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LABORATORY PREPARATION OF SEVERAL KINDS OF NUCLEAR FUEL MICROSPHERES USING A SOL-GEL METHOD

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ABSTRACT

A sol-gel method was developed for laboratory preparation of microspheres of nuclear fuel materials having novel compositions or properties. Fired microspheres of UO_2, ThO_2 and mixed ThO_2-UO_2 having porosities ranging up to 44%, of UO_2-W, UO_2-Mo, and ThO_2-Mo cermets, of mixed UO_2-ZrO_2 containing up to 67 mole % ZrO_2, and of ZrC and mixed ZrC-ZrN were prepared. All of these products are potentially useful in reactor fuel applications. The laboratory procedures appear to be easily adaptable to larger-scale applications.

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INTRODUCTION

The purpose of this work was to develop a rapid laboratory method for making microspheres of nuclear fuel materials, mostly oxides, and to use the method for the preparation and preliminary evaluation of several products. A method which proved very useful for this purpose was developed. The method is a sol-gel process, but it differs significantly from sol-gel processes in use at Oak Ridge National Laboratory (ORNL)[1] and at several other laboratories and plants[2-7]. Features which make this new method attractive for laboratory use are simplicity, flexibility, and the ability to control anion concentration in the gel microspheres before they are fired. These features make it possible not only to investigate and evaluate, in a preliminary manner, many types of microsphere products, but also to "build" into the microspheres properties such as controlled porosity.

Microspheres of nuclear fuel materials containing admixed materials to increase their strength or thermal conductivity or to raise their melting temperature, and microspheres with controlled porosity are needed for evaluation as nuclear fuels. Hopefully, some of these new products will exhibit superior performance as nuclear fuels.

Among the types of microspheres prepared were porous UO_2 and ThO_2; UO_2-Mo, UO_2-W, and ThO_2-Mo cermets; mixed UO_2-ZrO_2 and ZrN-ZrC; and ZrC. These products were examined by microscopy, porosities were measured using mercury porosimetry, photomicrographs of sections and chemical analyses were made, and resistances to crushing were determined. The results of these evaluations are given along with a description of the procedures used.

DESCRIPTION OF THE METHOD USED TO PREPARE MICROSPHERES

All of the microspheres described in this work were prepared by the procedures outlined in Figure 1. In the sphere forming procedure, a stream of sol was forced from a syringe into a layer of 2-ethyl-1-hexanol (2EH) floating on 15 M NH_4OH. The sol dispersed into droplets in the 2EH and the droplets fell into the 15 M NH_4OH where they gelled. The gelled microspheres

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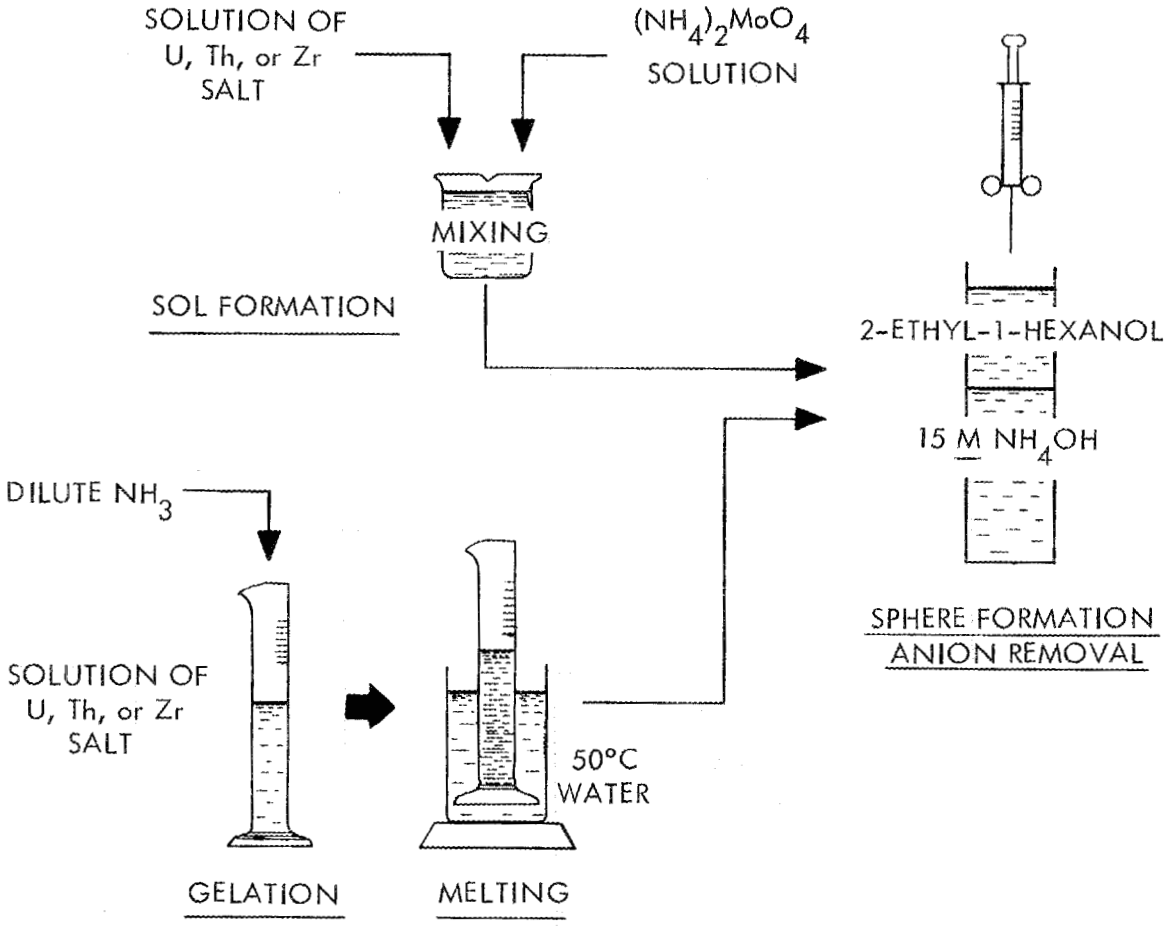

Fig. 1. Two Methods for Making Sols and One for Spheres Were Used.

did not agglomerate or otherwise change shape in the 15 M NH_4OH. Anions in the gelled spheres were leached out by the concentrated ammonium hydroxide. The gel spheres were dried and fired, usually for 1 hr at 1250-1300°C in argon purified over hot copper. In some cases 4% H_2-Ar was used.

It was discovered that sols form when ammonium molybdate solutions are mixed with solutions of uranium, thorium, or zirconium salts. The fundamental reasons that such sols form are not known, but the sols proved to be excellent starting materials for forming certain types of products, as will be shown below. A second method for making sols (Fig. 1, bottom) almost as simple as that described above, consisted of bubbling diluted ammonia gas into solutions of uranium, thorium, or zirconium salts until gelation occurred, then melting the gel at about 50°C to convert it to a free-flowing sol. All of the products described in this report were made from sols prepared by one of these two methods.

In some cases, minor variations in sol preparation were used. For example, sols containing zirconium were prepared by stopping the ammonia flow just before gelation occurred because the gels containing zirconium often could not be converted to sols by warming. In addition, good spheres could not be made from sols containing zirconium or thorium, made by the method shown in the lower half of Fig. 1, unless the sols were heated to 70-90°C for about 1 hr. Presumably, this treatment caused at least a partial conversion of amorphous sol into small crystallites.

In Fig. 2, the procedure used in this work is compared with the ORNL sol-gel process.[1] The other sol-gel processes, which have been described in publications,[2-7] are quite similar to the ORNL process. In the first step, anions are removed from a salt of uranium, thorium or zirconium by heating in air or water vapor, by alkaline precipitation followed by washing, or by solvent extraction, dialysis, or ion exchange. The product is peptized with water or dilute electrolyte solution to form a sol which is fed through a needle into an organic liquid where sol droplets are formed and dried to yield gel microspheres. In the procedure used in this work, sol is made by either of the two methods outlined in Fig. 1, and microspheres are formed by feeding this sol into the layered 2-ethyl-1-hexanol (2EH) and 15 M NH_4OH. Anion removal actually is part of the sphere forming step.

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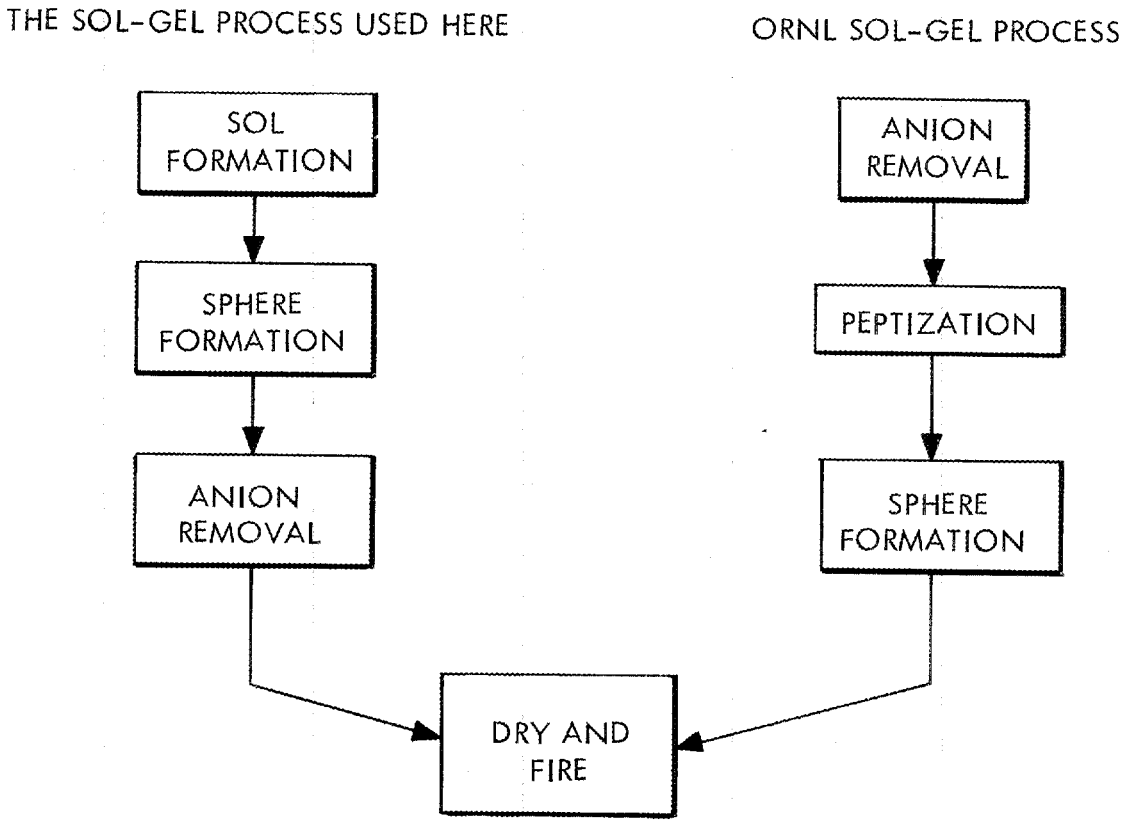

Fig. 2. Comparison of the Microsphere Preparation Method with the ORNL Sol-Gel Process.

The main advantage offered by this new method is the saving in time and effort required to investigate new sols. For example, the anion removal step requires no effort by the experimenter. In most of the cases described below, anion removal was accomplished by leaving the gel spheres in 15 M NH_4OH overnight. Microscopic investigation of the wet gel spheres immediately after formation will reveal if a new sol is working well enough to indicate that firing and evaluation of the fired product will be worthwhile. If the wet gel spheres appear to have unsatisfactory shapes, surfaces, or strength, they are discarded. Thus, the effect of several variables, such as sol concentration, on the forming operation can be evaluated rapidly.

Because it is not necessary to control water or surfactant content in the 2EH, the 2EH need not be circulated through a purification system and only a small amount (a layer about 3 inches thick) is required. No surfactant is needed because agglomeration of the droplets in the 2EH is not a problem. The droplets fall through the 2EH in a fraction of a second and therefore do not have an opportunity to agglomerate. The 2EH serves only to disperse the sol into droplets; it does not serve as a drying medium in this system as it does in the ORNL system outlined in Fig. 2. Therefore, the 2EH may be water-saturated.

The anion removal step may be terminated at any desired residual anion concentration by removing the gelled spheres from the ammonium hydroxide at the proper time. Results which are given later show that in some cases the residual ion concentration may be more important than has been previously realized.

Quantities of spheres sufficient for laboratory evaluation (about 20 g) can be formed in less than 5 min. The products described here were all made by applying pressure to a syringe by hand. To achieve better control over the sphere sizes, the use of a constant-speed feeding device would be necessary. Needles with bore diameters between 0.02 and 0.05 cm were used. The sphere size obtained depends on the velocity with which the stream of sol is introduced in to the 2EH rather than on needle size. This point will be discussed in more detail in the next section.

CONTROL OF MICROSPHERE SIZE[8]

The greater the velocity of the stream of sol entering the 2EH, the smaller are the spheres formed. An experiment was performed in which colored water droplets were pumped into 2EH, with a controlled-speed syringe drive. The dispersed droplets were photographed, and the photographs were examined with a microscope to determine the droplet sizes. The results are shown in Fig. 3. The variation of radius with velocity cannot be explained by a simple theory such as that given in the appendix. However, it is clear, from the results in Fig. 3, that the droplet size, and therefore the product size, can be controlled by controlling the velocity with which the sol is introduced into the 2EH.

POROUS UO_2 MICROSPHERES MADE BY VOLATILIZING MoO_3[9]

Porous UO_2 microspheres were made by firing UO_2 gel spheres containing hydrous MoO_3. The sols and gel spheres were prepared by the method outlined in Fig. 1 (top of figure). Upon firing, MoO_3 volatilized leaving pores in the product. A firing temperature of 1000°C for 1 hr in argon results in volatilization of about 98% of the molybdenum, and a temperature of 1300°C was used to desorb the remaining MoO_3 from the porous product.

In a typical preparation, a sol 1 M in uranium was prepared by mixing 1.6 M U^{4+} chloride solution with $(NH_4)_2MoO_4$ solution. The U^{4+} solution was made by dissolving UCl_3 in water. The UCl_3 reacts with water to form U^{4+}. The Mo/U atomic ratios were adjusted between 0.1 and 0.8. A U^{4+} chloride sol, prepared by the method shown in the lower part of Fig. 1, could be used in place of the solution; the results were the same in either case. Microspheres were prepared as described above (see Fig. 1) and left standing in 15 M NH_4OH for 20 hr. Upon removal from the 15 M NH_4OH, the atomic ratio of Cl^-/U had decreased from an initial value of 3 in the sol to about 0.01. For sols with a Mo/U atomic ratio of 0.3 or more, the Mo/U ratio had decreased to about one-half the original value. When the Mo/U ratio in the sol was 0.1, only about one-third of the molybdenum leached out in the 15 M NH_4OH.

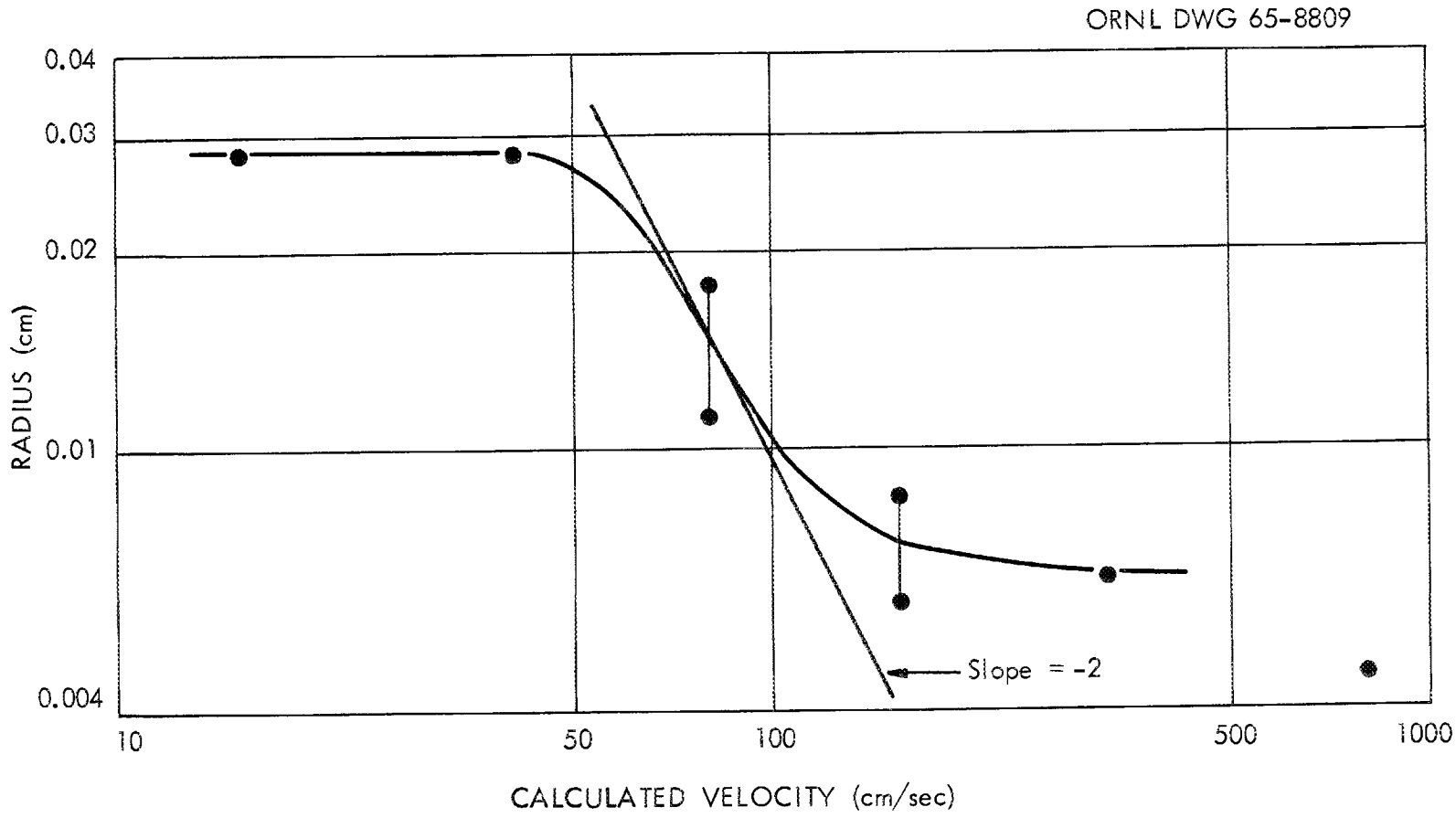

Fig. 3. The Slope of the Log-Log Plot of Radius vs Velocity Equals (-2) when the Velocity is About 80 cm per sec.

The porosity of the product increased rapidly with increasing Mo/U atomic ratios in the sol from 5% for sols containing no Mo to 30% at a ratio of 0.3 (Fig. 4). Greater amounts of molybdenum in the sol resulted in only a small increase in porosity.

As would be expected, the crush strengths of 300 μ spheres decreased rapidly (from 1700 g to about 300 g) as the porosity increased from 5% to 30%.

The density of the product not penetrated by mercury was close to 100% of theoretical, showing that nearly all of the pores were open to the surface.

Some typical examples of the section of the porous products are shown in Fig. 5. The porosity was increased from 19 to 34% by increasing the Mo/U atomic ratio in the sol from 0.1 to 0.8. Almost all pore diameters fell in the range 1 to 10 μ, with the smaller pores predominant for the lower porosities. The N_2 surface areas were 0.1 m^2/g or less, and decreased slightly with increasing porosity, due to the increase in pore size with increasing porosity.

An example of a section of a UO_2 microsphere of low porosity, 1.3%, is shown for comparison purposes in Fig. 6. The spheres from which this section was taken were prepared by the method shown in Fig. 1 (bottom).

POROUS ThO_2 MICROSPHERES MADE BY VOLATILIZING MoO_4

Porous ThO_2 microspheres were prepared by the same method described in the previous section for porous UO_2 microspheres, with 1 M $Th(NO_3)_4$ solution in place of the U^{4+} chloride solution. The thorium concentration in the sols was 0.7 M. The maximum Mo/Th atomic ratio used was 0.6; higher ratios resulted in sols that could not be converted to gel spheres because they were too viscous. For ratios less than 0.3, the $(NH_4)_2$ MoO_4 solution was mixed into thoria sols prepared by using ammonia (bottom method in Fig. 1). At these low ratios, sols prepared by simply mixing $Th(NO_3)_4$ solution with $(NH_4)_2$ MoO_4 solution resulted in elliptical rather than spherical product. Leaching in 15 M NH_4OH decreased the ratio of nitrate ions to thorium atoms from 4 in the sol to 0.01 in the gel spheres but did not effect the Mo/Th atomic ratios.

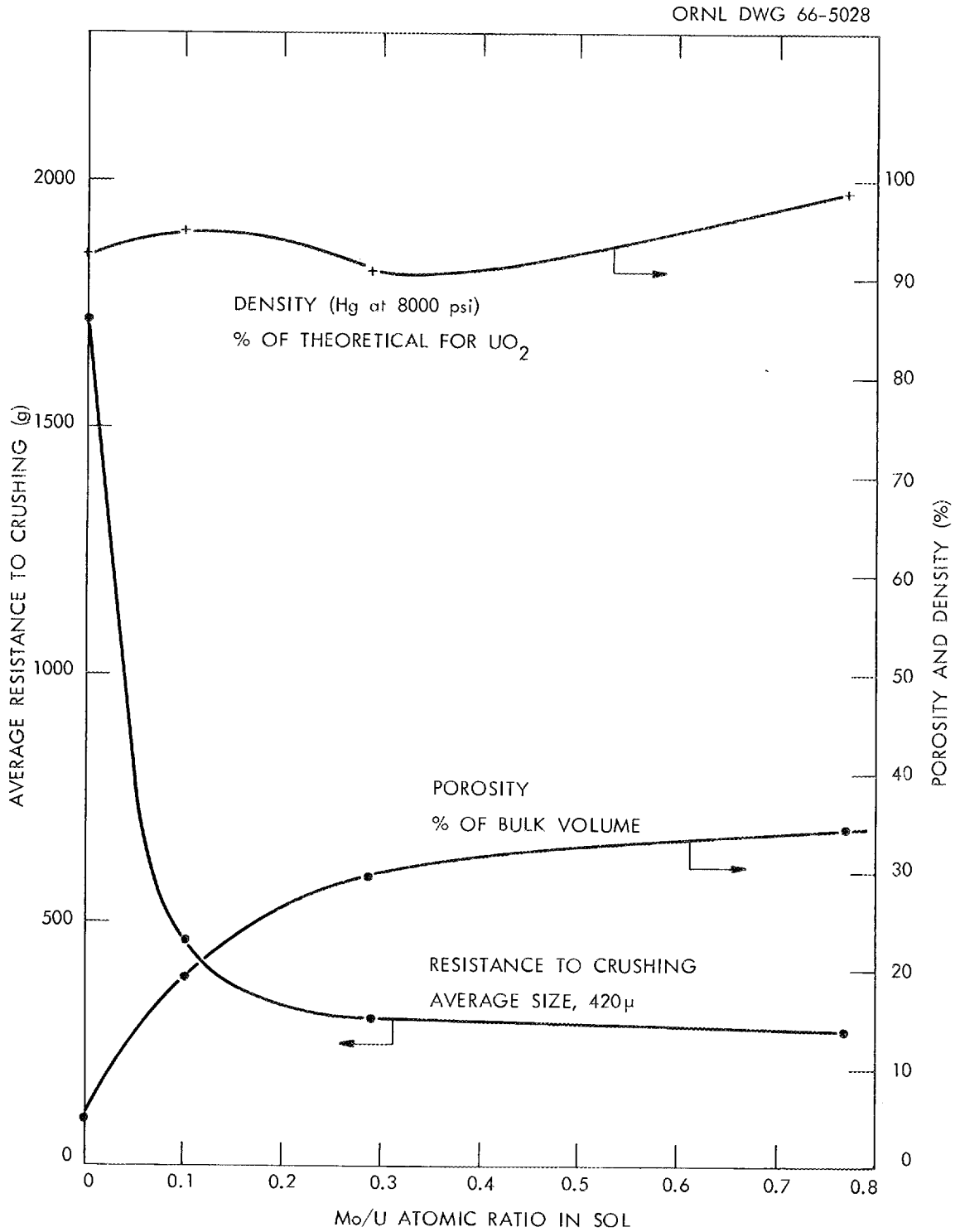

Fig. 4. Porosity Increases and Resistance to Crushing Decreases in the Fired Product as Mo/U Atomic Ratios in the Sol Increase.

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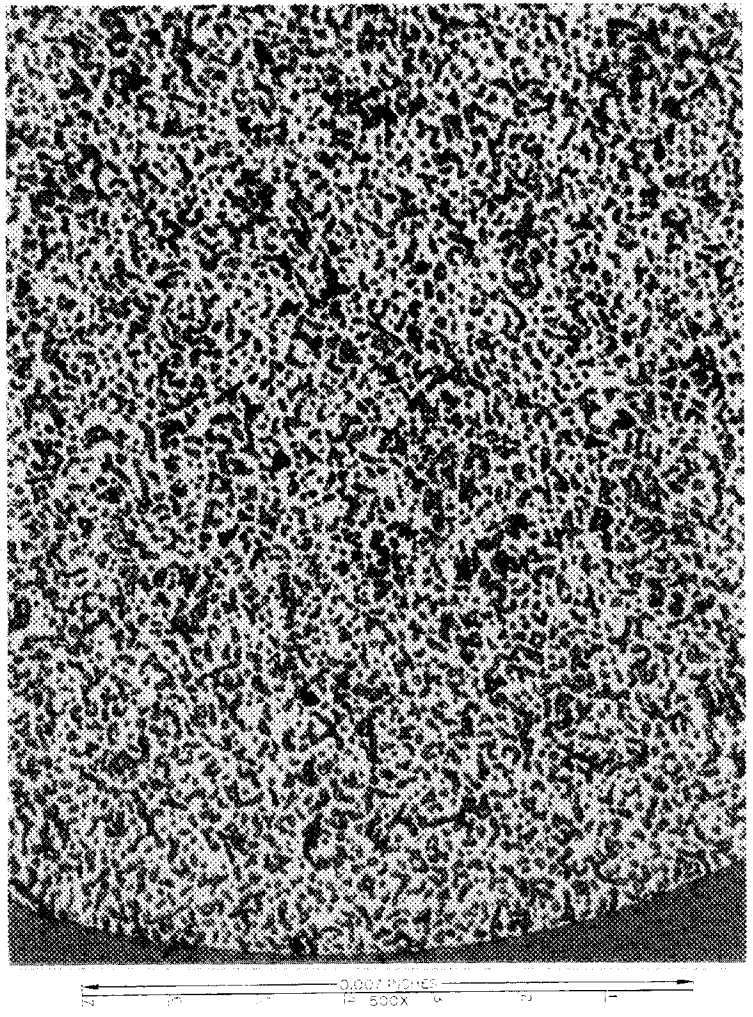

(a)

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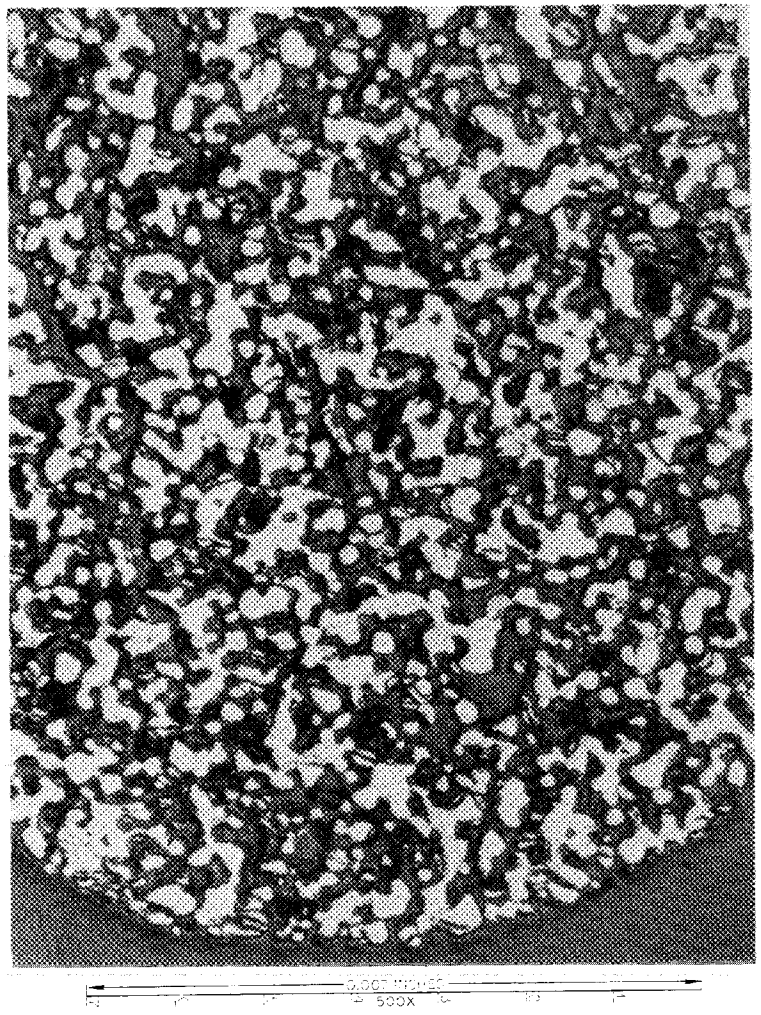

(b)

Fig. 5. Fired Microspheres from a U^{4+} chloride - $(NH_4)_2 MoO_3$ Sol. Mo/U atom ratios: (A) 0.1, (B) 0.8. Porosities: (A) 19% (B) 34%.

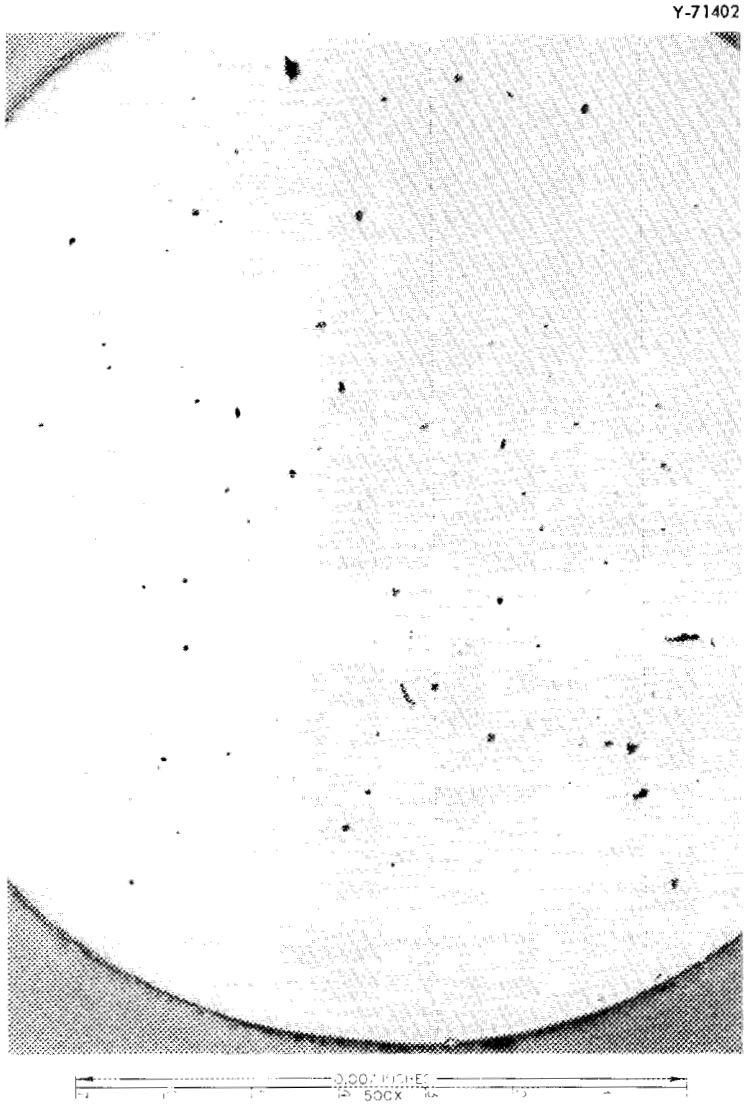

Fig. 6. Fired Microsphere from a U^{4+} Chloride Sol. Porosity is 1.3%.

The porosity of the product was over 20% when the Mo/Th atomic ratio in the sol was only 0.1 and showed no dependency on the amount of molybdenum in the sol over the range of ratios between 0.1 and 0.6 (Fig. 7). Some variable other than the amount of molybdenum caused the porosity to scatter between 12 and 33%. This variable is probably the rate of mixing of the thorium and molybdenum solutions. The sol forms very rapidly and, to obtain a uniform sol, the rate of mixing must be rapid. The sol preparation step needs further investigation.

Up to 0.1 Mo/Th the resistance to crushing decreased with increasing porosity, as expected, and the density of the ThO_2 not penetrated by mercury was usually nearly 100% of theoretical, showing that most of the pores were open to the surface. At higher Mo/Th, however, the products with lower porosity usually had lower crush strength and lower density, indicating that here some pores were not open to the surface.

Porous spheres of mixed UO_2-ThO_2 (20-80%) were also made by the same procedure, with the exception that a 0.8 M $Th(NO_3)_4$ -- 0.2 M $UO_2(NO_3)_2$ rather than 1 M $Th(NO_3)_4$ was mixed with ammonium molybdate solution.

In Fig. 8, photomicrographs of sectioned porous ThO_2 and UO_2-ThO_2 (20-80%) spheres, with 33% and 43% porosity, respectively, are shown. These spheres were made from sols containing 0.6 atom of Mo per mole of Th + U. The respective crush strengths (average of five measurements) for 300 μ spheres were 460 and 250 g. It is apparent that the pores are quite uniformly distributed.

POROUS UO_2 MICROSPHERES MADE BY VOLATILIZING CHLORIDE

It was discovered that the volatilization of residual chloride during firing of UO_2 gel spheres not only produced controllable porosity similar to that obtained by volatilization of MoO_3, but also resulted in a greater range of porosity of 1 to 44%.

The sol and spheres were prepared by the method outlined in the bottom of Fig. 1, starting with 1.0 to 1.7 M U^{4+} chloride solutions. The volume of 15 M NH_4OH used was varied to cause different residual chloride concentrations in the gelled spheres. As the volume of 15 M NH_4OH increased, the amount of chloride in the gelled spheres (Fig. 9) and the porosity of

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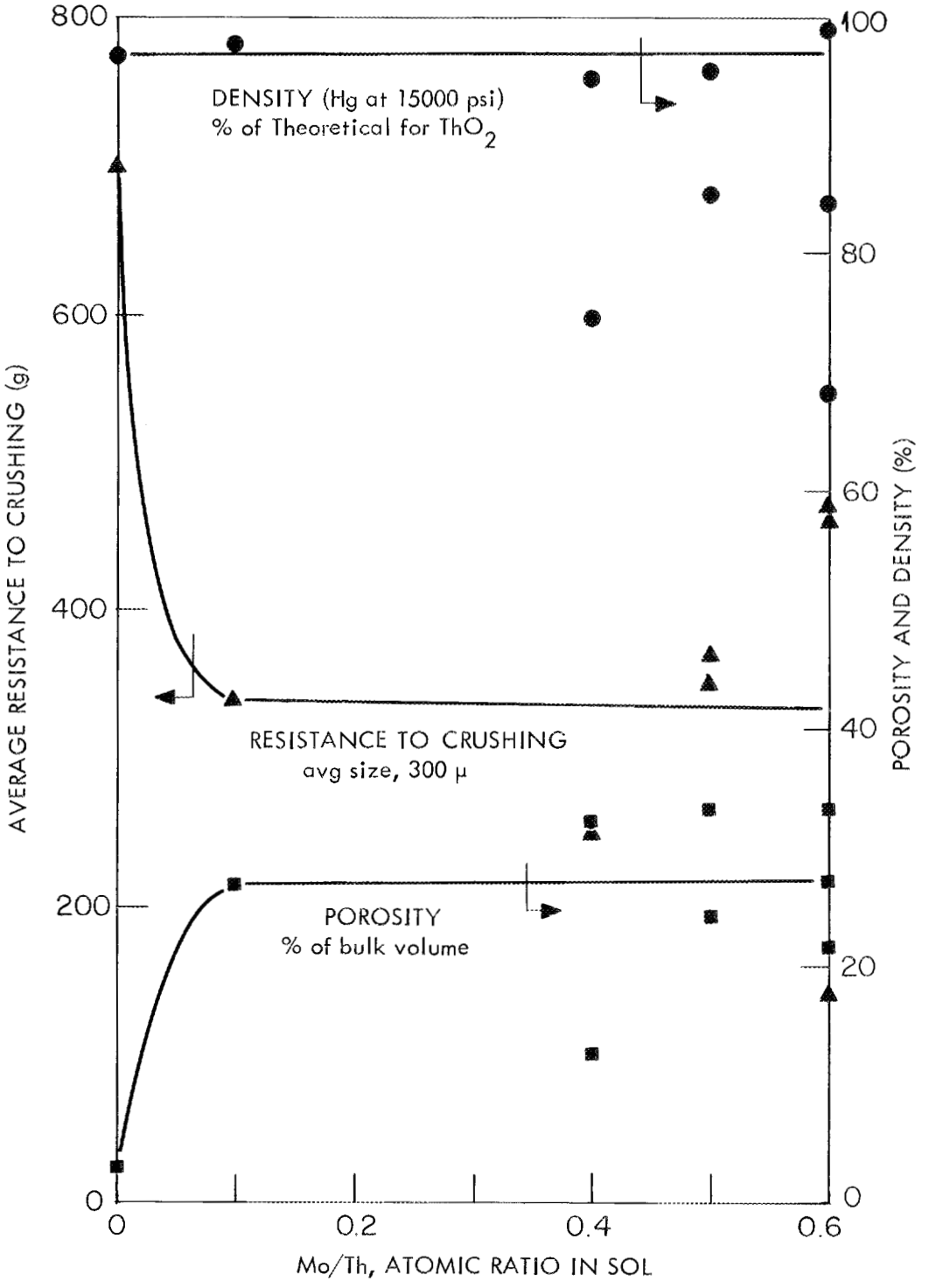

Fig. 7. Porosity Increases and Resistance to Crushing Decreases in the Fired Product as Mo/Th Atomic Ratios in the Sol Increase.

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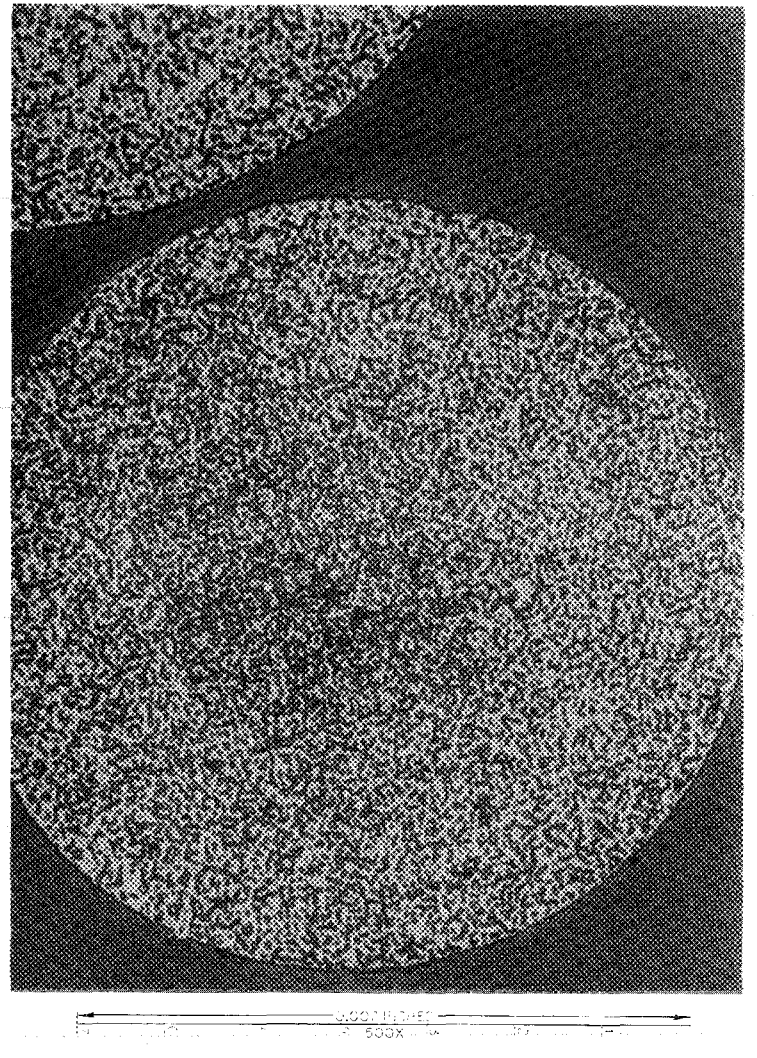

(a)

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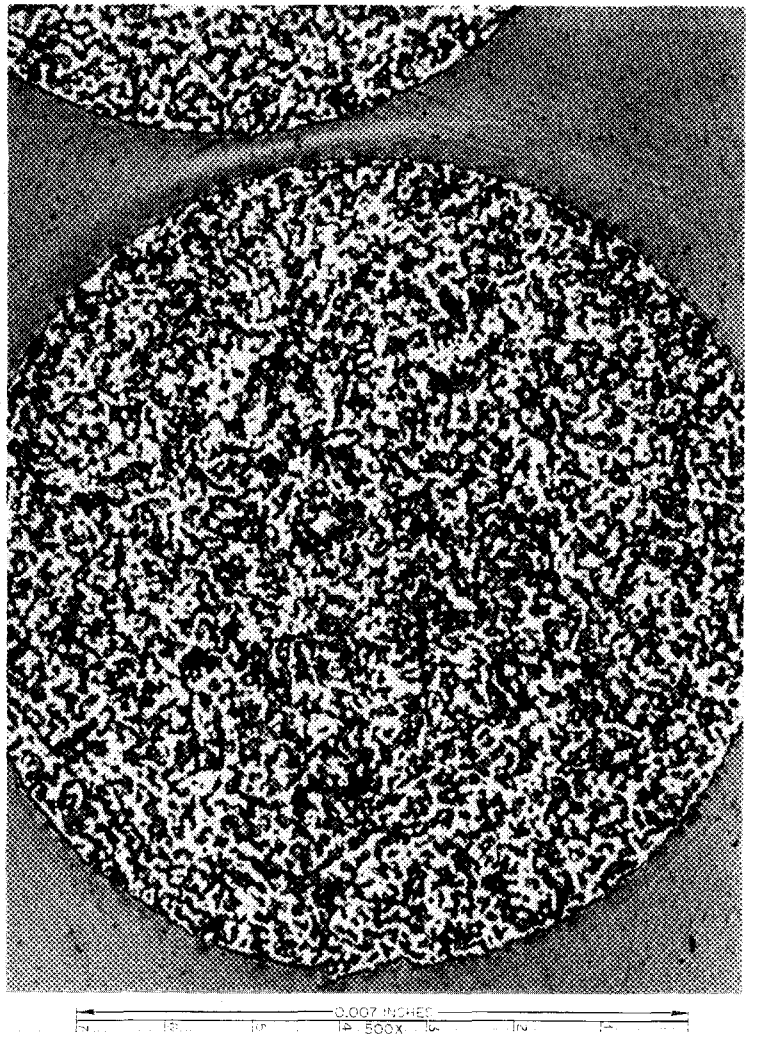

(b)

Fig. 8. Fired ThO_2(A) and UO_2-ThO_2 (20%-80%) Microspheres, made from Sols Containing 0.6 atom of Mo per atom of Th + U. Porosities: (A) 33%, (B) 43%.

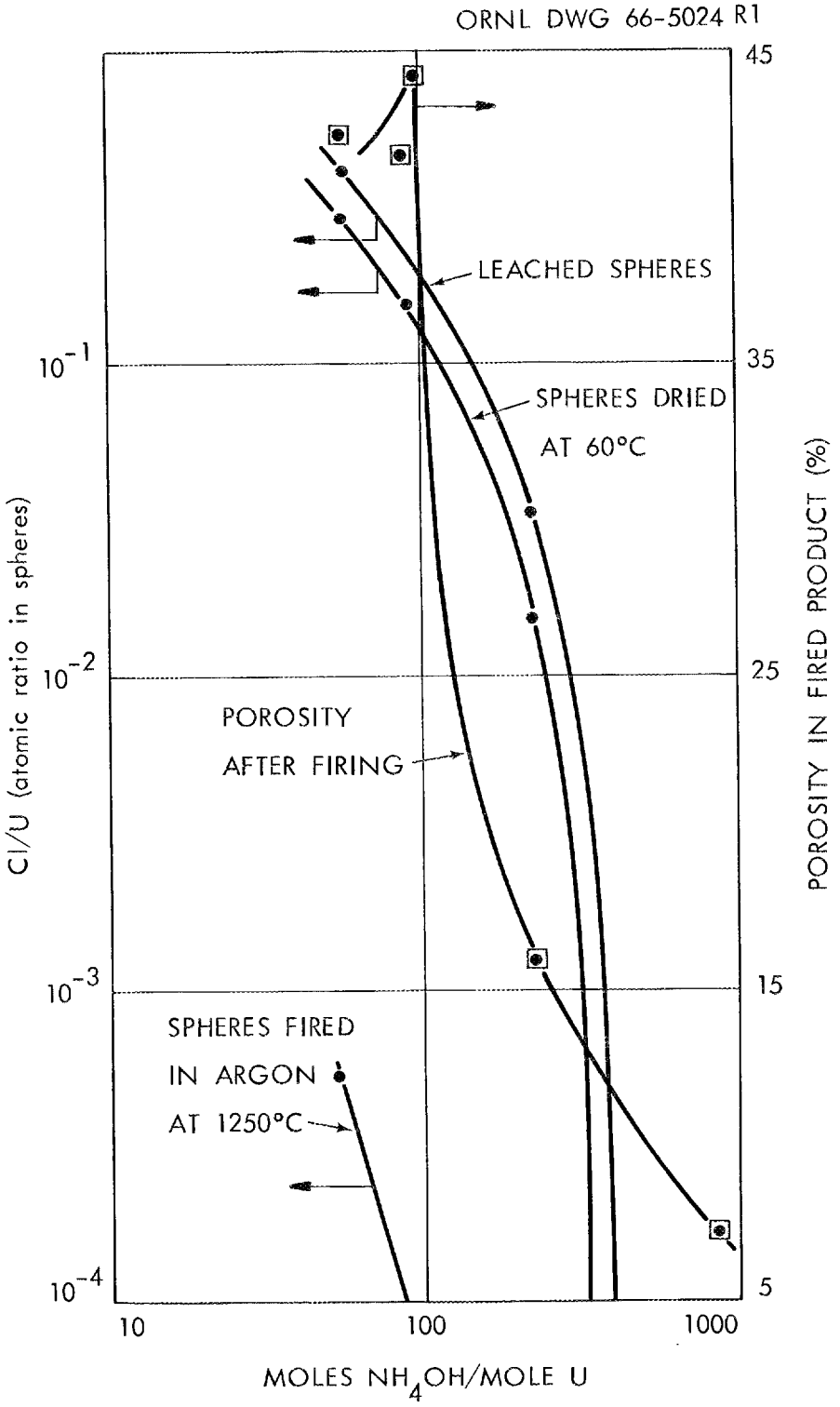

Fig. 9. The Amount of Chloride in the UO_2 Gel Spheres Decreases with the Amount of 15 M NH_4OH Used as Leachant.

the product (Fig. 10) fired in argon both decreased. Oven-drying removed very little chloride, but firing reduced the Cl/U atomic ratio in the product to less than 10^{-4} (about 10 ppm) if the ratio in the gel spheres was as low as 0.2. The excess oxygen in the fired product, calculated as % UO_3, ranged between 0.3 and 3% UO_3.

The porosity in the fired product reached a maximum of 44% when the Cl/U atomic ratio in the gel spheres was about 0.3 (Fig. 10). If the ratio was increased to between 0.3 and 0.4, the porosity decreased rather than increased, because the pore structure began to break up. At ratios higher than 0.43, the product was a powder. At ratios below 10^{-4}, too low to measure by the analytical methods used, the products still had porosities 2 to 7%. Evidently very small amounts of chloride in the gel spheres result in several percent porosity in the product.

In a typical preparation (porosity, 27%), 93% of the pore diameters were in the range 0.3 to 1.6 μ, about 3% were larger than 9 μ and 2% were smaller than 0.6 μ. The remaining 2% fell between 1.6 and 3.9 μ.

Resistance to crushing in 300 μ spheres was maximum (over 1700 g) at 5% porosity, dropping to 800 g at 1% porosity and to 100 g at the porosity maximum of 44% (Fig. 11). The two circled points near 42% porosity in Fig. 11 represent product from the gel spheres in which the Cl/U atomic ratio was greater than 0.2 before firing. Here the onset of deterioration into powder lowered both the resistance to crushing and the porosities.

Examples of sections of fired UO_2 microspheres with 44% porosity, the highest attained, are shown in Fig. 12. The photograph taken at lower magnification shows that the porosity is uniformly distributed. An example of product in which the pore structure has started to break up (Cl/U atomic ratio in leached spheres was 0.4) is given in Fig. 13. This product still retained its spherical shape but had practically no strength. Its color was red, rather than the black color typical of UO_2.

CERMET MICROSPHERES OF UO_2-Mo, UO_2-W AND ThO_2-Mo

The main purpose for introducing metal into nuclear fuels oxide microspheres is to increase the thermal conductivity. Therefore, to

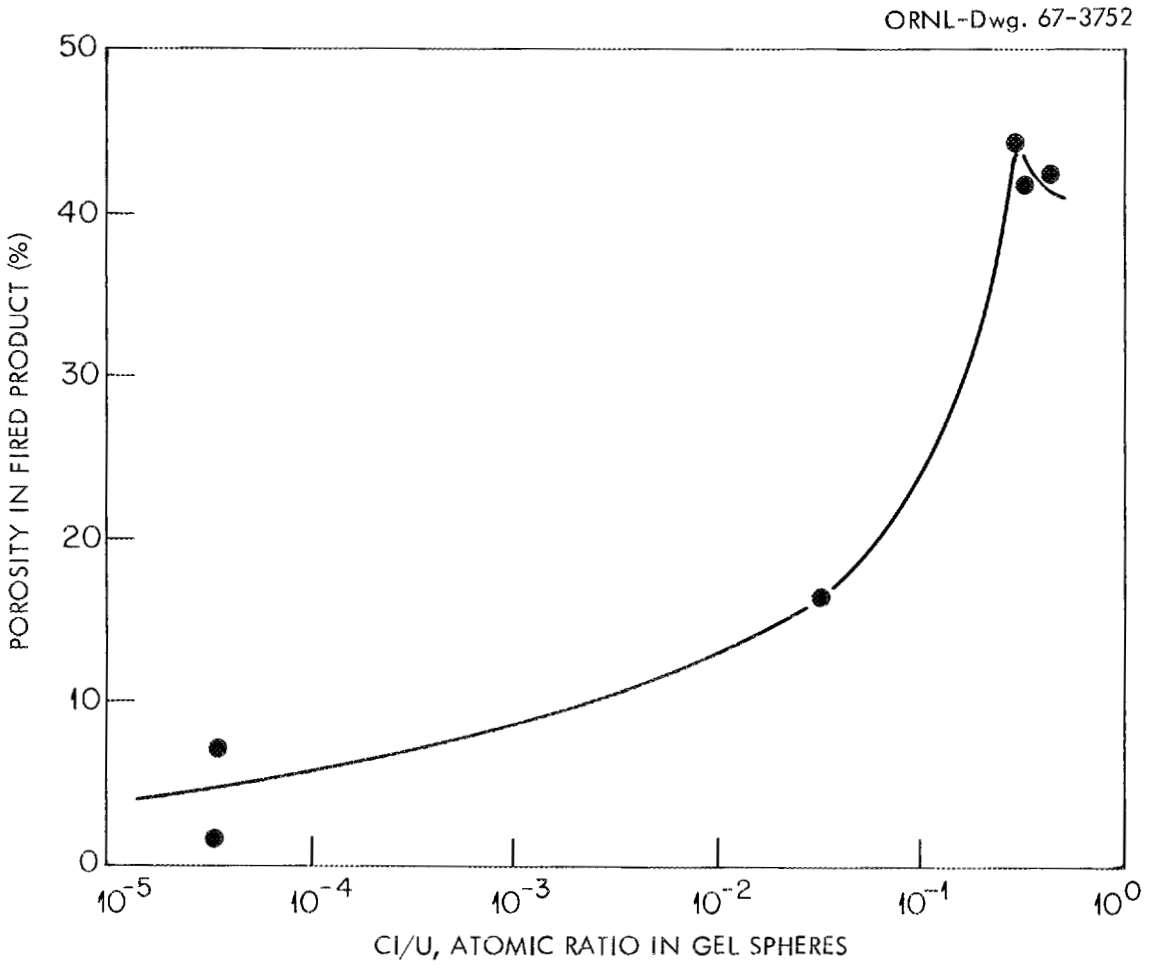

Fig. 10. Porosity in the Fired UO_2 Increases with the Amount of Chloride Left in the Gel Spheres.

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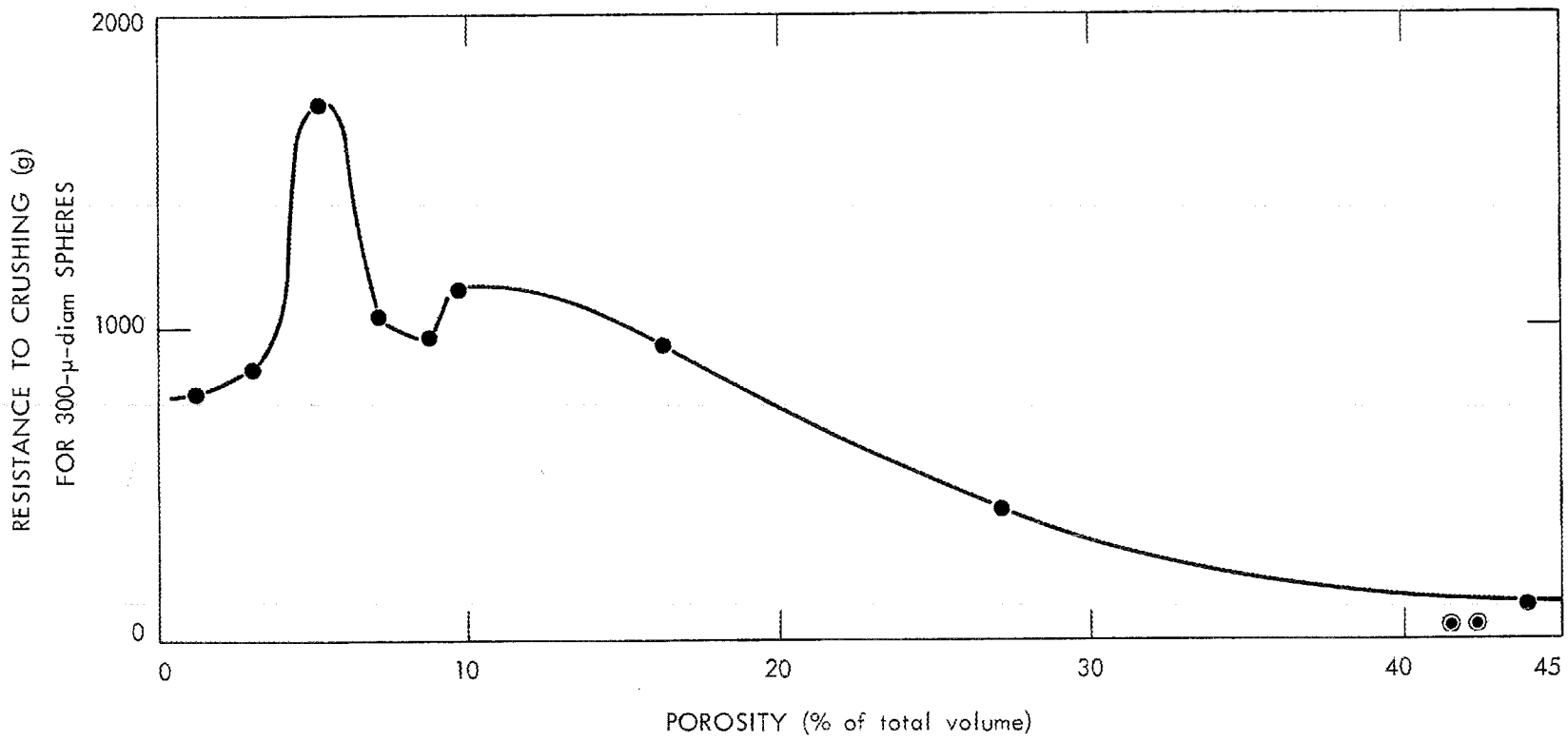
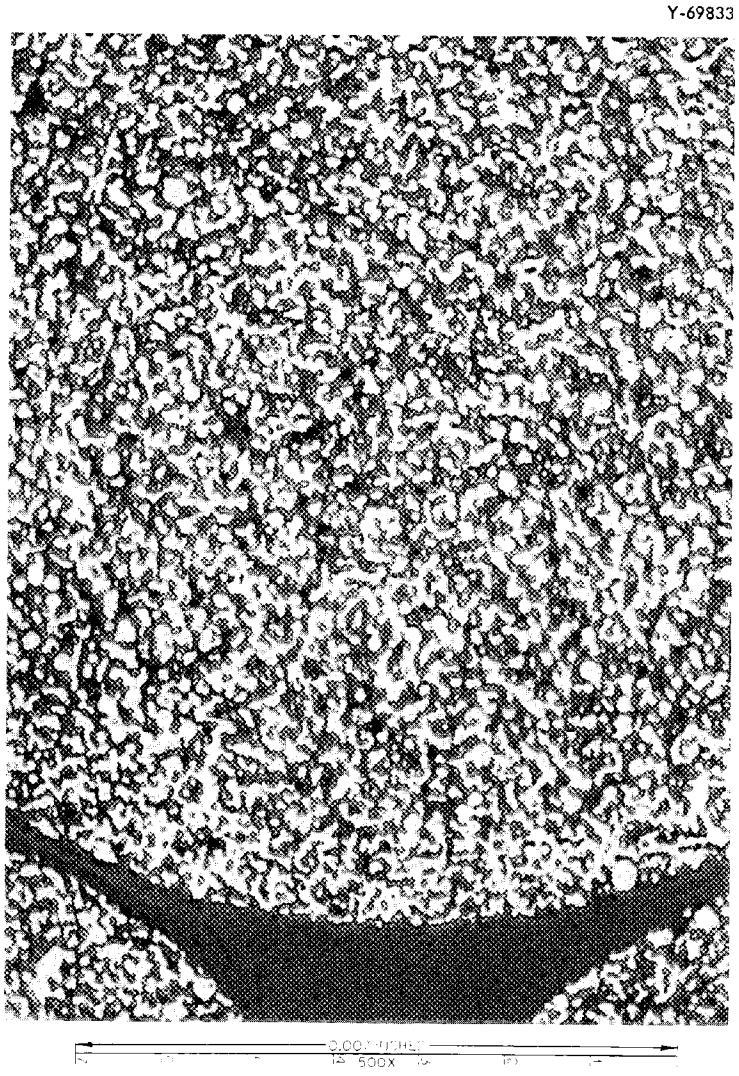


Fig. 11. Resistance to Crushing in the Fired UO_2 Microspheres Increases as the Porosity Increases to 5%, then Decreases with Increasing Porosity.



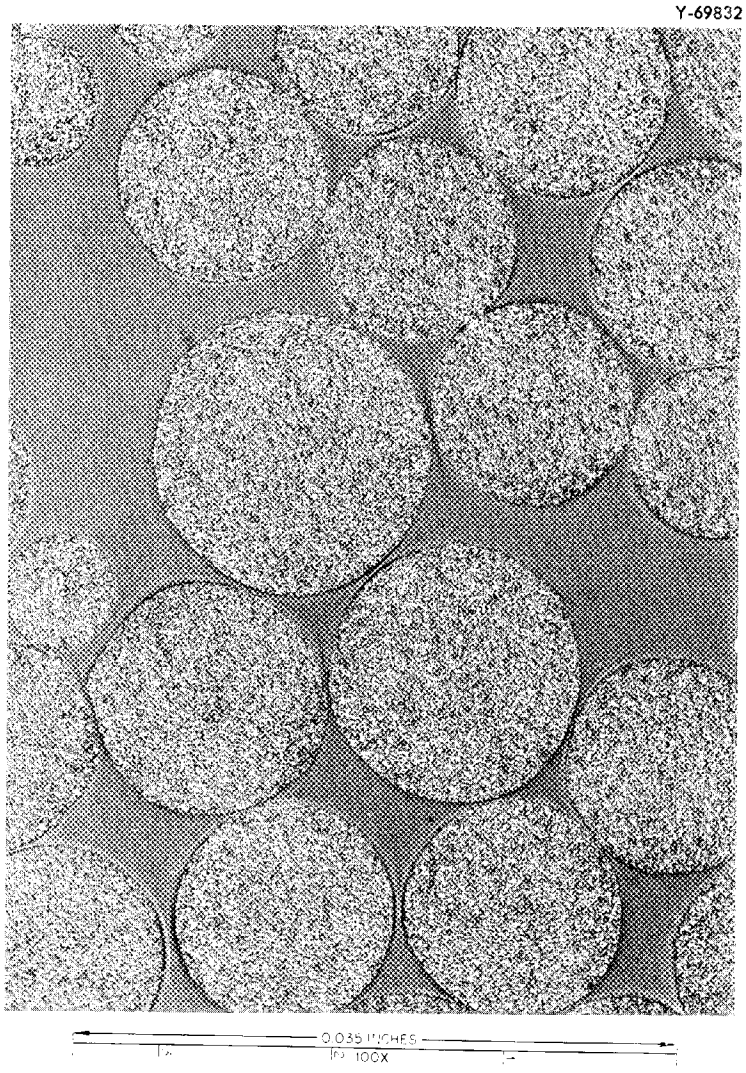


Fig. 12. Fired UO_2 Microspheres with 44% Porosity.

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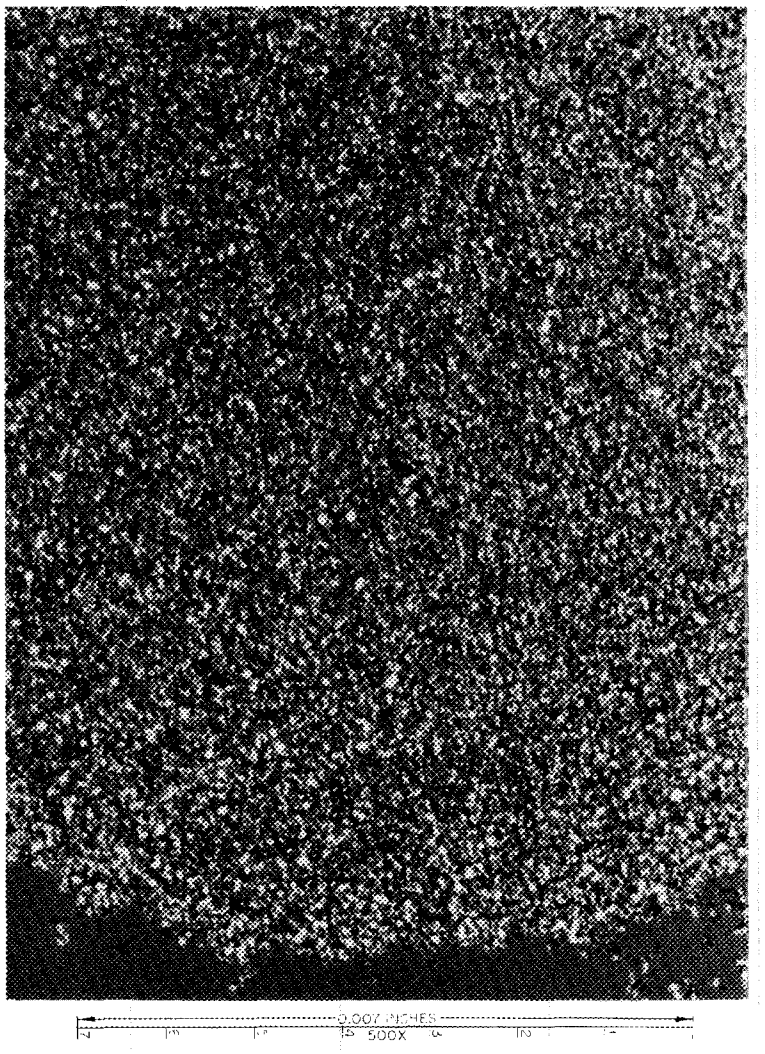

Fig. 13. Example of Fired UO_2 in which the Pore Structure Has Begun to Break Up. Porosity is 42.5%.

obtain a potentially useful product it is necessary to learn not only how to make strong, well-shaped microspheres but also how to make a product with good thermal conductivity. The visual observation of a continuous metal phase in photomicrographs of polished sections indicates good thermal conductivity.

In the examples described below, the structure was too fine to determine if the metal phase was continuous, even at 1000 times magnification. The absence of any visible metal aggregates is encouraging. Electrical conductivity much higher than expected for oxides was observed in electron microprobe measurements. These results are sufficiently promising to warrant further development work. In particular, a good method for measuring the thermal conductivity of the microspheres is needed.

The method used to prepare sol for UO_2-Mo product was the same as that described above for making porous UO_2 microspheres by volatilizing MoO_3. The major difference in the preparation occurred in the firing step. Firing was carried out in a reducing atmosphere (4% H_2-Ar, 1250°C for 1/2 hr) in order to reduce the MoO_3 to metal rather than volatilizing it.

No structural details could be discerned from photomicrographs of polished sections taken at 1000 times magnification (Fig. 14). Thus, it is not possible to determine if there is a continuous molybdenum or UO_2 phase. On the other hand it is apparent that there are no large aggregates of metal. Some crystallite growth was made visible by the polishing process. Chemical analysis showed that the product from which Fig. 14 was taken contained about one-half atom of molybdenum per mole of UO_2. The resistance to crushing of 300 μ spheres was about 600 g. The density, determined with mercury at 25°C, was 10.16, or 94% of the density calculated from the theoretical densities of UO_2 and molybdenum. X-ray analyses showed the presence of molybdenum metal and no molybdenum oxide.

A very similar procedure was used to make UO_2-W microspheres. Enough 7 M ammonium metatungstate solution was mixed with 1 M U^{4+} chloride solution to yield a sol containing about one atom of W per atom of UO_2. This sol is not stable and must be formed into spheres quickly. Because the sol is acidic, precipitation of tungstic acid begins within about 10 minutes. The forming and firing procedure were unchanged from that described

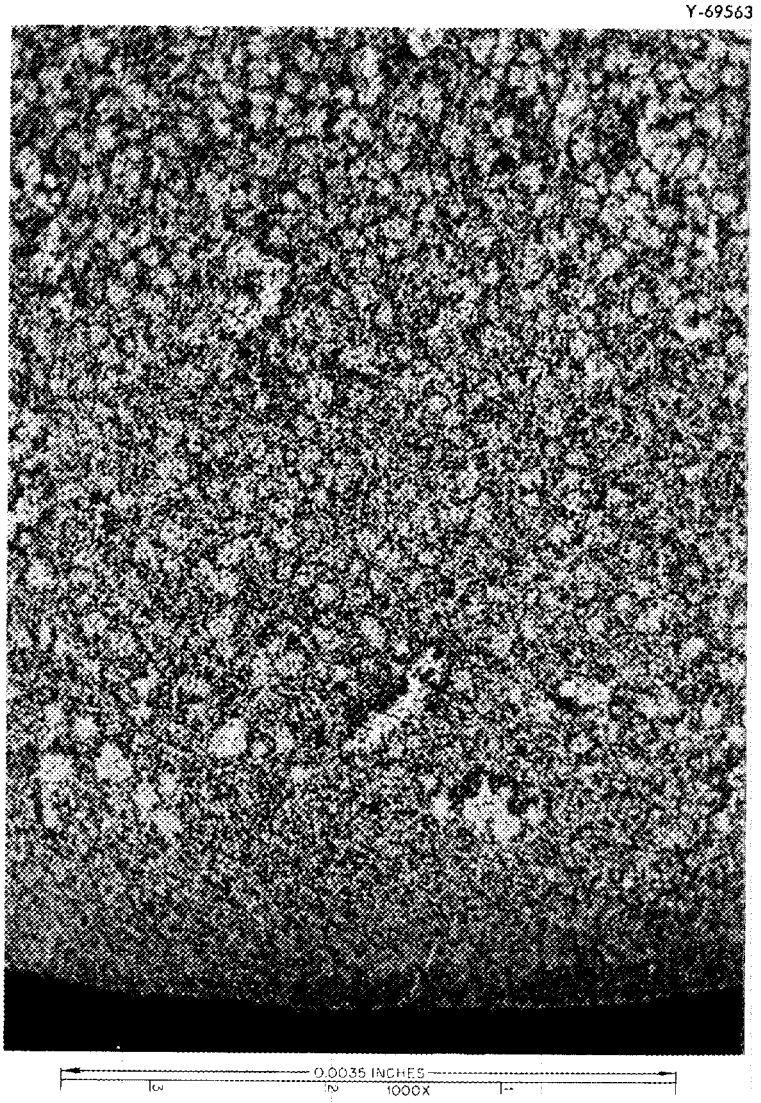

Fig. 14. Fired Cermet Microsphere of 65 mole % UO_2-35 mole % Mo.

above for the UO_2-Mo case. The products also appear to be very similar (Fig. 15). Again, no structural details can be discerned from the photomicrograph of polished sections, with the exception that some crystallite growth is evident. The resistance to crushing of 200 μ spheres was about 500 g. Chemical analysis of the fired product showed 0.9 atom of W per mole of UO_2.

The method used to prepare sol for ThO_2-Mo product was the same as that described above for making porous ThO_2 microspheres by volatilizing MoO_3. Firing was performed in a reducing atmosphere (4% H_2-Ar 1150°C for 1 hr). Again, no structural details could be discerned from photomicrographs of polished sections (Fig. 16) except that crystallite growth was evident. The crystallites can be seen quite clearly in photographs at lower magnification (right side of Fig. 16). Chemical analyses showed the product contained about one-half atom of Mo per mole of ThO_2. The resistance to crushing of 300 μ spheres was 500 g. X-ray analysis showed molybdenum metal and no molybdenum oxide. Electron microprobe examination did not reveal any inhomogeneity in the product. This examination did show that the electrical conductivity of the specimens was much higher than that of pure thoria.

MICROSPHERES OF UO_2 FROM UO_3 GELS

The preparation of UO_2 microspheres would be much simpler if they could be made directly from U^{6+} solutions. Because U^{6+} sols are not stable, it has always been necessary to reduce the U^{6+} to U^{4+} before making a sol. It was found that U^{6+} sols, which were suitable for forming gel spheres, could be made by the method in Fig. 1 (bottom) if sugar or glycerine were introduced into the U^{6+} solution before the NH_3 gas was introduced. Precipitation (probably of ammonium diuranate) began after 15 min, and it was necessary to form the sols into spheres quickly before this precipitation started.

Approximately 6 atoms of carbon (as sucrose or glycerine) were used per atom of uranium. The gelled spheres could be thoroughly dried without damage, but the evolution of organic material during firing left cracks which weakened the product (Fig. 17). The fired product contained

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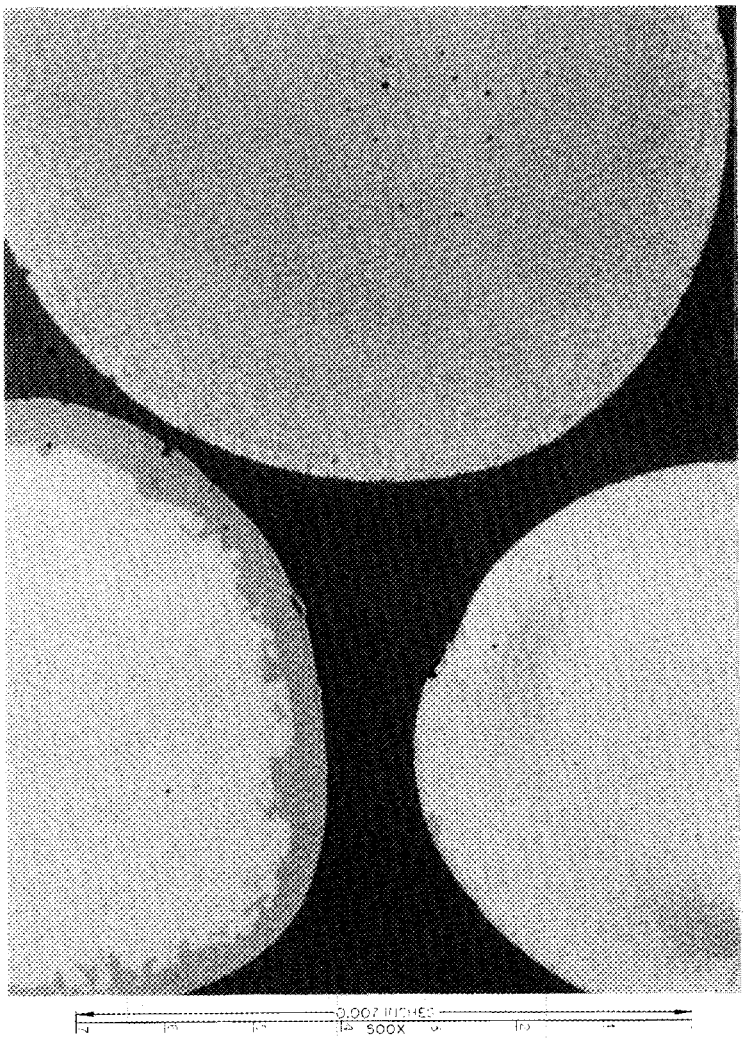

Fig. 15. Fired Cermet Microspheres of 55 mole % UO_2-45 mole % W.

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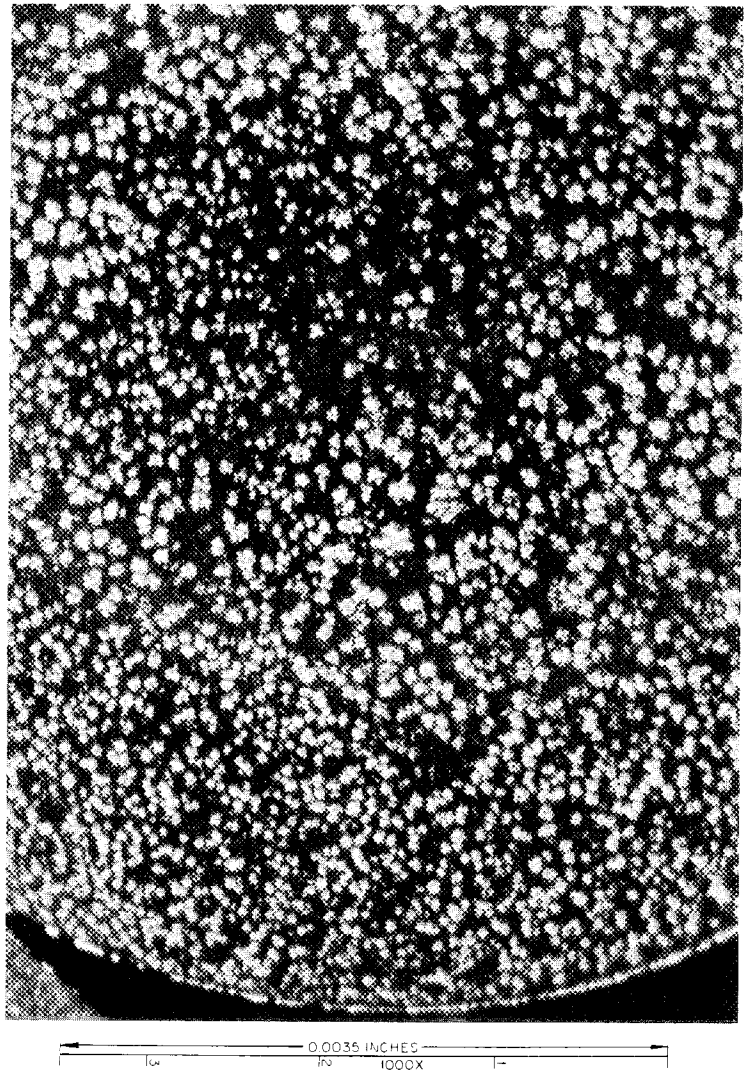

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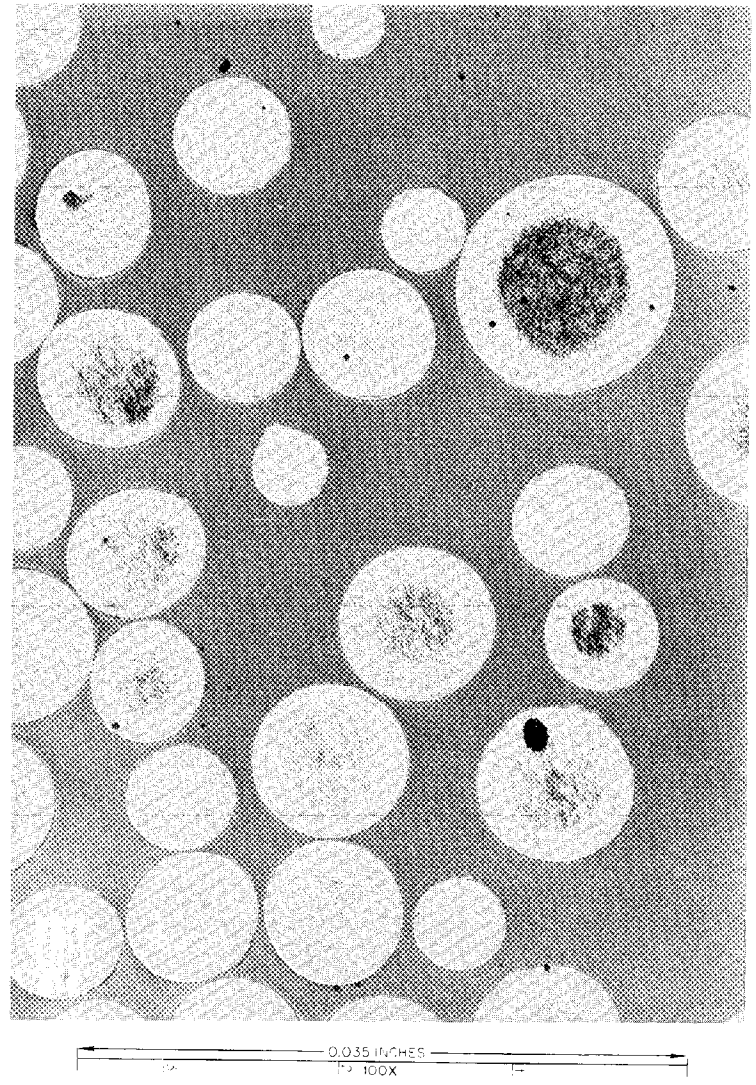

Fig. 16. Fired Cermet Microspheres of 65 mole % Th-35 mole % Mo.

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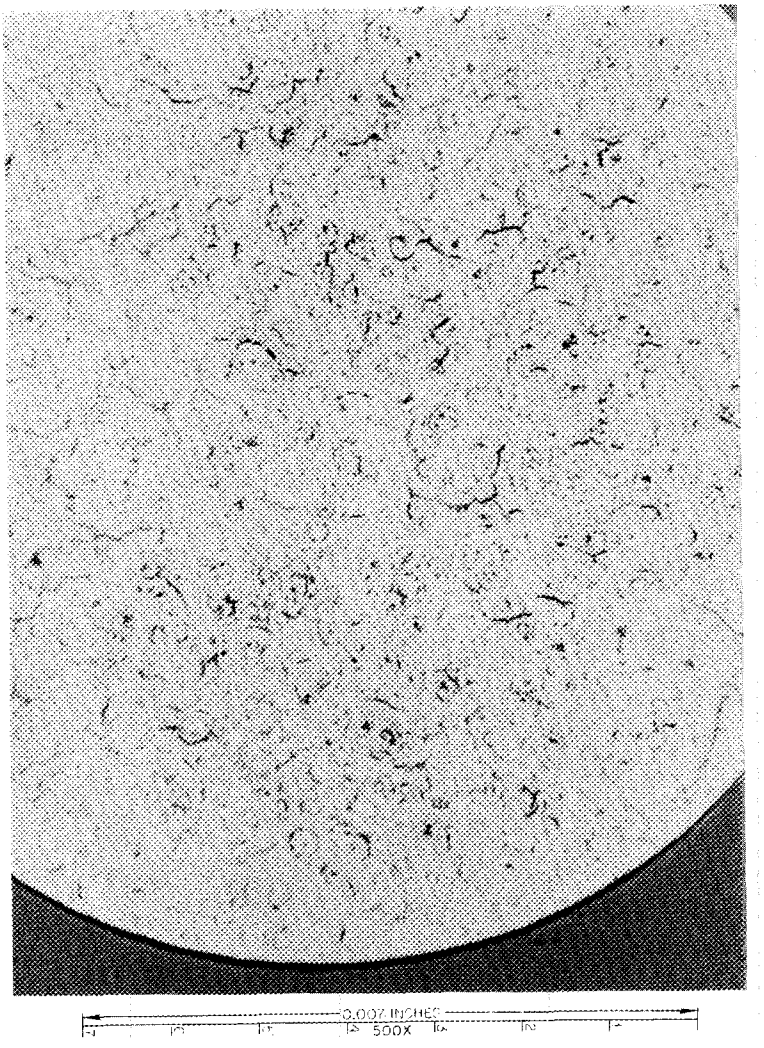

Fig. 17. Fired UO_2 Microspheres Made from UO_3 Gel.

as much as 3 (using sucrose) to as little as 0.1 (using glycerine) atoms of carbon per molecule of UO_2.

The sol used for the product in Fig. 17 was made by mixing 15 ml of 1.4 M $UO_2(NO_3)_2$ with 2.4 ml of glycerine and 5 ml of 1% Carbopol* thickener (an organic material added to increase the strength of the gelled spheres in the ammonium hydroxide). Ammonia diluted with air was introduced until droplets formed from the resultant sol would cross the 2EH-15 M NH_4OH interface. (This was a sol pH of about 3). The spheres were leached in 15 M NH_4OH overnight. After leaching, there were 3.3 atoms of carbon per atom of uranium. The gel spheres were fired to 800°C in argon, cooled, and cracked spheres were removed. No further breakage was observed upon firing to 1300°C in argon for 1 hr, indicating that the transformation of UO_3 into UO_2 can be achieved satisfactorily by firing at high temperature. Because of the many imperfections in the product (Fig. 17) the resistance to crushing was only 140 g for 300 μ spheres.

In general, this approach to making UO_2 microspheres appears promising, but improvements in yield and quality are needed.

MICROSPHERES MADE FROM SOLS CONTAINING ZIRCONIUM

The incorporation of zirconium compounds into nuclear fuel microspheres is sometimes desirable to increase the strength of the product, or, possibly in future applications, to improve the high temperature properties. For example, the melting point of zirconium monocarbide is 3420°C.

Microspheres of 20 mole % ZrO_2 - 80 mole % UO_2 were formed from a ZrO_2 sol mixed with $UO_2(NO_3)_2$ solution. The ZrO_2 sol was prepared from 1.6 M $ZrO(NO_3)_2$ solution by the method of Fig. 1 (bottom). The mixed sol and solution was 0.25 M in Zr and 1 M in $UO_2(NO_3)_2$. Spheres were formed by the method already described. The gel spheres were fired for 1 hr at 1150°C in 4% H_2 - Ar. High porosity in the product (Fig. 18), 44%, resulted in a low resistance to crushing of about 500 g for spheres 400 μ in diameter. The pores were almost all between 0.015 and 0.1 μ in diameter and therefore are too small to be seen clearly in Fig. 18. Very likely, the transformation of UO_3 to UO_2 during firing caused this porosity in the product. Thus, the main objective in adding ZrO_2 to UO_2 spheres, to

*Product of B. F. Goodrich Chemical Company.

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Fig. 18. Fired Microsphere of 20 mole % ZrO_2-80 mole % UO_2 Made from ZrO_2-UO_3 Gel.

increase strength, was not achieved. On the other hand, the spheres are quite strong in comparison to the highly porous UO_2 and ThO_2 products described earlier.

Gel spheres containing 40 mole % ZrO_2 and 60 mole % UO_3, of excellent shape and appearance, were also prepared. However, these spheres cracked during firing.

To make stronger microspheres of UO_2 - ZrO_2, it was necessary to mix ZrO_2 sol, prepared as above, with UO_2 sol, prepared from 1 M U^{4+} chloride sol by the method already described (Fig. 1, bottom), rather than with $UO_2(NO_3)_2$ solution. With the same firing conditions, product was prepared containing 33, 50, and 67 mole % ZrO_2 (Fig. 19). At 33% ZrO_2 the product was a mixture of black and yellow spheres, some of which were cracked. At 50% ZrO_2 some of the spheres had a glossy surface and some were frosted. At 67% ZrO_2, all were frosted. The resistance to crushing of all three products approached 2 kg at 400 μ diameter, except that the black spheres containing 33% ZrO_2 were much weaker.

A photomicrograph of a polished section of a sphere of 50 mole % ZrO_2 - 50 mole % UO_2 (Fig. 20) indicates the material is a single phase, with no visible pores.

Microspheres of ZrC and mixed ZrC and ZrN were also made. The sol and gel spheres were prepared in essentially the same way for both products; only the firing atmospheres and temperatures were different. A ZrO_2 sol was prepared as in Fig. 1 (bottom) and Spheron 9 graphite was dispersed into the sol using an ultrasonic probe. The sol used for preparing ZrC microspheres contained three atoms of carbon for each atom of zirconium; that used for preparing mixed ZrC-ZrN contained only two.

Sol containing 3 atoms of carbon per atom of zirconium was formed into gel spheres by the method shown in Fig. 1. Heptane was used in place of 2-ethylhexanol. The gel spheres were fired 1 hr in argon at 1800°C. The gel spheres remained spherical during the transformation to ZrC (Fig. 21). X-ray analysis showed ZrC and no ZrO_2.

Sol containing 2 atoms of carbon per atom of zirconium was formed into gel spheres in the same way. After firing for 1 hr at 1500°C in N_2 at 1 atm, the product was examined and found to be spheres coated with golden ZrN, but the spheres were unreacted on the inside. Firing was

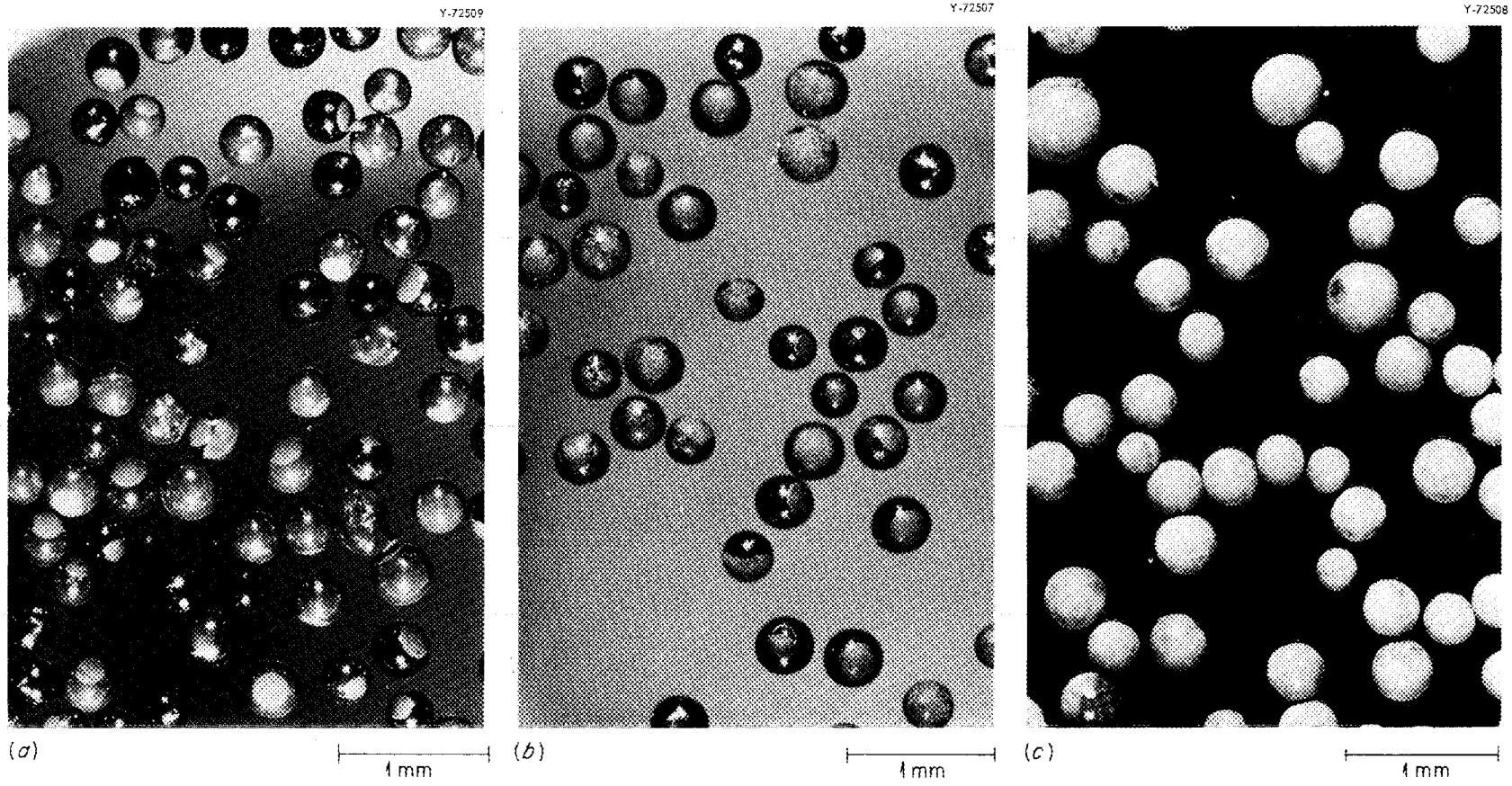

Fig. 19. Fired Microspheres of UO_2-ZrO_2. (A) 33% ZrO_2, (B) 50% ZrO_2, (C) 67% ZrO_2.

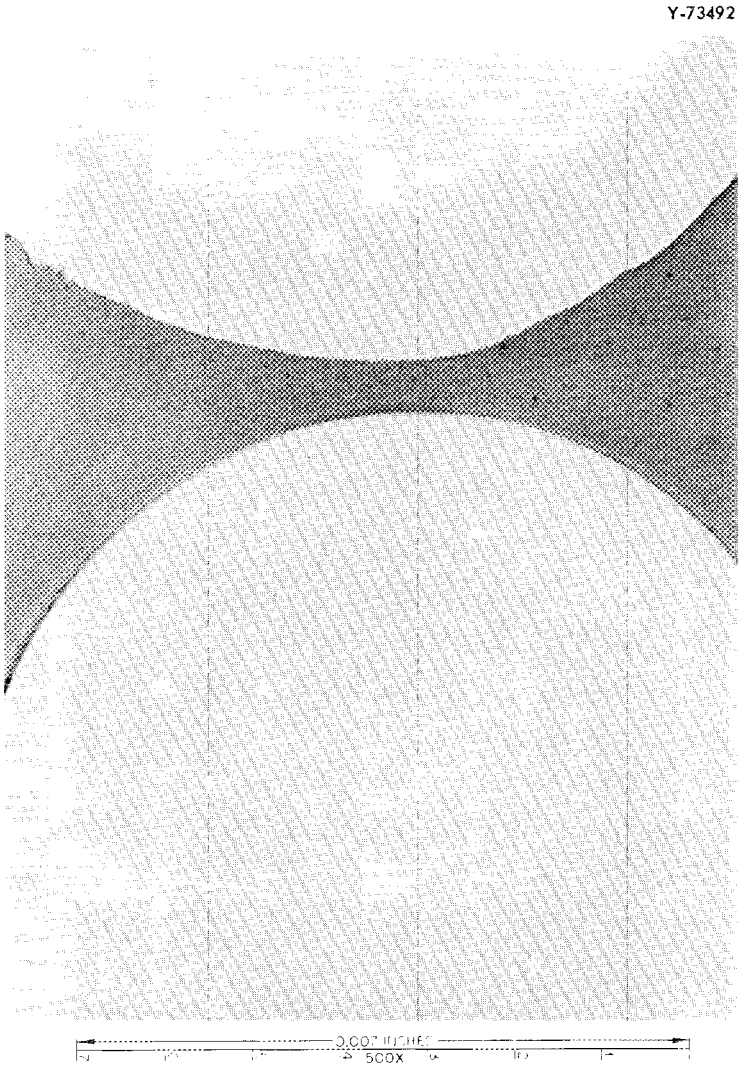

Fig. 20. Fired Microspheres of 50 mole % ZrO_2-50 mole % UO_2.

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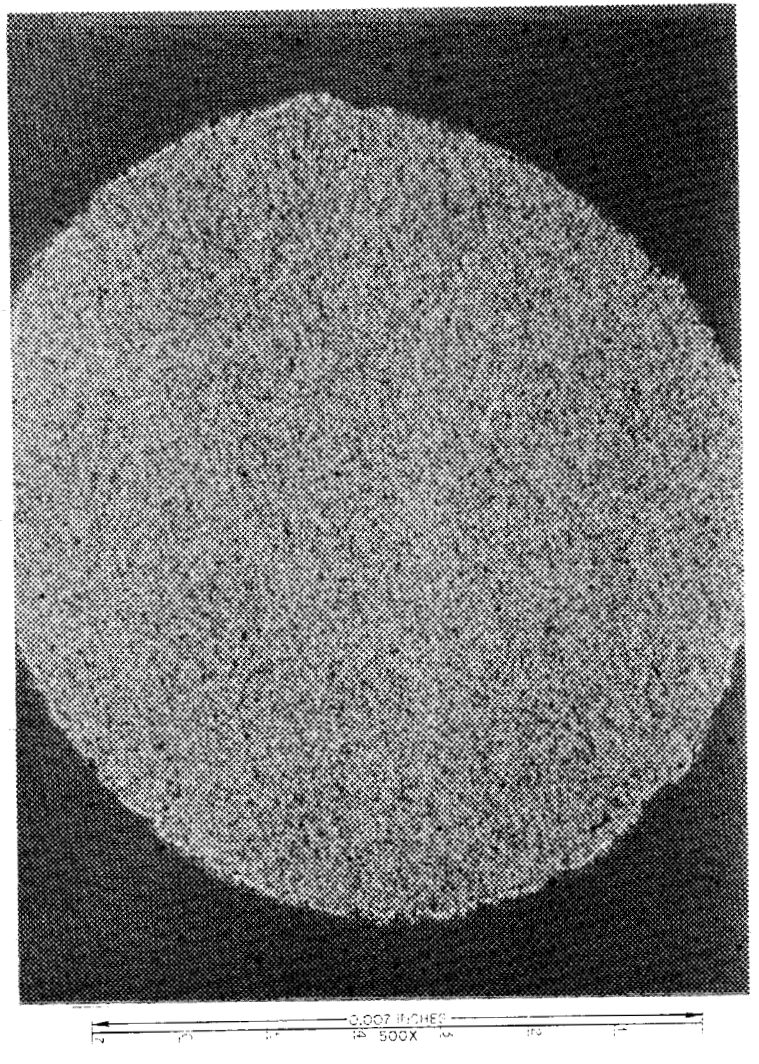

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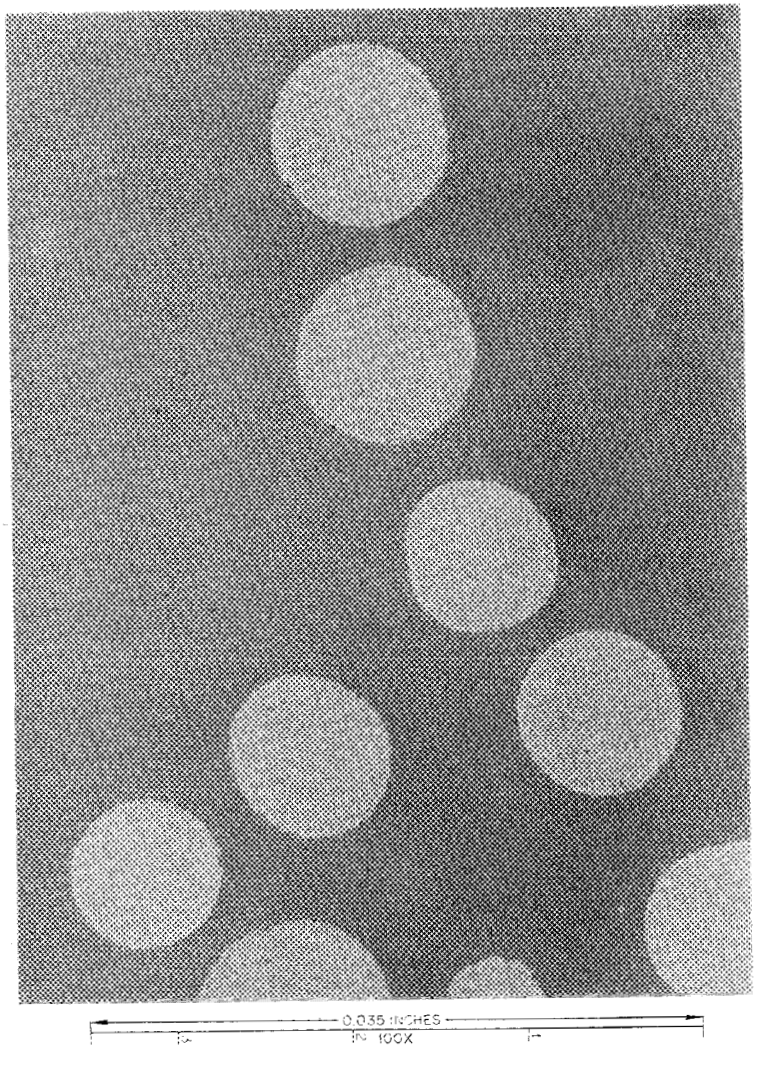

Fig. 21. Fired Microspheres for ZrC Made from ZrO_2-C Gel Spheres.

continued 3 more hrs at 1600°C. After this treatment, the spheres appeared uniform throughout and were dark-violet in color. Although ZrN was the expected product, chemical analysis indicated the product to be $ZrC_{1.35}N_{0.53}$. No ZrO_2 was found.

CONCLUSIONS

A sol-gel method was developed and proved very useful for laboratory preparation of microspheres of nuclear fuel materials having novel compositions or properties. The range of products which have been described in this report support the conclusion that sol-gel processes have a wide applicability and great flexibility as preparative methods for nuclear fuel materials in microsphere form.

The fired products which were prepared in microsphere form include porous UO_2, ThO_2 and mixed ThO_2-UO_2, with porosities ranging as high as 44%; cermets of UO_2-W, UO_2-Mo, and ThO_2-Mo; mixed UO_2-ZrO_2 containing up to 67 mole % ZrO_2; and ZrC and mixed ZrC-ZrN.

Preliminary characterization tests indicate that these products might all find future use in reactor fuel applications. However, much further testing of both irradiated and non-irradiated products will be necessary before firm conclusions can be drawn concerning the usefulness of any of these products.

The preparative methods developed in this work, while they are highly satisfactory for laboratory use, have not been tested on larger scale. Nevertheless, the simplicity of these methods, and their similarity to sol-gel processes which have been scaled-up, suggest that the products described above could be prepared on larger scale without encountering very serious problems.

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APPENDIX

ATTEMPT TO RELATE LIQUID DROP SIZE TO THE KINETIC ENERGY OF THE ENTERING SOL STREAM

A mathematical model was derived in an attempt to relate the fact that the size of the spheres formed decreased as the velocity of the stream of sol entering the 2-ethyl hexanol increased. Two major assumptions were made in the derivation:

1. The sol has no energy other than kinetic energy, which can be determined by measuring the velocity with which it enters the 2EH, and
2. all the kinetic energy is used in making spheres.

From the theory of the maximum bubble pressure method for measuring surface tension,[10] the pressure inside a droplet at equilibrium is

$$P = \frac{2\gamma}{r} \tag{1}$$

where γ is the interfacial tension and r is the radius of the droplet. Multiplying by volume (cc) and setting Eq (1) equal to kinetic energy, one obtains

$$\frac{mv^2}{2} = \frac{2\ \gamma\ (cc)}{r} \tag{2}$$

By rearranging and substituting density D for m/cc the equation becomes

$$r = \frac{4\ \gamma}{v^2 D} \tag{3}$$

or

$$\log r = -2 \log v + \log 4\ \gamma/D. \tag{4}$$

Therefore a plot of log r vs log v should have a slope of (-2). This derivation and equation can be found in physical chemistry textbooks dealing with surface tension[11].

The experimental results showed that this model did not work well except perhaps for a very narrow range of velocities near the center of the graph in Fig. 3. At low pumping velocities, gravitational force accelerated the sol, so that the maximum droplet radius that could be obtained was about 300 μ, corresponding to a solution velocity of 50 cm/sec.

At solution velocities greater than 100 cm/sec, much energy was used up in processes other than droplet formation, and the droplet radii did not decrease as rapidly with increasing solution velocity as predicted by Eq (4). It was concluded that Eq (4) cannot be used very satisfactorily for predicting behavior of real systems since it does not take into consideration all of the important energy terms for this process.

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