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THE STABILITY OF FISSILE-FERTILE OXIDE SOLID SOLUTIONS IN AIR

by

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ABSTRACT

The stability of (UTh)O₂, (PuTh)O₂, and (PuUTh)O₂ solid solutions when heated to high temperatures in air is reviewed and discussed. (PuTh)O₂ 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 U₃O₈. U₃O₈ formation is to be avoided if maximum dimensional stability is required. (UTh)O₂ compositions containing 50 m/o or more of ThO₂ 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 \(U_9O_8-y\) 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 UO₂-ThO₂ 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
UO₂ 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
UO₂ contents, including departure from Vegard's Law.

4. UO₂-ThO₂-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)O₂ solid solutions containing 40 m/o or more of ThO₂ remain
single-phase fluorite at all temperatures when heated in air. The corresponding
equilibrium composition varies from (Uo.6ThO.4)O₂ to ThO₂.

(ii) (UTh)O₂ compositions containing less than 40 m/o ThO₂ 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 (UaOs plus
fluorite solid solution) even at 1350°C.

Gilpatrick and others (1964) reported the ThO₂-UO₂ (equivalent to ThO₂-UO₂-O)
system more fully. The following conclusions can be drawn from this work:

(i) At 900°C or below, the minimum ThO₂ content for maintenance of a
fluorite solid solution at 0.2 atm pressure of oxygen is 40 m/o; the
corresponding equilibrium composition is (Uo.6ThO.4)O₂-ar. At 1200°C, only
33 m/o ThO₂ is required ((Uo.7ThO.3)O₂-ae), while at 1500°C the composition
(Uo.5ThO.5)O₂-ar is still single-phase fluorite.

(ii) No compositions containing less than 40 m/o ThO₂ will be single-phase
fluorite in the presence of 0.2 atm pressure of O₂ 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 ThO₂ content for which (UTh)O₂ will remain single-
phase fluorite on oxidation in air. The equilibrium composition varies from
(Uo.6ThO.4)O₂-ar to ThO₂.

(ii) (UTh)O₂ solid solutions containing 50-65 m/o UO₂ may gain some excess
oxygen and still remain single-phase fluorite up to a composition of (UTh)O₂-ar.
For UO₂ 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 UaOs
formation.

(iii) Upon further oxidation in air at 1200°C, (UTh)O₂ solid solutions
containing more than 50 m/o UO₂ give orthorhombic UaOs plus cubic (UTh)O₂-ar.
(iv) The equilibrium solubility of oxygen in (UTh)O₂ varies little with
temperature in the range ambient to 1200°C.

The lower limit of ThO₂ 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), 39.6 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 ThO₂ solid
solutions may have been metastable, and that the low ThO₂ content necessary for
stabilisation was probably due to the complete absence of UaOs in their initial
mixtures; the presence of some UaOs could possibly nucleate UaOs precipitation
at ThO₂ contents above 22 m/o. The same authors also observed that a solid
solution containing 34 m/o ThO₂ became two-phase on oxidation in O₂ at 120
atmospheres pressure, and that solid solutions containing 50 m/o or more ThO₂
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 ThO₂ however appears to have been established as the ThO₂ 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 ThO₂
content as low as 2 m/o "stabilised" (UTh)O₂ against flaking and powdering even
when oxidised to the composition (UTh)O₂-ar, 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

UO₂-ThO₂ 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 U₄O₉ 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 ThO₂ 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)O₂ solid solutions may be sintered in oxygen or air if they contain 50 m/o or more of ThO₂; UO₂-ThO₂ powders prepared by calcination of co-precipitated preparations can probably be sintered in air if they contain 50 m/o or more of ThO₂, since the degree of initial solution will often be sufficient to prevent U₄O₉ formation during heating. Cooling in H₂, or reheating and cooling in H₂, will be necessary to obtain a stoichiometric composition.

Lynch and others (1960) state that U₃O₈-ThO₂ powder mixtures may be sintered in air if they contain more than 29.6 m/o ThO₂. The U₃O₈ to U₄O₇ transition above 1000°C does not break the compact; the solid solution then forms as the temperature is raised and U₄O₉ does not reform on cooling. This technique is a convenient one for fabrication of UO₂-ThO₂. As before, the sintered product will be non-stoichiometric unless cooled, or reheated and cooled, in H₂. Also, in view of the phase diagram information discussed in Section 4.1, 50 m/o ThO₂ 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)O₂ solid solutions depends on the UO₂ 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 ThO₂.

Values for uranium valency reported from four investigations are given in Table 1. From these results it can be seen that (UTh)O₂ with ThO₂ 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 UO₂+x and (UTh)O₂+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 UO₂ is approximately 5.47 Å, while that of U₄O₉ is 5.44 Å (Gronwold 1955). The figures of Anderson and others (1954) for (UTh)O₂+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)O₂+x solid solutions is that uranium can be lost at significant rates by evaporation of UO₂. Workers at the General Electric Co. (1964) have studied the vapour pressure of UO₂ over (UTh)O₂+x at various temperatures in air, and some of their results are given in Table 3. PuO₂ was found to be a much more efficient additive for reducing uranium loss than was ThO₂, which merely acted as an ideal solid solution diluent for UO₂.

Solutions containing YO₂ showed considerable departure from ideal behaviour and in this way reduced the UO₂ 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 UO₂ content in (UTh)O₂+x, and 1 m/o for 60 m/o UO₂.

5. PuO₂ - BASED SYSTEMS

PuO₂ is a fluorite-type oxide. It readily loses oxygen on heating in vacuum, neutral, or reducing atmospheres to form PuO₁.₉₉ or one of the three forms of Pu₂O₃, but can incorporate excess oxygen only up to Pu₂O₃.₈₃ (Drummond and Welch 1957). Pu₂O₃ and ThO₂ form a complete series of solid solutions (Wittenburg 1963); their oxidation-reduction behaviour has not been reported but at least at high ThO₂:Pu₂O₃ ratios they would remain stoichiometric within close limits when heated in air. PuO₂ and UO₂ form a complete series of solid solutions. According to Brett and Russell (1963), compositions containing 20 m/o or more of Pu₂O₃ oxidise to form only single-phase fluorite phases with a uranium valency of up to 5; at lower PuO₂ contents an orthorhombic U₄O₇-type phase was also formed. Compositions containing 20 m/o or more Pu₂O₃ can form two phases, an
oxygen-deficient "UO$_3$ - 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 UO$_2$-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. (PuUTh)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


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


<table>
<thead>
<tr>
<th>Authors</th>
<th>ThO₂ Content</th>
<th>Uranium Valency</th>
<th>Conditions</th>
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<td>Anderson and others (1954)</td>
<td>24</td>
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<td>After oxidation in air, or in O₂ at 5-15 cm pressure, at up to 1400°C</td>
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<td>~4.5</td>
<td>Maximum valency, after oxidation in air at 1200°C</td>
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**TABLE 3**

**VAPOUR PRESSURE OF UO₂ OVER (UTh)O₂+x**

(General Electric Co. 1964)

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<tr>
<th>UO₂:ThO₂ Mole Ratio</th>
<th>Temperature (°C)</th>
<th>Vapour Pressure x 10⁷ (atm)</th>
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<td>1:1</td>
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