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A DIFFERENTIAL THERMAL ANALYSIS STUDY
OF U_3Si-Al AND U_3Si_2-Al REACTIONS

by

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ABSTRACT

As part of the Reduced Enrichment Research and Test Reactor (RERTR) program, high density uranium compounds are being evaluated as possible replacements for the fuels currently in use. U_3Si and U_3Si_2 powders dispersed in an Al matrix and roll bonded within 6061 Al alloy clad have performed well under irradiation in the ORR. A consideration of the heats of reaction between the silicides and the Al components of a reactor fuel plate has now been addressed.

By following standard quantitative differential thermal analysis (DTA) procedures, it has been demonstrated that neither silicide shows any measurable heat of reaction until the solidus temperature of 6061 (582°C) is exceeded. On heating, the exothermic reaction is quenched by the endothermic change of state as the Al species melt. All detectable events take place in the temperature regime from ~580 to ~660°C.

The heats of reaction per gram of fuel ranged from 304 ± 18 J for samples with 32 vol.% U_3Si_2 in the fuel zone to 486 ± 54 J for samples containing 45 vol.% U_3Si in the fuel zone.

I. INTRODUCTION

The Argonne National Laboratory (ANL) is managing the U.S. Reduced Enrichment Research and Test Reactor (RERTR) program to develop proliferation-resistant fuels. The main thrust of this effort is directed toward a reduction of ^{235}U enrichment of the uranium employed in the fuel alloys from >90% (currently employed) to <20% (typically $19.7 \pm 0.2\%$). As a consequence of this enrichment reduction, an increase in the total amount of uranium contained in a fuel element is required. However, at the lower enrichment, the total U required in an element for the most advanced reactors exceeds the amount that can be fabricated with present fuels and manufacturing techniques. For plate-type elements, the present fuels include powders of U_3O_8 or "UAL" (a U-Al alloy at about the composition of UAl_3 , i.e., ~70 wt.% U) dispersed in a matrix of commercially pure Al powder and roll bonded within a cladding of 6061 aluminum alloy. The plates so generated, which might typically be ~3 in. (~76 mm) wide by ~26 in. (~660 mm)

long and 0.050 to 0.060 in. (1.27 to 1.52 mm) thick, are assembled into a fuel element for insertion into the reactor core.

In order to meet the requirements of the most demanding reactors, a fuel alloy development effort was, and still is, an important aspect of the RERTR Program. The work in the Materials Science and Technology Division of ANL has focused on uranium silicides, U_3Si , U_3Si_2 , and " U_3SiAl " (a ternary alloy of U + 3.5 wt.% Si + 1.5 wt.% Al). The silicides have high densities and high uranium contents and are quite corrosion resistant in hot water -- the normal coolant for these reactors.

A description of the fuel alloy development work with silicide powders and "miniplates" is detailed in Ref. 1; comparable information on work with low-enrichment U_3O_8 may be found in Ref. 2. As a result of irradiation experience with fuel plates containing uranium silicides, the fuel alloys U_3Si and U_3Si_2 have emerged as contenders for satisfying the goals of the program; U_3SiAl has been abandoned as a fuel alloy powder for plate-type elements.

Once the silicides were determined to have a significant potential for commercial use, considerations beyond those of fabricability and stability in a normal irradiation environment had to be addressed. One such concern is the stability of the silicide-plus-aluminum mixture under off-normal conditions where the fuel element might be heated up to and beyond the melting point of Al. That is, what reactions might occur and what heat evolution might be expected to accompany such reactions? One³ report suggests that uranium silicides react rapidly with Al at $\sim 620^\circ C$.

The purpose of this study, then, was to determine by differential thermal analysis (DTA) techniques the temperature regime and enthalpies associated with reactions that occur between the silicide fuel particles and the aluminum matrix as well as the 6061 clad at elevated temperatures. A similar study has already been conducted for U_3O_8 -type fuel plates.⁴

II. REACTIONS

In Al plus U_3Si or U_3Si_2 dispersion fuels (in the absence of oxygen), three possible reaction products are UAl_2 , UAl_3 , and UAl_4 . At least three concurrent possibilities may be examined. First, the formation of free Si can be postulated, although it has never been observed to form. Second, the Si may form USi_3 . Third, the Si may substitute in the lattice of UAl_3 to form $U(Al,Si)_3$. The third possibility is the one that has been documented in phase equilibria studies by A. E. Dwight.⁵

/ For a reaction between one mole of U_3Si and a stoichiometric amount of Al, at least six equations can be written and balanced for a complete reaction. These are recorded in Table I. In Eqs. (4) through (6) the formation of USi_3 in combination with UAl_2 , UAl_3 , or UAl_4 is shown. This is a bookkeeping simplification since, as noted above, it has been demonstrated that USi_3 as a discrete phase is not formed, but $U(Al,Si)_3$ is the product.

Table II summarizes a similar set of six equations for possible reactions between U_3Si_2 and Al. Completely analogous to the discussion of $U_3Si + Al$ reactions, the most predictable event is the formation of UAl_3 which dissolves Si to form $U(Al, Si)_3$, i.e., reaction (11).

All reactions are diffusion controlled, and in each case the reaction products are less dense than the reacting phases. This inevitably leads to a growth of the fuel zone volume and, consequently, the fuel plate.

Table I. Possible $U_3Si + Aluminum$ Reactions

$U_3Si + 6 Al$	\rightarrow	$3 UAl_2 + Si$	(1)
$U_3Si + 9 Al$	\rightarrow	$3 UAl_3 + Si$	(2)
$U_3Si + 12 Al$	\rightarrow	$3 UAl_4 + Si$	(3)
$U_3Si + \frac{16}{3} Al$	\rightarrow	$\frac{8}{3} UAl_2 + \frac{1}{3} USi_3$	(4)
$U_3Si + 8 Al$	\rightarrow	$\frac{8}{3} UAl_3 + \frac{1}{3} USi_3$	(5)
$U_3Si + \frac{32}{3} Al$	\rightarrow	$\frac{8}{3} UAl_4 + \frac{1}{3} USi_3$	(6)

Table II. Possible $U_3Si_2 + Aluminum$ Reactions

$U_3Si_2 + 6 Al$	\rightarrow	$3 UAl_2 + 2 Si$	(7)
$U_3Si_2 + 9 Al$	\rightarrow	$3 UAl_3 + 2 Si$	(8)
$U_3Si_2 + 12 Al$	\rightarrow	$3 UAl_4 + 2 Si$	(9)
$U_3Si_2 + \frac{14}{3} Al$	\rightarrow	$\frac{7}{3} UAl_2 + \frac{2}{3} USi_3$	(10)
$U_3Si_2 + 7 Al$	\rightarrow	$\frac{7}{3} UAl_3 + \frac{2}{3} USi_3$	(11)
$U_3Si_2 + \frac{28}{3} Al$	\rightarrow	$\frac{7}{3} UAl_4 + \frac{2}{3} USi_3$	(12)

III. SAMPLE PREPARATION

The materials used to produce the samples for this study included Alcan MD101, a nominally -325 mesh commercially pure Al powder, and -100 mesh U_3Si (U + 4 wt.% Si) and U_3Si_2 (U + 7.5 wt.% Si) powders. The silicide powders were produced at ANL using high purity depleted uranium following procedures described in Ref. 1.

The powders were combined in accordance with the matrix shown in Table III. Silicide fuel was 15% -325 mesh (<45 μm , "fines") and 85% -100 + 325 mesh (<150 μm and >45 μm).

Table III. Test Matrix for Differential Thermal Analysis (DTA) Specimens

Identification Code	Matrix	Fuel	Vol.% Fuel in Fuel Zone	Total U in Fuel Zone, g-cm ²³
CS-6061-16 thru 24	None	None	0	0
CS-MD101-29 thru 32	MD101	None	0	0
CS-B-89 thru 94	MD101	U_3Si	32	4.7
CS-B-95 thru 100	MD101	U_3Si	45	6.6
CS-X-105 thru 110	MD101	U_3Si_2	32	3.6
CS-X-113 thru 118	MD101	U_3Si_2	45	5.1

Individual charges were weighed into screw-top glass vials, sealed, and mixed in a V-blender for a minimum of 3 h. After mixing, the charges were compacted with pressures ranging from 9 to 31 tons per in.² (~ 12 to ~ 44 kg/mm²) in a cylindrical die [0.75 in. (19.0 mm) diameter]. The compacts were ~ 0.133 in. (~ 3.38 mm) high x 0.753 in. (19.0 mm) diameter with ~ 14 vol.% porosity. After compacting, the samples were placed into holes drilled in a 6061 Al frame [6 x 8 in. (152 x 203 mm)] and covered top and bottom with 6061 Al cover plates. All 6061 hardware was chemically cleaned just prior to assembly to remove the oxide film. The assembly was then peripherally welded (leaving some gaps for air to escape) and roll-bonded by hot rolling, 20-25% reduction per pass, for seven passes. The hot rolling was followed by a one-hour blister test anneal at 485°C. Finally, the assemblies were cold rolled $\sim 19\%$ to 0.060 in. (1.52 mm). Hardware at various steps in the fabrication procedure is shown in Fig. 1.

The finished plates have an elliptical fuel zone [~ 0.75 x 4.8 in. (~ 19 x 122 mm)]; the overall dimensions are ~ 2 x 6 in. (~ 51 x 152 mm).

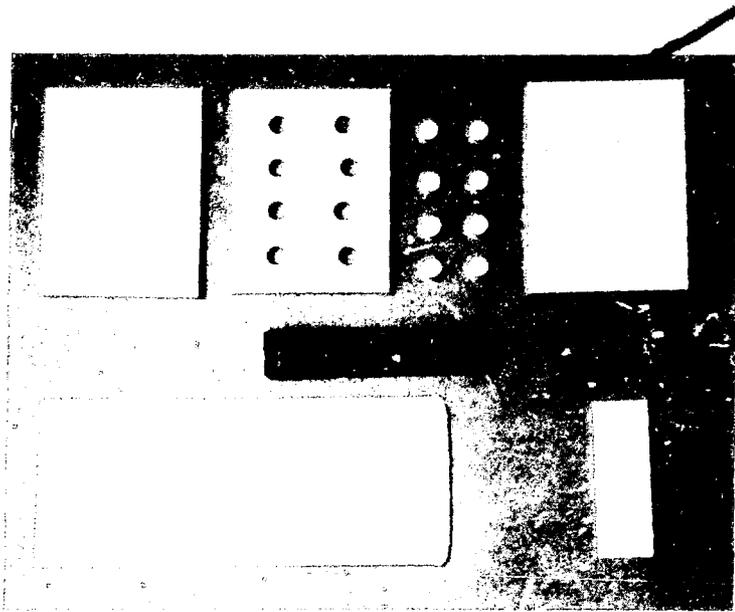


Fig. 1. Compatibility Study Components before Assembly (Top), after Rolling and Partial Shearing (Lower, Left), and Finished Plate (Bottom, Right).

Fuel zone volumes, silicide concentration values, and porosities of the fuel zones were calculated from the known quantities, chemistries, and densities of the components, and immersion densities measured in distilled water for several plates in each category. Radiographic films of the silicide plates were made to determine fuel location and homogeneity. Samples were manually punched out of uniform areas using a commercially available punch; the resulting sample geometry is illustrated in Fig. 2. As reference standards, similar discs were produced from plates which contained no "fuel." That is, samples were taken from plates wherein the fuel zone was 100% MD101 Al and from plates that were solid 6061 Al or pure Al. All samples, with or without fuel, were 0.060 in. (1.52 mm) thick.

IV. EQUIPMENT AND CALIBRATION

The system employed for this study was a Rigaku TG 2000 - a unit capable of being heated to 1500°C. Sample and reference pans were aluminum oxide and the atmosphere was high purity helium obtained by passing 99.999% pure helium through a six-foot (≈2 meters) length of 3/16 in. (4.8 mm) copper tubing filled with 60/80 mesh chromatographic grade molecular sieve material. The copper tubing was coiled and immersed in liquid nitrogen.

The thermo-gravimetric analysis (TGA) section of the system, which was not used for this study, was joined to the DTA portion and terminated in a 3/4 in. (14.0 mm) "T" at the back of the unit. One leg of the "T" was con-

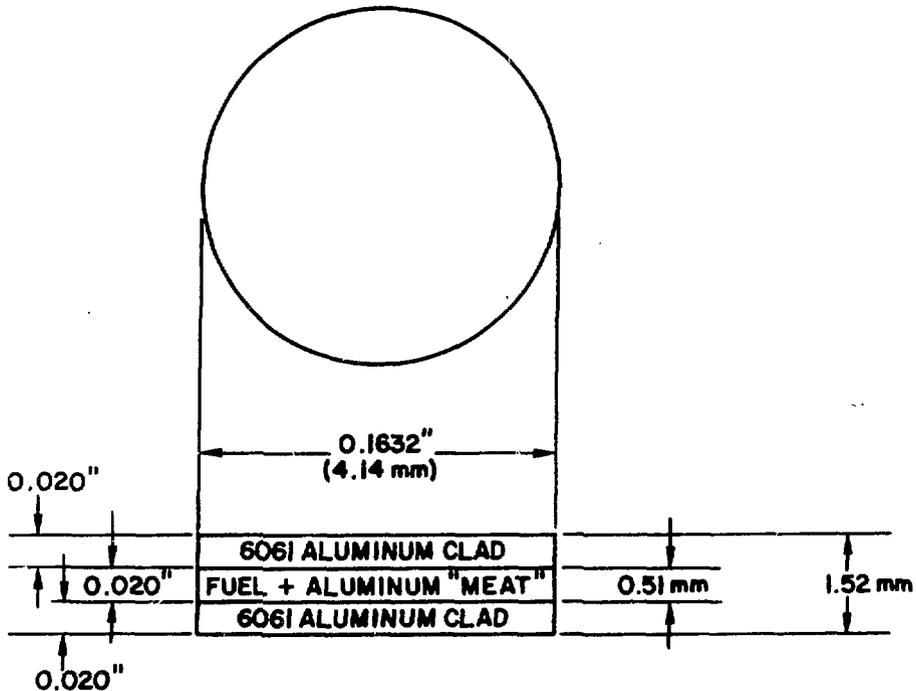
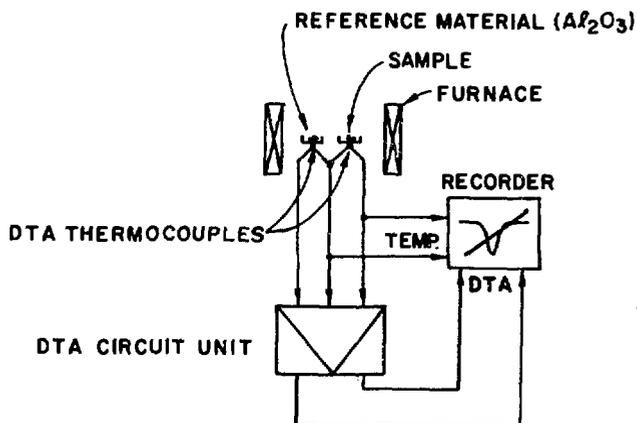


Fig. 2. Geometry of Samples Used for DTA Study.
Dimensions are Nominal.

nected to a 1405 Sargent-Welch mechanical vacuum pump while the other leg went to a flow meter that could be isolated from the vacuum by a three-port stopcock. The system is illustrated schematically in Figs. 3 and 4.

Helium flow was split, each half controlled by a Nupro metering valve and measured by the flow meter. One half of the helium (total flow rate 100 cm³/min) was directed down through the alumina protection tube which enclosed the sample and reference pans while the other half purged the TGA section. Prior to initiating helium flow, the entire system, including the 1/8 in. (3.2 mm) copper line leading to the main valve on the helium cylinder, was evacuated to approximately "0" torr (as read on a 0-1500 torr Helicoid absolute pressure gage). The vacuum pump was then isolated and the helium flow initiated. When the absolute pressure reached approximately 800 torr, the packless valve on the delivery side of the regulator (Matheson 3104-580) was closed and the vacuum pumping reinitiated. Three evacuation and purge cycles preceded each DTA run.

Once every seven to ten days the molecular sieve trap was regenerated. This regeneration consisted of heating the copper coil in place in an electrical resistance furnace to 200°C while purging with helium. The duration of heating was at least overnight (16 h) and occasionally over the weekend (64 h).



SCHEMATIC PRINCIPLE OF DIFFERENTIAL THERMAL ANALYSIS (DTA) MEASUREMENTS

Fig. 3. Schematic Representation of DTA Unit.

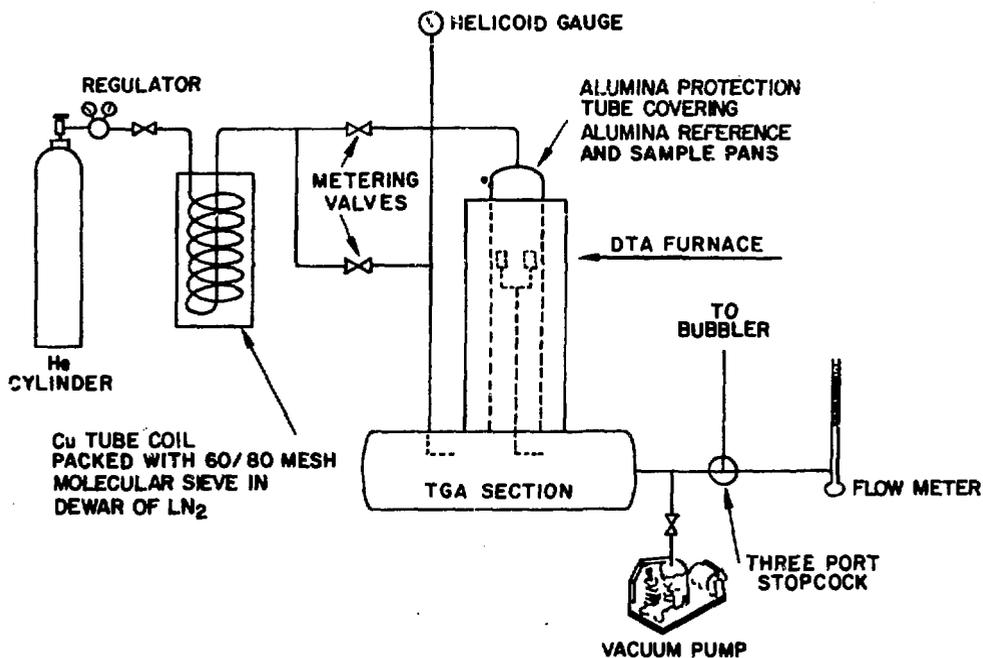


Fig. 4. Detailed Schematic of DTA Apparatus.

Techniques and procedures described in Ref. 4 were used as guides for calibration in this work; all heating and cooling were controlled at the rate of 10°C per minute. Initially an instrument factor vs. temperature curve was generated using zinc, aluminum, silver, gold, copper, uranium, and gadolinium. During these calibrations it was found that copper wetted the alumina pan and gadolinium reacted with the alumina. Therefore, the Cu and Gd points were not used. The results of the calibration are shown in Table IV.

The instrument factor (I.F.) is defined in the following way:

$$\text{I.F.} = \frac{(\Delta H_f)(\text{Mass of Sample})(\text{Chart Speed})}{(\text{Instrumentation Amplification Setting})(\text{Endotherm Area})}$$

Heat of Fusion (ΔH_f) in joules per gram.

Mass of sample in grams.

Chart Speed in centimeters per minute.

Instrument Amplification Setting in microvolts (usually 25 or 50).

Endotherm area (on melting) in square centimeters (measured by cut-and-weigh and/or calibrated planimeter).

When making calibration runs, the specimen was cycled through at least two melts and two freezes to approximately 150°C above and below the melting (freezing) point. The five point calibration plot was tested with a high-purity antimony sample. Because of its relatively high vapor pressure, antimony was melted only once and then heated to ~675°C. The experimentally determined heat of fusion for Sb was 158 J/g, which compares very well with a literature value of 163 J/g.

After observing that the reaction temperature range for fuel plate pellets was always in the 600-700°C range for all of the different types of specimens, internal standards of Sb and Al were run frequently during this study to ensure that minor instrument calibration deviations were being properly monitored and used in the calculations.

V. RESULTS AND DISCUSSION

Having established an instrument factor-vs.-temperature relationship, the heats of fusion (ΔH_f) were determined for samples taken from a piece of "pure" 6061 as well as from a plate that only had MD101 Al as the "meat." Following procedures described for the instrument calibration, the data summarized in Table V were generated. The onset of melting and peak temperatures recorded for these runs compare with literature values of 582°C for the solidus temperature and 652°C for the liquidus temperature of 6061; the melting point of pure Al is 660°C.

Table IV. Calibration Results

Metal	Mass, ug	Accepted ΔH_f , J/g	Measured ΔH_f , J/g	Onset of Melting, °C	Peak Temp., °C	Accepted Melting Point, °C	Instrument Factor	
							Calculated	Regression Best Fit ^a
Zn	51.0	112.0 ^{b,c}	-	429 429	435 435	419.6	0.02636 0.02720	0.02677
Al	49.5	397.0 ^c	-	e 666	e 675	660.4	0.02636 0.02576	0.02618
Ag	51.0	104.7 ^b	-	963 963	975 972	961.9	0.02808 0.02766	0.02732
Au	49.6	63.7 ^b	-	1068 1068	1080 1077	1064.4	0.03113 0.03265	0.03281
U	49.0	38.4 ^d	-	1134	1140	1133	0.03852	0.03806
Sb	51.3	163.2 ^b	158.1	633	639	630.8	0.0266	

^aStatistically derived from the calculated instrument factors and used as the IF for calculating ΔH values for test samples.

^bSupplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Hultgren, Orr, and Kelley, Univ. of California, Berkeley, CA, Nov. 1970.

^cJANAF Thermochemical Tables. Dow Chemical Co., Midland, MI. Al - June 30, 1979, Zn - Dec. 31, 1978.

^dThe Chemical Thermodynamics of Actinide Elements and Components, Part 1, The Actinide Elements, Oetting, Rand, Ackerman, International Atomic Energy Agency, Vienna, 1976.

^eMechanical failure of temperature plot but not of differential temperature plot.

Table V. Summary of Data from Plate Samples with No Silicide Fuel^a

Sample Type	No. of Runs	ΔH_f , J/g	Onset of Melting, °C	Peak Temperature, °C
6061	4	349 ± 23	633 ± 2	657 ± 2
6061 + MD101 Meat	2	372 ± 3	642 ± 3	660 ± 0

^aAll data determined from heating thermograms.

Illustrative thermograms for pure Al and 6061 are shown in Figs. 5 and 6; a similar plot for a MD101 Al meat disc is shown in Fig. 7.

Three discs produced from each of four compatibility study plates were run next. The first heating cycle was initiated at room temperature and carried to ~850°C. The sample was then cooled at the rate of 10°C per minute to ~400°C, and a second heating cycle to 850°C followed. After a second cool to ~400°C, a third and final heating cycle to 850°C was conducted. For one sample of each fuel and volume percent, heating was allowed to proceed to ~1300°C, at which point the study of that particular material was considered complete and the sample was cooled to room temperature.

Typical curves for the first and second heating cycles of a 32-vol.% U_3Si disc and a 45-vol.% U_3Si_2 disc are shown in Figs. 8 through 11. What was uniformly clear in all thermograms is that with two exceptions no distinguishable event was ever observed at a temperature below the solidus temperature of 6061 (582°C) and that the reaction between the silicide and the aluminum (MD101 + 6061) proceeded at a detectable rate only after liquid had formed in the sample. No event (exothermic or endothermic) was ever detected above ~660°C.

There must have been some solid state reaction between the particles and the aluminum. The degree of reaction and amount of heat liberated during this solid state reaction, however, was too small to be detected by the DTA apparatus. The total heating time for a sample taken from room temperature to 600°C was only one hour, and it has been demonstrated in other studies that no metallographically detectable reaction zone has been observed in specimens heated for this length of time in the solid state.

The data for the twelve fuel alloy discs are summarized in Tables VI and VII. Unfolding the exothermic heat of reaction of the silicide from the endothermic heat of fusion of the aluminum was done in the following manner:

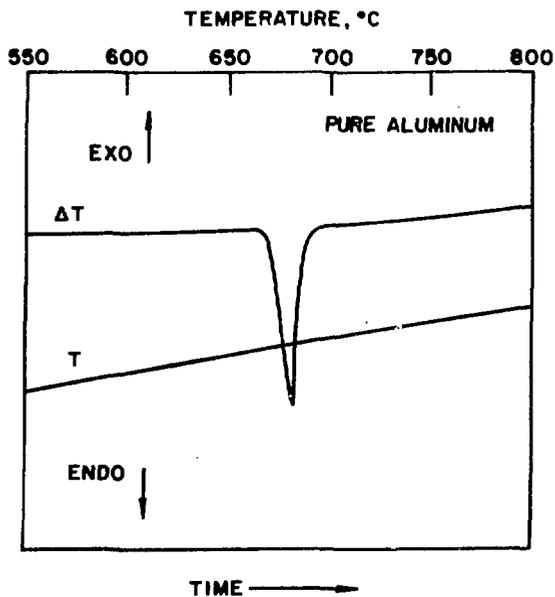


Fig. 5. Thermogram for Pure Aluminum.

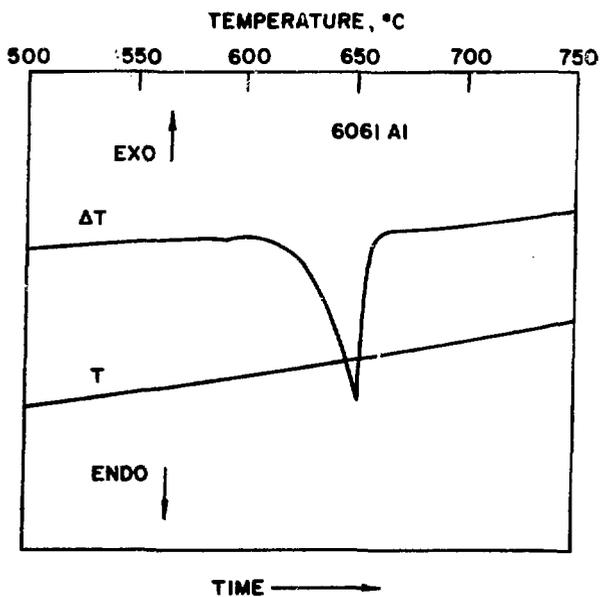


Fig. 6. Thermogram for 6061 Al.

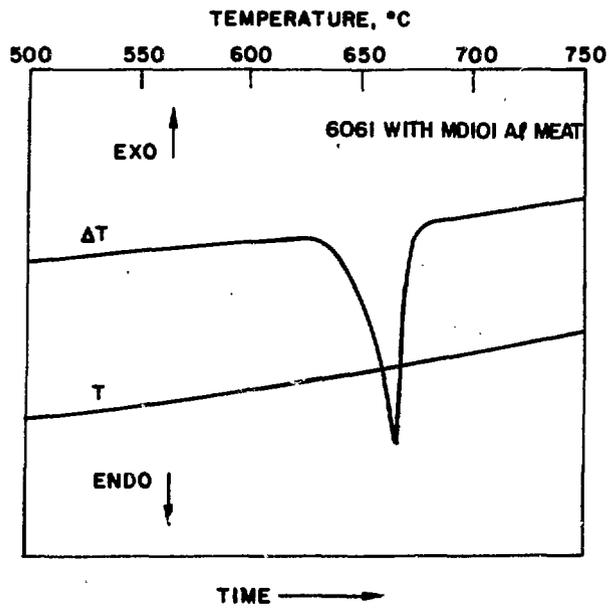


Fig. 7. Thermogram for MD101 Meat Sample.

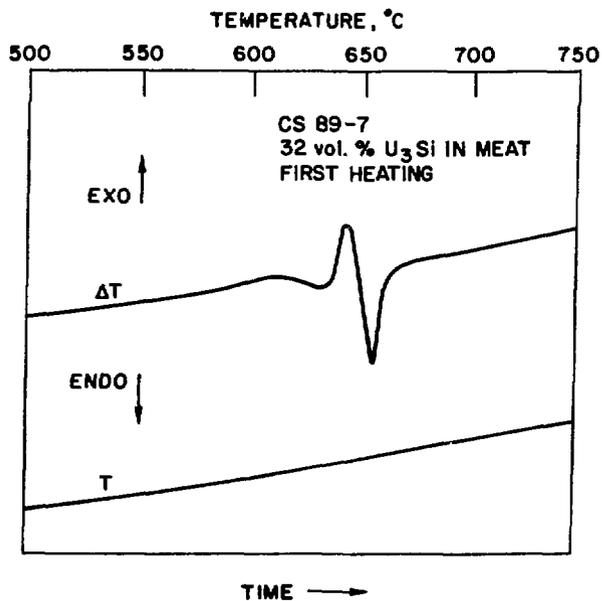


Fig. 8. Thermogram for 32-vol.% U_3Si in Meat Sample.

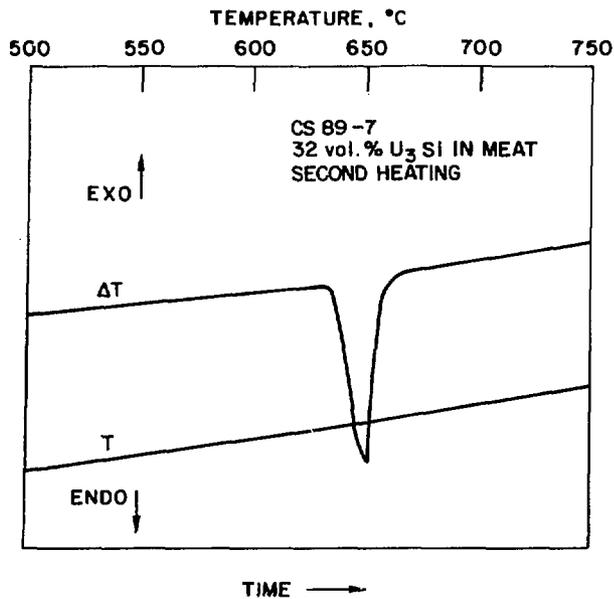


Fig. 9. Thermogram for Second Heating of the Same Specimen as Shown in Fig. 8.

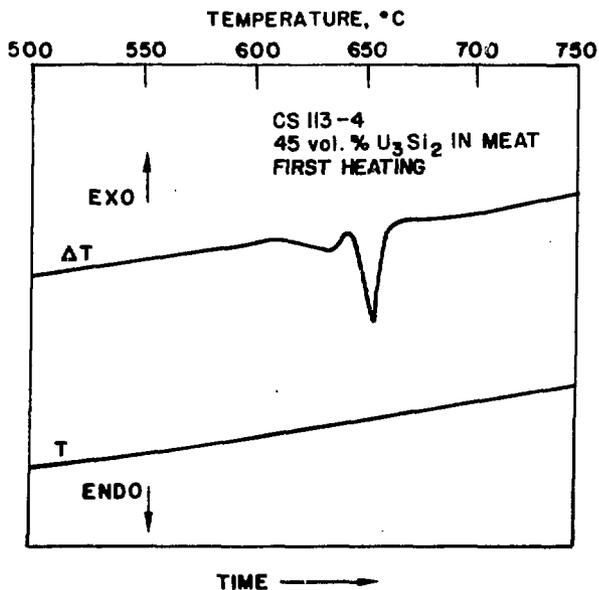


Fig. 10. Thermogram for 45-vol.% U_3Si_2 in Meat Sample.

Table VI. Data on Fuel-Containing Samples for DTA Study

Sample No.	Type of Fuel	Vol.% Fuel in Meat ^a	Vol.% Voids in Meat	Vol.% MD101 in Meat	Mass of Sample, mg	Mass of Fuel, mg	Mass of MD101, mg	Mass of 6061 Clad, mg	Calculated ΔH_f for MD101 + 6061, J
CS105-4	U ₃ Si ₂	32.0	6.0	62.0	73.5	24.16	10.36	38.98	17.72
-5		(3.6 gU/cm ³)			72.6	22.94	9.84	39.83	17.81
-8					74.0	24.84	10.65	38.51	17.67
CS113-1	U ₃ Si ₂	45.0	12.4	42.6	82.1	36.83	7.72	37.56	16.17
-2		(5.1 gU/cm ³)			81.2	35.57	7.45	38.18	16.28
-4					82.2	36.97	7.74	37.49	16.16
CS89-4	U ₃ Si	32.0	7.0	61.0	81.6	33.10	11.21	37.29	17.46
-5		(4.7 gU/cm ³)			79.1	29.90	10.13	39.07	17.66
-7					78.9	29.65	10.04	39.21	17.67
CS96-1	U ₃ Si	45.0	13.9	41.1	91.5	46.68	7.57	37.24	16.00
-3		(6.6 gU/cm ³)			92.1	47.46	7.70	36.93	15.95
-5					90.7	45.64	7.40	37.66	16.08

^aParentetical values are total U contained per unit volume of the fuel zone (= meat).

Table VII. DTA Data and Heats of Reaction for Fueled Samples

Sample No.	Fuel in Heat	Calculated ΔH_f for MD101 + 6061, J	Onset Temperature First Heating, °C	Endothermic			Exothermic			ΔH for Reaction, J/g of fuel	Mean, J/g of fuel	Sample Standard Deviation, J/g
				ΔH_1 First Heating, J	ΔH_2 Second Heating, J	ΔH_3 Third Heating, J	ΔH_1 (MD101 + 6061) - ΔH_1 , J	$\Delta H_3 - \Delta H_2$, J	$[\Delta H_1$ (MD101 + 6061) - ΔH_1] + $(\Delta H_3 - \Delta H_2)$, J			
CS105-4	32 vol.% U_3Si_2	17.72	595	9.75	15.84	15.98	7.97	0.14	8.11	336		
-5		17.81	600	11.10	14.43	14.91	6.71	0.48	7.19	313		
-8		17.67	585	7.78	16.17	16.04	9.89	-	9.89	398	349	±44
CS113-1	45 vol.% U_3Si_2	16.17	575	5.69	13.29	(a)	10.48	-	10.48	285		
-2		16.28	590	5.31	11.08	(a)	10.97	-	10.97	308		
-4		16.16	595	4.53	11.21	11.41	11.63	0.20	11.83	320	304	±18
CS 89-4	32 vol.% U_3Si	17.46	560	3.54	11.47	11.93	13.92	0.46	14.38	435		
-5		17.66	590	4.07	11.16	11.96	13.59	0.80	14.39	481		
-7		17.67	580	2.04	12.40	12.87	15.63	0.47	16.10	543	486	±54
CS 96-1	45 vol.% U_3Si	16.00	570	-0.77	7.15	7.47	16.77	0.32	17.09	366		
-3		15.95	605	-2.12	8.65	9.12	18.07	0.47	18.54	391		
-5		16.08	600	-0.66	9.38	9.94	16.74	0.56	17.30	379	379	±13

^aThird melting cycle not run.

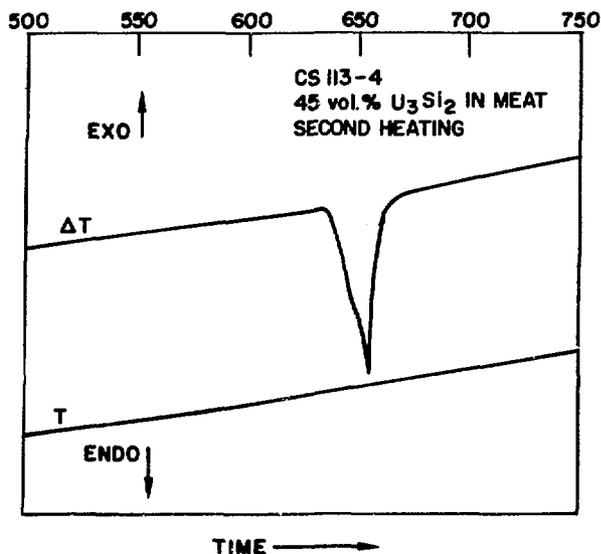


Fig. 11. Thermogram for Second Heating of the Same Specimen as Shown in Fig. 10.

1. Each sample was assumed to be exactly of the geometry shown in Fig. 2. Numerous measurements supported this. Each disc was assumed to contain in its "meat" the volume percents of fuel, MD101, and voids shown in Table VI. These numbers were derived from the known quantities of material used and immersion density measurements made on plates in each category.

2. Each pellet was weighed to the nearest 0.1 mg. The volume of the meat in each pellet was calculated as follows:

$$M_s = V_m \rho_m + V_c \rho_c \quad (13)$$

$$V_s = V_m + V_c \quad (14)$$

$$\text{Substituting for } V_c, \quad M_s = V_m \rho_m + (V_s - V_m) \rho_c \quad (15)$$

$$\text{Rearranging Eq. (15), } V_m \rho_m - V_m \rho_c = M_s - V_s \rho_c \quad (16)$$

$$\text{Simplifying Eq. (16), } V_m (\rho_m - \rho_c) = M_s - V_s \rho_c \quad (17)$$

$$\text{Solving for } V_m, \quad V_m = \frac{M_s - V_s \rho_c}{\rho_m - \rho_c} \quad (18)$$

In Eqs. (13) through (18), the following apply:

M_s = Mass of sample in grams,

V_s = Volume of sample in cubic centimeters (= 0.020568 cm³),

V_m = Volume of meat in sample in cubic centimeters,

V_c = Volume of clad in sample in cubic centimeters,

ρ_c = Density of 6061 clad (= 2.71 g/cm³), and

ρ_m = Density of meat in sample in grams per cubic centimeter.

Values for ρ_m were calculated using the volume percent (fractions) of fuel and MD101 shown in Table VI and the established densities of the meat components:

$$U_3Si_2 - 12.2 \text{ g/cm}^3,$$

$$U_3Si - 15.2 \text{ g/cm}^3, \text{ and}$$

$$MD101 - 2.70 \text{ g/cm}^3.$$

The ρ_m values for 32 and 45 vol.% U_3Si_2 in the meat are 5.58 and 6.64 g/cm³, respectively. For 32 and 45 vol.% U_3Si in the meat, the ρ_m values are 6.51 and 7.95 g/cm³, respectively.

Having established V_m , the masses of fuel, MD101, and 6061 were easily calculated by substituting the densities and volume fractions of each of the components into a simple conversion formula.

3. The heating thermograms for each of the three heating cycles were analyzed, and the net ΔH values for each were determined. The values are shown in Table VII.

4. A ΔH value was calculated for the mass of MD101 and 6061 in each pellet. For these calculations a ΔH_f value of 397 J/g was used for the MD101, and the experimentally determined value of 349 J/g was used for the ΔH_f of 6061.

5. The ΔH value measured for the first heating cycle (ΔH_1) was subtracted from the ΔH_f value for (MD101 + 6061). This became the ΔH value for the exothermic reaction between the silicide and the MD101 + 6061 during the first heating cycle and is shown in Table VII.

6. If no further reaction occurred, the thermograms for ΔH_2 and ΔH_3 should have been identical. That is, if the reaction was completed on the first heating, then subsequent thermograms would be a result of the ΔH of melting of the remaining aluminum species. However, with one exception (CS-105-8) there was a greater endothermic ΔH in heating cycle three than for the same sample in the second heating cycle. Therefore, the difference between ΔH_3 and ΔH_2 ($\Delta H_3 - \Delta H_2$, in Table VII) was ascribed to the completion of the reaction of the fuel with the aluminum. These (small) ΔH values were added to the value noted in Item 5 above and became the total ΔH for the fuel-aluminum reaction.

7. The total ΔH values described in Item 6 were divided by the grams of fuel present in each disc and became the enthalpy of reaction for the fuel. These values are shown in Table VII. Note that the values are recorded without a negative sign but are described as exothermic.

The arithmetic mean value for each set of samples is shown as is the sample standard deviation calculated for the three discs from each plate.

According to the phase equilibria work of A. E. Dwight,⁵ the reaction should place the composition of the reacted disc in the $U(Si,Al)_3 + Al$ field for all four conditions tested. Thus, the heat of reaction for each fuel type should be a constant and not depend on the volume percent of fuel present, at least within the limits studied in this work.

Nevertheless, for each fuel type the mean enthalpies of reaction are higher for the lower volume percent fuel. This might, for example, be the result of a change in reaction kinetics as the fuel-to-aluminum ratio is changed. If part of the reaction occurred at a very slow rate, DTA might not detect the heat released. If this was in fact the case, the true heats of reaction would be somewhat larger than the measured values. No analytical modeling has been performed on which to base such an extrapolation.

The column in Table VII identified as "Onset Temperature First Heating, °C" requires some amplification. As stated in Sec. IV, the conventions for treating DTA thermograms described in Ref. 4 were used for all calibrating pure metals as well as for 6061. The procedure requires drawing tangents to the ΔT line and the "V"-shaped curve resulting from the endothermic (on melting) ΔH of fusion. Because the melting of the 6061 and Al initiates and is superimposed on the reaction exotherm, it is very difficult to define accurately an "onset of reaction" temperature. It was not unusual to have thermograms of the type shown in Fig. 8, where the onset of the reaction caused a very slight but detectable exotherm which was immediately quenched by the endotherm of melting of the aluminum components of the specimen. However, other thermograms displayed no initial exotherm; instead, the "onset temperature" was that for an endothermic event. Therefore, the "Onset ..." temperatures recorded in Table VII represent the first event on heating identified by the tangent-construction technique and in effect identify the first departure from linearity for the ΔT plot.

It is clear that all detectable exothermic as well as endothermic events take place in the $\sim 570^\circ$ to $< 700^\circ C$ temperature regime.

VI. SOURCES OF UNCERTAINTY

A number of assumptions and calculations were made in determining the heats of reaction. Each assumption is a potential source of error in the final value. For example, the description of each fuel zone as being exactly of the volume percent of fuel and porosity indicated and being uniformly of the geometry shown in Fig. 2 cannot be proven; it is, nevertheless, a reasonable assumption.

Tests were run with pure Al samples at 5°C as well as 20°C per minute heating and cooling rates. In some cases the instrument amplification setting was changed. None of these experimental runs resulted in data different from those recorded in Table V. It is possible that the heats of reaction could have been different from those recorded here if other heating rates had been used for fueled samples. It is believed that if differences do exist as a function of heating rate, such differences would be small.

The variations in ΔH value from disc to disc for a given fuel and concentration and for different concentrations of fuel in the meat might be a function of fuel particle size. There was no way to define the effect of this variable in this study.

A. Instrumentation Calibration

As mentioned elsewhere in the text, the instrument calibration curve was checked frequently during the data collection period using Sb and pure Al as reference points covering the major temperature range of interest (650-660°C) for these fuels. The uncertainty in the instrument constant did not exceed $\pm 2\%$.

B. Temperature Calibration of Thermograms

Uncertainties in determining relative temperature readings for endotherms (and exotherms) using the Rigaku scale are estimated to be $\pm 0.5\%$. Absolute temperatures are measured by the instrument platinum-rhodium thermocouple and during this study were reproducible to $\pm 0.5\%$.

C. Measurement of Peak Areas

Measurement of peak areas was done by two methods: by the cut-and-weigh technique and by planimeter. The differences in the two methods was less than $\pm 1\%$. Reproducibility of a particular method was dependent upon which event was being evaluated or, basically, the size of the endotherm (or exotherm) area. Typically, the reproducibility of the "first event" was $\pm 2.5\%$. The second melt, usually being better defined than the first, was reproducible to $\pm 1\%$. Very small exotherms associated with some specimens (e.g., CS-89-7) were difficult to measure precisely but this area represented only a small fraction ($< 1\%$) of the total area determined for the calculations. The combined uncertainty in the calculations due to measurement of peak areas is estimated to be $\leq \pm 3\%$.

VII. COMPARISONS WITH THE LITERATURE

The only other DTA studies of the uranium silicide plus aluminum reactions were conducted by S. Nazaré.⁶ Nazaré's work was with samples similar to the ones used in this study as well as with pellets without clad which consisted of pressed powders of U_3Si or U_3Si_2 with an amount of Al powder to simulate a U loading of 4.0 gU/cm^3 . The tests were conducted in an "inert gas" with a heating rate of 5°C per minute up to a maximum temperature of $\sim 740^\circ\text{C}$. Most notably, Nazaré also found that the melting of the matrix plus clad did occur in the same temperature regime as the silicide plus aluminum reaction. On heating, he shows an "onset of exotherm" for plate discs at 620°C and a peak exotherm at 630°C to 635°C , followed immediately by an endotherm of larger magnitude, peaking at 650° to 660°C . No reaction of any type is indicated above 660°C .

Nazaré did not thermally cycle the samples in his DTA work, but he does state that the reaction was presumably not totally completed after one heating and cooling cycle. The scope of his studies did not include unfolding the ΔH for the fuel plus Al reaction from the data. Therefore, a quantitative comparison of his work and the studies recorded here is not possible. The data presented by Nazaré appear to be in consonance with the results of this study.

VIII. SUMMARY AND CONCLUSIONS

The heats of reaction between U_3Si or U_3Si_2 and an Al + 6061 matrix have been determined by quantitative differential thermal analysis. Using discs punched from 0.060 in. (1.52 mm) plates with a 0.020 in. (0.51 mm) thick fuel zone, the enthalpies at two concentrations of each silicide were determined.

The exothermic ΔH values unfolded from the experimental curves are:

<u>Meat</u>	<u>ΔH, J per gram of fuel</u>
32 vol.% U_3Si_2	349 ± 44
45 vol.% U_3Si_2	304 ± 18
32 vol.% U_3Si	486 ± 54
45 vol.% U_3Si	379 ± 13

On heating, the U_3Si + Al as well as the U_3Si_2 + Al reactions are initiated by the formation of some liquid. That is, no event was observed in the DTA plots until the solidus temperature of 6061 (582°C) was exceeded. In the temperature regime from 582°C to $\sim 660^\circ\text{C}$ the endothermic melting of 6061 and the MD101 Al is superimposed on the exothermic reaction between the fuel and the aluminum species. The net effect for fuel loadings up to $\sim 5 \text{ gU/cm}^3$ is always an endotherm. For samples at 45 vol.% U_3Si in the fuel zone ($\sim 6.6 \text{ gU per cm}^3$), the net effect for the first heating was a very slight exotherm.

For all specimens tested, a very slight reaction between the fuel particles and the aluminum occurred during a second heating cycle during which the reaction is completed; subsequent heating cycles up to as high as 1300°C demonstrated only the endothermic melting of the residual aluminum species.

The results of this study are in agreement with qualitative DTA studies conducted by one other independent investigator.⁶

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