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EXPLOSIONS OCCURRING DURING
CHEMICAL ETCHING OR PICKLING
OF URANIUM-ZIRCONIUM ALLOYS

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Authorizing Official
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December 19, 1952

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts

EXPLOSIONS OCCURRING DURING CHEMICAL ETCHING
OR PICKLING OF URANIUM-ZIRCONIUM ALLOYS

by H. P. Roth

Some time ago several comparatively minor explosions occurred at the Atomic Energy Commission Metallurgical Project at M.I.T. At least two of these explosions inflicted acid burns upon personnel involved. It is considered advisable that any available information relative to these explosions be disseminated. The exact cause or reaction which brought about these explosions is not understood. Therefore, this presents only the facts as recorded or best remembered relative to each explosion and no attempt is made to explain the chemical reaction involved. Observations and comments are included for their possible value.

General Information

A total of five explosions occurred in various departments of the laboratory. All involved the chemical etching of cast and extruded uranium-zirconium alloys of high uranium content in nitric acid baths. In three cases the uranium content of the alloy was the same, i.e., approximately 79% by weight. In the other cases the uranium content was higher, i.e., 82% and 91% by weight. M.I.T. chemical analyses gave the following results in weight percentage for those alloys which exploded:

Weight Percentage for Alloys Which Exploded

U	Zr	Fe	C
78.9	20.8	.07	.20
81.8	17.1	.20	.14
91.0	8.7	.06	.06

EXPLOSION # 1Personnel involved:

H. Sawyer

Date:

February 1, 1951

Alloy composition:

79 wt.% uranium, approximately

Sample condition and size:

Piece of extruded rod from M.I.T. alloy billet #980.

Dark, oxide coating on exterior of piece. Copper jacket had been mechanically removed. Size of samples about $1/4 \times 1/8 \times 3/4$ inch.

Acid bath,composition:

Concentrated nitric acid. 150 ml. approximate total volume.

temperature:

Below boiling. Not precisely controlled. Kept warm by placing over flame at intervals.

heating medium:

Bunsen burner with two wire screens for deflecting flame.

container:

Pyrex crystallizing dish within outer glass dish containing water bath.

introduction of other implements such as tongs, stirrer,
etc.:

Tongs (Cenco stainless steel) had been used but were not immersed at time of explosion.

age:

Fresh bath in which about two samples had been etched immediately prior to explosion. Previous bath prepared and discarded same day after several samples because of discoloration and accumulation of sediment.

time of sample immersion prior to explosion:

3 or 4 minutes.

Nature of explosion,

flash:

Small, bright flash.

sound:

Sharp crack.

force and damage:

Glass containers shattered. Most of acid solution driven forcefully upward to top of hood, falling to head, back of neck, shoulders and hands of operator standing a foot or two away.

Other information:

Purpose of etching, to clean off oxide coating for x-ray and chemical analysis of clean metal remaining.

EXPLOSION # 2Personnel involved:

A. R. Kaufmann

Date:

February 1, 1951. Approximately 15 minutes after Explosion #1.

Alloy composition:

Same sample piece as involved in Explosion #1

Sample condition and size:

Same sample piece as involved in Explosion #1

Acid bath,composition:temperature:heating medium:container:

Probably cooled to room temperature

introduction of other implements such as tongs, stirrer, etc:

Stainless steel tongs.

age:time of sample immersion prior to explosion:

} See other information below.

Nature of explosion,flash:

Small, white flash.

sound:

Sharp crack.

force and damage:

Force mild, damage none. Not sufficient acid present for great spattering.

EXPLOSION # 2, Cont'd

Other information:

Shortly after Explosion # 1 there was an inspection of the scene. The sample remained in a small amount of acid bath, probably about 8 ml. of solution, within a portion of broken container on sink bench. An attempt was made to remove the sample piece of metal from debris when a second explosion occurred. Water was immediately poured over all.

EXPLOSION # 3Personnel involved:

R. B. Russell

Date:

February, 1951

Alloy composition:

91 wt.% uranium, approximately.

Sample condition and size:

Piece of extruded rod from M.I.T. alloy billet #981. Black scale on exterior. Copper jacket had been mechanically removed. Sample size about $1/4 \times 1/8 \times 3/4$ inch.

Acid bath,composition:

Concentrated nitric acid, between 10 and 100 ml. total volume.

temperature:

Room temperature.

heating medium:

None.

container:

Pyrex crystallizing dish.

introduction of other implements such as tongs, stirrer,etc.:

Tongs had been inserted previously.

age:

Freshly prepared.

EXPLOSION # 3, Cont'd.

time of sample immersion prior to explosion:

About 4 minutes.

Nature of explosion,

flash:

Not observed.

sound:

Like a "mud" explosion or a loud cough.

force and damage:

Container not broken. Most of acid forcefully shot upward to top of etching hood. Operator sustained burns on shoulders, neck and hands.

Other information:

Purpose of etching was to clean off oxide coating to reveal clean metal for x-ray examination.

EXPLOSION # 4

Personnel involved:

E. B. Read

Date:

March, 1951

Alloy composition:

79 wt.% uranium approximately.

Sample condition and size:

Thick, dark oxide coating. Material from same rod
as in Explosion # 1.

Acid bath,

composition:

50-50 concentrated nitric acid and water by volume,
plus a few drops of hydrofluoric acid added shortly
before explosion. 150 ml. approximate total volume.

temperature:

Not more than 50-60°C.

heating medium:

Sand bath.

container:

Pyrex beaker.

introduction of other implements such as tongs, stirrer,
etc.

None.

age:

Freshly prepared.

EXPLOSION # 4, Cont'd.

time of sample immersion prior to explosion:

Several minutes in nitric acid water only. Reaction was slow. A minute or two after the few drops of hydrofluoric were added, beaker was lifted by hand and rotated which caused swirling of mixture and sample within, when explosion occurred.

Nature of explosion:

flash:

Bright.

sound:

force and damage:

Beaker did not break. Force threw most of acid upward and it fell on arms and clothing of operator.

other information:

Purpose was to clean off metal prior to chemical analysis.

EXPLOSION # 5Personnel involved:

W. Paynton

Date:

February, 1952

Alloy composition:

82 wt.% uranium, approximately.

Sample condition and size:

From M.I.T. alloy billet #979, extruded rod 1/2 inch in diameter and 2 feet long, encased in a copper jacket. One end showed a clean, transverse cut.

The opposite end, which was origin of explosion, had the characteristic appearance of the leading end of an extruded uranium rod. The copper jacket receded about a half inch from the end leaving the uranium alloy exposed. This was badly blackened, apparently by a heavy oxide coating.

Acid bath,composition:

A large volume of concentrated nitric acid and tap water. Proportions approximately 50-50.

temperature:

Room temperature.

heating medium:

None.

container:

Vented stainless steel pickling tank approximately 7 feet

EXPLOSION # 5, Cont'd.

long, 6 inches wide and $7\frac{1}{2}$ inches deep, hooded with plate glass on top surface and transite sides hinged to drop open.

introduction of other implements such as tongs, stirrer, etc.:

Tongs were immersed. See second item below entitled "Time of sample immersion".

Age:

Freshly prepared prior to etching 2 rods each approximately 3 feet long. These rods contained about 30 wt. % uranium in zirconium and were jacketed with copper. They did not explode.

time of sample immersion prior to explosion:

Approximately 10 minutes. Only the leading end of the rod had been cleared of copper. This exploded upon contact with air when lifted up with stainless steel tongs.

Nature of explosion,

flash:

Blue flame.

sound:

Deep, fairly powerful.

force and damage:

Blew out one side of hood. Splashed acid within hood and out at side. Some acid splashed on operator's hand and clothing.

EXPLOSION # 5. Cont'dOther information:

There was another rod with copper jacket in the bath at the same time with the one which exploded. It was primarily zirconium, 99.72 wt.%. The purpose was to remove the copper jackets by pickling. After the explosion the rods were allowed to remain in the pickling solution for several minutes. Then water was introduced to dilute the acid and the drain plug was withdrawn.

OBSERVATIONS AND COMMENTS

The main conditions attendant in all these occurrences were the presence of a fairly heavy, dark-colored oxide coating and the addition of nitric acid. Pieces of the same alloy were later etched or dissolved for various tests in the same acid baths after all traces of flaky oxide coating were removed by grinding or machining. No difficulties were encountered in etching.

The nature of the explosion is not understood and no clear explanation has been proposed and proven to be correct. It is not the purpose of the investigator gathering these facts to encourage the use of nitric acid with any high uranium-zirconium metal whether the thick oxide coating be present or not. It has been noted that this coating when particularly thick does not seem to be readily attacked by the acid. Rather, it appears to build up, being removed only after a long etching period and then not uniformly. The metal beneath the layer becomes attacked in certain spots allowing the acid to penetrate beneath the coating which finally comes away from the metal in black flakes rather than as a solute. This brings forth another thought. It may be that an essential factor in this type of explosion is extremely clean metal of certain composition. This may be why explosion does not occur immediately upon contact with the acid.

Temperature did not seem to be the vital factor. Neither

an open flame nor friction seemed to be essential. Copper was not always visibly present, nor was hydrofluoric acid always present in the solutions. It might be deduced in the case of Explosion #4 that the addition of hydrofluoric acid may have contributed to combustion by increased attack of the zirconium content attended by release of hydrogen. Also, there may possibly have been more localized heating due to this reaction. These did not seem to be vital points in view of the fact that hydrofluoric acid was not introduced into the other baths involved.

It is to be noted that uranium-zirconium alloys of 60 wt.% uranium and less were etched and pickled on numerous occasions and with varying strengths of nitric acid without ill effects. This is not to imply that they need not be handled with due caution. It is also of interest that alloys in this range as well as those causing these explosions were all immersed in various perchloric acid solutions without mishap. This was during electrolysis in an attempt to produce a surface with a polish of sufficiently high reflectivity for microscopic examination. In most of these cases it is not likely that heavy oxide coatings were present.

Recommendations:

It is strongly recommended that all uranium-zirconium alloys of greater than 75 wt.% uranium content be kept out of nitric acid.