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RESEARCH ESTABLISHMENT
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THE STABILITY OF FISSILE-FERTILE OXIDE SOLID SOLUTIONS IN AIR

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ABSTRACT

The stability of $(UTh)O_2$, $(PuTh)O_2$, and $(PuUTh)O_2$ solid solutions when heated to high temperatures in air is reviewed and discussed. $(PuTh)O_2$ is chemically stable under these conditions, but compositions containing uranium oxidise to give either a non-stoichiometric fluorite phase containing excess oxygen, or to this phase plus orthorhombic U_3O_8. U_3O_8 formation is to be avoided if maximum dimensional stability is required. $(UTh)O_2$ compositions containing 50 m/o or more of ThO_2 do not form an orthorhombic phase under any conditions of oxidation. Information on the extent of non-stoichiometry and the effects of excess oxygen on unit cell volume, bulk volume, and the rate of uranium loss at high temperatures is also reviewed.

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(General Electric Co. 1964)

1. INTRODUCTION

In some high temperature gas-cooled reactor designs, an all-ceramic fuel element which could be operated in ambient air rather than in a purified gas may have attractive advantages. As a basis for an assessment of the chemical stability in air of the fissile-fertile part of such elements, it is assumed that a dispersion of $(UTh)O_2$, $(PuTh)O_2$, or $(PuUTh)O_2$ in BeO may be required to operate at temperatures up to 1200°C in air. This would present no corrosion problem with $(PuTh)O_2$, which is completely stable in air, but compositions containing uranium may oxidise to give either non-stoichiometric oxide solid solutions or second phases.

In this report the stability of UO_2 and of $(UTh)O_2$ solid solutions is reviewed and discussed. The oxygen stability of $(PuUTh)O_2$ has not been reported in the literature, but some predictions are made on its behaviour on the basis of results for $(UTh)O_2$. The structural description of non-stoichiometry, which is outside the scope of this review, is not discussed. The formula UO_{2+x} as used here includes the closely related face-centred cubic phases U_4O_9, U_4O_{9-x}, and "non-stoichiometric UO_2".

2. UO_2

Pure UO_2, which has a fluorite (cubic) structure, readily oxidises to U_3O_8 in air at temperatures above 250°C. At temperatures above 1000°C, orthorhombic U_3O_{8-y} and cubic UO_{2+x} can exist in equilibrium, and, as the temperature is raised, the oxygen pressure at which UO_{2+x} is the stable phase becomes higher (Chapman and Meadows 1964). The oxidation of UO_2 to U_3O_8 is accompanied by a 36 per cent. increase in volume, which is sufficient to cause fragmentation of the body. Fabricated UO_2 cannot therefore be exposed to air at temperatures above 250°C unless the oxygen pressure is sufficiently low for UO_{2+x} to be the stable phase. The allowable oxygen pressure increases with increasing temperature; it is 10^{-3} atmospheres at 1200°C and 10^{-1} atm at 1450°C.

Addition of other oxides which form fluorite solid solutions with UO_2 can stabilise the fluorite structure, prevent the formation of orthorhombic phases, and allow solid bodies to be heated in air at all temperatures without fragmentation. ThO_2 is one material capable of stabilising the fluorite structure as discussed below.

3. UO_2-ThO_2 SYSTEM

Lambertson and others (1953) measured the liquidus and solidus temperatures for the UO_2-ThO_2 system, found that complete solid solution occurred, and reported only minor variations from the theoretical curves. Mumpton and Roy (1960), however, have suggested that solid solutions containing more than 60 m/o UO_2 may be metastable, the two stable phases being fluorite solid solutions of different compositions. Christensen (1963) and Cohen and Berman (1966) reported complete solid solution but significant deviation from ideal behaviour at high UO_2 contents, including departure from Vegard's Law.

4. UO_2-ThO_2-O SYSTEM

4.1 Phase Diagrams

There are some inconsistencies in the earlier literature and three recent phase diagrams will be discussed first.

Mumpton and Roy (1960) presented a tentative phase diagram from which the following conclusions can be drawn:

(i) $(UTh)O_2$ solid solutions containing 40 m/o or more of ThO_2 remain single-phase fluorite at all temperatures when heated in air. The corresponding equilibrium composition varies from $(U_{0.6}Th_{0.4})O_{2.4}$ to $ThO_{2.0}$.

(ii) $(UTh)O_2$ compositions containing less than 40 m/o ThO_2 may gain some excess oxygen on heating and still retain a fluorite structure at 1350°C. However, this may disproportionate to two fluorite phases on cooling. Further oxidation may result in the formation of a two-phase structure (U_3O_8 plus fluorite solid solution) even at 1350°C.

Gilpatrick and others (1964) reported the ThO_2-UO_3 (equivalent to ThO_2-UO_2-O) system more fully. The following conclusions can be drawn from this work:

(i) At 900°C or below, the minimum ThO_2 content for maintenance of a fluorite solid solution at 0.2 atm pressure of oxygen is 40 m/o; the corresponding equilibrium composition is $(U_{0.6}Th_{0.4})O_{2.27}$. At 1300°C, only 33 m/o ThO_2 is required $\left((U_{0.67}Th_{0.33})O_{2.28}\right)$, while at 1500°C the composition $(U_{0.93}Th_{0.07})O_{2.37}$ is still single-phase fluorite.

(ii) No compositions containing less than 40 m/o ThO_2 will be single-phase fluorite in the presence of 0.2 atm pressure of O_2 under all conditions of heating.

Mumpton and Roy, and Gilpatrick and co-workers, are thus in close agreement except for differences in the oxygen content of oxidised solid solutions.

The most recent phase study has been that of Cohen and Berman (1966). Their

results indicate that:

(i) 50 m/o is the minimum ThO_2 content for which $(UTh)O_2$ will remain single-phase fluorite on oxidation in air. The equilibrium composition varies from $(U_{0.5}Th_{0.5})O_{2.25}$ to $ThO_{2.0}$.

(ii) $(UTh)O_2$ solid solutions containing 50-65 m/o UO_2 may gain some excess oxygen and still remain single-phase fluorite up to a composition of $(UTh)O_{2.25}$. For UO_2 contents above 65 m/o the same applies but this fluorite structure may be metastable if the oxygen-to-metal ratio is above 2.18. Under slow-cooling conditions, two cubic phases may appear, but true equilibrium may involve U_3O_8 formation.

(iii) Upon further oxidation in air at 1200°C, $(UTh)O_2$ solid solutions containing more than 50 m/o UO_2 give orthorhombic U_3O_8 plus cubic $(UTh)O_{2.25}$.

(iv) The equilibrium solubility of oxygen in $(UTh)O_2$ varies little with temperature in the range ambient to 1200°C.

The lower limit of ThO_2 content above which all solid solutions remain fluorite even after oxidation in air at atmospheric pressure had previously been reported as 22 m/o (Anderson and others 1954), 40.5 m/o (Handwerk and others 1957), 29.6 m/o (Lynch and others 1960), and 43.5 m/o (Hund and Niessen 1952). Anderson and his co-authors suggested that, in effect, their low ThO_2 solid solutions may have been metastable, and that the low ThO_2 content necessary for stabilisation was probably due to the complete absence of U_3O_8 in their initial mixtures; the presence of some U_3O_8 could possibly nucleate U_3O_8 precipitation at ThO_2 contents above 22 m/o. The same authors also observed that a solid solution containing 34 m/o ThO_2 became two-phase on oxidation in O_2 at 120 atmospheres pressure, and that solid solutions containing 50 m/o or more ThO_2 remained fluorite under all conditions of temperature and atmosphere.

Many of the inconsistencies in the literature probably arise from the apparent difficulty of attaining equilibrium, particularly near phase boundaries. 50 m/o ThO_2 however appears to have been established as the ThO_2 content below which second phases can occur under some conditions of oxidation, but above which no second phases have ever been observed.

It is interesting to note that Cohen and Berman (1966) found that a ThO_2 content as low as 2 m/o "stabilised" $(UTh)O_2$ against flaking and powdering even when oxidised to the composition $(UTh)O_{2.61}$, where an orthorhombic phase would certainly be present. However, in the following discussion it is assumed that formation of a second phase at any stage of fabrication, or during operation under reactor conditions in air, is undesirable.

4.2 Fabrication

UO_2-ThO_2 powder mixtures must be sintered in either a neutral or a reducing atmosphere; use of an oxidising atmosphere would result in specimen fragmentation due to U_3O_8 formation during heating. Depending on the intimacy of the original mixture, a partial to complete solid solution will form during inert or reducing atmosphere sintering. If this is complete and if the ThO_2 content is 50 m/o or higher, the material could be cooled in an oxidising atmosphere if desired; however, cooling in a reducing atmosphere is necessary if a completely stoichiometric solid solution is required.

Pre-formed $(UTh)O_2$ solid solutions may be sintered in oxygen or air if they contain 50 m/o or more of ThO_2; UO_2-ThO_2 powders prepared by calcination of co-precipitated preparations can probably be sintered in air if they contain 50 m/o or more of ThO_2, since the degree of initial solution will often be sufficient to prevent U_3O_8 formation during heating. Cooling in H_2, or reheating and cooling in H_2, will be necessary to obtain a stoichiometric composition.

Lynch and others (1960) state that U_3O_8-ThO_2 powder mixtures may be sintered in air if they contain more than 29.6 m/o ThO_2. The U_3O_8 to UO_{2+x} transition above 1000°C does not break the compact; the solid solution then forms as the temperature is raised and U_3O_8 does not reform on cooling. This technique is a convenient one for fabrication of UO_2-ThO_2. As before, the sintered product will be non-stoichiometric unless cooled, or reheated and cooled, in H_2. Also, in view of the phase diagram information discussed in Section 4.1, 50 m/o ThO_2 would be a safer lower limit if a single-phase fluorite structure is required under all conditions.

4.3 The Degree of Non-Stoichiometry Attained

The degree of non-stoichiometry of partially-oxidised $(UTh)O_2$ solid solutions depends on the UO_2 content, the partial pressure of oxygen in the atmosphere, the temperature, and the extent to which equilibrium has been achieved. The excess oxygen content can conveniently be expressed as apparent uranium valency, assuming a fixed valency of 4 for ThO_2.

Values for uranium valency reported from four investigations are given in Table 1. From these results it can be seen that $(UTh)O_2$ with ThO_2 contents in the range 50-90 m/o will oxidise, when heated in air at 1200°C, to a uranium valency of 5.0 ± 0.1.

4.4 Effect of Non-Stoichiometry on Density

As the uranium valency in both UO_{2+x} and $(UTh)O_{2+x}$ increases, the lattice parameter of the fluorite unit cell decreases; this is accompanied by an increase in density and a decrease in volume. For example, the lattice parameter of UO_2 is approximately 5.47 Å, while that of U_4O_9 is 5.44 Å (Gronwold 1955). The figures of Anderson and others (1954) for $(UTh)O_{2+x}$ indicate that this contraction occurs only between uranium valencies of 4 and 5. Above 5, the lattice expands again slightly. Some examples of their results are given in Table 2, which also includes results from a U.S.A.E.C. report (1962) and from Cohen and Berman (1966). The maximum decrease in volume which can occur on oxidation is about 2 per cent.

4.5 Rate of Uranium Loss

One of the undesirable properties of $(UTh)O_{2+x}$ solid solutions is that uranium can be lost at significant rates by evaporation of UO_3. Workers at the General Electric Co. (1964) have studied the vapour pressure of UO_3 over $(UTh)O_{2+x}$ at various temperatures in air, and some of their results are given in Table 3. Y_2O_3 was found to be a much more efficient additive for reducing uranium loss than was ThO_2, which merely acted as an ideal solid solution diluent for UO_2. Solutions containing Y_2O_3 showed considerable departure from ideal behaviour and in this way reduced the UO_2 vapour pressure further than would be expected from dilution effects only.

Cohen and Berman (1966) reported uranium loss figures from two urania-rich compositions heated in air at 1200°C for 72 hours. These losses were 3 m/o for a 90 m/o UO_2 content in $(UTh)O_{2+x}$, and 1 m/o for 60 m/o UO_2.

5. PuO_2 - BASED SYSTEMS

PuO_2 is a fluorite-type oxide. It readily loses oxygen on heating in vacuum, neutral, or reducing atmospheres to form $PuO_{1.98}$ or one of the three forms of Pu_2O_3, but can incorporate excess oxygen only up to $PuO_{2.09}$ (Drummond and Welch 1957). PuO_2 and ThO_2 form a complete series of solid solutions (Wittenburg 1963); their oxidation-reduction behaviour has not been reported but at least at high ThO_2:PuO_2 ratios they would remain stoichiometric within close limits when heated in air. PuO_2 and UO_2 form a complete series of solid solutions. According to Brett and Russell (1963), compositions containing 20 m/o or more of PuO_2 oxidise to form only single-phase fluorite phases with a uranium valency of up to 5; at lower PuO_2 contents an orthorhombic U_3O_8-type phase was also formed. Compositions containing 20 m/o or more PuO_2 can form two phases, an oxygen-deficient "UO_2 - $PuO_{1.62}$" phase in addition to fluorite $(PuU)O_2$, on heating in hydrogen or on argon arc-melting.

The existence of a ternary solid solution, $(PuUTh)O_2$, is likely although this has not been confirmed in the literature. Its oxidation-reduction behaviour would be complex, but as a first approximation the behaviour of PuO_2 and ThO_2 in stabilising UO_2 against oxidation can be taken as identical; the total PuO_2 + ThO_2 content would in this treatment be considered to be all ThO_2. The higher the ThO_2:PuO_2 ratio, the more this procedure will be justified.

6. SUMMARY AND CONCLUSIONS

1. $(UTh)O_2$ solid solutions containing 50 m/o or more of ThO_2 remain single-phase fluorite on oxidation in air under all conditions of temperature.

2. UO_2-ThO_2 powder mixtures must be sintered in a neutral or reducing atmosphere. Preformed $(UTh)O_2$ solid solutions, including some co-precipitated powders, may be sintered in air if desired. The same applies to U_3O_8-ThO_2 mixtures.

3. All air-sintered, air-cooled, or air-annealed $(UTh)O_2$ will contain excess oxygen, in an amount usually close to that which corresponds to an apparent uranium valency of 5.

4. Oxidation of stoichiometric $(UTh)O_2$ causes a reduction in volume and an increase in density. The reduction in volume depends on the uranium content, but may be up to 2 per cent.

5. UO_3 volatilises from $(UTh)O_2$ solid solutions heated in air.

6. $(PuTh)O_2$ solid solutions remain near-stoichiometric when heated in air, but can probably become sub-stoichiometric or two-phase in vacuum, neutral, or reducing atmospheres.

7. The behaviour of $(PuUTh)O_2$ solid solution in air may be approximated by assuming that the PuO_2 + ThO_2 content is all ThO_2. The higher the ThO_2:PuO_2 ratio, the more this procedure will be justified.

7. REFERENCES

Anderson, J.S., Edgington, D.N., Roberts, L.E.J., and Wait, E. (1954). - J.Chem. Soc. 1954 : 3324.

Brett, N.H., and Russell, L.E. (1963). - Trans. Brit. Ceram. Soc. 62 : 97.

Chapman, A.T., and Meadows, R.E. (1964). - J. Am. Ceram. Soc. 47 : 614.

Christensen, J.A. (1963). - HW76559, p.11.5

Cohen, I., and Berman, R.M. (1966). - J. Nucl. Mat. 18 : 77.

Drummond, J.L., and Welch, G.A., (1957). - J. Chem. Soc. 1957 : 4781.

General Electric Co. (1964). - GEMP 34A.

Gilpatrick, L.O., Stone, H.H., and Secoy, C.H. (1964). - ORNL 3591, p.160.

Gronwold, F. (1955). - J. Inorg. Nucl. Chem. 1 : 357.

Handwerk, J.H., Abernathy, L.L., and Bach, R.A. (1957). - Am. Ceram. Soc. Bull. 36 : 99.

Hund, F., and Niessen, G. (1952). - Z. Electrochem. 56 : 972.

Lambertson, W.A., Mueller, M.H., and Gunzel, F.H. Jr. (1953). - J. Am. Ceram. Soc. 36 : 397.

Lynch, E.D., Handwerk, J.H., and Hoenig, C.L. (1960). - J. Am. Ceram. Soc. 43 : 520.

Mumpton, F.A., and Roy, R. (1960). - J. Am. Ceram. Soc. 43 : 239.

U.S.A.E.C. (1962). - TID 11295 2nd Edition, p.87.

Wittenberg, L.J. (1963). - MLM-1162.

TABLE 1

VALUES OF URANIUM VALENCY IN $(UTh)O_{2+x}$

Authors	ThO_2 Content	Uranium Valency	Conditions
Anderson and others (1954)	24	4.88	After oxidation in air, or in O_2 at 5-15 cm pressure, at up to 1400°C
	34	5.07	
	50	5.21	
	62	5.16	
	75	5.31	
	85	5.36	
	97	4.94	
	99	4.51	
Cohen and Berman (1966)	<10	~4.5	Maximum valency, after oxidation in air at 1200°C
	40	4.84	
	50	4.95	
	60	5.00	
	70	5.06	
	80	5.04	
	90	4.90	
	100	4.00	
Gilpatrick and others (1964)	30	4.9	At 1475°C, 0.2 atm O_2
	40	4.9	Below 900°C, "
	50	5.0	At 1500°C, "
	50	5.0	Below 900°C, "
	60	5.1	" " "
Lynch and others (1960)	30	4.9	Below 400°C in air
	30	4.8	At 800°C " "
	30	4.7	At 1250°C " "
	70	5.04	Below 400°C, as fabricated
	70	4.96	At 800°C, heating, in air
	70	4.68	At 1250°C, in air
	70	4.84	At 800°C, cooling, in air
	70	4.96	Below 400°C, " " "

TABLE 2

DATA ON THE OXIDATION OF $(UTh)O_2$ SOLID SOLUTIONS

ThO_2 Content (m/o)	Uranium Valency after Partial or Complete Oxidation	Corresponding Decrease in Volume (%)	Reference
85	4.5	0.16	Anderson and others (1954)
85	5.0	0.25	
85	5.4	0.16	
62	4.5	0.7	
62	5.0	0.8	
62	5.4	0.5	
50	5.2	1.3	
22	4.9	2.0	
80	5.2	0.5	U.S.A.E.C. (1962)
60	5.1	1.4	
50	5.0	1.9	
40	5.0	1.9	
30	5.0	2.1	
80	5.04	0.5	Cohen and Berman (1966)
70	5.06	0.8	
60	5.00	1.4	
50	4.95	1.9	
30	4.7	1.5	
20	4.6	1.5	
10	4.5	1.4	

TABLE 3

VAPOUR PRESSURE OF UO_3 OVER $(UTh)O_{2+x}$

(General Electric Co. 1964)

UO_2:ThO_2 Mole Ratio	Temperature (°C)	Vapour Pressure x 10^7 (atm)
1:1	1400	400
1:3	"	200
1:15	"	50
1:1	1200	11
1:3	"	9
1:15	"	7