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EXPLOSIONS INVOLVING PICKLING OF
ZIRCONIUM AND URANIUM ALLOYS

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W. J. Hurford

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EXPLOSIONS INVOLVING PICKLING OF
ZIRCONIUM AND URANIUM ALLOYS

W. J. Hurford

Introduction

During the AEC Metallurgical Information Meeting, held at Brookhaven National Laboratory in April, 1953, a request was made for an informal meeting to discuss explosion hazards involved in etching and pickling zirconium and uranium and their alloys. During the meeting it was evident that the personnel participating did not have complete information concerning the incidents at their laboratories; therefore, a request was made that reports be written by the participating laboratories and consolidated in a single report for general distribution. This report is a consolidation of information received from the various laboratories. In the interest of expediting the report, the comments of each laboratory are presented essentially as submitted. Attention is called to the following USAEC safety notices:

Serious Accidents, No. 39 (March 19, 1953), No. 44
(April 1, 1953)

Accident and Fire Prevention Information (February 26, 1953)

AMES LABORATORY

O. N. Carlson

An attempt to dissolve uranium which had adhered to the outside of a zirconium jacketed uranium slug was made using concentrated HNO_3 . The acid was contained in a plastic beaker. The explosion took place while no one was in attendance, but acid had been thrown out of the beaker and had sprayed the whole interior of the hood. Apparently, the explosion was caused by acid attack on the diffusion area between the uranium and zirconium metals.

Several minor explosions were also encountered on metallographic specimens of U-Zr-Nb ternary alloys. The exact compositions of the alloys which exploded were not noted. It is known that the composition ranges were the following:

5 to 17 wt % Zr

0.5 to 10 wt % Nb

Remainder U

The alloys had been pickled in dilute HNO_3 for approximately 15 minutes after which they were dried in acetone. During this treatment they had become covered with a grey surface film which upon being scratched or scraped exploded with a small "bang" like a fire cracker accompanied with a bright flash. The samples did not break apart; it appeared to be only a surface phenomenon.

These alloys had been annealed at 850°C and slow cooled.

108-3

BATTELLE MEMORIAL INSTITUTE

F. A. Rough

Experiences at Battelle Memorial Institute with pickling of uranium alloys are summarized as follows:

The explosions which have occurred resulted during pickling operations with 10 to 20 weight per cent zirconium alloys. There were two types: (1) Explosions in the pickling bath, and (2) Explosions where the alloy was transferred to the rinse water and was under or partially under the water.

The former was the most commonly encountered and has been observed in aqueous solutions of 50 volume per cent HNO_3 with small additions of HF . Apparently, all these pickling-bath explosions have occurred where vigorous chemical reaction raised the solution temperature. Difficulty has been encountered both with as-cast and hot-rolled alloys. In most of the cases, a number of pieces of the alloy were being pickled in the same bath. Ventilated hoods were used during pickling. An explosion of similar nature occurred some years ago during pickling of a 5 weight per cent niobium alloy in concentrated nitric acid.

The explosions which occurred in the rinse water resulted where mild-steel-jacketed 10 and 20 weight per cent zirconium alloys were dejacketed in aqueous 50 volume per cent HNO_3 solution. After the iron was removed by vigorous chemical action, the bare alloy rod was transferred to the wash water where the explosion occurred.

No difficulties have been encountered in the following cases: 108-4

- a. Metallographic etching operations involving zirconium alloys from 0 to 100 weight per cent and using a number of methods including HNO_3 - HF combinations.

- b. Pickling of rolled 20 weight per cent zirconium ternary alloys containing varying amounts of molybdenum, niobium, titanium, tin, and thorium. This was done in aqueous solution of 50 volume per cent HNO_3 with addition of about 25 grams per liter of NH_4F or NH_4HF_2 . Vigorous reaction and elevated temperatures were involved.
- c. Room-temperature pickling of numerous small machined samples of all compositions of zirconium alloys and other binaries in aqueous solution of 50 volume per cent HNO_3 .
- d. Pickling of large amount of 5 weight per cent zirconium and smaller amounts of 30 to 100 weight per cent zirconium alloy in hot aqueous solutions of 50 volume per cent HNO_3 containing small amounts of HF .
- e. Pickling of oxide-coated samples of a wide variety of binary alloys including zirconium alloys up to 1 or 2 weight per cent. This was done in aqueous 50 volume per cent HNO_3 .
- f. Dejacketing mild-steel-jacketed 1 and 2 weight per cent zirconium alloy rods in hot aqueous 50 volume per cent nitric acid.
- g. Pickling of large quantities of rolled biscuit uranium in hot aqueous 50 volume per cent HNO_3 .

BRIDGEPORT BRASS COMPANY

E. J. Hennessey and R. M. Treco

Description of Zirconium Pickling Accident of May, 1952

Material: Bureau of Mines Sponge Zirconium

Dimensions: 10" long x 1" O.D. x .015" wall, one end closed.

Treatment: Deep-drawn after annealing with 25% reduction in wall thickness.

After drawing washed in hot water to remove soap lubricant, followed by vapor-blasting to remove oxide in Cro-Hone unit using 200-mesh alundum abrasive. Cold-water rinse after vapor-blasting.

Surface Condition: Gray matte finish, rougher than original oxide surface.

Pickling Solution: 2 l. 1:1 conc. HNO_3

200 ml. HF (48%)

Mixed 4 hours prior to use in Polyethylene container.

Temperature at Start: Room temperature.

Description of Accident: Can was immersed completely in solution with bottom down and held in nichrome tongs. Evolution of brown fumes occurred in 2-3 seconds; a jet of acid erupted from the interior of the tube after about 10 seconds throwing acid as high as 4 feet. Subsequent examination of the can showed extensive solution of the wall along one side leaving large irregular-shaped holes.

Prior to pickling this can, three of four similarly treated cans had been cleaned without incident. No difference could be detected between previous cans and the last one. No sound or flash accompanied the eruption.

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Comments: Metal was in cold-worked condition suggesting a stress-corrosion mechanism. While solution was cold at start, there was heating up from the previous cans. However, similar operations have not resulted in further accidents, although as many as 5 cans have been pickled in one bath. There was no evidence of metallic pieces flying out of the bath and it was concluded that the missing metal had completely dissolved.

In future work the pickling solution has been inhibited with 400 mg/l of Rohm and Haas Triton X-100 and water-jacketed to maintain a temperature of about 12°C. In this inhibited bath as many as 25 similar cans have been pickled without incident.

HANFORD WORKS

J. J. Cadwell

While chemically cleaning five wafers of uranium - 1% zirconium alloy with a concentrated nitric acid solution contained in a polyethylene beaker, a violent reaction occurred blowing acid out of a beaker. The procedure used to etch the alloy wafers was the procedure used routinely for pickling uranium samples. The wafers had been in the concentrated nitric acid media for approximately 30 minutes prior to the incident. A short time before the incident, it was noted that the reaction in the vessel was proceeding vigorously. The contents of the beaker were emptied into a sink and the wafers rinsed with cold water. When the vessel was set aside in the fume hood, a puff of flame emerged from the reaction flask.

After examining the wafers, it was decided that further chemical cleaning was needed and they were again covered with cold concentrated nitric acid. After a short time (of the order of several minutes) the wafers were examined at the fume hood. Upon tipping the beaker a violent reaction occurred, blowing the acid out of the beaker. The reaction beaker which remained in the hood facilities was being observed from a distance of approximately 20 feet when a subsequent explosion occurred. The wafers were then removed from the reaction beaker and gradually immersed in water to prevent further explosions.

It has been observed by members of the Analytical Services group that there is a dangerous reaction between uranium and concentrated nitric acid if the metal and acid volumes are comparable. This reaction apparently does not occur when large volumes or dilute solutions of nitric acid are used to chemically clean relatively small volumes of uranium metal.

The present method of pickling uranium-zirconium alloys has been suspended.

108-8

KNOLLS ATOMIC POWER LABORATORY

D. W. White

With regard to the problem on explosion of zirconium and zirconium-uranium alloys, we have not encountered any evidence of this problem. However, it may be that we have not worked with these materials under such a wide variety of conditions where one might run into this trouble.

We have noticed somewhat similar behavior with pure uranium having quite a lot of oxide on the surface. Upon immersing such material in concentrated nitric acid, we have frequently noticed that it reacts very vigorously or perhaps even violently.

With regard to the "season cracking" phenomenon that has been observed with zirconium-uranium alloys, we have encountered a rather similar behavior with uranium-chromium alloys, which has been discussed in report KAPL-595. When massive pieces of uranium-chromium alloys (containing the order of 1% chromium) are transformed from the beta to the alpha phase under non-isothermal conditions, cracking of the sort described for uranium-zirconium alloys is very apt to occur.

108-9

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

B. R. Russell

In 1952, Roth⁽¹⁾ reported several incidents of explosions while etching uranium-rich zirconium-uranium alloys. Explosions between uranium powder or turnings and nitric acid have been noted in the literature.⁽²⁾ Recently such hazards to workers have been considered serious enough to summarize additional experiences with these alloys since the earlier report. These notes are designed to describe conditions sufficient to cause an explosion with an 80% wt. uranium alloy.

A copper-jacketed uranium alloy, No. 980, was extruded to a final size of 7/16" diameter rod (1/2" O.D. including jacket) at about 600°C. The analysis was:

	<u>Wt.%</u>	<u>At.%</u>
U	78.9	57.4
Zr	20.8	39.5
Fe	0.07	0.2
C	0.20	2.9

The copper jacket was stripped off a length of the rod and 1/16" x 3/4" x 7/16" longitudinal plates were prepared. The plates were ground with various abrasives from No. 24X Norton Metalite belt to as fine as No. 00 Behr-Manning (Norton) polishing paper.

- (1). Roth, H. P., "Explosions Occuring During Chemical Etching and Pickling of Uranium-Zirconium Alloys," MIT-1105 (Dec. 19, 1952).
- (2). Rodden, C. J., et al., Analytical Chemistry of the Manhattan Project, National Nuclear Energy Series, Div. VIII, v. 1, (McGraw-Hill Book Co., Inc., New York, N.Y., 1950), pp. 6-7.
- 108-10

These pieces were tested by dropping them into white concentrated nitric acid from a height of not more than four inches above the surface of the acid in a 100 ml Pyrex beaker.

Neither the surface finish nor state of oxidation was further investigated when it was found that a metastable surface could be put on the alloy at will, starting with a clean, freshly ground sample.

A typical preparation follows:

One of the plates was ground until all traces of surface stains were removed. After the sample was dropped into white concentrated nitric acid (complete immersion), there was no explosion, so exposure was prolonged for five minutes while the acid turned pale yellow. The beaker was deluged with tap water, rinsed with i-propyl alcohol and dried. The oxide (?) film, a very light tan, looked exactly the same as that on freshly-cut uranium exposed to the air for a short time. The film was so light that a casual observer might have called the sample still "bright". The dried sample was again dropped into fresh white concentrated nitric acid and this time there was the characteristic orange-white flash, a report, acid sprayed around, and brown fumes were evolved. After the beaker had been drowned in tap water, one could see a fine black blast-coating on the beaker wall and on the sample itself. The specimen was dried, dropped again into fresh acid, and the explosion repeated with another coating added to the first.

The coatings are not particularly pyrophoric when scratched with a sharp file, although they sparkled brilliantly compared to the original as-ground surface. A Norelco x-ray diffractometer scan of the two active surfaces (sample area 3/4" x 7/16") coated with the products of from two to ten explosions (but still reactive)

showed the following d-spacings in A with CuK radiation:

	<u>Int.*</u>	<u>d, Å</u>	
	strong	3.056	UO ₂ ?
	v. weak	2.811	
	medium	2.649	"
	medium	2.486	"
	weak	2.330	
	medium	1.867	"
broad	medium	1.595	"

*Intensities are of little importance since the sample is not random.

It is believed that these lines are partly explained by a somewhat distorted UO₂ (and possibly ZrO₂) coat. No UH₃ lines⁽³⁾ were found. If the black coat be a mixture of UO₂-ZrO₂, it is difficult to see why the urania does not dissolve in the concentrated acid. The normal uranium oxides dissolve readily in nitric acid without any explosions.

That the degree of shock or impact is a factor in starting the detonation can easily be demonstrated by the fact that very small or light (a gram or less) pieces are exploded less easily than larger (four grams or more) in the dropping test. A clear example of the effect of shock was observed when 3 ml of acid was poured over one of the larger pieces (which had previously exploded by dropping) without exploding, but when the piece was probed with the stainless steel tongs, it exploded.

It would seem to be very difficult to make out a case for the rapid burning of hydrogen itself in these explosions, since there is hardly time for enough gas to accumulate. Indeed, one can point out the danger from this source

(3). Warf, J. C., "Chemical Properties of Uranium Hydride," AECD-2997, (Sept. 29, 1949), p.34.

108-12

in dissolving uranium-silicon (e.g. 4% wt. Si) alloys in warm concentrated hydrochloric acid. The escaping hydrogen bubbles explode at the surface of the sample and also of the liquid with enough violence to spatter. If the acid is diluted 1:1 with water, the reaction rate is low enough to be safe,⁽⁴⁾ although actually concentrated nitric acid is recommended⁽⁵⁾ for dissolving the sample for chemical analysis.

In summary we should state that we have never observed the explosion of uranium, uranium alloys (including zirconium alloys), nor zirconium in the massive dry condition. Detonations at M.I.T. with uranium-zirconium have only been associated with contact with nitric acid, and at that only a reactive surface sensitive to mechanical shock seems to be involved. Whether this surface is a catalyst for the violent decomposition of nitric acid, or whether some metastable compound (such as metallo-nitrogen compound or hydrazine⁽²⁾) accumulated and developed by immersion in nitric acid itself explodes, cannot be stated without further work. The possibility of the generation of UH_3 was considered, in view of its well-known instability,⁽⁶⁾⁽⁷⁾ but it could not be detected by preliminary x-ray tests on active surfaces.

Finally, it should be emphasized that NO SURFACE PREPARATION CAN BE CONSIDERED SAFE AGAINST EXPLOSIONS EVEN WITH MOMENTARY CONTACT WITH CONCENTRATED NITRIC ACID. In conducting tests, the experimenter should be warned to wear a transparent helmet, since the ordinary face mask will not protect the victim against falling acid spray.

(4). Personal communication from Mr. Charles Allbright.

(5). Ref. 2, p. 219.

(6). Hartman, I., Nagy, J., Jacobson, M., "Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium and their Hydrides," BM-RI-4835 (Dec. 1951).

(7). Ref. 3, p. 52.

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SYLVANIA ELECTRIC PRODUCTS INCORPORATED

A. S. Kalish

At our Bayside Laboratories we have been fortunate in having no difficulty with explosions involving zirconium or any alloys even in the powder form. During the grinding of the powder in a steel mortar and pestle we have had very minor flash fires which involved only the few grams of powder in the mortar and were carried no further. No difficulty of any kind has been encountered with zirconium or its alloys in the solid form even where considerable pickling has been done.

At our Photoflash Lamp Division some severe flash fires have been encountered during the drying operation of very fine zirconium powder or of the fine zirconium powder mixed with oxidizing agents. This material is now handled with special equipment described by W. C. Fink, "A Laboratory for the Production of Zirconium Ignition Pastes for Photographic Flashlamps". The Sylvania Technologist, Vol. 5, No. 1, Jan. 1952, p. 7-9.

The problem with these powders, however, is probably peculiar to the photoflash lamp industry and not necessarily pertinent to work on solid zirconium where the chief difficulty seems to be in the pickling operation. One clue, however, is that the powder is unusually dangerous just at the point of becoming dry from the wet condition. Perhaps after pickling it is during the drying that the zirconium is liable to burn or explode.

108-18

WESTINGHOUSE ATOMIC POWER DIVISION

F. R. Lorenz

The first experience with explosions while etching uranium-zirconium alloys in nitric acid occurred at WAPD in December, 1952, while cleaning the black material from the surface of some material which had been hot rolled from a lithium-potassium-sodium carbonate salt bath. A 8.7% (wt.) zirconium alloy was treated with no trouble, but a 27.7% zirconium alloy gave several violent eruptions of the acid solution (50% HNO_3 by volume) and broke the Pyrex beakers in which the work was being done. The circumstances attending the explosions seemed to point to the touching off of the reaction by a spark during movement and handling of small pieces of the alloy.

In January, 1953, additional difficulties were once again encountered and this time the 8.7% zirconium alloy was the material in process. About 20 rods, 1/4" square and 8" long, were being prepared for remelting after having been rolled at 1500°F from the carbonate salt bath. Again the etching was done in a fresh solution of 50% HNO_3 (volume), and the processing was done in a 2-1/2" x 12" x 18" Pyrex tray (unheated, although heat is generated by the reaction). All of the rods had been placed in the solution and after about 4 minutes the first one was removed with metal tongs, rinsed under running water, scrubbed with a wire brush to remove salts which were left on the surface, rinsed again and set aside to dry. There was considerable sparking during the brushing operation. Six additional pieces were processed in this manner, then two pieces were removed from the solution to be rinsed and were accidentally dropped into the stone sink. The resultant explosion, accompanied by a bright flash, blew some water out of the sink. These

pieces were then brushed and rinsed again. All of the rods had a grey appearance after the scrub and rinse. A few succeeding pieces were done with no trouble, but a later one exploded while being scrubbed and was knocked out of the hand of the technician doing the pickling. In order to stop the dangerous work in process, it was necessary to remove the balance of the rods from the pickling solution. Three pieces were removed with metal tongs and immediately there was an explosion and flash which ejected most of the acid from the tray. The remaining pieces were removed by handling them one at a time with rubber gloves. These were rinsed in running water and set aside. Next when several pieces which had been etched, scrubbed and set aside to dry (for about 45 minutes) were moved slightly, there was a very loud explosion and bright yellow flash. About 15 minutes later, these same pieces were moved one at a time with no trouble, except one which was intentionally maltreated by striking it on the floor, resulting in a bang and bright flash which seemed to cover the entire surface.

At present, these alloys are handled by either wet blasting or anodic treatment in concentrated sulphuric acid. Etching in nitric acid after wet blasting the oxide off still causes explosions. The anodic treatment gives a bright surface and has not caused any explosions. All of the explosions which have been experienced at WAPD seem to have been a surface effect and in some manner associated with friction or shock induced during handling.

Attention is called to a reference in "Reactions of Uranium with Aqueous Acid Solutions"* in which the authors state that "since nitric acid vapors or nitrogen dioxide can react with uranium with explosive violence, it is necessary to add finely divided uranium to the nitric acid in small portions to avoid accidents".

*The Chemistry of Uranium: Part I, Katz and Rabinowitch, 1st Ed., 1951