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REACTIVITY OF CERTAIN URANIUM OXIDES
WITH ALUMINUM

Terminal Report

By
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February 10, 1958

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ABSTRACT

The reaction between uranium dioxide and aluminum has been studied at 600°C and below. At 600°C the visible reaction occurred within a few hours, while, for example, at 500°C and below, the specimens had to be at temperature for several days in order to show signs of any reaction. The method of manufacture of uranium dioxide had a pronounced effect on its compatibility. Granulated and high-fired oxides showed lowest, and the steam-treated oxide showed maximum, reactivity. The fact that finer oxide powder particles react faster than coarse ones was according to expectations. Mallinckrodt U₃O₈ powder of very fine particle size reacted severely with aluminum during a 1-1/2-hr test at 610°C.

I. INTRODUCTION

The work covered by this report consisted of a study of the compatibility of aluminum with some oxides of uranium at elevated temperatures. Uranium dioxide made by several different processes was evaluated in these studies and Mallinckrodt U_3O_8 was also subject of tests.

Since brazing of aluminum-clad fuel elements containing a core of uranium dioxide dispersed in aluminum usually is carried out at approximately 600°C , most experimental work for the tests described below was performed at this temperature. A limited amount of tests was carried out at other temperatures between 450° and 610°C .

Other variables in these tests, besides the process of manufacture and the reaction temperature, were: the amount of the oxide, the size of the oxide particles, and the time at temperature of the oxide-aluminum mixtures.

II. PREPARATION OF SAMPLES

The following raw materials were used for these tests:

- 1) Aluminum: ALCOA type HP-120 powder, -325 mesh size
- 2) Uranium dioxide*
 - a) Mallinckrodt-AEC Production Grade - prepared from calcined uranyl nitrate (-325, -140 +325 mesh)
 - b) Mallinckrodt High-Fired - prepared from calcined ammonium diuranate high fired at 1700°C . Contains 1/2% TiO_2 (-325, -140 +325 mesh)
 - c) Granulated - preparation similar to high-fired Mallinckrodt. Contains 3% CaF_2 in place of TiO_2 (-140 +325 mesh)
 - d) AEC Production Grade Arc Melted and Comminuted (-325, -140 +325 mesh)

* In the following, UO_2 is written for the uranium dioxide, although it can be assumed that the oxygen content was above the stoichiometric compound, Type UO_{2+x} . The surplus x of oxygen was probably not uniform in all the oxide powders used for these tests.

- e) Hydrothermal (Geneva Oxide) - prepared from calcined ammonium diuranate. $\text{UO}_3\text{-H}_2\text{O}$ intermediate, prepared in autoclave and high fired at $1600^\circ\text{-}1700^\circ\text{C}$ to UO_2 (-140 +325 mesh)
 - f) Steam-oxidized - prepared by oxidation of uranium in autoclave (-325 mesh). (Particles of this material were considerably smaller than other uranium dioxides tested.)
- 3) U_3O_8 made by Mallinckrodt, -325 mesh size, containing a large amount of very fine particles.

Initial work was concentrated on a comparison of the reactivities of uranium dioxide manufactured by various processes. A standard composition of 54 w/o UO_2 - 46 w/o Al was chosen. This is the approximate composition of 20% enriched MTR-type fuel plates containing UO_2 .

The particular uranium dioxide and the -325 mesh aluminum powder were weighed out and tumble-mixed in glass bottles for two hours. Specimens were cold pressed at 36 tsi in a 2" x 1/2" single-action V-block die, with no lubricant. These core compacts were then inserted in type 1100 aluminum picture frames and covered with plates of the same material. The cover plates were spot-welded into place and the assembled specimens were then hot rolled at 600°C to a final core size of 2" x 2" x 0.020". It is estimated that each compact spent approximately one hour at or near 600°C during the preheating and rolling operations. This time has not been taken into consideration in reporting the results obtained, and should be considered in any quantitative analysis of the data.

Other samples tested were manufactured as full-size MTR-type fuel plates. These included plates containing 32.8 w/o UO_2 (-325 mesh Mallinckrodt High Fired), 34.5 w/o U_3O_8 (-325 mesh Mallinckrodt), and UO_2 -bearing segmented gradient fuel plates containing 70 w/o UO_2 , 40 w/o UO_2 and 10 w/o UO_2 sections (-325 mesh Mallinckrodt High Fired).

The 32.8 w/o UO_2 and 34.5 w/o U_3O_8 -containing compacts were compacted at 36 tsi in a 3.25" x 2.375" die. The resultant UO_2 -containing compacts were 0.175" thick and the U_3O_8 -containing compacts were 0.190" thick. These core compacts were also assembled in type 1100 aluminum picture frames and covered with type 1100 aluminum plates 0.097" thick.

These plates were hot rolled at 600°C to a thickness of 0.054" and given a cold finishing pass to 0.050". The final core thickness of these plates was 0.030" with 0.010" of aluminum cladding top and bottom.

Manufacturing procedures for the gradient fuel plates were identical to those described above. Estimated time at 600°C during preheating for hot rolling for all the above plates was again one hour.

III. EXPERIMENTAL PROCEDURE

Two series of coupon specimens made with AEC Production Grade UO_2 were placed in an air furnace at 600°C. One group was made using -325 mesh UO_2 and the other contained -140 +325 mesh UO_2 . One specimen from each group was removed after each of the following times: 5, 15 and 30 minutes, and 1, 8, and 24 hours. All specimens were observed macroscopically and metallographically and were compared with unreacted controls. Since no reaction between aluminum and uranium dioxide was observed at times up to and including one hour, the latter was set as the shortest time for which data were taken in subsequent runs.

Similar tests on coupon specimens made with other types of UO_2 provided data on the UO_2 -Al reaction at various times between 1 and 16 hours.

In order to obtain data on the time required for the initiation of reaction between UO_2 and aluminum at 500°C, the 40 w/o UO_2 and 70 w/o UO_2 areas of two gradient fuel plates were held at this temperature. Samples were removed at 1, 2, 4 and 7 days and were compared metallographically with untreated controls.

In order to compare Mallinckrodt U_3O_8 with Mallinckrodt High-Fired UO_2 , plates containing 32.8 w/o UO_2 and 34.5 w/o U_3O_8 were held at 450°C for three hours and at 610°C for 1.5 hours. The plates were visually observed and samples of each type were studied metallographically after each heat treatment.

IV. DISCUSSION OF RESULTS

Examinations of the UO_2 -Al specimens after heat treatments were performed in two ways. The specimens were examined visually for gross distortion. In all cases where such distortion was observed, it took the form of a bulge in the center, as shown in Fig. 1.

The specimens were then examined metallographically under high magnification (500-700X). At the start of reaction, a light-colored reaction product could be seen around the UO_2 particles. As the reaction progressed, larger areas of what had been UO_2 appeared as reaction product. There appeared to be porosity in the specimens after severe reaction. Visible distortion did not occur until some time after the reaction product was first observed metallographically.

A. 54 w/o UO_2 Coupons Tested at 600°C

Data obtained in these experiments indicate that the time for initiation of reaction between UO_2 and Al depends on the manufacturing history of the uranium dioxide. Reaction rate is dependent on the UO_2 particle size. Results obtained with various types of UO_2 are described below.

(1) Mallinckrodt-AEC Production Grade UO_2

Fig. 2a is a photomicrograph of a control specimen made with -140 +325 mesh Production Grade UO_2 . After one hour at 600°C, no reaction was apparent in specimens containing UO_2 of -325 mesh or -140 +325 mesh particle size (Figs. 3a and 2b). After eight hours, considerable reaction had occurred in the -325 mesh specimen. (Figs. 3a and 3b). Some reaction had also taken place in the -140 +325 mesh specimen (Fig. 2c), but particles of UO_2 , around which there was no reaction product at all, could still be seen. After 24 hours at 600°C, considerably more reaction was apparent in the -140 +325 mesh specimen (Fig. 2d). All grains of UO_2 appeared to be reacting. Although the photomicrograph of the -325 mesh specimen taken after 24 hours (Fig. 3c) shows little difference in appearance from that taken after 8 hours, over-all observation of the specimens indicated that more reaction had occurred at the longer time.

(2) Mallinckrodt High-Fired UO_2

Time for initiation of reaction in High-Fired UO_2 -Al specimens made with -325 mesh and -140 +325 mesh was between 1 and 2 hours. This reaction was slight and there was no distortion of the specimens. After six hours at 600°C, the reaction had progressed considerably, but it was not as severe as that observed in samples made from production grade UO_2 . Figs. 4 and 5 show the micro-

structure of high-fired UO_2 -Al specimens as fabricated and after six-hour treatment.

(3) Granulated UO_2

Granulated UO_2 appeared to be the least reactive of the oxides studied. Specimens made with -140 +325 mesh material showed no reaction after one hour at 600°C , and only slight reaction with no observable distortion after an eight-hour run.

(4) Production Grade UO_2 - Arc Melted and Comminuted
(Arc melting and mechanical comminution at Sylcor Labs.)

This material was very reactive in the presence of aluminum. Compacts made with -140 +325 mesh UO_2 of this type showed slight reaction after one hour at temperature. The reaction was practically complete within four hours. Figs. 6a, b and c show the progress of this reaction. Fig. 7a shows a control specimen made with -325 mesh arc-melted UO_2 . After one hour at 600°C , the reaction was severe (Fig. 7b) and the specimen was distorted. Fig. 7c, taken after sixteen hours at temperature, shows that the reaction is about complete.

(5) Hydrothermal UO_2 (Geneva Oxide)

Geneva oxide is also quite reactive in the presence of aluminum at 600°C . Compacts containing -140 +325 mesh UO_2 started to react within one hour. After four hours, the reaction was largely completed. Figs. 8a, b and c show the stages of this reaction.

(6) Steam-oxidized UO_2

Steam-oxidized UO_2 was the most reactive of the oxides studied. This was at least partially due to the extremely fine particle size of the material manufactured by this process (Fig. 9a). After two hours at temperature, the specimen showed severe distortion and gross reaction. An observation at six hours (Fig. 9b) showed the reaction to be complete.

B. Gradient Fuel Plates Tested at 500°C

Tests at 500°C of 40 w/o UO_2 -Al and 70 w/o UO_2 -Al sections of gradient fuel plates indicated that considerably longer time

is required for initiation of an Al — UO_2 reaction at this lower temperature. As expected, reaction rate is much smaller at 500°C than at 600°C . Some reaction was observed in the 70 w/o UO_2 compartment after four days at temperature. After seven days at 500°C , some distortion was evident in the sample, but the reaction had not proceeded too far. Figs. 10a, b and c show the structure of the UO_2 -Al core as fabricated and after four and seven days.

No reaction was observed in the 40 w/o UO_2 segment during the seven-day duration of the test, as can be seen from Figs. 11a and b.

C. Comparison of High-Fired UO_2 with Mallinckrodt U_3O_8

Fig. 12a shows the core structure of a 34.5 w/o U_3O_8 -Al plate as manufactured. The size of the individual U_3O_8 particles was extremely small and there was a tendency to form agglomerates of U_3O_8 during tumble-mixing and fabrication. Heating of these plates at 450°C for three hours resulted in no reaction between the U_3O_8 and aluminum (Fig. 12b), and no distortion of plates. However, when these specimens were given an additional treatment of 1-1/2 hours at 610°C , large blisters were observed on the surface. Diameters of these blisters varied from 1/2 inch to 1-1/2 inches. Figs. 12c and 12d show the structure of the core in an unblistered area and in the vicinity of one of the blisters. The U_3O_8 appears to be completely reacted.

By comparison, Figs. 13a, b and c show the structure of cores containing 32.8 w/o UO_2 -Al which were tested along with the U_3O_8 -Al plates. There was no reaction between UO_2 and aluminum after three hours at 450°C , and only a slight reaction after the additional treatment of 1-1/2 hours at 610°C . The reaction product formed in the U_3O_8 plates does not appear to be UO_2 . It is likely that this product is the same one that results from the UO_2 -Al reaction.

V. CONCLUSIONS

The reaction of uranium dioxide with aluminum has been studied at 450° , 500° and 600°C . In most cases reaction at 600°C occurred within a few hours, whereas reactions at 500° were hardly observed before a time period of several days. The method of manufacturing UO_2 has a pronounced effect on its reactivity. Granulated and high-fired material showed minimum reactivity with aluminum, and the highest reactivity was observed with

steam-treated UO_2 . For comparison purposes, tests were also made with Mallinckrodt U_3O_8 of extremely fine particle size, which, among the specimens tested, showed the highest degree of reactivity to aluminum. Investigations of the UO_2 -Al interaction at elevated temperatures, as described in this report, demonstrate that the time required for onset of reaction depends on (a) the process of manufacture of the oxide; (b) additions to the oxide, such as TiO_2 or CaF_2 ; (c) the particle size of the oxide; (d) the particle shape of the oxide; and (e) the reaction temperature.

With respect to the manufacturing process of the UO_2 particles, the reactivity ranks as follows (starting with the least reactive material):

- 1) Granulated UO_2
- 2) Mallinckrodt high-fired UO_2
- 3) Mallinckrodt-AEC production grade UO_2
- 4) Hydrothermal UO_2
- 5) AEC production grade UO_2 - arc melted and comminuted
- 6) Steam oxidized UO_2

Small additions of CaF_2 or TiO_2 to UO_2 seem to have a beneficial effect on its stability.

Metallographic investigations showed clearly that in many instances small UO_2 particles in a specimen were already reacting while some larger particles still appeared unaffected.

Elongation of UO_2 particles (usually of agglomerates) during the rolling process results in the formation of stringers, and on account of the larger surface area the reaction occurs considerably faster.

An unusual result observed in the UO_2 -Al specimen tested at 500°C was that reaction was observed in the 70 w/o UO_2 specimens while none was apparent in the 40 w/o UO_2 plates. Further work is necessary to clear up this point.

The Mallinckrodt U_3O_8 that was tested is definitely more reactive with aluminum than are the various types of UO_2 .

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Fig. 1 Photograph of 70 w/o UO_2 -Al specimen after 16 hours at 600°C . Bulge in center is typical of the distortion resulting from UO_2 -Al reaction.

Plate #4129

a) Unreacted

Plate 18848

b) Heated at 600°C for 1 hr.

Plate 18852

c) Heated at 600°C for 8 hrs.

Plate 18853

d) Heated at 600°C for 24 hrs.

Plate 18854

Fig. 2 Core section containing 54 w/o UO_2 in Al, made from -140 +325 mesh size Mallinckrodt AEC production grade UO_2

Mag. 500X

a) Heated at 600°C for 1 hr.

Plate 18849

b) Heated at 600°C for 8 hrs.

Plate 18850

c) Heated at 600°C for 24 hrs.

Plate 18851

Fig. 3 Core section containing 54 w/o UO_2 in Al, made from -325 mesh size Mallinckrodt-AEC production grade UO_2 Mag. 500X

a) Not heated (unreacted)

Plate 18174

b) Heated at 600°C for 6 hrs.

Plate 18175

Fig. 4 Core section containing 54 w/o UO_2 in Al, made from -140 +325 mesh size Mallinckrodt high-fired UO_2
Mag. 500X

a) Not heated (unreacted)

Plate 18170

b) Heated at 600°C for 6 hrs. Plate 18171

Fig. 5 Core section containing 54 w/o UO_2 in Al, made from -325 mesh size Mallinckrodt high-fired UO_2 Mag. 500X

a) Not heated (unreacted)

Plate 18203

b) Heated at 600°C for 1 hr.

Plate 18204

c) Heated at 600°C for 4 hrs.

Plate 18205

Fig. 6 Core section containing 54 w/o UO_2 in Al, made from production-grade UO_2 , arc melted and comminuted to -140 +325 mesh size Mag. 500X

a) Not heated (unreacted)

Plate 18206

b) Heated at 600°C for 1 hr.

Plate 18207

c) Heated at 600°C for 16 hrs. Plate 18208

Fig. 7 Core section containing 54 w/o UO_2 in Al, made from production-grade UO_2 , arc melted and comminuted to -325 mesh size Mag. 500X

a) Not heated (unreacted)

Plate 18200

b) Heated at 600°C for 1 hr.

Plate 18201

c) Heated at 600°C for 4 hrs.

Plate 18202

Fig. 8 Core section containing 54 w/o UO_2 in Al; UO_2 made from -140 +325 mesh size hydrothermal uranium oxide
Mag. 500X

a) Not heated

Plate 18172

b) Heated at 500°C for 6 hrs. Plate 18173

Fig. 9 Core section containing 54 w/o UO_2 in Al; UO_2 made by steam oxidation of uranium powders
Mag. 500X

a) Not heated (unreacted) Plate 19030

b) Heated at 500°C for 4 days Plate 19031

c) Heated at 500°C for 7 days Plate 19032

Fig. 10 Core section containing 70 w/o UO_2 in Al; -325 mesh size
Mallinckrodt high-fired UO_2 Mag. 500X

a) Not heated

Plate 19028

b) Heated at 500°C for 7 days

Plate 19029

Fig. 11 Core section containing 40 w/o UO_2 in Al; -325 mesh size
Mallinckrodt high-fired UO_2 Mag. 500X

a) Not heated

Plate 18998

b) Heated at 450°C for 3 hrs.

Plate 18999

c) Heated at 450°C for 3 hrs. + 1-1/2 hrs.
at 610°C (unblistered area) Plate 19000

d) Heated at 450°C for 3 hrs. + 1-1/2 hrs.
at 610°C (near blistered area) Plate 19001

Fig. 12 Core section containing 34.5 w/o U_3O_8 in Al; -325 mesh size
Mallinckrodt U_3O_8 Mag. 500X

a) Not heated

Plate 18995

b) Heated at 450°C for 3 hrs.

Plate 18996

c) Heated at 450°C for 3 hrs. + 1-1/2 hrs.
at 610°C

Plate 18997

Fig. 13 Core section containing 32.8% UO_2 in Al; -325 mesh size
Mallinckrodt high-fired UO_2 Mag. 500X