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A QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS STUDY OF THE U_3O_8-Al THERMITE REACTION

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ABSTRACT

Concerns about proliferation resistance of nuclear fuel cycles and fuels have prompted a reinvestigation of U_3O_8-Al cermet fuels currently being used in research and test reactors. In particular, higher loadings of U_3O_8 are being considered. These new fuel compositions are in the region of maximum possible thermal energy release from the high-temperature "thermite" reaction between the U_3O_8 and aluminum components. This study was initiated to quantitatively measure the amount of reaction heat evolved.

A differential thermal analysis system was calibrated with materials of known heat of reaction. Subsequently, specimens of high-uranium-loaded U_3O_8-Al powder mixtures were analyzed. Thermite reaction heat measured for these specimens was much lower than expected. For example, for a 79 wt % U_3O_8 mixture, reaction heat measured was about 84 J/g, whereas 1.1 kJ/g was calculated from thermodynamics. Specimens of simulated fuel plates showed similar low results. Possible reason(s) for this behavior are discussed in the report.

When miniature fuel plates were heated in air in electrical resistance furnaces, (1) on heating to about 640°C the aluminum cladding melted and flowed away from the U_3O_8-bearing (meat) region of the plates, (2) the meat remained integral even when heated to 1400°C but warped under its own weight, and (3) no violent thermal effects, explosions, or gas releases were observed. The main conclusions drawn from these experiments are the following:

1. Measured heats of reaction evolved from high-uranium U_3O_8-Al mixtures at temperatures near 900°C are low compared with the thermal energy required to initiate the reactions. This fact indicates that the chemical heating effect on a reactor fuel core in an accident situation is small.
2. The lack of disruptive thermite reaction effects in heated miniature fuel plates indicates that switching from the current low U_3O_8 loading to higher levels does not add a significant chemical reaction hazard to other considerations of safe reactor operation.

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INTRODUCTION

Cermet Fuel Concept

Cermet nuclear fuels of uranium have been utilized in research and test reactors since the late 1950s. The cermet concept incorporates the desirable properties of both the pure ceramic and the metallic materials without retaining the worst of their poorer qualities. For example, ceramic UO_2 and U_3O_8 offer excellent stability under neutron irradiation in comparison to many uranium alloys yet are too mechanically unstable to be used alone in plate-type fuels. When these ceramics are mixed with a metal, however, the metallic phases of aluminum, stainless steel, or zirconium alloys provide ductility, fabricability, and high thermal conductivity in the fuel element.

Research efforts expended at Oak Ridge National Laboratory in the 1950s and 1960s yielded a readily fabricable and acceptably stable cermet fuel form. The end product, a U_3O_8 plate-type fuel element, found application in the Puerto Rico Nuclear Center Reactor (circa 1960), the High Flux Isotope Reactor (1965, continuing), and more recently in the High Flux Beam Reactor, the National Bureau of Standards Reactor, and the Oak Ridge Research Reactor. In these elements, dispersed U_3O_8 fuel particles are surrounded by a continuous aluminum metal phase, which serves the above-mentioned purposes and also acts as a fission product release barrier. This fueled region, called the "meat," is clad with aluminum alloy 6061. The usual fuel is 93% enriched in ^{235}U with the U_3O_8 occupying about 20 vol % (about 40 wt %) of the "meat."

In the 1970s, the concerns about proliferation resistance of fuels and fuel cycles led to an effort to utilize lower enrichment levels, (e.g., <20% ^{235}U). To maintain flux and power levels, a concomitant increase in the volume loading of the U_3O_8 is required. The maximal concentration of U_3O_8 in the meat that is currently under development at ORNL is about 43 vol % (about 75 wt %) U_3O_8, depending on fabrication voids. Several potential problems are brought on by this change, such as decreased fabricability, unproven irradiation behavior, lower thermal conductivity, and a composition in the region of maximum calculated potential energy release from the thermite reaction. The object of the study reported here is to determine the actual magnitude of this heat release, which is related to safety of the reactor in the event of an over-temperature excursion.

Thermite Reaction

It was recognized in the 1950s that the phase assemblage aluminum-urania constituted a nonequilibrium mixture, and thus that a cermet fuel would ultimately tend to change phases with potentially dangerous consequences. This is the thermite reaction. However, at temperatures up to 500°C little reaction occurs, and up to the aluminum melting point at about 660°C the worst behavior noted was time-dependent reaction leading sometimes to fuel-plate swelling and warpage.[1,2] This reaction was only of significance to fuel fabricators who had to braze fuel elements at temperatures of about 600°C. Operating temperatues of the fuel plates in-reactor were much lower than this, often less than 100°C, so that the potential thermite reaction was inconsequential except in the event of a loss-of-coolant accident. In view of this possibility, studies of the thermal behavior of the U_3O_8-Al system were undertaken.

The major features of reactions between aluminum and U_3O_8 were delineated by Fleming and co-workers[3–5] at Georgia Institute of Technology, and researchers at Argonne National Laboratory[6,7] investigated the consequences of thermite reactions in fuel plates. Other investigations in this area were performed by workers at the Savannah River Laboratory[8,9] and in Germany.[10–13] These studies were used as a basis for safety analyses of Al-U_3O_8-fueled reactors, such as the Oak Ridge Reactor.[14]

Fleming and Johnson[3] enumerated the possible reactions between U_3O_8 and aluminum as follows:

$$U_3O_8 + 4/3\ Al \rightarrow 2/3\ Al_2O_3 + 3UO_2\ , \tag{1}$$

$$U_3O_8 + 16/3\ Al \rightarrow 8/3\ Al_2O_3 + 3U\ , \tag{2}$$

$$U_3O_8 + 34/3\ Al \rightarrow 8/3\ Al_2O_3 + 3UAl_2\ , \tag{3}$$

$$U_3O_8 + 43/3\ Al \rightarrow 8/3\ Al_2O_3 + 3UAl_3\ , \qquad (4)$$

$$U_3O_8 + 52/3\ Al \rightarrow 8/3\ Al_2O_3 + 3UAl_4\ , \qquad (5)$$

The weight (mole) percent aluminum required for completion of reactions (1) through (5) as written are, respectively, 4.1 (57.1), 14.6 (84.2), 26.6 (91.9), 31.5 (93.5), and 35.7 (94.5). They studied compositions from 6 to 65 wt % Al with U_3O_8, these mixtures being in the form of pressed pellets. Based on thermochemical calculations and assuming complete reaction of the limiting reactant, they computed the "estimated maximum credible energy release" from various U_3O_8-Al compositions. Their results are shown in Fig. 1. The potential heat release effects, on moving from the current dispersion fuel compositions (60 to 75 wt % Al) to the newer developmental high loadings of U_3O_8 (25 to 35 wt % Al), are obvious from this figure. Their initial differental thermal analysis (DTA) study[3] of several compositions indeed showed behavior qualitatively similar to Fig. 1. However, they did not do quantitative work to determine the amount

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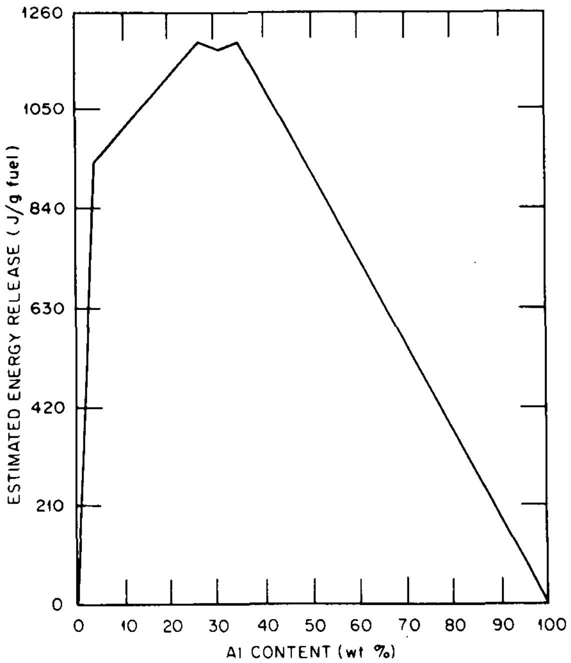

Fig. 1. Estimated Maximum Energy Release From U_3O_8-Al Reaction Mixtures. Redrawn from: J. D. Fleming and J. W. Johnson, "Exothermic Reaction in Al-U_3O_8 Composites," pp. 649–66 in *Research Reactor Fuel Element Conference*, TID-7642, Book 2, 1962.

of heat *actually* released. Differential thermal analysis scans showed the reaction heat apparently concentrated in one small temperature range, the "ignition" temperature. This temperature ranged from about 800 to 1000°C, increasing as the U_3O_8 level increased from 75 to 85 wt % U_3O_8 as shown in Table 1.

Table 1. Effect of U_3O_8 Content on Thermite Reaction Ignition[a]

U_3O_8 content (wt %)	Ignition temperature (°C)	Relative peak area
85.4	993	1.0
79.5	932	1.7
74.5	932	2.2

[a] Source: J. D. Fleming and J. W. Johnson, "Aluminum-U_3O_8 Exothermic Reactions," *Nucleonics* 21(5): 84–85 (1963).

Fleming et al., in the final program report,[5] determined that the U_3O_8 reaction with aluminum occurs in at least two stages, an initial very rapid reduction of U_3O_8 to UO_2, followed by a slower reaction forming uranium-aluminum compounds. They hypothesized that the initial reaction leaves a barrier of Al_2O_3 and UO_2 around the still-solid U_3O_8 particles, hindering further reaction with the molten aluminum. These layers were actually observed in some specimens. They further proposed that the secondary reaction is controlled by the rate of diffusion of aluminum to the reaction zone. Hence, the exotherms they observed in heating of U_3O_8-Al mixtures were probably from only the initial, rapid portion of the reaction. Slower, diffusion-controlled reactions would generally release heat so slowly that experimental measurement by DTA techniques would be difficult. For that matter, they are not likely to cause large temperature increases in a fuel element heated to the ignition temperature.

A final observation[5] of relevance to fuel elements was the retention shape and some strength in experimental fuel plates after heating above the aluminum melting point. This residual strength increased by a factor of 4 after completion of the thermite reaction.

Investigations at ANL[6] again indicated a two-stage nature to the U_3O_8-Al thermite reaction, with three-fourths of the reaction heat released in the first stage reduction to UO_2. They also determined that a definite particle-size effect occurred, with smaller U_3O_8 particle sizes yielding more rapid and complete reaction. More importantly, it was found that heat treatment below 650°C of an U_3O_8-Al compact, instead of passivating the U_3O_8-Al interface and retarding reaction, actually caused more intense reaction and higher heat release rates. Apparently, this heat treatment retards the reaction until further heating causes a breakdown in the passivated layer and, at the higher temperature, reaction occurs more quickly. This fact has considerable implications for fuel plates, because their fabrication entails hot-rolling and heat-treating steps that may worsen the potential reaction consequences.

A further study at ANL[7] dispelled many of the fears concerning the behavior of U_3O_8-Al dispersion-type fuel elements that use fully enriched uranium. These experiments involved nuclear heating of High Flux Isotope Reactor (HFIR) fuel-plate sections (41 wt % U_3O_8 in the "meat," 27 wt % including cladding) in the Transient Reactor Test Facility. Their experiments and results are summarized as follows:

> Experiments were performed over a range of fission energy input from 133—1062 cal/g in 30°C, 120°C, and 285°C water. The samples retained their plate-like shape at fission energy inputs as high as 440 cal/g even though an energy of 230 cal/g was sufficient to melt the aluminum cladding and the aluminum in the matrix of the fuel. The extent of reaction for the fuel samples that received 440 cal/g or less of energy was <2.5%, with the exception of one sample in 285°C water which reacted to the extent of 11.8%. Samples subjected to energies greater than about 500 cal/g lost their resemblance to plates. In this energy range, two samples irradiated in 30°C water fragmented and reacted to the extent of 28.4 and 74.6%, respectively; samples irradiated in 120 and 285°C water formed single large globules and reacted from 91 to 94%. Results with the HFIR fuel were generally similar to those from previous studies with aluminum-uranium alloy fuel except that the cermet fuel retained a plate-like shape at energies up to 440 cal/g. The results indicated that the aluminum-U_3O_8 thermite reaction may not be an important energy source in the transient meltdown of the cermet fuel.

Other studies aimed at elucidating the mechanism of the reactions were conducted elsewhere. Rollig,[10] in his study of the analogous UO_2-Al reaction, in the presence of excess aluminum, decided that after an initial interface reaction coats the UO_2 with Al_2O_3 and some uranium-aluminum compound, the remainder of the reaction is rate-limited by aluminum ion diffusion. This statement is in agreement with that of Fleming et al.[5] Similar conclusions regarding U_3O_8 were reached by Ondracek and Patrassi[12] in an excellent summary of reaction mechanism data.

Later studies of U_3O_8-Al reactions were stimulated by experiences at the Savannah River Plant in which exothermic reactions occurred in mixtures of alkali-uranates with aluminum. Gray and Kerrigan[8,9] examined the reactions by DTA, along with thermogravimetric- and evolved-gas analyses (TGA and EGA, respectively). Phases were identified by x-ray diffraction and electron microprobe techniques. They found[8] the initial exothermic reaction of U_3O_8 and aluminum leading to formation of UO_2 to occur around 600°C, this reaction being quenched by the endothermic melting of the aluminum at 660°C. The larger exothermic reaction began around 950°C, and led to formation of $UAl_4 + Al_2O_3$. For batches of scrap powders consisting largely of UO_3 or U_3O_8 mixed with aluminum and heated, they estimated that 1.7 to 2.1 kJ/g of mixture was released in the higher temperature (>800°C) reaction.[9] The end products were Al_2O_3, UO_2, and uranium aluminides, largely in agreement with other investigators.

In summary, the thermite reaction between U_3O_8 and aluminum is composition-dependent regarding total possible heat release, ignition temperature, and residual phases. The "reaction" is likely to be at least two separate reactions; the first being rapid and involving interfacial formation of UO_2 and Al_2O_3 on the U_3O_8 particles, the later reaction(s) involving formation of UAl_2, UAl_3, and/or UAl_4. The latter reaction(s) are likely to be diffusion-controlled and are not therefore sources of large instantaneous energy releases; that is, their self-heating effects are small.

EXPERIMENTAL APPROACH

The questions relating to highly loaded U_3O_8 elements then are the following: (1) how much heat is released (and how quickly) on heating a fuel plate beyond its operating limits, (2) at what temperature is the majority of this heat released, and (3) what effect does this heat release have on the operability and safety of the reactor? This report will present results of experiments designed to determine quantitative answers to the first two questions. The third question will be answered only very qualitatively.

A differential thermal analysis system was used to measure the temperatures at which the thermite and other reactions occur and to quantitatively determine the enthalpy changes during these reactions. Two U_3O_8-Al powder mixtures of differing composition were first evaluated, followed by samples punched directly from fabricated U_3O_8-Al miniature fuel plates (miniplates). X-ray diffraction phase analysis was used in an attempt to define the reactions taking place on heating one of the powder samples. Finally, a few complete miniplates were heated in electric furnaces to observe the mechanical behavior of a fuel plate on heating through the thermite reaction temperature range.

EQUIPMENT AND PROCEDURES

X-Ray Diffraction

Phase identification for a few selected samples of reacted U_3O_8-Al was performed by x-ray diffraction analysis. Samples were ground to pass through a 200-mesh screen (U.S. Sieve Series) and mounted on a silicon single crystal to reduce the x-ray background. The silicon was oriented in such a way as to provide no contribution to the x-ray spectrum. A vertical Norelco diffractometer using copper radiation with a graphite crystal differential beam monochromator was used to provide the x-ray data. Data collection was at a 2Θ-scan rate of 37 μrad/s with a 6-s integrating time, providing a final plot of diffracted intensity against 2Θ. The peak positions were measured manually and compared to standard patterns for known phases.

Differential Thermal Analysis

Preliminary experiments were performed with a Dupont Model 900 Thermal Analyzer, while most of the work including all quantitative studies utilized a Dupont Model 990 Thermal Analysis System. This system includes a furnace capable of attaining 1600°C at a programmed constant rate, while maintaining the test specimens under any given atmosphere. Sample temperature and differential temperatures are fed into a controller-programmer-recorder module that allows selection of numerous data readout options. Thermograms were customarily recorded as ΔT and T versus time with a 2-pen recorder.

A diagram of the furnace, thermocouples, and specimens is given in Fig. 2 and serves to illustrate the theory of DTA operation. The material

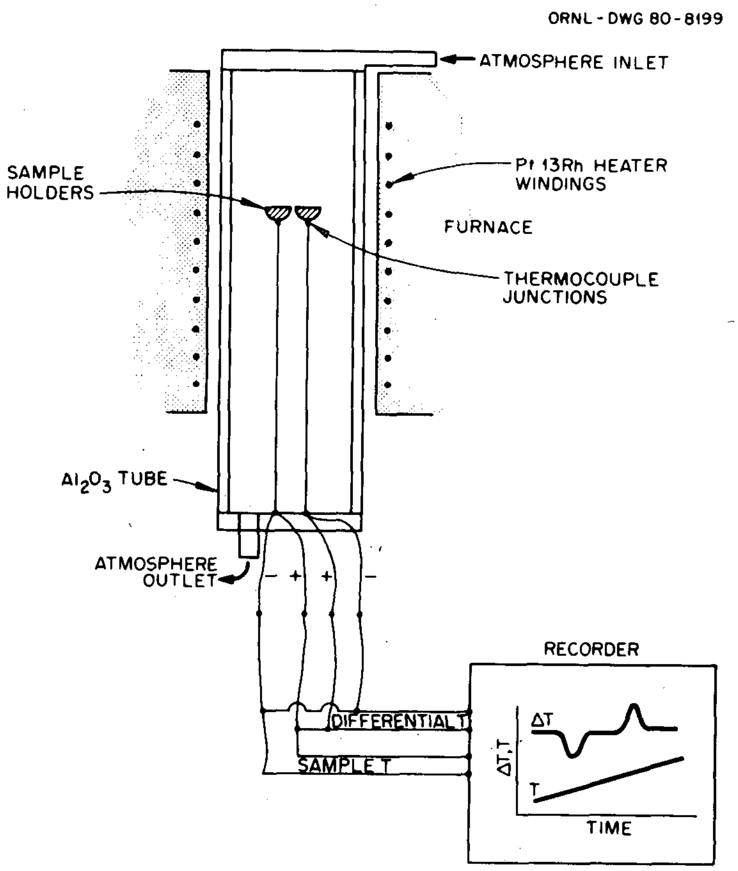

Fig. 2. Schematic Diagram of a Differential Thermal Analysis System. Power supply, programmer, and controller are not indicated.

whose thermal effects are to be observed is placed into an Al_2O_3 cup which is placed into intimate contact with the sample thermocouple. A thermally inert material (in this case granular high-fired Al_2O_3) is similarly located next to the sample in its own cup. The furnace tube is placed around the sample and reference, and proper atmosphere is established. The furnace is then heated at a constant rate until the desired temperature is reached.

If the sample and reference materials have identical heat capacity, density, thermal conductivity, and heat transfer coefficients, the differential temperature will be constant and the display will be a horizontal line, because the temperature difference between the samples will remain the same as heating progresses. If their conductivities, densities, and/or heat capacities differ, the temperature sensed by the sample and reference thermocouples will differ and a ΔT signal will be generated. Ordinarily, these effects are observed as an offset from zero or a constant slope on the ΔT versus time curve, and the instrument can be compensated for these effects. When the heat capacity changes suddenly in the course of heating, as at a phase transformation or thermally activated reaction, there will again be generated a ΔT signal. As the transformation or reaction proceeds, the sample temperature differs more and more from the (continuously increasing) reference material temperatures and the ΔT signal increases. As the reaction ceases, the ΔT signal will disappear. If the reaction is endothermic, the heating thermogram will exhibit a negative deviation (valley) from zero ΔT as the sample absorbs heat while remaining at the same temperature and the reference material temperature increases. This is typified by melting behavior and certain phase reactions. Conversely, some changes of state or reactions are characterized by exothermic (heat-liberating) effects and a positive ΔT change occurs (peak).

Several conventions exist among thermal analysis workers regarding the measurement of reaction "onset" temperatures and also concerning construction of the baseline under a peak for measurement of areas encompassed in the ΔT-time region. It is necessary for correlation of data from one laboratory to the next to use a given set of these conventions, although as long as they are specified in the data it does not matter which set is used. This is even more true when, as in this report, all data reported are relative to data taken on standards using the same equipment and conventions. The onset temperature of a reaction and the baseline construction conventions used are illustrated in Fig. 3.

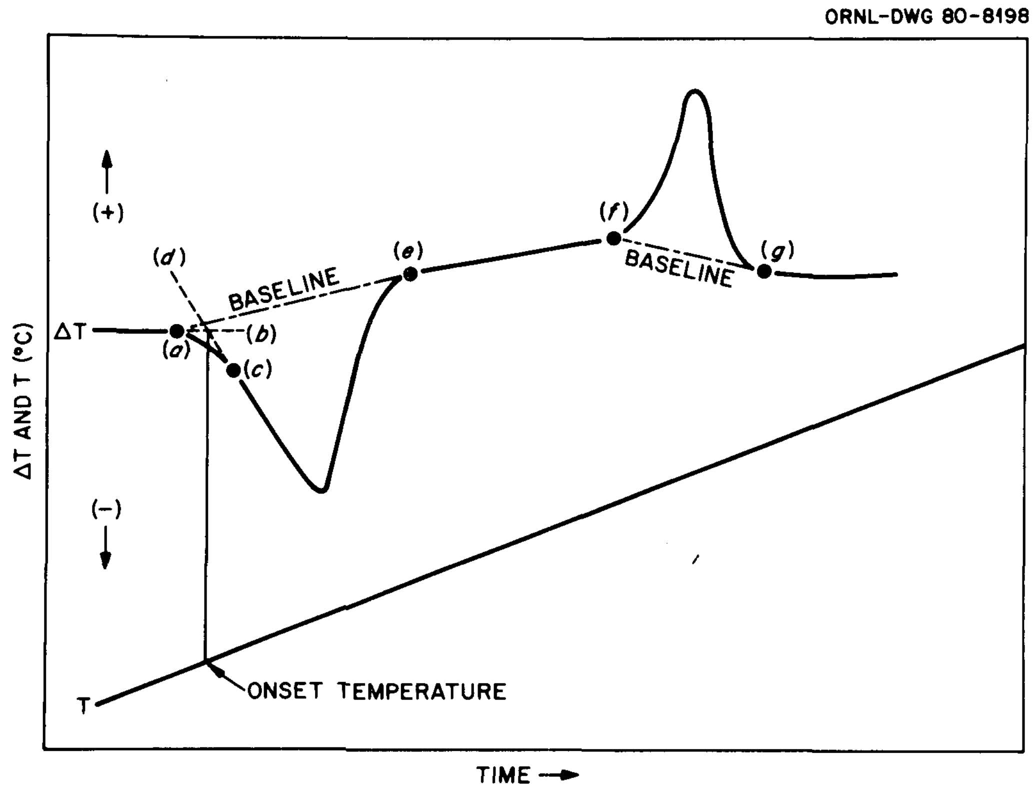

Fig. 3. Differential Thermogram Illustrating Definition of "Baseline" and "Onset Temperature."

The onset temperature is determined by constructing the continuance of the lower temperature baseline past the thermal event (a to b in the figure) and finding on it the intersection with the back-extrapolated peak or valley wall (c to d). The smoothed baseline is drawn from the point where the peak or valley first deviates from the baseline to the point where it returns to a normal baseline. These are illustrated by lines a—e, and f—g in Fig. 3.

The area (A) encompassed by a thermal event on a thermogram is proportional to the enthalpy of transformation or reaction of the sample (ΔH), the mass of the sample (M) and the speed with which the pen moves along the time axis (C). It is inversely proportional to the ΔT-axis sensitivity (ΔT_y). Thus, one can write

$$A = \frac{1}{(E)} \frac{(\Delta H)(M)(C)}{(\Delta T_y)} , \tag{6}$$

where E is a constant at any given temperature and is related to the ease of heat flow from the furnace into the sample and reference materials. It is called the heat flow calibration constant. Now, if one wishes to calculate a heat of transformation or reaction (ΔH), a measured area under the peak from a known weight of sample will allow its calculation if E is known for the DTA system at that temperature. Consequently, one must determine E as a function of temperature, which is best accomplished by measuring peak areas from materials of known ΔH. This was the procedure followed in this study.

Samples of NBS Standard Reference Materials Sn, Zn, Al, Cu, and Pb, along with high-purity Ag and Au, were used as both temperature and ΔH standards. From 10 to 65 mg of sample was weighed into an Al_2O_3 cup and heated to above the melting temperature at 10°C/min heating rate. Granular high-fired Al_2O_3 was used as a reference material. A flow of 50 cm^3/min Ar (at STP) was directed down over the materials during the run. The sample was melted once in this fashion while recording the thermogram, then rerun after cooling to below the melting point. This procedure eliminates problems encountered in using powdered metal (versus solid chunks) where sintering may occur before melting the powders, absorbing heat and giving erroneous ΔH values. Peak areas were measured from the thermogram traces with a calibrated planimeter. Some specimens were run several times to verify repeatability on the same sample, and E for some materials was measured on several separate samples. Results of the calibration runs are presented in Table 2, and some typical thermogram traces are shown in Fig. 4. The E versus T data were analyzed by least squares regression analysis using several formulas. The best fit (highest correlation coefficient) was obtained with the relation

$$E = (2.79 \times 10^{-1})\ T^{0.8217} , \tag{7}$$

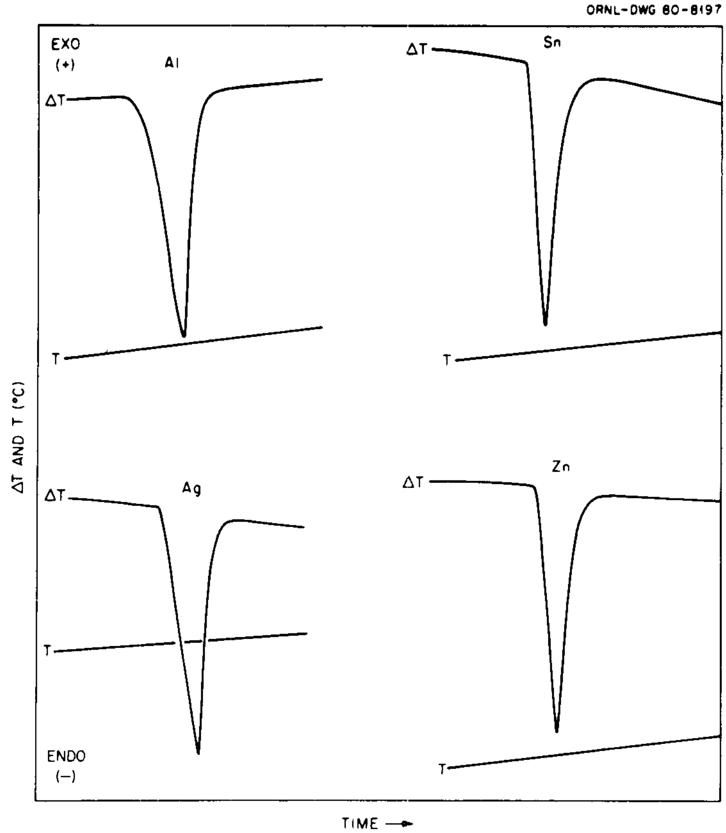

Fig. 4. Typical Thermograms of Metals Used for DTA Calibration.

Table 2. Results of Calibration of Thermal Analyzer

Material	Melting temperature[a] (°C)	Observed onset temperature (°C)	ΔH Melting[b] (J/g)	Sample weight (mg)	Calculated E ($\mathrm{JV^{-1}\ min^{-1}}$)
Sn	231.9	233	59	39.2	28
Pb	327.5	326	23	43.4	32
Zn	419.6	429	113	25.1	37
Al	660.4	663	397	20.5	49
Al	660.4	658	397	30.4	56
Al	660.4	658	397	30.4	58
Al	660.4	658	397	19.2	55
Al	660.4	658	397	19.2	54
Ag	961.9	969	111	35.7	84
Ag	961.9	968	111	35.7	87
Ag	961.9	960	111	35.7	84
Au	1064.4	1068	63	35.1	80
Cu	1083.4	1082	205	27.4	99
Cu	1083.4	1078	205	29.9	80

[a] IPTS 1968 Primary Fixed Points and Secondary Reference Points.

[b] From Table 2.2, page 63, in *CRC Handbook of Materials Science, Vol. I: General Properties*, C. T. Lynch, Ed., CRC Press, Cleveland, Ohio, 1974.

where E is in J/V·min and T is in °C. Data points from Table 2 are plotted in Fig. 5, and the line represented by Eq. (7) is superimposed to show the correlation.

As the test of accuracy of the procedure, two materials with known ΔH were selected and treated as unknowns. These were chosen to have transformations in the same temperature range where the thermite reaction peaks occur. Samples of germanium metal and $SrCO_3$ powders were analyzed by the above procedures, measuring peak areas by planimeter and selecting E values from Eq. (7) at the appropriate temperatures. The ΔHs calculated are compared to literature values in Table 3. The agreement between literature and calculated values is excellent for this type of analysis, error being less than 7%.

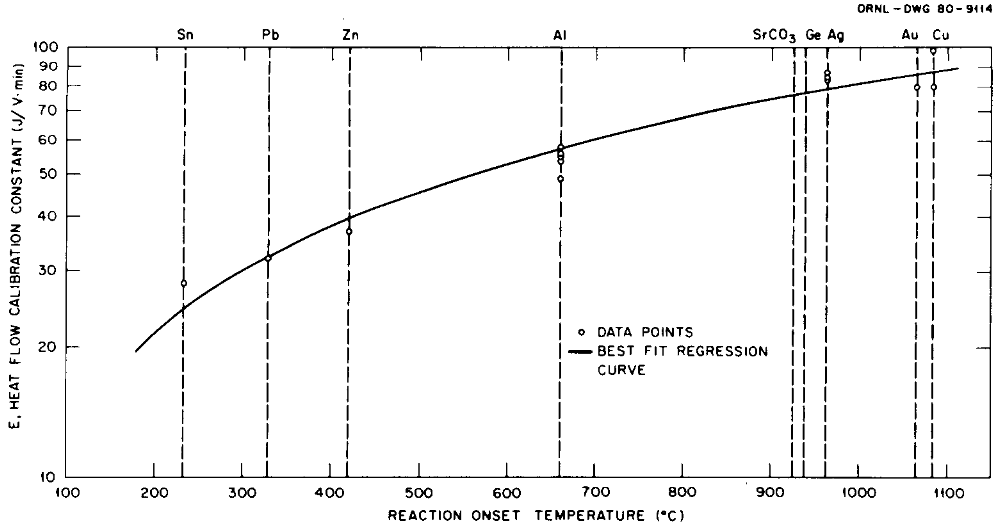

Fig. 5. Heat Flow Calibration Constant (E) Versus Reaction Temperature Showing Data Points and Best-Fit Curve.

Table 3. Comparison of Calculated ΔH Values to Literature Values for Unknowns

Material	Transformation temperature, °C		E-value used (JV^{-1} min^{-1})	ΔH (J/g)	
	Literature	Observed		Literature	Calculated
Ge	937[a]	943	77.4	477[a]	472
$SrCO_3$	925[b]	935	77.0	116[b]	109

[a] From Table 2.2, p. 63, in *CRC Handbook of Materials Science, Vol. I: General Properties*, C. T. Lynch, Ed., CRC Press, Cleveland, Ohio, 1974.

[b] R. C. Mackenzie and P.F.S. Ritchie, "Peak Areas and Heats of Transition of DTA Temperature Standards," *Therm. Anal.* 1: 441–52 (1971).

Sample Preparation

Two trial compositions of mixed powders were examined. The first was a mixture of 50 wt % U_3O_8 powder-50 wt % Alcoa 101 Al powder (vacuum degassed at 500°C). This mixture, designated 50/50, was used primarily to test effects of instrumental and sample preparation parameters on thermogram quality. No particular care to control particle sizes was exercised. Both powders were of average particle size — less than 44-μm equivalent spherical diameter. Using the Model 900 Thermal Analyzer (the Model 990 was not yet available), it was determined that the most reproducible thermograms were obtained with a sample prepared by blending the powders in an oblique blender, pressing into a pellet at 138 MPa, and crushing to pass a screen with 500-μm openings. Heating rate also played a role in thermogram reproducibility, and 10°C/min was chosen as an optimum rate. Using these parameters, this material was run in the DTA system several times, with heating being discontinued at several temperatures on successive samples. Samples were then subjected to x-ray diffraction analysis for phase identification after the runs.

To better approximate the meat region of a maximal U_3O_8-loaded fuel plate, a second composition was prepared from the same materials in the same way. This was 79 wt % U_3O_8-21 wt % Al (79/21 mixture). It was quantitatively analyzed on the new Model 990 Thermal Analyzer System.

Finally, miniplates were fabricated by the conventional processes of powder-blending, pressing, cladding, rolling, and heat-treating. The essential steps were:

1. weighing and blending the U_3O_8 powder (the principal particle size is 44 to 88 μm with about 25 wt % <44 μm) with the aluminum powder (principal particle size is 0 to 44 μm) for each fuel compact,
2. cold pressing at 414 MPa (60,000 psi) to form the green compacts,
3. degassing the compacts at 590°C and less than 7 Pa (0.05 torr) for 1 h to remove pressing lubricant and adsorbed gases,
4. assembling the degassed compacts into frames and welding on cover plates of Alclad 6061 aluminum alloy to form the rolling billet,

5. cladding by hot roll bonding at 495°C,
6. annealing at 495°C for 1 h to soften and also to test for blistering,
7. cold rolling to a reduction in thickness of 20% (total reduction in thickness is 87.5%), and
8. heat treating to the "0" temper for aluminum alloy 6061.

Specimens were punched out of two of these miniplates, both of which had 75 wt % U_3O_8 in the "meat," and a total of 52 or 63 wt % Al, respectively, including cladding. These specimens would closely represent the actual fuel element in a reactor compared to the blended powder materials, because the plate specimens had undergone the same fabrication procedures a fuel plate would receive. Other complete miniplates were heated in an electrical resistance furnace in air and visually monitored to determine macroeffects of heating through the thermite reaction temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

Powder Mixtures

50 wt % U_3O_8 composition

A typical ΔT-T thermogram obtained with the Model 900 Thermal Analysis System for this composition is shown in Fig. 6. Clearly discernible features on it are the following:

1. an exotherm on heating with a peak at about 620°C, followed closely by,
2. a sharp endothermic peak at 656°C,
3. a broad exotherm beginning near 850°C with a peak at 985°C,
4. exothermic activity around 1300°C and greater, and
5. a sharp exotherm on cooling at about 640°C.

Based on the literature data described previously, one can ascribe (1), (2), (3), and (5), respectively, to the initial

$$U_3O_8 + 4/3\ Al \rightarrow 3UO_2 + 2/3\ Al_2O_3 \qquad [(1)\ p.\ 3]$$

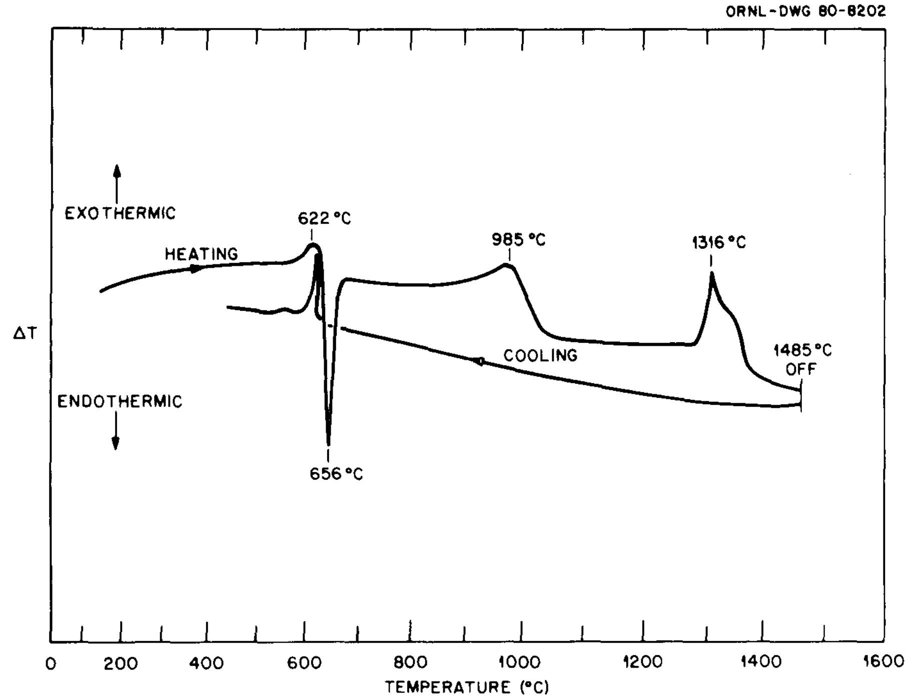

Fig. 6. Typical Thermogram of a 50/50 Mixture as Recorded With the Model 900 DTA System.

reaction,[3] which is obscured by the heat absorbed by melting of aluminum (~660°C), followed by the secondary thermite reaction peak at greater than 800°C, and finally the 640°C freezing exotherm aluminum on cooling. The latter is smaller than the melting endotherm (in peak areas) because part of the aluminum has been consumed in reaction with U_3O_8. Not all aluminum has been reacted because, according to possible reactions (1)–(5), (pp. 3–4) the 50 wt % Al in this mix is in excess of that required to convert all U_3O_8 to other products. Also, one will notice the relative size of the secondary thermite peak area in relation to the aluminum melting endotherm. That is to say, the thermite reaction heat evolved is not far greater than the heat absorbed by the melting of the aluminum.

The other feature, (4), on the thermogram has not been reported in the literature. Its origin is unknown at present.

In an attempt to define the phases present after each of these reactions, several other specimens of this composition were heated in the DTA to temperatures beyond the peaks, cooled rapidly, and analyzed by x-ray diffraction. Phase analysis results are presented in Table 4.

Table 4. Phases Present in 50/50 Mixture After Heating to Given Temperatures

Temperature attained (°C)	Phases present
25	Al, U_3O_8
725	Al, U_3O_8
1250	Al, U_3O_8, Al_2O_3
1350	Al, U_3O_8, UAl_2, UO_2, Al_2O_3

After heating to 725°C, the molten aluminum should have reacted partially with the U_3O_8 particles, according to previous investigators, resulting in appearance of UO_2 and Al_2O_3. However, they described this process as a surface reaction phenomenon, resulting in a thin layer of reaction products. If this layer comprised less than about 5 to 10 wt % of the mix, our x-ray diffraction technique may not have been sensitive enough to detect the product phase. Hence, the absence of UO_2 and Al_2O_3 phases at 725°C does not necessarily mean they were not produced. A more sensitive technique, such as electron microprobe or transmission electron microscope analysis, may be required to detect these phases.

After heating beyond the 850 to 1000°C peak, x-ray diffraction shows the presence of Al_2O_3. It is not until after the 1300°C exotherm that sufficient reaction occurs to allow observation of UAl_2 in the reaction products. The appearance of this phase would be puzzling in an equilibrium reaction situation, because one would expect to find UAl_4 in the presence of excess aluminum. The fact that even after exposure to 1350°C there is still U_3O_8 remaining indicated that equilibrium was not achieved. Because the reaction is probably diffusion-controlled, it may be that the UAl_2 is merely the primary phase between the U_3O_8 and aluminum phases, and given time, more aluminum would diffuse into the U_3O_8 particle through the UAl_2 layer and convert it to UAl_3 and finally UAl_4.

Several duplicate DTA runs were made on this material, during which it became apparent that the approximate 900 and 1300°C exotherms varied widely in onset temperature, peak shape, and duration. This was particularly true of the highest temperature exotherm (circa 1300°C). Onset temperature varied from 1100 to 1300°C, geometry at times being extremely narrow and sharp, and at others shallow and broad, including fine structure (extra peaks). In many cases, the peak area surpassed that of the approximately 800 to 1000°C peak, while at other times it was less. The origin of this exotherm is still unknown, and certainly is of complex nature.

79 wt % U_3O_8 composition

Mixed powders of 79 wt % U_3O_8–21 wt % Al were pressed into pellets and crushed for DTA examination. Four *T*–Δ*T*–time thermograms were obtained from four separate specimens. A tabulation of major features is given in Table 5. Peak areas are for comparison of aluminum melting endotherm to thermite exotherm in any one run, and cannot be compared between runs, because the sample weights varied from run to run. One thermogram is shown in Fig. 7. It has the same characteristic features as the thermogram of the 50/50 mixture (Fig. 6), except that the thermite peak at 800 to 900°C is now smaller in extent than the aluminum melting endotherm. Also, the highest temperature exotherm now is better defined, showing in all four cases two distinct peaks. They occur at lower temperatures than for the 50/50 composition. The shoulder on the low-temperature side of the aluminum melting endotherm, previously ascribed to reaction (1), now appears less distinct in comparison and was absent in runs for two of the samples.

Table 5. Results of Differential Thermal Analysis of 79/21 Aluminum Specimens

Run number	Aluminum melting endotherm		Thermite reaction exotherm		Others
	Onset *T* (°C)	Peak area (cm^2)	Onset *T* (°C)	Peak area (cm^2)	Peak *T* (°C)
1	654	7.77	881	5.32	1223, 1263
2	654	7.82	880	5.18	1224, 1249
15	654	6.89	880	9.11	1223, 1245
17	654	8.02	883	14.37	1213, 1250

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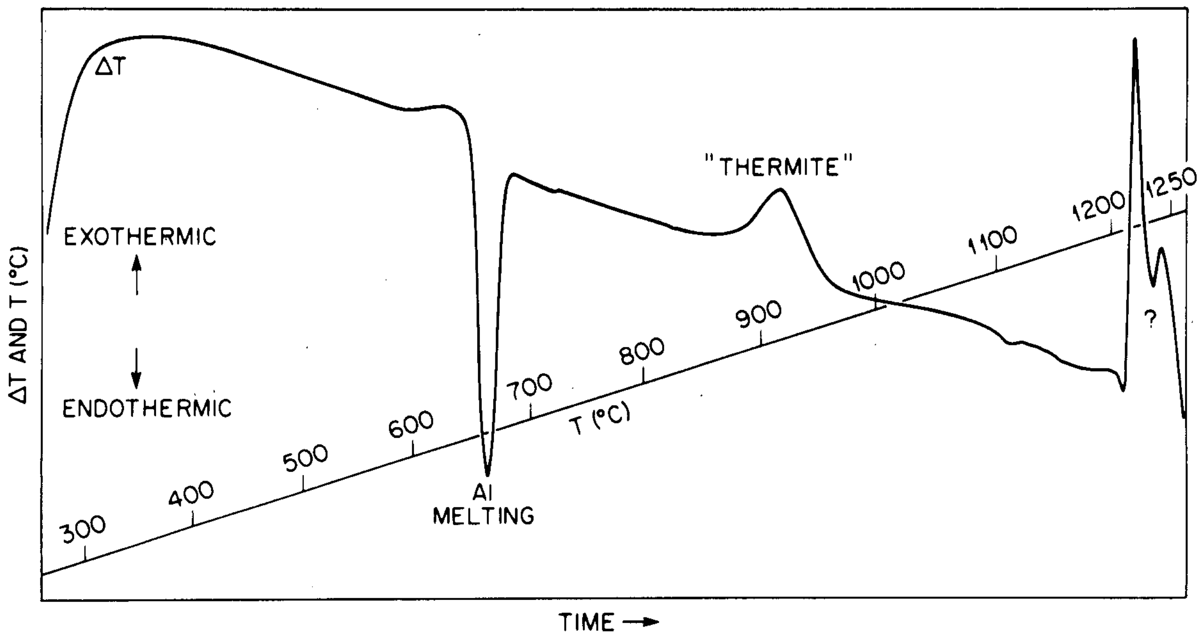

Fig. 7. Typical Thermogram of 79/21 Mixture as Recorded With the Model 990 DTA System.

As a further test of the accuracy of the DTA heat of reaction calibration, these specimens were quantitatively analyzed. The area encompassed by the aluminum melting endotherm was measured, and along with the known weight of aluminum in the mixture in the sample, appropriate instrumental parameters (C, ΔT_y) and the E-value from Eq. (7), the ΔH (melting) for aluminum was measured. Results of these calculations are presented in Table 6. The close correlation between calculated and known values for these mixtures implies two facts: first, the procedure and calibration are correct; and second, very little aluminum reacts to form Al_2O_3 by the time the melting point is reached. In other words, if reaction (1) does occur at temperatures lower than the aluminum melting point, only a very small fraction of aluminum is involved. This result is in agreement with the fact that no Al_2O_3 was detected by x-ray diffraction in the 50/50 composition heated to 725°C.

Run 15 yielded a significantly lower value of ΔH (melting) than the other three, and the suspected reason for this was an experimental weighing error. As is shown in Table 6, the thermite ΔH is also lower for this run, which supports this possibility.

Using the E-value at the appropriate temperature, known C, ΔT_y, and sample weight, ΔH for the area under the thermite exotherm was calculated

Table 6. Results of DTA Examination of 79/21 Specimens

Run number	Aluminum melting onset temperature (°C)	Calculated ΔH[a] (J/g)	Thermite reaction heat (J/g)	
			Calculated	From Fleming and Johnson[b]
1	654	394	79.1	1090
2	654	390	76.1	1090
15	654	357	55.6	1090
17	654	403	85.4	1090

[a] Compare to 397 J/g literature value.

[b] J. D. Fleming and J. W. Johnson, "Exothermic Reactions in Al-U_3O_8 Composites," pp. 649–66 in *Research Reactor Fuel Element Conference*, TID-7642, Book 2, 1962.

for each of the four runs. Results are presented in Table 6, along with the calculated "maximum credible energy release" value for this composition from Fleming and Johnson.[3]

Obviously, all of the potentially available reaction heat is not released in the observed temperature range of about 880 to 1000°C. The reason is unknown, but there are several possibilities:

1. Heat release rate is a function of heating rate, and faster rates would probably result in larger concentrated heat releases. Up to the 20°C/min rate evaluated in this test, however, no significant effect is observed.
2. Reaction rate and thus heat release is probably inversely proportional to U_3O_8 particle size, and finer particles than those used could result in larger thermal energy releases.
3. The heat of reaction calculation of Fleming and Johnson[3] assumed complete reaction, which was not the case here (see x-ray results, Table 4).
4. Their data for heats of formation were overestimates, based on the best information available at the time. This is possibly the case for UAl_2 and UAl_3, and UAl_4 especially, though not by a factor of about 15 as would be required here.[15]
5. Part of the "thermite" reaction thermal energy release may well be represented in the exotherms occurring at the higher temperatures. These peaks occur at temperatures beyond the range of calibration of our instrument, so estimating the heat involved is impossible.

6. Diffusion-controlled reactions, as these are presumed to be, may simply proceed too slowly to exhibit measurable thermal energy release.

If one uses the heats of reaction calculated from these thermograms for aluminum melting and the thermite reaction, the 21% Al in such a fuel absorbs about 85 J/g fuel on melting, while the thermite reaction heat evolved is a maximum of 85 J/g fuel. Considering then the potential heat effects of the thermite reaction, one could conclude that its effect will be negligible compared to the heat required:

1. to heat the fuel from operating temperature to the melting point of aluminum,
2. to melt the aluminum, and
3. to heat the resulting mass to about 880°C.

However, if that much heat were available in the reactor from decay heating, then, depending on the heating rate and other factors, the thermite reaction at about 880°C could perhaps produce enough heat to initiate the exothermic reactions at greater than 1200°C, which in turn would produce even more heat. Tests to corroborate this concept were then formulated. First, samples of miniplates were quantitatively analyzed by DTA, then entire miniplates were heated in an electric furnace and visually observed.

Miniplates

Differential thermal analysis

Specimens punched from two different miniplates were quantitatively analyzed by DTA. Typical thermograms from each of the (estimated nominal) 52 and 63% Al plates are given in Fig. 8. As with the 79/21 composition, the peak areas were analyzed for thermite reaction heat, using only the main peak at around 900°C. Also, the peak area encompassed in the aluminum melting endotherm was analyzed to provide an estimate of the weight percent aluminum (total) in the specimen. Results are presented in Table 7. Thermite reaction heats are compared to Fleming and Johnson's calculations[3] in Table 8. Again, as with the powder mixtures, the measured thermite reaction heat is very low compared to the calculated maximum possible value.

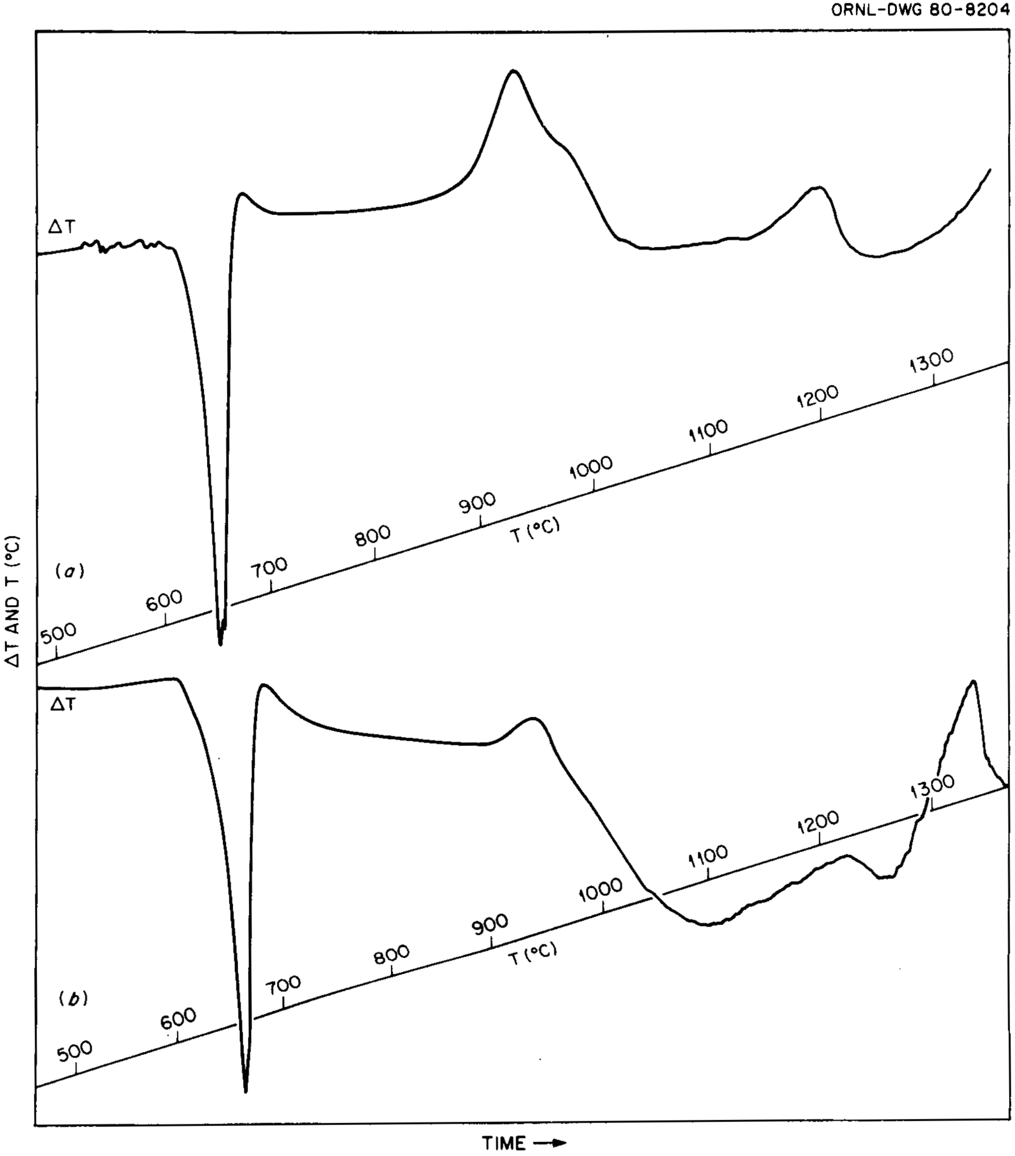

Fig. 8. Typical Thermograms of U_3O_8-Al Miniplate Specimens as Recorded with the Model 990 DTA System. (a) Nominally estimated aluminum content of 52 wt %. (b) Nominally estimated aluminum content of 63 wt %.

Table 7. DTA Results From Miniplate Specimens

Specimen number	Run number	Aluminum content, wt %		Thermite reaction		Other peaks
		Estimated[a]	Calculated	Onset *T*, °C	Δ*H*, J/g	Peak *T*, °C
14-3-1	28	52	[b]	898	165	~1330
14-3-2	29	52	50.1	880	398	~1200
14-3-3	30	52	55.1	904	264	
14-3-4	35	52	[b]	872	381	~1300
14-3-5	36	52	59.9	892	123	
14-3-6	37	52	57.4	895	120	
		Average =	55.6		243	
16-1-1	31	63	[b]	901	77	~1220
16-1-2	32	63	67.5	908	48	1220, 1330
16-1-3	33	63	67.3	904	92	1170, 1320
16-1-4	34	63	66.7	896	68	1220, 1330
		Average =	67.2		71	

[a] Estimated from weight percent aluminum in core and average cladding thickness.

[b] Peak was off-chart; area could not be measured.

Table 8. Comparison of Measured Thermite Reaction Heats to Literature Values

Total aluminum content (wt %)	Thermite reaction heats (J/g fuel)	
	Measured	Literature[a]
52–56	243	830–900
63–67	71	650–710

[a] J. D. Fleming and J. W. Johnson, "Exothermic Reactions in Al-U_3O_8 Composites," pp. 649–66 in *Research Reactor Fuel Element Conference*, TID-7642, Book 2, 1962.

The calculation of total aluminum content based upon the heat effect was close to the estimated value in both cases, as expected. This DTA technique was sensitive enough to detect the fact that there were two types of aluminum present, the cladding of aluminum alloy 6061 and the matrix ("meat") material of 101 aluminum. This is evidenced by the double-peak nature of the aluminum melting endotherm [Fig. 8(a)]. The low-temperature shoulder observed previously on this endotherm is essentially absent, which may indicate that the initial reaction between U_3O_8 and aluminum [reaction (1)] may have been initiated during plate rolling or annealing, and hence was not occurring upon sample heating in the DTA furnace.

The higher temperature exotherms observed with the 79/21 and 50/50 powder mixes are extremely variable in these samples. Their nature and origins are unknown.

Heating tests

Four separate miniplates (roughly 25 by 50 by 1.5 mm thick) were heated in electrical resistance furnaces in air to determine the effects of heating an element beyond the 800 to 1000°C thermite reaction temperature range. The first was held upright in a bed of sand, heated slowly overnight to 500°C, then heated to 1020°C in 2 h. The plate slumped over at 710°C, after the aluminum cladding had been observed to melt. No further changes in appearance were noted. After cooling, the still integral plate was sectioned lengthwise. Visual examination showed three distinct layers of material; the two outer cladding layers, each of which had formed into a pool near the center of the plate, and the inner "meat" which, though reacted, was still intact; that is, no "explosions" or large displacements of material had occurred.

The second miniplate was laid in a hemicylindrical quartz reaction boat and heated to 1110°C from a preheat level of 500°C in 21 min. This would give an average heating rate of about 30°C/min, or three times as fast as the rate used on the DTA runs. The plate slumped into the boat at about 690°C, with no further observable occurrences. On cooling, this plate also was integral. There had been a slight axially downward tilt to the specimen during heating, and the aluminum cladding had flowed in that direction and was solidified there. This left the U_3O_8-Al reaction products in the meat exposed. The meat was hard and strong in this state. No evidence of unusual thermal behavior was found.

The third miniplate was treated similarly, this time with a thermocouple in contact with the plate. It was heated from 500 to 1050°C in 30 min. After 5 min, the plate had reached the cladding melting temperature (~650°C) at which temperature a thermal arrest was observed. No other thermal effects were observed on heating. On cooling, a change in slope of the temperature-time curve indicated freezing of the aluminum. As with the second plate, this specimen had the meat exposed, and though warped it was integral. The aluminum cladding had flowed to the bottom of the quartz boat yet it retained adherence to the meat.

Since there were DTA exotherms noted previously at greater than 1200°C for specimens taken from this type of plate, a fourth miniplate was rapidly heated to 1405°C (106 min from 500°C). A thermal arrest was noted only at about 640 to 650°C. After cooling, the plate appeared similar to the previous two, except that warpage was more severe.

These four miniplate experiments showed no major disruptive effects that could be ascribed to the thermite reaction. This is as expected from the DTA experiments. It is interesting to note that in the latter three of these experiments the meat was essentially exposed to the atmosphere, not in contact with the aluminum of the cladding. Hence the meat, 75 wt % U_3O_8-25 wt % Al, was allowed to thermally react by itself, without the diluting effect of the aluminum cladding. This composition is one of those calculated by Fleming and Johnson[3] (Fig. 1) to exhibit maximal energy release upon reaction. The fact that the meat showed no ill effects other than warping after heating to 1400°C is encouraging, indicating that the thermite reaction in this type of fuel plate is not likely to pose any safety problems.

SUMMARY AND CONCLUSIONS

Summary

Differential thermal analysis, x-ray diffraction, and in-furnace heating experiments were performed on powder mixtures and miniature fuel plates of compositions ranging from 50 wt % U_3O_8-50 wt % Al to 79 wt % U_3O_8-21 wt % Al. The DTA experiments showed the following:

1. On heating, U_3O_8-Al mixtures of these compositions exhibit several distinct thermal energy releases or absorptions. These include an exotherm between 600°C and the melting point of aluminum, an endotherm on

melting of aluminum, an exotherm at a temperature near 900°C, and one or two more exotherms at temperatures greater than 1200°C.

2. Quantitative analysis of the areas encompassed within these exo- and endotherms yields good accuracy ($<10\%$ error) for values of the heats of transformation.

3. Using the quantitative analysis technique described, heats of reaction for three U_3O_8-Al compositions were calculated. These results were all much lower than values described in the literature, based on thermochemical considerations.

X-ray diffraction analysis of samples of a 50/50 composition heated to various temperatures showed no reaction products after heating to 725°C. After heating to 1250°C, Al_2O_3 was observed, and after 1350°C, UO_2 and UAl_2 were found in the reaction products.

When miniature fuel plates were heated in air in electrical resistance furnaces, (1) on heating to about 640°C the cladding aluminum melted and flowed away from the meat, (2) the meat remained integral even when heated to 1400°C but warped under its own weight, and (3) no violent thermal effects, explosions, or gas releases were observed.

Conclusions

The main conclusions drawn from these experiments are the following:

1. Measured heats of reaction evolved from high-uranium U_3O_8-Al mixtures at temperatures near 900°C are low compared with the thermal energy required to initiate the reactions.

2. The first conclusion plus the lack of disruptive thermite reaction effects in heated miniature fuel plates indicates that switching from the present low U_3O_8 loading to higher levels does not add a significant chemical reaction hazard to other considerations of safe reactor operation.

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