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A DTA, TGA, AND METALLURGICAL STUDY OF THE EXOTHERMIC REACTIONS BETWEEN ALUMINUM AND URANIUM COMPOUNDS: THE SOLID STATE REACTIONS OF URANIUM OXIDES AND URANATES WITH ALUMINUM

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ABSTRACT

The exothermic reactions of the type A + BC → AC + B between aluminum and βUO_3, αU_3O_8, αNa_2UO_4, $Na_2U_2O_7$, $N_2U_7O_{24}$, and MUO_4 (where M = Mg, Ca, Sr, or Ba) were studied using the techniques of differential thermal analysis (DTA), thermogravimetric evolved gas analysis (TGA-EGA), x-ray diffractometry, optical microscopy, and electron microprobe analysis. Two types of exothermic reactions were observed: The first type is a solid-state reaction occurring at the interfaces between particles in the compacted powders, beginning at or near the temperature at which the uranium compound undergoes either a first- or second-order transition. Only U_3O_8, UO_3 and those uranates having pseudo-hexagonal layers of $[UO_2(O_{1.5})]^-$ groups undergo this first type of reaction. The second type of reaction is the reduction of the solid uranium compounds (all crystal structures) by liquid aluminum beginning at 800 to 900°C.

INTRODUCTION

The preparation and crystallographic properties of several alkali and alkaline-earth metal uranates have been described in the literature.[1-13] These studies have divided the uranates into roughly three crystal systems and have shown that one crystal system of uranates is related to the structure of αU_3O_8. However, no systematic study of the uranates has been reported, and only one thermal study[2] of pure $Na_2U_2O_7$ has been made. Also, no attempts have previously been made to determine thermal property differences among the three crystal systems of uranates, nor to determine the thermal relationships of the pseudo-hexagonal uranates to αU_3O_8. Because recent experience at the Savannah River Plant[14] revealed the pseudo-hexagonal uranates $Na_2U_2O_7$ and $Na_6U_7O_{24}$ will react exothermically in the solid state with aluminum, a systematic thermal study of the aluminothermic reactions of the three crystal classes of uranates and their relationships to αU_3O_8 and βUO_3 was begun at the Savannah River Laboratory.

EXPERIMENTAL

Preparation of Samples

The oxides (βUO_3[1] and αU_3O_8[1]) and the uranates [$Na_2U_2O_7$,[2] $Na_6U_7O_{24}$,[2] αNa_2UO_4,[2] and MUO_4 (where M = Mg,[3] Ca,[4] Sr,[4] or Ba[5])] were prepared by methods given in the literature. Samples were then prepared by blending a uranium compound with Type 101 aluminum powder on an equal weight ratio and compacting the blend to greater than 70% of theoretical density. For the differential thermal analysis (DTA) studies, the pellets were broken and 10 mg segments used as samples. Samples for x-ray, optical microscopy, and electron microprobe studies were unbroken pellets that had been heated on a thermal balance for extended periods of time near the reaction temperatures. A powder diffraction technique was used to identify the major products after samples had been ground. Samples for optical microscopy and electron microprobe studies were mounted as whole pellets and then polished by normal techniques.

Instrumental

Differential thermal analyses were carried out in both argon and 4% H_2-96% He atmospheres on a model DTA-202 (R. L. Stone Div., Tracor, Inc., Austin, Texas) system. Thermogravimetric evolved gas analyses (TGA-EGA) were carried out in both helium and 4% H_2-96% He atmospheres on a modified Model RH electrobalance (Cahn Instrument Co., Paramount, California) with the evolved gases fed to a Model MS-10 mass spectrograph (AEI Scientific Apparatus Corp., Elmhurst, Illinois). X-ray diffractometry was performed on a 2.5 kw x-ray generator and a vertical goniometer (North American Phillips Co., Inc., New York, New York). Microprobe analyses were made with a MAC 400 electron probe microanalyzer (Material Analysis Corporation, Palo Alto, California).

DISCUSSION AND INTERPRETATION OF RESULTS

Al-Uranium Oxide Reactions

A typical DTA curve for an Al-U_3O_8 compact is shown in Figure 1. The thermal reactions were easily explained by referring to previously published results. The first two endotherms were the result of transitions of impurities in the αU_3O_8. In agreement with Notz, et al.,[15] the first endotherm is the result of the nonreversible transition of the impurity βU_3O_8 to αU_3O_8. Using both DTA and a hot stage x-ray diffractometer, Notz[15] was able to show that orthorhombic αU_3O_8 undergoes a second-order transition (no detectable heat of transition) to hexagonal U_3O_8. The transition was complete at 250°C. The second endotherm was shown to be attributable to the impurity uranyl nitrate.

The exothermic reaction beginning at about 600°C was studied by Fleming and Johnson.[16] By varying the aluminum to U_3O_8 ratio and the static heating time at 600°C, they were able to show by x-ray diffraction that the products were UO_2 and Al_2O_3. They attributed these products to the following reaction:

$$3U_3O_8(s) + 4Al(s) = 2Al_2O_3(s) + 9UO_2(s) \qquad (1)$$

Handwerk, et al.[17] found the reaction to be incomplete and postulated the formation of an aluminum oxide barrier around the reacting U_3O_8 particles. Other published data[18],[19] suggest that UAl_4 is also formed in this reaction. However, we found x-ray diffraction evidence for UO_2 but not for UAl_4 (which is difficult to detect). These reactions were quenched when the aluminum melted at 660°C, as shown by the endothermic peak.

Fleming and Johnson[16] have also studied the rather spectacular complete reduction of U_3O_8 by liquid aluminum. As shown in Figure 1, this exothermic reaction begins at about 950°C. Again by varying the aluminum to U_3O_8 ratio, Fleming and Johnson[16] were able to show the following reactions occurred in addition to Reaction 1 above:

$$3U_3O_8(s) + 16Al(\ell) = 8Al_2O_3(s) + 9U(\ell) \qquad (2)$$

$$3U_3O_8(s) + 34Al(\ell) = 8Al_2O_3(s) + 9UAl_2(\ell) \qquad (3)$$

$$3U_3O_8(s) + 43Al(\ell) = 8Al_2O_3(s) + 9UAl_3(\ell) \qquad (4)$$

$$3U_3O_8(s) + 52Al(\ell) = 8Al_2O_3(s) + 9UAl_4(\ell) \qquad (5)$$

Using pellets containing 50 wt % Al, Reaction 5 is the predominant reaction.

A typical DTA curve for an Al-βUO_3 compact is shown in Figure 2. This system has not been previously reported in the literature. TGA-EGA showed the first two nonreversible endotherms were caused by loss of water. As UO_3 does react with water at room temperature to form $UO_2(OH)_2 \cdot H_2O$, the first endotherm at about 100°C is postulated to be the dehydration of $UO_2(OH)_2 \cdot H_2O$ to $UO_2(OH)_2$. The second endotherm at about 280°C is postulated to be the dehydroxylation of $UO_2(OH)_2$ to UO_3. At about 400°C, UO_3 begins to lose oxygen via the reaction:

$$3UO_3(s) = \alpha U_3O_8(s) + 1/2\ O_2(g) \qquad (6)$$

to completion (Figure 3, Curve C). However, when the reacted pellet was ground and recompacted before obtaining a differential thermogram, additional exothermic reaction occurred. X-ray diffraction of the ground pellets showed the major constituents to be the starting materials: aluminum and $Na_2U_2O_7$. From this, we concluded that the reaction was a surface reaction only. For verification, the profiles of aluminum and uranium concentrations were obtained with the electron microprobe. The profiles were obtained by starting the scan in an aluminum grain, traversing the particle interface, through a $Na_2U_2O_7$ particle, across the opposite interface, and into a second aluminum grain. Figure 5 shows these scans. In the unreacted pellet, the concentration profile shows very sharp boundaries between aluminum and uranium. In the reacted pellets, however, there is a layer containing both aluminum and uranium at the interface. Although verifying experiments were not made, the solid state reduction of the uranium oxides is assumed to occur at the particle interfaces since the reactions as well as x-ray data are similar.

The low temperature exothermic reactions between aluminum and uranates were also studied as a function of method of preparation, for as the preparation varies, the concentration of the major impurity $Na_6U_7O_{24}$ also varies. No attempt was made to quantify the $Na_6U_7O_{24}$ content other than by measuring the relative intensities of the x-ray lines and changes observed in thermal analysis data. The DTA curves for compacts of $Na_2U_2O_7$

prepared by three different methods are shown in Figure 6. For Product B, the intensity ratio of x-ray lines for $Na_6U_7O_{24}$ with respect to $Na_2U_2O_7$ was about 1/10. The DTA curve shows two distinct peaks for the low temperature exotherm at about 225°C; the first peak is attributed to $Na_6U_7O_{24}$, and the second peak is attributed to $Na_2U_2O_7$. For Product A, the intensity of x-ray lines for $Na_6U_7O_{24}$ increased to about 1/5 of the intensity of the $Na_2U_2O_7$ lines, and the DTA curve shows one rather sharp peak. For Product C, x-ray lines for $Na_6U_7O_{24}$ could not be detected, and the DTA curve shows a single broad peak for the low temperature exotherm. From the DTA curves, it is concluded that $Na_6U_7O_{24}$ undergoes essentially the same low temperature exothermic reactions with aluminum as does $Na_2U_2O_7$, with probable formation of αU_3O_8 (Reaction 9).

The second exothermic reaction between $Na_2U_2O_7$ and aluminum begins at approximately 600°C (Figure 3, Curve B). This reaction is very similar to the U_3O_8-Al reaction, and the partial reduction of uranium is quenched when the aluminum melts (endotherm at 660°C). The third exothermic reaction is the complete reduction of the uranium compounds to the U-Al alloy. The following set of reactions is proposed to account for the three exotherms observed with Al-$Na_2U_2O_7$ compacts:

The U_3O_8 that is formed begins to react with aluminum via Reaction 1 above. These reactions were quenched when the aluminum melted at 660°C as shown by the endothermic peak. The exothermic peak starting at about 900°C then was the result of Reactions 2 through 5 above.

Al-Uranate Reactions

Typical DTA curves for $Na_2U_2O_7$, $Na_2U_2O_7$-Al compacts, and reaction residues are shown in Figure 3.

No thermal events were noted for $Na_2U_2O_7$ (Curve A). However, when heated in the high temperature x-ray diffraction camera,[2] $Na_2U_2O_7$ exhibited second-order, reversible, phase changes at 365 and 1075°C; these were observed through small changes in x-ray patterns. In complete agreement with Cordfunke and Loopstra,[2] DTA and TGA experiments showed that $Na_2U_2O_7$ was thermally stable to at least 1200°C.

When $Na_2U_2O_7$ was compacted with aluminum powder, three exothermic reactions were observed (Curve B). The first reaction began at about 225°C. X-ray diffraction and electron-probe analysis of compacts (which had been held at 360°C for about 16 hours) showed this solid state reaction occurred only at the particle interfaces. Typical microstructures of unreacted and reacted pellets are shown in Figure 4. The unreacted pellet contained large round grains of silvery aluminum and orange $Na_2U_2O_7$. The reacted pellet contained silvery grains and black particles with very irregular edges. When the reacted pellet was broken and a differential thermogram run, the reaction went

$$9Na_2U_2O_7(s) + 4Al(s) \xrightarrow{\sim 250°C} 9Na_2O(s) + 2Al_2O_3(s) + 6\alpha\text{-}U_3O_8(s) \qquad (9)$$

$$3\alpha U_3O_8(s) + 4Al(s) \xrightarrow{\sim 600\text{-}640°C} 2Al_2O_3(s) + 9UO_2(s) \qquad (10)$$

$$Na_2U_2O_7(s) + 4Al\ (\ell) \xrightarrow{>900°C} Na_2O(s) + 2Al_2O_3(s) + 2U\ (\ell) \qquad (11)$$

$$Na_2U_2O_7(s) + 8Al\ (\ell) \xrightarrow{>900°C} Na_2O(s) + 2Al_2O_3(s) + 2UAl_2(\ell) \qquad (12)$$

$$Na_2U_2O_7(s) + 10Al\ (\ell) \xrightarrow{>900°C} Na_2O(s) + 2Al_2O_3(s) + 2UAl_3(\ell) \qquad (13)$$

$$Na_2U_2O_7(s) + 12Al\ (\ell) \xrightarrow{>900°C} Na_2O(s) + 2Al_2O_3(s) + 2UAl_4(\ell) \qquad (14)$$

The uranates $Na_2U_2O_7$,[2] $Na_6U_7O_{24}$,[2] $CaUO_4$,[4] and $SrUO_4$[4] have a structure consisting of pseudo-hexagonal layers of $[UO_2(O_{1.5})]^-$ groups. With a similar structure, it is not surprising that prepared samples of $CaUO_4$ and $SrUO_4$ also underwent low temperature, solid state, exothermic reactions with aluminum similar to those of $Na_2U_2O_7$. However, those uranates which have a completely different crystal structure do not undergo solid state reactions with aluminum. For example, αNa_2UO_4 and $MgUO_4$ crystallize in the orthorhombic system possessing infinite $UO_2(O_2)^{2-}$ chains, whereas $BaUO_4$ has pseudo-tetragonal layers of $UO_2(O_2)^{2-}$. Neither of the latter three uranates reacted with aluminum below about 800°C.

Above 800°C, all three crystal systems of uranates did react with aluminum to yield a U-Al alloy. The alloy formed depended only on the uranium to aluminum ratio present.

Summary of Reactions of Aluminum with Uranium Oxides and with Uranates

UO_3 and U_3O_8 undergo solid-state reactions with aluminum between 630 and 660°C. These reduction reactions are slow, occurring only at the particle interfaces of the compacted powders, and are quenched by the melting of aluminum at 660°C. The reduction of uranium oxides by liquid aluminum then begins at about 900°C.

The uranates $Na_2U_2O_7$, $Na_6U_7U_{24}$, $CaUO_4$, and $SrUO_4$ (pseudo-hexagonal crystal structure) react with aluminum in the solid state; αNa_2UO_4 and $MgBaUO_4$ (orthorhombic crystal system) and $BaUO_4$ (pseudo-tetragonal crystal system) do not react with aluminum in the solid state. The solid-state reductions of uranates also occur only at the particle interfaces of the compacted powders, and are quenched by the melting of aluminum at 660°C. The further reduction of uranates by liquid aluminum begins at about 800°C.

Each of the above solid-state reductions begins near the temperature at which the uranium compound is undergoing a phase transformation.

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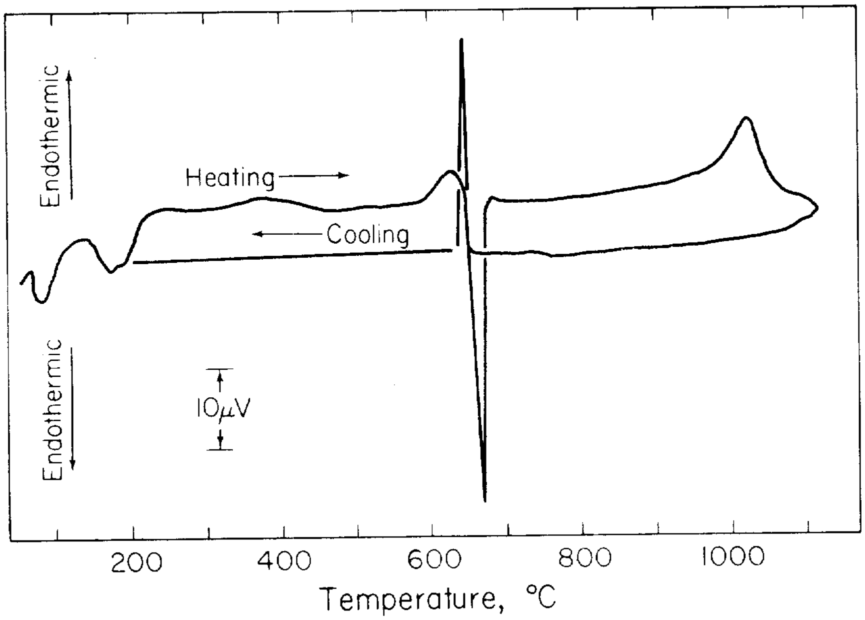


FIG. 1 DTA Curves for an Al-U_3O_8 Compact

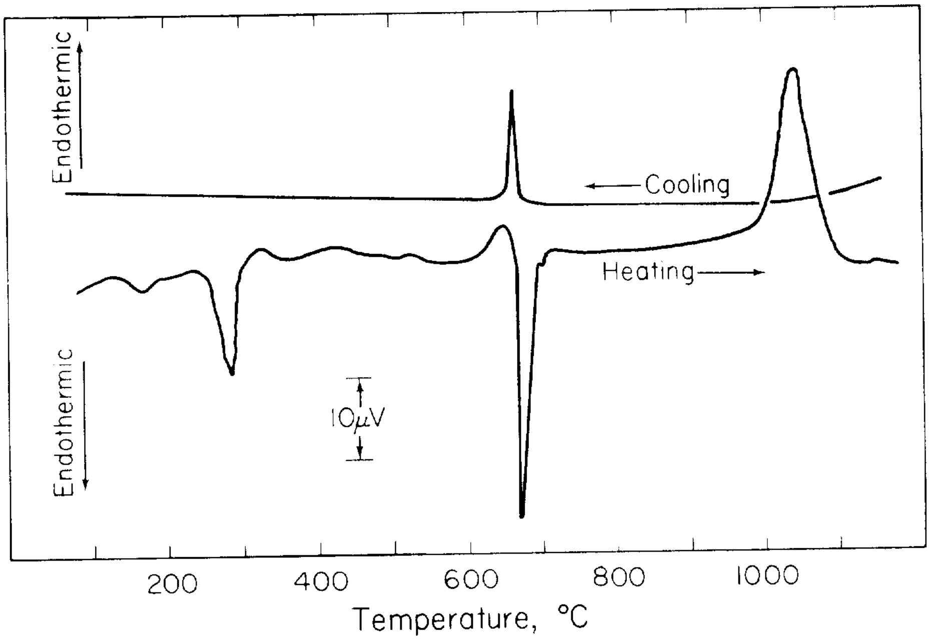


FIG. 2 DTA Curves for an Al-UO_3 Compact

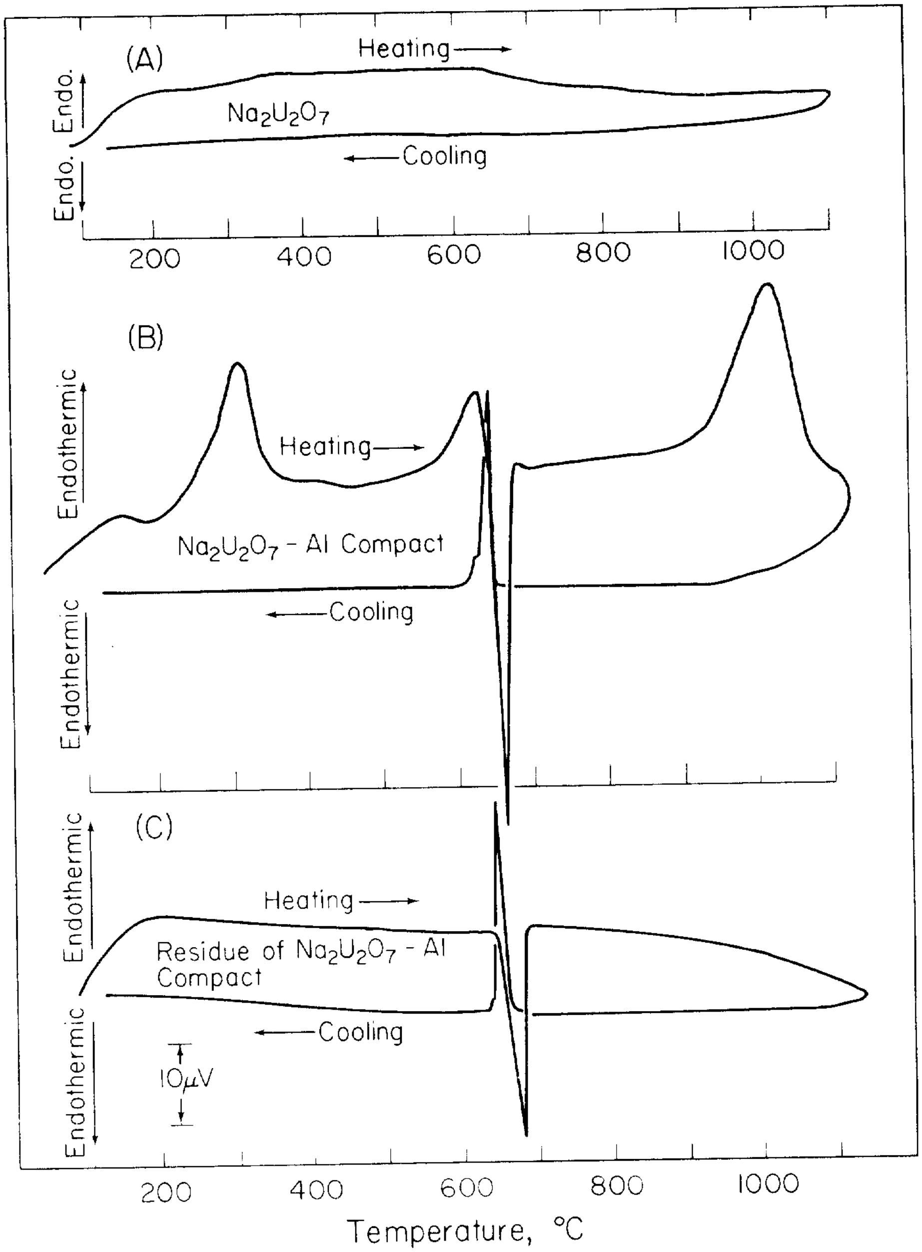
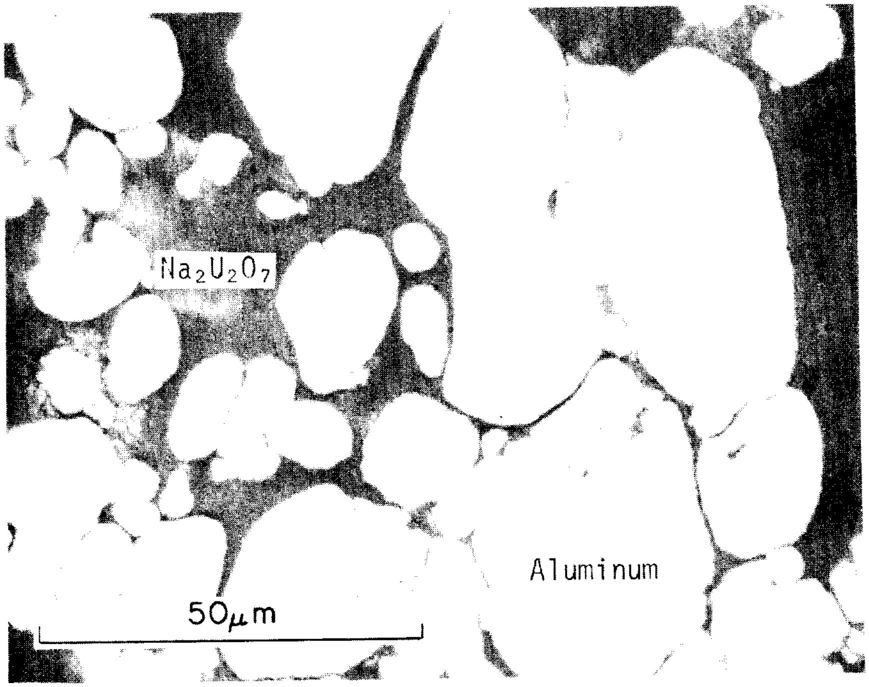
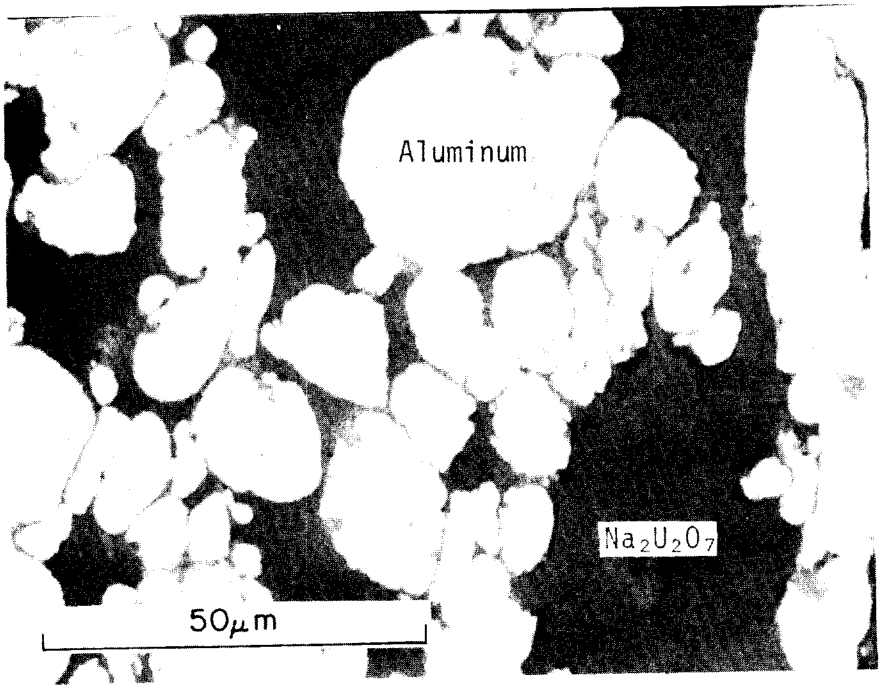


FIG. 3 DTA Curves for $Na_2U_2O_7$, $Na_2U_2O_7$-Al Compact, and Reaction Residue



a. Unreacted (as-pressed)



b. Reacted (heated 16 hr at 360°C)

FIG. 4 Microstructures of Al-$Na_2U_2O_7$ Pellets

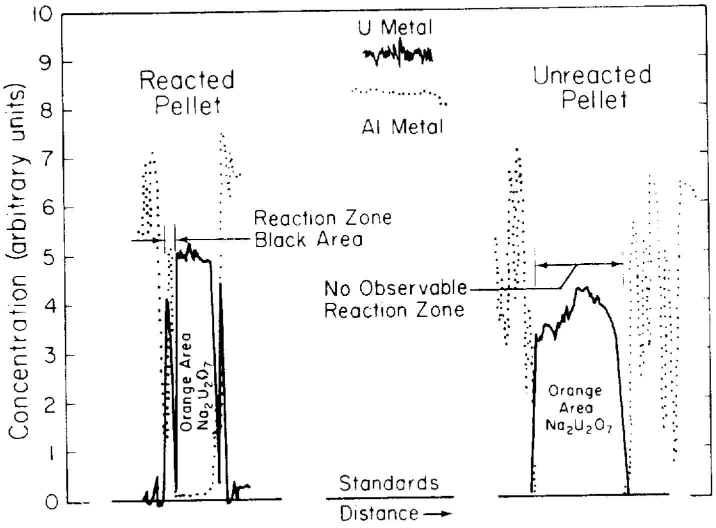


FIG. 5 Electron Microprobe Scan of Al-$Na_2U_2O_7$ Pellets Showing Interfacial Reaction Zone

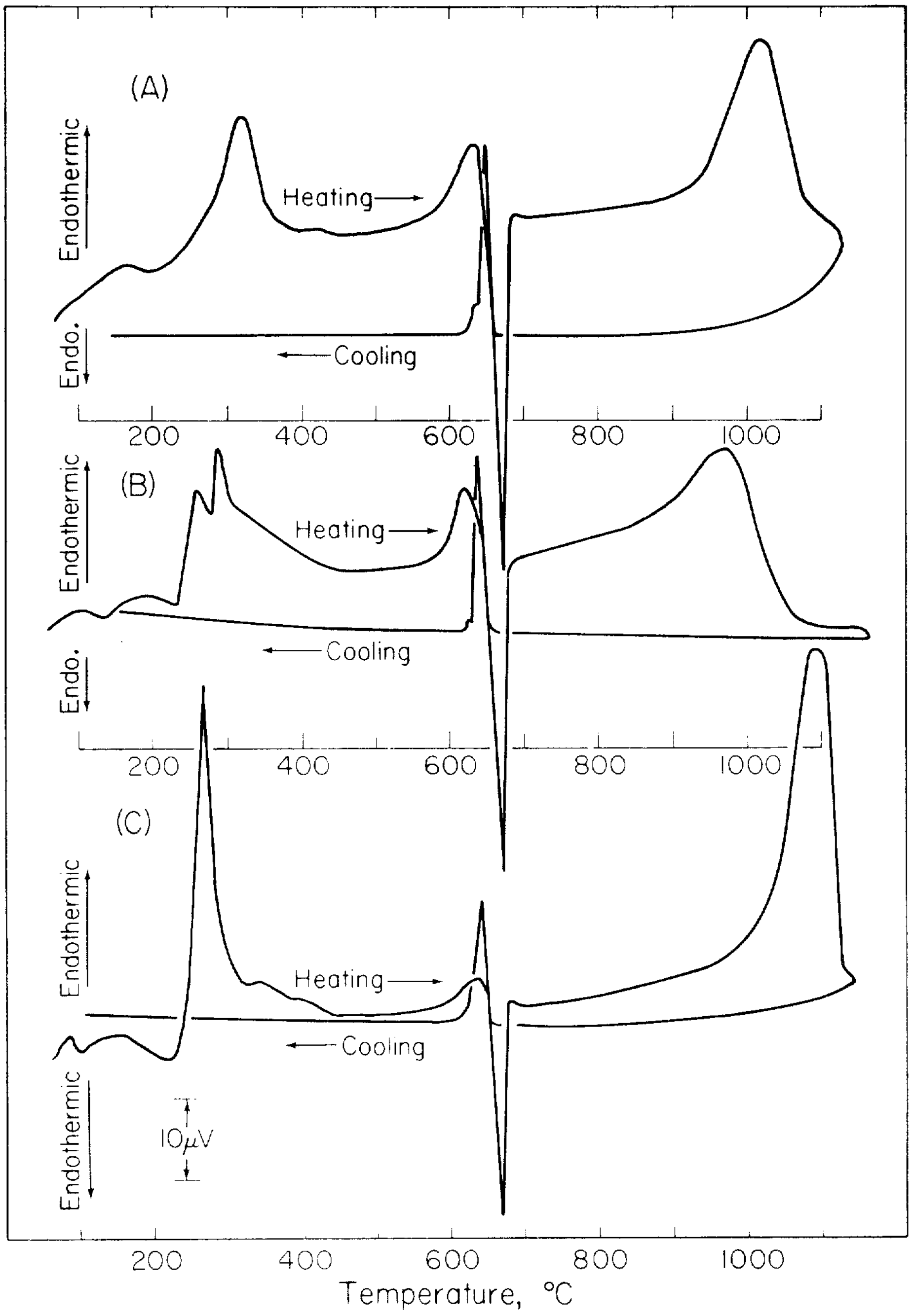


FIG. 6 DTA Curves of Mixtures of $Na_2U_2O_7$ - $Na_6U_7O_{24}$ - Al in Pressed Compacts