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CERAMIC NUCLEAR FUELS IN THE SYSTEM $\text{ZrO}_2\text{-CaO-UO}_2$

by

J. H. Handwerk, G. D. White,
and D. C. Hill

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ABSTRACT

Potential nuclear fuels in the system $\text{ZrO}_2\text{-CaO-}\text{UO}_2$ were investigated. Cubic fluorite-type solid solutions, as indicated by X-ray diffraction patterns, were formed by sintering CaO-stabilized ZrO_2 and U_3O_8 compacts in either air or hydrogen. A continuous solid solution was found between urania and stabilized zirconia with hydrogen sintering at 1750°C . Air sintering produced a limited region of solid solution in the stabilized zirconia portion of the system at 1450°C . Results on phase identification, oxidation behavior, and water corrosion are presented.

INTRODUCTION

The success of reactors fueled with urania⁽¹⁾ and thoria-uranium⁽²⁾ has stimulated interest in other refractory oxide systems for nuclear power applications. The systems of interest would be those in which UO_2 is combined with a second refractory oxide having good chemical stability and a low neutron cross section. The more common oxides which fulfill these general criteria are magnesia, alumina, and zirconia.

The addition of a second inert oxide to urania would lower the uranium atom concentration of the fuel. This dilution would tend to complicate the design of a reactor. It can be justified, however, if the fuel is to be used as a high burnup spike in the reactor core or if the additive will enhance certain properties of the urania, such as its resistance to oxidation.

Cubic fluorite UO_2 when subjected to a slight oxidizing atmosphere will eventually oxidize to U_3O_8 . This oxidation is accompanied by a volume expansion which may disrupt fuel elements comprised of UO_2 . Oxidized urania also exhibits an appreciable vapor pressure at temperatures in excess of 1200°C , and has demonstrated inferior fission product retention and irradiation stability when compared with UO_2 .

The stability of urania under oxidizing conditions may be improved by the formation of a stable refractory compound or by the formation of a solid solution which would inhibit the oxidation of the urania. This investigation had as one of its objectives a cursory study of compositions in the

systems $\text{MgO-}\text{UO}_2$, $\text{Al}_2\text{O}_3\text{-}\text{UO}_2$, and $\text{ZrO}_2\text{-}\text{UO}_2$ to determine if suitable nuclear fuels could be formed. This preliminary work was directed towards the preparation of compositions in the various systems, and the evaluation of some of these compositions under oxidizing and reducing conditions. These studies indicated that solid solutions in the system $\text{ZrO}_2\text{-}\text{UO}_2$ would have potential use as nuclear fuels, and, therefore, the work was concentrated in this system. The results of the other preliminary work, however, are reported, since they may be of interest in guiding future work.

PRELIMINARY INVESTIGATIONS

Mixtures of $\text{MgO-U}_3\text{O}_8$ and $\text{Al}_2\text{O}_3\text{-U}_3\text{O}_8$

Mixtures in the binary systems $\text{MgO-}\text{UO}_2$ and $\text{Al}_2\text{O}_3\text{-}\text{UO}_2$ were prepared by mixing from 10 to 70 w/o UO_2 (added as an equivalent amount of U_3O_8) with either fused crushed MgO or Al_2O_3 . The mixtures were dry blended in a pebble mill and were then cold pressed into pellets. The pellets thus formed were sintered in air at temperatures ranging from 1400 to 1750°C.

The mixtures of U_3O_8 and MgO which contained less than 30 w/o UO_2 produced good pellets on sintering, whereas those mixtures containing more than 30 w/o UO_2 appeared to have numerous cracks and were quite friable. Microscopic examination revealed that mixtures were two phase following sintering; no evidence of compound formation or solid solution as reported by Lambertson and Mueller⁽³⁾ was observed. This was not unexpected since the mixtures studied were heated rather rapidly to the sintering temperature, furnace cooled to room temperature, and then examined. By means of this procedure the mixtures were in all probability not at equilibrium. Several specimens were exposed to 300°C water and were found to disintegrate in a few hours. For this reason it did not appear that a stable solid solution could be prepared from MgO and U_3O_8 which would be corrosion resistant to water, and work in this system was abandoned.

Mixtures of U_3O_8 and Al_2O_3 containing up to 50 w/o UO_2 sintered into good pellets. Above 50 w/o UO_2 the pellets appeared to have numerous small cracks, were rather soft, and were easily crushed. Microscopic examination of these mixtures revealed that all compositions were a heterogeneous mixture of Al_2O_3 and an oxidized UO_2 . Both phases were readily distinguishable, although the Al_2O_3 phase was discolored by what appeared to be diffusion of urania into the alumina grains. As there was no evidence of compound or solid solution formation in the mixtures examined in this system, it appeared that no suitable fuels could be formed.

Mixtures of $\text{ZrO}_2\text{-}\text{UO}_2$

A unique series of solid solutions has been reported in the system $\text{ZrO}_2\text{-}\text{UO}_2$. Lambertson and Mueller⁽⁴⁾ found that more than 40 m/o ZrO_2

can be incorporated in the cubic fluorite structure of UO_2 , and that tetragonal ZrO_2 can dissolve about 20 m/o UO_2 at temperatures greater than 1500°C . Wolten⁽⁵⁾ also investigated the system and deduced that continuous fluorite-type solid solution between end members existed at temperatures greater than 1900°C . This investigator also reported that tetragonal solid solutions between the limits 15 to 20 m/o UO_2 were stable down to room temperature. Voronov et al.,⁽⁶⁾ reported solid solution limits of 15 m/o ZrO_2 in UO_2 and 15 m/o UO_2 in ZrO_2 . These investigators reported that prolonged heat treatments at elevated temperatures (25 to 200 hr at 1400 to 1500°C) were necessary for compositions to approach equilibrium conditions. The suggested phase diagram for the system $\text{UO}_2\text{-ZrO}_2$ is shown in Figure 1.

106-6474

Figure 1. Phase Equilibrium Diagram for the System $\text{UO}_2\text{-ZrO}_2$ (after Voronov et al.)

and ZrO_2 , and from this investigation it would appear that sound pellets could not be made in a single sintering operation.

The volume instability can be prevented by reacting zirconia with such oxides as CaO , CeO_2 , MgO , Y_2O_3 , and other rare earth oxides. These oxides form solid solutions with zirconia in either the tetragonal or cubic fluorite-type crystal systems. Of these oxides CaO and MgO are the most common, and it has been reported⁽⁸⁾ that 15 to 28 m/o CaO in zirconia will form cubic solid solutions which are stable up to the liquidus temperature. Two phase regions have been reported above and below these compositional limits, as shown in Figure 2.

Belle⁽⁷⁾ investigated two-phase monoclinic-tetragonal compositions in the system $\text{ZrO}_2\text{-UO}_2$ which contained less than 15 m/o UO_2 . Disintegration of sintered compacts was observed after relatively short exposure to high-temperature water. Apparently the transformation temperature of monoclinic zirconia was lowered due to urania solid solution, and detrimental volume changes occurred during corrosion testing. This behavior in these monoclinic-tetragonal compositions would serve to limit their usefulness as nuclear reactor fuels. However, to evaluate this behavior, a mixture of 90 w/o ZrO_2 and 10 w/o UO_2 (added as an equivalent amount of U_3O_8) was prepared. This mixture was cold pressed and sintered in air at 1450°C . Pellets then formed developed numerous small cracks during sintering which was attributed to the monoclinic-tetragonal inversion of zirconia, which took place at approximately 1000°C . X-ray diffraction patterns indicated the incomplete reaction of the U_3O_8

Figure 2. Phase Equilibrium Diagram for the System ZrO_2 -CaO (after Duwez et al.)

In the preliminary investigations, mixtures of 10 to 20 w/o UO_2 (added as U_3O_8) and ZrO_2 stabilized with 10 w/o MgO were compacted and sintered in air at temperatures ranging from 1400 to 1700°C. Pellets formed from these mixtures sintered without visible defects; however, X-ray diffraction patterns indicated incomplete formation of solid solution. A similar series of mixtures prepared from CaO-stabilized zirconia appeared to form a more complete solid solution on the single sintering used. For this reason this investigation was confined to the evaluation of compositions in the systems ZrO_2 -CaO- UO_2 , with most attention directed toward the zirconia-rich portion of the system.

PROCEDURE

Compositions in the system ZrO_2 -CaO- UO_2 were prepared from mixtures of low-hafnium, high-purity ZrO_2 ,* reagent-grade CaCO_3 , and U_3O_8 . The compositions investigated are shown in Figure 3. Specimens corresponding to these compositions were prepared by two techniques.

Figure 3
Compositions Investigated in the System ZrO_2 -CaO- UO_2 .

106-4597

*Obtained from the Wah Chang Chemical Corporation, Albany, Oregon.

The first method was to press mixtures of calcia-stabilized ZrO_2 and U_3O_8 . The zirconia was stabilized prior to mixing with U_3O_8 to avoid the volume change during sintering caused by the inversion from monoclinic to tetragonal zirconia. Various mixtures of zirconia-calcia (Table I) were prepared by dry milling ZrO_2 and CaCO_3 . These mixtures were calcined in air at 1450°C for 8 hr, and X-ray diffraction patterns were taken to identify the structures present.

Table I

CALCIA-STABILIZED ZIRCONIA COMPOSITIONS

CaO, w/o	ZrO ₂ , w/o	CaO, m/o	ZrO ₂ , m/o	Structures Present
8.0	92.0	16.0	84.0	sFCC + wM
10.0	90.0	20.0	80.0	FCC
15.0	85.0	28.0	72.0	sFCC + wCaZrO ₃
20.0	80.0	35.0	65.0	sFCC + mCaZrO ₃
30.0	70.0	48.0	52.0	wFCC + sCaZrO ₃

LEGEND: FCC - Fluorite-type Solid Solution
M - Monoclinic Zirconia
s - Strong Pattern
m - Medium Pattern
w - Weak Pattern

The calcined calcia-stabilized zirconia was in the form of a soft clinker and could be easily crushed. This material was mixed with U_3O_8 by dry milling for 3 hr.

The second method used to prepare the ternary compositions was to calcine in air, at temperatures from 1400 to 1700°C , mixtures of ZrO_2 , CaCO_3 , and U_3O_8 . Initially, the calcined material was crushed by wet grinding in a porcelain pebble mill for from 18 to 24 hr, followed by dewatering and drying of the slurry; however, specimens formed from these mixtures were found to contain an estimated 8 to 10 v/o of a phase which had been liquid during sintering. This liquid phase leads to a typical microstructure in these sintered compacts as shown in Figure 4. To minimize the liquid phase, the calcined material was wet ground in rubber-lined pebble mills with stabilized zirconia as the grinding medium. Examination of specimens prepared from this material revealed that they were virtually free of liquid phase.

26065

250X

Figure 4. Microstructure of a ZrO_2 -9.5 w/o CaO -5 w/o UO_2 Composition Sintered in Air at 1725°C for 4 Hr.

The powders were in some instances mixed with 3 w/o polyethylene glycol* prior to pressing to improve pressing characteristics and the green strength of the compacts. Specimens in the form of right cylinders were pressed in a hardened steel die at pressures ranging from 7,000 to 30,000 psi and in an isostatic chamber at 50,000 psi. Pellets were sintered (from 1350°C to 1750°C) in hydrogen on sheet molybdenum and in air on platinum or in stabilized zirconia crucibles. Crystalline structures present in the sintered compacts were identified from X-ray diffraction patterns, and lattice parameters of fluorite-type structured solid solutions were calculated from back-reflection lines.

Studies on the oxidation behavior of the ternary mixtures were limited to compositions along the tie-line (Figure 3) connecting the binary composition 20 m/o CaO -80 m/o ZrO_2 with UO_2 . Urania content (added as U_3O_8) varied from 4.3 to 77.5 m/o UO_2 . Compacts, without the binder addition, were pressed isostatically at 50,000 psi and were sintered in hydrogen for 4 hr at 1650°C . Weight-loss data were taken on the sintered pellets to calculate the stoichiometry or oxygen-to-metal atom ratio of each composition. X-ray diffraction data were taken to confirm solid-solution formation. Pellets were crushed to minus 200 mesh, and powders were oxidized at 800°C and 1000°C for 126 and 96 hr, respectively. A few compositions

*Carbowax 4000. Obtained from Union Carbide Chemical Company, South Charleston, West Virginia.

were oxidized at 1200°C to 1400°C for 50 hr. Weight changes were measured and oxygen-to-metal atom ratios were calculated on the assumption that weight gains were due entirely to oxidation of U^{4+} ions. Structural changes resulting from oxidation were determined from X-ray diffraction data.

Water corrosion studies were performed on the composition 5 m/o UO_2 -9.5 m/o CaO -85.5 m/o ZrO_2 . Pellets were formed at 20,000 psi and were sintered in air for 4 hr at 1650°C. Also, this mixture was calcined for 4 hr at 1650°C and was ground in a pebble mill to pass a 325 mesh screen. Pellets were pressed at 20,000 psi and were sintered in air for 4 hr at 1725°C. Two specimens from each heat treatment were subjected to static autoclave tests in degassed distilled water and in air-saturated distilled water at 360°C and 2700 psi. Two specimens of each heat treatment were steam corroded at 540°C and 600 psi. Cumulative weight data were taken at approximately 30-day intervals for exposure up to 105 days.

DISCUSSION AND RESULTS

The phases resulting from the reaction of the various calcia-zirconia compositions at 1450°C are listed in Table I. The results indicate that for the time and temperature of reaction used a 16-m/o addition of calcia was insufficient to form a product composed only of the fluorite-type structure; however, a 20-m/o additive of calcia resulted in a product with only the fluorite-type structure present. Larger additions of calcia resulted in the formation of orthorhombic calcium zirconate in addition to the fluorite-type solid solution. These reacted calcia-zirconia compositions mixed with U_3O_8 as well as a calcined mixture of ZrO_2 , $CaCO_3$ and U_3O_8 were used in this investigation of the ZrO_2 - CaO - UO_2 system. Specimens prepared from either material were essentially the same, for the heat treatments used in sintering were sufficiently prolonged to allow the compositions to approach equilibrium.

Phase Identification

With urania additions to CaO -stabilized zirconia, solid solubility was observed over a considerable portion of the system ZrO_2 - CaO - UO_2 when compacts were sintered in hydrogen at 1750°C, as may be observed in Figure 5.

A two-phase region, fluorite solid solution plus $CaZrO_3$, was found above the single-phase fluorite region. The boundary line between fluorite-type solid solution and the two-phase fluorite-type and tetragonal zirconia areas was predicted from previous UO_2 - ZrO_2 and CaO - ZrO_2 phase investigations.^(3,5,7) Compositions containing more than 50 m/o UO_2 along the tie-line from UO_2 to 35 m/o CaO -65 m/o ZrO_2 were single-phase fluorite-type solid solutions. The same condition existed above 27 m/o UO_2 along the tie-line from UO_2 to 28 m/o CaO -72 m/o ZrO_2 . Complete solid

106-4595

Figure 5. Fluorite Solid Solution Limits for ZrO_2 - CaO - U_3O_8 Mixtures Fired in Hydrogen at 1750°C for 6 Hr.

28 m/o CaO -72 m/o ZrO_2 and in compositions containing more than 15 m/o UO_2 along the tie-line from UO_2 to 20 m/o CaO -80 m/o ZrO_2 . Calcium uranate and monoclinic zirconia existed at higher urania concentrations.

106-6475

Figure 6. Lattice Parameters for the System $(\text{Zr}_{0.80}\text{Ca}_{0.20})\text{O}_{1.80}$ - UO_2

solution was noted, at all urania contents, along the tie-line from UO_2 to 20 m/o CaO -80 m/o ZrO_2 . Lattice parameters from the compositions along the tie-line UO_2 -($\text{Zr}_{0.80}\text{Ca}_{0.20}$) $\text{O}_{1.80}$ were calculated from X-ray back-reflection data. As shown in Figure 6, the parameters deviated slightly from ideal solid solution values.

A relatively small region of solid solution existed in the CaO -stabilized zirconia portion of the ternary system urania-zirconia-calcia when compacts were air sintered at 1450°C . This region is shown in Figure 7. Fluorite-type solid solutions were not formed by air-sintering techniques in compositions containing more than 20 m/o UO_2 along the tie-line from UO_2 to

106-4593

Figure 7. Fluorite Solid Solution Limits for ZrO_2 - CaO - U_3O_8 Mixtures Fired in Air at 1450°C for 6 Hr.

106-6473

Figure 8. Differences in Lattice Parameters for Unoxidized and Oxidized Compositions in the System $(\text{Zr}_{0.80}\text{Ca}_{0.20})\text{O}_{1.80}-\text{UO}_2$.

tion of U_3O_8 was found in oxidized powders containing more than 70 m/o urania.

When powders were oxidized at 1000°C , the fluorite structural stability was limited to compositions containing less than 20 m/o urania. X-ray diffraction patterns for oxidized compositions of 27 to 58 m/o urania contained lines for hexagonal U_3O_8 , monoclinic ZrO_2 , and rhombohedral CaUO_4 .

Oxygen-to-metal atom ratios of oxidized powders, calculated from weight-change data, are shown in Figure 9. The stoichiometry of the initial compositions prepared by hydrogen sintering at 1650°C is also given for comparison. Fluorite-type structures which were stable when oxidized at 800°C had oxygen-to-metal atom ratios of less than 2.05 for compositions containing up to 35 m/o urania. The 1000°C oxidation

Oxidation Behavior

X-ray diffraction and weight-change data were utilized to determine structural stability and stoichiometry of oxidized compositions. Differences in lattice parameters in the system $\text{UO}_2-(\text{Zr}_{0.80}\text{Ca}_{0.20})\text{O}_{1.80}$ were noted between unoxidized compositions and compositions oxidized at 800°C . Contraction of the unit cell, as shown in Figure 8, was observed for oxidized compositions containing up to 30 m/o urania. Similar results have been reported for the systems thoria-urania⁽⁹⁾ and ceria-urania.⁽¹⁰⁾ When higher urania compositions (35 to 60 m/o urania) were analyzed, a body-centered cubic structure and hexagonal U_3O_8 were evident from X-ray diffraction patterns. Only the hexagonal modifica-

106-6471

Figure 9. The Effect of Atmosphere on the Oxygen to Metal Atom Ratios in the System $(\text{Zr}_{0.80}\text{Ca}_{0.20})\text{O}_{1.80}-\text{UO}_2$.

treatment led to compositions having ratios less than 2.00 exhibited structural stability. From these data it may be deduced that structural stability exists for all compositions having ratios below 2.00 to 2.05. Limited weight-change data at higher temperatures (1200°C to 1400°C) indicate oxygen-to-metal atom ratios intermediate to the 800°C and 1000°C curves. The possibility of urania volatility increases with increasing temperature making accurate expression of oxygen-to-metal atom ratios difficult.

Water Corrosion

Cumulative weight-change data for low-urania compositions subjected to water and steam environments, shown in Table II, indicated good corrosion resistance. Only slight edge chipping of the pellets and some surface discoloration from autoclave deposits were noted after long exposure times. There was no appreciable difference in behavior with the degassed or with the air-saturated distilled water.

Table II

WATER CORROSION DATA FOR 85.5% ZrO₂-9.5% CaO-5% UO₂ (m/o) COMPOSITION

Water Environment			Sintering Temp, °C	Density, gm/cm ³	Exposure Time, days	Average Weight Change, gm/cm ²
Type	Temp, °C	Pressure, psi				
Degassed, Distilled	360	2700	1650	5.14	32	-0.22
					93	-0.23
					185	-0.14
			1725	5.18	45	-0.55
					105	+0.34
					225	-0.42
Air-saturated, Distilled	360	2700	1650	5.14	32	-0.10
					93	-0.21
					185	-1.29*
			1725	5.18	45	-0.38
					105	+0.88**
					225	-0.03
Saturated Steam	540	600	1650	5.14	35	-0.20
					64	-0.26
					97	-0.38
			1725	5.18	41	-0.09
					105	-0.16
					167	-0.26

*Excessive Edge Chipping Noted.

**Surface Deposits Present.

SUMMARY

Compositions in the ternary system $\text{ZrO}_2\text{-CaO-}\text{UO}_2$ containing less than 30 w/o urania could be sintered in air; compositions of higher urania content were sintered successfully only in a hydrogen atmosphere. A fluorite-type structure solid solution of $\text{UO}_2\text{-CaO}$ -stabilized zirconia existed over much of the ternary system when samples were fired in hydrogen.

In oxidation tests at 800°C , up to 35 m/o urania was compatible with the fluorite-type structure. In tests at 1000°C , only 20 m/o urania was accommodated in the structure. The $\text{ZrO}_2\text{-CaO-}\text{UO}_2$ compositions investigated were strongly resistant to corrosion by water or steam environments.

ADDENDUM

The investigation reported here led to the manufacture of the fuel for the EBWR Spike Fuel Elements. The specimens for the fuel pins were in the form of right cylinders, 0.813 cm in diameter and about 1.27 cm in length. They were fabricated by compacting a mixture of U_3O_8 , CaCO_3 , and ZrO_2 , and sintering at 1675°C in air. The sintered pellets contained the cubic fluorite-type solid solution and had a chemical composition of 9.01 w/o UO_2 (93% enriched), 9.07 w/o CaO , and 81.92 w/o ZrO_2 . Approximately 150,000 specimens were manufactured. The description of this work has been previously reported in ANL-6168.⁽¹¹⁾

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