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SUBJECT: Explosive Reactions During Reprocessing of Reactor Fuels Containing Uranium and Zirconium or Niobium

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FROM: T. A. Gens

ABSTRACT

Small particles of zirconium formed during mechanical operations, have caused serious industrial explosions. Particles of this type will not be encountered during aqueous chemical reprocessing. However, small particles of metallic phases rich in zirconium or niobium, produced by selective leaching of a more reactive uranium-rich phase, can enter into violently explosive reactions.

The conditions under which explosions with zirconium-bearing alloys may be expected during chemical reprocessing have been defined in the literature. The uranium-zirconium alloys containing less than 30 wt % zirconium are hazardous when they contact nitric acid. Laboratory work has shown that potentially explosive zirconium alloys may be safely dissolved in nitric acid if enough fluoride ion is added to maintain a mole ratio of fluoride to dissolved zirconium of four. Niobium-bearing fuel alloys can also explode after contacting nitric acid, but the conditions which produce explosions have not yet been studied thoroughly. Dissolution studies with the EBWR alloy (93.5% U, 5% Zr, 1.5% Nb) indicate that hazardous niobium alloys can also be processed safely in nitric acid by addition of enough fluoride to prevent formation of surface deposits.

The ternary phase diagram for zirconium-uranium-oxygen shows that the epsilon phase is unstable at the interface between a zirconium or a Zircaloy-2 cladding and a uranium oxide core. These fuels can be processed by techniques which require contact with nitric acid without fear of epsilon-phase explosions.

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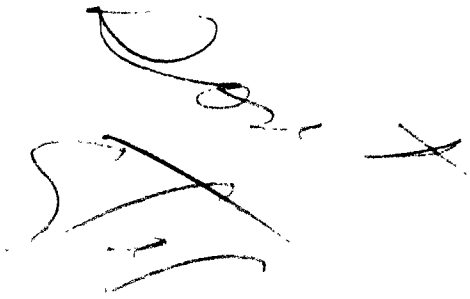


1.0 INTRODUCTION

All explosions involve intimate contact between an oxidizer and a reducer. In nuclear fuel reprocessing, such a condition sometimes occurs when finely divided or porous metal contacts nitric acid, oxygen, or even air. The large reaction surface required for explosions can be produced by machining metal into small pieces or by selective dissolution of the matrix material of an alloy to expose a large surface area of a less-rapidly dissolved phase. The activation energy required to initiate the explosive reaction can then be provided locally by a spark or blow, if sufficient oxidizer is present.

To avoid explosions, and the disastrous consequences that could be expected in reprocessing radioactive fuel, the conditions under which explosions occur must be understood. A survey of the literature has provided an insight into these conditions. Some questions left unanswered in the literature have been investigated in the laboratory.

2.0 EXPLOSIVE OXIDATION OF ZIRCONIUM MACHINED INTO FINE PARTICLES

Serious industrial accidents have occurred with zirconium machined into small particles (1). In hydrofluoric acid dissolution (the only chemical reprocessing method for zirconium in use on a production basis) and in the newer chemical reprocessing methods being developed for zirconium, such as the Zircex (2) and Zirflex (3) processes, the attack is uniform. No fine metallic particles are produced. A temperature above 1000°C is required to ignite massive zirconium metal (4). At this temperature and in the presence of air or oxygen, massive zirconium metal burns rather than explodes, since the surface-to-mass ratio is very low. The various zirconium alloys may be expected to have ignition behavior quite similar to zirconium metal. In cases where fuels are chopped or sheared into small pieces prior to leaching (5), smaller fragments will probably be produced. These fragments should be disposed of before large quantities collect.

3.0 SELECTIVE DISSOLUTION OF THE MATRIX MATERIAL TO EXPOSE A LESS-READILY DISSOLVED PHASE

To obtain an explosive reaction by fine particles during dissolution of reactor fuel alloys, it is necessary to have conditions such that

$$R_M - R_L > 0, \qquad (1)$$

where R_M and R_L are the rates of dissolution of the metallic matrix and a less-readily dissolved phase, respectively. Nitric acid is the only dissolving medium now in common use in which expression (1) is known to become large enough to lead to explosions during fuel reprocessing.

The epsilon phase explosions with uranium-zirconium alloys are the best known, but similar explosions can probably be expected with any alloy which contains phases that dissolve at different rates.

3.1 The Epsilon Phase in Uranium-Zirconium Alloys

With the epsilon phase in uranium-zirconium alloys (Fig. 1), the term R_L is smaller than R_M in nitric acid. A method of estimating the amount of epsilon phase to be expected under a steady-state processing condition has been developed (6). The black particles of epsilon phase, which coat the surface of the alloy during dissolution, can be passivated by slow oxidation to a gray zirconia-urania solid solution and can also dissolve slowly, if the necessary activation energy for explosion is not supplied.

The epsilon phase can form when the solubility of zirconium in α-uranium is exceeded (about one atom per cent or 0.4 wt % up to 600°C) (7,8). The composition of the epsilon phase is about 2-3 zirconium atoms per uranium atom (9) or 50 wt % zirconium (see Fig. 1).

Approximately 30 wt % is the upper limit (10) of zirconium concentration at which uranium alloys can be dissolved in nitric acid. Experiments in this laboratory showed that a uranium alloy containing 35 wt % zirconium was unreactive toward refluxing 15 M HNO_3 while an alloy containing 25 wt % zirconium began dissolving rapidly at 60°C, and an alloy containing 15 wt % zirconium dissolved readily without heating. Thus, no explosions occur with alloys containing more than 30 wt % zirconium since the epsilon phase becomes the major component and no dissolution occurs. Contact with nitric acid need only last a few minutes with uranium-zirconium alloys of about 20 wt % zirconium to produce a potentially explosive surface deposit (8).

Some experimenters have reported that explosions with uranium-zirconium alloys do not occur in mixed nitric acid and hydrofluoric acid (8,10). Others have reported explosions (10). This discrepancy in experimental results can be explained if consideration is given to the amount of fluoride in solution which is not complexed by zirconium. A fluoride-to-zirconium mole ratio (F/Zr) in solution of more than four is usually maintained. At these high fluoride concentrations, the epsilon phase dissolves as rapidly as it is exposed, and the conditions required for explosion (expression 1) do not occur (8,11). As the F/Zr ratio in solution decreases to below four, the term R_L in expression (1) becomes smaller. At some F/Zr ratio below four the value of expression (1) becomes appreciable and explosions are possible. Experiments were performed to determine the highest F/Zr ratio at which explosions would occur. A uranium alloy containing 25 wt %

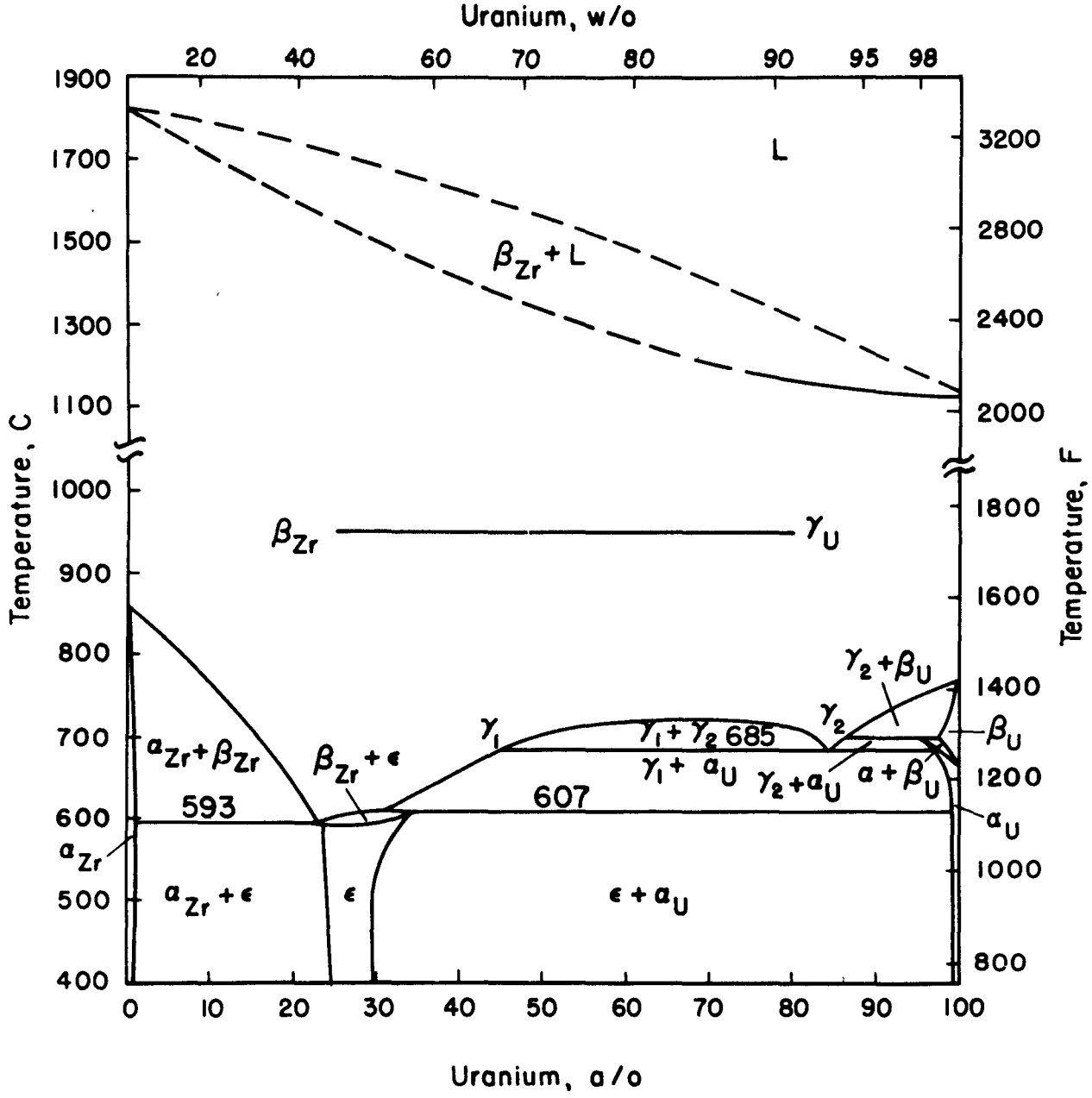


Fig. 1. Uranium-Zirconium Binary Phase Diagram from BMI-1092, page 12.

zirconium, which exploded readily in nitric acid, was used. The highest F/Zr ratio at which explosions occurred was 3.1. At this ratio the explosion was very small. At lower F/Zr ratios, much more surface deposit collected, and the explosions were much more violent. The lowest F/Zr ratio which is safe will vary, since the terms in expression (1) vary with alloy and acid concentration.

Therefore, failure to maintain sufficient fluoride while reprocessing hazardous alloys with mixed nitric acid and hydrofluoric acid can lead to explosions. At low fluoride concentrations, the explosion hazard should be considered very similar to that in pure nitric acid. In all cases, there apparently is no explosion hazard if a F/Zr ratio of 4 in solution can be maintained with certainty throughout the dissolution and if no fluoride-complexing agent other than zirconium is present.

3.2 The Epsilon Phase in Uranium Dioxide Fuels Clad in Zirconium or Zircaloy - 2

Diffusion of uranium into a zirconium or Zircaloy-2 cladding at points of contact between the cladding and a uranium dioxide core can form a region containing some epsilon phase (12). This consideration has caused much concern in reprocessing of PWR blanket rods (13).

By maintaining excellent contact for a period of a year or more at temperatures of 600°C or below, a phase can be formed at the interface containing more uranium than zirconium (12). At temperatures above 600°C, much uranium diffuses farther into the cladding. Since the rate of diffusion (12) becomes very slow at the coolant temperature of about 350°C, (14) there is little possibility that an appreciable quantity of uranium will diffuse completely through the cladding. The epsilon phase is found only in specimens which have been heated to temperatures of over 700°C. This phase does not form at the interface, but is found in isolated spikes in grain boundaries several mils inside the cladding. The high oxygen content at the interface (12) probably is responsible for the absence of epsilon phase at the interface. The ternary phase diagram (Fig. 2 Ref. 9) shows that the epsilon phase is unstable at oxygen concentrations greater than 2 atom % and cannot exist at oxygen concentrations greater than 15 atom %. If it could be assumed that material containing only about 30 wt % zirconium and about 70 wt % uranium forms at the interface, it would be expected that this interface material would dissolve in nitric acid. However, this assumption is unsound, because under ideal contact conditions for 37 days at 700°C, only 10 wt % uranium was found at the interface (15). Nitric acid dissolution of such material containing less than 30 wt % zirconium might expose the area in which the epsilon spikes are isolated within a zirconium matrix, but the zirconium matrix will not dissolve in

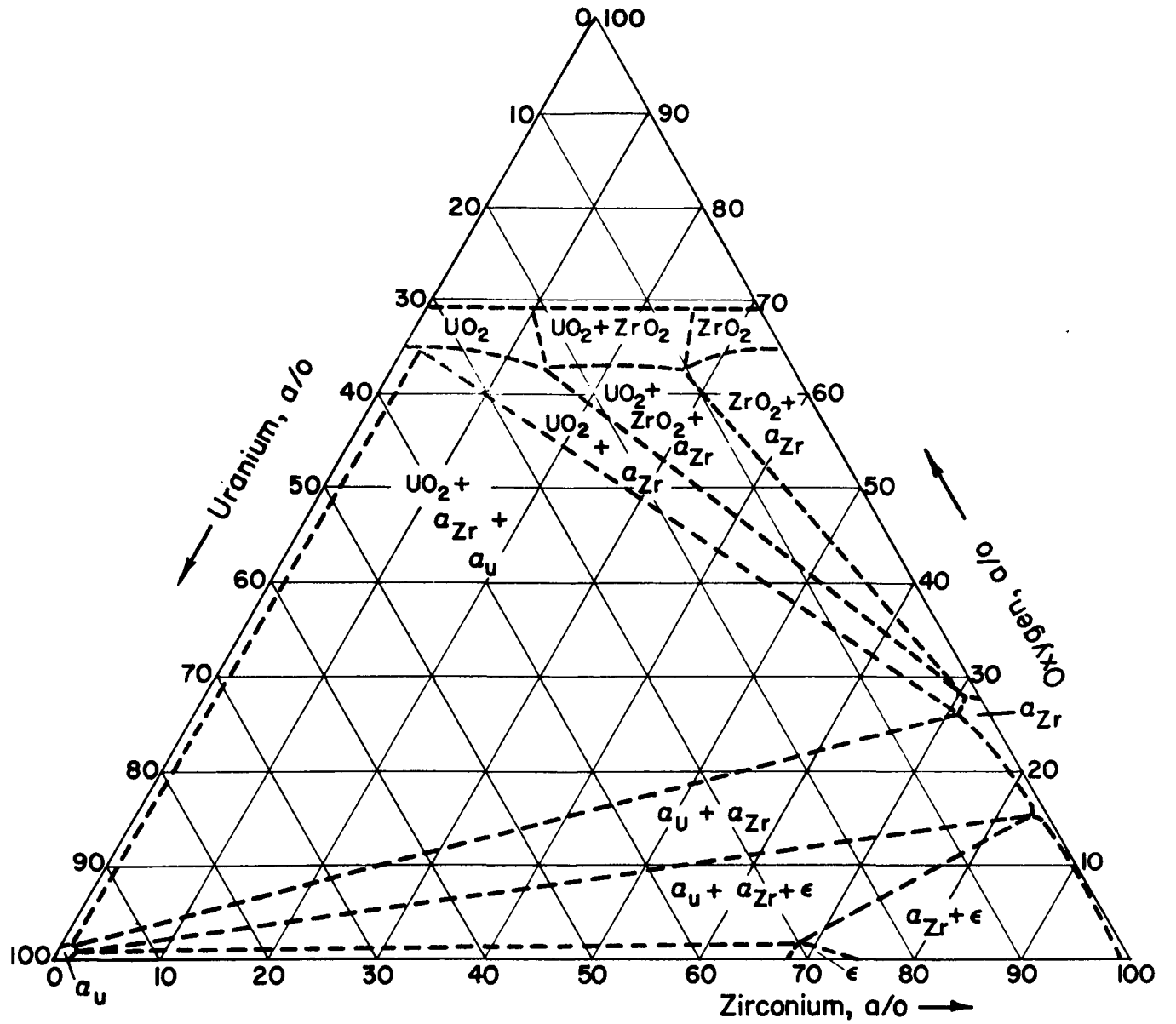


Fig. 2. Uranium-Zirconium-Oxygen Ternary Phase Diagram at 550°C from BMI-1092, page 17.

nitric acid and there is no possibility of exposing small particles of epsilon phase to the acid. Thus, there is no possibility of epsilon-phase explosions. An additional convincing argument is that no epsilon phase explosions have been reported with the PWR blanket rod (16).

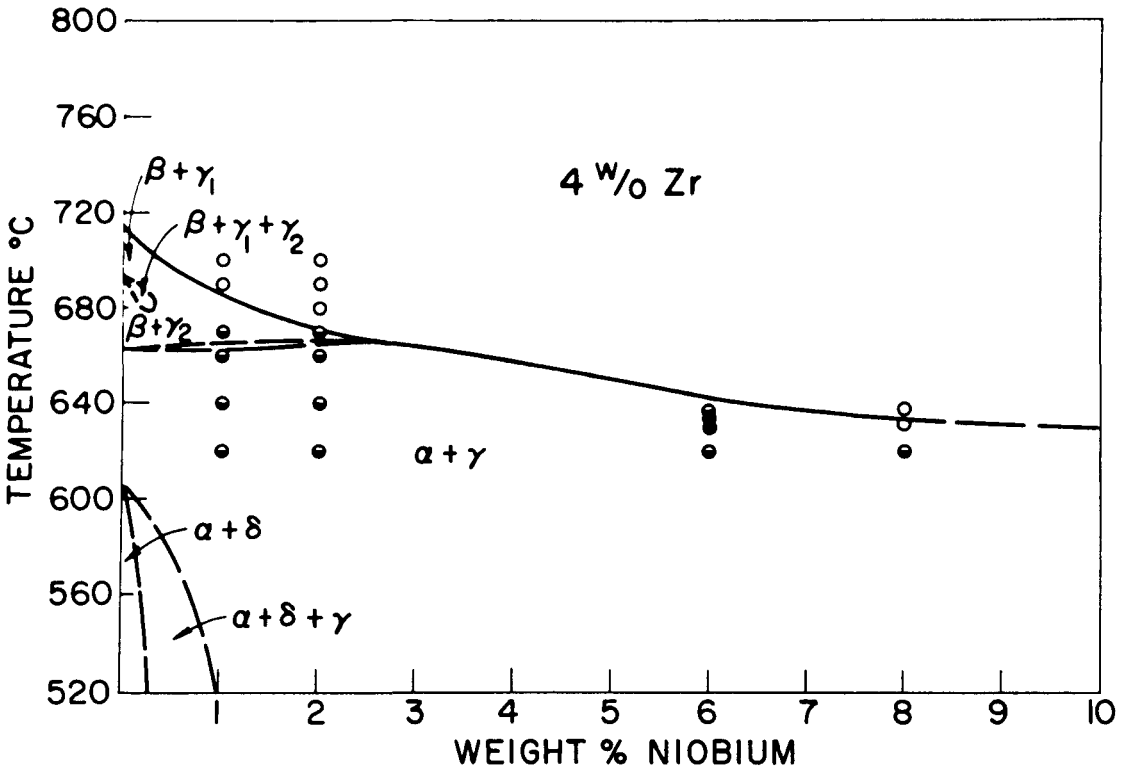
3.3 Nitric Acid-Insoluble Phases in Uranium Alloys Containing Niobium

Certain niobium-uranium alloys can explode after contacting nitric acid (17). Samples of a uranium alloy containing 10 wt % niobium were dissolved in refluxing 15 M HNO_3. Much sludge collected but no explosions could be produced. This alloy would not dissolve in cold nitric acid. Apparently, the explosive properties of the alloy are modified by the previous heat treatments. The best opinion available is that explosions which occur with alloys of uranium and niobium are very similar in nature to those which occur with uranium-zirconium alloys (18).

The EBWR alloy (93.5% U --5% Zr --1.5% Nb) has a composition which resembles that of the hazardous uranium-zirconium alloys. Phase diagrams (Fig. 3) for the U-Zr-Nb system show that the composition of the EBWR alloy is such that it falls approximately on the boundary of the delta phase (19). The delta phase has about the same composition as the epsilon phase. In laboratory investigations, surface deposits capable of entering into very violent explosive reactions were produced upon dissolving this alloy in nitric acid. The Zircaloy-2 cladding from EBWR plate was removed in hydrofluoric acid and the core alloy was refluxed 1/2 hr or longer in 15 M HNO_3. Sometimes a blow was sufficient to initiate the explosion. Other times a spark from a Tesla Coil was required, and on several occasions no explosion could be produced. In many experiments in which a F/Zr ratio of four or greater was maintained throughout dissolution in mixed HF-HNO_3, no surface deposit formed and no explosions occurred. In only one such experiment, (F/Zr = 4.3), did an explosion occur, and in this case the fluoride was very dilute (0.076 M) and complexed by equimolar quantities of aluminum.

4.0 METALLURGICAL TREATMENT TO REMOVE THE LESS-READILY DISSOLVED PHASE

The epsilon phase is stable at room temperature but disappears completely at temperatures above 607°C (Fig. 1). Thus the effects of the epsilon phase are much more apparent in alloys that are annealed or hot-worked below 600°C than in alloys that are quenched (7,8). It has been reported that some alloys which are usually hazardous cannot be exploded in nitric acid if they have been quenched from high temperatures (6,8). The EBWR alloy, when quenched rapidly, contains only a single phase (20). In this laboratory, uranium alloys containing 15 and 20 wt % zirconium, which were quenched during



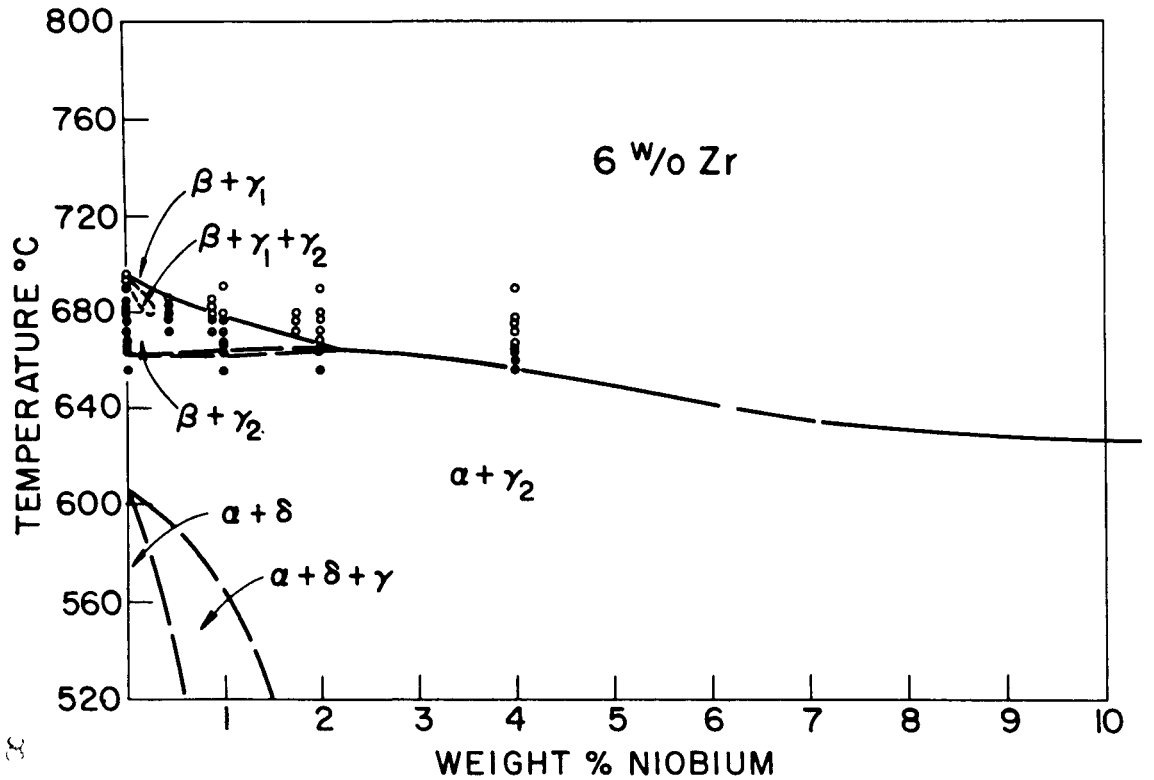


Fig. 3. Uranium-Zirconium-Niobium Phase Diagrams from ANL-5581, page 42.

preparation, would not explode in nitric acid. An alloy containing 25 wt % zirconium, annealed at 525°C for 24 hr, exploded readily. Quenching of fuel alloys at a sufficiently rapid rate might ensure the absence of any significant amount of the less-readily dissolved phase, and if transformation to this phase should then be sufficiently slow at storage or reprocessing temperatures, there would be no explosion hazard. If the insoluble phase is transformed rapidly enough at high temperatures, the Zircex Process (2) might be operated well above 600°C, and the products cooled rapidly enough to prevent formation of the insoluble phase. Thus any unreacted alloy subjected to this treatment could be allowed to contact nitric acid without danger of explosions. A detailed knowledge of rates of formation of the less-readily dissolved phase at various temperatures is needed. Research closely related to this problem is underway at Battelle Memorial Institute (21) and at the Westinghouse Bettis Plant (22,23).

5.0 CONCLUSIONS

Zirconium alloys containing low weight percentages of uranium and the PWR type fuels (Zircaloy-2 clad uranium dioxide) can be safely reprocessed by techniques which use nitric acid. Fuel alloys which contain a large amount of uranium and small amounts of other metals are hazardous. Uranium-zirconium alloys containing less than 30 wt % zirconium, the EBWR alloy (93.5% U, 5% Zr, 1.5% Nb), and some uranium-niobium alloys are among the alloys which can explode after contacting nitric acid. These fuels which are hazardous in nitric acid can be reprocessed safely by techniques which do not use nitric acid, for example the Zirflex (3) or Zircex (2) processes. Water, rather than nitric acid, should be used to dissolve the chloride residue of the Zircex hydrochlorination of hazardous alloys, to prevent explosions should the alloy not have been completely hydrochlorinated. Further investigations should be made concerning the possibilities of quenching of hazardous alloys so that they may be safely contacted with nitric acid.

This discussion is concerned mainly with two explosion hazards, the epsilon phase explosions (and the related case with niobium-bearing alloys), and the explosive oxidation of finely machined metal fragments. Explosion hazards in fuel reprocessing may exist with reagents other than nitric acid. For example, anhydrous hydrogen chloride in ethyl acetate reportedly can be used to isolate quantities of a pyrophoric minor metallic phase by selective dissolution of the uranium-zirconium matrix (8).

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