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PHASE RELATIONS
IN
CRYSTALLINE CERAMIC
NUCLEAR WASTE FORMS
THE SYSTEM $\text{UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2\text{-ThO}_2$
AT 1200°C IN AIR

DOE Research and Development Report

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Rockwell International

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THE SYSTEM $\text{UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2\text{-ThO}_2$
AT 1200°C IN AIR

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ABSTRACT

Steady-state phase relations in the system UO_{2+x} - CeO_2 - ZrO_2 - ThO_2 were determined for application to phase relations in the high-level crystalline ceramic nuclear waste form "Supercalcine-Ceramics." Samples were treated at 1200°C at an oxygen partial pressure of 0.21 atm and a total pressure of 1 atm. Phase assemblages were found to be composed of cubic solid solutions of the fluorite structure type, solid solutions based on ZrO_2 , and orthorhombic solid solutions based on U_3O_8 .

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1.0 INTRODUCTION

Crystalline ceramics for use in nuclear waste disposal have been under study for some time and are receiving increased attention today.⁽¹⁻⁷⁾ One important radionuclide host phase in the ceramics developed by McCarthy and coworkers^(3,4,8-13) is a solid solution of the fluorite* (CaF_2) structure type, which is assumed by the minerals uraninite $[(\text{U,Th,RE})\text{O}_{2+x}]$ and thorianite $[(\text{Th,U,RE})\text{O}_{2+x}]$.^(4,8-13) This phase, along with a rare earth (RE) orthophosphate phase isostructural with the mineral monazite $[(\text{Ce,La,Y,Th})\text{PO}_4]$, would contain most of the long-lived alpha-emitting nuclides of Th, U, Np, Pu, Am, and Cm.⁽¹⁴⁾ Compositions of present and future nuclear wastes will vary in the relative amounts of the elements that crystallize in the F_{ss} phase. Therefore, to facilitate the design of such ceramics, a study of phase relations in the system $\text{UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2\text{-ThO}_2\text{-RE}_2\text{O}_3$ ($\text{RE}=\text{Nd,Gd}$) in air and at a typical crystallization temperature of 1200°C has been undertaken. The subsystem to be described here is the system $\text{UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2\text{-ThO}_2$ as determined from samples fired at 1200°C in air at a total pressure of 1 atm.

*The shorthand term " F_{ss} " will be used throughout to denote a cubic solid solution of the fluorite structure type. Similarly, " Z_{ss} " and " $(\text{U}_3\text{O}_8)_{\text{ss}}$ " will be used to denote solid solutions based on ZrO_2 and U_3O_8 , respectively. In all cases, the term "solid solution" refers to an atomically mixed phase that is crystalline.

2.0 LITERATURE

A comprehensive literature survey was conducted for previous work on systems relevant to this study. A number of papers on the constituent metal oxide and binary oxide systems were found, but no higher order systems appear to have been studied. Descriptions of the end members and reported two-component systems are summarized below.

2.1 U-O

The phase relations among the uranium oxides are extremely complex and have been the subject of a great deal of experimental work. Smith et al.⁽¹⁵⁾ have recently compiled and evaluated the literature on this subject. Stoichiometric UO_2 crystallizes in the fluorite structure with a room temperature cubic cell constant of 5.4701 Å.⁽¹⁶⁾ Upon heating in the presence of oxygen, the U^{4+} present in the UO_2 oxidizes to 5+ or 6+ with charge balance provided by ionized oxygen interstitials with an accompanying decrease in the unit cell size.⁽¹⁷⁾ The fluorite structure is retained up to a composition of about $\text{UO}_{2.25}$ where, upon further oxidation, other phases begin to appear.⁽¹⁵⁾ At 1200°C in air, the equilibrium phase of uranium oxide is a phase of the approximate stoichiometry U_3O_8 .⁽¹⁸⁾ This phase was prepared by Pepin and Smith,⁽¹⁹⁾ and the x-ray powder pattern was indexed on the basis of an orthorhombic unit cell similar to that reported by Aykan and Sleight.⁽²⁰⁾ This phase appears to range in stoichiometry from $\text{UO}_{2.60}$ to $\text{UO}_{2.67}$ ⁽¹⁵⁾ with $\text{UO}_{2.62}$ reported to be the equilibrium composition in air at 1200°C.⁽²¹⁾

2.2 Ce-O

The cerium ion exists in two principal valence states, 3+ and 4+, corresponding to the oxides Ce_2O_3 and CeO_2 . Bevan and Kordis⁽²²⁾ have studied the phase relations in the Ce-O system and have observed a single-phase fluorite structure field extending from pure CeO_2 to about $\text{CeO}_{1.73}$ at temperatures greater than 1023°C. Sorensen⁽²³⁾ has studied the system from 900 to 1400°C

and provides data from which it can be concluded that the value of x in CeO_{2-x} is small (<0.001) at 1200°C and atmospheric oxygen pressure. Pure CeO_2 has a room temperature cubic cell constant of $5.4110 \text{ \AA}$.⁽²⁴⁾

2.3 ZrO_2

Zirconia is known to exist in three polymorphs. Mumpton and Roy⁽²⁵⁾ report the inversion from the tetragonal form to the room temperature monoclinic form to display marked thermal hysteresis. Using HfO_2 -free zirconia, they placed the inversion temperature at 1170°C during heating and 1040°C during cooling. Smith and Cline⁽²⁶⁾ have established the existence of a cubic polymorph stable at temperatures greater than about 2300°C . The high-temperature cubic form crystallizes with the fluorite structure with room temperature cubic cell constants of 5.09 and $5.10 \text{ \AA}$ as measured by Katz⁽²⁷⁾ and by Boganov, Rudenko, and Makarov,⁽²⁸⁾ respectively. ZrO_2 is essentially stoichiometric in air and must be fired at oxygen partial pressures of less than 10^{-5} torr to form an oxygen-deficient phase.⁽²⁹⁾

2.4 ThO_2

Thorium dioxide exists as a fluorite-structured oxide up to its melting point at about 3200°C .⁽³⁰⁾ The room temperature cubic cell constant of ThO_2 has been reported to be $5.5975 \text{ \AA}$ by Vogel and Kempter.⁽³¹⁾ Hammou and Deportes⁽³²⁾ have shown that ThO_2 is also essentially stoichiometric in air.

2.5 $\text{UO}_{2+x}-\text{CeO}_2^*$

Data from Hund, Wagner, and Peetz⁽³³⁾ indicate that the system at 1200°C in air consists of a single-phase region of (F_{ss}) extending from pure CeO_2 to

*Systems including uranium oxide will be referred to as "pseudo" systems due to the additional variable of atmospheric oxygen. For example, this system has two metal oxide end members, but is "pseudobinary" rather than "binary." The notation " UO_{2+x} " will be used for the uranium oxide end member for the same reason.

about 63 mol % UO_{2+x} . At higher UO_{2+x} concentrations a region of $[\text{F}_{\text{ss}} + (\text{U}_3\text{O}_8)_{\text{ss}}]$ occurs. Paul⁽³⁴⁾ observed no solubility of CeO_2 in U_3O_8 at 1250°C in 1 atm oxygen.

2.6 $\text{UO}_{2+x}\text{-ZrO}_2$

Ochs,⁽³⁵⁾ Verbetskii and Kovba,⁽³⁶⁾ and Mumpton and Roy⁽²⁵⁾ have studied the system $\text{UO}_{2+x}\text{-ZrO}_2$ in air at temperatures around 1200°C and provide data from which it can be concluded that the system at 1200°C in air consists almost entirely of $[(\text{U}_3\text{O}_8)_{\text{ss}} + \text{Z}_{\text{ss}}]$ with little or no solubility of either end member in the other.

2.7 $\text{UO}_{2+x}\text{-ThO}_2$

This system has been studied in air by Cohen and Berman,⁽³⁷⁾ Mumpton and Roy,⁽²⁵⁾ Friedman and Thoma,⁽³⁸⁾ Hund and Niessen,⁽³⁹⁾ and at 1 atm oxygen by Paul and Keller.⁽⁴⁰⁾ All the authors report a two-phase region of $[(\text{U}_3\text{O}_8)_{\text{ss}} + \text{F}_{\text{ss}}]$ at high UO_{2+x} concentrations and a single-phase region of (F_{ss}) extending to pure ThO_2 at lower UO_{2+x} concentrations. There is a good deal of disagreement as to the placement of phase boundaries in this system. The $(\text{F}_{\text{ss}})\text{-(F}_{\text{ss}} + \text{U}_3\text{O}_8)_{\text{ss}}$ phase boundary at 1200°C in air was placed at 50, 65, and 56 mol % UO_{2+x} by Cohen and Berman,⁽³⁷⁾ Friedman and Thoma,⁽³⁸⁾ and Hund and Niessen,⁽³⁹⁾ respectively. ThO_2 was found to be insoluble in U_3O_8 in 1 atm oxygen at 1250°C by Paul and Keller.⁽⁴⁰⁾

2.8 $\text{CeO}_2\text{-ZrO}_2$

The system $\text{CeO}_2\text{-ZrO}_2$ has been extensively studied, but few papers were found dealing with the temperature range about 1200°C. Data from all the authors surveyed⁽⁴¹⁻⁴⁵⁾ show that at 1200°C CeO_2 has ~20 mol % solubility in tetragonal ZrO_2 and that ZrO_2 has ~20 to 30 mol % solubility in CeO_2 , with a broad region of $(\text{F}_{\text{ss}} + \text{Z}_{\text{ss}})$ being the dominant feature of the system. Negas et al.⁽⁴⁵⁾ report the system to be pseudobinary at high temperatures because

of the tendency of the $(\text{Ce,Zr})\text{O}_2$ solid solutions to reduce to $(\text{Ce,Zr})\text{O}_{2-x}$ in air at temperatures greater than 1000°C . The system at 1200°C in air, however, will be considered a binary system as the value of x in $(\text{Ce,Zr})\text{O}_{2-x}$ is reported to be small (≤ 0.04) at 1200°C .⁽⁴⁵⁾

2.9 CeO_2 - ThO_2

Subsolidus relations in the system CeO_2 - ThO_2 have been studied by Passerini,⁽⁴⁶⁾ Whitfield, Roman, and Palmer,⁽⁴⁷⁾ Hammou et al.,⁽⁴⁸⁾ and Hoch and Sub Yoon.⁽⁴⁹⁾ All agree that the system consists of a complete solid solution series of the fluorite structure type. Compiled cell constant data indicate that the variation of cell constant is a linear function of composition throughout the system.

2.10 ZrO_2 - ThO_2

All five authors^(25,50-53) reporting work in this system agree that ThO_2 and ZrO_2 show only a slight mutual solubility at 1200°C . Solubilities range from a low of 2 mol % for each end member as estimated by Mumpton and Roy⁽²⁵⁾ to ~5 mol % as shown in the phase diagram of Sakurai and Arashi.⁽⁵¹⁾ The system at 1200°C consists of a two-phase region of $(\text{F}_{\text{ss}}+\text{Z}_{\text{ss}})$ extending almost to the pure end members.

3.0 EXPERIMENTAL

Determination of the pseudoquaternary system proceeded in a stepwise fashion. The binary and pseudobinary systems were first determined to evaluate reported work and to place phase boundaries accurately at 1200°C. Phase relations in the four three-component systems were then studied. Finally, six ThO₂ composition sections* at 10 mol % intervals from 10 to 60 mol % ThO₂ were determined to explore pseudoquaternary relations. A large number of samples were needed to place phase boundaries with confidence. Approximately 20 samples were used to fix phase relations in the two-component systems, 100 to 150 to determine three-component systems and 10 per ThO₂ composition section in the pseudoquaternary tetrahedron. Since it takes more data to place phase boundaries in higher order systems, the estimated accuracy of the placement of the phase boundaries decreases when going from two-component (estimated at ±1 mol %) to three-component (±2 mol %) to the pseudoquaternary ThO₂ composition sections, where phase boundaries are estimated to be accurate to within ±5 mol %.

Samples were prepared by mixing appropriate volumes of standardized aqueous solutions of the metal nitrates. The mixtures were dried and then calcined at ~500°C to drive off the nitrogen oxides. The residue was an x-ray amorphous mixture of the oxides, which was then ground in an agate mortar, pressed into pellets, and fired at 1200°C in a SiC resistance-type furnace for 1 to 2 weeks on platinum foil trays supported by refractory firebrick. Temperature during firing was monitored using a type S thermocouple that was calibrated relative to a similar thermocouple that was standardized using the melting points of gold and diopside. Temperature during firing of all samples was observed to fluctuate by not more than ±3 degrees about 1200°C. Cooling to room temperature was accomplished by removing the pellets from the furnace and pulling the platinum trays onto a cooled copper plate. The pellets were observed to cool to a temperature less than red hot (about 600°C) in less than 5 s.

*The term "composition section" refers to a diagram in which the concentration of the specified end member is held constant.

After firing and cooling to room temperature, all samples were subjected to two x-ray powder diffraction analyses, the first to detect phase assemblages and the second to fix the cubic F_{ss} cell constants. In both cases, standard x-ray powder diffractometers utilizing copper K-alpha radiation ($\lambda_{\alpha} = 1.54178 \text{ \AA}$) were used. Phase assemblages were determined by high-sensitivity scans at 2° two-theta per minute from 60 to 20° two-theta. Room temperature F_{ss} cell constants were measured by a second scan with an internal standard of Er_2O_3 ($a_0 = 10.5501 \text{ \AA}$), which had been calibrated relative to a silicon standard (National Bureau of Standards Standard Reference Material Number 640, $a_0 = 5.43088 \text{ \AA}$). Erbia was used as an internal standard because it crystallizes with the fluorite-related C-type rare earth oxide structure with major reflections occurring in the two-theta range of F_{ss} with comparable intensities when mixed 1:1 by volume with the sample. F_{ss} cell constants were determined by scanning the (111) peak of the F_{ss} and the (222) peak of the Er_2O_3 internal standard at $1/5^\circ$ two-theta per minute, correcting the observed F_{ss} peak relative to the internal standard, and applying the usual geometrical relations to determine the unit cell edge. This technique enabled the measurement of the F_{ss} reflection to within $\pm 0.005^\circ$ two-theta, making the reported F_{ss} cell constants accurate to within $\pm 0.002 \text{ \AA}$.

Steady-state, if not necessarily equilibrium, conditions were verified by refiring a number of selected compositions from each system for an additional period of ~ 1 week. The samples were cooled and examined as before. Phase assemblages were found to be unchanged. The comparison of the F_{ss} cell constants was found in all cases to be within the range of error of the measurement technique used, indicating that steady-state conditions had been attained after the initial firings.

Reproducibility was checked by firing 60 new compositions in all systems and examining as before. Both phase assemblages and cell constants were observed to agree with the phase diagrams constructed with the data from the initial firings.

The effect of the cooling rate on phase relations was also investigated. Four samples of compositions at the center of each three-component system and in the pseudoquaternary system were prepared. After firing for 1 week at 1200°C in air, each composition was cooled to room temperature in four different ways. A rapid cooling was accomplished by quickly removing the pellets from the furnace and dropping them in a pool of mercury. The pellets were observed to cool to room temperature almost immediately. A slow cool was accomplished by removing the pellets from the furnace but leaving the platinum foil trays on the refractory firebrick support. The samples were observed to cool to a temperature less than red hot in about 10 min. The third cooling rate, intermediate between the two already described, was the method used for the samples used to determine phase relations. The fourth cooling rate, the slowest used, was accomplished by turning off the furnace while leaving the samples inside. The furnace was observed to cool at an initial rate of 50°C/h and reached room temperature overnight. After cooling, all samples were examined by x-ray diffraction to determine phase assemblages and F_{ss} cell constants. A comparison of the samples that had undergone different cooling rates showed no difference in phase assemblages and no detectable difference in F_{ss} cell constants.

4.0 RESULTS

Data on phase assemblages and F_{ss} cell constants were used to place phase boundaries. The "parametric method" described by Cullity⁽⁵⁴⁾ was used in and near phase fields including F_{ss} . This method is advantageous as it avoids the problem of the limited sensitivity of x-ray diffraction to minor phases and enables the accurate placement of phase boundaries. An example of the utility of this technique in placing phase boundaries and plotting F_{ss} cell constant isopleths* is shown in Figures 1, 2, and 3 for the system $\text{ThO}_2\text{-CeO}_2\text{-ZrO}_2$. The "method of disappearing phases," also described by Cullity, was used to place phase boundaries at low F_{ss} concentrations and in phase regions where no F_{ss} is stable. A description and discussion of each three-component system and phase relations in the pseudoquaternary system follow.

4.1 $\text{ThO}_2\text{-CeO}_2\text{-ZrO}_2$

The system $\text{ThO}_2\text{-CeO}_2\text{-ZrO}_2$ is presented in Figure 4. It consists of a region of (F_{ss}) extending from the $\text{ThO}_2\text{-CeO}_2$ binary system towards ZrO_2 . At higher ZrO_2 concentrations a two-phase region of ($F_{ss}+Z_{ss}$) appears extending up to a single-phase region of (Z_{ss}) occurring near the ZrO_2 apex. Cell constant isopleths in the ($F_{ss}+Z_{ss}$) and (F_{ss}) regions were drawn using the data presented in Figures 2 and 3, respectively. The (F_{ss})-($F_{ss}+Z_{ss}$) phase boundary was placed using the plot in Figure 1. The (Z_{ss})-($F_{ss}+Z_{ss}$) boundary was determined using only phase assemblage data and is therefore dashed in as it was less accurately placed than the other phase boundaries.

Phase relations in the bounding binary system $\text{CeO}_2\text{-ThO}_2$ were found to agree well with the literature with a complete solid solution series observed with the F_{ss} cell constants a linear function of composition. Phase relations in the system $\text{ZrO}_2\text{-ThO}_2$ were also found to agree with the literature with

*The term "cell constant isopleth" refers to lines superimposed on the phase diagrams denoting regions of the system where the F_{ss} cell parameter is constant with composition. Cell constant isopleths are included in the phase diagrams as additional information to facilitate their use.

9364-3

Figure 1. Plot of the F_{ss} cell constants as a function of composition for various ThO_2 composition sections in the system ThO_2 - CeO_2 - ZrO_2 . The $(F_{ss}) - (F_{ss} + Z_{ss})$ phase boundary was placed at breaks in the curves as indicated by the dashed line. The numbers on the plots correspond to the ThO_2 concentration.

9364-4

Figure 2. Plot of the F_{ss} cell constants as a function of composition for various ZrO_2 composition sections in the system $\text{ThO}_2\text{-CeO}_2\text{-ZrO}_2$. The plots were used to draw F_{ss} cell constant isopleths in the two-phase ($F_{ss} + Z_{ss}$) region. The numbers on the plots correspond to the ZrO_2 concentration.

9364-5

Figure 3. Plot of the F_{ss} cell constants as a function of composition for various ZrO_2 composition sections in the single-phase (F_{ss}) region of the system $ThO_2-CeO_2-ZrO_2$. The plots were used to fix the F_{ss} cell constant isopleths in the (F_{ss}) phase field. The numbers on the plots correspond to the ZrO_2 concentration.

Figure 4. Steady-state phase relation diagram for the system $\text{ThO}_2\text{-CeO}_2\text{-ZrO}_2$ as determined from samples fired at 1200°C in air. Cubic F_{ss} cell constant isopleths are plotted as a function of composition. Phase boundaries that were placed using the "parametric method" are drawn in solid lines; those placed by other techniques are drawn in dashed lines.

1 to 2 mol % solid solubility of each end member in the other observed. Phase boundaries in the $\text{CeO}_2\text{-ZrO}_2$ system, however, are significantly displaced relative to the values found by other authors. Phase boundaries were observed at 15 and 88 mol % ZrO_2 for the $(F_{ss})\text{-(}F_{ss}+Z_{ss}\text{)}$ and $(F_{ss}+Z_{ss})\text{-(}Z_{ss}\text{)}$ boundaries while data compiled from the literature suggest ~25 and 80 mol %. This discrepancy can be attributed to the use of the more precise "cell constant" technique in this study. Authors reporting work in this system appear to have placed the phase boundaries using only phase assemblage data or by extrapolation from data obtained at other temperatures.

The effect of the size difference of the ions in this system is evident in the behavior of the single-phase F_{ss} field. Shannon's⁽⁵⁵⁾ values for the effective ionic radii of Th^{4+} , Ce^{4+} , and Zr^{4+} in eightfold coordination are 1.05, 0.97, and 0.84 Å, respectively. Th^{4+} has a much larger ionic radius than does Zr^{4+} , with Ce^{4+} falling in between. Based solely on an ionic size argument, a larger solid solution range in the system $\text{CeO}_2\text{-ZrO}_2$ would be expected compared with $\text{ThO}_2\text{-ZrO}_2$ as is observed in the diagram. The difference in ionic size between Th^{4+} and Zr^{4+} appears to have a large effect on phase relations in other systems, as will be seen later.

4.2 $\text{CeO}_2\text{-UO}_{2+x}\text{-ZrO}_2$

The system $\text{CeO}_2\text{-UO}_{2+x}\text{-ZrO}_2$, presented in Figure 5, is more complex. It comprises regions of (F_{ss}) , $(F_{ss}+Z_{ss})$, and (Z_{ss}) extending from the $\text{CeO}_2\text{-ZrO}_2$ binary incorporating increasing amounts of UO_{2+x} into solid solution up to the three-phase region of $[F_{ss}+Z_{ss}+(\text{U}_3\text{O}_8)_{ss}]$ and the two-phase region of $[F_{ss}+(\text{U}_3\text{O}_8)_{ss}]$. These regions extend almost to pure UO_{2+x} where a single-phase region of $(\text{U}_3\text{O}_8)_{ss}$ is stable. Cell constant isopleths and the $(F_{ss})\text{-(}F_{ss}+Z_{ss}\text{)}$ and $[F_{ss})\text{-(}F_{ss}+(\text{U}_3\text{O}_8)_{ss}]$ phase boundaries were drawn based on F_{ss} cell constant data. The three-phase region of $[F_{ss}+Z_{ss}+(\text{U}_3\text{O}_8)_{ss}]$ was placed solely on the basis of phase assemblage data and is dashed in as it was not as accurately placed as the other boundaries.

9364-8

Figure 6. Steady-state phase relation diagram for the system UO_{2+x} - ThO_2 - ZrO_2 as determined from samples fired at 1200°C in air. Cubic F_{ss} cell constant isopleths are plotted as a function of composition. Phase boundaries that were placed using the "parametric method" are drawn in solid lines; those placed by other techniques are drawn in dashed lines.

Phase relations in the bounding system $\text{UO}_{2+x}\text{-ZrO}_2$ agreed well with the literature. The system was observed to consist almost entirely of orthorhombic $(\text{U}_3\text{O}_8)_{ss}$ and (Z_{ss}) with little or no solid solution between the end members. A small degree of solid solubility was detected by a small shift of high-angle diffraction maxima relative to the pure compounds and was estimated at 1 mol % for each end member. Phase relations in the system $\text{UO}_{2+x}\text{-CeO}_2$ were found to differ from those reported by Hund, Wagner, and Peetz.⁽³³⁾ The $(F_{ss})\text{--}[F_{ss}+(\text{U}_3\text{O}_8)_{ss}]$ phase boundary placed in this study at 55 mol % UO_{2+x} contrasts with the value of 63 mol % observed by Hund et al. It is not clear, however, whether they performed their study in air or pure oxygen. The disagreement in phase boundary placement may therefore be attributable to the effect of the different oxygen partial pressures. Although not reported by Paul,⁽³⁴⁾ some solubility of CeO_2 was observed in U_3O_8 with the $[F_{ss}+(\text{U}_3\text{O}_8)_{ss}]\text{--}[(\text{U}_3\text{O}_8)_{ss}]$ phase boundary placed at 6 mol % CeO_2 .

This system is, in the strictest sense, a quaternary system involving phase relations between three metal oxides and atmospheric oxygen. While this system is drawn in the manner of a ternary system, it is in reality a projection of phase relations along the air oxygen isobar in the larger system of the pure metals and oxygen. The odd shape of the $(F_{ss})\text{--}(F_{ss}+Z_{ss})$ phase boundary and the unusual behavior of the cell constant isopleths (they must be straight in a true ternary system) in the $(F_{ss}+Z_{ss})$ region can be attributed to the combined effects of the substitution of ions of different radius and oxygen solid solution in the F_{ss} with the accompanying effect on the unit cell size.

4.3 $\text{UO}_{2+x}\text{-ThO}_2\text{-ZrO}_2$

This system, presented in Figure 6, is the most complex of the three-component systems studied. As uranium oxide is added to the $\text{ZrO}_2\text{-ThO}_2$ binary, the region of $(F_{ss}+Z_{ss})$ is broadened. With the addition of more UO_{2+x} , a three-phase region of $(2 \times F_{ss}+Z_{ss})$ occurs bounded by regions of $(2 \times F_{ss})$ and (Z_{ss}) . The cell constants of the fluorite solid solutions in the three-phase region are ~ 5.57 and $5.33 \text{ \AA}$. As the concentration of UO_{2+x} is increased, a

large lobe of single-phase (F_{ss}) extends from the UO_{2+x} - ThO_2 binary towards ZrO_2 , with a region of ($F_{ss}+Z_{ss}$) occurring at higher ZrO_2 concentrations. Upon adding still more UO_{2+x} , regions including $(U_3O_8)_{ss}$ form the phase assemblages [$F_{ss}+Z_{ss}+(U_3O_8)_{ss}$] and [$F_{ss}+U_3O_8)_{ss}$]. At nearly 100 mol % UO_{2+x} a small field of $(U_3O_8)_{ss}$ is stable. All phase boundaries and cell constant isopleths except those denoting single-phase regions of (Z_{ss}) and $(U_3O_8)_{ss}$ were placed using cell constant data. Approximate cell constant isopleths are drawn in the ($2 \times F_{ss}$) field.

Phase relations in the UO_{2+x} - ThO_2 system were in good agreement with the literature. The (F_{ss})-[$F_{ss}+(U_3O_8)_{ss}$] phase boundary was placed at 60 mol % UO_{2+x} in this study, while Hund and Niessen⁽³⁹⁾ and Friedman and Thoma⁽³⁸⁾ place it at about 56 and 65 mol % UO_{2+x} , respectively.

The outstanding feature of this system is the occurrence of phase assemblages including two fluorite solid solutions. The existence of these phase assemblages was confirmed by additional firings in the ($2 \times F_{ss}$) and ($2 \times F_{ss}+Z_{ss}$) phase fields. The existence of this phase assemblage is probably a consequence of the large ionic size difference of Th^{4+} and Zr^{4+} . One of the fluorites in the three-phase region of ($2 \times F_{ss}+Z_{ss}$) has a cell constant of about 5.57 Å, close to that of pure ThO_2 . The other fluorite, whose composition is richer in ZrO_2 and UO_{2+x} , has a cell constant of about 5.33 Å, smaller than that of pure UO_2 (5.4701 Å)⁽¹⁶⁾ but larger than that of room temperature cubic ZrO_2 (5.09 to 5.10 Å).⁽²⁷⁻²⁸⁾ The large size difference of the unit cells of these phases, due to the large difference in ionic size of Th^{4+} and Zr^{4+} , is a possible cause for the absence of complete solid solution between them and the existence of phase fields that include two fluorite solid solutions. Another reason may be the effect of interstitial oxygen. The F_{ss} with a cell edge of 5.57 Å has a composition that is rich in ThO_2 . This solid solution would be expected to contain little additional oxygen as there is little uranium present to charge-compensate. The 5.33-Å fluorite, on the other hand, contains about 33 mol % uranium oxide and would readily incorporate additional oxygen to form a grossly defective solid solution. The occurrence of an oxygen interstitial defect structure in one F_{ss} and not the other may act to stabilize

one fluorite relative to the other, thereby forming the observed miscibility gap. The more probable explanation is the former, however, as two-fluorite phase assemblages have also been observed in the uranium-free systems $\text{Gd}_2\text{O}_3\text{-CeO}_2\text{-ZrO}_2$ and $\text{Gd}_2\text{O}_3\text{-ThO}_2\text{-ZrO}_2$.⁽⁵⁶⁾

4.4 $\text{CeO}_2\text{-ThO}_2\text{-UO}_{2+x}$

The system $\text{CeO}_2\text{-ThO}_2\text{-UO}_{2+x}$, presented in Figure 7, consists of a single-phase region of (F_{ss}) extending from the $\text{CeO}_2\text{-ThO}_2$ binary to about the 60 mol % UO_{2+x} composition section where a two-phase region of $[\text{F}_{\text{ss}}+(\text{U}_3\text{O}_8)_{\text{ss}}]$ is stable. A single-phase region of $(\text{U}_3\text{O}_8)_{\text{ss}}$ appears near the pure uranium oxide end member with the phase boundary dashed in as it was not determined using the method of cell constants. F_{ss} cell constants were observed to vary smoothly with composition throughout the system.

4.5 $\text{UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2\text{-ThO}_2$

Phase relations in portions of the pseudoquaternary system, as determined by ThO_2 composition sections, are presented in Figures 8 through 13. Phase relations were determined solely by phase assemblage data; hence, the phase boundaries in the ThO_2 compositions sections are drawn as dashed lines. Phase boundaries are estimated, however, to be placed to within ± 5 mol % of their true position. This was established by several additional samples with compositions in close proximity to the phase boundaries. The pseudoquaternary system behaves as would be expected based on the bounding three-component systems. No new phases or phase assemblages were observed, with the only unknown aspect of the system being the magnitude of penetration of the three-component phase fields into the pseudoquaternary volume.

Phase relations within the four-component system are complex and difficult to draw. The pseudoquaternary phase relations can, however, be visualized using the system $\text{CeO}_2\text{-UO}_{2+x}\text{-ZrO}_2$ as a base and observing the change in phase fields as ThO_2 is added, as illustrated in the ThO_2 composition sections of

Figure 7. Steady-state phase relation diagram for the system $\text{CeO}_2\text{-ThO}_2\text{-UO}_{2+x}$ as determined from samples fired at 1200°C in air. Cubic F_{ss} cell constant isopleths are plotted as a function of composition. Phase boundaries that were placed using the "parametric method" are drawn in solid lines; those placed by other techniques are drawn in dashed lines.

9364-10

Figure 8. Phase relation diagram of the 10 mol % ThO₂ composition section of the system UO_{2+x}-CeO₂-ZrO₂-ThO₂ based on samples fired at 1200°C in air. Phase boundaries are drawn solely on phase assemblages observed by X-ray powder diffraction and are therefore drawn as dashed lines.

9364-11

Figure 9. Phase relation diagram of the 20 mol % ThO_2 composition section of the system $\text{UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2\text{-ThO}_2$ based on samples fired at 1200°C in air. Phase boundaries are drawn solely on phase assemblages observed by X-ray powder diffraction and are therefore drawn as dashed lines.

Figure 10. Phase relation diagram of the 30 mol % ThO₂ composition section of the system UO_{2+x}-CeO₂-ZrO₂-ThO₂ based on samples fired at 1200°C in air. Phase boundaries are drawn solely on phase assemblages observed by X-ray powder diffraction and are therefore drawn as dashed lines.

Figure 11. Phase relation diagram of the 40 mol % ThO_2 composition section of the system $\text{UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2\text{-ThO}_2$ based on samples fired at 1200°C in air. Phase boundaries are drawn solely on phase assemblages observed by X-ray powder diffraction and are therefore drawn as dashed lines.

Figure 12. Phase relation diagram of the 50 mol % ThO_2 composition section of the system UO_{2+x} - CeO_2 - ZrO_2 - ThO_2 based on samples fired at 1200°C in air. Phase boundaries are drawn solely on phase assemblages observed by X-ray powder diffraction and are therefore drawn as dashed lines.

9364-15

Figure 13. Phase relation diagram of the 60 mol % ThO₂ composition section of the system UO_{2+x}-CeO₂-ZrO₂-ThO₂ based on samples fired at 1200°C in air. Phase boundaries are drawn solely on phase assemblages observed by X-ray powder diffraction and are therefore drawn as dashed lines.

Figures 8 through 13. When 10 mol % ThO_2 is added to the system $\text{CeO}_2\text{-UO}_{2+x}\text{-ZrO}_2$, the concentration of UO_{2+x} is decreased, thereby shrinking the phase fields including $(\text{U}_3\text{O}_8)_{\text{ss}}$. A $(2 \times F_{\text{ss}} + Z_{\text{ss}})$ region also appears near the zirconia apex. With the addition of progressively more ThO_2 , the $(2 \times F_{\text{ss}} + Z_{\text{ss}})$ region expands and the $[F_{\text{ss}} + Z_{\text{ss}} + (\text{U}_3\text{O}_8)_{\text{ss}}]$ and $[F_{\text{ss}} + (\text{U}_3\text{O}_8)_{\text{ss}}]$ fields shrink in proportion to the rest of the system up to the 40 mol % ThO_2 composition section where no $(\text{U}_3\text{O}_8)_{\text{ss}}$ is stable. At 40 mol % ThO_2 , the system comprises a single-phase region of (F_{ss}) , a two-phase region of $(F_{\text{ss}} + Z_{\text{ss}})$, and a three-phase region of $(2 \times F_{\text{ss}} + Z_{\text{ss}})$. Between the 40 and 50 mol % ThO_2 sections, the $(2 \times F_{\text{ss}} + Z_{\text{ss}})$ phase field contacts the single-phase (F_{ss}) region phase boundary forming a two-phase region of $(2 \times F_{\text{ss}})$. With the addition of still more ThO_2 , the phase assemblages remain the same, with the $(2 \times F_{\text{ss}})$ region expanding slightly. Sections of ThO_2 concentration greater than 60 mol % ThO_2 were not investigated, but an examination of the system $\text{UO}_{2+x}\text{-ThO}_2\text{-ZrO}_2$ (Figure 6) indicates that the basic phase assemblage of Figure 13 remains stable with a contraction of both the $(2 \times F_{\text{ss}} + Z_{\text{ss}})$ and $(2 \times F_{\text{ss}})$ fields up to the 90 mol % ThO_2 section where only phase fields of $(F_{\text{ss}} + Z_{\text{ss}})$ and (F_{ss}) are stable. These phase assemblages remain stable up to about the 98 mol % ThO_2 composition section where a single-phase (F_{ss}) region is entered which extends to pure ThO_2 .

5.0 DISCUSSION AND CONCLUSIONS

Phase relations in the system $\text{UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2\text{-ThO}_2$ as fired at 1200°C in air have been determined. Highly reactive x-ray amorphous starting materials and firing times of up to several weeks were used to attain steady-state conditions. The achievement of steady-state conditions was proven by refiring a number of selected compositions in all subsystems. A number of different cooling rates were observed to have no detectable effect on the observed phase relations. It is possible, however, that the phase relations described in this paper are not the equilibrium phase relations but metastable relations due to the attainment of a persistent metastable state. It is for this reason that the diagrams produced are described as "phase relation" diagrams rather than "phase equilibrium" diagrams. The attainment of a metastable state would not be unexpected because of the highly refractory nature of the oxides in this system. Very long firings of compositions in this system may result in new phase relations, particularly by oxygen defect ordering to form, for example, phases similar to U_4O_9 .⁽⁵⁷⁾ Very long firings are not, however, of interest in the processing of crystalline high-level nuclear waste ceramics.

Cooling rates slower than those used in this study will be used in the processing of crystalline waste forms. A caution on the use of these diagrams for that application should therefore be noted. The F_{ss} cell constants may vary substantially if slower cooling rates are used. The values of the F_{ss} cell constants are dependent on the radii of the ions that constitute the unit cell. Upon cooling, diffusion of oxygen in or out of the F_{ss} may occur. To preserve electroneutrality, oxygen diffusion would be accompanied by a change of the uranium valence state. Shannon's⁽⁵⁵⁾ values of the effective ionic radii for U^{4+} and U^{6+} in eightfold coordination (1.00 Å and 0.86 Å, respectively) show that there is a substantial change in the uranium ionic radius with valence. This may produce different F_{ss} cell constants. Since slower cooling rates would result in the attainment of phase assemblages representative of temperatures less than 1200°C , the values of the F_{ss} cell constants would be changed relative to the cell constants reported here. This effect would be most pronounced at high uranium concentrations where more uranium is present to change valence state with oxygen diffusion.

While slower cooling rates may change the F_{ss} cell constants, the phase assemblages will probably not change. Both metal and oxygen ion diffusion on cooling are necessary to form new phase assemblages. Kingery, Bowen, and Uhlmann⁽⁵⁸⁾ show, however, that the oxygen diffusion coefficients at 1200°C in fluorite structured oxides are about nine orders of magnitude greater than those for the metal ions. The values for the metal ions are so low that adequate atomic mobility for new phase formation on cooling is improbable. Therefore, a change of F_{ss} cell constant by oxygen diffusion is more likely to occur than the formation of new phase assemblages. If the cooling rate is so slow that the formation of new phase assemblages is a possibility, the phase diagrams presented here may still be applied. Slower cooling rates will result in the attainment of phase relations characteristic of temperatures lower than 1200°C. A common feature of all the binary systems constituting this pseudoquaternary system is that the expanse of regions of two phases increases with decreasing temperature. An example is the system CeO_2-ZrO_2 where Negas et al.⁽⁴⁵⁾ report the $(F_{ss}+Z_{ss})$ phase field to have a breadth of about 50 mol % at 1200°C, which expands to a breadth of about 53 mol % at 1100°C. Assuming that similar behavior occurs in the pseudoquaternary system, cooling rates slow enough to result in new phase assemblages would result in phase relations similar to those described here, but with multiphase fields expanded at the expense of single-phase regions.

In summary, the phase diagrams presented here are expected to describe phase relations at 1200°C in air. The phase diagrams can also be used to interpret data obtained at other temperatures and from slower cooling rates.

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