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by

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STUDY OF THE U_3O_8-Al THERMITE REACTION AND STRENGTH OF REACTOR FUEL TUBES

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ABSTRACT

Research and test reactors are presently operated with aluminum-clad fuel elements containing highly enriched uranium-aluminum alloy cores. To lower the enrichment and still maintain reactivity, the uranium content of the fuel element will need to be higher than currently achievable with alloy fuels. This will necessitate conversion to other forms such as U_3O_8-aluminum cermets.

Above the aluminum melting point, U_3O_8 and aluminum undergo an exothermic thermite reaction and cermet fuel cores tend to keep their original shape. Both factors could affect the course and consequences of a reactor accident, and prompted an investigation of the behavior of cermet fuels at elevated temperatures. Tests were carried out using pellets and extruded tube sections with 53 wt % U_3O_8 in aluminum. This content correspondends to a theoretical uranium density of 1.9 g/cc.

Results indicate that the termite reaction occurs at about 900°C in air without a violent effect. The heat of reaction was approximately 123 cal/g of U_3O_8-aluminum fuel. Tensile and compressive strength of the fuel tube section is low above 660°C. In tension, sections failed at about the aluminum melting point. In compression with 2 psi average axial stress, failure occurred at 917°C, while 7 psi average axial stress produced failure at 669°C.

INTRODUCTION

Uraniun-aluminum alloy cores exhibit different physical characteristics from U_3O_8-aluminum cermet cores when heated above the melting point of aluminum. The uranium-aluminum alloy simply melts along with the cladding at approximately 660°C, whereas the cermet element may maintain its shape at higher temperatures. Aluminum also reduces U_3O_8 above 900°C to form UAl_x compounds with a release of thermal energy. This exothermic reaction, sometimes referred to as a thermite reaction, may affect the reactor safety analysis and charge design. The release of energy could contribute to the heat load on the reactor confinement system following a full core meltdown, and the melting or slumping behavior could alter the course of a transient accompanied by failure of safety rods. Due to reported differences in cermet behavior[1-3], this study[4] was undertaken to evaluate the nature of the thermite reaction for U_3O_8 produced from denitrated uranyl nitrate solution and to determine the strength of a fuel tube above the melting point of aluminum.

EXPERIMENTAL PROCEDURE

Experiments were carried out at the Savannah River Laboratory using depleted U_3O_8 and atomized commercial Alcoa 101 aluminum powders. Typical particle size distribution for the U_3O_8 powder was from 10 µm to 149 µm, with no more than 30% less than 44 µm. The particle size ranges for special tests are indicated on the figures. The U_3O_8 powder was produced by denitrating uranyl nitrate solution to form UO_3 which was then heated at 800°C for 6 hours in a low grade nitrogen atmosphere. The density and surface area of the oxide powder were 7.3 g/cc and 0.2 m^2/g, respectively. About 90% of the aluminum particles were less than 44 µm.

Cold pressed pellets and coextruded tube sections were tested. Pellets one inch (2.5 cm) in height and diameter were mechanically compacted to about 85% of theoretical density from blended U_3O_8 and aluminum powders. Aluminum sterate was used as a die lubricant for compaction. The tube diameters are given in Table 1 for the three tube fuel assembly.

Table 1. Tube Diameters for the Three-Tube Assembly

Fuel Tube	Diameter*, inches (cm) Outside	Inside
Outer	3.700 (9.398)	3.434 (8.722)
Middle	2.936 (7.457)	2.590 (6.579)
Inner	2.048 (5.202)	1.718 (4.364)

* 0.030 (0.076) inch cladding on tube surfaces.

Specimens were heated using both slow and rapid heating rates. For slow heating, the specimens were placed in a furnace at room temperature and heated in air at about 21°C per minute. Rapid heating was accomplished by putting the specimen in a preheated 1300°C furnace. The average heating rate was calculated to be about 780°C/minute up to the melting point of aluminum.

The average static stress to cause failure was determined for outer cermet tubes under compressive and tensile loading. The compressive strength of the core was obtained by heating in air three inch (7.6 cm) long tube sections with weights placed on top of the specimens. The heating rate was about 21°C/minute. The tensile strength was determined using five feet (1.5 m) long outer tubes. The center section of approximately two feet (60 cm) was heated in air using a resistance furnace (1°C/min). Weights were hung from the bottom of the tube. The average compressive and tensile stresses were calculated by dividing the applied load by the nominal cross sectional area of the core.

After completing the reaction and strength studies, a large scale test was made to determine if increasing the number of tubes affected the maximum temperature and if a larger specimen would collapse above 660°C. For the test, 19 assembled tubes 18 inches long with 45 and 57 wt % U_3O_8-aluminum cores were placed in a 1000°C preheated furnace. The array is shown in Figure 1. The steel band was put loosely around the tubes to keep them from toppling while loading the furnace. The tubes were placed in a stainless steel tray to catch the molten aluminum and debris. Thermocouples recorded the temperature in the middle tube of each layer.

RESULTS AND DISCUSSION

Thermite Reaction

Pellets

Typical time-temperature curves are shown in Figure 2 for pellets containing 53 wt % U_3O_8 with different size U_3O_8 particles. Both the maximum temperature and the oxide particle size are indicated on the figure. Also shown is the furnace temperature near the specimens. Although the furnace was set at 1300°C, the temperature near the samples was about 1250°C due to a thermal gradient.

Between 600 and 700°C, the aluminum melted and exuded from the pellet. When the thermite reaction occurred at the ignition temperature between 900 and 1000°C, the specimen glowed "white hot". But no violent reactions as reported by Fleming and Johnson[1] were observed for any of the 53 wt % U_3O_8-aluminum pellets. This observation is consistent with the data of Baker[2], et al. indicating that no violent reactions occur for 30 to 90 wt % U_3O_8-aluminum pellets.

The pellets reached the reaction temperature in 1 to 2 minutes. After the reaction began, the peak temperature was reached in 10 to 20 seconds. The maximum self-heating rate was about 70°C/sec. After completing the reaction, the temperature of the pellet decreased, approaching the furnace temperature. Pellets were heated up to 30 minutes with no other exothermic reactions detected.

The maximum temperature of the pellets was a function of the particle size of the oxide as reported by Baker, et al. The highest temperature recorded was 1600°C and occurred for pellets with all fine (<44 μm) U_3O_8 particles. Extrapolation of Baker's data gave a peak temperature of about 1500°C for a 53 wt % pellet. The measured peak temperature was 350°C higher than the recorded furnace temperature. Increasing the average size of the U_3O_8 particles to 64 μm resulted in a maximum temperature of 1330°C. The maximum temperature for pellets with <44 to 149 μm particle size distribution was 1400°C, 200°C less than for the specimen with all fine U_3O_8 particles.

The oxide particle size controls the reaction rate because the reaction begins at the uranium oxide-aluminum interface. Increasing the U_3O_8 particle size decreases the contact surface area between the reactants which reduces the rate of reaction and lowers the instantaneous energy release. The extent of the reaction for large particles is also affected because once reaction products form around the particle surface, further reactions between U_3O_8 and aluminum require diffusion of reacting elements through the barrier. For pellets containing the full range of oxide particle sizes, two reactions occurred and resulted most likely from differences in the U_3O_8 particle size distribution.

A test was also made by plunging a pellet with fine U_3O_8 particles into a 1000°C furnace. The 1000°C temperature was considered the upper bound for thermite ignition. Upon completion of the reaction, the peak temperature was 1370°C. The pellets were heated to temperature by thermal energy from both the furnace and the exothermic reaction. The energy released for rapidly heated pellets with fine U_3O_8 particles appeared somewhat independent of the furnace temperature. After the exothermic reaction, pellet temperatures increased 370°C above the furnace temperature at 1000°C and increased 350°C above the furnace temperature at 1250°C.

The energy released during the U_3O_8-aluminum reaction was estimated from temperature-time graphs to be about 123 cal/g of U_3O_8-aluminum for 53 wt % U_3O_8 pellets. Pasto[5], et al. recently reported an experimental value of 95 cal/g of fuel for 52 wt % U_3O_8 in aluminum. The maximum heat released from the reaction of a 20 kg U_3O_8-aluminum core, assuming no dilution by the aluminum cladding, is about the same as the cumulative decay heat from a 540 MWD fuel assembly during the first 30 seconds after shutdown.

Tube Sections

To determine the effect of the thermite reaction during overheating of reactor fuel, tests were conducted using three inch (7.6 cm) long tube sections. Both slow and rapid heating rates were used. A typical time-temperature curve for a slowly heated outer tube section with a 53 wt % U_3O_8-aluminum core is shown in Figure 3. No reactions were detected up to approximately 660°C where the aluminum cladding and the aluminum in the core melted as indicated by the almost isothermal part of the curve. After the aluminum melted, the temperature of the core again approached the furnace temperature indicated by the dotted line. At about 875°C an exothermic reaction started. The heating rate at this time was about 7°C/min. Between 875 and 925°C, two small reactions occurred and were reproducible. It is conceivable that the double reaction resulted from the particle size distribution because about 30% of the U_3O_8 particles were fines. The kinetics of the reaction were slow, requiring approximately 7 minutes for completion. The maximum increase in the temperature of the tube section was only 25°C above the furnace temperature. Tubular specimens have been heated slowly to 1375°C and showed no further reactions.

The time-temperature curve for a rapidly heated outer tube section is shown in Figure 4. The curve for a pellet having identical composition and similar oxide particle size distribution is also shown for comparison. The peak temperature of 1290°C for the tube section was about 50°C above the furnace temperature or 110°C lower than for the pellet. The effective oxide content is diluted by the aluminum cladding. If all the aluminum cladding remained on the tube section after melting, the oxide concentration would decrease from 53 to 23 wt %. However, some of the molten aluminum runs off the specimen so that the effective concentration is between these values. Baker has shown that the peak temperature is a function of the composition and from his data, a peak temperature of 1290°C would imply an effective composition of 35 wt % U_3O_8.

Specimen Microstructure

The microstructure and reaction products were studied using scanning electron microscopy and x-ray energy spectroscopy. Specimens as-fabricated and specimens heated to 675°C both showed discrete particles of U_3O_8 in the aluminum matrix. Heating to 1375°C resulted in essentially a complete U_3O_8-aluminum reaction. The microstructure no longer consisted of U_3O_8 particles but an uranium-aluminum phase (UAl_x) with some residual aluminum. Small faceted particles containing aluminum, probably Al_2O_3, were also observed.

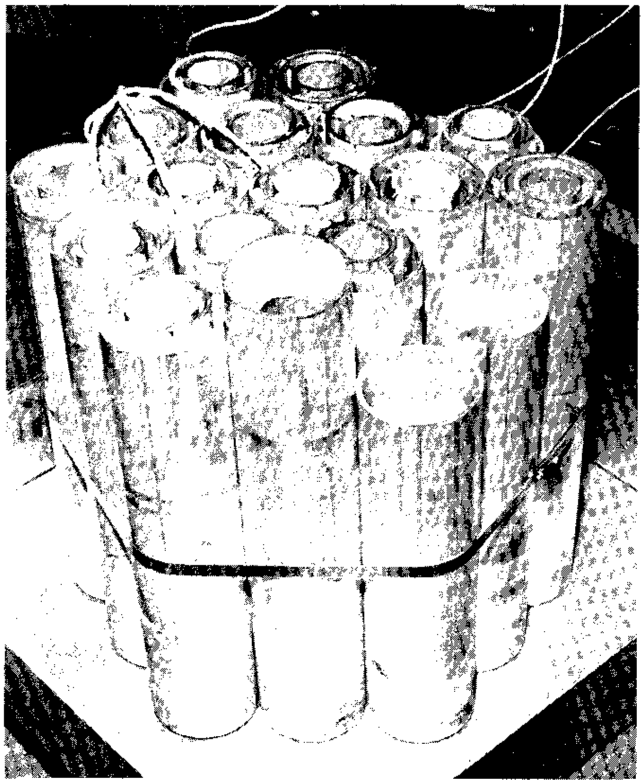

Fig. 1. Array of 19 Assembled Tube Sections

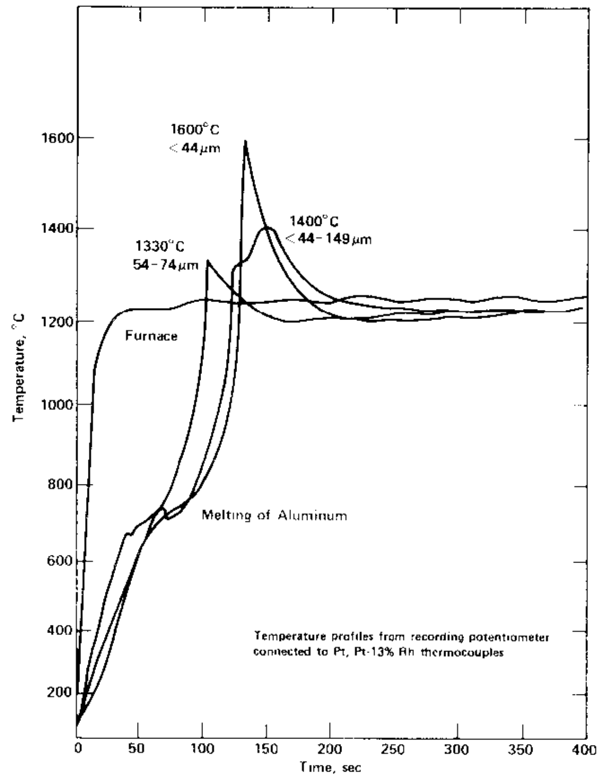

Fig. 2. Effect of U_3O_8 Particle Size on Thermal Reactions in Rapidly Heated 53 Wt % U_3O_8-Al Pellets

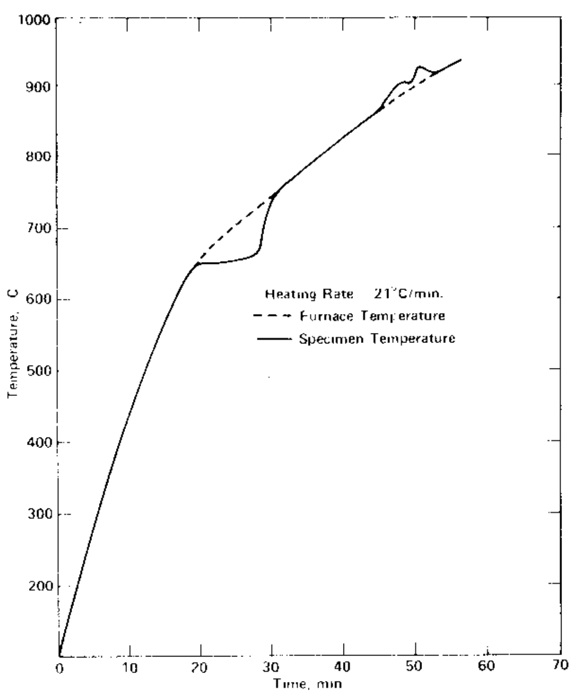

Fig. 3. Temperature of Slowly Heated Outer Tube Section with a 53 Wt % U_3O_8-Al Core

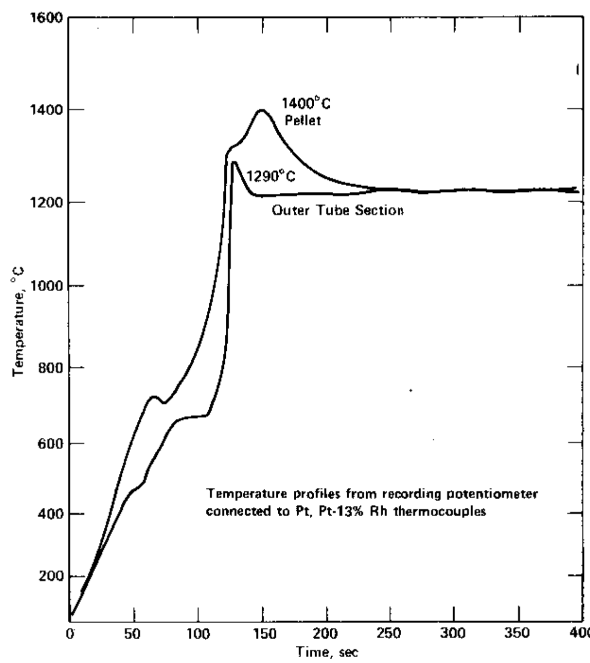

Fig. 4. Comparison Between Time-Temperature Curves for a 53 Wt % U_3O_8-Al Pellet and on Outer Tube Section Plunged into a Preheated Furnace

Strength of Cermet Fuel

Cermet fuel elements maintain their shape above the melting point of aluminum because of the aluminum oxide or U_3O_8 network as postulated by Fleming and Johnson. The average stress to collapse the reactor fuel element is critical to the operating safety of cermet fuel in case of a core meltdown. The significance of the compressive or tensile strength depends on the manner in which the fuel is held in the reactor core and the applied load.

Compressive Strength

The average axial compressive stress to collapse an outer tube heated above the melting point of aluminum is given in Table 2 for a 53 wt % U_3O_8-aluminum core. The compressive strength decreases from 11 psi near 660°C to 2 psi at 917°C which is within the thermite ignition temperature range of 900 to 1000°C. With no applied load, the three inch cermet specimen did not collapse at 1375°C, but bulged at the top. During removal from the furnace, however, one side collapsed from movement or vibration. The aluminum from the cladding and core accumulated at the bottom of the specimen. For comparison, a 35 wt % uranium-aluminum alloy core collapsed at 670°C with no applied load.

Table 2. Average Axial Compressive Stress and Temperature to Collapse 53 wt % U_3O_8-Al and 35 wt % U-Al Outer Tubes in Air

Applied Load, lbs	(kg)	Compressive Stress in the Core, psi	(MPa)	Collapse Temperature, °C U_3O_8-Al	U-AL
0		-		1375*	670
1.5	(0.7)	2	(0.01)	917	-
3	(1.4)	4	(0.03)	915	-
6	(2.7)	7	(0.05)	669	-
8.5	(3.9)	11	(0.08)	667	-

* Collapsed when removed from furnace.

During irradiation, U_3O_8 and aluminum form U-Al intermetallic compounds by a diffusion controlled low temperature reaction. To simulate the microstructure of an irradiated fuel tube, 53 wt % U_3O_8-Al tube sections were heated in air at 1000°C for 1 hour with no applied load to form reaction products. X-ray diffraction confirmed the presence of UAl_4, UAl_3, Al_2O_3, and residual Al; no U_3O_8 was found. Specimens were then reheated in the furnace and collapsed at 755 and 660°C with 2 and 9 psi average axial stress, respectively.

Tensile Strength

U_3O_8-Al tubular sections with 1.5 and 3 lb (0.68 and 1.36 kg) applied tensile loads failed at 668 and 669°C, respectively. The average stress in the core was calculated to be 2 and 4 psi. Doubling the applied load had no effect on the failure temperature because the tensile strength of the core is low when the aluminum melts. In fact, in the limit the tensile strength of the specimen should be equal to the surface tension of the molten aluminum metal unless affected by an interlocking oxide network. Because the failure occurred at low stress near the aluminum melting point, it is concluded that the influence of the oxide structure on the tensile strength is relatively small.

Large Scale Test

The strength of the cermet core is low above the melting point of aluminum. To determine if the weight of the tube would cause it to collapse, 18-inch-long sections of the three-tube assembly were heated in a 1000°C preheated furnace. The calculated axial stress at the bottom of the tubes was about 2.5 psi, assuming only the aluminum cladding melted and ran off the sections. The 2.5 psi stress corresponded to the static failure load at about 917°C.

The time-temperature curves for the specimens were similar to previously reported curves except that the assemblies in the center of the array heated more slowly. At about 985°C, the exothermic reaction was detected. The peak temperature recorded was approximately 1400°C for the 57 wt % tube. There was no sighthole to observe the tubes, so the furnace was shut down and the door opened. The tubes had collapsed as shown in Figure 5.

For water-cooled assemblies, stresses are present from a frictional surface drag due to the flow of coolant over the surfaces, as well as from the weight of the tube. In a low temperature reactor operating at near atmospheric pressure, two phase flow will develop at about 130 to 150°C, and the surface temperature of the tube will increase rapidly. The flow instability will decrease the frictional drag but pressure surges will develop, producing vibration and high cyclic stresses until the tubes fail.

Subcooled burnout tests have been carried out at the Savannah River Laboratory using 1-inch diameter tubes containing 55 wt % depleted U_3O_8-aluminum and 35 wt % depleted uranium-aluminum alloy cores. The tubes were electrically heated in the laboratory under pool-boiling conditions. The burnout tests were made to compare the time-temperature history and microstructures of alloy and cermet tubes.

Particles from the melted region were identified as containing UAl_3 and fine eutectic regions of high uranium content. This suggested that the temperature for the alloy core was between 730 and 900°C. Similar temperatures were reached by cermet tubes; however, no evidence of a thermite reaction was observed. The particles produced were granular in shape and ranged in size from about 1 to 240 mils (0.03 to 6.1 mm) with an average size of 50 mils (1.3 mm).

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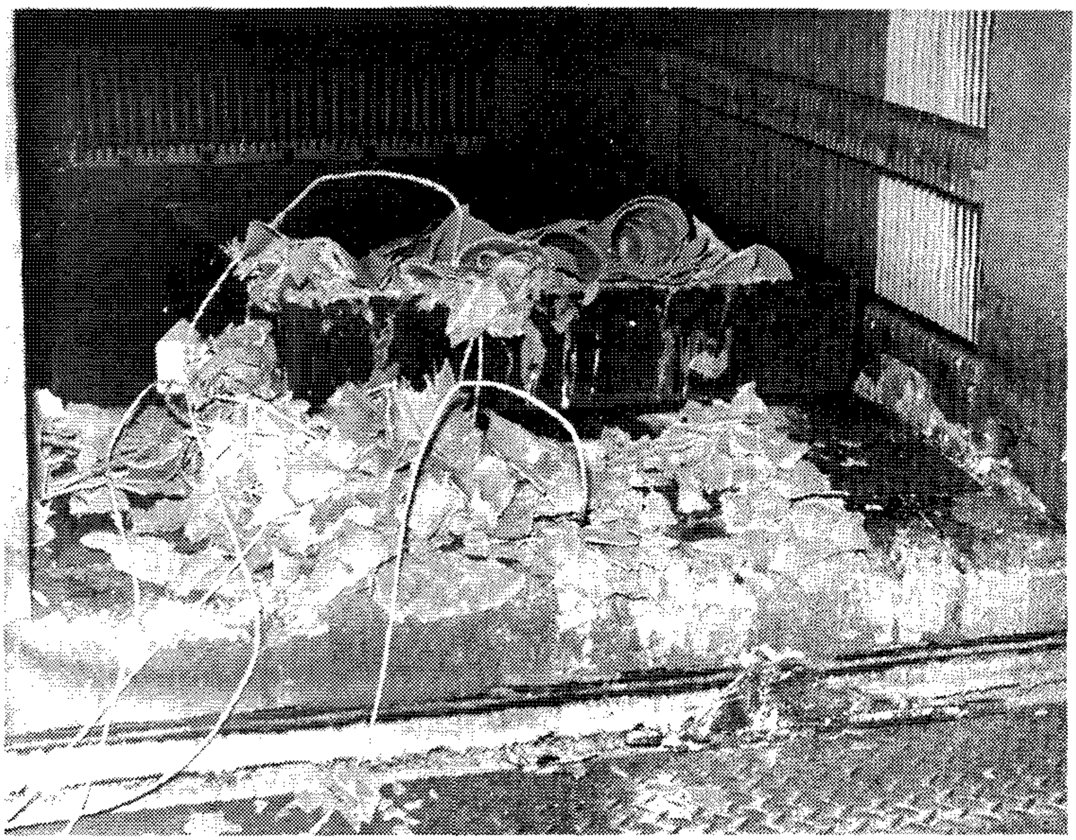

Fig. 5. Collapsed U_3O_8-Al Tubes in 1000°C Furnace

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