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CHEMICAL REACTIONS DURING ThO_2
AND ThO_2 - UO_2 FUEL FABRICATION

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ABSTRACT**Chemical Reactions During ThO₂
and ThO₂-UO₂ Fuel Fabrication****J. C. Clayton****Westinghouse Electric Corporation
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The chemical reactions that occurred during the various processing steps used in the fabrication of thorium and thorium-uranium fuel pellets for the Shippingport Light Water Breeder Reactor are discussed. These include (1) precipitation and pyrolysis of thorium oxalate, (2) precipitation, calcination, and hydrogen reduction of ammonium diuranate, (3) comminution, granulation with an organic binder, and cold compaction of ThO₂ and ThO₂-UO₂ powders, (4) decarburization of the organic binder in CO₂ at temperatures up to 925°C, and (5) sintering in moist hydrogen at temperatures up to 1790°C.

Thorium oxalate precipitation and pyrolysis temperatures were the primary process variables for controlling the resulting thorium powder properties. Coprecipitated metal sulfates were converted to transition metal sulfides during calcining — the conversion of thorium oxalate to thorium oxide. The critical variable for controlling the uranium powder properties was the hydrogen reduction temperature. During the decomposition and hydrogen reduction of ammonium diuranate to UO₂ at 625°C, stable coprecipitated phosphates, like Ca₃(PO₄)₂, survived. Metal phosphide formation then occurred during CO₂ pretreatment by carbon reduction of the phosphates.

Thermodynamic analyses showed that the efficiency of carbon removal from cold-compacted ThO₂ and ThO₂-UO₂ pellets by CO₂ oxidation increases with temperature and, at temperatures around 900°C, substantially complete oxidation of carbon to carbon monoxide gas should occur. The carbon content of ThO₂ and ThO₂-UO₂ fuels was further reduced during the initial heating in the hydrogen sintering cycle through the formation of methane gas. Additions of water vapor to the hydrogen sintering atmosphere also aided in carbon removal. Experimental measurements (gas chromatography and carbon analyses) were in agreement with the thermodynamic predictions. However, minute amounts of metallic sulfides and phosphides survived the high-temperature hydrogen sintering treatment and have been identified by electron microprobe and X-ray analyses. These compounds were formed as a result of chemical reactions among various cation and anion impurities that were present in the ThO₂ and UO₂ powders. Chemical reactions occurred between the transition metals Fe, Cr, and Ni and residual sulfate in the case of ThO₂ and phosphate in the case of UO₂.

CHEMICAL REACTIONS DURING THORIA AND THORIA-URANIA FUEL FABRICATION

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SUMMARY

Thoria was the fertile fuel in the Shippingport Light Water Breeder Reactor (LWBR) and was the base oxide for thoria-uranium fuels. A practical process was developed for producing high density ThO_2 and $\text{ThO}_2\text{-UO}_2$ fuel pellets. The chemical reactions that occurred during the various processing steps are discussed.

INTRODUCTION

The processing steps used in the fabrication of thoria and thoria-uranium fuel pellets for the Shippingport LWBR included (1) precipitation and pyrolysis of thorium oxalate, (2) precipitation, calcination, and hydrogen reduction of ammonium diuranate, (3) comminution, granulation with an organic binder, and cold compaction of ThO_2 and $\text{ThO}_2\text{-UO}_2$ powders, (4) decarburization of the organic binder in CO_2 at temperatures up to 925°C , and (5) sintering in moist hydrogen at temperatures up to 1790°C .

BACKGROUND

Thorium oxalate precipitation and pyrolysis temperatures were the primary process variables for controlling the resulting thoria powder properties. The thorium oxalate precipitation temperature affected surface area, bulk density, particle size and size distribution not only of the precipitated thorium oxalate but also of the calcined ThO_2 powder [1,2]. Lower precipitation temperatures resulted in greater surface areas, smaller particle sizes, and lower bulk densities for calcined ThO_2 powders. Lower calcination temperatures favored a more active powder that consisted of porous particles with large surface area. The uranium powder was prepared by converting purified uranyl nitrate into oxide through precipitation and direct hydrogen reduction of ammonium diuranate. The critical variable for controlling UO_2 powder properties was the hydrogen reduction temperature.

THORIUM OXALATE PRECIPITATION AND CALCINATION

Oxalic acid, the reagent used to precipitate thorium oxalate from thorium nitrate solution, contains up to 500 ppm residual sulfate in the form of alkali and alkaline earth metal sulfates. Some of this sulfate is carried along with the precipitated thorium oxalate. For example, sulfate is quite strongly coprecipitated with calcium oxalate due to the low solubility of calcium sulfate. Other available cations can also coprecipitate with sulfate. In addition, this type of anion coprecipitation is enhanced by precipitation in hot solutions. The LWBR thorium oxalate was precipitated at 38°C , thus making sulfate coprecipitation more likely.

During calcining (the conversion of the thorium oxalate to thorium oxide) the metal sulfates are converted to a mixture of the sulfides of chromium, iron, and nickel. These metals are the main elements in Inconel, the alloy used as a container in the calcining operation, and in the stainless steel hardware used in the thorium oxalate precipitation.

The calcination temperatures for the thoria with calcium sintering aid additions and for the binary thoria (no calcium additions) were 954°C and 1038°C , respectively. The chemical reaction that occurs [3] is $\text{MSO}_4 + 4\text{C} \rightarrow \text{MS} + 4\text{CO}$ where M represents Cr, Fe, Ni or possibly Th. Carbon is available as a result of oxalate decomposition.

The free energies of formation for some of these transition metal sulfides [4,5] are

ΔG , Free Energy of Formation (calories/mole)

Sulfide	400°C	797°C	954°C	1038°C
FeS	-27,457	-22,471	-20,438	-19,368
FeS ₂	-13,065	+4900	+11,865	+15,645
NiS	-23,401	-16,227	> mp	> mp
Ni ₃ S ₂	-26,493	-18,750	> mp	> mp
ThS ₂	-135,635	-133,650	-132,865	-132,445

All of the sulfides could form at the lower temperatures, but, because of their relatively low melting points (790-797°C), little if any nickel sulfide formation would be expected.

AMMONIUM DIURANATE PRECIPITATION AND REDUCTION

The sole reason for using thorium in nuclear reactors is that thorium can be converted by neutron capture into fissile U-233, an isotope of uranium that does not exist in nature. However, phosphate is picked up by tributyl phosphate extraction of uranyl nitrate during purification and separation of U-233 from the various fission products. Some of this phosphate is carried along with the precipitated ammonium diuranate. For example, uranyl phosphate and mixed phosphates are readily precipitated in aqueous solutions [6]. Most cations precipitate phosphates. As with the sulfate, anion coprecipitation is enhanced in hot solutions. The LWBR ammonium diuranate was precipitated at 52°C.

During hydrogen reduction of ammonium diuranate to UO₂ at 625°C, the less stable phosphates with low melting points decompose, melt, and vaporize while the stable phosphates, like Ca₃(PO₄)₂, survive.

DECARBURIZATION PRETREATMENT AND SINTERING REACTIONS

The single ThO₂ or blended ThO₂-UO₂ powders were next comminuted in a reduction process (micronizing) that involved the collision of like particles in a rubber-lined chamber. Some metallic (Fe, Ni, Cr), carbon, and sulfur pickup from the micronizer was detected, especially with multimicronizing. The comminuted powders were agglomerated with an organic binder to form millimeter-size, free-flowing globules that were pressed into pellets. The binder was removed during a decarburization heat treatment in carbon dioxide (425°C for ThO₂; 925°C for ThO₂-UO₂).

The organic binder used for LWBR fuels was Carbowax 6000, a polyethylene glycol polymer in the form of a linear chain of oxygen-linked ethyl groups. On heating, Carbowax 6000 decomposes into volatile gases, carbon, and partially pyrolyzed polymer residues. Below 400°C, burnout removal of binder, although incomplete, is primarily by polymer chain degradation into volatile products. A four hour, 425°C, CO₂ pretreatment of ThO₂ and ThO₂-UO₂ results in 50% removal of binder carbon as volatiles. Around 600°C, elemental carbon is the main residue; and the chemical reaction for its removal is oxidation by CO₂.

During developmental work that preceded manufacture of LWBR fuel pellets, effluent gases were examined by gas chromatography for a series of laboratory pretreatment runs in which green thorla pellets were heated in flowing CO₂ to remove the Carbowax binder. Methane was detected at or near room temperature. Around 280°C, the higher hydrocarbons appeared. Carbon monoxide and water vapor, also detected in the effluent stream at these temperatures, are probably Carbowax decomposition products, although they could have resulted from chemical reactions such as CO₂ + H₂ → CO + H₂O and 2C + O₂ → 2CO. At higher temperatures (600-925°C) the main residue was elemental carbon, which is removed by oxidation to carbon monoxide according to the reaction C + CO₂ → 2CO. The presence of water and oxygen throughout the pretreatment indicates that they also aid in carbon removal by the reactions C + H₂O → CO + H₂, 2C + O₂ → 2CO, and C + O₂ → CO₂. All of these reactions were found to be thermodynamically possible (Figures 1 and 2). Thus, the efficiency of carbon removal from green ThO₂ and ThO₂-UO₂ pellets by oxidation reactions increases with temperature and, at

temperatures around 900°C, thermodynamic considerations indicate that substantially complete oxidation of carbon should occur.

However, pellet coring was initially observed in large (2-cm diameter) thorium pellets during LWBR production startup. Pellet coring is characterized by low density in the geometric center of the pellet and is associated with large pores, high pore frequency, and lack of grain structure [7]. Pellet coring results from a high rate of temperature rise during sintering combined with a high residual carbon content in the residual pellet. Under these conditions, pellet surfaces densify before the carbonaceous products within the central region can diffuse to the pellet surface and react with the hydrogen atmosphere. This sintering at the surface traps the carbonaceous products inside the pellet, prevents their escape, and allows excessive internal pressure buildup that can lead to swelling or fracture and to lack of densification in that region. Thorium pellet coring was corrected by the use of wet hydrogen to remove residual carbon, by loading the pellets in an open array for pretreatment and sintering, and by the use of a lower pellet heating rate in sintering.

During the CO₂ pretreatment cycle, carbon will not combine with LWBR fuel oxides to form actinide carbides (Figures 3 and 4). In fact, any uranium or thorium carbides initially present should be oxidized to UO₂ or ThO₂ by the CO₂ [1]. Stoichiometric UO₂ can be further oxidized by the CO₂, but the subsequent hydrogen sintering reduces the hyperstoichiometric oxide to the stoichiometric condition as well as removes the residual carbon.

The carbon content of the LWBR fuels was further reduced during the initial heating (low temperature region) in the hydrogen sintering cycle through formation of methane by the reaction, $C + 2H_2 \rightarrow CH_4$. Additions of water vapor to the hydrogen sintering atmosphere also enhanced carbon removal in the ThO₂ and ThO₂-UO₂ pellets (Figure 2). Most of the carbon detected in pretreated and even sintered pellets was identified as CO₂ chemically adsorbed on pellet surfaces.

SULFUR PRETREATMENT AND SINTERING REACTIONS

During pretreatment, any oxygen present in the CO₂ atmosphere could convert the sulfides into metal oxides by the reactions $2MS + 3O_2 \rightarrow 2MO + 2SO_2$ and $ThS_2 + 3O_2 \rightarrow ThO_2 + 2SO_2$. The free energies for these reactions [4] are tabulated below. The pretreatment temperature for ThO₂-UO₂ reaches 925°C and thus further loss of NIS could occur during pretreatment. It is known that the sulfides of chromium are easily attacked by oxidizing agents but not by reducing agents. For example, CrS is stable in hydrogen at 1200°C, but, when heated in air or oxygen, it decomposes into chromic oxide and SO₂.

ΔG Oxidation Reaction (calories/mole)

Sulfide	25°C	400°C	797°C	925°C
NIS	-206,081	-188,551	-170,267	>mp
FeS	-213,085	-199,215	-183,382	-178,430
ThS ₂	-305,785	-278,878	-250,148	-240,948

During hydrogen sintering at temperatures up to 1790°C, the following reactions can occur [3,4]:

1. Loss of sulfur, melting and vaporization of transition metal sulfides. The melting point data predict a greater loss of NIS and FeS than CrS during the sintering process.
2. Reduction of sulfides through the reaction $MS + H_2 \rightarrow M + H_2S$. The free energies for transition metal reduction reactions [4] are listed below, and the thermodynamic data indicate that metal sulfide reduction becomes more likely as the sintering temperature increases.

ΔG Reduction Reaction (calories/mole)

Sulfide	25°C	400°C	797°C	1197°C
NiS	+11,791	+9,766	+7,278	> mp
FeS	+14,452	+13,822	+13,522	+13,115

3. Oxidation of sulfides by the water vapor in the sintering atmosphere through the reactions $MS + H_2O \rightarrow MO + H_2S$ and $ThS_2 + 2H_2O \rightarrow ThO_2 + 2H_2S$. Some free energies for this type of reaction are given below [4,5].

ΔG Oxidation Reaction (calories/mole)

Sulfide	25°C	400°C	797°C	1197°C
FeS	+11,853	+11,917	+12,532	+12,685
NiS	+15,355	+17,249	+18,910	> mp
ThS ₂	-68,994	-55,829	-42,062	-28,295

Because the free energies of the transition metal sulfide water vapor oxidation reactions are positive and increase with increasing temperature, in contrast to ThS₂, water vapor oxidation of the transition metal oxides seems unlikely.

PHOSPHOROUS PRETREATMENT AND SINTERING REACTIONS

Metal phosphide formation can occur during CO₂ pretreatment by carbon reduction of the phosphates by the reactions $MPO_4 + 4C \rightarrow MP + 4CO$ and $M_3(PO_4)_2 + 8C \rightarrow M_3P_2 + 8CO$. CrP and Fe₂P have been prepared by carbon reduction of their phosphates. In addition, any oxygen present in the CO₂ atmosphere could convert the metallic impurity phosphides into metal oxides and phosphorous oxides. The phosphorous oxides could then react with the actinide oxides to form mixed UO₂-P₂O₅ and ThO₂-P₂O₅ systems in the 400-925°C temperature range [8-11].

Most metals form phosphides, and metal phosphide formation can occur by several reactions [10] during the initial stages of hydrogen sintering as follows:

1. Phosphate reduction by the reaction $MPO_4 + 4H_2 \rightarrow MP + 4H_2O$.
2. Direct reaction of the elements by the reactions $M + P \rightarrow MP$, $M + 2P \rightarrow MP_2$, and $3M + 4P \rightarrow M_3P_4$. Phosphorous can combine with the common metallic impurities (Fe, Ni, Cr) in LWBR fuels to form phosphides. The compounds UP, UP₂, and Th₃P₄ can also form by direct combination of the elements.
3. Solid solution formation. Phosphorous dissolves extensively in iron and steel, and iron is present in the Inconel and stainless steel contaminants in the thorium powder. The phase diagram of the iron-phosphorous system exhibits a liquid region in the temperature range of 1050-1550°C.

During the intermediate and final stages of hydrogen sintering at temperatures up to 1790°C, the reactions that can occur [6,8-10] are melting and vaporization of the metallic impurity phosphides but not the actinide phosphides, conversion of the higher phosphides to lower phosphides, and reduction and decomposition of the less stable phosphides. Fe₃P₄, when heated in hydrogen, is reduced to FeP. UP₂ and U₃P₄ convert to monophosphides at high temperatures.

FUEL PELLET ANALYSES

Minute quantities of impurity inclusions survived high-temperature hydrogen sintering and were detected in representative ThO_2 and $\text{ThO}_2\text{-UO}_2$ pellets by scanning electron microscope (SEM) and electron microprobe examination. Occasional metallic inclusions were identified as Cr-Fe-Ni alloys. Compound impurity inclusions, primarily concentrated at grain boundary triple junctions, differed in composition in the two oxides. In ThO_2 the major constituent was CrS associated with minor amounts of Fe and Ni. In the $\text{ThO}_2\text{-UO}_2$ fuel, the major constituent was phosphorous associated with Fe and Ni. CrS was also present. The amount of impurity inclusions as determined by SEM and microprobe techniques was consonant with bulk chemical analyses. The absence of any definite evidence of either thorium or uranium in the impurity inclusions indicates that the impurities did not react with the matrix during sintering. Sulfide impurities from source thorium nitrate have also been identified in sintered ThO_2 and $\text{ThO}_2\text{-UO}_2$ microspheres [12].

CONCLUSIONS

Minute amounts of metallic sulfides and phosphides, identified in sintered ThO_2 and $\text{ThO}_2\text{-UO}_2$ fuel pellets, were formed during the manufacturing process as a result of chemical reactions among various cation and anion impurities that were present in the ThO_2 and UO_2 powders. Chemical reactions occurred between the transition metals Fe, Cr, and Ni and residual sulfate in the case of ThO_2 and phosphate in the case of UO_2 .

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Figure 1

Figure 2

Figure 3

Figure 4