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DEVELOPMENT OF MIXED-NITRIDE FUEL MATERIALS OBTAINED BY CARBOTHERMIC REDUCTION OF OXIDES(a)

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DEVELOPMENT OF MIXED-NITRIDE FUEL MATERIALS OBTAINED BY CARBOTHERMIC REDUCTION OF OXIDES

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Mononitrides of uranium and plutonium are recognized as possessing many of the properties which are desirable for fast reactor fuel applications. The well known attributes of nitrides, including high metal atom density, high thermal conductivity, and refractoriness relative to other ceramic fuel systems, have established a high level of interest in documenting the performance and economic potential of these materials. A monocarbide and a mononitride fuel system have a close genetic relationship and their known properties point to generally similar performance potential. In more detailed comparisons of the two fuel systems for fast reactor use, the question of relative economics has often appeared. In a recent study on fuel cycle considerations for a similar carbide and nitride fueled fast breeder, Fletcher and Greenborg (of BNW) have concluded that the nitride fuel cycle is competitive with the carbide only if an alternative to synthesis of nitrides from pure U and Pu metals is available. An increase of approximately 25% in fuel fabrication costs between the case of metal compared with oxide starting material for conversion to nitride was shown by their analysis. Thus, in the light of ~~present~~ existing fuel cycle technology, the only realistic nitride fuel material is one obtained from the oxide. We are reporting here on materials studies and laboratory-scale development work which provides a basis for evaluation of a realistic mixed nitride fuel system.

In pursuing a carbothermic reduction scheme for nitride synthesis, the parallel between this process and the carbothermic synthesis of carbides is immediately obvious. At this point, we conceive of the conversion and fabrication requirements for carbides and nitrides as involving virtually equivalent processes, equipment and scale-up problems.

CARBOTHERMIC SYNTHESIS

The general reactions used for synthesis of nitrides, both from the metal and from oxide, are shown in Table I. Major differences in the two schemes, aside from starting material, are the higher temperatures and the necessity for rapid removal of the CO reaction product in the case of the carbothermic method.

Previous studies and development work on the carbothermic synthesis of uranium nitride have been carried out by several investigators.(1,2) Hyde's group at Harwell(3) made an extensive study of carbothermic reduction of UO_2 to yield nitride or carbonitride, using both hydrocarbon and solid forms of carbon. A reasonable conversion to uranium nitride was achieved in a graphite fluidized-bed reactor. The best nitride composition achieved was $U(N_{0.96}C_{0.04})$ from an oxide-carbon mixture. The oxide-butane reaction produced considerably higher carbon levels if high oxide conversion was achieved.

Our approach to the synthesis of mixed nitride from the oxide is patterned after the British work with several basic changes in the technique. These basic differences involve the use of a refractory metal rather than a graphite reactor and the addition of composition control reactions following the primary conversion.

In a reaction of this kind, the efficiency of gas-solid contact and removal of gaseous reaction products (i.e., CO - CH_4) is very important. The reactor vessal which we have developed is shown in the schematic drawing, Figure 1. Tungsten was chosen as the reactor material for its compatibility with the reactants, products and atmospheres involved in our reaction sequences. In this system, gases flow vertically through the particle bed, which is supported on a porous tungsten plate. Flow conditions are maintained such that the bed does not reach a truly fluidized condition. The reactor vessel now in use is approximately 2 inches O.D. and 5 inches long.

Figure $\overset{3}{2}$ depicts the physical arrangement of the reactor and supporting systems. A graphite resistance furnace is used with the reactor, with a blanket of pure helium gas inside the furnace. Reactive gases flowing toward the reactor are purified to reduce oxygen and water content to less than 1 ppm and monitored for purity. After passing through the reactor, effluent gases are monitored for carbon monoxide or methane content. The furnace temperature is programmable and automatically controlled; reactor temperature is measured independently by thermocouple.

We begin our conversion sequence by charging the reactor with 50 grams of approximately 1/2 mm particles comprised of an intimate oxide-carbon mixture. The synthesis process ~~is comprised~~ consists essentially of the following three simplified reactions:

$$MO_2 + 2C + 1/2\ N_{2(g)} \xrightarrow[1600°C]{} MN + 2CO \mid M(CN);C \qquad (1)$$

M = U,Pu or U+Pu

$$C \xrightarrow[1200°C]{H_{2(g)}} CH_{4(g)} \qquad (2)$$

$$M(CN) \xrightarrow[100°C \le T \le 1200°C]{H_{2(\;)}} MN_{>1.0} + C \qquad (3)$$

In the reaction (1) the primary conversion to yield the mononitride plus carbon monoxide is shown. A slight excess of carbon (4-8 mole%) is used in the starting material to obtain more complete conversion of the oxide. This excess is retained in the product as both uncombined (free) carbon and combined carbon in solution in a carbonitride phase. Reaction (2) is used to remove the uncombined (free) carbon. Following this reaction, a nitrogen flow is established and reaction (3) occurs, in which combined carbon is displaced from the carbonitride solid solution, primarily by formation of higher nitrides with low carbon solubility. In the final stage, reaction (2) is repeated to remove the carbon released in reaction (3) and decomposition of higher nitrides is achieved in helium at 1500°C before cooling.

The product obtained from this process is a single phase uranium or (U,Pu) nitride (or carbonitride) in the form of porous friable particles of approximately the same size as the oxide-carbon particles. Chemical compositions for three successive standard runs of mixed nitride are given in Table II; the composition of a uranium nitride synthesized under the same conditions is also shown. We feel that the uniformity in anion content (within 0.05 - 0.1 wt% between batches) represents good reproducibility for a fuel preparation process. The effectiveness of the hydrogen-nitrogen-hydrogen sequence for removal of both free and combined carbon has been confirmed by analyzing the chemical composition of material after each step in the sequence. We have observed carbon contents to be reduced from 1.3 wt% after primary conversion to 0.3 wt% after the complete sequence, with an accompanying decrease in lattice parameter of 0.010 Å.

TABLE II

COMPOSITIONS OF NITRIDES OBTAINED BY CARBOTHERMIC REDUCTION

	U/Pu	N_2	O_2	C	Lattice Parameter
UPCN-4	4.0	5.22	0.10	0.17	**4,893**
UPCN-6	4.0	5.30	0.06	0.18	**4.893**
UPCN-7	4.0	5.33	0.19	0.22	**4.893**
UPCN-8	4.0	5.32	0.14	0.28	**4.894**
UCN-2	**U only**	4.84*	0.04	0.25	**4.890**

$U_{0.8}Pu_{0.2}N$

*

SINTERING BEHAVIOR

Our initial work with mixed nitride fuel materials involved synthesis of the individual nitrides (UN and PuN) from the respective metals using the standard metal-hydride-nitride methods. Typically, the UN and PuN thus obtained contained 100 to 400 ppm carbon and less than 500 ppm oxygen. In developing the carbothermic synthesis of nitrides we were interested in the effect on sintering behavior of the differences in the two materials, especially **differences in** carbon content. We have merely applied the same sintering **procedures** developed for metal-derived nitrides to carbothermic nitrides to obtain a qualitative evaluation of relative sinterability.

In order to sinter mixed nitrides to high densities, we have found that it is necessary to ball mill the material for periods of up to 100 hours. In the case of metal-derived nitrides this operation serves to yield a homogeneous physical mixture of UN and PuN particles; since the carbothermic nitrides are already in the form of a (U,Pu)N solid solution, only minor homogenization is obtained by milling. In both cases, however, ball milling and pressing operations increase oxygen content by 1000 to 2000 ppm.

Sintering atmospheres of argon, helium, and nitrogen have been used with no significant differences noted between sintering results in the various atmospheres. A truly quantitative evaluation of sintering kinetics has not been obtained for these systems due to the difficulty of reproducible communication and storage of active powders. However, our results indicate that densities between 85 - 94% TD may be obtained by sintering for 3 to 6 hours at temperatures between 1700 and 1900°C. For a powder of given activity, the shorter times and lower temperatures yield densities in the mid-80's (% TD) while the full 6 hours at 1900°C is required to achieve densities between 92 and 95% TD.

As specific examples of results obtained in sintering mixed nitrides we may refer to the data in Table II. For the two sintering runs with carbothermic material and the one run with metal-derived material, the similarity in densities achieved with sintering between 1800 and 1900°C for 4 to 6 hours is readily apparent. Note also that the carbothermic material (UPCN-2) with relatively high carbon and oxygen content shows no significant deviation from the other compositions in its sintering behavior. A change in composition during sintering of carbothermic material has been observed, as indicated by the change in carbon and oxygen content shown in Table II. We hypothesize that this phenomenon results from a further reaction of carbon and oxygen in the pellets during the vacuum offgas period at 1250° to 1400°C in 10^{-5} torr used in the heatup portion of the sintering cycle. The reduction in carbon and oxygen content during sintering brings the composition of sintered carbothermic nitrides into close correspondence with compositions of sintered metal-derived material.

Figure 7 show microstructures of sintered mixed nitrides obtained from both synthesis routes. Accounting for the density difference, virtually the same microstructure is obtained with either material. Note that both contain a fine, randomly dispersed oxide phase; differences in shading of nitride grains is due to staining by the etchant.

TABLE III

DATA ON SINTERING OF MIXED NITRIDES

(Ratio U:Pu = 4:1)

Run	Sintering Conditions	Average Density	Composition ( )				
			Sintered			Before Sintering	
			N_2	O_2	C	O_2	C
UPCN-2 (Carbothermic)	Helium 4 hr - 1800°C	~87% TD	4.24	0.89	0.60	--	0.81
UPCN-4 (Carbothermic)	Nitrogen 4 hr - 1900°C	~94% TD	5.27	0.30	0.11	0.40	0.18
MNP-39 (Metal-Derived)	Helium 6 hr - 1850°C	~89% TD	5.25	0.24	0.06	--	--

PHYSICAL AND CHEMICAL PROPERTIES

In evaluating the physical and chemical properties of carbothermic mixed nitrides we have thus far concentrated on three very important fuel characteristics: thermal conductivity, melting [illegible] the fuel-cladding compatibility. The approach has been to first measure properties of a typical metal-derived nitride fuel material and then measure the same properties on carbothermic nitrides. This actually comprises a preliminary evaluation of the effect of composition (especially with respect to carbon and oxygen) on properties, either in terms of concern with "impurity" levels or intentional formulation of carbonitride or carboxynitride.

Thermal Conductivity

The thermal conductivity of the uranium-plutonium nitride samples was determined indirectly by measuring thermal diffusivity and calculating thermal conductivity from the relationship

$$K = \alpha \rho C_p$$

where α = thermal diffusivity, ρ = density and C_p = heat capacity. This method was employed instead of direct steady-state methods because: (1) it required only small test specimens and (2) a large temperature range could be covered in a relatively short period of time. Moreover, since the primary goal of these measurements was to compare samples produced from different processes and with different oxygen and carbon impurity levels, the relative thermal conduction was established from direct comparisons of thermal diffusivity.

Thermal diffusivity was measured from 200-1600°C using the "flash" method developed by Parker, et al at the U. S. Naval Radiological Defense Laboratory. Instead of a flash lamp, our apparatus employs a ruby laser to transiently heat one surface of a small sample, 0.25" dia. by 0.030-0.040" thick. The subsequent temperature increase on the rear surface of the sample was measured with an indium antimonide infrared detector and thermal diffusivity was calculated from the relationship

$$\alpha = \frac{A L^2}{t_{1/2}}$$

where L = sample thickness, A - a value which varies with heat loss and $t_{1/2}$ = the time to one-half maximum temperature rise measured at the rear surface. Values for A were determined using Cowan's method. Ambient sample temperature was established in moly-rhenium wound tube furnace which was enclosed and continuously purged with either helium or argon - 8% hydrogen to prevent oxidation of the sample.

The thermal diffusivity data determined in this study is shown in Figure 5. Unlike the thermal diffusivity of dielectic materials which decreases with temperature, the thermal diffusivity of the nitride increases because of electronic contributions to the conduction process. In this respect, the thermal conductivity of the mixed nitride is very similar to that of the mixed carbide which varies little with temperature.

The thermal diffusivities of the three samples agreed surprisingly well in spite of the large variation in oxygen and carbon contents. This result was somewhat unexpected since increases in impurity content normally result in decreases in thermal conduction. Bates, at our laboratory, has observed an appreciable decrease in the thermal diffusivity of uranium oxycarbides with increases in oxygen content within the oxygen solubility range. Although we are unable presently to explain our results, the data do show that the thermal diffusivity of carbothermic nitrides is comparable or better than that of nitrides produced from metals.

Calculated thermal conductivity is shown as a function of temperature in Figure 6. We used the heat capacity of UN reported by ______ since no data are currently available for the mixed nitride. However, the heat capacity of the mixed nitride should not be too different from that of UN because of the similarities of uranium and plutonium and their compounds.

The data were corrected to theoretical density using Biancherias( ) equation. Although a large variety of densities have not been used in thermal diffusivity measurements, Biancherias correction appears to work reasonably well.

Since the thermal conductivity of the mixed nitride has not been measured directly we cannot compare our calculated results with steady-state data. However, our results do agree reasonably well in magnitude with the thermal conductivity data reported by ____________________ at ____________________ for uranium-plutonium carbides.

Melting Behavior

Melting studies have been conducted in [illegible] - [illegible] pseudobinary system involving nitrogen pressures from 1 to 1[illegible] atmospheres. A high pressure, cold wall furnace employing a resistance [illegible] tungsten Vee filament was used. Temperatures were measured with a micro optical pyrometer sighted on the filament and liquid formation was observed visually. Calibration of the system was based on known melting points of high purity refractory metals and compounds.

The results of melting determinations on several nitride materials are shown in Figure 7. Note that with UN and PuN, a slope to the left is observed in the plot of log P_{N_2} versus 1/T. This indicates the pressure dependence of the decomposition reaction

$$MN_{(s)} \rightarrow M_{(liq)} + 1/2\ N_{2(g)}\uparrow \quad .$$

An inflection to a vertical on this curve indicates the pressure required to yield congruent melting of the nitride according to the reaction

$$MN_{(s)} \rightarrow MN_{(liq)} \quad .$$

As expected, the curve for the mixed nitride falls between that of UN and PuN. Curves for other high purity (U,Pu)N compositions (unsintered) followed the same pattern, including the definite slope to the left.

Unexpectedly, the data from liquid formation of sintered mixed nitrides does not fit this pattern. The points from all compositions (See Table   ) studied appear to be independent of nitrogen pressure above one atmosphere and fall within the temperature range of 2760 - 2800°C. In the pressure range covered, the [illegible] decomposition behavior as observed with UN and PuN does not appear to occur in these sintered materials. The explanation is probably involved with the effect of carbon and oxygen in the fuel material relative to a high purity nitride. Pressure dependence over [illegible] in the range below one atmosphere is presently under study and should lead to a more comprehensive interpretation. It is apparent that carbon and oxygen as "impurities" in the nitride fuel materials have no significant effect on the melting temperature, at least for concentrations up to 6000 ppm C and 9000 ppm O_2.

Compatibility

The compatibility of both metal-derived and carbothermic nitride fuel materials with sodium and 304 stainless has been evaluated at typical fast breeder conditions. In this work, typical 0.020 inch diameter fuel pellets were placed in sections of 0.025 inch O.D. 304 stainless steel tubing and sodium bonded in the same loop used for bonding pin sections for irradiation. In several cases, the same assembly with helium rather than sodium bond was used as a control sample. Pin sections were doubly encapsulated and sealed in argon filled ampules for heat treatment.

Conditions used for the tests were standardized on two time periods (100 and 1000 hours) and two temperatures (650 and 1000°C). The 100-hour tests were used to obtain preliminary information to support irradiation projects. The 1000-hour tests were assumed adequate to provide indication of chemical interaction under isothermal conditions. Examination was by metallographic techniques, including a special technique for viewing sodium in the annulus.

Tests were run under the above conditions of time and temperature with metal-derived nitrides with compositions typical of those previously discussed and densities between 85 and 90% TD. No changes in interfaces of either fuel or cladding were observed after 1000 hours at 650° and 1000°C; nor were any chemical or mass transport effects noted.

Similar tests were conducted with two carbothermic nitrides, including a sample containing 6000 ppm carbon and 9000 ppm oxide. The results with the [illegible]therm[illegible]terial with a sodium bond were equivalent to the case with [illegible] nitride. Figure ___ shows fuel and cladding interfaces from [illegible]tion [illegible] the compatibility capsule containing the high carbon and oxygen sample. The fuel surface is completely unchanged, as is the cladding surface.

The only noticeable change in cladding microstructure is an increase in grain size due to the time-temperature conditions.

We conclude from these results that, under isothermal conditions, no incompatibility exists between mixed nitrides and 304 stainless steel in the presence of sodium. This stability is unchanged when the nitride contains carbon and oxygen levels considerably higher than compositions which can be reproducibly obtained by carbothermic reduction.

SYNTHESIS REACTIONS FOR URANIUM-PLUTONIUM NITRIDES

Metal Derived:

$$U + 1.5H_2 \xrightarrow[\text{1 atm.}]{\text{26-300 }^{o}\text{C}} UH_3 \xrightarrow[10^{-5}\text{ torr}]{\text{300 }^{o}\text{C}} 3U + 2N_2 \xrightarrow[\substack{\text{1 atm.}\\ \text{(Static)}}]{\text{300-800 }^{o}\text{C}} UN + U_2N_3$$

$$U_2N_3 \xrightarrow[10^{-5}\text{ torr}]{\text{1200 }^{o}\text{C}} 2UN + 1/2N_2 \nearrow$$

$$Pu + (1.\ \tfrac{X}{2})\ H_2 \xrightarrow[\text{1 atm.}]{\text{26 }^{o}\text{C}} PuH_{2.x} + N_2 \xrightarrow[\substack{\text{1 atm.}\\ \text{(Flowing)}}]{\text{100-800 }^{o}\text{C}} PuN + (1.0\ \tfrac{X}{2})\ H_2$$

Carbothermic Reduction:

$$MO_2 + 2C + 1/2N_2 \xrightarrow{\text{1200-2000 }^{o}\text{C}} MN + 2CO \nearrow$$

$M = U, Pu$

Fig. 1

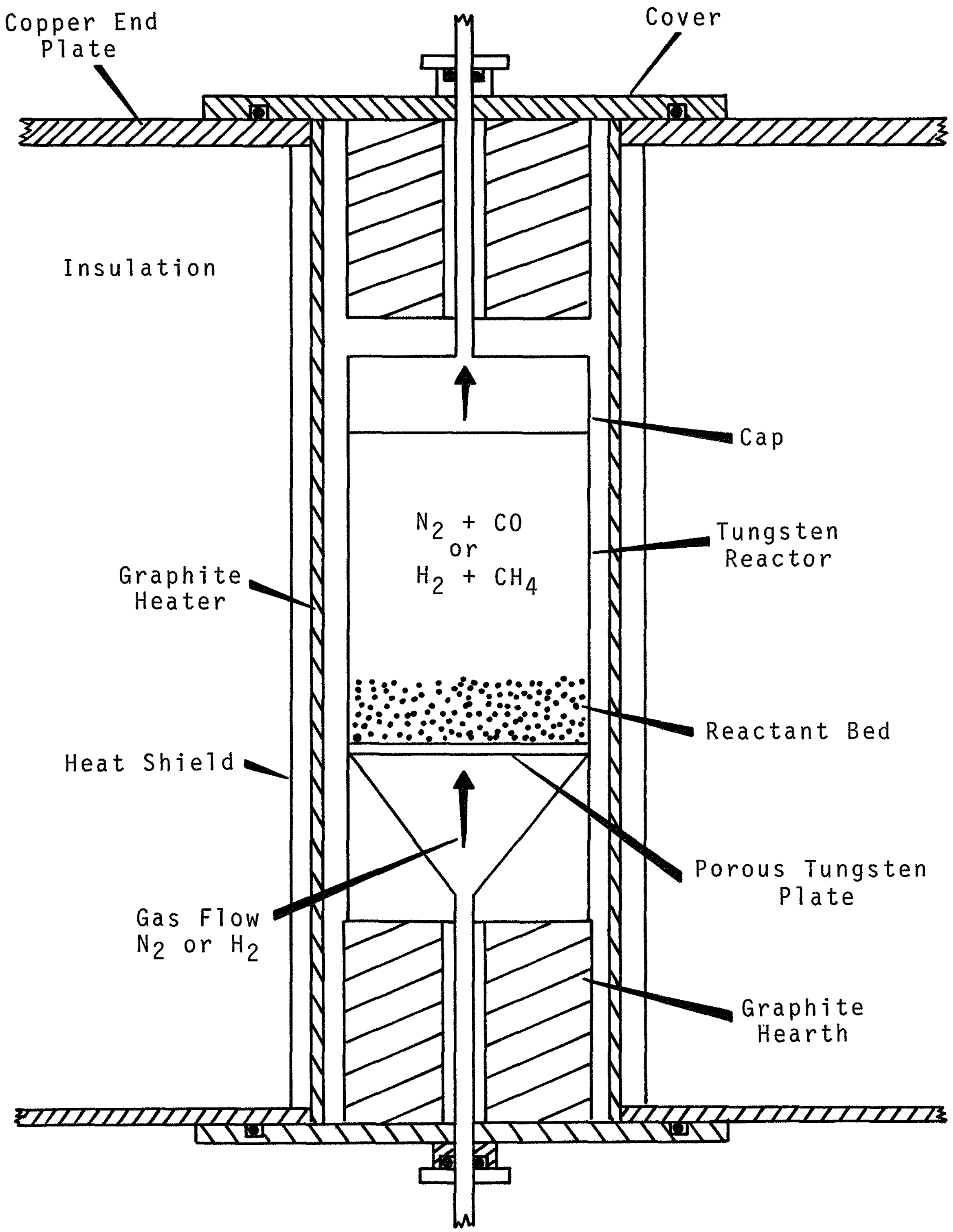

Copper End Plate
Cover
Insulation
Cap
N_2 + CO or H_2 + CH_4
Tungsten Reactor
Graphite Heater
Reactant Bed
Heat Shield
Porous Tungsten Plate
Gas Flow N_2 or H_2
Graphite Hearth

Fig. 2

PARTICLE BED REACTOR SYSTEM FOR CARBOTHERMIC SYNTHESIS OF URANIUM – PLUTONIUM NITRIDES

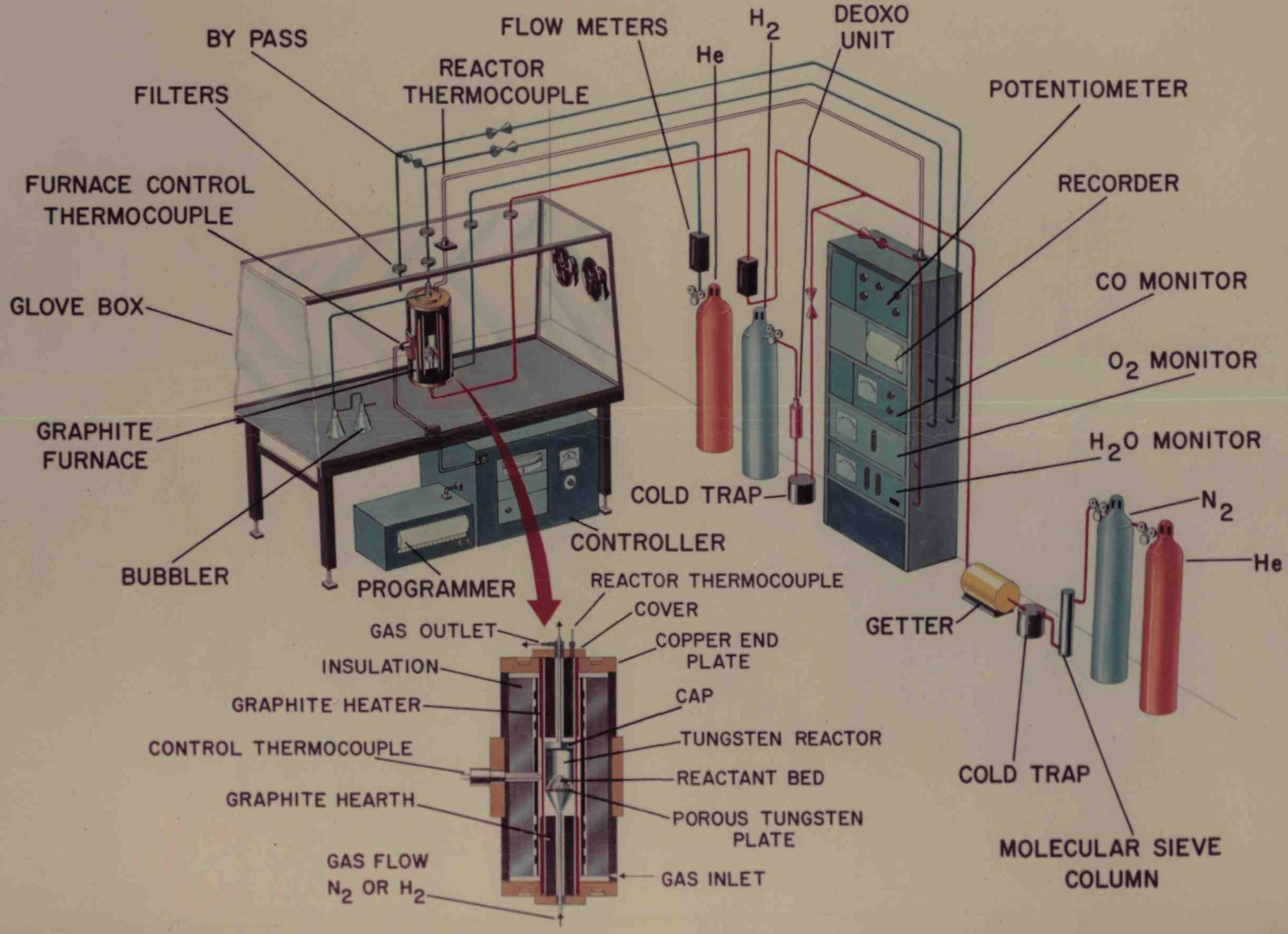
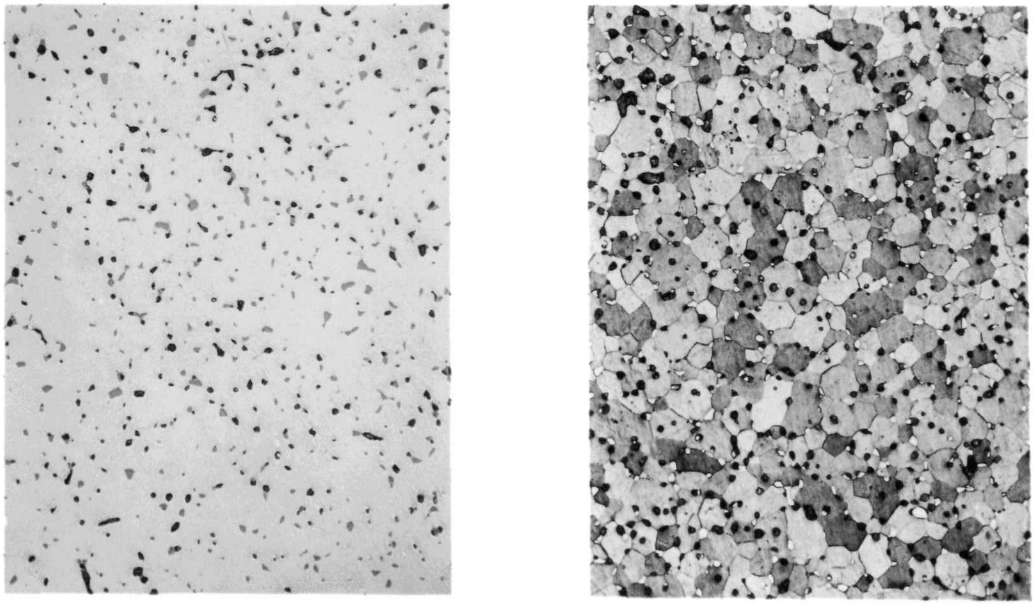


Fig. 3

SINTERED CARBOTHERMIC NITRIDE
UPCN-4S



UNETCHED 500X

ETCHED 500X

COMPOSITION

AFTER SYNTHESIS		AFTER SINTERING
5.15 WT%	N_2	5.30 WT%
1050 PPM	O_2	3000 PPM
1775 PPM	C	1150 PPM
4.893	a_0	4.891

SINTERED - 1900°C 1 ATM N_2

DENSITY - 13.3 GM/CC OR ~94% T. D.

FIG. 4

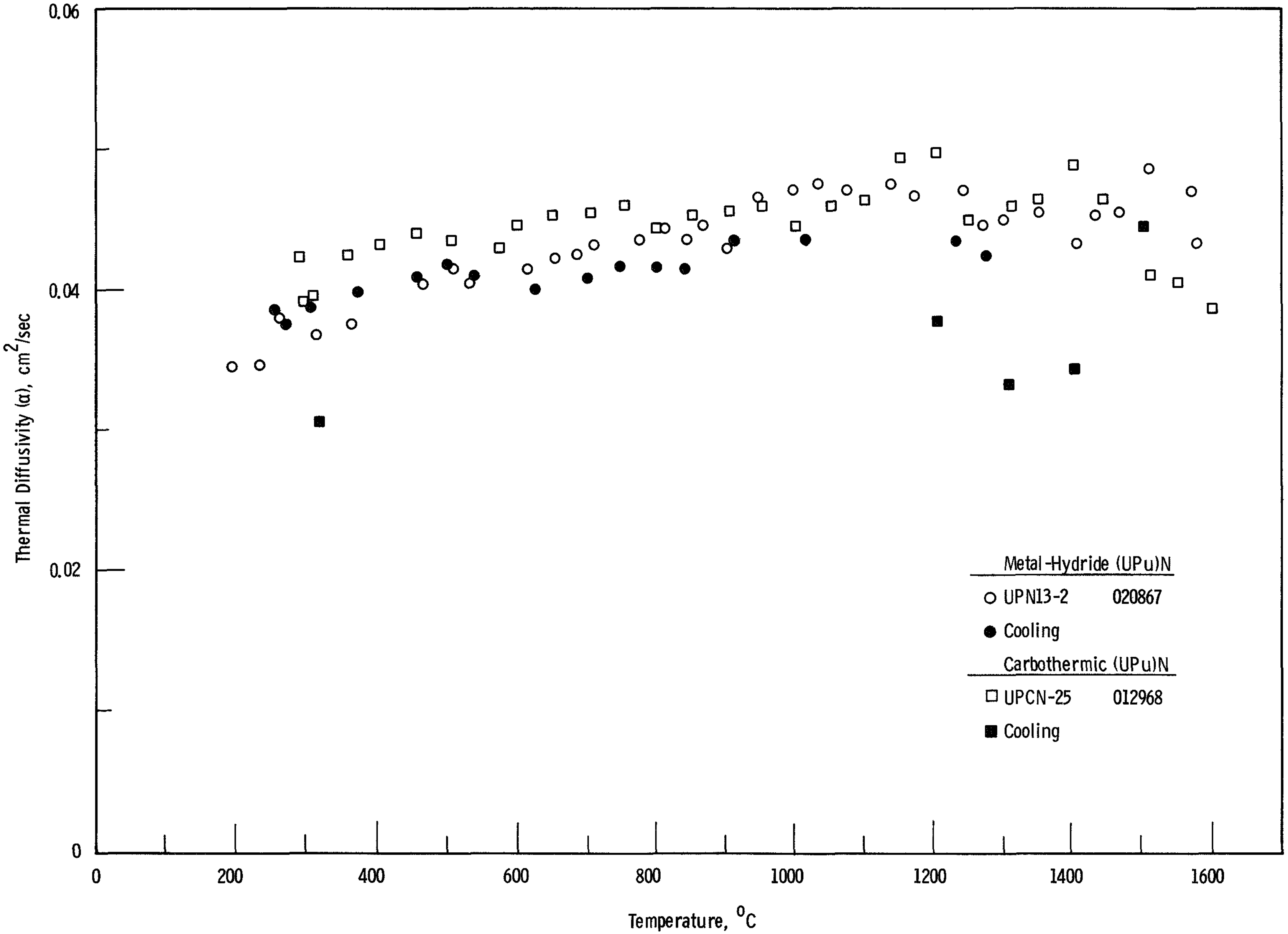

0.06
0.04
0.02
0
Thermal Diffusivity (α), cm²/sec
0
200
400
600
800
1000
1200
1400
1600
Temperature, °C
Metal-Hydride (UPu)N
○ UPN13-2 020867
● Cooling
Carbothermic (UPu)N
□ UPCN-25 012968
■ Cooling

FIG. 5

THERMAL CONDUCTIVITY OF $(U_{0.8}Pu_{0.2})N$

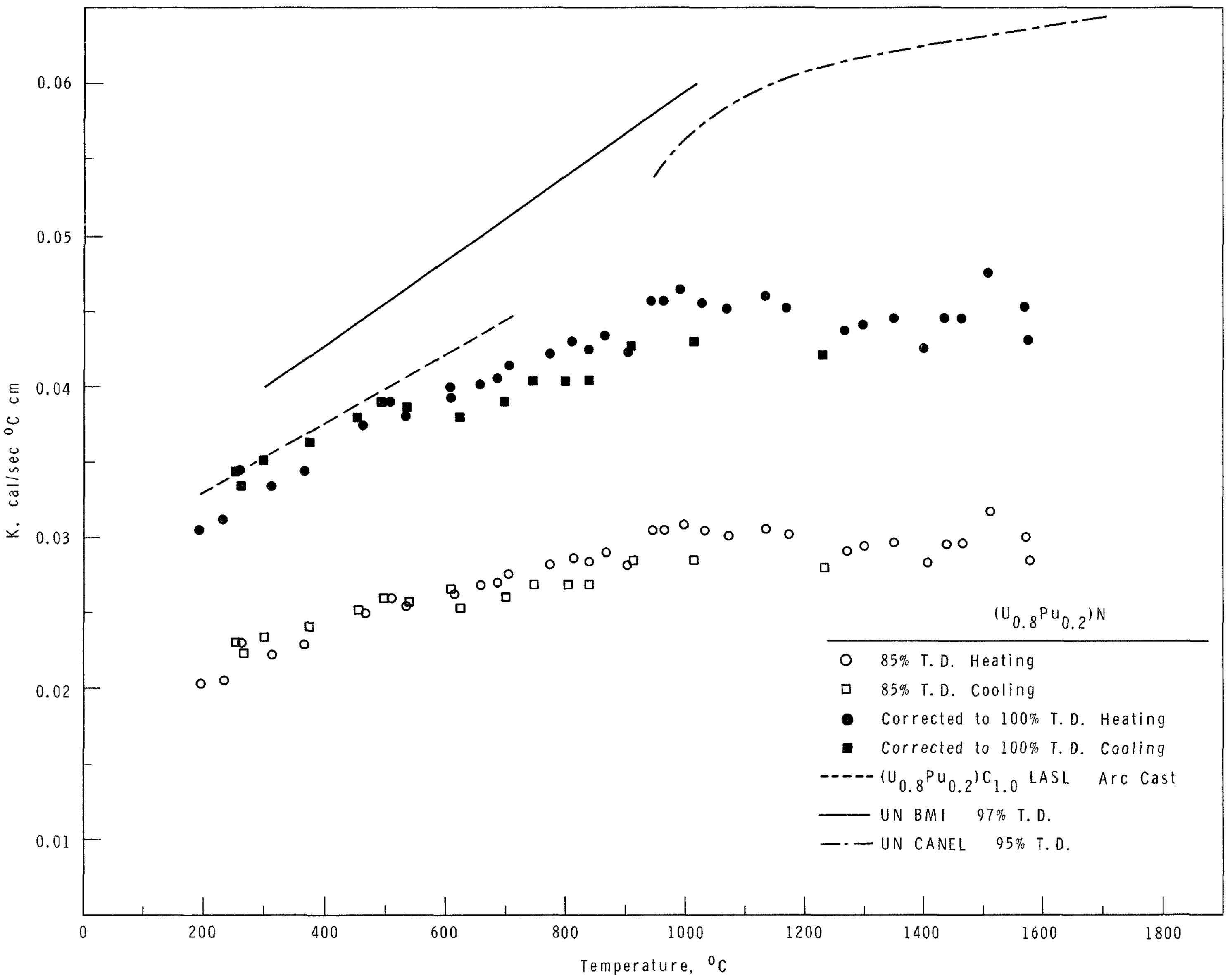


FIG. 6

DECOMPOSITION AND MELTING OF U, Pu NITRIDES

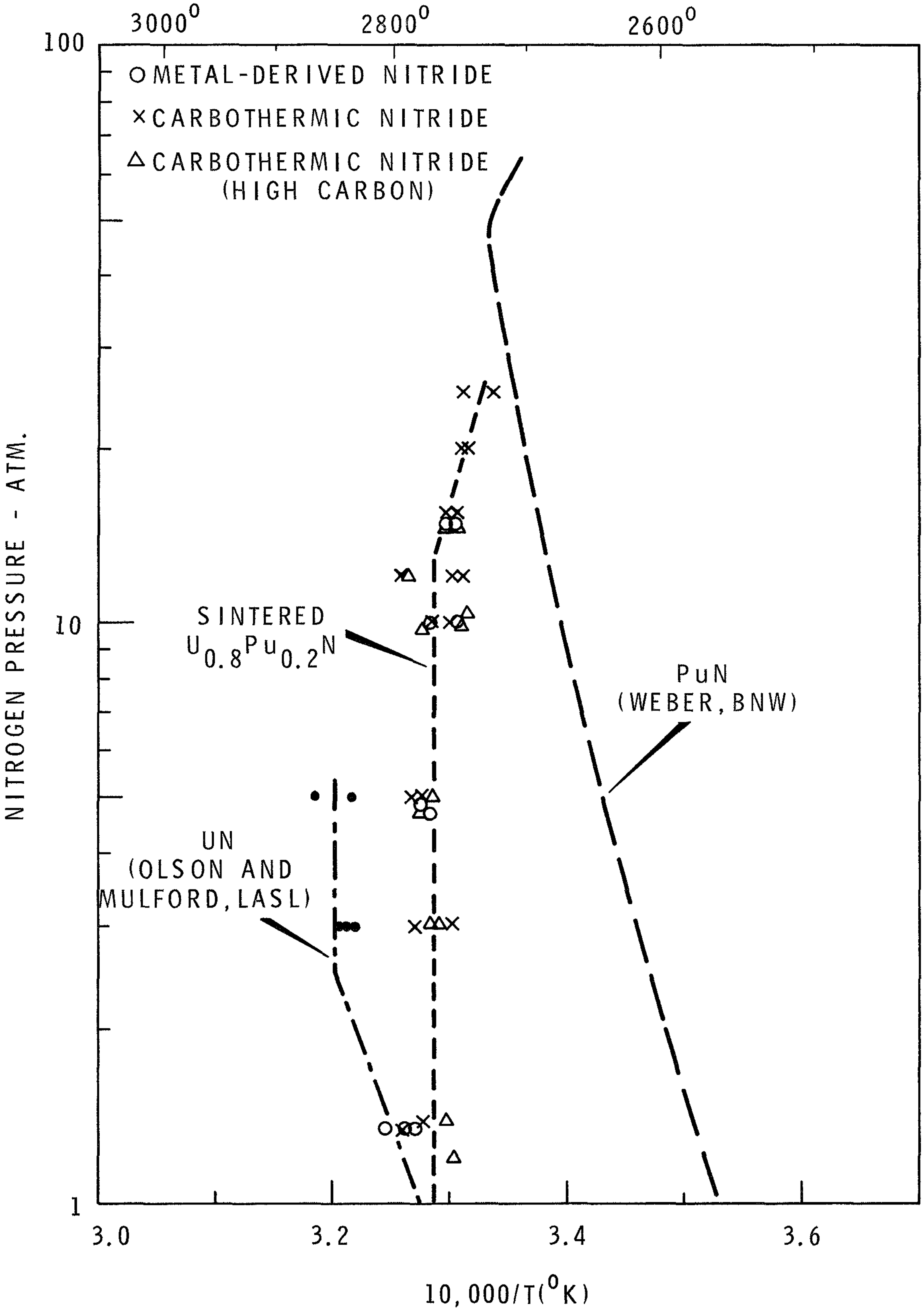
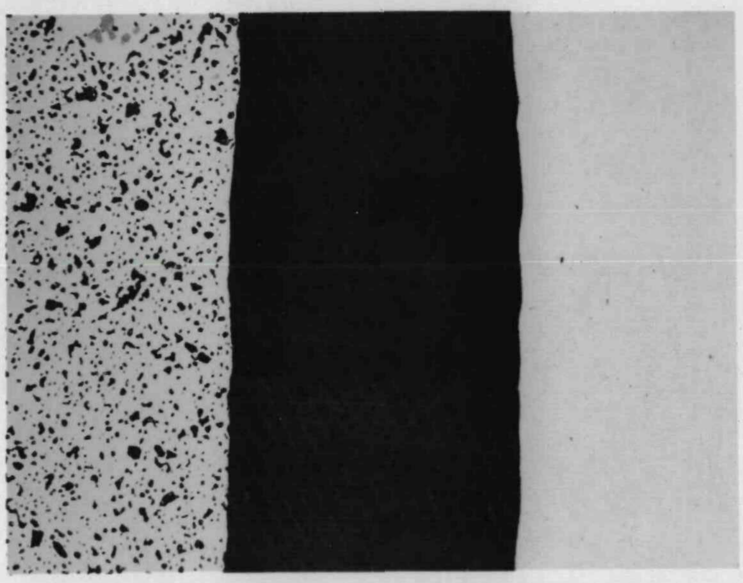


Fig. 7

MICROGRAPHS FROM HIGH CARBON MIXED NITRIDE COMPATABILITY TEST



FUEL ANNULUS CLAD
(Na REMOVED)

RADIAL SECTION (250X)

ETCHED 304 SS CLADDING (150X)

FIG. 8