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THE IDENTIFICATION AND CHARACTERIZATION OF EXPLOSIVE RESIDUES
PRODUCED BY DISSOLUTION OF URANIUM-ZIRCONIUM ALLOYS

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THE IDENTIFICATION AND CHARACTERIZATION OF EXPLOSIVE RESIDUES
PRODUCED BY DISSOLUTION OF URANIUM-ZIRCONIUM ALLOYS

I. INTRODUCTION

Hurford⁽¹⁾ has recently summarized the experiences of investigators at various AEC sites who have, in the course of their work with uranium-zirconium alloys, noted explosive reactions when these alloys were treated with nitric acid. In general, these workers observed that nitric acid pickling of uranium-zirconium alloys produced gray or black residues on the metal surface. These films were found to be extremely sensitive to shock, and, in some cases, detonated with sufficient violence to break glassware.

Uranium-zirconium alloys have a number of desirable properties with respect to their use as fuel elements for various reactors. The formation and detonation of explosive films which could occur during chemical processing of such irradiated fuel elements is thus of considerable importance. For this reason, an experimental investigation was carried out to identify and characterize the nature of the explosive surfaces. The results obtained are presented in this paper; the application to the problem of explosion hazards in dissolving processes, however, appears in a separate report.⁽²⁾

It should also be noted that, concurrent with this investigation, similar programs have been underway at both Argonne National Laboratory and Ames Laboratory. Insofar as was possible, results obtained in this investigation have been compared with results obtained at these other sites.

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- (1) Hurford, W. J., Explosions Involving Pickling of Zirconium and Uranium Alloys, WAPD-84, May 28, 1953. (~~Confidential~~).
- (2) Schulz, W. W., Scott, F. A., and Voiland, E. E., Explosion Hazards in the Nitric Acid Dissolution of Uranium-Zirconium Alloy Fuel Elements, HW-32365, July 20, 1954. (~~Secret~~).

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II. SUMMARY AND CONCLUSIONS

The properties of explosive residues formed during the dissolution of certain uranium-zirconium alloys were investigated. The composition and reactions of such residues and factors affecting their formation are discussed. The following conclusions were drawn:

1. Explosive residues are formed on the surfaces of annealed uranium-zirconium alloys as the result of the preferential attack of the alpha uranium phase.
2. Residues are isolated in a very finely divided state, and explosions occur as the result of a rapid oxidation process.
3. The residues isolated in this investigation consisted of a mixture of (a) an explosive component which has been identified with an intermetallic compound of uranium and zirconium (epsilon phase), (b) an inert component believed to be a solid solution of zirconium and uranium oxides, and (c) zirconium carbide, an impurity resulting from the use of graphite crucibles and molds during alloy preparation.
4. Residues derived from slow-cooled or annealed alloys contain predominantly the epsilon phase. Residues isolated from gamma quenched alloys were not explosive and are believed to be principally solid solutions of uranium and zirconium oxides.
5. The composition of the pure intermetallic compound is approximately UZr_2 .
6. The intermetallic compound was tentatively assigned a body centered cubic structure with $a = 6.16 \text{ \AA}$.
7. UZr_2 is desensitized by nitric-acid. The rate of desensitization increases with increasing acidity and temperature.
8. Uranium-zirconium alloys can be completely dissolved in nitric acid solutions containing sufficient fluoride or fluosilicate ion to react with the zirconium.

III. EXPERIMENTAL

A. Preparation and Isolation of Explosive Residues

1. Alloy Description

Explosive residues were prepared and isolated from a number of different uranium-zirconium alloys. The major portion of the experimental work, however, was performed with material isolated from a 1.59 weight per cent alloy (Alloy 1) prepared at Hanford by personnel of the Fuel Technology Sub-Section. This particular alloy was prepared by fusion of an alloy of higher zirconium concentration with uranium. The resulting alloy was cast in a graphite mold and furnace cooled.

Explosive films were also isolated from 4.9 weight per cent and 8.7 weight per cent alloys (Alloys 2 and 3) obtained from the Ames Laboratory. These alloys were prepared by co-reduction of uranium tetrafluoride and zirconium tetrafluoride. After melting in a graphite crucible, the alloy was poured into a graphite mold, quenched, and cut into 1/4 inch lengths. Lengths of both alloys were heated at 850 C for two hours and then water quenched. Alloy 2 was then annealed at 750 C for two hours, at 600 C for two hours, and at 500 C for twenty hours, while Alloy 3 was annealed at 750 C for two hours, at 650 C for two hours, and at 500 C for only two hours.

Experiments were also carried out with samples of the 4.9 weight per cent and 8.7 weight per cent alloys which had not been annealed after being water quenched from 850 C. Residues isolated from these two unannealed alloys (Alloys 4 and 5) were not explosive. The effect of the heat treatment of the alloy on the production of explosive residues is more fully discussed later (cf. page 11).

Photomicrographs of the alloys used in this investigation are shown in the Appendix.

2. Procedures for Residue Preparation

Preliminary experiments revealed that explosive films readily formed on the surfaces of Alloys 1, 2, and 3 when specimens of these alloys were immersed in 6-15.7 M HNO_3 at 50-100 C for 5-20 minutes. Similarly, explosive films could be produced by treatment with hydrochloric acid or by anodic dissolution in a variety of electrolytes. Workers at Argonne report⁽³⁾ that explosive residues can also be prepared by dissolution of uranium-zirconium alloys in ethyl acetate solutions of anhydrous hydrogen chloride. These results indicate that formation of explosive residues from annealed uranium-zirconium alloys occurs with reagents which preferentially dissolve the uranium-rich phase.

On the other hand, it was observed that uranium-zirconium alloys could be completely dissolved in nitric acid if about four moles of fluoride ion were added (as hydrofluoric acid) per mole of zirconium. Dissolution under these conditions resulted in shiny metallic surfaces without formation of any film or residue. Similar results were obtained with nitric acid solutions containing ammonium fluosilicate. Nitric-hydrofluoric acid dissolution of uranium-zirconium alloys has been extensively studied at Argonne⁽⁴⁾ as a method for the safe dissolution of the uranium-zirconium alloys (two weight per cent zirconium) contemplated for use as EBR fuel elements.

Although various procedures served for the isolation of residues, further experiments showed that the explosive nature of these residues was strongly dependent on the exact conditions of preparation. Complete dissolution of the uranium-rich phase from a portion of the 1.59 weight per cent alloy in 15.7 M HNO_3 left a residue which was completely inert

(3) Summary Report, Chemical Engineering Division, July, August, and September, 1953, ANL-5169, December 1, 1953. Page 47. (Secret).

(4) Summary Report, Chemical Engineering Division, October, November, and December, 1953, ANL-5213, February 1, 1954. Pages 6-10. (Secret).

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when sparked with a Tesla coil. Conversely, the residue left on the surface of the same alloy after only twenty minutes immersion in boiling 15.7 M HNO_3 detonated with a brilliant flash and a loud report. Residues of different sensitivity could be produced at lower acidities and temperatures. These results indicated the necessity for a quantitative measure of the explosive property.

3. Determination of Residue Sensitivity

It was found that the explosive property could be conveniently measured by determining the weight of oxygen taken up when a known weight of residue was detonated in an atmosphere of pure oxygen. The explosive property was denoted by the term "sensitivity" and was arbitrarily defined as the milligrams of oxygen taken up per 100 milligrams of residue reacted. Experimentally, sensitivity was determined by transferring 20-100 milligrams of residue to a weighed vessel and evacuating to about 10^{-5} millimeters mercury pressure. A known pressure of oxygen was then admitted, and the reaction initiated with the spark from a Tesla coil. The amount of oxygen taken up was determined from the gain in weight and was also calculated from the ideal gas equation after measurement of the change in oxygen pressure and the volume of the vessel. The calculated and measured weight gains generally agreed to within five per cent.

Some results of the application of the sensitivity test to residues obtained from Alloys 1, 2, and 3 under a variety of conditions are shown in Table I.

On the basis of oxygen uptake the most sensitive residue was prepared from Alloy 1 by anodic dissolution (0.3 amp/cm^2) in 1 M HNO_3 . Under these conditions the residue adhered to the alloy surface in the form of a black powder which was easily scraped off at the conclusion of electrolysis. Residues prepared by this technique were washed thoroughly with water and acetone, air dried, and stored under vacuum for subsequent identification and characterization.

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TABLE I
RESIDUE SENSITIVITY

Weight oxygen taken up determined as indicated in the text (page 10).

<u>Alloy Number</u>	<u>Residue Preparation</u>	<u>Sensitivity (mg O₂/100 mg Residue)</u>
1	Anodic dissolution in 1 <u>M</u> HNO ₃ 1 hour, 5 amperes.	17.
1	Nitric acid pickling 10 <u>M</u> HNO ₃ , 20 min., 100 C.	12.
1	Nitric acid pickling 15.7 <u>M</u> HNO ₃ , 20 min., 100 C.	10.
1	Anodic dissolution in 30% H ₃ PO ₄ 1 hour, 15 amperes.	10.
1	Anodic dissolution in 0.5 <u>M</u> citric acid 1 1/2 hours, 10 amperes.	4.
2	Anodic dissolution in 1 <u>M</u> HNO ₃ 1 hour, 5 amperes.	3.
3	Anodic dissolution in 1 <u>M</u> HNO ₃ 1 hour, 5 amperes.	7.
3	Nitric acid pickling 8 <u>M</u> HNO ₃ 1 hour, 80 C.	5.

Anodic dissolution in 1 M HNO₃ was also found to yield more sensitive residues from Alloys 2 and 3 than the other procedures tested. However, the sensitivity of these residues was considerably less than that prepared from the 1.59 weight per cent alloy.

4. Effects of Alloy Heat Treatment on Residue Sensitivity

As indicated earlier, residues isolated from the quenched alloys were not sensitive. This observation is in agreement with results obtained at Ames. Investigators there report⁽⁵⁾ that explosive films could not be produced on alloys quenched from 725 C but could be formed if the alloy was annealed at 625 C or lower before pickling.

(5) Quarterly Summary Research Report in Metallurgy, April, May, and June, 1953, ISC-396, November 16, 1953. Page 33. (Secret).

A further difference between quenched and annealed alloys was that only small quantities of residue could be prepared from the quenched alloys. Thus, dissolution of samples of the 8.7 weight per cent quenched and annealed alloys in boiling 13-14 M HNO_3 produced residues corresponding respectively to one and ten per cent of the initial weights of alloy taken. Experiments at Argonne have also shown that annealed alloys yield larger quantities of residue.⁽⁶⁾

The experiments with the quenched alloys thus demonstrated the dependence of residue sensitivity on the prior heat treatment of the alloy. These experiments also suggested that a further heat treatment of the annealed alloys, 2 and 3, might be beneficial with respect to the preparation of more sensitive residues from these two alloys. Accordingly, samples of Alloys 2 and 3, as well as samples of the two quenched alloys, 4 and 5 were sealed in an evacuated quartz tube, placed in a muffle furnace, and subjected to the following heat treatment: seven hours at 850 C, nine hours at 700 C, seven hours at 625-650 C, ten hours at 575-600 C, and furnace cooling to room temperature. Residues were then prepared by anodic dissolution in 1 M HNO_3 , and sensitivities were determined as before. Table II lists the results obtained. For comparison, the sensitivity of residues from the 1.59 weight per cent alloy is also shown.

(6) ANL-5169. IBID. Page 47.

TABLE II
INFLUENCE OF ALLOY HEAT TREATMENT ON RESIDUE SENSITIVITY

Heat Treatment:		7 hours at 850 C	
		9 hours at 700 C	
		7 hours at 625-650 C	
		10 hours at 575-600 C	
Alloy Number	Zirconium Wt. - Per Cent	Residue Sensitivity (mg O ₂ /100 mg)	
		Before Heat Treatment	After Heat Treatment
1	1.59	17.	(a)
2	4.9	3.	18.
3	8.7	7.	14.
4	4.9	(b)	18.
5	8.7	(b)	14.

(a) Alloy not heat treated

(b) Residues completely inert before heat treatment

The data in Table II show that, in each case, heat treatment resulted in the production of more highly sensitive residues. In the case of Alloys 2 and 4, residues isolated after heat treatment were as sensitive as those prepared from the 1.59 weight per cent alloy. The result for Alloy 4 is particularly noteworthy in that, prior to heat treatment, residues from this alloy were totally insensitive. More highly sensitive residues were also derived from the 8.7 weight per cent alloys, 3 and 5; these alloy residues were, however, still less sensitive than those from the other alloys.

A satisfactory explanation for the variation of residue sensitivity with alloy heat treatment may be developed from a consideration of the uranium-zirconium constitutional diagram (Figure 1). This diagram represents the consensus of a group of representatives from several laboratories at a meeting in March 1954. The participating laboratories were Ames, Battelle Memorial Institute, Argonne National Laboratory, Sylvania, Knolls Atomic Power Laboratory, Massachusetts Institute of

Technology, Westinghouse Atomic Power Division, and National Bureau of Standards. At the top of the diagram, the inset section at the left represents the early work of Dr. A. R. Kaufmann, the section at the right that of F. A. Rough and A. A. Bauer. We are indebted to Dr. Rough for the copy reproduced in this document.

Examination of the phase diagram shows that the only phases to be expected at room temperature, when equilibrium conditions exist, are the alpha and epsilon phases. The phase diagram also shows that the epsilon phase in alloys of low zirconium content corresponds to an intermetallic compound of the approximate composition, UZr_2 . Analyses of residues exhibiting maximum sensitivity (cf. page 23) indicate Zr/U mole ratios of 1.9 to 2.4. This is strong evidence to indicate that the preparation of sensitive residues corresponds to the isolation of the epsilon phase.

In the event that equilibrium has not been established in the annealed alloy, the metastable gamma phase may co-exist with the alpha and epsilon phases. The exact quantities of each will depend on the time of annealing, the kinetic aspects of the phase transformation, and on the zirconium content of the alloy. The behavior of these three phases upon anodic dissolution of the alloy in 1 M HNO_3 may be considered to be as follows: the alpha phase, which may contain as much as 0.3 weight per cent dissolved zirconium, is rapidly attacked and almost completely dissolves, leaving a small amount of inert residue. The gamma phase is inhomogeneously attacked leaving an insensitive residue. The epsilon phase is only slowly attacked and is isolated as a sensitive residue. The net result is the isolation of a sensitive intermetallic compound diluted with inert material. The amount of oxygen taken up by a particular residue thus depends on the amount of inert material present and thus ultimately on the heat treatment of the alloy.

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B. Characterization of Residues

1. X-Ray Diffraction Analysis

The x-ray diffraction powder patterns of various sensitive and insensitive residues were obtained to characterize these residues. Such patterns were invaluable in comparing sensitive and insensitive residues obtained either from different alloys or by different methods of preparation.

Table III is a compilation of d values, line intensities, and tentative hkl assignments of the patterns of representative sensitive residues. The similarity of sensitive residues is evident in Table III, and is even more apparent when the actual diffraction films are observed. Table III contains all of the lines appearing in the x-ray patterns of sensitive residues.

In the characterization of the sensitive residues, lines corresponding to a face centered cubic material were indexed. This component was identified as zirconium monocarbide by comparison of the diffraction pattern with the catalogued ASTM values.* It may be concluded from the relative ratios of the zirconium monocarbide lines that the carbide content of sensitive residues is small and varies in sensitive residues derived from different alloys.

The occurrence of zirconium monocarbide in sensitive residues is not surprising since all of the alloys used were melted and cast in graphite crucibles. Furthermore, zirconium monocarbide would be expected to be relatively inert under the mild conditions used to prepare sensitive residues, and, accordingly, would be isolated with the inter-metallic compound.

*A personal communication from Dr. F. A. Rough at Battelle Memorial Institute indicates that the pattern might result from the zirconium analogue of the slightly distorted cubic hafnium hydride, but from the mode of preparation this seems unlikely.

TABLE III

X-RAY DIFFRACTION PATTERNS OF SENSITIVE RESIDUESResidue 1 - Prepared by anodic dissolution of Alloy 1 in 1 M HNO₃.Residue 2 - Prepared by pickling Alloy 1 in 8 M HNO₃ for 10 mins. at 80 C.Residue 3 - Prepared by anodic dissolution of Alloy 4 in 1 M HNO₃ after heat treatment described on Page 11.

hkl Assignment		Residue 1		Residue 2		Residue 3	
hkl ^(a)	hkl ^(b)	$\frac{d}{\text{\AA}}$	Intensity	$\frac{d}{\text{\AA}}$	Intensity	$\frac{d}{\text{\AA}}$	Intensity
110		4.30	VW	---	---	---	---
200		3.01	MVB	3.01	MVB	3.01	MVB
	111	2.65	W	2.69	M	2.65	W
211		2.55	VS	2.51	S	2.55	S
	200	2.39	W	2.33	M	---	---
220		---	---	2.16	VW	2.10	VW
310		1.98	M	1.95	M	1.95	S
		1.85 ^(d)	VW	1.84 ^(d)	VW	1.85 ^(d)	VW
222		1.80	M	1.77	M	1.79	S
321	220	1.66	W	1.65	M	1.63	M
411-330		1.46	W	1.45	M	1.45	M
	311	---	---	1.40	M	1.42	W
	222	1.35	VW	1.34	VW	1.35	VW
332		1.33	M	1.31	M	1.32	M
422		1.26	W	1.25	W	1.26	M
	400	1.16	W	1.16	W	1.16	W
521		1.12	W	1.12	W	1.12	VW
	321	1.07	VW	1.07	W	---	---
530-433		1.05	VW	1.06	W	---	---
	420	---	---	1.04	W	1.03	W
442-600		---	---	1.02	W	---	---
620		---	---	0.97	W	---	---
541	422	0.95	MB	0.95	MB	---	---

(a) Body centered cubic

(b) Face centered cubic

(c) Legend of Intensities

S = Strong

W = Weak

B = Broad

M = Medium

V = Very

(d) This line is believed to arise from small amounts of oxide diluent.
See Page 17 and Table V.

The lines remaining after elimination of those due to zirconium monocarbide were indexed (with the exception of one line at $\underline{d} = 1.85 \text{ \AA}$) on a bodycentered cubic system with a unit cell of 6.16 Å. Calculated and found values for $\sin^2 \theta$ are tabulated in Table IV. This structure was assumed to be that of the epsilon phase in the uranium-zirconium system.

Inspection of the films showed the unindexed line at $\underline{d} = 1.85 \text{ \AA}$ to be extremely diffuse, and it was noted that it corresponded to the second strongest line of the x-ray pattern of insensitive residues. The strongest line of the insensitive residue patterns occurs as a similar diffuse line in the region $\underline{d} = 3.02 \text{ \AA}$ and is undoubtedly responsible for the diffuse, complex band at $\underline{d} = 3.01 \text{ \AA}$ to $3.07 \text{ \AA}$ in the patterns of the sensitive powder. Rough⁽⁷⁾ reports only a very weak line at $\underline{d} = 3.07 \text{ \AA}$ in the x-ray pattern of the epsilon phase of an uranium-49 weight per cent zirconium alloy.

Rough's data on the epsilon phase includes all of the lines in the body centered cubic pattern of this study except the lines with $\underline{d}$ values of 1.65 Å and 0.95 Å. This disagreement is not serious, however, since these lines may also be assigned to the face centered cubic component, ZrC. Rough also includes lines with $\underline{d}$ values of 1.16 Å (W) and 1.54 Å (VW) in the pattern of the epsilon phase. Mueller⁽⁸⁾ also feels that the 1.54 Å and 1.16 Å lines should be included along with a line at $\underline{d} = 1.21 \text{ \AA}$. No lines with $\underline{d}$ values of 1.54 Å and 1.21 Å were found in any of the patterns of sensitive residues reported here.

The assignment of the line with a $\underline{d}$ value of 1.16 Å is critical since a cubic configuration cannot be assigned to the epsilon phase if this line is included in its pattern. As indicated in Table III, assignment of this line to the face centered cubic zirconium carbide pattern was made, and thus, it

(7) Rough, F. A., Re: Uranium-Zirconium Constitutional Diagram, GEH-21364, August 31, 1954 (Confidential).

(8) Personal Communication from Dr. M. H. Mueller, Argonne National Laboratory.

TABLE IVCALCULATED AND EXPERIMENTAL $\sin^2 \theta$ VALUES FOR THE
BODY CENTERED CUBIC COMPONENT OF SENSITIVE RESIDUES

hkl	Intensity ^(a)	$\sin^2 \theta$	
		Found	Calculated
110	W	0.0316	0.0314
200	S	0.0630	0.0628
211	S	0.0939	0.0942
220	W	0.1267	0.1256
310	M	0.1565	0.1570
222	M	0.1878	0.1884
321	M	0.2187	0.2198
411 (330)	M	0.2829	0.2826
332	M	0.3446	0.3454
422	W	0.3770	0.3768
521	W	0.4703	0.4710
530 (433)	W	0.5323	0.5338
442 (600)	W	0.5670	0.5652
620	W	0.6268	0.6280
541	M	0.6605	0.6594

(a) Legend of Intensities

S = Strong
M = Medium
W = Weak

was possible to ascribe a body centered cubic structure to the epsilon phase. In view of the disagreement between the various investigators over the inclusion of the line corresponding to a d value of 1.16 Å, however, the authors feel that sufficient data are not available at this time to unequivocally decide the real structure of the epsilon phase. Nevertheless, the near identity of the x-ray patterns of sensitive residues with Rough's epsilon phase alloy does indicate a high percentage of epsilon phase in the sensitive residue.

From x-ray diffraction analyses it is highly probable that the sensitive residues isolated by anodic dissolution consist principally of finely divided epsilon phase uranium-zirconium alloy, contaminated by varying amounts of zirconium monocarbide and inert oxide.

X-ray diffraction data for various insensitive residues are listed in Table V. The x-ray patterns indicate that the same material is produced when quenched alloys are pickled in nitric acid or when sensitive residues are either leached in nitric acid or ignited in oxygen. It is believed that these inert residues are principally solid solutions of uranium and zirconium oxides. Little success, however, was attained in characterizing the x-ray diffraction patterns. Identification of the inert residues with the $\text{UO}_2\text{-ZrO}_2$ system⁽⁹⁾ was unsuccessful. On the other hand, investigators at Argonne National Laboratory⁽¹⁰⁾ have isolated residues from the reaction of various uranium-zirconium alloys with nitric acid which they have analyzed by x-ray diffraction as $\text{UO}_2\text{-ZrO}_2$ mixed oxide phases.

2. Chemical Composition

The samples of sensitive residues were dissolved in a 1:1 mixture of concentrated nitric and hydrofluoric acids. The excess hydrofluoric acid was then removed by fuming with perchloric acid followed by fuming with acidified boric acid. Uranium and zirconium hydroxides were precipitated and converted to the chloride by addition of hydrochloric acid. The insensitive residues could not be completely dissolved in nitric acid or nitric-hydrofluoric acid mixtures. They were fused with potassium pyrosulfate, and the uranium and zirconium precipitated twice as the hydroxide before final conversion to the chloride system. Uranium in these solutions was determined by titration with chromium (II) sulfate. Zirconium was determined by titration with sodium versenate (alizerol cyanone RC indicator) according to the method of Fritz and Fulda⁽¹¹⁾.

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- (9) Lambertson, W. A. and Mueller, M. H., Uranium Oxide Phase Equilibrium Systems: III, $\text{UO}_2\text{-ZrO}_2$, J. Am. Ceram. Soc., 36, 365, (1953).
- (10) Personal Communication from Dr. M. H. Mueller, Argonne National Laboratory.
- (11) Fritz, J. S. and Fulda, M. O., Titrimetric Determination of Zirconium, ISC-382, July 28, 1953. (Unclassified).

TABLE V

X-RAY DIFFRACTION PATTERNS OF INSENSITIVE RESIDUES

- Residue 1 - Prepared by heating sensitive residue from heat treated Alloy 4 in boiling 15.7 M HNO_3 for 5 hours.
 Residue 2 - Prepared by nitric acid pickling of Alloy 5.
 Residue 3 - Prepared by heating sensitive residue from Alloy 1 in boiling 10 M HNO_3 for 8 minutes.
 Residue 4 - Prepared by ignition of sensitive residue from Alloy 1 in oxygen.

Residue 1		Residue 2		Residue 3		Residue 4	
d	Intensity ^(a)	d	Intensity	d	Intensity	d	Intensity
$\text{\AA}$		$\text{\AA}$		$\text{\AA}$		$\text{\AA}$	
---	---	4.13	W	4.15	M	4.09	M
3.67	W	3.72	W	3.67	M	3.69	M
3.35	W	---	---	3.36	W	3.37	M
3.02	S	3.00	S	3.02	S	3.02	S
2.64	M	2.67	S	2.64	M	2.67	M
2.54	W	2.58	W	2.55	W	2.55	M
---	---	2.47	M	---	---	---	---
2.32	W	2.32	M	---	---	---	---
1.91	W	1.88	W	1.89	W	1.90	M
1.82	S	1.84	M	1.82	VS	1.84	S
1.73	W	1.74	W	---	---	1.75	W
1.69	W	1.68	W	---	---	1.69	W
1.61	M	1.60	W	1.63	M	1.67	M
---	---	1.58	M	---	---	---	---
1.53	M	1.54	M	1.54	M	1.55	S
1.50	M	1.51	W	1.51	M	---	---
1.47	M	1.47	W	1.47	M	1.47	W
---	---	1.42	W	---	---	1.42	VW
---	---	1.29	W	---	---	1.28	VW
1.24	W	1.27	VW	1.26	W	---	---
1.23	W	---	---	1.24	W	1.23	W
1.20	W	1.19	W	1.21	M	1.21	W
---	---	1.15	W	1.16	M	1.15	W
---	---	1.12	W	1.12	W	1.12	VW
---	---	---	---	1.02	W	---	---
---	---	---	---	0.99	W	0.99	W
---	---	---	---	0.96	VW	0.91	VW

(a) Legend of Intensities

S = Strong
 M = Medium
 W = Weak
 V = Very

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The precision of the analytical methods was determined from a series of analyses of exploded residues which had been partially densitized by nitric acid (cf. page 26). These samples showed no trend in Zr/U ratio with variation in experimental conditions, and their x-ray diffraction patterns were identical. The average of determinations of twelve samples of these exploded inert residues derived from Alloy 1 is listed in Table VI. The average deviation from the mean was three per cent for zirconium, two per cent for uranium, and two per cent for total uranium-zirconium. The methods were never tested on standards comparable to the experimental samples although mixtures of uranium dioxide, zirconium dioxide and solutions containing hydrofluoric acid were used.

Results of analyses of various residues are listed in Table VI. Although the precision of the determinations (performed in duplicate) for each type of residue is good, the Zr/U ratios obtained from the sensitive residues are in each case less than the ratios from their exploded counterparts. Since any fractionation of uranium and zirconium during the oxidation is inconceivable, this discrepancy must stem from a bias in the analytical method as applied to these samples. However, if credence is placed in either set of values for the Zr/U ratio, it is observed that an increase in sensitivity is associated with a decrease in Zr/U ratio.

Consideration of the uranium-zirconium phase diagram and the effect of alloy heat treatment on sensitivity lead to the identification of the explosive component of residues as the epsilon phase. In all of the sensitive residues isolated in this investigation, however, the epsilon phase was never isolated in a pure state but was always found associated with a small amount of zirconium carbide and with varying amounts of uranium-zirconium mixed oxides. Assuming that the composition of the epsilon phase is UZr_2 and the oxidation products are UO_2 and ZrO_2 , the residue corresponding to a sensitivity of 17.5 mg O_2 /100 mg contains 77 per cent epsilon phase.

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TABLE VI
CHEMICAL ANALYSIS OF VARIOUS RESIDUES^(a)

Alloy		Residue Type	Residue Analysis (per cent)			Zr/U Ratio	Sensitivity (mg O ₂ /100 mg residue)
No.	w/o Zr		Zirconium	Uranium	Sum		
1	1.59	Sensitive	46.9	51.2	98.1	2.4	} Avg. 17.5
1	1.59	Sensitive	47.9	50.5	98.4	2.5	
1	1.59	Sensitive	45.8	49.9	95.7	2.4	
1	1.59	Inert - Exploded ^(b)	39.4	40.2	79.6	2.6	
2	4.9	Sensitive	44.8	35.	79.8	3.3	3.
2	4.9	Sensitive	47.	36.	83.	3.4	3.
2	4.9	Inert - Exploded	49.7	32.3	82.0	4.0	--
3	8.7	Sensitive	43.9	36.4	80.3	3.2	6.7
3	8.7	Sensitive	44.2	37.0	81.2	3.1	6.9
3	8.7	Inert - Exploded	45.4	32.1	77.5	3.7	--
3	8.7	Inert - Exploded	44.8	32.1	76.9	3.6	--
3	8.7	Inert - Exploded	44.7	31.8	76.5	3.7	--
4-HT ^(c)	4.9	Sensitive	43.0	51.1	94.1	2.2	18.
4-HT	4.9	Inert - Exploded	35.6	41.4	77.0	2.2	--
5	8.7	Inert - HNO ₃ desensitized	48.9	34.0	82.9	3.8	--
5-HT	8.7	Sensitive	43.4	49.3	92.7	2.3	14.
5-HT	8.7	Inert - Exploded	36.4	38.7	75.1	2.5	--

(a) Sensitive residues derived by anodic dissolution in 1 M HNO₃.

(b) Average of 12 analyses (cf. text, page 22)

(c) 'HT' indicates alloy after heat treatment described on page 11.

X-ray data show the epsilon phase to predominate in residues from Alloy 1 and Alloy 4-HT in which minimum Zr/U ratios occur. In residues from Alloys 5-HT, 3 and 2, however, the epsilon phase content decreases in the order listed and the Zr/U ratios increase. Thus a higher content of epsilon phase in a sensitive residue is accompanied by a decrease in Zr/U ratio. The relationship between epsilon phase content, sensitivity, and Zr/U ratios indicate that the composition of the pure intermetallic compound is very close to UZr_2 .

The higher Zr/U ratios associated with residues of lower epsilon content are to be expected if the oxide component in such residues is richer in zirconium than the epsilon phase. This belief is supported by the fact that a completely inert residue having a Zr/U ratio of 3.8 was derived from Alloy 4 (gamma quenched) having a Zr/U ratio of 0.25.

3. Reactions of Explosive Residues with Nitric Acid

Early attempts to prepare sensitive residues by pickling techniques indicated that explosive residues are appreciably desensitized in hot nitric acid solutions. Consequently, in the dissolution of the bulk alloy, an equilibrium concentration of the explosive material results from the concurrent production and removal of the sensitive material. Since some knowledge of the magnitude of this steady state concentration is necessary to estimate the extent of the explosion hazard, a series of exploratory experiments was performed to outline the kinetics of the desensitization process. Furthermore, it was hoped that the kinetic behavior might provide additional information concerning the nature of the sensitive material.

Several batches of residue were prepared by anodic dissolution of Alloy 1 in 1 M HNO_3 . They were then combined and the sensitivity determined. Weighed samples of this starting material were then introduced into ten milliliter portions of nitric acid solutions in which the concentration of acid was varied from zero to 13 moles per liter. The reaction was

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allowed to proceed for a measured time at a fixed temperature and was then quenched by the addition of an excess of cold water. The residue was washed by decantation with water and acetone, air dried and weighed. The amount of oxygen consumed by an aliquot of this partially desensitized residue was then determined. The resulting exploded residue was analyzed for uranium and zirconium. Data obtained are listed in Table VII.

The partially desensitized residues could not be readily recovered quantitatively. In order to correct the weights of the recovered residues for the losses incurred in the manipulative procedure it was necessary to take into account the fact that dissolution, as well as desensitization, occurs when sensitive residues are treated with nitric acid. Evidence of dissolution was obtained from qualitative tests of the supernatant solutions. In those solutions of higher acidity traces of uranium and zirconium were found. These qualitative tests indicated that dissolution was slight at lower acidities and temperatures. In these latter experiments some manipulative losses were observed, and 90 per cent of the stoichiometric weight of residue was recovered. The 90 per cent recovery factor was, therefore, used to correct all weights of partially desensitized residues. The assumption of a 90 per cent recovery factor introduces a slight uncertainty in the quantity of recovered residue, and, consequently, a slight uncertainty in the value for the amount of epsilon phase remaining.

An estimate of the fraction of sensitive residue dissolved could have been obtained from analyses of the supernatant solutions. Unfortunately, at the time these experiments were carried out no adequate analytical method for the determination of small quantities of zirconium was available. In lieu of direct experimental values the dissolution losses were calculated in the following manner. The weights of recovered residues (on the basis of a 90 per cent recovery factor) were corrected for the gain in weight caused by the partial oxidation. It is possible to make this correction since x-ray data and chemical analysis show that the same

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TABLE VII

DESENSITIZATION AND DISSOLUTION OF SENSITIVE RESIDUES IN NITRIC ACID

(Unless otherwise indicated experiments carried out at 100-104 C with residue isolated from Alloy 1 by anodic dissolution in 1 M HNO_3)

HNO_3 M	Time in HNO_3 (min)	Sensitive Residue (mg)		Partially Desensitized Residue (mg)			Fraction Epsilon Remaining	Fraction Sensitive Residue Dissolved(d)	Zr/U Ratio in Exploded Residue
		Weight	Epsilon Content(a)	Weight(b)	Sensitivity (mg O_2 /100 mg)	Epsilon Content(c)			
13	2	104.6	81.	104.	7.7	35.	0.44	0.10	2.5
13	4	97.1	75.	87.	5.6	21.	0.28	0.20	2.6
10	5	95.3	73.	90.	3.9	15.	0.21	0.19	2.8
10	8	80.5	62.	72.	2.4	8.	0.12	0.24	2.5
10	20	72.9	56.	55.	negligible	negligible	negligible	0.37	2.6
7	10	81.4	63.	76.	4.5	15.	0.24	0.18	2.7
7	10	47.7	37.	41.	5.1	9.	0.25	0.25	2.6
7	18	90.0	69.	81.	1.3	5.	0.07	0.35	2.6
7	4	119.4	36. (e)	114.	3.4	17.	0.48	negligible	3.7
7	8	70.6	21. (e)	73.	2.0	6.4	0.30	negligible	3.6
2	16	111.4	86.	116.	10.2	52.	0.60	0.03	2.6
2	40	97.8	75.	102.	3.3	15.	0.20	0.10	2.6
0	60	47.5	37.	47.	11.1	23.	0.62	0.07	2.5
7	18(60 C)	57.3	44.	59.	12.1	31.	0.71	0.02	2.5
7	18(80 C)	50.5	39.	48.	5.1	11.	0.28	0.17	2.5
2	20(0.75 M UNH)	54.0	42.	53.	7.9	18.	0.44	0.11	2.4
2	20(1.5 M UNH)	62.6	48.	61.	3.7	10.	0.20	0.16	2.6

- (a) Residues from Alloy 1 were calculated from their oxygen consumption to contain 77 per cent UZr_2 .
 (b) Corrected for manipulative losses. 90 per cent recovery assumed.
 (c) Calculated on the basis that 1 mg O_2 consumed is equivalent to 4.38 mg UZr_2 .
 (d) Derived from difference between initial weight sensitive residue and weight of partially desensitized residue after correction for weight gain due to partial oxidation.
 (e) Residues from Alloy 3 were calculated from their oxygen consumption to contain 29 per cent UZr_2 .

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product is formed by nitric acid desensitization and by explosion in oxygen. The weight increase due to nitric acid oxidation is obtained from the difference in sensitivity before and after partial desensitization. The difference between the initial weight of sensitive residue and the corrected weight of recovered sensitive residue was then taken to be the dissolution loss. Values computed in this manner are shown in Table VII. These values cannot be considered too reliable, however, since the uncertainty involved in assuming a 90 per cent recovery factor enters into their estimation. They do, however, indicate that dissolution occurs at a slower rate than desensitization.

Attempts to systematize the data obtained at the boiling temperatures resulted in the curves depicted in Figure 2 which show an apparent first order dependence of the densensitization process on the amount of sensitive material. The rate constants derived from these curves are listed in Table VIII.

TABLE VIII
FIRST ORDER REACTION RATE CONSTANTS FOR THE DENSENSITIZATION OF EXPLOSIVE RESIDUES BY NITRIC ACID

<u>Nitric Acid</u> <u>M</u>	<u>k^(a)</u> <u>min⁻¹</u>	<u>k/HNO₃</u>
2	0.038	0.02
7	0.15	0.02
10	0.28	0.03
13	0.33	0.03

(a) k is the constant in the expression $-\frac{dA}{dt} = kA$, in which A represents the explosive residue content.

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Inspection of this table shows an approximate linear relationship between these rate constants and the nitric acid molarity. This relationship leads to the following expression which relates explosive residue, nitric acid concentration (moles/liter), and time of reaction (minutes) at the boiling temperature: $\log A/A_0 = -(0.012 [HNO_3] - 0.008)t$.

The effect of a decrease in temperature is a diminution of desensitization rate. The relative rates at 60, 80 and 104 C are very roughly 1, 4, and 11. On the other hand, the addition of excess nitrate as uranyl nitrate results in an increase in the desensitization rate.

Although residues derived from Alloy 1 were the principal material used in this study, two experiments were performed with residue from Alloy 3. As shown in Figure 2, the kinetic behavior of this residue was identical with that from Alloy 1 despite its much smaller initial sensitivity. This strongly confirms that sensitive residues are mixtures of at least two components. One is explodable and is common to both sensitive residues. The remaining material is inert and acts as a diluent for the reactive material. It is also interesting to note that the dissolution rate of the residues from Alloy 3 is much less than those from Alloy 1.

Although much conjecture is possible, the mechanism of the desensitization reaction cannot be established on the basis of the available data. The reaction is heterogeneous and might be expected to follow zero order kinetics with the rate being dependent on particle size and possibly, under some conditions, on a diffusion step. It is, therefore, surprising that first order kinetics should be found and until verified should be considered only tentatively established. The relationships, however, are empirically valid and can be used in the estimation of explosive residue content in the nitric acid dissolution of U-Zr alloys.

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FIGURE 2

RATES OF DESENSITIZATION OF EXPLOSIVE RESIDUES IN
SOLUTIONS OF VARYING NITRIC ACID CONCENTRATION

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IV. ACKNOWLEDGEMENT

The authors wish to acknowledge the cooperation of I. M. Brickey of the Fuel Technology Sub-Section in preparing the uranium - 1.59 weight per cent zirconium alloy. Acknowledgement is also made to D. W. Brite of the Chemistry Unit for the development of analytical procedures for the determination of zirconium in the various residues.

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APPENDIX

Photomicrographs of the various alloys used in this investigation are shown in Figures 1-12. Specimens were etched by two to five seconds electropolishing in a bath consisting of five parts phosphoric acid, five parts ethylene glycol, and eight parts ethyl alcohol.

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FIGURE 1-ALLOY 1-CAST
URANIUM-ZIRCONIUM AL-
LOY CONTAINING 1.59 PER-
CENT ZIRCONIUM. SLOW
COOLED. SENSITIVITY--
17 mg O₂/100 mg residue.

250 X

FIGURE 2 - ALLOY 1 AT
GREATER MAGNIFICATION
1000X

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FIGURE 3 - ALLOY 1 AFTER
25 HOUR ANNEALING AT 550 C
AND WATER QUENCHING FROM
550 C. RESIDUE COMPLETELY
INERT.

250X

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FIGURE 4 - ALLOY 1.
WATER QUENCHED FROM
800C AFTER 15 MINUTES AT
THIS TEMPERATURE.

250 X

FIGURE 5-ALLOY 2-CAST
URANIUM-ZIRCONIUM
ALLOY CONTAINING 4.9
PERCENT ZIRCONIUM.
(cf. P. 8 FOR HEAT TREAT-
MENT SCHEDULE) SENSI-
TIVITY-3mg O₂/100 mg
residue.

250 X

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FIGURE 6-ALLOY 4-SPECI-
MEN OF ALLOY 2 AFTER
QUENCHING FROM 850 C.
RESIDUE COMPLETELY
INERT.

250 X

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FIGURE 7-ALLOY 4 AFTER
HEAT TREATMENT DE-
SCRIBED ON P. 12 SENSI-
TIVITY-18 mg O₂/100 mg.
RESIDUE.

250 X

FIGURE 8-SAME SPECIMEN
AS IN FIGURE 7 AT A
GREATER MAGNIFICATION.
1000 X

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FIGURE 9-ALLOY 3-CAST
URANIUM ZIRCONIUM
ALLOY CONTAINING 8.7
PERCENT ZIRCONIUM. (cf.
P. 8 FOR HEAT TREAT-
MENT SCHEDULE.) SENSI-
TIVITY--7 mg O₂/100 mg
RESIDUE.

250 X

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FIGURE 10-ALLOY #5-
SPECIMEN OF ALLOY 3
AFTER QUENCHING FROM
850 C. RESIDUE COM-
PLETELY INERT.

250 X

FIGURE 11-ALLOY 5 AFTER
HEAT TREATMENT DES-
CRIBED ON P. 12. SENSI-
TIVITY--14 mg O₂/100 mg
RESIDUE.

250 X

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FIGURE 12-SAME SPECIMEN
AS IN FIGURE 11 AT A
GREATER MAGNIFICATION,
1000 X

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ABSTRACT

The properties of residues produced by nitric acid dissolution of uranium-zirconium alloys containing 1.5, 4.9, and 8.7 weight per cent zirconium were investigated.

Residues from annealed alloys consisted principally of a finely divided explosive component which was identified as an intermetallic compound (epsilon phase) with the approximate composition UZr_2 . Also present were small amounts of zirconium carbide formed in the alloy preparation and an inert material believed to be a solid solution of uranium and zirconium oxides produced by the attack of nitric acid on U-Zr solid solution phases.

Partially annealed alloys produced residues with less epsilon content and more inert oxide, while the residues from gamma quenched alloys were non-explosive and consisted primarily of the inert oxide.

On the basis of x-ray diffraction data, the epsilon phase has been assigned a body centered cubic structure with $a = 6.16 \text{ \AA}$.

Both desensitization and dissolution occur when the intermetallic compound reacts with nitric acid. Kinetic studies indicate the rate of desensitization to be first order with respect to the explosive compound and nitric acid. The rate of dissolution is markedly slower than the rate of desensitization.

Metallographic and x-ray diffraction data are included.

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