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LABORATORY PREPARATION OF URANIUM NITRIDE MICROSPHERES BY A SOL-GEL TECHNIQUE

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OAK RIDGE NATIONAL LABORATORY
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UNION CARBIDE CORPORATION
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Chemical Development Section B

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ABSTRACT

Methods were successfully developed for preparing urania-carbon sols and converting these sols into gel microspheres. Two methods were investigated for converting the gel microspheres into UN microspheres: (1) heating the gel microspheres in nitrogen to produce uranium nitride directly, and (2) heating in argon to produce uranium carbide, then in nitrogen to produce uranium nitride from the carbide. Both methods appear promising. The second method always yields a product containing carbon.

1. INTRODUCTION

The purpose of this work was to explore the possibility of preparing microspheres of uranium nitride from gel microspheres of mixed uranium oxide and carbon. Microspheres of UN are potentially attractive as a reactor fuel. Therefore, in addition to simply preparing UN microspheres, it was desired to prepare UN microspheres that have good fabricability. This implies high crushing strength and good size control. It also implies controlled, though not necessarily high, density.

Aqueous urania-carbon sols with good sphere-forming characteristics were prepared after determining appropriate conditions for adding carbon to UO_2 sols to form stable and fluid dispersions at carbon to uranium ratios of 2.0 through 2.4. Conditions were also established for forming gel microspheres from the UO_2-C sol. The forming procedure closely resembled that described elsewhere for forming thoria[1,2] and urania[3] gel microspheres. The UO_2-C gel microspheres were converted to UN microspheres by heating them in a stream of nitrogen. In an alternative method, the UO_2-C gel microspheres were first converted to uranium carbide by heating them in a stream of argon, and then the uranium carbide microspheres were converted to UN by heating them in a stream of nitrogen.

The preparation of UO_2 sols is described in detail in another report;[3] therefore, no description of this first step in the preparation of UN microspheres is given here.

Additional work is planned to establish in more detail the effects of reaction temperature and time and the carbon-to-uranium ratios in the gel on the properties and purity of the microspheres. The removal of excess carbon by reaction with hydrogen will be investigated in more detail. Extensive characterization of the microspheres with respect to properties such as density, hardness, strength, and purity is also planned. In future work, the preparation of UN microspheres having a range of densities and composed of a mixture of UN and UC will be investigated.

2. PREPARATION OF UO_2-CARBON SOL

2.1 Preliminary Studies

An ultrasonic generator and sonic converter device, hereafter referred to as a sonifier, was used for dispersing carbon into the urania sol. Spheron 9 carbon black (Table 1) was used in the study.

Table 1. Properties of Spheron 9 Carbon Black[a]

Surface Area (m^2/g)	Particle Diameter By Elect. Micros.	Particle Diameter By Nitrogen Adsorption	% Volatile Matter	% Fixed Carbon	pH[b]	Apparent Density of Pellets (lb/ft^3)
109	290	320	5.0	95.0	4.5	22

[a] Cabot Corporation, Boston, Massachusetts, "Carbon Black Pigments."

[b] Determined with a glass electrode in a carbon-black—water sludge (ASTM designation: D1512). Under these conditions, pH is related to the amount of carbon-oxygen complexes on the surface of the carbon black.

Much of the preliminary work included the use of surfactants, since other workers[4] had reported the surfactants useful in producing carbon dispersions of low viscosity. Tween 80 (a polyoxyethylene sorbitan monooleate) and Renex 30 (a nonionic ether of polyoxyethylene and a branched alcohol) were the two surfactants used.

In a typical experiment, a volume of natural UO_2 sol was placed in a container of such configuration as to accommodate the step horn of the sonifier. The surfactant was added to the sol, followed by the addition of Spheron 9 carbon. When the tip of the sonifier was immersed in the sol, the high density of vibrational energy delivered at the tip of the sonifier caused a fairly rapid increase in the temperature of the sol. It was thus necessary to immerse the container in an ice bath. To inhibit oxidation of the UO_2 sol, all experiments were performed in an argon atmosphere.

Some experimental results using surfactants are listed in Table 2. In run S-2 an attempt was made to decrease the viscosity of the dispersion by increasing the concentration of the surfactant. It can be noted that it was not possible to maintain a fluid system when a 1.35 M UO_2 sol was used in the presence of these surfactants.

A 1.16 M UO_2 sol was next diluted to about 0.58 M, and the experiments listed in Table 2 were repeated. Results from these dispersions at the lower concentrations showed that the time required for the dispersions to become thixotropic was increased but that the length of time the dispersion retained sufficient fluidity to permit sphere forming was still too short. The dispersion had a tendency to thicken when handled.

Dispersions were made next without surfactants. The procedure for dispersing the sol was not changed. Table 3 lists results. The UO_2-carbon dispersions, in which the contact time with the sonifier was 25 to 30 min, remained fluid and stable for periods of greater than 24 hr. No evidence of settling out was detected during this period. However, dispersion for 60 min with the sonifier thickened the sol.

2.2 Preparation of the UO_2-C Sols Used in the Preparation of UN Microspheres

When a 1.09 M UO_2 sol (Table 4) was allowed to set overnight, the mixture became thixotropic. Dilution of the sol with water was necessary

Table 2. Effect of Surfactants on Urania-Carbon (Spheron 9) Sol Dispersions

UO_2 sol = 1.35 M
Moles NO_3^-/mole U = 0.077
Moles $COOH^-$/mole U = ~0.033
Carbon = 2.7 M plus 5% excess crude carbon

Run No.	Volume (ml)	Surface-Active Agent	Vol % of Surfactant Used	Dispersing Time (min)	Remarks
S-1	75	Renex 30	0.8	60	Became thixotropic within 15 min after stopping sonifier
S-2	75	Renex 30	2.0	60	Same effect
S-3	75	Renex 30	0.8	30	Became thixotropic within 1 hr after stopping sonifier
S-4	75	Tween 80	0.8	60	Sol thickened before the 60 min mixing time was completed

Table 3. UO_2-Carbon (Spheron 9) Sol Dispersions (No Surfactants)

UO_2 = 0.58 M
Moles NO_3^-/mole U = 0.095
Moles $COOH^-$/mole U = 0.262
Carbon = 1.16 M plus 5% excess crude carbon

Run No.	Volume (ml)	C/U Ratio	Dispersing Time (min)	Remarks
SX-1	75	2.0:1	60	Sol thickened after dispersion
SX-2	75	2.0:1	30	Formed a thin dispersion; sol remained fluid overnight; microscopic examination showed that a homogeneous dispersion had been obtained in the 0.5 hr dispersing time
SX-3	75	2.2:1	25	Same as those above
SX-4	75	2.4:1	25	Same as those above

Table 4. Composition of Urania Sol Before Dilution

Total U (moles/liter)	U^{4+} (%)	Moles NO_3^- per Mole U	Moles COOH per Mole U	Specific Gravity
1.093	76.5	0.019	0.10	1.2742

to restore fluidity. After a fluid system was obtained, several batches of UO_2-carbon sols having a carbon-uranium atom ratio of 2.3:1 were prepared. The required weight of carbon was added to the 0.825 M sol, and a further dilution with water was made to a final concentration of approximately 0.55 M for each batch prepared.

Twelve 100-ml batches of urania-carbon sol were prepared. Each batch was placed in an ice bath and mixed with the sonifier for 30 min. Good dispersions were obtained in all cases.

3. FORMATION OF UO_2-CARBON GEL MICROSPHERES

The apparatus used, and a procedure which resembles that used in forming the UO_2-C gel microspheres have been described in detail in other reports.[1,2,3] Therefore, only the process details required to apply this apparatus and procedure to the formation of UO_2-C gel microspheres will be described here.

The UO_2-C gel microspheres were formed in 2-in.-diam forming column. The forming medium was a 94.5 vol % 2-ethyl-1-hexanol—5 vol % 2-octanol—0.5 vol % Amine-O mixture. The UO_2-C sol was fed into the gelling column through a two-fluid nozzle at flow rates of 1.2 cc/min to 2.5 cc/min. Column backflow of the forming medium was 0.8 gal/min. Partial removal of water from the gelled spheres took place in the column and further drying was accomplished in flowing argon at approximately 120°C for 16 hr. Microscopy showed that the spheres had smooth surfaces. Average size of the spheres was about 300 μ.

4. CONVERSION OF UO_2-CARBON GEL MICROSPHERES TO UN MICROSPHERES

4.1 Two Methods for Making UN Microspheres

There are two methods by which UO_2-C gel microspheres can be converted to UN microspheres. One method could, in theory, yield pure UN; the other yields a product in which 1 g-atom of carbon is produced for each g-atom of UN.

By the first method, the UO_2-C gel microspheres are heated in a stream of nitrogen and react as shown below:

$$UO_2 + 2C + 1/2N_2 \longrightarrow UN + 2CO . \tag{1}$$

Three g-atoms of C are required per mole of UO_3, if any UO_3 is present. If no excess carbon is present [that is, no more than 2 g-atoms of C per mole of UO_2 (or 3 per mole UO_3)], the product should be fairly pure UN. Actually, some UO_2 is usually found in the product when temperatures of only 1500 to 1600°C are used, even if excess carbon is used. Others, working with powders, have made this same observation.[5]

By the second method, the UO_2 is first converted to carbide in a stream of inert gas by the reaction:

$$UO_2 + 3C \longrightarrow UC + 2CO . \tag{2}$$

Four g-atoms of C are required per mole UO_3, if any UO_3 is present. The UC is then treated with N_2 to form UN by the reaction:

$$UC + 1/2N_2 \longrightarrow UN + C . \tag{3}$$

The carbon in the UC intermediate product remains in the final product.

4.2 Conversion by a Single Reaction

Although reaction (1) has been found to proceed very well with powdered UO_2 and carbon mixtures,[5] it was found that a problem develops when attempts are made to carry out this reaction on the UO_2-C gel microspheres. The microspheres rapidly become coated with a very thin, mirror-like layer of UN which impedes the entry of nitrogen to the interior and consequently prevents formation of UN on the inside of the microspheres. The coating can be rendered pervious to N_2 by temperature cycling to form and decompose higher nitrides.

The coating appears to most effectively inhibit the nitriding of the interior of the microspheres when the microspheres are almost perfectly spherical and without surface defects. In runs 1, 3, and 4 (Table 5), the UO_2-C gel microspheres were formed in a small forming column. Microscopy showed pitting and variation from the desired spherical shape. A larger fraction of these microspheres was converted to nitride than in later runs using more nearly perfect microspheres, even though higher temperatures and longer reaction times were used in the later runs. For example, in the first run, x-ray analyses indicated the product was almost pure UN, and in run (3) the N/U atomic ratio in the product was 0.88.

In all the runs so far, the microspheres retained their shape, and no sintering of the microspheres was observed during the conversion to nitride.

In attempts to convert the well-formed microspheres to nitride [runs (6) through (13), Table (5)], it was learned that only partial conversion was possible at temperatures as high as 1650°C and reaction times as long as 4 hr. Microscopy revealed that, in every case, the spheres had a glossy silver coat but were black on the inside. Both the starting material, UO_2 + C gel, and uranium carbide are black while UN is silvery.

4.2.1 Penetration of the UN Coat

The results of experiments described above indicate that the formation of UN microspheres by reaction (1) was prevented by the formation of a coating of UN which the N_2 could not penetrate. Therefore, experiments were performed in which temperature cycling was investigated as a possible method of disrupting the coating. The reasoning involved is that, as the temperature is lowered from the 1600°C reaction temperature, UN

Table 5. Results of Attempts to Convert UO_2-C Gel Microspheres into UN Microspheres by Heating in N_2

C/U atomic ratios between 2.2 and 2.7

Run	Temp. (°C)	Time (hr)	Product N/U, Atomic Ratio	Special Conditions
1	1500	3	--	Gel microspheres prepared in laboratory forming column
3	1500	3	0.88	
4	1500	2	0.62	
6	1550	4	0.59	
6C	1550	4	0.64	
7A	1550	4	0.50	
7B	1550	4	0.51	
8A	1550	4	0.35	
8B	1550	4	0.40	
9	1600	1	0.73	
10	1600	4	0.10	
11	1600	4	0.36	
12	1650	4	0.25	
13	1650	4	0.20	
14	1600	5	0.80	Cooled to 950°C after 2 hr, then reheated to 1600°C
16	1600	5	0.92	
18	1600	4	0.81	Reactions (2) and (3), 2 hr each

does not remain stable in the presence of N_2. Rather, it picks up N_2 gradually, until, at 1000°C and 1 atm of N_2 for example, the equilibrium phase contains over 1.6 atoms of nitrogen per atom of uranium.[6] Reheating to 1600°C will decompose the higher nitrides into UN. Such a cycle should (and in fact did) disrupt the UN coat enough so that it can be penetrated by N_2 gas.

A batch of UO_2-C gel microspheres were dried in a stream of argon at 600°C for 3 hr and carefully analysed for use in investigating the problem of the UN coating. Although the original sol contained 2.3 atoms of carbon per atom of uranium, the dried gel microspheres contained 2.7, due to organic material picked up from the forming column (Table 6). Analyses were also made to determine the valences of the uranium in the gel microspheres. The results are given as wt % UO_2 and UO_3. Quantitative analyses of these microspheres were made difficult by the fact that the microspheres adsorb the surrounding atmosphere (argon in this case) to the extent that they lost over 4% of their room-temperature weight when they are heated to 400°C. Consequently, this weight loss must be determined, as well as the amounts of uranium, carbon, and oxygen present. If this weight loss is not determined, the sum of the weights of uranium, carbon, and oxygen will amount to only about 96 wt % of the spheres at room temperature.

A sample of these microspheres was heated for 2 hr in N_2 at 1600°C. Some were removed, cooled to room temperature under N_2, and examined under the microscope. A photograph of these microspheres in which one microsphere was broken open (Fig. 1) shows the thin, glossy UN coat and the black interior.

Table 6. Composition of UO_2-C Gel Microspheres Used in Runs 14, 16, and 18

Sample	C/U Atomic Ratio
1	2.693
2	2.742
3	2.770
4	2.786
Average values:	UO_2 — 39.67 wt % UO_3 — 46.15 wt %

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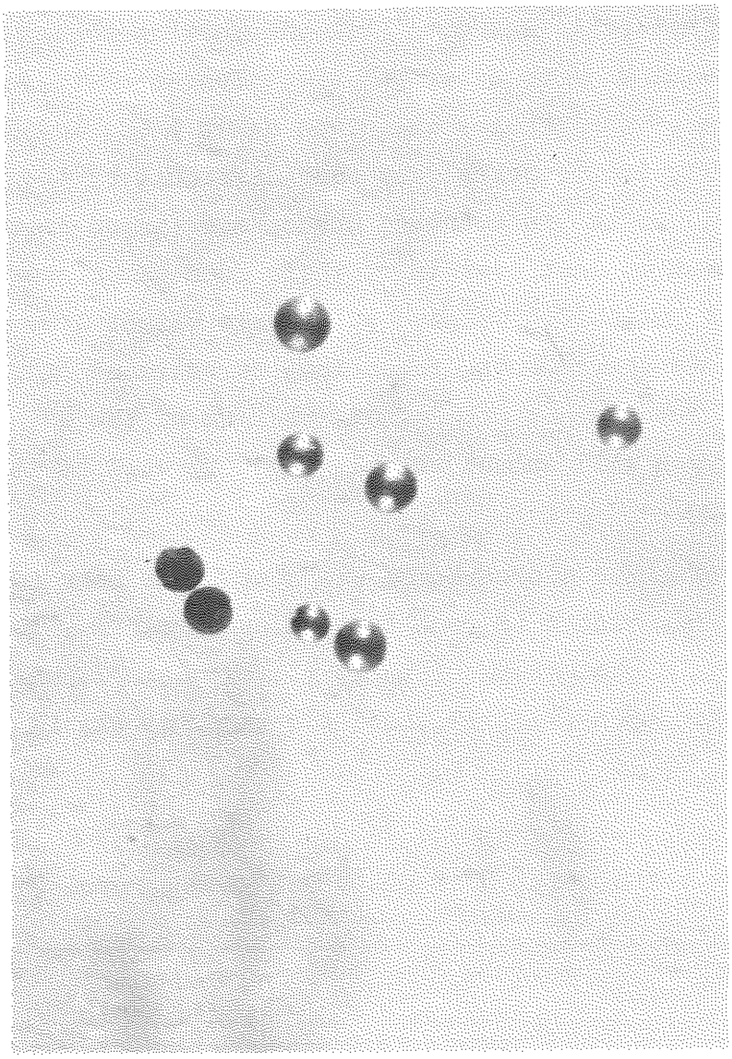

Fig. 1. After a 2-hr Treatment of UO_2-C Gel Microspheres in N_2 at 1600°C, the Microspheres are Coated with Silver-Colored UN, While the Interior of Broken Spheres (Lower Left) are the Black Color of Carbon, UO_2, and Uranium Carbide.

The microspheres not removed from the furnace were cooled to 950°C with N_2 flowing and held overnight at this temperature. The temperature was then increased to 1600°C for 3 more hours.

Complete conversion to nitride was not expected in this run because some contamination of the argon atmosphere by air during the sampling after the first 2-hr treatment was unavoidable. It has been observed that the microspheres react rapidly with air, even at room temperature, when they have been partially converted to carbide. X-ray analyses showed the product was a mixture of uranium nitride and UO_2. Uranium carbide was not identified. Despite this unavoidable contamination of the argon, the N/U atomic ratio in the final product was 0.8 (run 14, Table 5), considerably higher than in previous comparable runs. The results of this run indicated that temperature cycling, with N_2 present, did indeed render the UN coating pervious to N_2.

Another run (run 16, Table 5) was made to confirm that penetration of the UN coat was accomplished by temperature cycling. The procedure was the same as described above for run 14, except that no sample was removed during the run. Even more complete conversion was achieved. Analyses showed the composition of the product to be $UN_{0.92}C_{0.13}$. This amount of carbon is slightly less than the calculated amount (0.18 atom of carbon per atom of uranium) that should be found in the product, based on the analyses in Table 6. The analyzed amounts of uranium, nitrogen, and carbon accounted for 99.9 wt % of the product microspheres. Thus, reaction (1) appears to have proceeded very nearly to completion. By starting with uranium oxide-carbon gel microspheres containing exactly enough carbon to remove all oxygen as CO, the preparation of pure UN microspheres should be possible.

The density of the UN microsphere product, measured by toluene displacement, was 13.66. The theoretical density of UN from x-ray measurements is 14.31.[7] This high density, 13.66, is higher than other workers have achieved with pure UN.[8]

Examination of the product (see Fig. 2) revealed microspheres of two colors. Those on top, as the microspheres lie in the firing boat,

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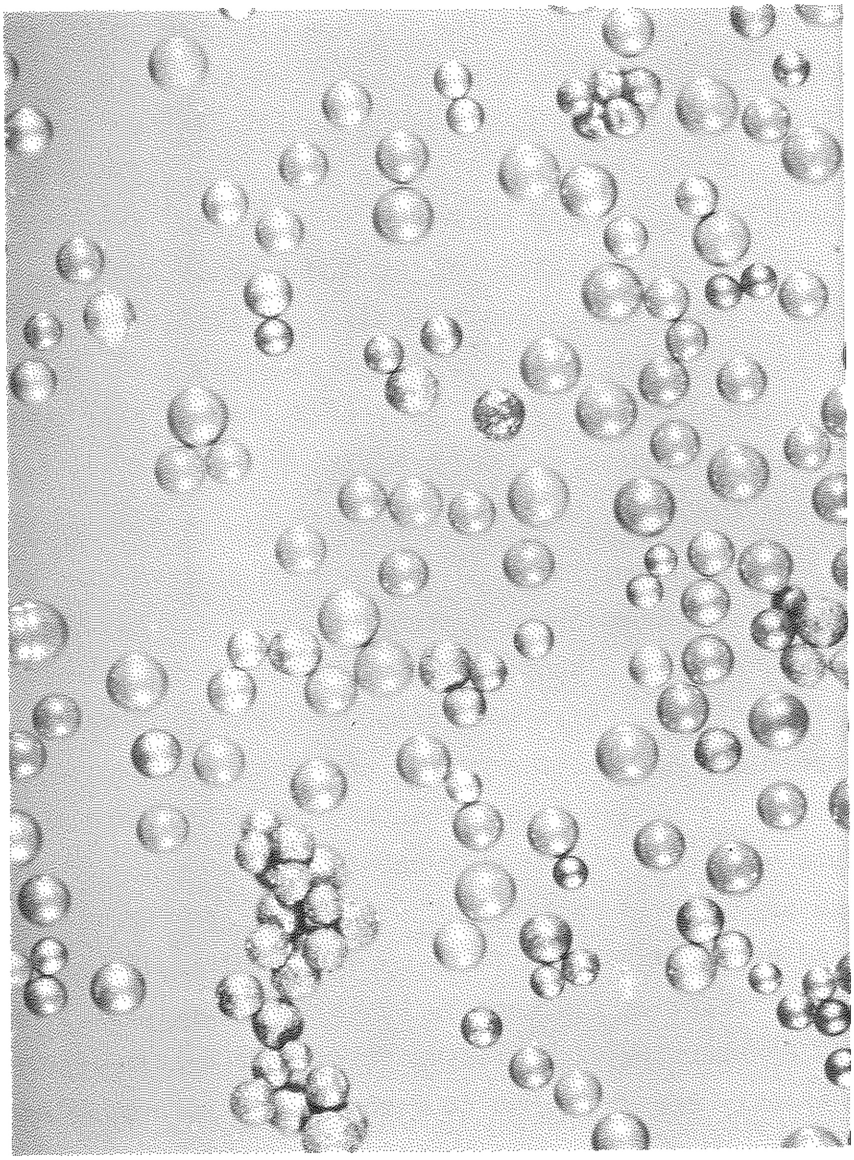

Fig. 2. Microspheres of UN Prepared by Firing UO_2-C Gel Microspheres in Nitrogen Gas. Magnification 33X.

were dark gray, while those underneath were silvery. This color difference is not very apparent in Fig. 2, but it will be shown more clearly later on photomicrographs. X-ray analysis indicated that a small amount of UO_2 was present in the dark-gray microspheres, while the silvery microspheres gave lines only for UN. This difference may be due to a small temperature variation in the microsphere bed, and it indicates that careful temperature control may be needed for complete conversion.

Some agglomerates of microspheres can be seen in Fig. 2. Such agglomerates were also observed in the UO_2-C gel microspheres before firing. Agglomeration occurs in the forming column when the Amine-O surfactant (see Sec 3) becomes depleted, and is corrected by adding more Amine-O to the forming medium. No sintering was observed in any of the UN microsphere products.

Measurements of crush strength revealed that the dark-gray microspheres were stronger than the silvery ones. Crush strengths, measured separately on five dark-gray microspheres, were between 240 and 460 g; those measured on silvery ones were between 100 and 250 g. The spheres had diameters in the range 100 to 250 μ. In these crush-strength measurements, the spheres had been removed from containers filled with argon and exposed to the laboratory atmosphere. Therefore, the low crush strengths may be caused by a small amount of surface reaction with the atmosphere, which weakens the spheres.

Photomicrographs were prepared from polished sections of the microspheres shown in Fig. 2, using bright-field illumination (Fig. 3) and polarized light (Fig. 4). The dark-gray and silvery microspheres mentioned above are easily distinguishable in these photomicrographs, but there are no visible structural differences to explain the difference in coloration. Some evidence of UO_2 and carbon was expected in the darker spheres, since the dark color suggests that these materials are present and x-ray analyses indicated the presence of some UO_2. The absence of any good evidence for UO_2 and carbon in the darker sections may be due to the poor polishing characteristics shown by these sections.

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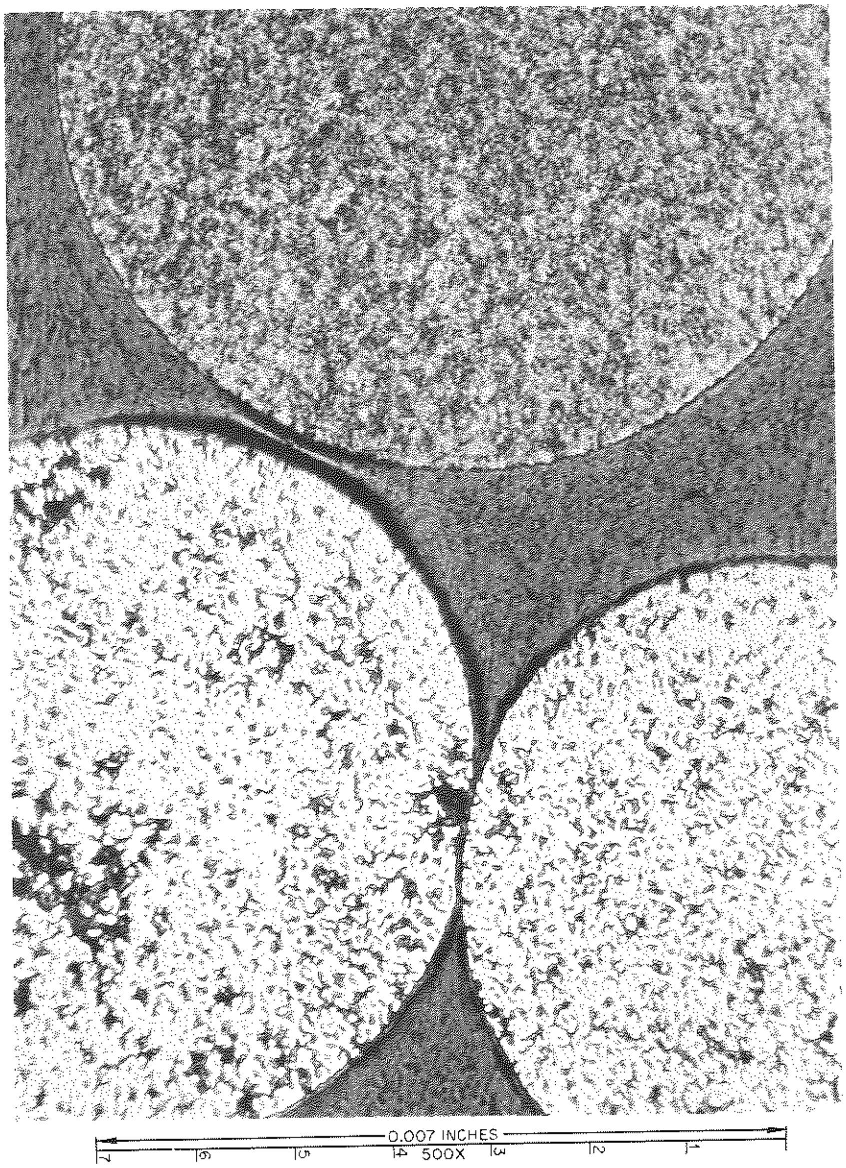

Fig. 3. Photomicrograph of Polished Sections of the Microspheres in Fig. 2, Using Bright Field Illumination.

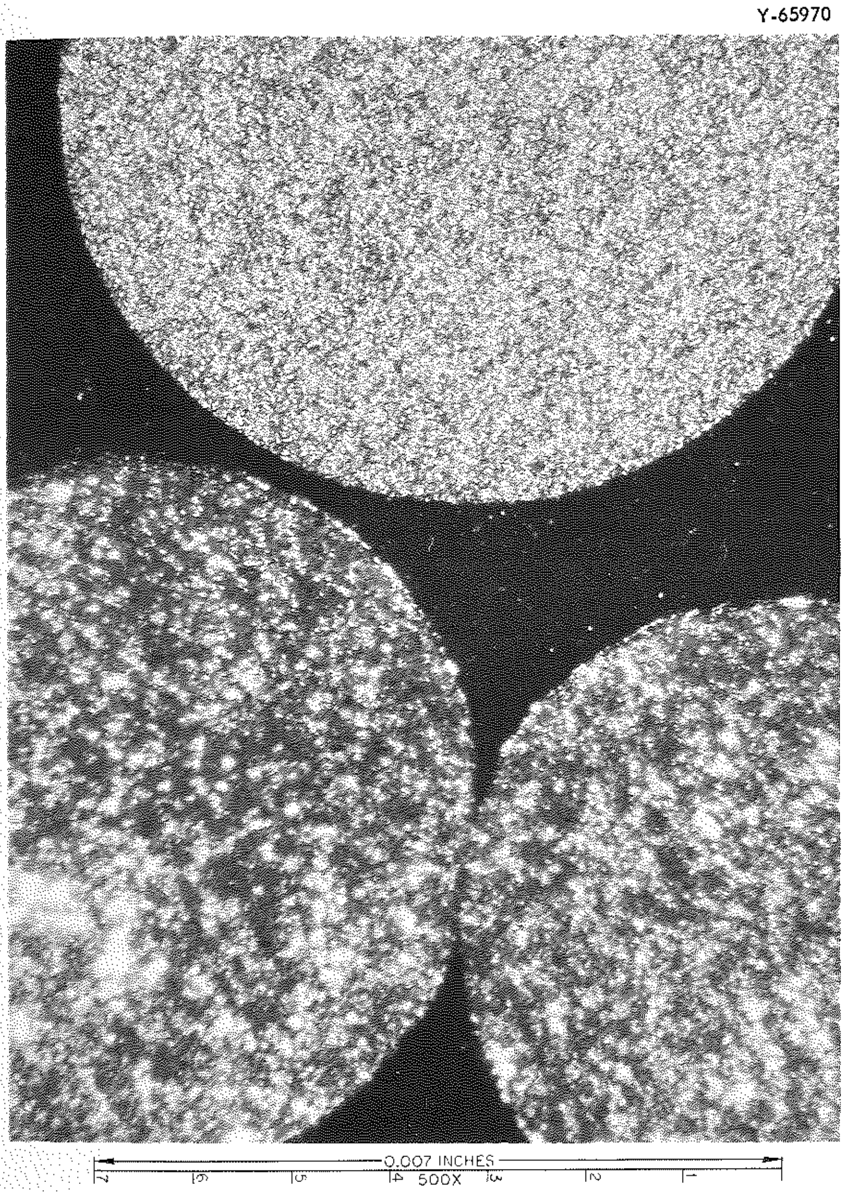

Fig. 4. Photomicrograph of Polished Sections of the Microspheres in Fig. 2, Using Polarized Light.

4.3 Conversion by Two-Step Method

Experiments in which the UO_2-C gel microspheres were first converted to uranium carbide [reaction (2)], then to nitride [reaction (3)], were quite promising. A run (run 18, Table 5) was made in which the gel microspheres were heated in argon for 2 hr at 1600°C to form carbide, then for 2 more hours in nitrogen gas at 1600°C to form nitride. The composition of the product was found by analysis to be $UN_{0.81}C_{0.40}O_{0.24}$. X-ray analyses indicated the product was mostly UN and contained some UO_2. No carbide or carbon x-ray patterns were found. The microspheres were silvery and well-shaped (Fig. 5). Some spheres were broken open and found to be the same color throughout. The density of these microspheres, measured by toluene displacement, was 12.43. Crush strengths, measured separately on five microspheres, were between 270 and 410 g. The spheres had diameters in the range 100 to 200 μ.

It is important to note that the carbon present in the UO_2-C gel microspheres (C/U atomic ratio = 2.7, see Table 6) was not enough for reaction (2) to go to completion, since this reaction requires 3 atoms of carbon per molecule of UO_2, and 4 atoms of carbon per molecule of UO_3. On the basis of the analyses presented in Table 6, an initial C/U atomic ratio of 2.7 should lead to a product having 0.73 atom of carbon, 0.73 atom of nitrogen, and 0.54 atom of oxygen per atom of uranium. Thus, the respective ratios achieved (0.81, 0.40, and 0.24) actually represent more conversion than could be expected if reactions (2) and (3) went to completion. It is apparent that additional reaction occurred by reaction (1) during the 2-hr nitrogen gas treatment. When UO_2-C gel microspheres are prepared in the future, with the correct amount of carbon for reaction (2) to go to completion, good conversion to UN by reaction (3) should be possible.

Photomicrographs of polished sections to the microspheres shown in Fig. 5 generally confirm the chemical and x-ray analyses, and, in addition, show a layer of nearly pure UN around the outside of the microspheres (Figs. 6, 7, and 8).

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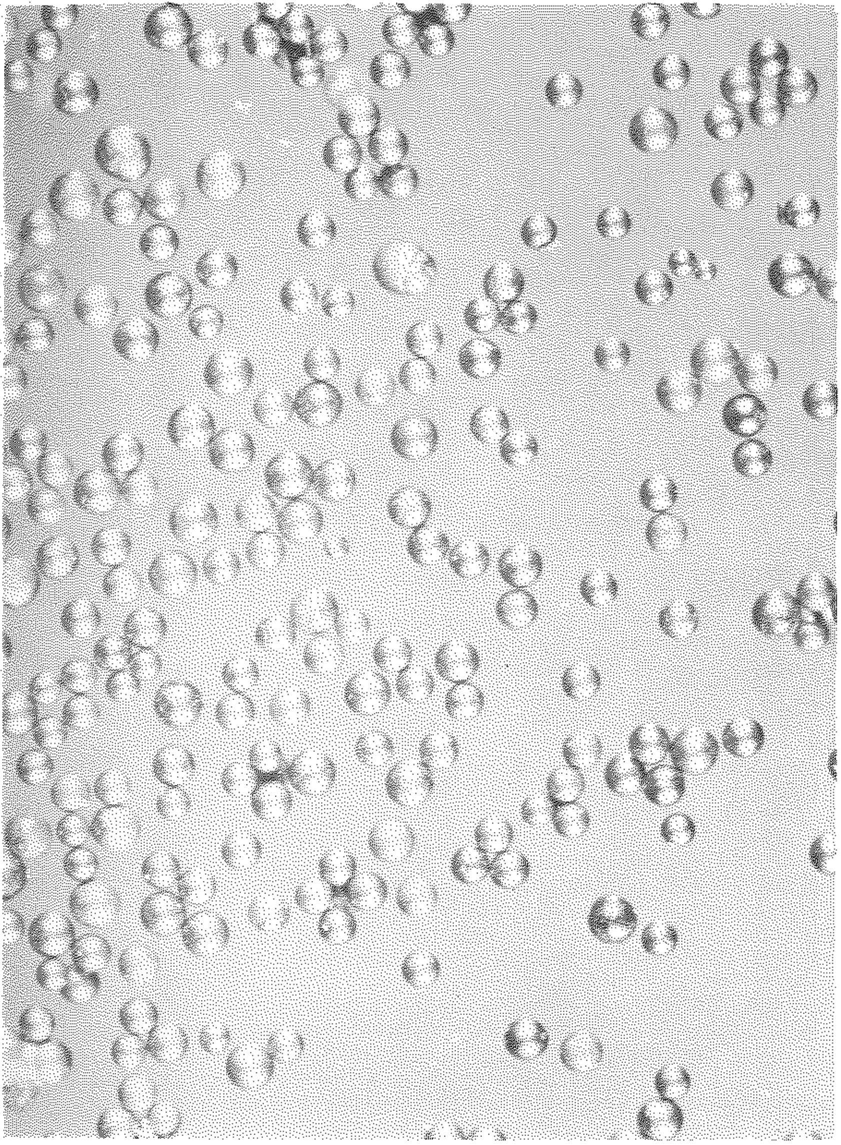

Fig. 5. Microspheres of UN Prepared by Firing UO_2-C Gel Microspheres, First in Argon, then in Nitrogen Gas. Magnification 33X.

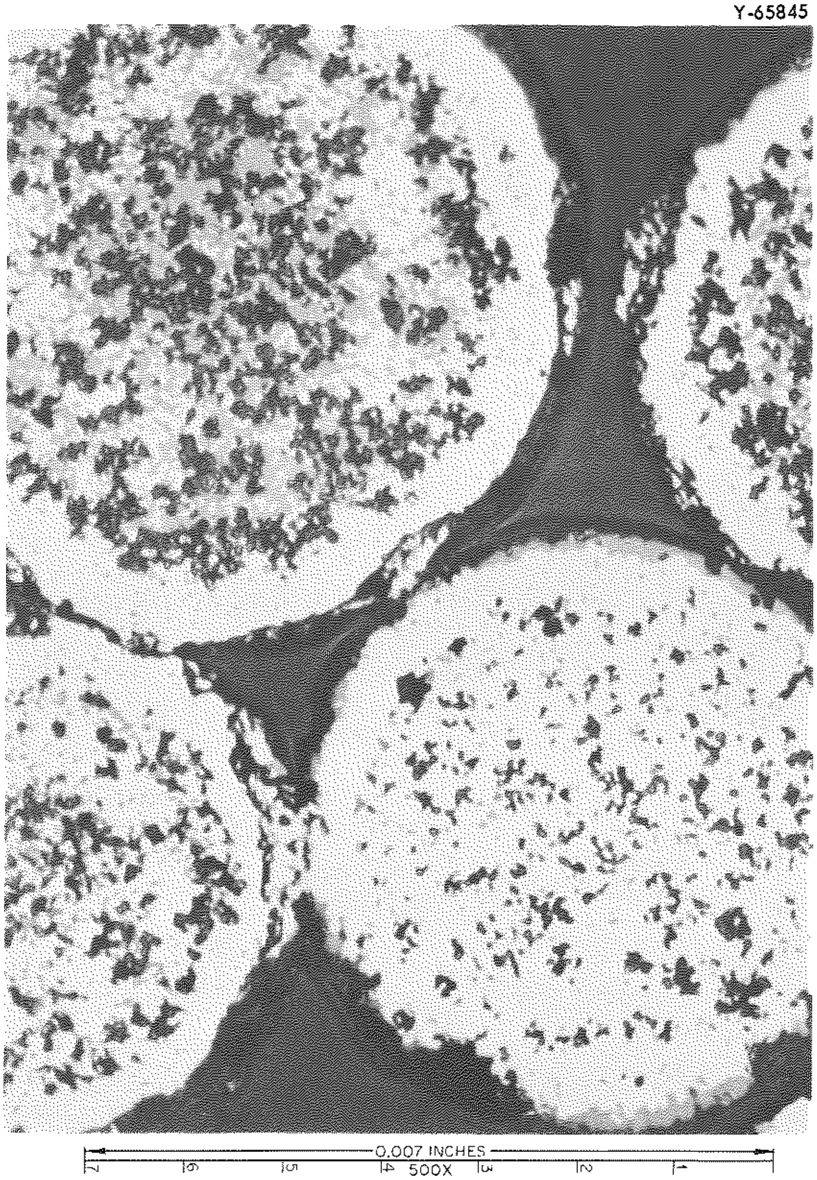

Fig. 6. Photomicrograph of Polished Sections of the Microspheres in Fig. 5, Using Bright-Field Illumination.

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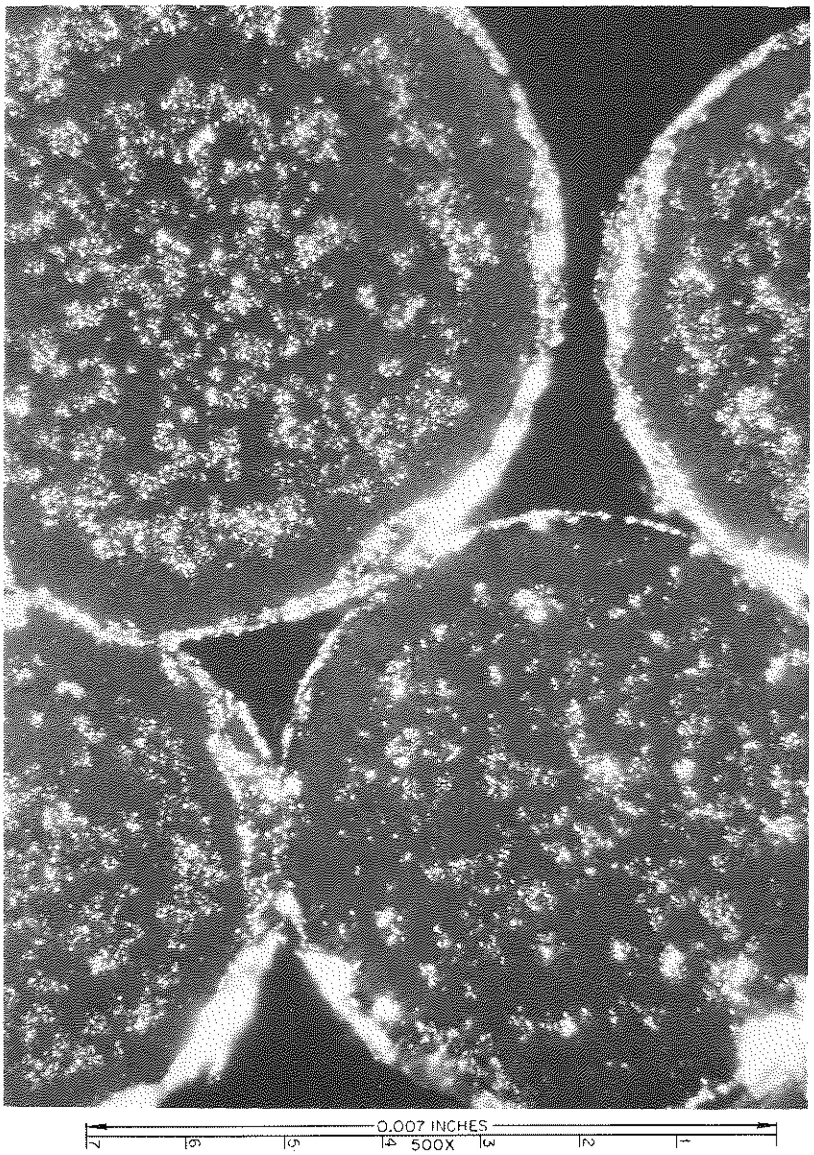

Fig. 7. Photomicrograph of Polished Sections to the Microspheres in Fig. 5, Using Polarized Light.

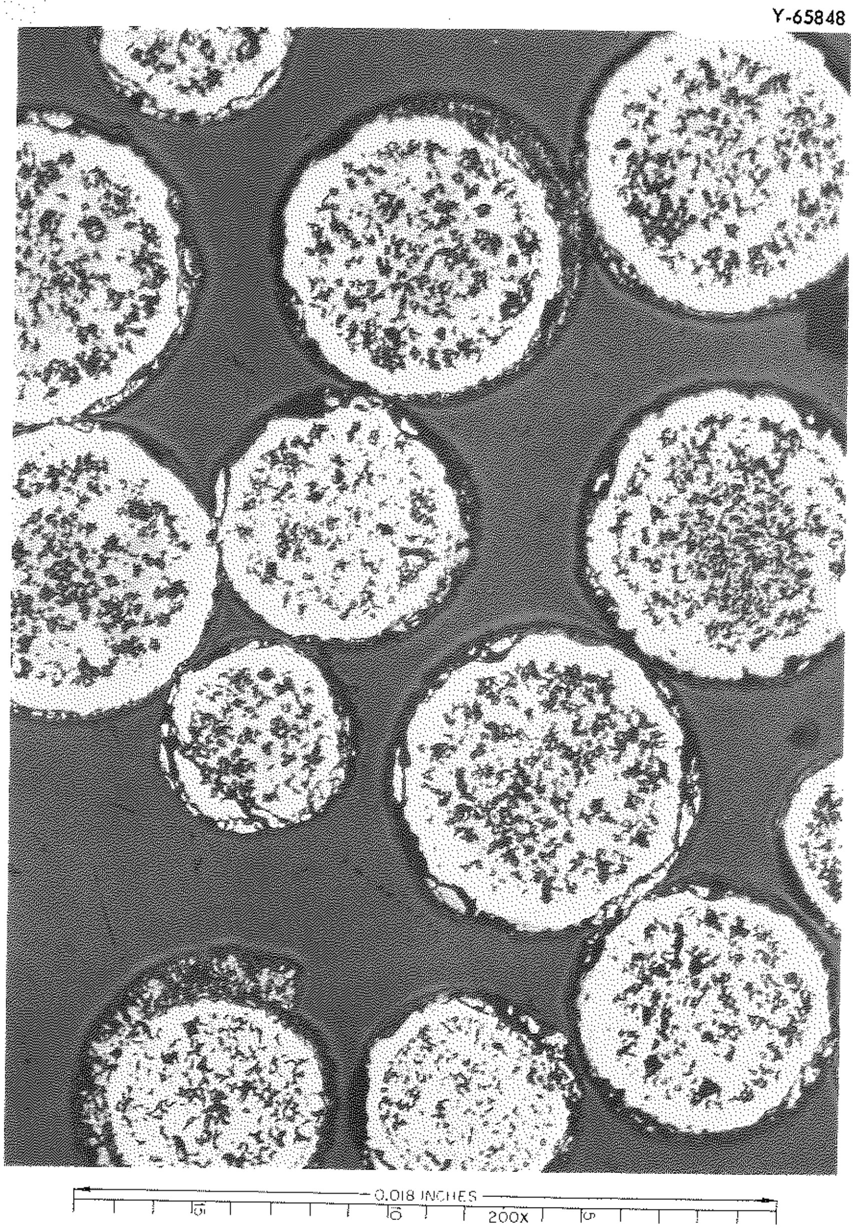

Fig. 8. Photomicrograph of Polished Sections of the Microspheres in Fig. 5, Using Bright-Field Illumination.

The UO_2 in the microspheres is visible as the gray material in Fig. 6, which is a bright-field photomicrograph. The major UN phase is white. The UO_2 near the outside of one section gives evidence of a slow reaction of the UN with the atmosphere at room temperature.

The layer of nearly pure UN around the outside of the microspheres may be caused by reaction (1) occurring slowly after reaction (2) and (3) have very nearly proceeded to completion. Reaction (1) would be expected to proceed slowly, since the UO_2 and carbon particles could come together only by diffusing through the UN matrix. It is not clear why reaction (1) should take place more rapidly near the outside of the microspheres. If the above explanation is correct, it suggests that the treatment in N_2 at 1600°C (2 hr for these microspheres) should be extended to allow reaction (1) to proceed into the center of the microspheres.

The dark spots in the polished sections in Fig. 6 might be either graphite particles or voids. A photomicrograph of the same sections taken with polarized light shows the presence of small graphite particles (Fig. 7).

A photomicrograph similar to Fig. 6 but taken at a lower magnification (Fig. 8) shows clearly the areas of pure UN near the outside of the microspheres.

Although this two-step method for converting UO_2-C gel microspheres to UN microspheres appears to work well, it has the possible disadvantage that carbon is left in the product. British workers have successfully reduced higher carbides of uranium to UC with hydrogen at 1000°C.[9] However, in the present study, microspheres of UN and carbon, prepared by the same method described above, were converted into powder by a 2-hr treatment with hydrogen at 1000°C. Carbon was removed, however, and was deposited in the reactor downstream from the UN powder.

5. CONCLUSIONS AND RECOMMENDATIONS

Methods were successfully developed for preparing UO_2-C sols and converting these sols into gel microspheres. Two methods were investigated for converting these microspheres into UN microspheres: (1) treating with a stream of N_2 at 1600°C, and (2) treating with a stream of argon at 1600°C followed by treating with N_2 at 1600°C. Both methods appear promising, but the second method always yields a product containing carbon.

In the first method, temperature cycling from 1600°C to about 1000°C and back to 1600°C is necessary to render pervious to N_2 a UN coat which forms on the gel microspheres when they are exposed to N_2 at 1600°C.

In the second method, further work is needed to develop a satisfactory method for removing the carbon in the microsphere product. A possible method, the use of hydrogen at atmospheric pressure and 1000°C, was tried; while it led to some carbon removal, it did not appear promising because it fractured the particles. However, other temperatures and lower hydrogen partial pressures should be tried.

Since the C/U ratio in the UO_2-C gel microspheres appears to be of critical importance in the preparation of pure UN microspheres, it will probably be necessary to control this ratio carefully. It will also be necessary to know accurately the uranium valence state, because the amount of carbon needed varies with the amounts of UO_2 and UO_3 present in the gel microspheres.

Information is needed concerning the rate at which the reaction yielding UN approach completion as a function of several variables: temperature, nitrogen gas partial pressure, CO partial pressure, C/U ratio in the gel microspheres, and size of the microspheres. The effects of these variables will be investigated with the aid of a controlled-atmosphere thermobalance.

The deliberate inclusion of excess carbon in the UO_2-C gel microspheres should be investigated, with the objective of forming microspheres containing solid solutions of UN and UC. Deliberate inclusion of material in the gel microspheres which volatilizes during firing should also be investigated as a means of producing UN microspheres of controlled porosity.

6. ACKNOWLEDGEMENTS

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