oxides and inert matrix aluminium oxide is of great importance. But up to now, information is incomplete. Results of experimental investigations of phase equilibria in the PuO_2-Al_2O_3 quasibinary system are presented in [1964Hou] (as quoted by [1965Far]) and [1965Hou] (reproduced also in [1967Ack]). The authors of [1965Hou] have prepared plutonium dioxide from the oxolate by calcining at 600°C. The used aluminium oxide was chemical reagent grade material. The PuO_2-Al_2O_3 powders were sintered in an oxygen atmosphere at 1250°C for 2 hours in thoria crucibles. The melting points of the pellets were determined and high temperature sintering was carried out in oxygen and argon atmospheres. The specimens were studied using metallography, X-ray diffraction and microprobe analysis. The melting behavior of the systems PuO_2-Al_2O_3 and $PuO_{1.61}$-Al_2O_3 as well as the character of the phase equilibria in the Al_2O_3-$PuO_{1.61}$-PuO_2 partial system over the temperature range 1727 to 2177°C were calculated by [1997Zha] using the Calphad method. Future experimental determinations of phase equilibria along the $PuO_{1.61}$-Al_2O_3 and PuO_2-Al_2O_3 sections as well as the melting behavior and solid state equilibria in the range of compositions including Al_2O_3 and plutonium oxides are necessary. This new information will become a theoretical basis for new practical applications of Al-O-Pu alloys.

Binary Systems

The Al-O system is accepted from [Mas2]. The constitution of the Al-Pu and O-Pu systems are mainly based on the data of [1989Kas] and [1990Wri], respectively, that serve also as the foundation of the [Mas2] handbook data concerning the corresponding systems. The O-Pu binary was slightly modified in [1997Zha], which accepted a temperature of 2300 ± 40°C for melting point of the "PuO_2" phase (of composition $PuO_{1.61}$) and a maximum point in the liquidus and solidus lines at 2475°C for the composition $PuO_{1.77}$.

Solid Phases

No ternary phases were found. Crystallographic data concerning the known unary and binary phases are listed in Table 1. No visible solubility of the third component in the binary phases was determined.

Quasibinary Systems

The phase diagram of the PuO_2-Al_2O_3 quasibinary system is presented in Fig. 1. It is based on the experimental results of [1964Hou] and [1965Hou] that were quoted in [1965Far] and [1967Ack] and was corrected slightly to take into account the accepted melting point of 2475°C for PuO_2. The PuO_2-Al_2O_3 phase diagram calculated by [1997Zha] is identical. This phase diagram was found to be simple eutectic

with very little terminal solid solubility and no ternary compounds. So, the mutual solubilities of PuO_2 in Al_2O_3 and Al_2O_3 in PuO_2 are 0.28 ± 0.2 and 0.14 ± 0.14 (mol%), respectively. The oxygen contents corresponding to the maximum solubilities are 60.019 and 66.661 (at.%), respectively. The eutectic temperature obtained by [1964Hou] and [1965Hou] is accepted as an average of those obtained from a series of specimens. No attempts were made by the authors to determine the liquidus because no crucible material could be found by them which did not react with these substances when molten and which was also stable in oxygen at the temperatures involved (> 2000°C). Thus, the liquidus curves are plotted in Fig. 1 as dotted lines.

Invariant Equilibria

On the basis of experimental investigations, [1964Hou, 1965Hou] found a three-phase invariant equilibrium $L \rightleftharpoons \alpha + \pi$ at a temperature of 1910 ± 15°C. The temperature of the invariant equilibrium involving the participation of liquid, the α and σ phases and, obviously, a fourth phase, was calculated by [1997Zha] to be 1776°C.

Isothermal Sections

Isothermal sections of the Al_2O_3-$PuO_{1.61}$-PuO_2 partial system were calculated by [1997Zha] for the temperature range from 1727 to 2177°C. During construction of these sections, results of their own calculations of the phase equilibria in the forming O-Pu binary system in the range of compositions 61.68 to 66.67 at.% O (between the σ and π phases) were used. They accepted the maximum point in the liquidus and solidus lines at 2475°C and 63.90 at.% O which contradicts the accepted data of [1990Wri, Mas2], and therefore, the data obtained by [1997Zha] need further experimental verification. The Al_2O_3-PuO_2-$PuO_{1.61}$ (PuO_{2-x}-Al_2O_3 at $0 \le x \le 0.39$) isothermal section calculated at 1877°C by [1997Zha] is shown in Fig. 2. The dashed line represents the projection of the eutectic valley.

Temperature – Composition Sections

It was assumed by [1997Zha] that the $PuO_{1.61}$-Al_2O_3 system is a simple eutectic like the PuO_2-Al_2O_3 section and that the liquid phase behaves ideally. With this assumption, the eutectic point was calculated to be at 1776°C and 52 mol% $PuO_{1.61}$ (60.87 at.% O). However, as at higher temperatures, the composition $PuO_{1.61}$ lies in the PuO_2 phase field (the CaF_2 type structure), the $PuO_{1.61}$-Al_2O_3 section would seem not to be quasibinary, and the eutectic temperature, probably, corresponds to the invariant four-phase process with participation of the liquid phase.

Thermodynamics

The Calphad technique was used by [1997Zha] for the calculation of phase equilibria with involving the plutonium oxides. The thermodynamic data used for Pu_2O_3, $PuO_{1.61}$ (solid) and PuO_2 were taken from the ECN-T base [1990Cor, 1997Zha]. The data for the liquid σ phase were estimated while those used for the α phase are from the SGTE database. The least-square optimization programs BINGSS and BINFKT [1995Luk,1997Zha] were used to perform the thermodynamic phase diagram optimization of the binary systems. Phase diagrams were then generated using the program MTDATA [1994Aea, 1997Zha] with the model parameters obtained in the optimization.

Notes on Materials Properties and Applications

In connection with high temperature reactor systems, the dispersion of plutonium oxides in various ceramic matrices, in particular, in Al_2O_3, the properties of the diluent (particularly its thermal conductivity) may be expected largely to determine the behavior of the fuel. The corresponding system is the Al-O-Pu.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al) (I) < 660.452, 1.013 bar	*cF*4 $Fm\bar{3}m$ Cu	*a* = 404.96	at 25°C [Mas2] dissolves less than $3\cdot10^{-8}$ at.% O at ~660°C and up to 1.6 at.% Pu at 650°C [Mas2]
(Al) (II) $2.05\cdot10^{5}$ bar	*hP*2 $P6_3/mmc$ Mg	*a* = 269.3 *c* = 439.8	at 25°C [Mas2]
(ηPu) (h_5) 640 - 483	*cI*2 $Im\bar{3}m$ W	*a* = 363.43	at 483°C [1990Wri] dissolves up to 10.5 at.% Al at 801°C [1989Kas]
(εPu) (h_4) 483 - 463	*tI*2 *I*4/*mmm* In	*a* = 332.61 *c* = 446.30	at 477°C [1990Wri] dissolves up to 0.25 at.% Al at 463°C [1989Kas]
(δPu) (h_3) 463 - 320	*cF*4 $Fm\bar{3}m$ Cu	*a* = 463.71	at 320°C [1990Wri] dissolves up to 14.5 at.% Al at 788°C [1989Kas]
(γPu) (h_2) 320 - 215	*oF*8 *Fddd* γPu	*a* = 315.87 *b* = 576.82 *c* = 1016.2	at 235°C [1990Wri]
(βPu) (h_1) 215 - 125	*mC*34 *C*2/*m* βPu	*a* = 928.4 *b* = 1046.3 *c* = 785.9 β = 92.13°	at 190°C [1990Wri]
(αPu) (r) < 125	*mP*16 $P2_1/m$ αPu	*a* = 618.3 *b* = 482.2 *c* = 1096.3 β = 101.97°	at 21°C [1990Wri]
α, Al_2O_3 2054 - < 500	*hR*30 $R\bar{3}m$ αAl_2O_3	*a* = 479 *c* = 1293	60 at.% O [1977Kri]
γ (Al-O)	*cF*56 $Fd\bar{3}m$ $MgAl_2O_4$		metastable; ~ 60 at.% O; labelled as "γAl_2O_3" [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
δ (Al-O)	-	-	metastable; ~ 60 at.% O; labelled as "δAl_2O_3" [Mas2]
θ (Al-O)	*m*** *C*2/*m* βGa_2O_3	-	metastable; ~ 60 at.% O; labelled as "θAl_2O_3" [Mas2]
κ (Al-O)	-	-	metastable; ~ 60 at.% O; labelled as "κAl_2O_3" [Mas2]
χ (Al-O)	*h*** *P*6$_3$/*mcm* or *P*6/*mmm* or *P*6$_3$/*mmc* χAl_2O_3	-	metastable; ~ 60 at.% O; labelled as "κAl_2O_3" [Mas2]
βPu_3Al (h) 560 - 195	*tP*4 *P*4/*mmm* $SrPb_3$	*a* = 449.9 *c* = 453.8	25 at.% Al [1989Kas]
		a = 453.0 *c* = 447.5	[E]
		a = 449.9 *c* = 453.6	[1959Boc]
αPu_3Al (r) < 195	*c***		25 at.% Al [1989Kas]
η, PuAl 590 - 193	*cI*58	*a* = 1076	50 at.% Al [1989Kas] [1959Boc]
β, $PuAl_2$ < 1540	*cF*24 *Fd*$\bar{3}$*m* Cu_2Mg	*a* = 783.1	66.7 at.% Al [1989Kas] [E]
$\delta Pu_{0.95}Al_3$ (h_3) 1420 - 1210	*cP*4 *Pm*$\bar{3}$*m* $AuCu_3$	*a* = 426.2	~76 at.% Al, labelled as "3H" [1989Kas]
$\gamma Pu_{0.95}Al_3$ (h_2) 1210 - 1027	*hP*24 *P*6$_3$/*mmc* $PuAl_3$	*a* = 608.3 *c* = 1441.0	~76 at.% Al, labelled as "6H" [1989Kas]
$\beta Pu_{0.95}Al_3$ (h_1) 1027 - 915	*hR*36 *R*$\bar{3}$*m*	*a* = 614.85 *c* = 2110.11	~76 at.% Al, labelled as "9Hβ" [1989Kas]
$\alpha Pu_{0.95}Al_3$ (r) < 915	*hR*36 *R*$\bar{3}$*m*	*a* = 615.02 *c* = 2117.44	~76 at.% Al, labelled as "9Hα" [1989Kas]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
λ, $Pu_{0.90}Al_4$	*oI*20	*a* = 439.6	~81.6 at.% Al [1989Kas]
< 925	*Imma*	*b* = 626.6	
	UAl_4	*c* = 1370.8	
			undergoes a second order transition at 645°C [1989Kas]
ν, Pu_2O_3	*hP*5		59.3 to 60.5 at.% O [1990Wri]
< 2080	$P\bar{3}m1$	*a* = 383.88	[1990Wri]
	La_2O_3	*c* = 595.94	
ρ, $PuO_{1.52}$	*cI*80	*a* = 1104.5	60.2 at.% O [1990Wri]
< 450	$Ia\bar{3}$		
	Mn_2O_3		
σ, $PuO_{1.61}$	*cI*80		61.7 to 63.0 at.% O [1990Wri]
1180 - 335	$Ia\bar{3}$	*a* = 1099.1	[1990Wri]
	Mn_2O_3		
π, PuO_2	*cF*12		60 to 66.7 at.% O [1990Wri, 1997Zha]
< 2425	$Fm\bar{3}m$		
	CaF_2	*a* = 539.6	[E]
		a = 539.26	[1962Pap, S]
		a = 539.53	[1963Lea, S]

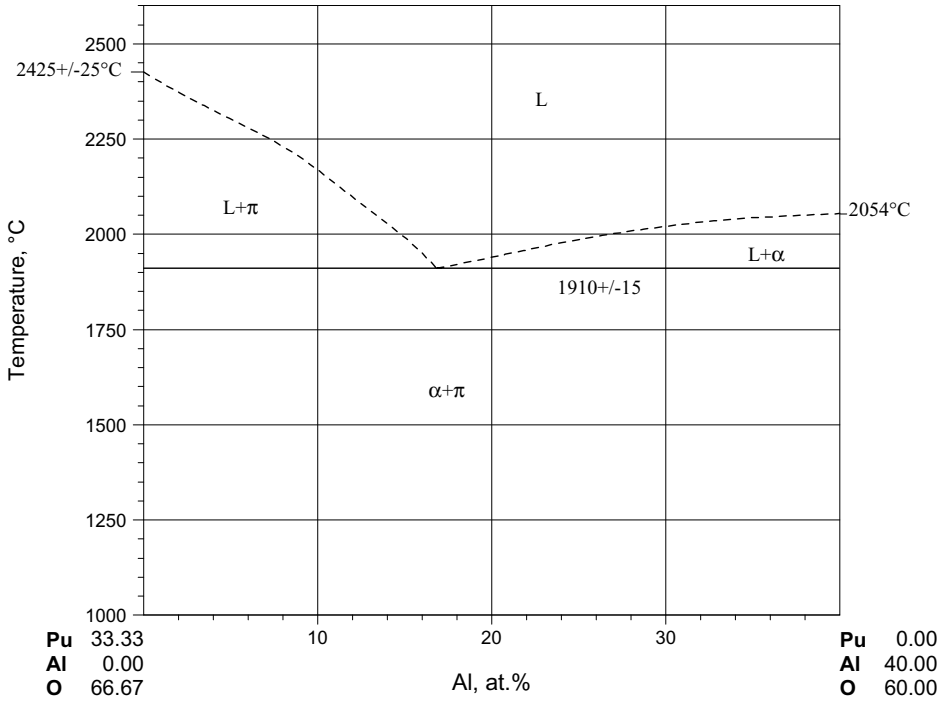

Fig. 1: Al-O-Pu. The PuO_2-Al_2O_3 quasibinary section

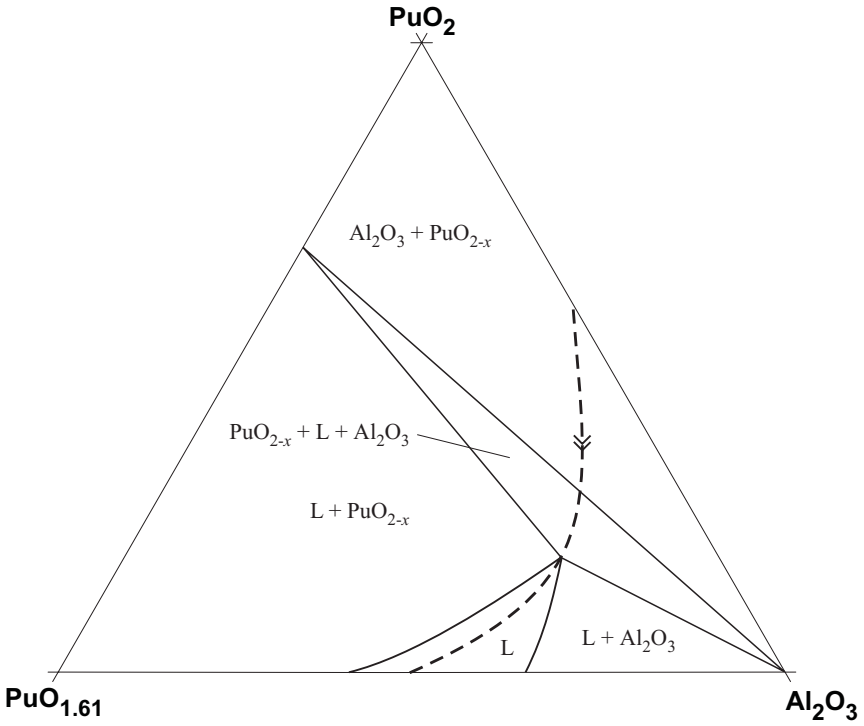

Fig. 2: Al-O-Pu. Schematic partial isothermal section calculated at 1877°C. Dashed line: projection of the eutectic valley