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FABRICATION OF URANIUM MONONITRIDE COMPACTS

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16. Abstract

Uranium mononitride (UN) compacts were fabricated by cold isostatic pressing and sintering, hot isostatic pressing, and hot extrusion. Fine UN (<1 μm) powder was used for the sintering studies. The effects of sintering temperature and time on the density, grain size, and oxygen and carbon content of the sintered compacts were studied. Coarse (70 to 150 μm) UN powder was compacted by hot isostatic pressing. The effects of pressing pressure, temperature, and canning materials were studied. Also, cursory studies were made on hot extrusion of the coarse UN powder and on machining of sintered compacts.

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FABRICATION OF URANIUM MONONITRIDE COMPACTS

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SUMMARY

Uranium mononitride (UN) is attractive for use in future lithium-cooled nuclear space power reactor concepts. It is necessary to consolidate the UN powder into compacts and machine the compacts to solid or hollow cylindrical pellets for precise assembly into cylindrical fuel pins.

Three methods of densifying UN powder into compacts were investigated. These methods were cold isostatic pressing and sintering, hot isostatic pressing, and hot extrusion. The first method consisted of cold isostatic pressing and sintering of fine (<1 μm) uranium nitride powder. Compacts of 82.5 to 97.8 percent of theoretical density were produced by varying sintering time and temperature. Grain size varied from 2×10^{-4} to 9×10^{-3} cm diameter (ASTM No. 14 to 4). A major problem in processing fine UN powder into compacts is its ready oxidation. The oxygen content of UN compacts, cold isostatically pressed without a binder, decreased during sintering in an argon-nitrogen atmosphere at temperatures up to 2300° C. The carbon content decreased with time at all sintering temperatures investigated.

The second method of densification was hot isostatic pressing of coarse (70 to 150 μm) uranium nitride powder. UN compacts with densities ranging from 95.5 to 99.8 percent of theoretical were produced by varying the pressure and temperature. A potential advantage of this method is that coarse uranium nitride powder picks up very little oxygen compared to fine uranium nitride powder. The carbon content averaged only 10 ppm higher than the starting material.

A cursory study was made on hot extrusion of the coarse uranium nitride powder. The feasibility was demonstrated but cracking occurred because molybdenum extrusion cans were used.

Two methods of machining UN compacts to tolerances required for assembling in fuel pins were tried. Solid and hollow cylinders can be machined to close tolerances by grinding and by electric discharge.

INTRODUCTION

Uranium mononitride (UN) offers promise as a nuclear fuel for future lithium-cooled space power reactors. The properties which make UN attractive for use as a nuclear reactor fuel are its high uranium density, high thermal conductivity, high melting point, and good chemical compatibility with lithium (refs. 1 to 3).

A major disadvantage of UN is that it is pyrophoric in a fine (<20 μm) powder state. Great care must be taken to exclude oxygen and water vapor while handling the UN powder to prevent contamination. Oxygen and water vapor can react with UN to form UO_2 (uranium dioxide), which is undesirable in lithium cooled reactors. If the fuel element cladding possessed a defect, the UO_2 could react with the lithium to form free uranium, which will attack the cladding material at the grain boundaries (refs. 4 and 5). Therefore, all fabrication processes to form UN compacts must be performed in dry boxes with a high purity inert gas atmosphere (<10 ppm each of oxgyen and water). However, after the UN powders are densified into compacts, very little oxygen pickup is observed in air.

Another impurity which seems to be associated with UN is carbon. Carbon could react with the cladding material and cause embrittlement. To prevent this interaction, carbon should be kept at a minimum.

Another disadvantage of UN is that it decomposes into uranium and nitrogen at elevated temperatures in the absence of a nitrogen atmosphere (ref. 6). This probably will not be a serious problem at the operating temperatures ($\leq 1300^{\circ}$ C) presently considered for space power reactors because the extent of decomposition is not significant below about 1500° C. For example, the decomposition pressure of nitrogen over UN at 1400° C is only 10^{-8} atmospheres (10^{-3} N/m^2) (ref. 6) If higher temperatures are needed, only a small nitrogen pressure is required to prevent decomposition.

For reactor designs having different temperature and burnup requirements, UN compacts of various densities and shapes may be needed. Reactors requiring low burnups could rely on the containment of fission products in high-strength, dense compacts. However, containment of the fission products in the fuel is difficult in reactors requiring high fuel burnups. This type of reactor may need either porous UN or dense UN in the shape of hollow cylinders to accommodate fuel swelling. In addition, a small grain size structure with evenly-distributed, interconnected, fine porosity is highly desirable in the fuel to facilitate fission gas release. Several investigators (refs. 1, 2, 3, 6, and 7) have done work on sintering or hot isostatic pressing of UN to product 95 percent dense compacts. But little information is available on the production of high purity UN compacts of various densities and shapes which may be required for lithium-cooled space power reactors.

The purpose of this study was to fabricate and characterize UN compacts made by various methods. Fabrication methods included cold isostatic pressing and sintering,

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TABLE I. - ANALYSES OF URANIUM NITRIDE POWDERS

	Powder lot		
	A	B	C
Physical analysis			
Particle surface area,[a] m^2/g	0.65	0.95	--------
Particle size,[b] μm	.54	.35	70 to 150
Major elements			
Uranium, wt %	94.26	94.20	94.39
Nitrogen, wt %	5.40	5.49	5.67
Oxygen, ppm	2450	2125	485
Carbon, ppm	93	665	80
Trace elements, ppm			
Aluminum	50	50	<20
Arsenic	.4	.4	-----
Boron	.6	2.0	-----
Calcium	7.0	7.0	<25
Chlorine	----	-----	10
Chromium	10	10	10
Cobalt	.1	1.0	<5.0
Copper	5.0	20	<6.0
Fluorine	----	-----	<10
Hydrogen	----	-----	75
Iron	30	100	50
Lead	.7	-----	<5.0
Magnesium	4.0	10	------
Manganese	30	30	<10
Molybdenum	----	-----	<10
Nickel	40	40	10
Phosphorous	.5	2.0	------
Platinum	----	3.0	------
Potassium	7.0	2.0	------
Silicon	30	100	<50
Sodium	4.0	1.0	------
Sulfur	----	-----	<10
Tin	----	-----	<5.0
Tungsten	----	1.0	<25
Zinc	7.0	10	------
Zirconium	----	1.0	<50

[a]Measured by BET method.
[b]Determined from surface area using formula
(4/surface area × density) for irregular particles.

hot isostatic pressing, and hot extrusion. The UN compacts were characterized by metallography, density, grain size, and chemical analysis. In addition, a machining study was conducted on the UN compacts.

FABRICATION OF SINTERED UN COMPACTS

Powder Characteristics

Uranium nitride[1] powder for this investigation was synthesized by the Oak Ridge National Laboratory. The powder synthesis process consisted of multiple hydriding steps of uranium metal and then final nitriding (refs. 3 and 7). Two lots of uranium nitride powder (A and B), which were similar in particle size distribution and purity, were used. The composition and particle size of these two powder lots are given in table I. Slight differences in the oxygen content in the two powder lots were observed (i. e., 2450 ppm for lot A and 2125 ppm for lot B). Great differences were observed in the carbon content in the two powder lots (i. e., 93 ppm for lot A and 665 ppm for lot B).

The nitrogen content reported by our chemical laboratory for both powder lots was about 5.5 weight percent, which is somewhat less than the nitrogen content of stoichiometric UN (5.56 wt % nitrogen). Oak Ridge National Laboratory, however, has indicated that the same type of powder normally contains about 6.5 weight percent nitrogen. Strong indications of both a UN phase and a U_2N_3 (uranium sesquinitride) phase were obtained by X-ray diffraction studies on the two powder lots. No U phase was detected. Thus, there seems to be an inconsistency in the accuracy of the nitrogen content which indicates that the analytical methods for nitrogen are not completely satisfactory. Even if excess nitrogen is present, however, it is not a problem because U_2N_3 is unstable at elevated temperatures. During the sintering operation, nitrogen is evolved and the end product is single phase UN, as indicated by the following:

$$U_2N_3 \rightarrow 2UN + \frac{1}{2} N_2$$
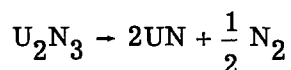
Consolidation of Powder

Uranium nitride powders and pressed compacts were handled in a high purity argon

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[1]The general term uranium nitride is used in this report for powders because the powders used were a mixture of uranium mononitride (UN) and uranium sesquinitride (U_2N_3).

atmosphere dry box. The oxygen and water contents of the argon atmosphere were less than 5 ppm each. Powder for each compact was tap-packed and vibrated into 1/2 inch (1.27 cm) diameter rubber tubes. The packed tubes were sealed, transferred, and pressed isostatically in water at 70 000 psi (480 MN/m^2). No compaction binder was used in this study. The pressed compacts were about 3/8 inch (0.95 cm) in diameter and 3 inch (7.62 cm) long. The pressed compacts were ~55 percent of theoretical density, and the pressed compacts had good green strength and could be easily handled.

The pressed compacts were further consolidated by sintering. Sintering was accomplished in an all-metal furnace consisting of a tungsten heating element with tungsten and molybdenum heat shields. Access to the furnace was through a flowing argon atmosphere dry box so that the pressed compacts were never exposed to air. The sintering schedule consisted of (1) heating to 1500° C in 3 hours, (2) heating from 1500° C to the sintering temperature (1700° to 2500° C) in 1 to 2 hours, (3) holding at sintering temperatures for 2 to 6 hours, (4) cooling to 1500° C in 1/2 hour, (5) holding at 1500° C for $1\frac{1}{2}$ hours, and (6) cooling to room temperature in about 1 hour.

The sintering atmosphere used was either high purity (<5 ppm oxygen and water) argon or an argon-nitrogen mixture. The gas atmosphere pressure was 1 atmosphere (100 KN/m^2) and the flow was regulated at 2×10^{-3} cubic foot per second (5.6×10^{-5} m^3/sec) corrected to standard temperature and pressure. All of the compacts were sintered in an argon atmosphere up to 1500° C and in a mixture of 67 percent nitrogen and 33 percent argon above 1500° C.

Characterization of Sintered UN Compacts

Two variables, sintering temperature and hold time, were studied in this investigation. These variables affected the density, grain size, and oxygen and carbon contents. After sintering the UN compacts were evaluated by metallography, density measurements, and chemical analysis. X-ray diffraction was not sensitive enough to detect any UO_2 phase. The N/U ratios of the sintered compacts varied between 0.943 and 1.01, but no correlation could be made because of the lack of precision and accuracy for the nitrogen and uranium analysis (see appendix for discussion of the methods of chemical analysis). Low nitrogen contents (or N/U ratios of less than 1) were reported for many of the samples. A low N/U ratio should result in free uranium being present in the microstructures, but only single phase UN was observed in microstructures examined by optical metallography.

Density and grain size. - The densities of the compacts reported were taken by the water displacement technique. The theoretical density used for UN in all of the density calculations was 14.32 grams per cubic centimeter. Grain sizes were taken by the

circle intercept method. Compacts with densities lower than 90 percent of theoretical were sprayed with clear lacquer to seal the pores. Several density measurements were repeated to check their reproducibility. Also, several densities were taken by calculating the volume from measured dimensions of a machined compact. These calculated densities from a machined compact confirmed those obtained by water displacement.

The effects of sintering temperatures and hold times on density and grain size are shown in figures 1 and 2. The sintered densities ranged from 82.5 to 97.8 percent of theoretical. The grain sizes varied from 2×10^{-4} to 9×10^{-3} centimeter in diameter (ASTM No. 14 to 4). The compact density and grain size increased with increasing sintering temperature for any given hold time. Similarly, compact density and grain size exhibited slight increases with longer hold times at any given temperature. The greatest increase in density and grain size occurred by increasing the sintering temperature with most of the densification and grain growth occurring in the first 2 hours of sintering. No appreciable difference could be attributed to the use of the two uranium nitride powder lots (A and B)

The effects of sintering temperatures on porosity and grain growth are shown in figure 3. The sintering time for these samples was held constant at 6 hours and the
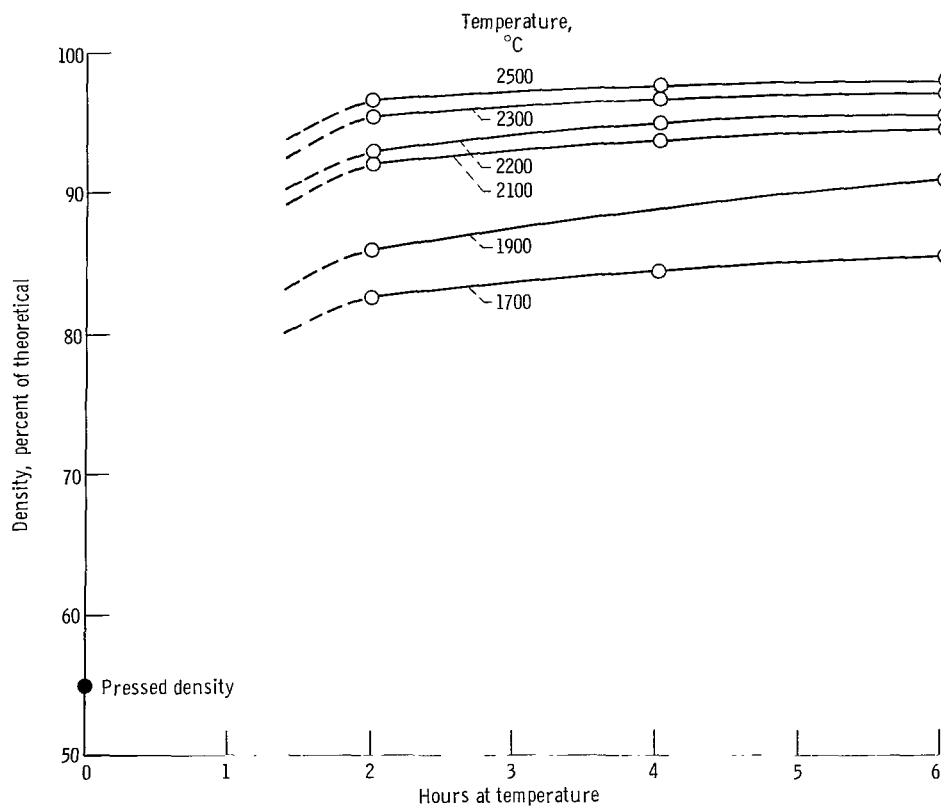
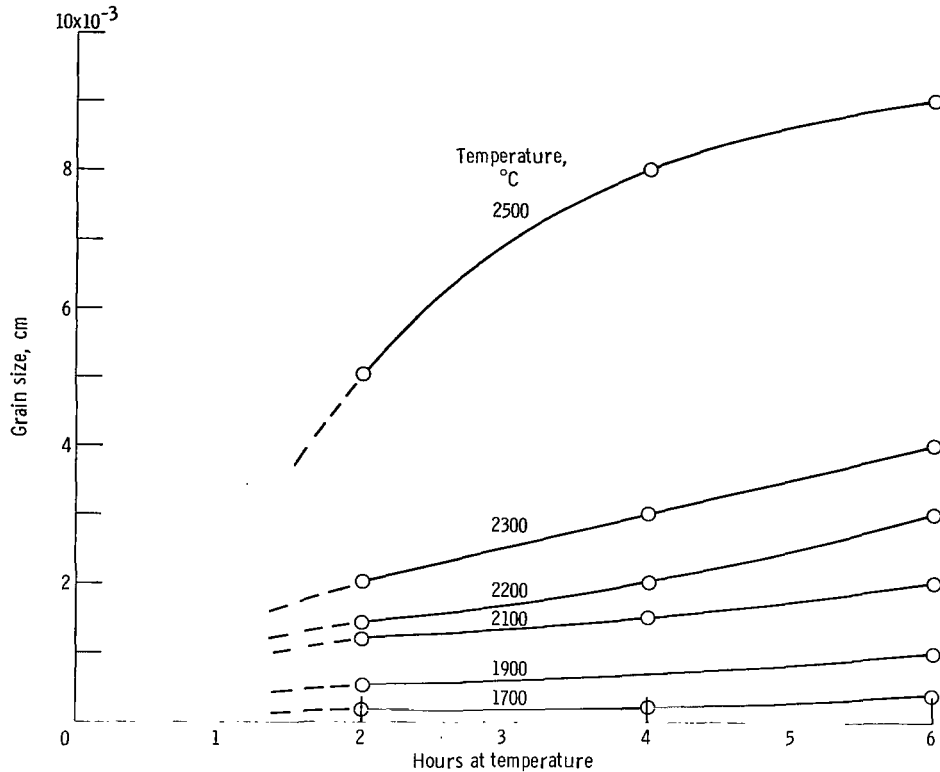Figure 1. - Effect of sintering time and temperature on sintered density of UN compacts.

Figure 2. – Effect of sintering time and temperature on grain size of sintered UN compacts.

temperature was varied from 1700° to 2500° C. The porosity decreases and the grain size increases as sintering temperature increases. Microstructures of UN compacts with a constant sintering temperature (2300° C) and hold times varied from 2 to 6 hours are presented in figure 4. Compact density and grain size increased slightly with longer hold times at any given temperature.

Oxygen and carbon content. – The inert gas fusion method was used to determine the oxygen content in the sintered UN compacts and the uranium nitride powders. No second phase (UO_2) was observed at a magnificantion of 500 in metallographic samples of compacts containing less than 1500 ppm of oxygen.

Figure 5 represents the effects of sintering temperature and hold times on oxygen content. Differences were observed in the two powder lots used in this study. The oxygen content of sintered compacts varied from 418 to 2500 ppm. During sintering powder lot A (2450 ppm oxygen initially) lost more of its oxygen than powder lot B (2125 ppm oxygen initially).
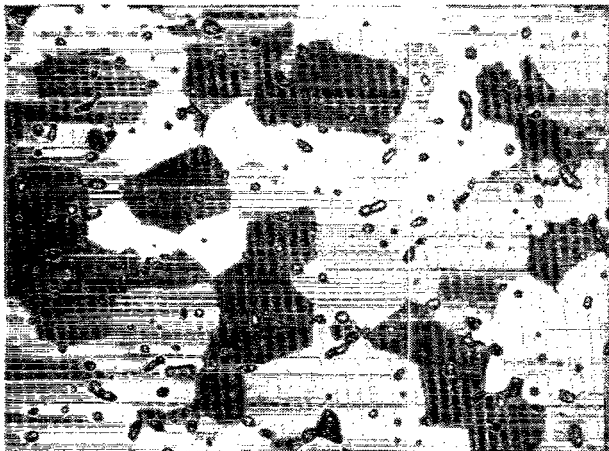
The reason for the different behavior of the two powder lots is not known, but it might be related to how the oxygen is present in the powders. Possibly, the oxygen in powder lot A is present mostly as adsorbed moisture on the surface of the powder. Dur-
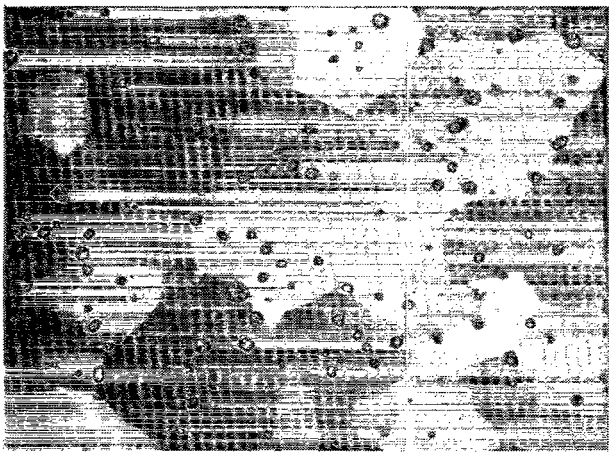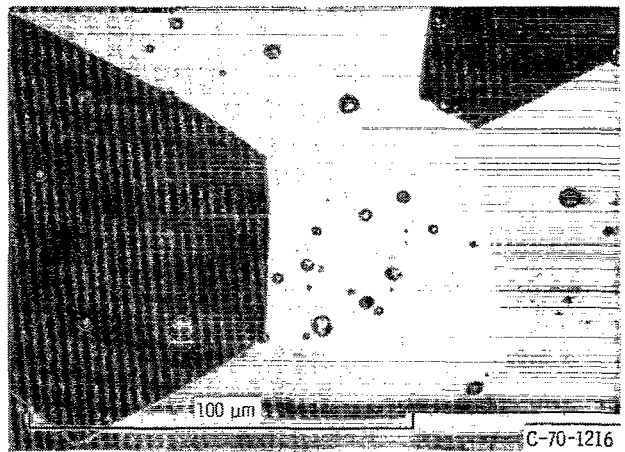
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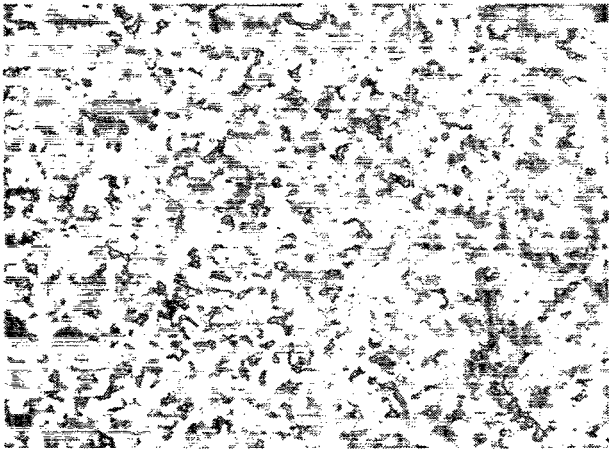
(a) 1700° C.
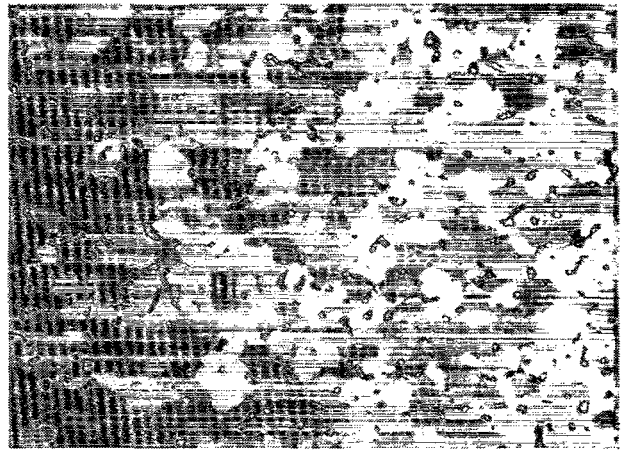
(b) 1900° C.

(c) 2100° C.
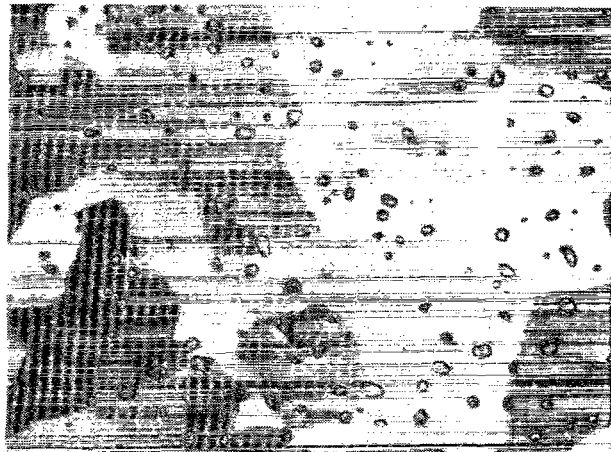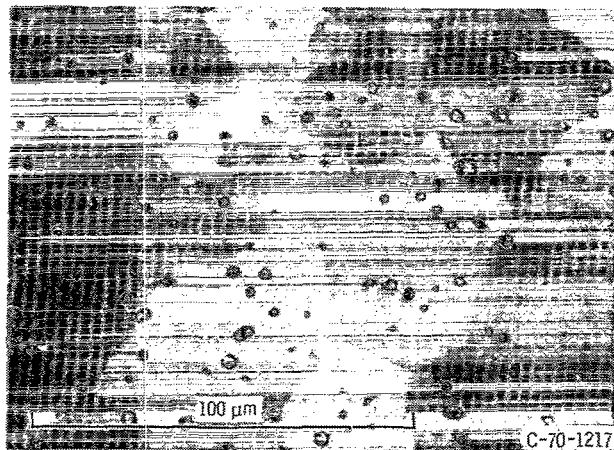
(d) 2200° C.

(e) 2300° C.

(f) 2500° C.

Figure 3. – Microstructures of compacts sintered at various temperatures for 6 hours. Etchant, 60 milliliters lactic acid, 24 milliliters nitric acid, and 2 milliliters hydrofluoric acid. X500.

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(a) 2 Hours.

(b) 4 Hours.

(c) 6 Hours.

Figure 4. – Microstructures of compacts sintered at various times at 2300° C. Etchant, 60 milliliters lactic acid, 24 milliliters nitric acid, and 2 milliliters hydrofluoric acid. X500.

ing sintering the moisture is driven off and the oxygen content drops. In powder lot B, however, the oxygen could be present as a stable UO_2 phase. It is also noted that there is a substantial decrease in oxygen content after 2 hours of sintering, with the exception of the compacts sintered at 2500° C. However, in all cases the oxygen content increased after 2 hours at sintering temperatures. The mechanism for the decrease in oxygen during the first 2 hours is not known, but two possibilities are (1) the oxygen can unite with the carbon impurity and be lost as CO, or (2) the oxygen may be present as water and be driven off as a water vapor. The concommitant reduction in carbon content observed in the analyses tends to support the carbon reduction theory. The rise in oxygen
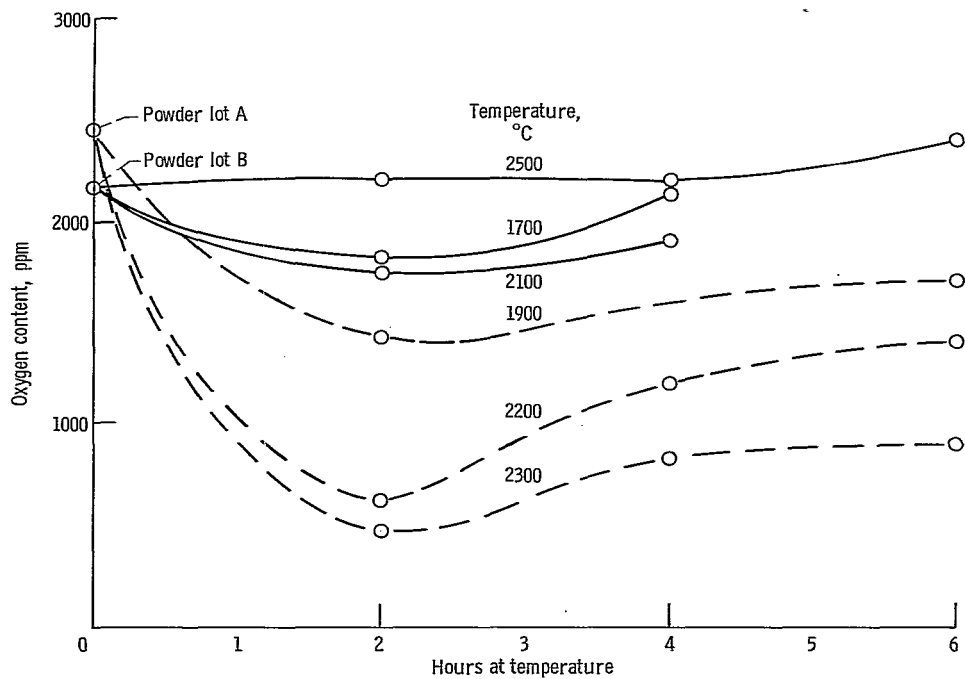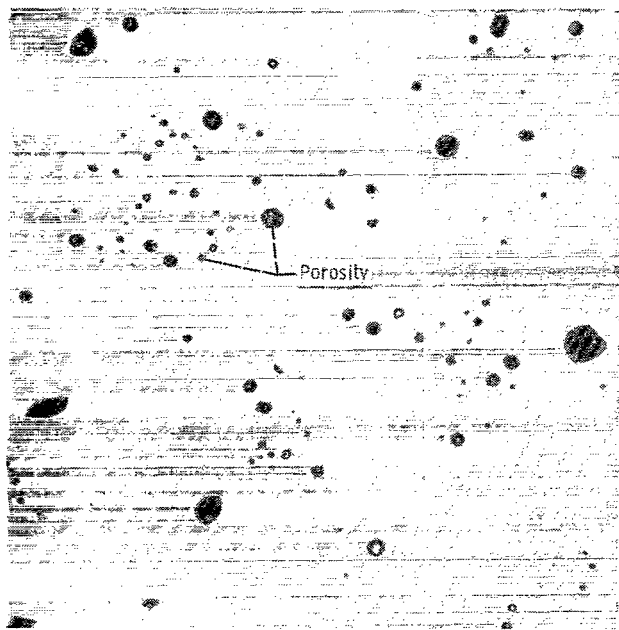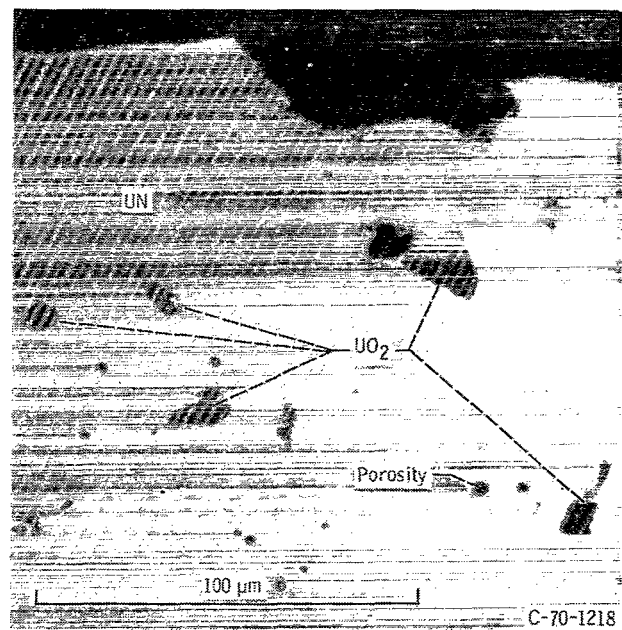
Figure 5. – Effect of sintering time and temperature on oxygen content of sintered UN compacts.

(a) Center of compact.

(b) Outer edge of compact.

Figure 6. – Unetched structure of UN compact sintered at 2500° C for 6 hours. X500.

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content after 2 hours at temperature may be attributed to the reaction of UN with the oxygen impurity of the furnace atmosphere.

The UN compacts sintered at 2500° C for 6 hours contained a UO_2 phase on the outer edge. This is illustrated in figure 6. Figure 6(a) shows the center of the compact sintered at 2500° C for 6 hours: there is no evidence of a UO_2 phase in the center of this sample. However, at the outer edge of the compact, as illustrated in figure 6(b), an appreciable amount of UO_2 was present. Because this UO_2 phase is on the outer edge only, the UN may have reacted with the oxygen impurity in the furnace atmosphere.

The carbon contents reported for the sintered compacts were determined by the combustion method. Triplicate samples were run and were in close agreement with each other. The effect of sintering temperature and hold times on carbon content is shown in figure 7. It should be noted that the two lots of powder had different carbon contents (93 ppm for lot A and 665 ppm for lot B). All of the sintering conditions resulted in reductions in carbon content with most of the decrease occurring during the first 2 hours of sintering. This is particularly apparent in the compacts produced from lot B powder with higher initial carbon content. The decrease in carbon content during
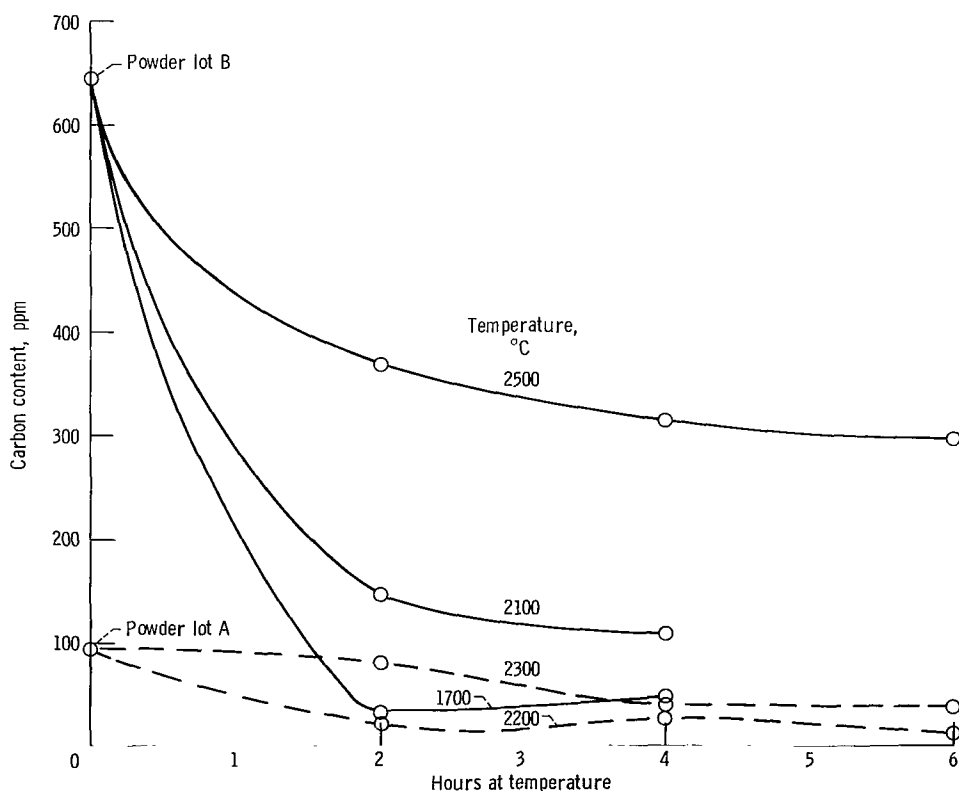

Figure 7. – Effect of sintering time and temperature on carbon content of sintered UN compacts.

sintering probably can be attributed to the carbon uniting with the oxygen impurity of the furnace atmosphere and also with the oxygen in the powder.

Discussion of Sintering Results

The sintering parameters selected for producing UN fuel should depend on the reactor application and on the fuel characteristics desired. The UN fuel could be in the form of dense hollow cylinders or a porous structure with interconnected porosity. In either case, a small grain size would be an advantage for better fission gas release. The oxygen and carbon contents should be kept as low as possible. Oxygen could cause problems if a fuel pin developed defects and lithium came in contact with the fuel, and carbon could cause embrittlement of the fuel cladding. The results of this investigation have shown that to keep the oxygen content at a minimum, the compacts should be sintered at temperatures less than 2500° C with hold times of 2 hours or less. These sintering conditions would still lower the carbon content considerably since most of the reduction in carbon occurred in the first 2 hours of sintering.

The results obtained from this sintering study indicate that both dense and porous UN structures can be fabricated. Since both the density and grain size increase with increasing temperature and hold time, it would be difficult to produce a dense structure with a small grain size. Thus, for a specific application, a compromise may be necessary between grain size and density. Low density (85 percent) compacts with a porous structure and a fine grain size can be produced by sintering the UN at lower temperatures (i. e. , 1900° C) This low density structure is ideal for fission gas release and for minimizing the effects of fuel swelling. However, because of the low sintering temperature, the structure may be unstable at the operating temperature of the reactor, and some sintering and densification could occur.

HOT ISOSTATIC PRESSING OF UN COMPACTS

Powder Characteristics

A coarse uranium nitride powder obtained from Nuclear Materials and Equipment Corporation was used for this investigation. This powder was made by direct nitriding of uranium metal chips. The uranium nitride particles were irregular in shape and were 70 to 150 micron in diameter. The composition and particle size are given in table I (powder lot C). This powder had a higher nitrogen content (5. 67 wt %) and lower oxygen (485 ppm) and carbon (90 ppm) contents than the finer powders used in the sintering

studies. Coarse powder was used for this study because it is less reactive (i.e., less surface area) than the fine powder used in the sintering study. Thus, oxygen contamination of the powder during processing should be less.

Fabrication

The coarse uranium nitride powder was loaded and vibrated into containment cans (1/4 in. or 0.6 cm diam by 3 in. or 7.6 cm long) of several different materials through a 0.050 inch (1.3 mm) diameter hole. Different canning materials were investigated because of difficulties in producing a crack-free compact. (Effects of different canning materials on cracking of compacts made from coarse uranium nitride powder and from sintered pellets will be discussed later.) After the cans were loaded, wire of the same composition as the containment can was inserted into the fill hole and the can was sealed in vacuum by electron beam welding. All cans were leak checked by first externally pressurizing with 50 psi (3.45×10^5 N/m^2) helium and then submerging the cans in alcohol to detect any helium bubbles from leaks. Before pressing the cans were wrapped in tantalum sheet to act as a getter to avoid contamination while pressing. The cans were hot isostatically pressed at various pressures and temperatures in a cold-walled autoclave with helium as the pressurizing gas.

Effects of Compaction Conditions

This study involved two variables: (1) pressing pressures of 15 000 psi (104 MN/m^2) and 30 000 psi (207 MN/m^2); and (2) temperatures of 1370°, 1535°, and 1650° C. Hold times at temperature were kept constant at 1 hour. These variables affected the density and the grain size of the UN compacts. Molybdenum tubes from a commercial supplier were used for canning material in this study. The inside surface of these tubes, although cleaned of the die lubricant from their manufacture, still contained a large amount of carbon. After pressing, the compacts were evaluated by metallography, density measurements, and chemical analyses. Only the center of the samples was used for the evaluations because of radial and circumferential cracking of the UN near the surface of the canning material.

Density. - The densities reported in this investigation were obtained by the water displacement technique. Several density measurements were made to check their reproducibility. Densities were also confirmed from the dimensions and weight of a machined compact.

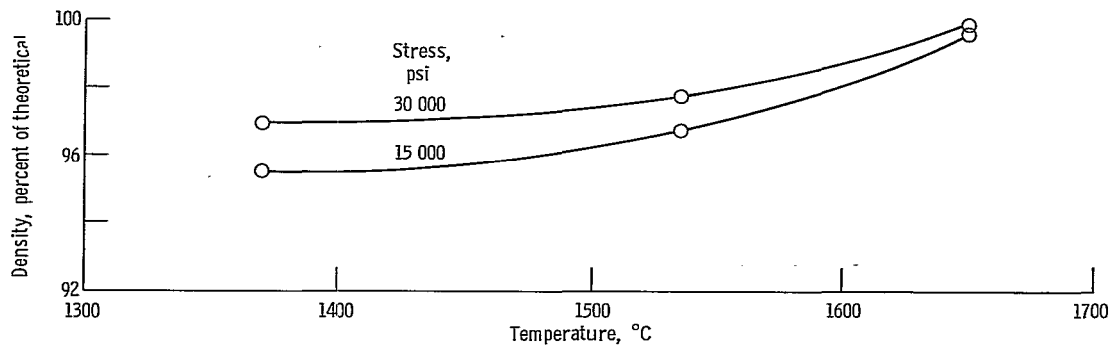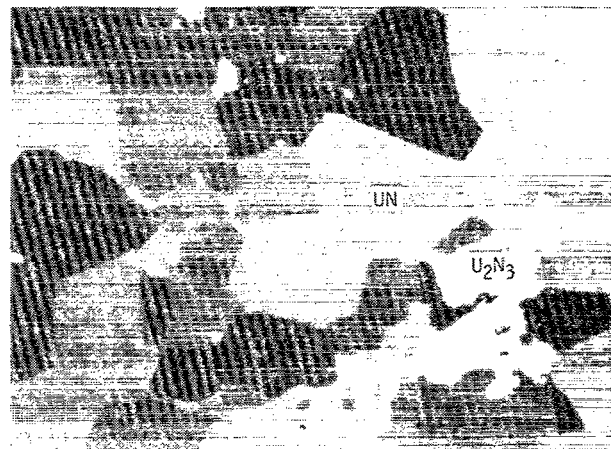The effect of pressure and temperature upon density of hot isostatically compacted
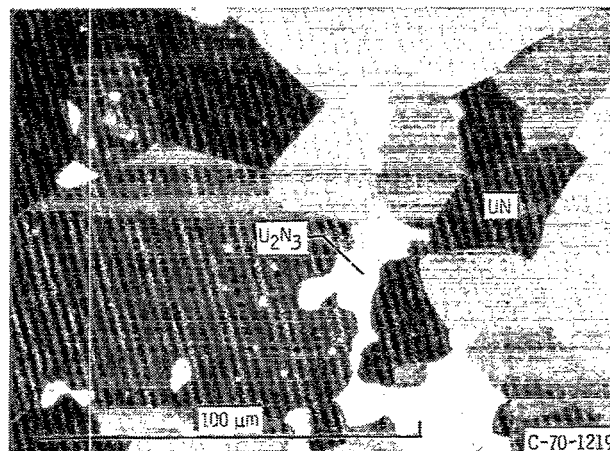
Figure 8. – Effect of pressing temperature and pressure on density of hot isostatic pressed UN compacts. Hold time at temperature, 1 hour.

(a) 1370° C; 96.9 percent of theoretical density.

(b) 1535° C; 98.2 percent of theoretical density.

(c) 1650° C; 99.8 percent of theoretical density.

Figure 9. – Microstructures of compacts hot isostatically pressed at 30 000 psi (207 MN/m^2). Etchant, 60 milliliters lactic acid, 24 milliliters nitric acid, and 2 milliliters hydrofluoric acid. X500.

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coarse uranium nitride powder is shown in figure 8. Densities varying from 95.5 percent of theoretical to almost theoretical density (99.8 percent) were achieved. Although no attempts were made in this study to achieve lower densities, I assume that lower densities could be achieved, if desired, either by lowering the pressure or the pressing temperature.

Microstructure and grain size. - Some typical microstructures of UN pressed at 30 000 psi (207 MN/m^2) and temperatures of 1400°, 1535°, and 1650° C are shown in figure 9. Note that in the etched structure, it is difficult to distinguish any porosity. But, to show that porosity is present, an unetched microstructure of the same compact as shown in figure 9(b) is shown in figure 10.
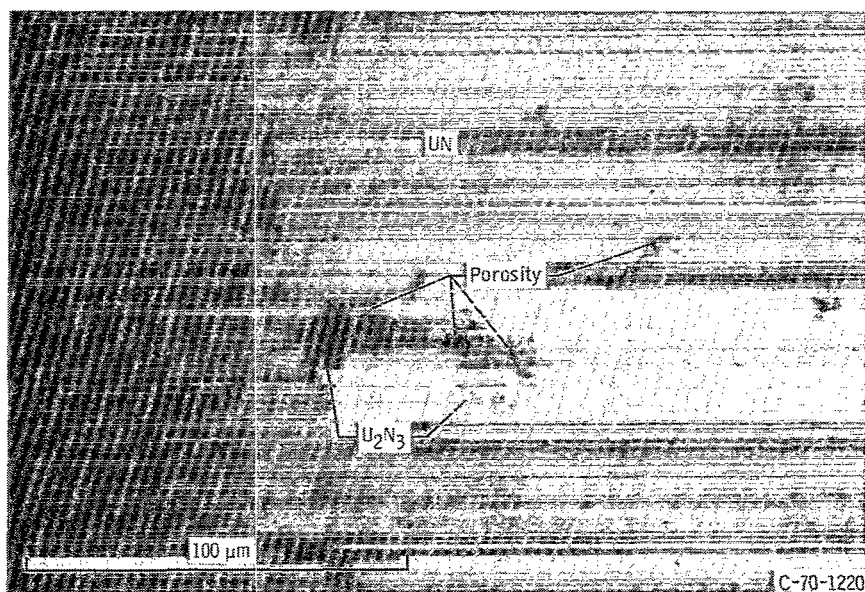

Figure 10. - Microstructure of compact hot isostatically pressed at 30 000 psi (207 MN/m^2) and 1535° C. Unetched; 96.2 percent of theoretical density. X500.

Figure 9 also indicates that the compaction temperature affects grain size. Specimens pressed at different pressures with the same pressing temperature were almost identical in grain size. However, in compacts pressed at different temperatures, grain sizes were much larger at 1650° C than at the two lower temperatures.

A second phase appeared in all of the pressed compacts. Electron microprobe analysis identified this phase as being similar to UN. The amount of nitrogen could not be identified because of uranium interference. But by metallographic examination, this second phase was identified as a U_2N_3 phase. The presence of U_2N_3 is not surprising

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in view of the high nitrogen content (5.67 percent) of the UN powder. Methods to eliminate this U_2N_3 phase will be discussed in detail later.

Effects of Canning Materials

Four types of canning materials were investigated in an attempt to produce a crack-free compact. These materials were (1) molybdenum cans made from tubes from a commercial vendor, (2) molybdenum cans made from high purity molybdenum sheet, (3) columbium - 1 percent zirconium (Cb-1 percent Zr) cans made from tubes from a commercial vendor, and (4) ingot iron cans machined from solid stock.

Two types of UN were pressed using each canning material: (1) sintered compacts (95 percent dense) made by sintering of fine uranium nitride powder (lot B), and (2) unsintered, coarse uranium nitride powder. A small amount of a UO_2 phase was observed in the sintered compacts before hot isostatic pressing. All pressings were made at 30 000 psi (207 MN/m^2) and 1370° C with a hold time of 1 hour. The pressing temperature of 1370° C was selected to stay appreciably below the melting point of the iron cans (1535° C). The compacts made from the coarse uranium nitride powder achieved a density of 96.9 percent of theoretical, but the sintered compacts did not increase in density after pressing. No appreciable difference in density could be noted as a result of the different canning materials.
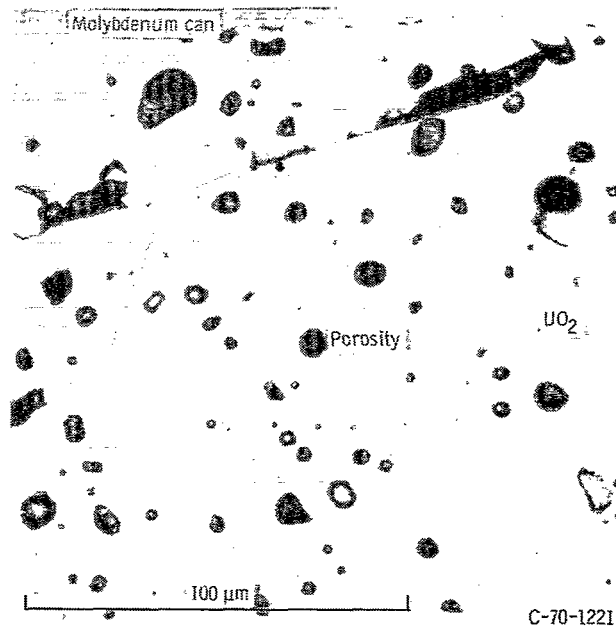
Compacts pressed in molybdenum cans made from a commercial tubing had severe radial and circumferential cracks in both pressed powders and sintered compacts (fig. 11). This cracking is attributed to the great difference between the total thermal expansion of molybdenum and UN and also to the possible bonding between UN and molybdenum at the interface. The UN compacts were subjected to tensile stresses upon cooling because the UN contracted more than the molybdenum can. The total thermal contraction of molybdenum from 1370° C to room temperature is 8.5×10^{-3} centimeter per centimeter, while the total thermal contraction for UN from 1370° C to room temperature is 13.0×10^{-3} centimeter per centimeter.

Cracking was less severe in both types of pressings (powder and sintered compacts) using the high purity molybdenum cans (fig. 12). The pressed sintered compact showed only circumferential cracking near the interface. The reasons for the lesser degree of cracking are not understood.

Compacts pressed in ingot-iron cans showed the best results. No cracking of the UN or separations between the UN and the can was observed (as illustrated in fig. 13). These UN compacts were subject to compressive stresses upon cooling because the iron can contracts more than the UN fuel. The total thermal contraction of iron from 1370° C to room temperature is 20.0×10^{-3} centimeter per centimeter (i.e., 7.0×10^{-3} cm/cm
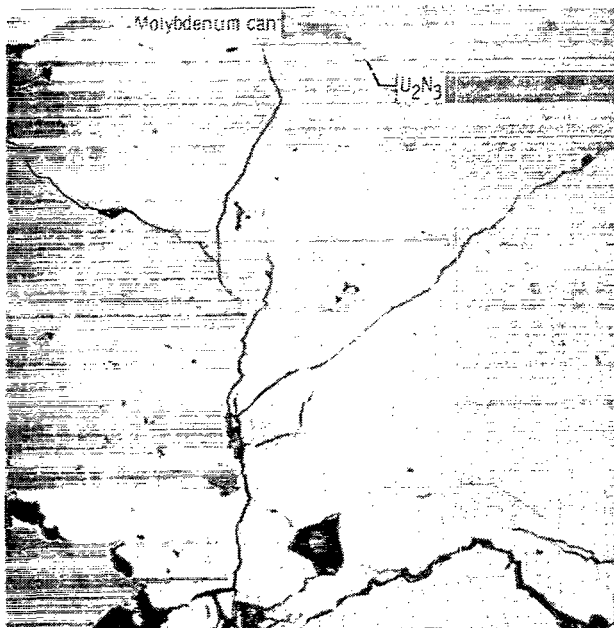
16

(a) Hot isostatically pressed coarse powder.

(b) Hot isostatically pressed UN pellet made from fine UN powder (cold isostatically pressed and sintered).

Figure 11. – UN compacts hot isostatically pressed in commercial molybdenum cans at 30 000 psi (207 MN/m^2) and 1370° C for 1 hour. Unetched. X500.

(a) Hot isostatically pressed coarse powder.

(b) Hot isostatically pressed UN pellet made from fine UN powder (cold isostatically pressed and sintered).

Figure 12. – UN compacts hot isostatically pressed in high purity molybdenum cans at 30 000 psi (207 MN/m^2) and 1370° C for 1 hour. Unetched. X500.
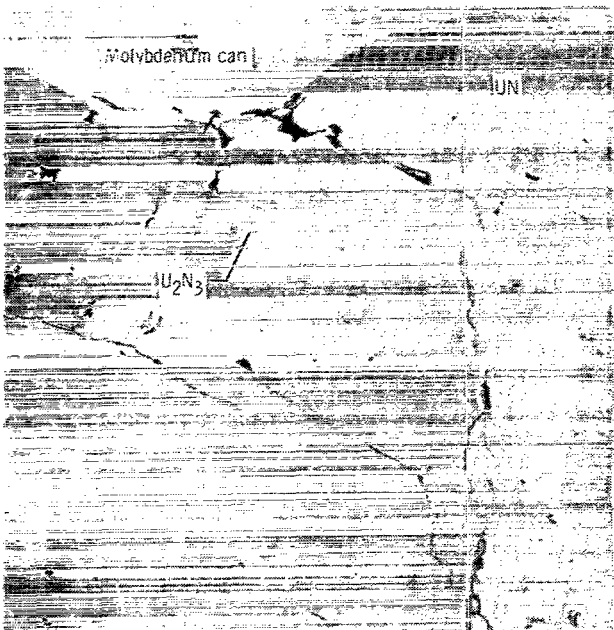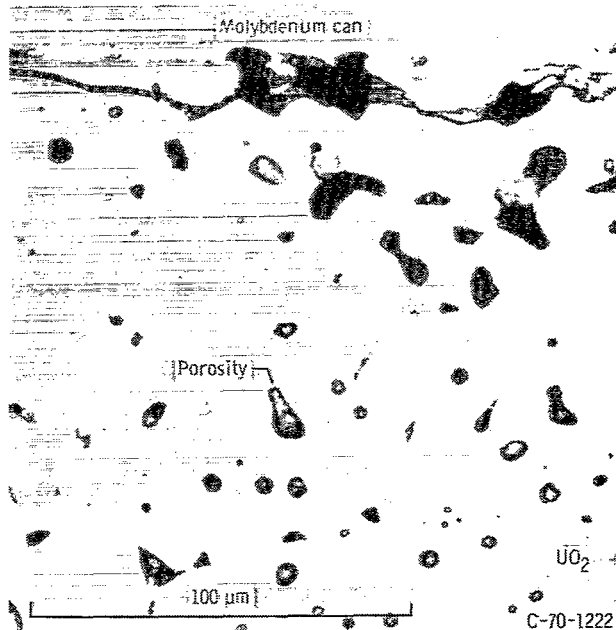
17

(a) Hot isostatically pressed coarse powder.

(b) Hot isostatically pressed UN pellet made from fine UN powder (cold isostatically pressed and sintered).

Figure 13. – UN compacts hot isostatically pressed in ingot iron cans at 30 000 psi (207 MN/m^2) and 1370° C for 1 hour. Unetched. X500.
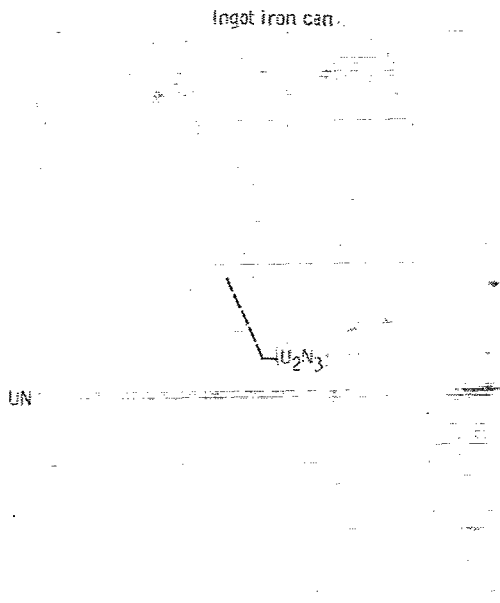

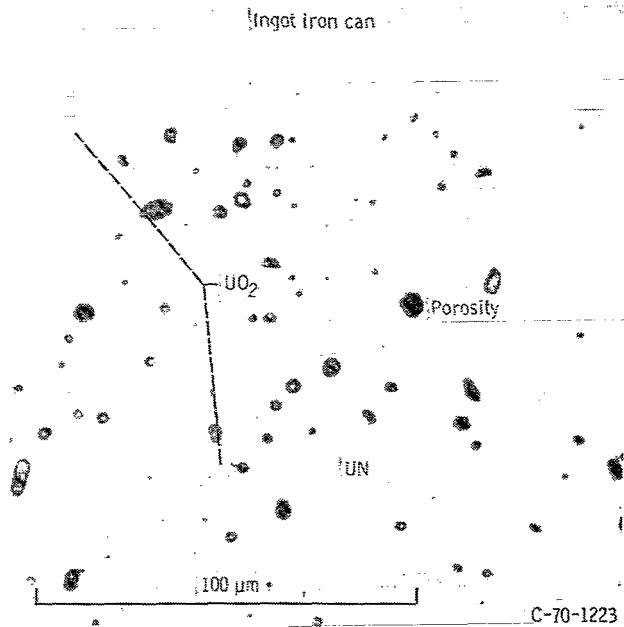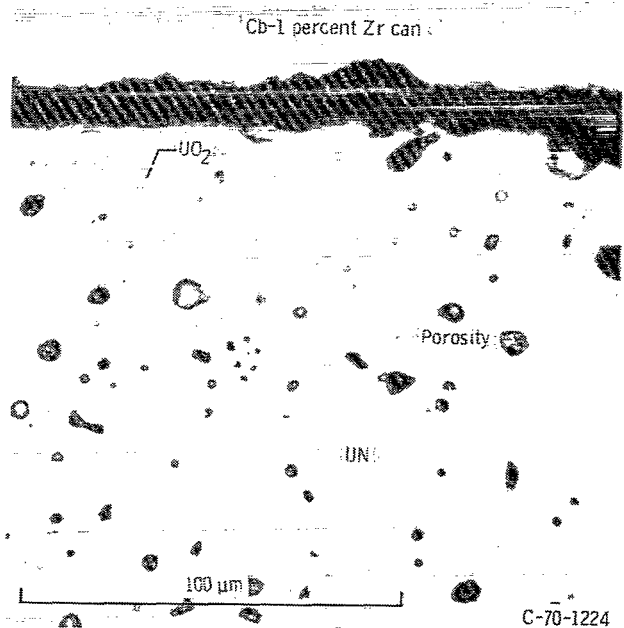(a) Hot isostatically pressed coarse powder.

(b) Hot isostatically pressed UN pellet made from fine UN powder (cold isostatically pressed and sintered).

Figure 14. – UN compacts hot isostatically pressed in columbium-1 percent zirconium cans at 30 000 psi (207 MN/m^2) and 1370° C for 1 hour. Unetched. X500.

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greater than that for UN). A very irregular interface between the UN compacts and the iron resulted from the softness of the iron at the compaction temperature. This effect was not observed where the pressed and sintered UN compact was used, presumably because the UN did not deform in this compaction attempt.

Compacts pressed in Cb - 1 percent Zr cans (fig. 14) also showed good promise in respect to avoiding cracking of the UN. However, the UN in the form of unsintered coarse powder did not completely densify. This probably was because a leak developed while pressing. No cracking in the UN samples could be detected, and there was no indication of bonding between the Cb - 1 percent Zr can and UN compacts. The separation between the UN and the Cb - 1 percent Zr can probably results from the tensile stresses caused by the lower thermal expansivity of the Cb - 1 percent Zr can $(11.5 \times 10^{-3}$ cm/cm at 1370° C). Apparently, the bonds between the UN and the Cb - 1 percent Zr cans were weaker than those achieved with the molybdenum cans.

This study of canning materials demonstrated that crack-free UN can be hot isostatically pressed in the size range studied here. But the limitations involved in using ingot iron and Cb - 1 percent Zr cans should be taken into account. Separations, which occur between the Cb - 1 percent Zr can and the UN, could be undesirable because of the possibilities of producing cracked compacts. If ingot iron is used as a canning material, a maximum practical temperature of only 1400° C can be used to avoid melting of the can because of the temperature gradient in the hot isostatic pressing furnace. This low temperature hinders densification. A maximum density of only 96.6 percent of theoretical was achieved in hot isostatically pressing coarse uranium nitride powder using ingot iron as a canning material.

Effect of Presintering

To produce a single phase UN compact, a test was set up to eliminate the U_2N_3 phase that was observed in the previous hot isostatic pressings. It was assumed that the U_2N_3 phase was formed because of the high nitrogen content (5.67 percent) in the coarse uranium nitride powder. A compact was prepared by cold hydrostatic pressing the coarse uranium nitride at 70 000 psi (480 MN/m^2) and sintering at 1700° C for 2 hours under the same conditions used for the sintering studies described earlier. The purpose of this heat treatment was to produce single phase UN, since U_2N_3 readily decomposes above 1500° C to form UN and nitrogen. After sintering, the compact was approximately 75 percent dense and contained no observable U_2N_3 phase (fig. 15). The sintered compact was loaded in an ingot iron can which was then electron beam welded in a vacuum. The compact was hot isostatically pressed at 30 000 psi (207 MN/m^2) and 1370° C with a hold time of 1 hour. Figure 16 confirms that the U_2N_3 phase was elim-
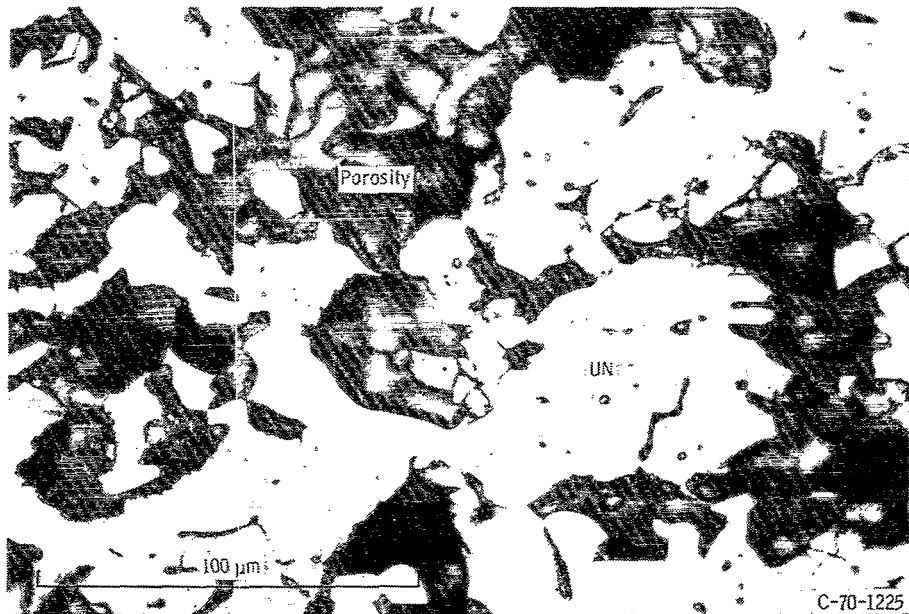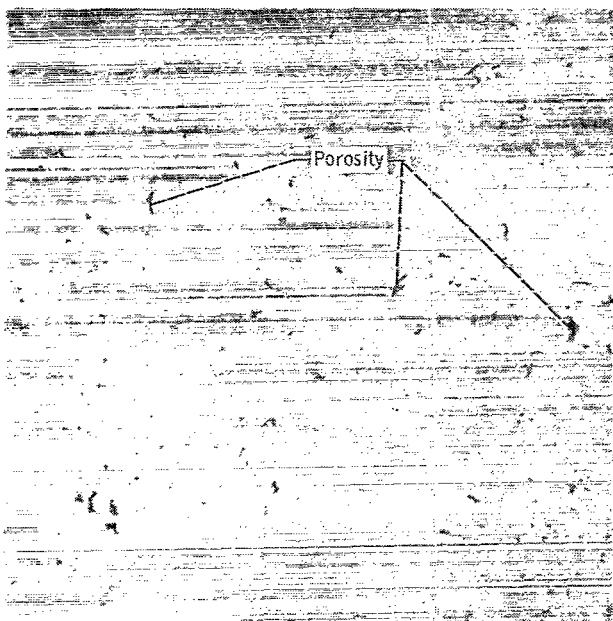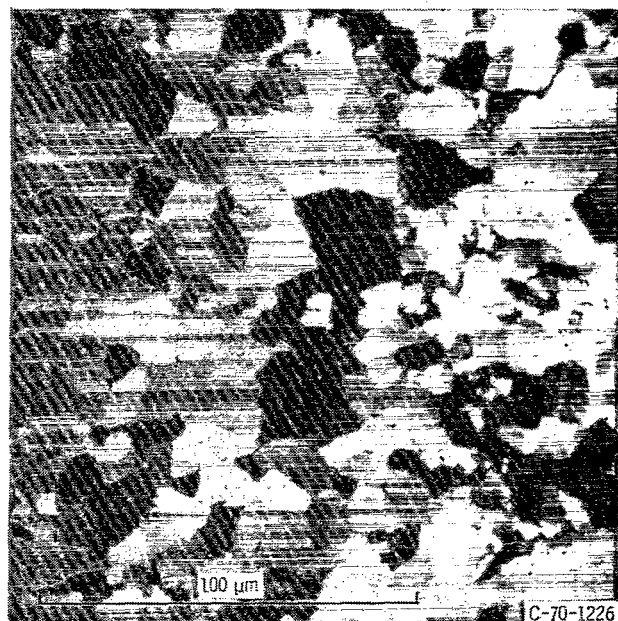
Figure 15. – Sintered UN compact made from coarse UN powder. Sintered at 1700° C for 2 hours. Unetched. X500.

(a) As polished.

(b) Etched. Etchant, 60 milliliters lactic acid, 24 milliliters nitric acid, and 2 milliliters hydrofluoric acid.

Figure 16. – Hot isostatically pressed UN compact (cold isostatically pressed and sintered at 1700° C before hot pressing). X500.

inated. The density of the compacts (96.2 percent of theoretical) was slightly lower than for a one-step hot-pressing of the UN powder (96.9 percent). This slight drop in density could be attributed to the fact that the particles were bonded together in sintering and hindered the movement of particles while pressing.

Chemical Analysis

Several of the hot isostatically pressed UN compacts were analyzed for oxygen, carbon, and nitrogen. The analyses indicate that there was no increase in oxygen content from the starting powder (485 ppm) since the average oxygen content of the compacted samples was 480 ppm. The carbon content of the compacts averaged 90 ppm, which is only slightly higher than the starting carbon content of the powder (80 ppm). The nitrogen content of the compact that was heat treated prior to hot isostatic pressing decreased from 5.67 to 5.46 weight percent N. This, together with a single phase microstructure, indicates that the UN is probably stoichiometric. It is concluded that a high purity single phase UN compact can be produced by hot isostatic pressing from high purity coarse powder containing excess nitrogen if the powder is heat treated properly to remove excess nitrogen prior to pressing.

EXTRUSION OF UN POWDER

The purpose of this study was to take a cursory look at extrusion of UN powder as a method for producing a fully dense UN compact. Five molybdenum extrusion cans loaded with the coarse uranium nitride powder (lot C) were extruded. The extrusion cans were 2.1 inches (5.3 cm) in outside diameter and 4.5 inches (11.5 cm) long and had inside dimensions of 1.25 inches (3.2 cm) diameter and 2.5 inches (6.4 cm) length. After loading, a molybdenum plug was inserted into the fill hole and electron beam welded in a vacuum. Four of the billets were extruded at 2200° C with 16:1, 12:1, 10:1, and 6:1 reduction ratios. The fifth billet was extruded at 1300° C with a reduction ratio of 6:1. The purpose of the latter extrusion was to see if UN powder could be extruded at a relatively low temperature.

All of the 2200° C extrusions showed promise, but cracking occurred in the UN because of the difference in thermal expansion and bonding between UN and molybdenum. This cracking is very similar to the cracking that occurred in hot isostatic pressing. Disregarding the cracking effect, UN powder can be extruded to very high densities. The microstructure of a UN sample extruded at 2200° C with a reduction ratio of only

Figure 17. – Crack-free area of UN compact made by extruding coarse UN powder in molybdenum cans at 2200° C with reduction ratio of 6:1. Etchant, 60 milliliters lactic acid, 24 milliliters nitric acid, and 2 milliliters hydrofluoric acid. X500.

6:1 is shown in figure 17. The highly dense, very coarse grain size structure is typical of extruded UN.

The extrusion at 1300° C with a reduction ratio of 6:1 did not appear promising. These extrusion conditions produced a severely-cracked partially-bonded structure. Although other attempts at 1300° C extrusion were not made, it is possible that higher reduction ratios and/or extrusion rates could result in better UN compacts at this extrusion temperature.

MACHINING OF UN COMPACTS

The purpose of this machining study was to precisely machine solid and hollow cylinders to close tolerances for easy assembly into cylindrical fuel pins. Two methods of machining 95 percent dense sintered UN compacts made from fine uranium nitride powder were investigated. These were grinding and electric discharge machining (EDM).

Centerless and cylindrical grinders with water as a coolant were used for the grinding studies. A soft 100-grit silicon carbide wheel produced the best grinding results. No precautions were needed to protect the UN from contamination. Visual examination indicated very little or no oxidation of the UN. This was confirmed by chemical analysis

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of representative samples. If necessary, the surface can be slightly sanded in an inert atmosphere dry box to eliminate any possible oxide on the surface.

Various sizes of UN compacts, ranging in diameter from 0.100 inch (0.25 cm) to 1/2 inch (1.3 cm) and approximately 3 inches (7.6 cm) long, were successfully ground. Tolerances could be held within ±0.0005 inch ($\pm 1.27 \times 10^{-3}$ cm). The surface finish was equivalent to 32 microinches rms (81.3×10^{-6} cm rms).

The EDM process was investigated as a possible machining method because, unlike most ceramics, UN has a sufficient electrical conductivity for the EDM process. Holes of various sizes and crosscuts were made in surface ground UN specimens. Examples are shown in figure 18. The surface finish produced by the EDM process can be con-

Figure 18. – Machined UN specimens by grinding and electric discharge machining. X2.

trolled by varying the frequency and the amount of capacitance while machining. The best surface finish (32 rms) was produced by using the finest feed (low capacitance and high frequency). Brass or tantalum electrodes produced the fastest cut and best surface of the materials tried.

Because carbon pickup from the oil bath on the surface of the work piece occurs in the EDM process, several samples were analyzed for carbon. The carbon content was increased about 75 ppm in each sample. However, after a few mils were ground from the EDM surface, the carbon content decreased to the original amount.

From the above machining results, it is concluded that UN compacts can be machined to produce shapes and tolerances which may be necessary for nuclear reactor fuel elements.

COMPARISON OF UN FABRICATION METHODS

Sintering of fine uranium nitride powder, hot isostatic pressing of coarse uranium nitride powder, and extursion of coarse uranium nitride powder were the three methods

used in this study to fabricate UN compacts. The purpose of this section of the report is to compare these three methods of fabricating UN compacts and to indicate areas needing further study.

Sintering of fine uranium nitride powder is the least expensive method of fabricating UN compacts. Hot isostatic pressing and extrusion are more expensive because of the complex equipment required and the cost of the expendable canning materials. Another advantage of sintering UN compacts is that a wide range of densities and grain sizes can be easily achieved. The amount of porosity in a sintered compact can be easily controlled. However, this porosity may not be evenly distributed and completely interconnected because the particles contain a range of particle sizes and are irregular in shape. The fines could cause agglomerated sintering to produce dense spots, and the irregular particles could cause stoppage of passages for complete interconnected porosity.

Unfortunately, the sintering process also has some disadvantages. The critical one is that very fine powder must be used to produce highly dense compacts and the fine powder is more prone to oxygen contamination. Thus, the handling and sintering steps must be carefully controlled. However, if low density compacts are desired, a coarser powder can be used and the possibility of contamination by oxygen can be reduced.

Hot isostatic pressing of coarse UN powder probably can be used to produce either highly dense or porous UN compacts. Low oxygen content compacts can be fabricated because large particles with a much smaller surface area can be used. No oxygen pickup was observed in the hot isostatic pressed UN compacts. Another advantage of the hot isostatic pressing method is that porosity can be controlled, and if the particles are shaped properly (i. e., spherical), interconnected porosity can be produced for fission gas venting purposes. However, if a very fine porosity and a small grain size are needed, this process has no advantages over sintering because very fine UN powder must be used. Additional work is needed to investigate lower compaction temperatures and measures.

The extrusion method probably could be developed to produce fully dense crack-free UN compacts. However, this would be an expensive method and would be limited to producing dense structures. Additional work is needed to investigate extrusion at lower temperatures, which should result in finer UN grain sizes. Lower extrusion temperatures would allow other canning materials to be used which might eliminate the cracking of the UN.

In summary, the fuel element requirements (e. g., fuel burnup, density, type of porosity, and purity level) will largely dictate the method of fabrication. At the present, more work is needed on the sintering method to produce compacts from larger particles. Stable porous UN compacts with fine interconnected porosity and a small grain structure could be made which would be ideal for fission gas release and fuel swelling. An additional advantage is that a coarse powder would be less prone to oxygen contamination.

Also, more work is needed to investigate hot pressing parameters of UN powders of various particle sizes and shapes (spherical and nonspherical) to produce the type of UN compacts that might be required in space power reactors.

CONCLUSIONS

Three methods of fabricating uranium mononitride (UN) compacts were investigated. These methods were cold isostatic pressing and sintering, hot isostatic pressing, and hot extrusion. Two methods for machining UN compacts, grinding and electric discharge machining, were also investigated.

The following major results were obtained using the method of cold isostatic pressing and sintering of fine uranium nitride powders.

1. UN compacts of densities ranging from 82.5 to 97.8 percent of theoretical were made by varying the sintering temperature and time. In all cases observed, most of the densification took place within the first 2 hours at sintering temperature.

2. The major contaminants (carbon and oxygen) in the UN and excess nitrogen can be reduced during sintering. There was a substantial decrease in oxygen content of the UN during the first 2 hours of sintering for all conditions except for the highest sintering temperature (2500° C) investigated. The lowest oxygen content obtained was 418 ppm after sintering for 2 hours at 2300° C. Sintering times of 2 hours or less are recommended to keep oxygen content to a minimum because for longer times the oxygen content increased above that observed in compacts sintered for 2 hours. The carbon content decreased with increasing time for all sintering temperatures with the greatest decrease occurring during the first 2 hours.

3. Fine uranium nitride powder can be cold isostatically pressed without binder to give compacts with good green strength for handling purposes.

4. Grain sizes between 2×10^{-4} and 9×10^{-3} centimeter (ASTM No. 14 to 4) were obtained by varying sintering temperature and time. Increasing the sintering temperature greatly increases the grain size of UN. In addition, increasing the time at temperature slightly increases the grain size.

The following major results were obtained using the method of hot isostatic pressing of coarse UN powder (70 to 150 μm diam).

1. Densities ranging from 95.5 to 99.8 percent of theoretical were produced by varying the pressure and temperature.

2. Low oxygen (<500 ppm) and carbon (90 ppm) content UN compacts were fabricated by hot isostatic pressing. There was essentially no oxygen or carbon pickup in the process.

3. Pressings made in ingot iron cans produced the best results. No cracking of the UN compacts or separations between the can and UN could be observed. However, a maximum practical pressing temperature of only 1400° C can be used because of the low melting point of iron. This temperature limits the densification of UN to about 97 percent of theoretical density.

4. Pressings using Cb - 1 percent Zr cans showed good promise with respect to the cracking of UN. No cracking in the UN could be detected but a separation between the can and UN compact was observed. This separation could be an undesirable because of the possibilities of producing a cracked compact.

5. Pressings made in molybdenum cans produced the poorest results. Severe radial and circumferential cracking of the UN was observed in all pressings using molybdenum cans.

The following results were obtained using only the hot extrusion of coarse uranium nitride powder.

1. The feasibility of producing theoretically dense UN compacts was demonstrated. However, methods to eliminate the cracking of the UN caused by the molybdenum extrusion cans will have to be developed.

2. All extrusions done at 2200° C produced extremely large grains. Further development work is needed at lower temperatures for smaller grain size structures.

The following major results were obtained from a machining study on UN compacts using grinding and electric discharge machining (EDM) methods.

1. Tolerances of ± 0.0005 inch ($\pm 1.27 \times 10^{-3}$ cm) can be held on diameters ranging from 0.1 inch (0.25 cm) to 1/2 inch (1.3 cm) by using cylindrical and centerless grinding. A surface finish of 32 microinches rms (81.3×10^{-6} cm rms) was achieved by grinding.

2. Holes and crosscuts were made by EDM. The surface finish was controlled in the EDM process by varying the frequency and capacitance of the equipment. A slight pickup of carbon by the EDM process was removed by grinding a few mils from the surface.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 16, 1970,
120-27.

APPENDIX - CHEMICAL ANALYSIS METHODS FOR UN

Generally accepted methods for chemical analysis of UN have not been developed to date and more work in standardizing procedures is needed to establish precise and accurate results. Since this investigation was not intended to be a study of the chemical analysis of UN, the best methods and handling techniques known to date were applied.

The following methods for chemical analysis of carbon, oxygen, and nitrogen were used in this report. The combustion method with a chromatographic finish was used for carbon; the inert gas fusion method was used for oxygen; and the Kjeldahl method was used for nitrogen. In the Kjeldahl method the sample was dissolved in a sulphuric acid (H_2SO_4), hydrofluoric acid (HF), and potassium chromate (K_2CrO_4) solution and this process was followed by the normal Kjeldahl distillation-volumetric finish. Triplicate samples were run on each. The average results are reported in this study. Great care was taken in the preparation of the samples for analysis. First of all, the samples to be analyzed were never exposed to air. Secondly, all samples were prepared in an inert gas dry box. The compacts were crushed and weighed into tin capsules. Then each sample was double sealed in plastic bottles to avoid possible contamination. Samples were removed from the inert gas dry box at the time the analysis was ready to be done.

Work done on the precision of the analyses of W-UN cermets (ref. 8) indicates that there is a 0.99 probability that the Kjeldahl analysis for nitrogen is within 3 percent of the average value. The precision for the oxygen analysis by the inert gas fusion method indicates that a 0.99 probability that the results are within 5.5 percent of the average value. The precision of the carbon analysis indicates that there is a 0.99 probability that they are within 7 to 10 percent of the average value. Because these statistics were taken on W-UN cermets, the accuracy of the nitrogen, carbon, and oxygen content could have been interferred with by tungsten. Thus, I believe that the precision of the analysis of the UN itself is probably much better. However, this does not verify that accuracy has been achieved in the chemical analysis. Analytical chemical results can be consistent, yet the values may not be correct. Results obtained for this study indicate that the analyses are consistent. But when the percentages of the elements were totaled there was a discrepancy. Totals varied both above and below 100 percent. When N/U ratios were calculated from the results obtained from the chemical analyses, the ratios varied from 0.943 to 1.01. This area of uncertainty gives an indication that more work is needed to improve the accuracy of the analyses of the major elements in UN.

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