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REACTIONS DURING THE PROCESSING OF U_3O_8-Al CERMET FUELS

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ABSTRACT:

The cermet fuel (U_3O_8 dispersed in Al) being considered for use in the Savannah River Site reactors is thermodynamically unstable due to the potential for a metallothermic reduction reaction. The exothermic reaction between U_3O_8 and Al produces approximately 225 calories of heat for every gram of oxide consumed. During processing of the U_3O_8-Al cermet fuels by Powder Metallurgy (P/M) techniques, a significant portion of the U_3O_8 is reduced to U_4O_9. The reaction between U_4O_9 and Al is also exothermic, however, the maximum heat released by the reaction is approximately 80 calories per gram of oxide reacted. Metallothermic reduction reactions for U_3O_8 /U_4O_9 /Al mixtures do not occur at the normal reactor operating temperature (~100 °C) or at temperatures below the melting point of aluminum (660 °C).

This report describes work performed to quantify the extent of reaction during P/M processing of the U_3O_8-Al cermet fuel, and to determine the effect of reduction to U_4O_9 on the metallothermic reduction reaction.

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REACTIONS DURING THE PROCESSING OF U_3O_8-Al CERMET FUELS

INTRODUCTION:

The ^{236}U concentration in the enriched uranium stockpile at the Savannah River Site (SRS) has slowly increased over the years of operation. To combat this buildup, blending the high ^{236}U material with other sources has been the standard practice. Eventually it will not be feasible or practical to blend high ^{236}U fuel with uranium from alternate sources. In this case, the uranium loading of the fuel tubes will need to be increased in order to obtain adequate performance from the high ^{236}U fuel.

Currently SRS reactor fuel tubes are made by coextruding an aluminum clad billet containing a U-Al alloy core. Maximum uranium loadings for this process are around 30 weight percent. Above 30% uranium loading, the fabrication process becomes increasingly difficult and less efficient. The Savannah River Laboratory has evaluated, tested, and proven powder metallurgy (P/M) as an alternate method for the production of fuel tubes containing up to approximately a 60 weight percent uranium loading.

The alternate fuel tube manufacturing process utilizes a compacted uranium oxide (as U_3O_8)-aluminum blend as a core material. The fuel tubes produced by the powder metallurgy process are often called cermet (**CER**amic-**MET**al) fuels. The manufacturing process for the cermet fuels consists of blending the U_3O_8 powder with a commercially available Al powder, isostatically compacting the powder mixture to form a cylindrical billet core, assembling the core into an aluminum billet, degassing the billet assembly, and coextruding to produce a thin-walled fuel tube.

It is well known that any oxide mixed with aluminum represents a potential thermodynamically unstable situation, which under very specific conditions can undergo an exothermic metallothermic oxidation-reduction reaction. The classical example of a metallothermic oxidation-reduction reaction is the "Thermite" reaction.[1] Unlike the U_3O_8-Al reaction, the classical "Thermite" reaction (iron oxide and aluminum) can ignite at temperatures significantly below the melting point of Al. Uranium oxide-aluminum mixtures exhibit reaction at temperatures well above the melting point of aluminum (660 °C). The cermet fuels are operated at temperatures well below the melting point of aluminum. Therefore, the thermodynamic instability of the cermet fuels is not a matter of concern for normal operation of the Low Temperature Heavy Water Reactors (LTHWR) at the Savannah River Site. The concern is with the potential for a metallothermic reaction in the event of a thermal excursion accompanying a reactor accident.

Cermet fuel is exposed to several high temperature, reduced atmosphere environments during its processing at the Savannah River Site.[2] These environments result in a partial reaction of the U_3O_8 and aluminum to yield sub-stoichiometric U_3O_8 and U_4O_9. This reduction lowers the energy liberated during an exothermic metallothermic reduction.[3] This report describes work conducted to quantify the extent of the processing reaction and to determine its effect on the metallothermic reduction reaction.

SUMMARY:

A significant solid-state reduction reaction occurs during the processing of U_3O_8-Al fuels by the Powder Metallurgy process. Current processing methods[2] yield extruded fuel tubes having a composition of approximately equal quantities of U_3O_8 and U_4O_9 in an aluminum matrix. Varying temperature, time, and pressure conditions were studied and results indicate that complete reduction of the U_3O_8 to U_4O_9 is possible with only slight modifications to the existing powder metallurgy flowsheet.

The reduction to U_4O_9 has a significant impact on the thermochemistry of the fuel mixture. Reduction of U_3O_8 to UO_2 by Al in a manner analogous to the classical "Thermite" reaction yields 225 calories of heat (theoretical) for every gram of oxide consumed. Similar reactions for U_4O_9 yield only 80 calories of heat for every gram of U_4O_9 reacted.

Mixtures of U_4O_9 and Al undergo metallothermic reduction at temperatures in the vicinity of 900 °C. Conversely, mixtures of U_3O_8 and Al do not react until temperatures of about 1150 °C are reached. The reaction onset temperatures for all mixtures of U_3O_8, U_4O_9, and Al examined in this work are well above the normal reactor operating temperature of approximately 100 °C and the melting point of aluminum (660 °C). Simple reduction to U_4O_9 does not decrease the reaction onset temperature to below Al-melting.

Solid-state reactions are diffusion controlled, and the rate depends on the diffusing species in the solids. Melting of the aluminum cladding and core matrix is required for a rapid reaction to occur in the cermet fuel proposed by the Savannah River Laboratory. Furthermore, reactions occurring during the Powder Metallurgy processing may effectively prevent metallothermic reduction by providing a reaction product (Al_2O_3, possible U-O-Al compounds, etc...) diffusion barrier between the core oxide particle and the aluminum matrix.

BACKGROUND:

Cermet fuels produced by powder metallurgy have been under development at the Savannah River Plant for the past 20 years. Cermet nuclear fuels and targets have also been used in a number of research and test reactors throughout the United States Department of Energy (DOE) complex, as well as in the international community. Currently, cermet fuels are used in the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory (ORNL) and in the High Flux Breeder Reactor (HFBR) at the Brookhaven National Laboratory (BNL). A great deal of attention was focused on cermet fuels during the Reduced Enrichment for Research and Test Reactors (RERTR) program in the 1970's. Faced with a decreasing supply of highly enriched uranium, alternate fuel forms needed to be developed. Along with various mixed oxide fuels, U_3O_8-Al mixtures were considered. By mixing U_3O_8 and aluminum powders together and processing by powder metallurgy techniques, higher uranium loadings are achievable. The maximum uranium loading achievable using powder metallurgy processing is estimated at 60-70 weight percent uranium. The conventional alloy casting process becomes inefficient above 30-35 percent uranium compositions. The ability to use higher uranium loadings makes it possible to employ low enriched fuels containing high ^{236}U fuels without compromising reactor performance.

A great deal of work was performed on U_3O_8-Al fuel mixtures before any test irradiations were conducted. The potential incompatibility of the U_3O_8 fuel particles with the aluminum matrix has been thoroughly examined by a number of researchers.[4-14] Reactions occurring between U_3O_8 and aluminum are diffusion controlled at temperatures below the melting point of aluminum (660 °C).[4] As the solid-state reaction proceeds, a product layer forms at the reactant interface. For U_3O_8-Al reactions, this reaction layer consists of Al_2O_3, U_4O_9, other sub-oxides of uranium, and possibly U-Al and U-O-Al compounds. As the reaction proceeds, this reaction layer grows, effectively inhibiting further reaction by increasing the diffusion distance.

The overall kinetics of the U_3O_8-Al reaction are controlled by a number of variables including temperature, heating rate, oxide thermal history, and oxide morphological characteristics. Reaction kinetics increase with decreasing oxide particle size.[4] This occurs due to the fact that smaller particles possess more surface area per unit weight. Surface area is related to particle size for spherical particles by the equation:

$$S = 6/pd \qquad (1)$$

Where: S = specific surface area (m^2/g)
d = particle diameter (m)
p = density (g/cm^3).

This increase in surface area increases the amount of contact with the aluminum matrix thereby increasing the available interface for reaction. Slower reactions occur for oxide fired at 800 °C rather than 1400 °C.[4] The increased reactivity of the low fired oxide may be attributed to its higher specific surface area. Figure 1 shows the amount of U_3O_8 reduced to U_4O_9 or UO_2 as a function of heating time at 600 °C as measured by quantitative metallography. The results shown in Figure 1 indicate significant reduction occurs for all oxides examined at times greater than 20 hours.

Numerous workers have examined the exothermic reactions which occur above the melting point of aluminum.[6-12] Fleming and Johnson[11] and Ondracek and Patrassi[12] report that the reaction occurs in two distinct steps. Both Fleming and Ondracek report the initial step as reduction to UO_2 followed by further reductions to U-Al solid solutions (Fleming) or UAl_x compounds (Ondracek). The first step in this reaction is the most energetic. The reaction thermochemistry is discussed in detail in the next section of this report.

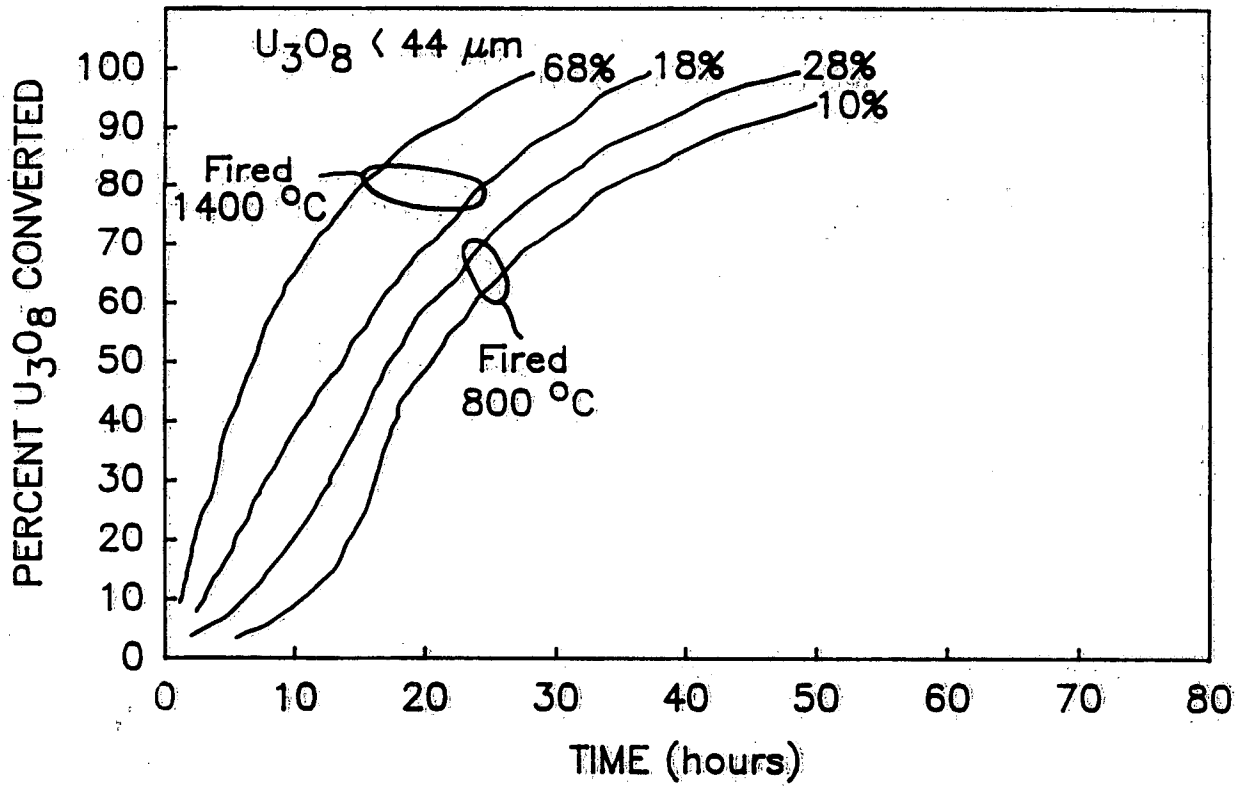


Figure 1 - Effect of time, temperature, oxide morphology, and oxide thermal history on U_3O_8-Al reactions (after reference 4).

During powder metallurgy processing, solid-state reactions occur that lower the maximum credible energy released in the event of metallothermic reduction reaction ignition. The primary focus of the work presented in this report is quantification of the reactions that occur during processing, and evaluation of the impact of these reactions on potential "Thermite-type" reactions.

REACTION THERMOCHEMISTRY:

Metallothermic Reduction Reactions:

The metallothermic reduction of uranium oxide by aluminum is described as a two step process. The process involves reduction of the higher oxide to UO_2, followed by further reduction to a uranium-aluminum alloy. The first step in the reduction process is more energetic than the second.

The initial step in the reduction of U_3O_8 by Al is shown below:

$$U_3O_8 + (4/3)\ Al \text{ ----> } 3\ UO_2 + (2/3)\ Al_2O_3 \qquad (2)$$

This reaction is exothermic and yields 225 calories of heat for every gram of U_3O_8 reacted. This reaction is much less energetic than the actual thermite reaction (iron oxide reduced to iron metal) which yields over 1200 calories of heat per gram of iron oxide reacted. The amount of heat generated during the metallothermic reduction of U_3O_8 is also insignificant when compared to the heat generated during normal reactor operation or radioactive decay.[15]

Current processing procedures for the oxide fuel tubes make it important to consider other uranium oxide species in addition to U_3O_8. Billets are degassed prior to extrusion to remove trapped gases. The solid state reaction between U_3O_8 and aluminum that occurs during billet outgassing is illustrated below:

$$(7/3)\ U_3O_8 + (19/9)\ Al \text{ ----> } U_4O_9 + U_3O_8 + Al + (5/9)\ Al_2O_3 \qquad (3)$$

During this processing step, a conversion to U_4O_9 occurs. This conversion may result in a particle configuration where a U_4O_9/Al_2O_3 reaction layer exists around a U_3O_8 particle. For this scenario, the reaction thermochemistry is markedly different.

In light of this transformation, it is necessary to examine the reaction occurring between the U_4O_9 outer layer and the aluminum matrix. This reaction is shown below:

$$U_4O_9 + (2/3)\ Al \text{ ----> } 4\ UO_2 + (1/3)\ Al_2O_3 \qquad (4)$$

Thermodynamically, this reaction may proceed as written (due to the negative free energy change), however it is less likely to occur due to the fact that the reaction free energy (90 kcal/mole) is less than that determined for U_3O_8-Al reaction (190 kcal/mole). The U_4O_9-Al reaction also yields much less heat (approximately 80 calories per gram of compound) than the similar reaction for U_3O_8 (225 calories per gram). This analysis indicates that the consideration of the U_4O_9 phase has a significant impact on the thermodynamics of the U-O-Al system.

It is important to note that the thermodynamic potentials in no way reflect the kinetics of the reactions. Although the chemical thermodynamics indicate that a reaction could take place because of the energy balance, many other factors contribute to the occurrence or rate of a reaction. For instance, the presence of "other" phases in a system may prevent a reaction from proceeding. Phases, such as the U_4O_9 coating on U_3O_8, may provide barriers which inhibit the propagation of thermodynamically possible reactions.

Adiabatic Temperature Calculations:

Adiabatic temperature calculations may be used to predict the maximum temperature resulting from a complete or an incomplete combustion reaction. There are two basic assumptions for making these calculations. They are:

1. The enthalpy of the reactants at the initial temperature, T_o equals the enthalpy of the products at the adiabatic temperature, T_{ad}, and

2. The system is thermally isolated.

The second assumption is especially important since it implies that none of the heat generated by the reaction is allowed to escape to the surrounding medium.

The general incomplete combustion reaction between U_3O_8 and aluminum is shown below:

$$U_3O_8 + (4/3 + x)\,Al \text{ ----> } 3\,UO_2 + (2/3)\,Al_2O_3 + x\,Al \qquad (5)$$

Based upon this reaction, the adiabatic temperature associated with the reduction reaction may be calculated from the following equation:

$$dH_R^\circ = \{(2/3)C_p(Al_2O_3) + 3C_p(UO_2) + x\,C_p(Al)\}dT \qquad (6)$$

Using the calculated heat of the reaction (dH_R°) at standard temperature and pressure, the adiabatic temperature rise for the reaction may be determined by integrating the specific heats of the products (C_p) using the initial and adiabatic temperatures as limits.

For an initial temperature of 373 °K (100 °C), the adiabatic temperature equals the melting point of aluminum at an oxide loading of 44 %. This oxide loading is near the current specified loading of the fuel core. However, when the fuel cladding is considered, the fuel rod assembly actually contains only 14 weight percent U_3O_8. Using this value, the calculations show that an initial temperature of over 500 °C is necessary for the adiabatic temperature to approach the melting point of aluminum. This temperature is much higher than any encountered during normal reactor operation, and suggests spontaneous ignition of the U_3O_8-Al metallothermic reduction reaction is unlikely during normal reactor operation or during significant temperature excursions.

It should be noted that the system is not thermally isolated during normal operation. Heat is removed from the system by the reactor core cooling system. Consideration of this heat removal makes it even more unlikely that any thermal energy produced by a local reaction of U_3O_8 and Al will result in reaction propagation.

EXPERIMENTAL PROCEDURE:

The purpose of this work was to quantify the extent of reaction during the processing of U_3O_8-Al cermet fuels by powder metallurgy. Secondary to examination of processing reactions, the effect of processing reactions on the metallothermic reduction reaction was investigated. In order to determine the extent of a processing reaction, a two-fold experimental program was performed. This program consisted of samples extracted from a depleted uranium oxide (DU_3O_8)-Al mixture during various stages of the actual powder metallurgy process. Analysis was also performed on samples cut from a compacted fuel core (before any processing) that were subjected to varied time, temperature, and pressure conditions. The feed powders and samples analyzed are described below.

Feed Powder Specifications:

The cermet fuels manufactured by the Savannah River Laboratory consist of U_3O_8 particles dispersed in an aluminum matrix. Typically, the U_3O_8 is produced by denitration of uranyl nitrate solutions. This thermal denitration produces UO_3 which is roasted at approximately 800 °C to yield nearly stoichiometric U_3O_8. The product U_3O_8 has an irregular morphology as illustrated in Figure 2a. The physical and chemical properties of the U_3O_8 produced by denitration of uranyl nitrate are summarized in Table I.

The aluminum powder used is Type 101 aluminum manufactured by the Aluminum Company of America.* The morphology of this powder is shown in Figure 2b. The average particle size of the 101 powder is approximately 20 microns. The physical and chemical characteristics of Type 101 aluminum are summarized in Table II.

Powder Metallurgy Process:

Figure 3 shows a generalized flowsheet of the Savannah River Laboratory powder metallurgy process. As indicated in Figure 3, four samples were extracted from this flowsheet at various stages of processing. Samples were removed from the as-mixed powder, and from the process after isostatic compaction, vacuum degassing, and extrusion and testing. The extracted samples were retained in sealed bags until analysis was performed.

Ampule Samples:

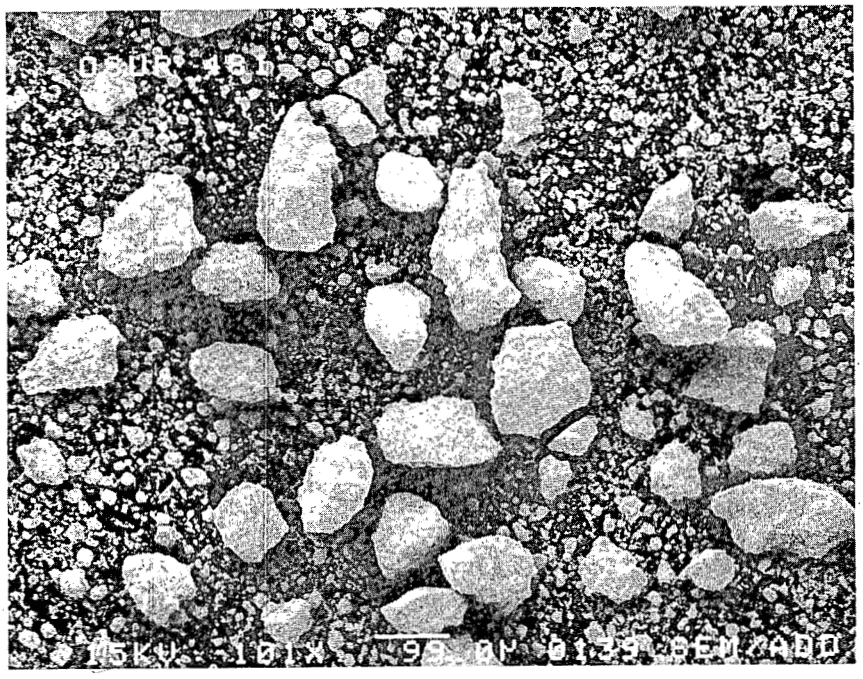
In order to determine more precisely the conditions where reaction occurs during vacuum degassing, a series of samples were exposed to various time, temperature, and pressure conditions. The vacuum degassing step requires that the billet be held at elevated temperatures at reduced pressures for significant periods of time. It has been postulated that the majority of the reduction reaction that occurs during processing occurs during the vacuum degassing step.[3]

The samples analyzed were extracted directly from an isostatically compacted billet core fabricated from the same powder blend that was used for the actual processed samples. The samples were exposed to temperatures ranging from 425 to 625 °C, at pressures ranging from 10^{-7} Torr to atmospheric (760 Torr) for times ranging from 2 to 96 hours. The environments were produced by encapsulating the U_3O_8-Al samples in fused quartz ampules, evacuating the ampule assembly to the desired pressure, and sealing the open end of the tube. Pressures were measured at the precise moment of ampule closure using an ionization gauge located near the open end of the ampule. This process is schematically illustrated in Figure 4.

Product Analysis:

The processed samples were analyzed by a variety of techniques. The phase assemblage of

*Aluminum Company of America, Pittsburgh, Pennsylvania.



a. U_3O_8 produced by thermal denitration of uranyl nitrate.

b. Alcoa Type 101 aluminum powder.

Figure 2 - Scanning electron micrographs (SEM) of constituent powders.

Table I

Properties of Typical Feed U_3O_8.

Physical Properties:

Density	
Apparent	2.0 g/cc
Tapped	4.0 g/cc
Average Particle Size	74-107 microns
Specific Surface Area	0.18-0.46 m^2/g

Screen Analysis

Mesh	Typical Range
+100	0-Trace
-100+200	25-50
-200+325	25-50
-325	10-40

Typical Chemical Analysis:

Compound	Typical
U_3O_8	99%
N	1000 ppm
Fe	73 ppm
P	100 ppm
W	100 ppm
Al	2 ppm
Cr	20 ppm
Other Metals, each	10 ppm

Table II

Properties of Type 101 Aluminum Powder.

Physical Properties:

Density	
Apparent	1.1 g/cc
Tapped	1.5 g/cc
Average Particle Size	17-24 microns
Specific Surface Area	0.15-0.25 m^2/g

Screen Analysis

Mesh	Typical Range
+100	0-Trace
-100+200	0-5
-200+325	10-25
-325	75-100

Typical Chemical Analysis:

Compound	Typical	Max Limit
Al	99.20	
Al_2O_3	0.6	
Fe	0.15	0.25
Si	0.07	0.15
Other Metals, each	0.01	0.03
Other Metals, total	-	0.15

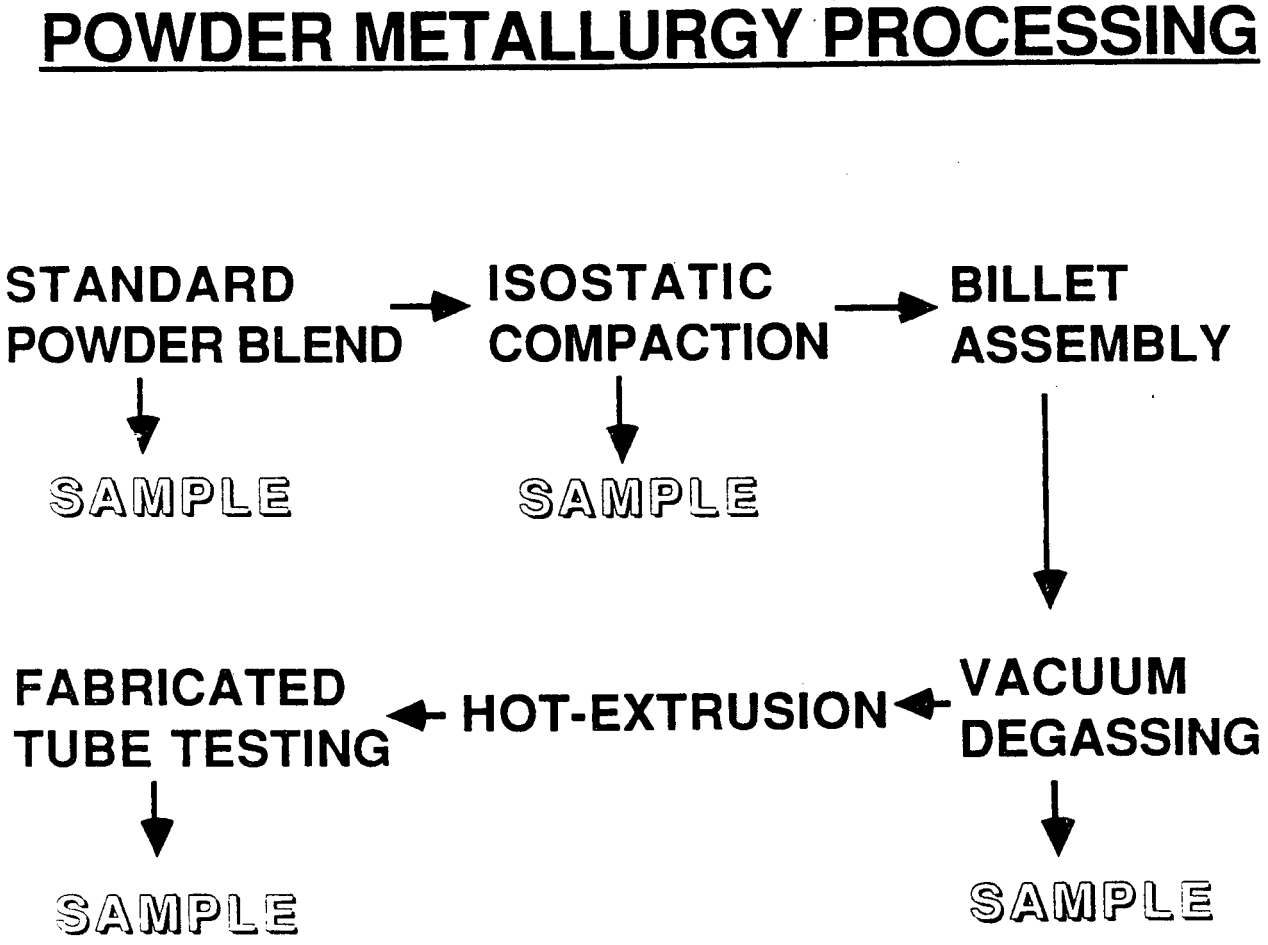


Figure 3 - Generalized flowsheet for the Powder Metallurgy process indicating points of sample extraction.

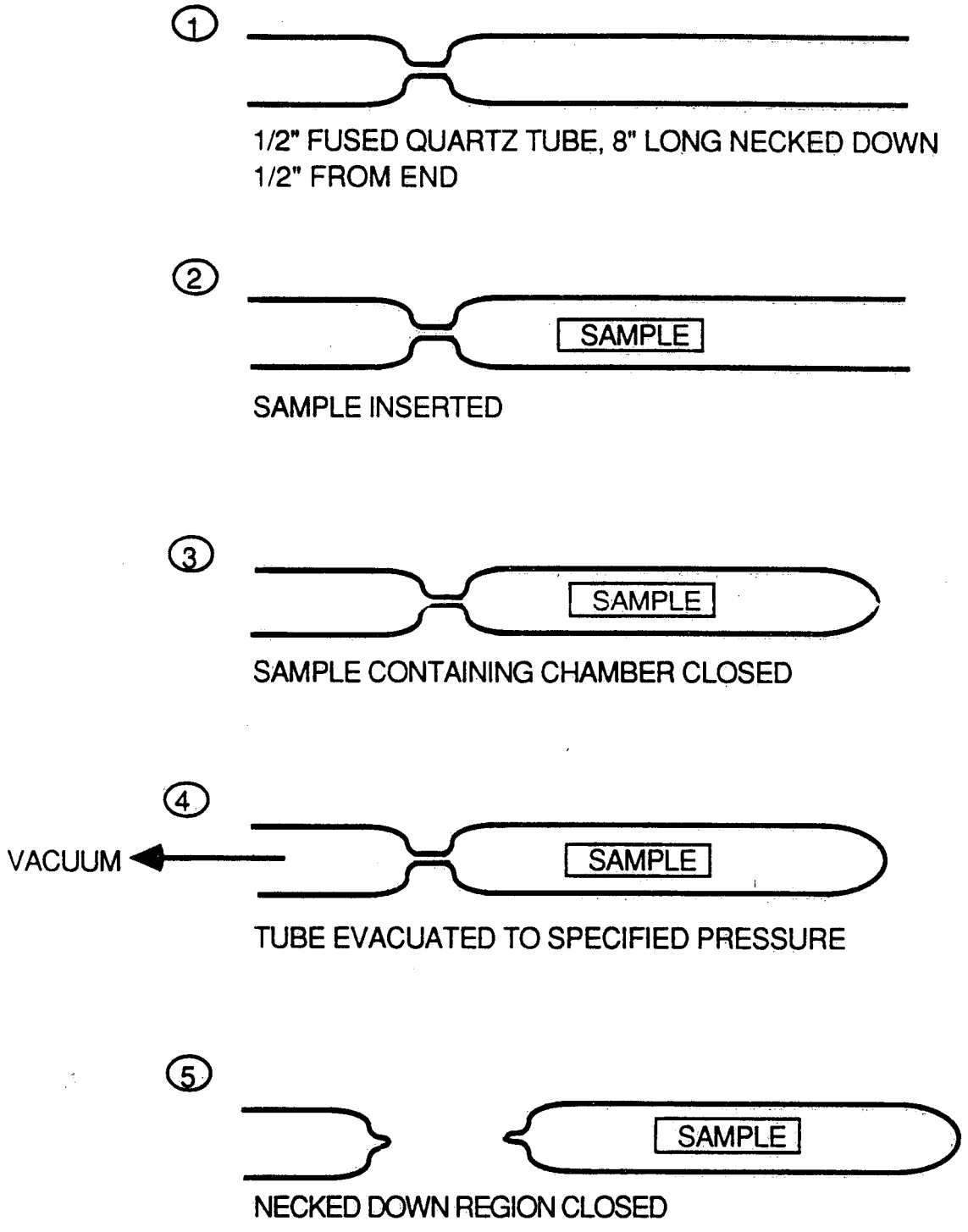


Figure 4 - Schematic depiction of sample encapsulation process.

each sample was determined using an 2.5 kW x-ray generator and a vertical goniometer.# The x-ray diffraction (XRD) results were used to determine semi-quantitative percent reduction by comparing peak heights for the primary U_3O_8 and U_4O_9 reflections, using the primary aluminum peak as an internal standard. The values reported for the percent oxides determined by this method are estimated to be valid within +/- 10%. Typical analyses were performed from 10 to 70 degrees two-theta at a rate of 1/2 degree two-theta per minute.

The metallothermic reduction reaction was analyzed using differential thermal analysis (DTA). The analyses were performed in a flowing nitrogen atmosphere using a Du Pont 1090 Differential Thermal Analyzer.+ Platinum sample cups were employed and the reference cup was filled with Al_2O_3. A temperature range of 100 °C to 1250 °C and back to 200 °C was examined at a scan rate of 20 °C/minute.

RESULTS AND DISCUSSION:

Actual Processed Samples:

X-Ray Diffraction:

The phase assemblage determined for the samples extracted from the actual powder metallurgy process are shown in Table III. As illustrated in Table III, isostatic compaction has no effect on the composition of the U_3O_8-Al blend. However, the results shown in Table III indicate that significant reduction does occur during the vacuum degassing process. After vacuum degassing, the core contains a mixture of U_3O_8, U_4O_9, and Al. Alumina was not detected due to the relatively small amount present (XRD cannot detect phases present at less than 2%) and also because the low symmetry of Al_2O_3 and low atomic number of Al do not generate strong diffraction patterns. The sample analyzed was held at the degassing temperature for a period of 36 hours. The degassed core has a composition of approximately 42% U_3O_8 and 58% U_4O_9. Based upon the semi-quantitative nature of the phase determination, the core may be considered a nearly equal mixture of U_3O_8 and U_4O_9.

Following extrusion, the core contains 58% U_3O_8 and 42% U_4O_9. These numbers again indicate that the core is an equal mix of $U_3O_8$and U_4O_9. While the higher percent U_3O_8 present suggests reoxidation, there are a number of factors which prevent such a conclusion. One inconsistency between the two sets of data is the fact that different billets were used for the two samples. While the powder blend was assumed identical, the actual distribution of fine particles (< 44 microns) may have been different. Processing conditions (particularly during vacuum degassing) may also have varied. Vacuum degassing times may vary from the nominal process specification by 12 to 24 hours. Another problem is associated with the difficulty in removing the aluminum coating from the extruded sample. The aluminum cladding is strongly bonded to the core following extrusion. Best attempts were made to fully remove the cladding before x-ray analysis, however it is likely that pieces of the cladding remained. These pieces increase the overall aluminum content of the sample and therefore affect the accuracy of the numbers.

The possibility of re-oxidation following vacuum degassing may not be totally dismissed. Billets are removed from the degassing ovens while they are still at maximum temperature. If even a small air leak exists in the cladding assembly or the degassing line, the core will be exposed to the atmosphere. Atmospheric oxygen contents are sufficient to cause partial oxidation to U_3O_8 particularly at elevated temperatures.

#Philips Corporation, New York, New York.

+DuPont Instruments Company, Wilmington, Delaware.

Table III

Phase Assemblage Determined After Various Stages of the Powder Metallurgy Process

Sample	Relative Oxide Content in Core U_3O_8	U_4O_9
Feed Powder	100%	0%
As-Compacted	100%	0%
Vacuum Degassed	42%	58%
Extruded	58%	42%

Table IV

Effect of Core Position on the U_4O_9 Content of Vacuum Degassed Sample.

Position	U_4O_9/Al Ratio
Outside	0.432
Center	0.424
Inside	0.439

The effect of radial core position on the reduction reaction was also examined for the degassed sample. Three samples were extracted from the core at various radial positions. Results from this analysis (expressed as ratios of the U_4O_9 peak to the aluminum peak) are shown in Table IV. These results suggest that reasonably uniform reduction occurs radially across the billet core during degassing.

Differential Thermal Analysis:

The x-ray diffraction analyses indicate that significant reduction occurs during vacuum degassing. The effect of this reaction on the overall system reactivity was determined using differential thermal analysis. A typical differential thermal analysis output for a mixture of U_3O_8 and Al is shown in Figure 5a. This plot shows the aluminum melting endotherm at approximately 660 °C followed by a strong exotherm due to the metallothermic reduction of U_3O_8 by Al at 1150-1200 °C. A similar plot for a section of the extruded fuel tube is illustrated in Figure 5b. This plot is very similar to that obtained for the initial powder blend except for the exothermic peak appearing at 900 °C. As discussed in the following section, this peak is attributed to the presence of U_4O_9 in the extruded sample.

Ampule Samples:

X-Ray Diffraction:

The results obtained for the actual processed samples indicate that reduction to U_4O_9 does occur during the processing of U_3O_8-Al cermet fuels by the existing powder metallurgy process flowsheet. The information obtained also confirms that reduction occurs primarily during vacuum degassing. Since vacuum degassing conditions vary greatly in a production environment, samples cut from the U_3O_8-Al core were exposed to known temperature, time, and pressure conditions in the laboratory.

The effect of vacuum degassing temperature on the percent reduction is shown in Figure 6. Although the reaction proceeds readily at all of the temperatures examined during the 24 hour time period of the test, only temperatures above 500 °C were sufficient to cause complete reduction of the available U_3O_8 to U_4O_9.

The effect of processing time on the reduction reaction is shown in Figure 7. The data indicate that the reduction of U_3O_8 by Al occurs fairly rapidly at 525 °C and 10^{-4} Torr. Reaction times greater than 10 hours are sufficient to cause complete reduction to U_4O_9 if the temperature is above 525 °C.

The effect of pressure is somewhat less defined. Figure 8 shows the effect of processing pressure on the percent reduction. A good deal of scatter exists in the data. This scatter may be a manifestation of the difficulty in obtaining an accurate pressure reading during the precise moment of ampule closure. The lack of a clear pressure dependence implies that the reaction is most likely solid-state diffusion controlled, however, the regression line indicates an increasing tendency for reduction with increasing ampule pressure. A step-like relationship may also be envisioned for the data shown in Figure 8.

The pressure dependence observed is somewhat puzzling since it is the opposite of that expected. Intuitively, one would expect in lower pressure environments that the aluminum would more actively seek oxygen from the U_3O_8 resulting in a greater amount of reduction. There are two possible explanations for the seemingly anomalous pressure dependence. The first possible explanation considers reactions of the Al powder with the environment. It is well known that a surface oxide layer exists on Al powder. This oxide layer contains aluminum oxide and aluminum hydroxides. Upon reduced pressure heating, the hydroxides decompose to aluminum oxide.[16] The decomposition reactions, which occur concurrently or in series, are:

$$Al_2O_3 \cdot 3\,H_2O \dashrightarrow Al_2O_3 + 3\,H_2O \qquad (7)$$

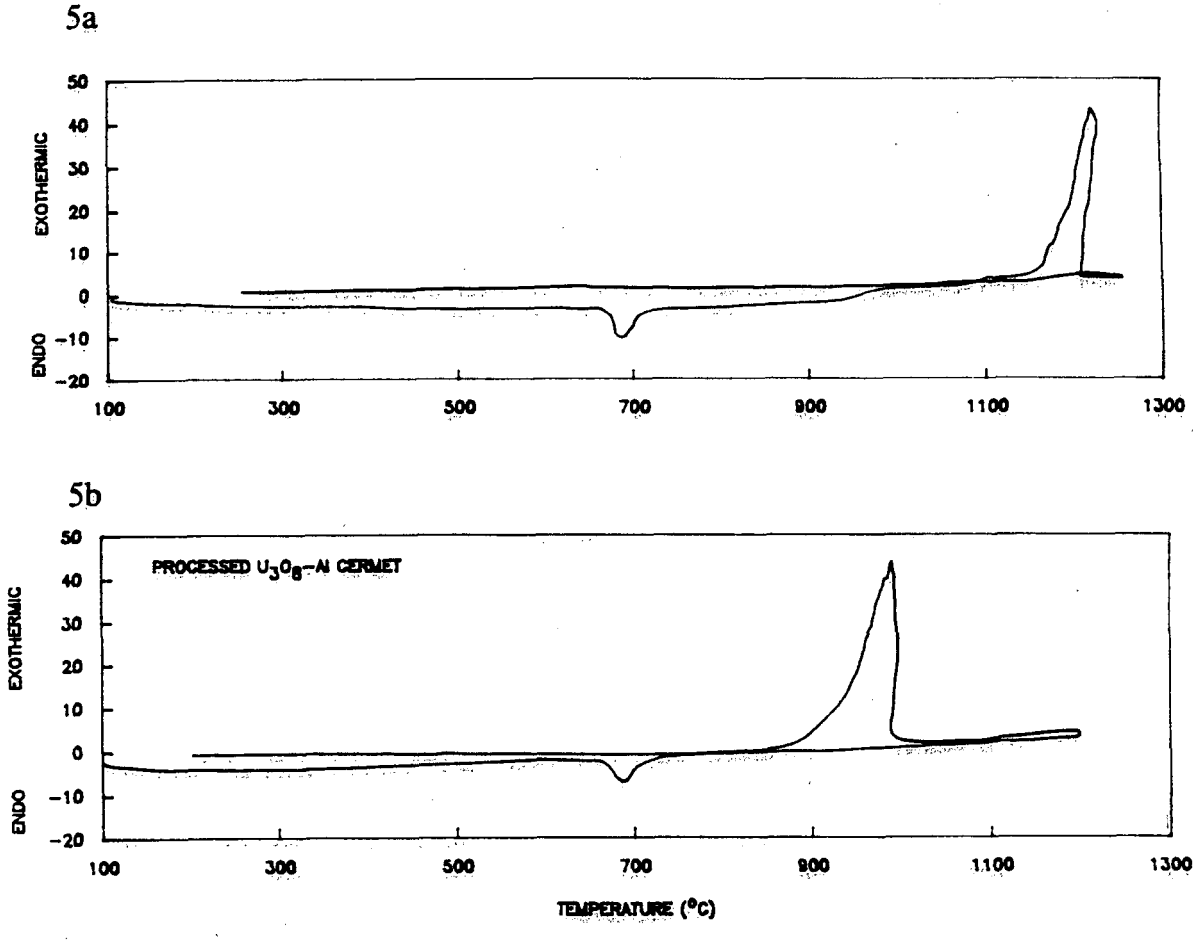


Figure 5 - Differential Thermal Analysis (DTA) output for an as-pressed U_3O_8-Al compact (a), and for an as extruded tube (b).

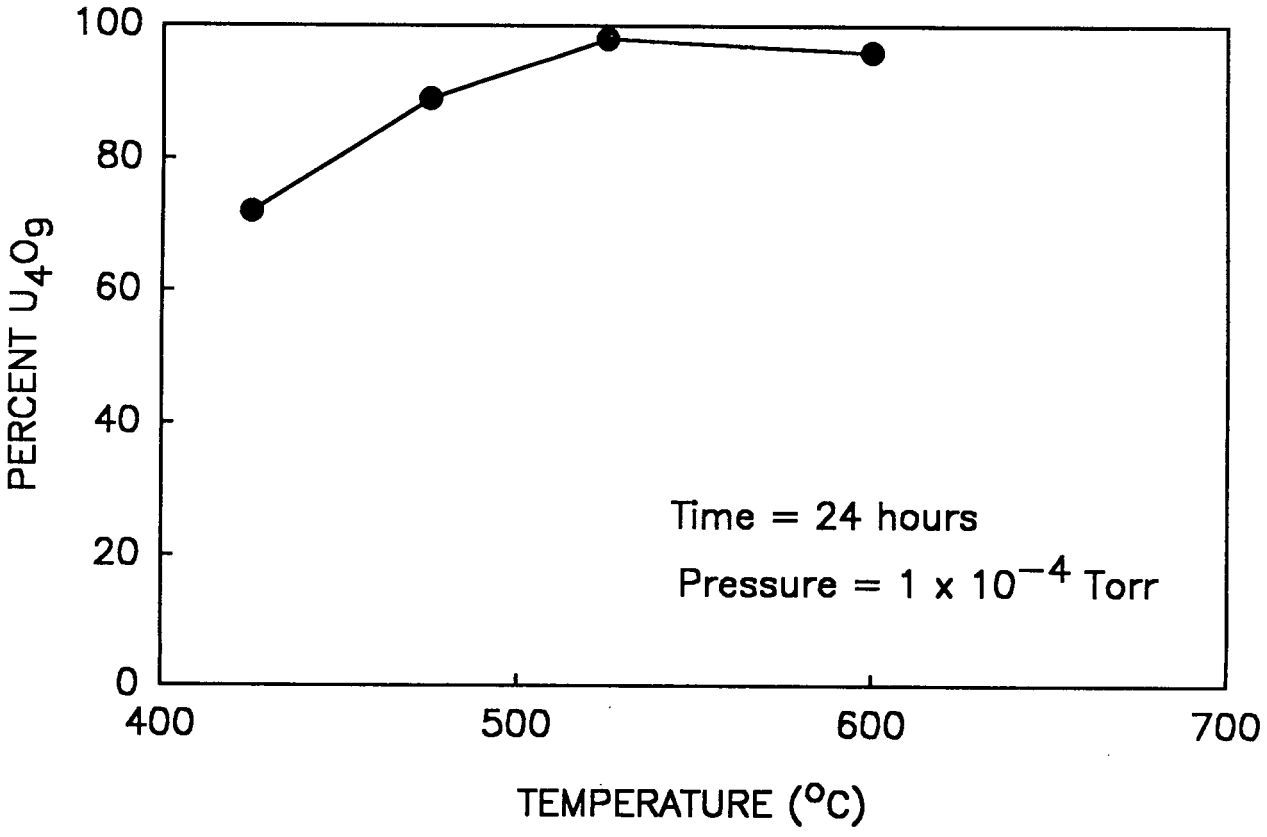


Figure 6 - Effect of processing temperature on U_3O_8-Al reactions.

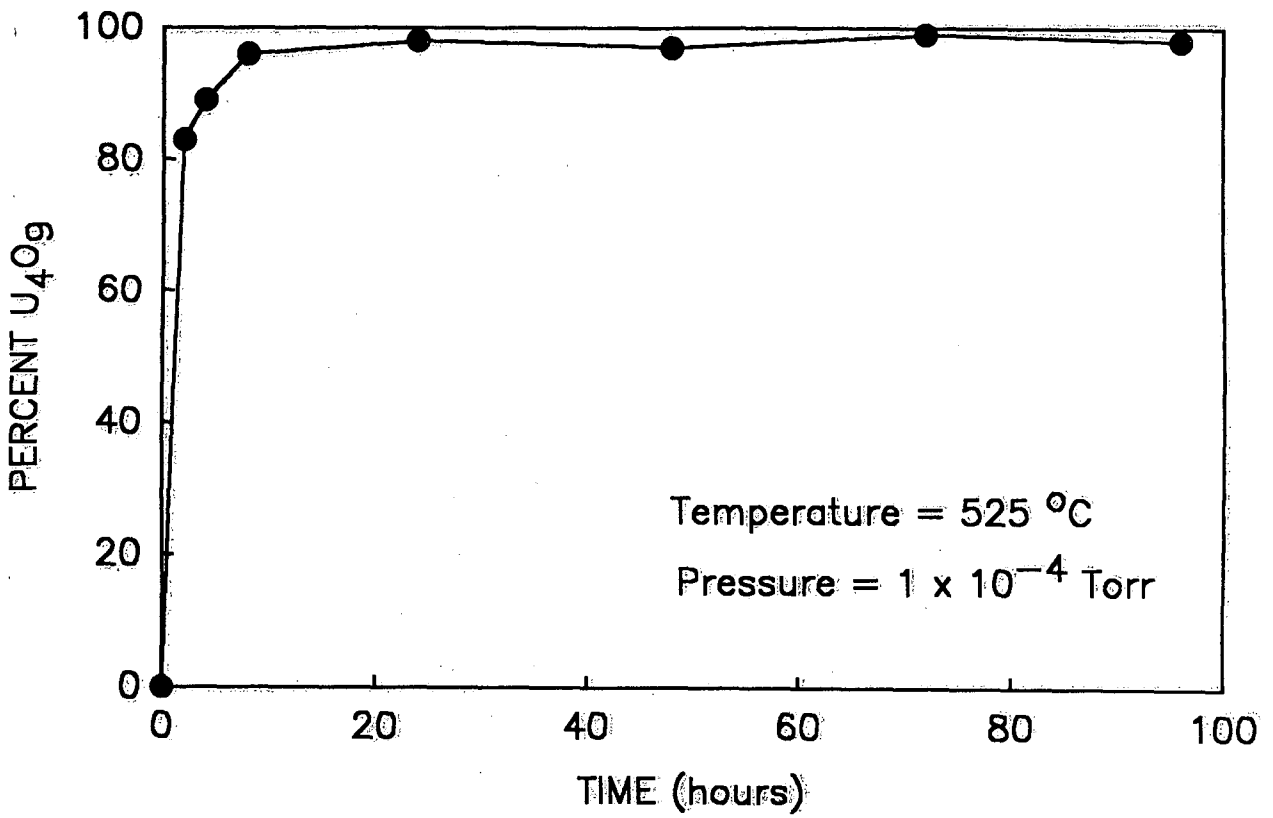


Figure 7 - Effect of processing time on U_3O_8-Al reactions.

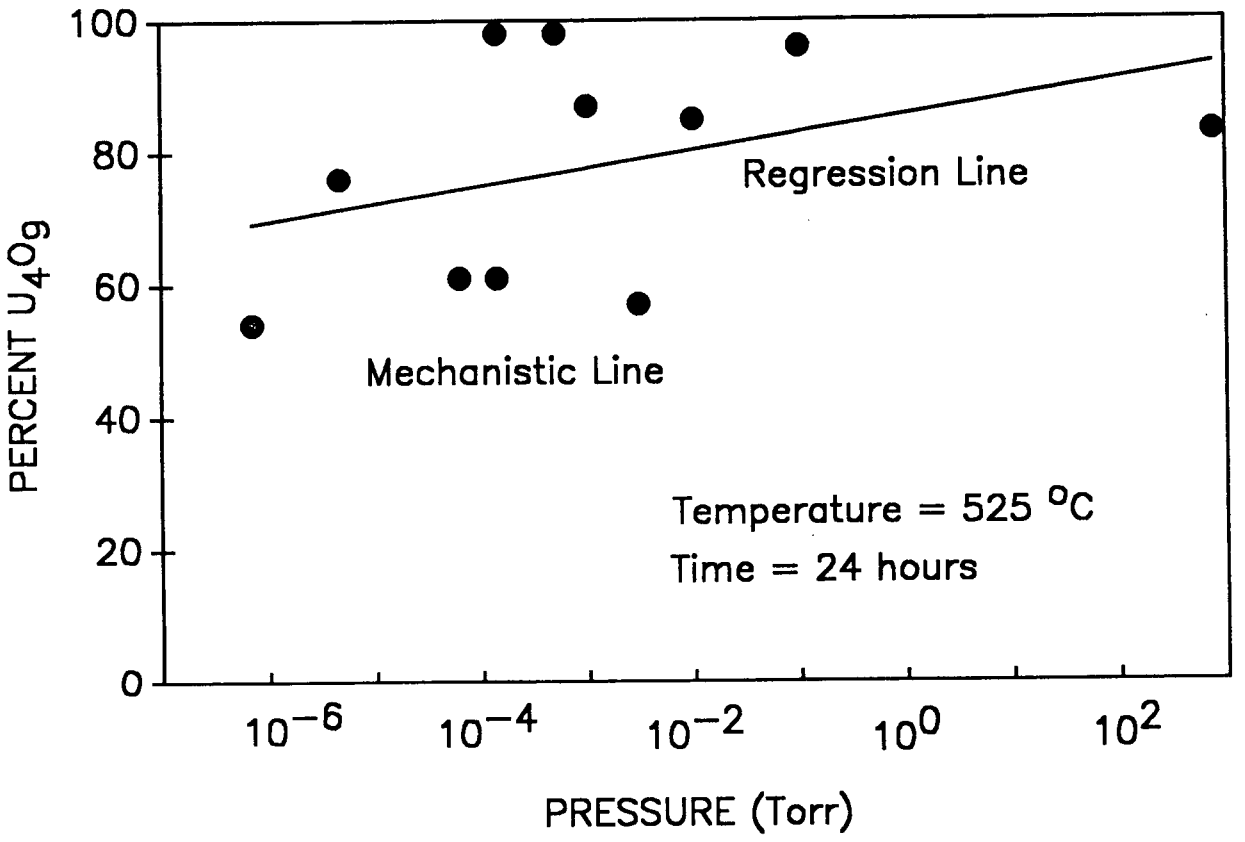


Figure 8 - Effect of processing pressure on U_3O_8-Al reactions.

$$Al_2O_3 \cdot 3\,H_2O \text{ --> } Al_2O_3 \cdot H_2O + 2\,H_2O \quad (8)$$

$$2\,Al + 6\,H_2O \text{ --> } Al_2O_3 \cdot 3\,H_2O + 3\,H_2 \quad (9)$$

$$Al_2O_3 \cdot H_2O \text{ --> } Al_2O_3 + H_2O \quad (10)$$

$$2\,Al + 3\,H_2O \text{ --> } Al_2O_3 + 3\,H_2 \quad (11)$$

The particular reactions of interest in this series are (9) and (11). These reactions show that hydrogen may be produced when Al is heated in the presence of water vapor. Kirchoff[17] and her coworkers have shown that aluminum powder exposed to air contains over 100 ppm adsorbed hydrogen. Once generated, this H_2 may reduce the U_3O_8 present to U_4O_9 by the reaction:

$$4\,U_3O_8 + 5\,H_2 \text{ --> } 3\,U_4O_9 + 5\,H_2O \quad (12)$$

The water vapor produced may then react with the excess aluminum present to form more hydrogen. In the higher pressure environments, there is likely to be more H_2O present. Increased H_2O would allow greater amounts of hydrogen to be generated according to equations (9) and (11). The larger amount of hydrogen present would subsequently lead to increased reduction of the U_3O_8 in the high pressure environments.

A second possible explanation focuses on the reactions that occur between U_3O_8 and Al during heating at reduced pressure. A reaction mechanism may be proposed. The unbalanced reactions of importance are shown here:

$$U_3O_8 + Al \text{ ----> } U_4O_9 + Al_2O_3 \quad (13)$$

$$Al + O_2 \text{ ----> } Al_2O_3 \quad (14)$$

$$U_3O_8 \text{ ----> } U_4O_9 + O_2 \quad (15)$$

In higher pressure environments, reaction (8) occurs to a large extent due to the increased amount of gaseous oxygen present. The oxidation of aluminum to Al_2O_3 results in a 30% density increase. Such an increase may cause a mechanical disruption in the compact which may increase the U_3O_8-Al contact and allow reduction to continue. Conversely, in low pressure environments, reaction (8) does not proceed as vigorously due to the lower amount of oxygen present. Consequently, reaction (7) becomes more important. This reaction also generates more dense reaction products but to a lesser extent, resulting in a lower degree of mechanical disruption. In this case, the reaction kinetics are controlled by solid-state diffusion across the product layer and incomplete reduction occurs. Reaction (9) does not become important until the oxygen partial pressure in the processing environment is lower than 10^{-11} Torr.[4]

Ampule studies indicate that significant reduction of U_3O_8 by aluminum occurs readily at elevated temperatures. The data also suggests that complete reduction to form a core of 100% U_4O_9 is possible with only slight modifications to the existing powder metallurgy flowsheet.

Differential Thermal Analysis:

The ampule samples were also used to determine the metallothermic reduction reaction onset temperature as a function of percent U_4O_9. The effect of percent U_4O_9 on the reaction onset temperature is illustrated in Figure 9. From the results obtained, U_4O_9 will react with aluminum in the vicinity of 850 to 900 °C, whereas U_3O_8 reacts in the range of 1150 to 1200 °C. The lower ignition temperature for U_4O_9 may be attributed to the fact that U_4O_9 has more tightly bound oxygen than U_3O_8. This implies that molten aluminum will not react as readily

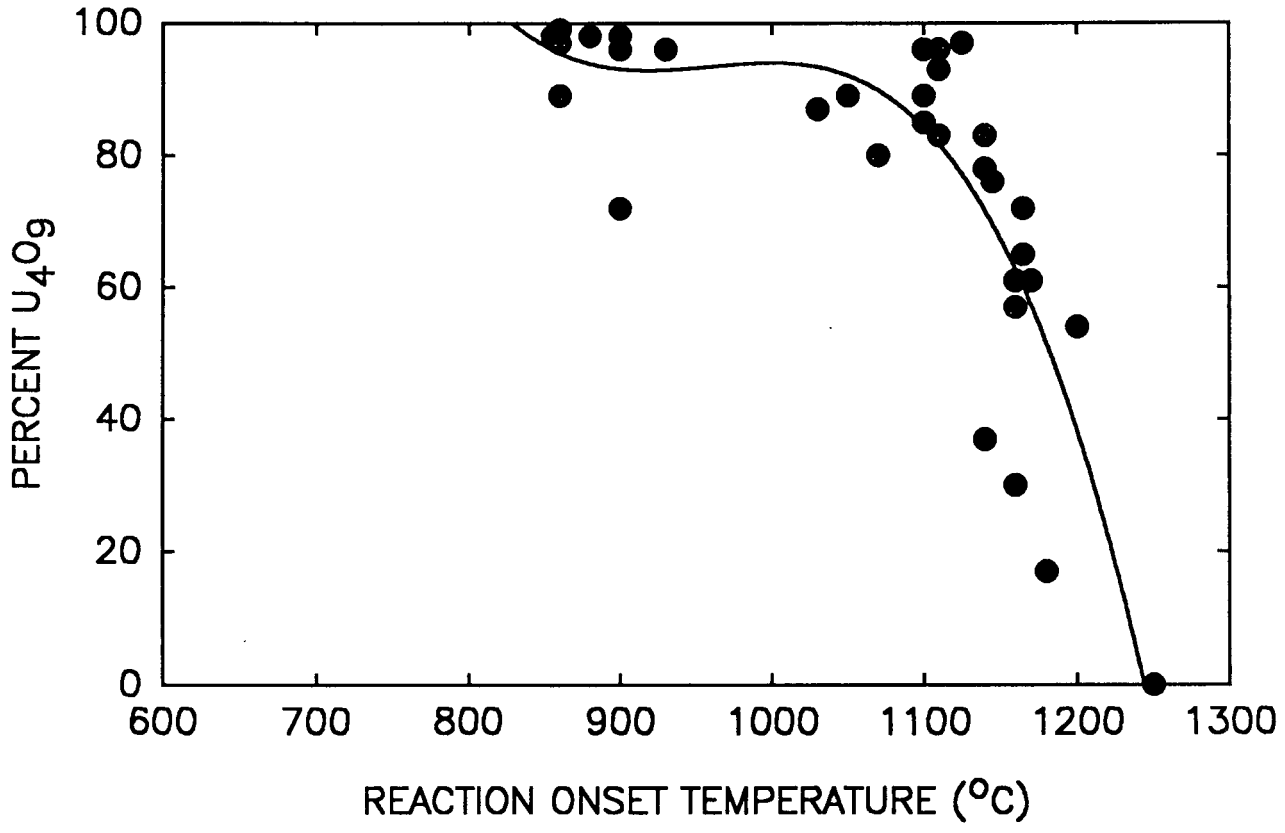


Figure 9 - Effect of percent U_4O_9 on the metallothermic reduction reaction onset temperature.

with the U_4O_9 to form the protective Al_2O_3 barrier around the particles which inhibits reaction propagation in fuel tubes. It is extremely important to note that the lowest reaction temperature observed is well above the aluminum melting temperature.

CONCLUSIONS:

The work reported shows that approximately 50% of the U_3O_8 present in an as-pressed cermet core is reduced to U_4O_9 during the processing of cermet fuels by the existing Powder Metallurgy flowsheet. The ampule studies have also indicated that reduction to 100% U_4O_9 is possible with only slight modifications to the existing flowsheet.

Thermodynamically, the reduction to U_4O_9 has a significant impact on the overall energetics of the system. Reduction to U_4O_9 lowers the maximum credible energy release in the event of metallothermic reduction by a factor of three, from 225 (for U_3O_8) to approximately 80 calories (for U_4O_9) per gram of oxide consumed.

Although the reduction to U_4O_9 does decrease the energetics of the system, there is also a slight loss of high temperature stability. The ignition point of U_4O_9-Al mixtures is approximately 200 °C less than that for similar mixture of U_3O_8 and aluminum. However, for any of the uranium oxide-aluminum mixtures examined, the lowest metallothermic reduction reaction ignition temperature was more than 200 degrees above the melting point of aluminum.

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