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PWAC-498
FABRICATION OF LOW DENSITY
URANIUM NITRIDE FOR HIGH
FISSION GAS RELEASE

AEC RESEARCH AND DEVELOPMENT REPORT

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PWAC-498
FABRICATION OF LOW DENSITY
URANIUM NITRIDE FOR HIGH
FISSION GAS RELEASE

AEC RESEARCH AND DEVELOPMENT REPORT

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FABRICATION OF LOW DENSITY
URANIUM NITRIDE FOR HIGH
FISSION GAS RELEASE

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Written By: S. D. Caplow
G. W. Lindemann
A. C. Schilling

Approved By:

L. M. Raring
L. M. Raring

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A. SUMMARY

A method of fabricating low density uranium nitride with a structure optimized for maximum fission gas release has been demonstrated on a laboratory scale. The structural features optimized are: 1) the virtually complete elimination of closed, transgranular porosity and 2) a reduction of the trapping sites for fission gases. The process involves three stages: 1) the fabrication of high density large-grained UN pellets by liquid phase sintering, 2) the chemical comminution of these pellets into coarse, essentially single-grained particles, and 3) the fabrication of a low density UN fuel body having the desired properties. As compared to earlier methods of fabricating low density UN, the method described resulted in 95% and more of the total porosity open to the surface, and a twenty-fold reduction in the grain boundary surface area.

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B. INTRODUCTION

This report is intended to summarize certain work done at Pratt & Whitney Aircraft Division, Connecticut Advanced Nuclear Engineering Laboratory, under Contract AT(30-1)-2789 on the development of fuels for the SNAP-50 reactor. In particular, this report describes a method of fabricating low density uranium nitride that is structurally optimized for high release of fission gases. These methods are derived from the practical experience gained from early fission gas release experiments and from the application of a postulated mechanism of fission gas release as determined under the Advanced Materials Program.

Ultimate performance of fuel fabricated by these methods would, of course, be determined by irradiation evaluation. Termination of the contract, however, made this impossible. It is the intent of this report to describe the analysis by which the structural requirements were determined and the methods of fabrication that were developed to achieve them.

Uranium nitride has among its properties a high melting point, high thermal conductivity and a high uranium loading. From an engineering point of view, these properties make UN an especially attractive reactor fuel. The additional factors of 1) a high degree of stability in contact with the lithium coolant, 2) compatibility in contact with tungsten-lined columbium alloys and 3) confidence, based on extrapolations from numerous irradiation experiments, of the ability of the fuel to meet the design requirements, had led to its selection as the candidate fuel for the SNAP-50 powerplant. Details of the progress made in the development of UN for the SNAP-50 program is discussed in Ref. 1.

In common with all reactor fuels, however, irradiation to high burnups results in matrix swelling - the degree being a characteristic of the particular fuel and of the reactor conditions. Among the effects of swelling are restriction to coolant flow and excessive stresses upon the fuel cladding. The result is that burnup limitations may become a design limiting criteria.

In addition to the fuel swelling contributed by the increase in atomic volume of the solid fission products over that of the parent atoms (Ref. 2), the gaseous fission products are of major concern. This results from the coalescence of the gaseous fission product atoms into bubbles as a result of the more rapid diffusion rates that occur at the high operating temperatures of most ceramic fuels. Upon coalescence into large bubbles, the gaseous atoms exert a pressure in accordance with the gas laws. The sum of these two forces are greater than those resulting from the volume of the atoms alone.

A UN fuel body, with a structure designed to optimize the release of fission gases from within the fuel matrix, is one of several methods that have been considered at CANEL for further enhancing the burn-up capabilities of UN and the operating levels of the SNAP-50 reactor*. The fission gases that are released would then be contained at a lower pressure in a plenum provided within the fuel element. Stronger tungsten alloys provide a means of minimizing the plenum size. It had been intended, up to the time of contract termination, to irradiate the fuel described in this report at the following conditions:

Fuel - 80% Dense UN
Clad - W-26 Re Alloy (no Barrier)
Clad Dimensions - 0.250" by 0.020 wall
Clad Surface Temperature - 2200F
Power Density - 1.4 Kw/cc
Burnup - 1.5 a/o U
Time - 2500 hours

*Ref. 3 discusses the irradiation program and Ref. 4 the reactor parametric studies of a low density UN fueled reactor.

C. STRUCTURAL REQUIREMENTS FOR MAXIMUM FISSION GAS RELEASE

1. Previous Experience Related to Fission Gas Release

Analysis of irradiation results generated under earlier irradiation programs led to the conclusion that intergranular porosity in sintered, high density UC (e.g., greater than 94%) became interconnected when the burnup and swelling reduced the density to 88% (Ref. 5). With this information, four UC capsules representing varying densities were irradiated. One objective was to determine the effect of fabricated density on fission gas release and swelling. The results available at the time of contract termination are summarized in Fig. 1. As expected, maximum fission gas release was obtained with the lowest density fuel (81% T.D.), although actual release (31%) was much less than desirable. These results, and a review of the metallographic structure demonstrated that the relationship between density change and gas release was not simply linear. This was substantiated by BET measurements on pretest low density UC: although surface areas became progressively larger as the density decreased, the microstructure, as seen in Fig. 2 before and after irradiation, was composed of numerous isolated pores and channels of small diameter. Communication of these pores with external surfaces was not complete and it was obvious that this accounted for the limited (31%) fission gas release. To improve performance, a quantitative measure of the percent interconnected porosity and of the pore diameter became more desirable than BET surface area measurements. A porosimetry technique was therefore used to measure the effects of fabrication and material parameters on the nature of the porosity.

Results similar to these were reported by General Atomics (Ref. 6): the retention of fission products increased with increased fuel density. Discrepancies in the amount of fission gas released from low density specimens was attributed to difference in the extent to which porosity was interconnected.

The structural requirements established from these analyses were that: 1) transgranular porosity made no contribution to fission gas release and should therefore be reduced or eliminated, and 2) intergranular porosity, to be effective, must be interconnected and open to the surface. Incorporating these features could be expected to significantly increase fission gas release by increasing accessibility to free surfaces.

2. Fission Gas Behavior in High Density UN

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Studies of fission gas behavior in high density UN, under the Advanced Fuels and Materials Program, showed that gas atoms first agglomerate to form bubbles which, in turn, migrate to grain boundaries. These bubbles are immobilized at the grain boundaries but they continue to grow in size as burnup continues (Ref. 7). If the bubbles are discrete, fuel swelling occurs as internal pressure increases. On the other hand, if the bubbles are interconnected, and particularly if they form a continuous passage with the surface, the gas can escape and swelling may thus be suppressed. In Ref. 8 it is shown that the probability of achieving interconnected porosity will be greater when the total grain boundary area is less (large grain size). Conversely, the greater the grain boundary area (small grain size), the more one would expect discrete gas bubbles. Incomplete gas release associated with the low density UC shown in Fig. 2 does not contradict this model; although the density of the fuel was relatively low (81% T.D.), porosity was not fully interconnected and gas release was not, therefore, completely effective. This was a fine grained fuel specimen (approximately 5 microns average) as compared to normal, high density UC (approximately 25-50 microns).

FIG 1

EFFECT OF PRETEST FUEL DENSITY ON IRRADIATION PERFORMANCE

(UC, 2200F SURFACE TEMPERATURE)

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<u>Capsule Number</u>	<u>Pretest Fuel Density (% Theor.)</u>	<u>Exposure (Hours)</u>	<u>Burnup (% U)</u>	<u>Gas Release (% Xe)</u>	<u>Pin Swelling (% per % B/U)</u>
523	81	940	0.87	30.6	1.73
520	85	2090	2.0(1)	N.A.(2)	2.49
521	89	1160	1.2(1)	N.A.(2)	3.98
524	93	540	0.63	1.8	1.28
534	94	3290	1.46	1.5	2.24

(1)Estimate

(2)N.A. - Not available

FIG 2

MICROSTRUCTURE OF LOW DENSITY UC
(81% THEORETICAL DENSITY)~~UNCLASSIFIED~~

AS FABRICATED

MAGNIFIED: 1000X

POST IRRADIATION

MAGNIFIED: 500X

PELLETS FABRICATED BY SINTERING FINE POWDER

Although not fully established by experimental data, a further phenomenon affecting gas behavior was observed under the Advanced Materials Program. This was that a presumably stable dispersed oxide phase could provide transgranular trapping sites for fission gases. This effect would thus be additive to the effect of a fine grain size in preventing the release of fission gases. The additional structural requirements established from these observations was that 1) the microstructure should be relatively coarse grained, and 2) the interstitial content should be low to reduce the possibility of high temperature oxide precipitates.

3. Summary of Structural Requirements

The preceding considerations led to definition of the following manufacturing objectives:

- a. Minimum transgranular porosity
- b. Intergranular porosity interconnected and open to the surface
- c. Large grain size
- d. Low oxygen content

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D. POROSIMETRY TECHNIQUES

The instrument employed was the Aminco-Winslow porosimeter. Operation is based on the principle that the open porosity is directly proportional to the amount of fluid (mercury) that can be forced into a pellet (Ref. 9). The surface tension opposition of any liquid into a small pore may be overcome by the application of an external pressure. The diameter of the pore is related to the pressure placed on the fluid by the following relationship:

$$(1) \quad D = \frac{-4 G \cos \Theta}{P}$$

where D is the diameter of the pore just enterable by the fluid of surface tension G, under an external pressure P and at a contact angle Θ with the material being tested. For this system, a contact angle of 140 degrees and a surface tension of 480 dynes/cm is given. The equation is thus reduced to:

$$(2) \quad D = \frac{175}{P}$$

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where D is in microns and P is in psia.

Figure 3 is a photograph of the apparatus. A penetrometer tube, used for measuring penetration, is shown lying on the stand. It consists of a capillary graduated in cc of mercury and has a sealed cup at one end within which the pellet is placed. For the low pressure measurements, the penetrometer tube is installed in the vacuum chamber on the left side of the apparatus; for the high pressures it is installed in the protected section on the right side of Fig. 3. This capillary is initially evacuated and then filled with mercury to a pressure of 6.3 psia. It is then isolated and pressurized by means of a screw press with isopropyl alcohol as the working fluid. As the pressure on the mercury-alcohol interface increases, the mercury is forced into the pore of the pellet and the extent of penetration is observed on the graduated capillary by the rising mercury column.

Pore diameter and pore size distribution are determined from equation (2) and from the ratio of the mercury penetration at a given pressure to the maximum penetration at 5000 psia. Fig. 4 is a typical pore size distribution curve for a sample of UN that had been sintered to approximately 80% of theoretical density. The range of measurable porosity is from 0.035 to 100 microns. Porosity less than 0.035 micron diameter was considered as closed. The percent of total void volume that is interconnected is determined from the ratio of the volume of mercury absorbed to the total void volume as determined by density measurement.

The exposed pore surface area can be determined from the measured pore diameter and open pore volume from the relation:

$$(3) \quad \text{Surface Area: } \frac{4 \times \text{Open Pore Volume}}{\text{Pore Diameter}}$$

which assumes cylindrical pores. From equation (3) it is apparent that the pore diameter should remain small in order to have the largest possible surface area for gases to be released. Keeping in mind the previously described structural requirement of large grain size (in order to minimize grain boundary surface area), a useful parameter for measuring the efficiency of different low density fuel is the ratio:

$$(4) \quad \frac{\text{Grain boundary surface area/unit volume (G)}}{\text{Pore surface area/unit volume (P)}}$$

FIG 3

AMINCO-WINSLOW POROSIMETER

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FIG 4

PORE SIZE DISTRIBUTION IN 80% DENSE UN

E. METHODS OF FABRICATING LOW DENSITY UN

Four different starting material conditions were evaluated: 1) fine powder, 2) coarse powder, 3) coarse, polycrystalline particles, and 4) coarse single crystal particles.

Process flow sheet used for these four starting materials is shown in Fig. 5. Methods and resultant microstructures are discussed in detail below. Results of the porosimetry analysis for the several methods are discussed in the section "Results and Conclusions".

1. Fine Powder

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In this approach, a lower green density of the fine powder compacts was investigated. This method is commonly used to produce low density bodies. The following description applies to uranium carbide as fabricated for earlier irradiation experiments but since properties of UC and UN powders as synthesized at CANEL are similar, the experiments were not repeated for uranium nitride.

Fine particles of uranium carbide powder were obtained by the synthesis method as described in Ref. 10. The median particle size was between four and seven microns as determined by sedimentation analysis. Electron microscopy showed that these particles were composed of an agglomerate of smaller particles measuring 0.1 to 1 microns in diameter. The desired 80% final density was obtained by cold pressing to only 45% of theoretical rather than 55 to 60% normally used for high density sintered fuel. The pellets were sintered, in vacuum, at 3300F. As expected, they were "hour glass" shaped after sintering and required centerless grinding and end facing. The microstructure is shown in Fig. 2. Fuel fabricated by this method shows individual high density grains but grain size averages only 5.5 microns, corresponding to the mean agglomerate size of the starting powder. A fine network of discrete, intergranular porosity was apparent at 1000X.

2. Coarse Powder

The objective in this approach was to increase the grain size while retaining intergranular porosity. Coarse powders were produced by a modification of the synthesis practice in which only three hydride-dehydride cycles were used (instead of nine) in reducing uranium metal to powder. The powder was screened for the -60 + 150 mesh fraction which was used in these tests.

The powder was pressed manually at 60-70 TSI under an inert atmosphere using a standard break-away die set lubricated with Welch Duo Seal Oil. Green density was 57-59% T.D., which permitted a higher final sintering temperature without exceeding the 80% density objective. This combination of low green density and higher sintering temperature produced a stronger pellet than obtained by means of a high green density and lower sintering temperature.

An investigation of sintering effects led to the development of the following cycle:

- a. Heat to 2800F in vacuum (5×10^{-4} mm or better) and hold at 2800F for one hour in order to decompose any residual sequinitride and remove surface oxide. Add nitrogen gas to approximately 8 inches vacuum at the end of the one hour hold to retard the decomposition of UN at the higher temperatures.

METHODS OF FABRICATING LOW DENSITY UN PROCESS FLOW SHEETS

FABRICATION FROM FINE POWDER

(9 CYCLES)

FABRICATION FROM COURSE POWDER

(3 CYCLES)

FABRICATION FROM COARSE POLYCRYSTALLINE PARTICLES

(9 CYCLES)

FABRICATION FROM COARSE MONOCRYSTALLINE PARTICLES

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FIG 5

- b. Heat at 3600F for two hours to promote maximum sintering without losing intergranular porosity. Cool to 2800F and evacuate so that the higher nitride will not form. Then allow the furnace to cool under a high vacuum for at least three hours.

The pellets were heated in tungsten crucibles in a graphite resistance heated furnace. The final density was approximately 80% T.D. The assintered pellets were then centerless ground and end faced. At this point geometric densities could be taken since the pellets represented uniform cylindrical shapes. For the purpose of capsule production the density requirements were 80% $\pm 1\%$.

As described later, pellets fabricated by this method showed considerable interconnected porosity. However, although the particle size of the starting powder was between 100 and 250 microns (corresponding to the mesh fraction), the grain size after sintering was only 10 microns. As with the fine powder starting material, grain size is believed to correspond to the starting powder size. The increase from 5.5 to 10 microns in going from fine powder to coarse powder could therefore be anticipated. In both instances, further grain growth is limited by the necessity to avoid excessive sintering temperatures, since this would tend to eliminate the internal porosity and increase density.

3. Coarse, Polycrystalline Particles

It was hoped to further increase grain size by this approach. High density UN pellets (greater than 94%) were fabricated, crushed, fractionated, and reprocessed to produce a low density specimen.

As indicated by Fig. 5, fine UN powder was manually pressed at 80 TSI to green densities in the 68 to 70% range. These pellets were then sintered conventionally in tungsten crucibles as follows:

- Heat to 2800F in vacuum (5×10^{-4} mm or better) as before and hold one hour at temperature. Admit nitrogen until a pressure of 22 inches is reached.
- Heat from 2800F to 3700F under the partial pressure of nitrogen and hold at 3700F for two hours to permit slow grain growth.
- Heat from 3700F to 4100F under nitrogen partial pressure and hold at 4100F for two hours so that densification of the pellet can be achieved.
- Furnace cool from 4100F to 2800F under nitrogen and then evacuate and continue to cool to room temperature.

This technique produced densities in the 95 to 97% range. Metallographic analyses showed single phase structures and chemical analyses less than 1000 ppm each of oxygen and carbon.

The pellets were next crushed under an inert atmosphere in a porcelain mortar and pestle and screened to obtain the -60 + 150 mesh fraction. The net yield was approximately 40%, even after recrushing the +60 mesh portion.

The coarse particles were pressed manually at 60 to 70 TSI to approximately 72 to 75% dense pellets. Lower green density pellets were too friable to handle. The pellets were then placed in tungsten crucibles and sintered as follows:

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- a. Heat to 2800F in vacuum. Hold at 2800F for one hour in vacuum and admit nitrogen to a pressure of 22 inches as before.
- b. Heat to 3800F and hold two hours under nitrogen partial pressure. Cool to 2800F, evacuate and continue cooling for at least three hours under vacuum.

The structures of pellets produced by this method are represented in Figs. 6 and 7. Fig. 6 shows the relatively uniform and interconnected porosity about each particle. Fig. 7 shows a single particle at a higher magnification to delineate the polycrystalline structure of the particle. This structure also shows considerable porosity "trapped" within the particle.

4. Coarse Single Crystalline Particles

This approach was attempted in view of the disappointing results shown by the first three methods. In this technique, advantage was taken of a molten uranium phase to provide a mechanism for growing large grains of essentially theoretical density. Since extraneous elements were not introduced in this method, purity was not compromised. The second step in this process reduced the coarse grained compact to single grained coarse particles of high specific density. These are then pressed and sintered to the final form. These essential steps are described in detail below:

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a. Liquid Phase Sintering

In this step liquid phase sintering was used to prepare a coarse-grained, highly dense UN body. The liquid phase was provided by adding free uranium powder to fine UN powder and then pressing and sintering this to a high density pellet. To determine the proper addition of uranium, two levels were tried: 19.6 and 58.3 w/o. These were sintered simultaneously with a control specimen as follows:

- (1) Heat to 2400F for five hours in vacuum to provide maximum mobility in the liquid uranium without excess evaporation. Add nitrogen to 8 inches vacuum as before to retard the high temperature decomposition of UN.
- (2) Heat from 2400F to 4100F in two hours under nitrogen partial pressure.
- (3) Furnace cool to 2800F and evacuate. Cool under vacuum to R.T. in approximately three hours.

The effect of this sintering treatment is shown in Fig. 8. The average grain size of the control specimen was 25 microns as compared to 95 microns for the sample containing the 19.6% uranium and 150 microns for the sample containing 58.3% uranium. Moreover, the control sample had sharp, angular grains whereas the "liquid phase sintered" specimens showed grains with rounded corners (19.6% U). The grain boundary phase, uranium, was important in the comminution of the pellet, as explained below.

The higher uranium content samples showed extensive reaction with the tungsten crucibles (the tungsten-uranium eutectic melts at approximately 2000F). For this reason work with the higher uranium material was abandoned and all subsequent work was done with approximately 20% uranium. This material sintered satisfactorily in tungsten crucibles.

MICROSTRUCTURE OF LOW DENSITY UN

FABRICATED BY SINTERING POLYCRYSTALLINE PARTICLES
79.6% DENSE

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AS POLISHED

MAGNIFIED: 100X

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MICROSTRUCTURE OF LOW DENSITY UN

FABRICATED BY SINTERING POLYCRYSTALLINE PARTICLES
79.6% DENSE

ETCHED

MAGNIFIED: 500X

SHOWS THE MULTI-GRAINED NATURE OF INDIVIDUAL PARTICLES
AND TRANSGRANULAR POROSITY

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FIG 7

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FIG 8
GRAIN GROWTH AS A FUNCTION OF COMPOSITION

LIQUID PHASE SINTERED UN
SINTERED AT 2400F FOR FOUR HOURS, 4100F FOR TWO HOURS

CONTROL

19.6 W/O U
METAL ADDITION

58.3 W/O U
METAL ADDITION

MAGNIFIED: 100X

A series of experiments was also conducted in an attempt to optimize sintering practices. Sintering at 2400F, 2800F, 3700F, 3900F and 4100F, for two and twelve hours was investigated. Results are summarized in Fig. 9 and the microstructures in Fig. 10. The microstructures suggest that grain growth occurs through absorption of less favorably oriented grains by adjacent grains. This indicates that a solution and reprecipitation mechanism is involved, with the liquid uranium phase serving as the transfer agent. Additionally, Figs. 10b and 10c, in particular, also suggest that a second growth mechanism, solid state diffusion between contacting particles, is occurring simultaneously.

It was also found that the nitrogen content increased with increasing sintering time or temperature (Fig. 9). This is thought to be due both to uranium evaporation and nitrogen enrichment by reaction with the cover gas. Based upon the results as summarized in Fig. 9, a two-step sintering cycle was selected to attain maximum grain growth. The effectiveness of the two step process is illustrated by comparison of run E-234, sintered two hours at 4100F, with run E-240, which was sintered in two steps: 2400F for five hours followed by 4100F for two hours. The first method developed an average grain size of 70 microns; the two step method produced an average grain size of 125 microns. In another trial (run E-244), grains as large as 220 microns were obtained by sintering first at 2400F (five hours) followed by a 4100F (12 hours) sinter. This cycle, in argon, was selected as standard procedure for the irradiation program. Argon was used instead of nitrogen in order to minimize the thickness of high density peripheral ring of large, columnar grains (Fig. 11). No free uranium was observed in the grain boundaries in this columnar region.

b. Chemical Comminution

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Having succeeded in producing a coarse grained UN body, it now became necessary to comminute this material to essentially mono-crystalline coarse particles. A number of crushing and screening techniques were tried and rejected. In addition to the other problems inherent in crushing, random fractures resulted in polycrystalline particles rather than single crystal particles. A hydriding-dehydriding technique, as used in the fuel synthesis for reducing uranium metal to powder, was tried. This was successful. The mechanism was dependent upon the successive hydriding and dehydriding of the intergranular uranium metal phase. The resultant volume change produced complete intergranular fracture to form essentially mono-crystalline coarse powder.

The coarse grained sintered UN was placed in a retort in the powder synthesis rigs and hydrided at 250F for 45 minutes. This was followed by vacuum dehydriding at 650F for 90 minutes. Experiments with repetitive hydride/dehydride cycles showed that pulverization was essentially complete after the second cycle. No further reduction in particle size was obtained with additional cycles. There was no apparent reaction between the hydrogen and the UN grain surface.

Approximately 45% of the product of this chemical comminution met the desired particle size range (100 to 250 microns); 50% was in the 400-600 micron range; and the remaining 5% were fines, produced from the free uranium metal. The 400-600 micron fraction came from the coarse columnar surface skin, previously mentioned. Mechanical crushing of this coarse fraction yielded an additional 20% in the acceptable particle size range. It is believed that further improvement in yield could be obtained either through additional sintering development to produce a coarser average grain size or by more discriminate crushing. Fig. 12 represents a typical sample of the powder product: examination in the etched condition showed an essentially single crystal structure with no transgranular porosity.

FIG 9

RESULTS OF LIQUID PHASE SINTERING EXPERIMENTS

EFFECTS OF TIME AND TEMPERATURE

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Batch No.	Sinter Cycle		Grain Size (Microns)			Nitrogen Content (w/o)
	Temperature	Time, hr	Liquid Phase Center	Edge	Control Grain	
E-225	2400	2	8	10	5	4.31, 4.26
E-227	2800	2	24	24	12	4.73, 4.77
E-231	3700	2	60	70	12	5.19, 5.16
E-236	3900	2	66	81	14	N.A.
E-234	4100	2	70	100	16	5.14, 5.04
E-224	2400	12	26	50	6	4.70, 4.76
E-232	2800	12	39	39	12	4.84
E-230	3700	12	85	110	15	5.17
E-235	3900	12	100	140	20	N.A.
E-233	4100	12	160	190	29	5.05, 5.11
E-240	2400 + 4100	5 2 N ₂	120	---	N.A.	4.88, 4.98
E-244	2400 + 4100	5 12 N ₂	220	---	N.A.	N.A.
E-245	2400 + 4100	5 12 A	210	---	N.A.	4.63, 4.82

FIG 10A

2870-260 2870-257
2870-262 2870-255

LIQUID PHASE SINTERED UN EFFECT OF TIME AND TEMPERATURE

RUN #E225 MAGNIFIED: 200X
SINTER CYCLE 2400F X 2 HR VAC
GRAIN SIZE 8μ

RUN #E227 MAGNIFIED: 200X
SINTER CYCLE 2800F X 2 HR VAC
GRAIN SIZE 24μ

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RUN #E224 MAGNIFIED: 200X
SINTER CYCLE 2400F X 12 HR VAC
GRAIN SIZE 26μ

RUN #E232 MAGNIFIED: 200X
SINTER CYCLE 2800F X 12 HR VAC
GRAIN SIZE 39μ

FIG 10B

2870-258 2870-263
2870-256 2870-261

LIQUID PHASE SINTERED UN EFFECT OF TIME AND TEMPERATURE

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RUN #E231 MAGNIFIED: 200X
SINTER CYCLE 3700F X 2 HR IN N₂
GRAIN SIZE 60 μ

RUN #E236 MAGNIFIED: 200X
SINTER CYCLE 3900F X 2 HR IN N₂
GRAIN SIZE 66 μ

RUN #E230 MAGNIFIED: 200X
SINTER CYCLE 3700F X 12 HR IN N₂
GRAIN SIZE 85 μ

RUN #E235 MAGNIFIED: 200X
SINTER CYCLE 3900F X 12 HR IN N₂
GRAIN SIZE 100 μ

FIG 10C

LIQUID PHASE SINTERED UN EFFECT OF TIME AND TEMPERATURE

RUN #E234
SINTER CYCLE 4100F X 2 HR IN N₂
GRAIN SIZE 70 μ

MAGNIFIED: 200X

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RUN #E233
SINTER CYCLE 4100F X 12 HR IN N₂
GRAIN SIZE 160 μ

MAGNIFIED: 200X

MACROSTRUCTURE OF LIQUID PHASE SINTERED UN

ETCHANT: 70 V/O LATIC ACID
28 V/O NITRIC ACID
2 V/O HYDROFLUORIC ACID

MAGNIFIED: 15X

SHOWS THE PERIPHERAL RING OF APPROXIMATELY 500 MICRON GRAINS AND
FREE URANIUM ALONG THE INTERIOR GRAIN BOUNDARIES

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FIG 11

P W A C - 498

2870-235

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MICROSTRUCTURE OF UN PARTICLES PRODUCED BY THE
LIQUID PHASE OPERATION AND CHEMICAL COMMINUTION

ETCHED

MAGNIFIED: 100X

IN THE ETCHED CONDITION, SHOWS THE SINGLE-GRAIN STRUCTURE OF
THE HIGH DENSITY PARTICLES

UNCLASSIFIED

P W A C - 498
FIG 12

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2870-231

c. Pellet Fabrication

The UN powder from the preceding operation was finally pressed and sintered to the desired pellet structure. The screened, coarse, single crystal UN powder was pressed to a density of 75 to 77% of theoretical and then sintered in tungsten crucibles as follows:

- (1) Heat to 2800F in vacuum, hold one hour. Admit nitrogen to a pressure of 22 inches.
- (2) Heat from 2800F to between 3600F and 4100F under 22 inches of nitrogen; hold two hours at temperature. (The specific temperature is determined by the sintering characteristics of a particular batch).
- (3) Cool to 2800F, evacuate, and continue cooling under vacuum.

Pellets produced by this technique were generally in the density range of $80\% \pm 1\%$ of theoretical. Structurally the porosity was confined to grain boundaries and uniformly distributed (Fig. 13). An occasional polycrystalline particle was observed (Fig. 14). These are attributed to the crushing of the peripheral ring.

Fig. 15 clearly shows the advantage of this method for the production of the desired structure as compared to other approaches investigated in the present work.

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MICROSTRUCTURE OF LOW DENSITY UN FABRICATED FROM MONOCRYSTALLINE PARTICLES

LOW MAGNIFICATION

ETCHED

MAGNIFIED: 100X

SHOWS THE PORE STRUCTURE AROUND UN PARTICLES AND THE LARGELY
SINGLE-GRAINED STRUCTURE OF EACH PARTICLE

UNCLASSIFIED

FIG 13

P W A C - 498

2870-212

MICROSTRUCTURE OF LOW DENSITY UN FABRICATED
FROM MONOCRYSTALLINE PARTICLES
HIGH MAGNIFICATION

UNCLASSIFIED

ETCHED

MAGNIFIED: 500X

SHOWS THE GENERAL ABSENCE OF TRANSGRANULAR POROSITY AND THE
STRUCTURE OF A PARTICLE CONTAINING MORE THAN ONE GRAIN

P W A C - 498
FIG 14

2870-216

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FIG 15

COMPOSITE OF MICROSTRUCTURES OF LOW DENSITY UN

METHOD A MAGNIFIED: 100X
SINTER FINE POWDER

METHOD B MAGNIFIED: 500X
SINTER COARSE POWDER

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METHOD C MAGNIFIED: 500X
SINTER POLYCRYSTALLINE PARTICLES

METHOD D MAGNIFIED: 500X
SINTER MONOCRYSTALLINE PARTICLES

F. RESULTS AND CONCLUSIONS

This investigation has developed a method for the fabrication of UN pellets with essentially no transgranular porosity, minimum grain boundary area, and a uniform network of intergranular porosity. Furthermore, close chemical control of impurities has been preserved in this process, as indicated by the following typical analyses:

Nitrogen: 5.20, 5.28 w/o
Oxygen: 1100, 1350 ppm
Carbon: 830 ppm

Four different approaches were investigated, based upon four types of starting materials. Results of the porosimetry analysis are summarized in Fig. 16. The first approach, which involved the sintering of fine powders, was unsuccessful because of the fine grain size (5.5 microns) and because the porosity was too widely distributed and not sufficiently interconnected (70%) to allow fission gases to escape before swelling became intolerable. In the second approach, increasing the particle size of the starting powder, did not give any real benefit over the fine powder material. Next, an attempt was made to increase the grain size and eliminate transgranular porosity by sintering at high temperature to produce a coarse grained structure. These pellets were crushed; the 105 to 250 micron fraction was reprocessed to a low density body. This technique coarsened the grain size only slightly (20 versus 10 microns) and, although the individual grains were of high density, resintering closed much of the open porosity (48% interconnected). Finally, an approach based upon liquid phase sintering was investigated to develop a coarse grained product with an intergranular uranium phase. When this product was processed through several hydride-dehydride cycles, it disintegrated to coarse, essentially mono-crystalline particles. A resintering process was then developed which produced the desired end product: 80% T.D.; interconnected porosity; and coarse mono-crystalline particles. A significant reduction in specific grain boundary area was achieved through this development ($600 \text{ cm}^2/\text{cm}^3$ versus $10,900 \text{ cm}^2/\text{cm}^3$). An increase in pore diameter from 0.8 microns to 4.0 microns also occurred. These comparisons are based upon material produced from fine powders as standard. As discussed previously, the ratio of grain boundary surface area to open pore surface area is significant with respect to the release of fission gases. A five-fold improvement was attained by means of the process developed. Since the larger pore diameter would be more stable than small pores - which may spheroidize and close during irradiation - the improvement may be even more significant.

In summary, the 50% improvement in open pore volume, twenty-fold increase in grain diameter, and five-fold improvement in G/P ratio are properties which could be expected to improve the irradiation stability of UN fuel.

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POROSIMETRY ANALYSIS OF LOW DENSITY (80%) SPECIMENS

<u>Starting Material</u>	<u>Density</u> <u>(% of Theor.)</u>	<u>Interconnected</u> <u>Porosity</u> <u>(% of Total)</u>	<u>Grain</u> <u>Diameter</u> <u>(microns)</u>	<u>Grain</u> <u>S.A./Vol.</u> <u>(cm²/cm³)</u>	<u>Median</u> <u>Pore</u> <u>Diameter</u> <u>(microns)</u>	<u>Pore</u> <u>S.A./Vol.</u> <u>(cm²/cm³)</u>	<u>G/P</u>
Fine Powder	79.36	71.12	5.5	1.09 x 10 ⁴	0.83	3.42 x 10 ⁴	0.319
Coarse Powder	82.53	66.80	10.0	0.60 x 10 ⁴	1.40	2.35 x 10 ⁴	0.255
Polycrystalline Particles	79.61	48.25	20.0	0.30 x 10 ⁴	4.80	0.40 x 10 ⁴	0.750
Monocrystalline Particles	80.07	95.43	100	0.06 x 10 ⁴	4.00	1.00 x 10 ⁴	0.058

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