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It has been occasionally observed, that, on dissolution in nitric acid, zirconium-jacketed uranium dioxide fuel elements react with explosive violence. It is the purpose of this report to investigate the causes of the explosion, to determine whether such extreme reactivity is a normal feature of Zr-UO₂ systems, to examine the possibility that irradiation may accelerate formation of the reactive species, and to suggest possible methods of alleviating the problem. The investigation is based on a survey of current literature (see Bibliography).

1. Explosion of Uranium-Zirconium Alloys

The extremely pyrophoric nature of uranium, zirconium, and their alloys has long been known (1). Recent experience with these materials has been summarized in several reports (2, 3, 4, 5, 5a, 6, 7). It has been demonstrated (5, 5a) that in the case of uranium-zirconium alloys, the explosive substance is the so-called ϵ -phase alloy (approximately U₃Zr₈). When high-uranium alloys are treated with nitric acid, the α -U phase is preferentially attacked, leaving on the surface a residue consisting of ϵ -phase admixed with an oxide phase. The explosion results from extremely rapid oxidation of the finely divided ϵ -phase residue. Explosive residues are formed not only by HNO₃ but also by aqueous HCl and by anhydrous HCl dissolved in ethyl acetate (5a, 8). On the other hand, addition of sufficient HF or (NH₄)₂SiF₆ to HNO₃ prevents the formation of such residues (9).

Thus, formation of ϵ -phase alloy by reaction of the Zr cladding with the UO₂ fuel element will lead to the likelihood of explosive reactions occurring on dissolution of the element in nitric acid. Prevention of the explosion by addition of F⁻ or of SiF₆⁼ is probably impractical since such additions prevent the desired separation of U and Zr.

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2. Thermodynamics of the Zr-UO₂ Reaction

Calculations have been made of the heat and free energy of the reaction.

assuming the phases to be pure and at standard conditions. The heat of formation of UO₂ at 298.16°K was taken from Huber, et. al. (10); the entropies of U and UO₂ at 298.16 were taken from the work of Jones, et. al. (11); high-temperature enthalpy and entropy increments of U and UO₂ were from the compilation of Kelley (12). These increments were based on heat capacity data of Moore and Kelley (13) and of Ginnings and Corruccini (14). North (15) has recently questioned their data on U, but, in view of the reputations of the U. S. workers and the general reliability of their technique, their work is preferred until more conclusive evidence of its incorrectness is presented. The heat of formation of ZrO₂ was that of Humphrey (16); the entropy of ZrO₂ at 298.16°K. was taken from the work of Kelley (17); that of Zr was a calculated value given by Rossini, et. al. (18); high temperature enthalpy and entropy increments were taken from Kelley's tables (12). These increments were based on the heat capacity data of Jaeger and Veenstra (19). The thermodynamic properties of oxygen were taken from standard reference works (12, 18). In Table I are given the heats and free energies of formation of UO₂ and of ZrO₂ as functions of temperature; and the heat and free energy of reaction (1). The uncertainties in the latter quantities are about ± 2 kcal./mole. Thus, ΔF for reaction (1) cannot be distinguished from zero throughout the temperature range of the table. Incidentally, the last values entered in each column of Table I represent approximately the upper limits in temperature of the necessary data. The findings of this calculation verify the remarks of McCreight (20) and of Williams, et. al. (21).

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Thermodynamic Properties of UO_2 and ZrO_2

T(°K)	UO_2^*		ZrO_2^*		Reaction (1)	
	$-\Delta H_f$ (kcal/mole)	$-\Delta F_f$ (kcal/mole)	$-\Delta H_f$ (kcal/mole)	$-\Delta F_f$ (kcal/mole)	ΔH (kcal/mole)	ΔF (kcal/mole)
298.16	259.2	246.6	261.5	247.7	- 2.3	- 1.2
400	258.9	242.3	261.4	243.0	- 2.4	- 0.8
500	258.6	238.1	261.2	238.5	- 2.6	- 0.3
600	258.3	234.1	261.0	234.2	- 2.7	- 0.1
700	258.0	230.0	260.8	229.5	- 2.8	0.6
800	257.8	226.1	260.6	225.0	- 2.8	1.1
900	257.6	222.1	260.5	220.6	- 2.9	1.5
935 (α -U)	257.6	220.7	260.5	219.0	- 2.9	1.6
935 (β -U)	258.3	220.7	260.5	219.0	- 2.2	1.6
1000	258.2	218.1	260.4	216.2	- 2.2	2.0
1045 (β -U)	258.0	216.3	260.3	214.2	- 2.3	2.1
1045 (γ -U)	259.2	216.3	260.3	214.2	- 1.1	2.1
1100	259.0	214.0	260.2	211.8	- 1.2	2.2
1135 (α -Zr)	258.9	212.6	260.3	210.3	- 1.4	2.2
1135 (β -Zr)	258.9	212.6	261.0	210.3	- 2.0	2.2
1200	258.7	209.9				
1300	258.3	205.8				

*Standard States:

UO_2 : Cubic crystals at 1 atm. pressure

ZrO_2 : Monoclinic crystals at 1 atm. pressure

U: $T < 935^\circ K.$
 $935 < T < 1045^\circ K.$
 $1045 < T < 1405^\circ K.$

α - crystals at 1 atm. pressure
 β - crystals at 1 atm. pressure
 γ - crystals at 1 atm. pressure

Zr: $T < 1135^\circ K.$
 $T > 1135^\circ K.$

α - crystals at 1 atm. pressure
 β - crystals at 1 atm. pressure

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3. Phase Relations in the U-Zr-O System

Experimental work has shown that the assumption of the previous section regarding the purity of the phases involved in reaction (1) is not-at-all justified. The uranium-zirconium binary system has been investigated by Rough, et. al. (22). They find that below about 600°C (about 1100°F) the only stable solid phases are α -U, α -Zr (so-called δ -phase), and so-called ϵ -phase (also sometimes called δ -phase). The composition of the latter phase is approximately represented by U_3Zr_8 , although its range of stability as a pure phase is from about UZr_2 to about UZr_3 . The similarity of this phase to U_3O_8 will be evident. The zirconium-oxygen binary system has been studied by Domagala and McPherson (23) from Zr to ZrO_2 . The only solid phases observed were Zr and ZrO_2 . The most interesting feature of the phase diagram is the very high solubility of oxygen in zirconium metal (29 atom.%). High concentrations of oxygen stabilize the α - (low temperature) form of Zr to a surprising degree. More than 18 atom % O raises the α - β transformation temperature from 862°C to the melting point (about 1975°C). The UO_2 - ZrO_2 pseudobinary system has been studied by Lambertson and Mueller (24). The phase diagram is characterized by appreciable mutual solubility of the two oxides with a fairly large miscibility gap. Finally, the Zr- UO_2 quasibinary system has been studied by Rough, et. al. (22), and by Saller, et. al. (25).

Consideration of all of the above work allowed Rough, et. al. (22), to construct tentative ternary isothermal sections of the U-Zr-O system. Their diagrams at 550°C and at 660°C are shown in Figs. 1 and 2. It will be seen from these sections that Zr will be expected to react with UO_2 and that U will be expected to react with ZrO_2 as well. The thermodynamic equilibrium for any given mixture of Zr and UO_2 can be predicted from the ternary phase diagrams. The section at 550°C (Fig. 1) is applicable at temperatures below 600°C (1100°F). The section at 660°C (Fig. 2) applies approximately from 600°C to the solidus temperature.

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Figure 1. Tentative Zirconium-Uranium-Oxygen Ternary Section at 550°C

TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION
AT 550 C

Figure 2. Tentative Zirconium-Uranium-Oxygen Ternary Section at 660°C

TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION
AT 660 C

4. Reaction Kinetics in the Zr-UO₂ System

Two studies (21, 26) have been made of Zr-UO₂ cermets. In both investigations it was concluded that reaction between the metal and oxide occurred. It has also been observed (27) that liquid uranium metal reacts with ZrO₂. A more thorough study of the kinetics of the Zr-UO₂ reaction has been made by Mallett, *et al.* (28), under the sponsorship of Westinghouse Atomic Power Division, in connection with the FWR program. Other more fragmentary studies have also been reported (29).

Mallett, *et al.* (28), found the rate of reaction between Zr and UO₂ to be very slow at 510°C (950°F) and at 593°C (1100°F), measurably fast at 704°C (1300°F), and very rapid at 1093°C (2000°F). Reduction occurs at the Zr-UO₂ interface, the product U and O diffusing into the zirconium phase. Oxygen appears to diffuse much more rapidly than does uranium. From their data at 1300°F, they give the following results for the distance of penetration of the various product phases into zirconium.

For movement of the interface: $d = 0.17 t^{1/2}$

For maximum penetration of the α -Zr + α -U phase:

$$d = 0.37 t^{1/2}$$

For maximum penetration of the α -Zr + ϵ phase:

$$d = 1.30 t^{1/2}$$

For maximum penetration of dissolved oxygen in the α -Zr phase:

$$d = 1.72 t^{1/2}$$

where t is the time in days and d is the distance of penetration in mils.

Using these results, they estimate the useful life of a zirconium jacket of 30 mils thickness to be about 300 days at 1300°F. At 2000°F, they estimate a useful life of about 60 hours. The useful life is defined as the time necessary for oxygen penetration through the cladding. They find that similar reactions occur with Zircalloy-2, although at slower rate.

5. Effects of Radiation on the Zr-U System

Radiation would be expected to affect the rate of the Zr-UO₂ reaction only through effects which it might have on diffusion rates of U and of O in Zr. The production of lattice defects by high-energy particles (fast neutrons and fission fragments) will tend to increase diffusion rates. Since α-Zr is a close-packed hexagonal metal (30), radiation damage will presumably create significant numbers of defects and hence increase diffusion rates. However, as the zirconium becomes saturated with oxygen, one would expect radiation-produced defects to be less important, compared with those introduced by the presence of the solute atoms. Thus, while the acceleration of the early stages of the reaction may be appreciable, at later stages the rates should be less affected. Furthermore, thermal motion of the atoms will tend to remove radiation-produced defects. This annealing will become more important at elevated temperatures. It seems likely that radiation will have only a small effect on the rate of reaction of zirconium with UO₂.

6. Conclusions

The above discussion makes it evident that reaction of zirconium with UO₂ is to be expected, whatever the temperature, and that the ε-phase alloy will be one of the products of the reaction. The reaction rate will be very slow - although not zero - as long as the Zr-UO₂ interface is held below about 600°C (1100°F). Nevertheless, it can confidently be predicted that formation of ε-phase will occur to some small degree in Zr-UO₂ fuel elements which are exposed to temperatures of power reactor interest. In particular, in the PWR, the Zr-UO₂ interface temperature is estimated to be 1300°F (28). Formation of ε-phase can probably be prevented readily enough by employing a diffusion barrier of some sort between the Zr and UO₂. For example, a thin layer of ZrO₂ would tend to prevent ε-phase formation. This barrier would eventually diffuse into the Zr metal phase but might still be a helpful measure. Other materials might be

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superior, e. g. SiC.

The grains of ϵ -phase formed by reaction of Zr and UO_2 can be expected to be very small and, therefore, very reactive. Thus, it must be anticipated that explosive reactions with HNO_3 are a reasonable likelihood. Certainly not every fuel element will be explosive; perhaps the great majority will not be; but occasional explosive elements will unquestionably be encountered. If formation of ϵ -phase is not prevented by use of a diffusion barrier of some sort, the best solution to the problem of explosive fuel elements seems to be to use a fuel element processing scheme not based on HNO_3 dissolution. In particular, the Zircex hydrochlorination (either gas or liquid-phase) comes to mind. The decision between use of diffusion barriers and use of HNO_3 -free processing methods seems to rest primarily on economic factors.

The work reported from Battelle (22, 28) seems to dispose of any necessity for an experimental program at ORNL on the Zr- UO_2 system. It should also be mentioned that ϵ -phase is a normal, stable component of the Zr-U system so that explosive reactions should be expected from alloys in this system, particularly from those near the pure metals in composition, where the grain size of ϵ -phase will be especially small. This tendency to explode will be less marked in gamma-quenched alloys but will probably occur anyway, especially in samples irradiated at 500 to 600°C.

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