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COATING OF UO_2 PARTICLES WITH BeO BY SOLUTION METHODS

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ABSTRACT

Spherical particles of beryllium oxide containing and enclosing UO_2 particles (-10 micron) were prepared by dispersing a suspension of UO_2 in a concentrated viscous solution of a basic beryllium salt in a liquid organic medium, drying, and firing. The spheres produced were porous and would require densification to make the beryllium oxide protective to the UO_2 . Precipitation of beryllium hydroxide or carbonate on UO_2 particles suspended in solutions of beryllium salts under various conditions produced no actual coating of the UO_2 particles.

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1.0 INTRODUCTION

Individual coating of each fuel particle (e.g., UO_2), in the fuel element of a gas-cooled reactor, with a material sufficiently dense to retain fission products would eliminate many of the fuel element design problems if the coating material had a low neutron cross section, good heat transfer properties, and good mechanical and thermal strength. Beryllium and aluminum oxides are potential coating materials, with beryllium oxide having a somewhat higher thermal stability. Small UO_2 particles have been successfully coated with aluminum oxide by hydrolysis of aluminum chloride with water vapor in a fluidized bed of UO_2 particles (1). Such a procedure is more difficult with beryllium oxide, however, since beryllium compounds hydrolyze only partially and produce basic salts which are sticky and viscous.

This work has investigated the possibility of coating UO_2 particles with beryllium compounds that can be ignited to refractory oxide by the use of beryllium compounds in liquid solution or suspension. Slurrying beryllium oxide with UO_2 or precipitating beryllium oxide or carbonate on aqueous suspended UO_2 produced no coating. Inclusion of UO_2 particles in a concentrated viscous solution of beryllium basic oxalate or formate followed by drying and firing this material did result in enclosing UO_2 particles in BeO . A method for producing this material in small spheres was developed. Possibilities for the use of the resulting semi-porous material include fusion to acceptable density, densification by resaturation with a beryllium basic salt followed by a second ignition, or use directly in the hot press production of ceramic fuel elements (2).

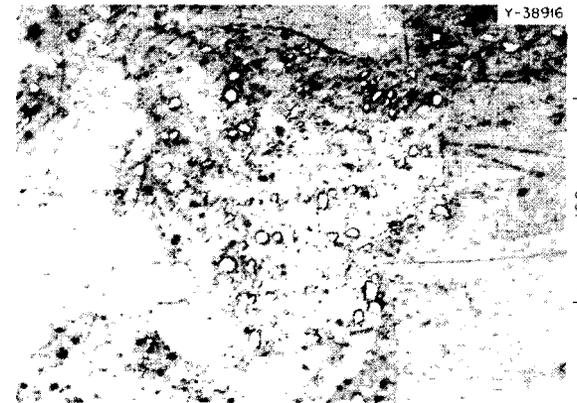
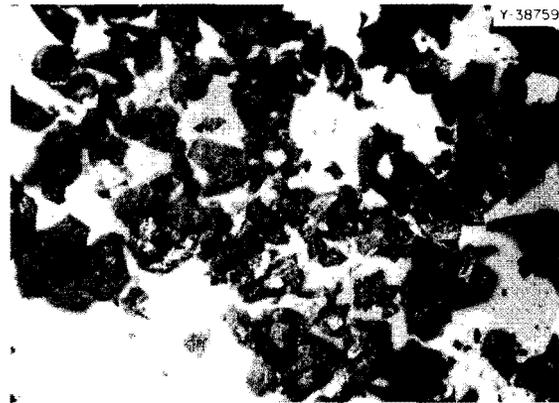
The author is indebted to G. N. Case for technical assistance in the experimental work, and to the Metals and Ceramics Division's Metallography Laboratory under the direction of R. J. Gray for the photomicrographs.

2.0 PRODUCTION OF SPHERICAL COATINGS

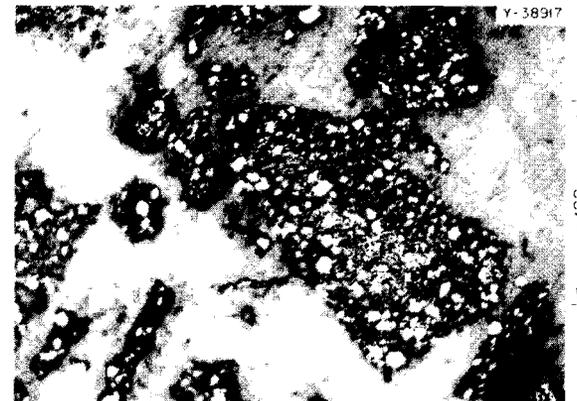
2.1 BeO from Decomposition of Basic Salts

The published chemistry of the basic beryllium salts indicated that they could contain a high ratio of BeO to acid anion. Of four basic salts examined, the basic oxalate and formate proved useful. Basic nitrate could not be ignited without oxidizing the UO_2 . Basic acetate was decomposed and ignited to BeO , but some of the material was volatile and large quantities of beryllium volatilized on heating. (Figure 1 shows UO_2 particles enclosed in a dense BeO matrix

14 Be - 1
UO₂ SUSPENDED IN A GLASS OF Be
BASIC ACETATE DRIED THEN HEATED
TO 1000°C FOR 3hr IN ARGON



14 Be - 2
ABOVE SAMPLE HEATED AN
ADDITIONAL 10hr AT 1300°C



DIRECT PHOTOGRAPH

POLISHED SECTION

Fig. 1. Basic Acetate Preparation.

prepared by slowly heating a sirup of basic beryllium acetate containing suspended UO_2 particles. The final temperature was 1000°C in 14 Be-1 and 1300°C in 14 Be-2.)

Basic beryllium salts of oxalic and formic acids were easily prepared by adding to a given number of equivalents of acid twice that number of equivalents of beryllium as hydroxide or basic carbonate.* This Be/acid ratio was used in all the subsequent tests. The beryllium compound dissolved completely in several hours with gentle heating. Beryllium concentrations of $\sim 10\text{ M}$ were easily attained with either compound; the solutions had the consistency of a thick sirup. Small particles ($<10\mu$) of UO_2 stirred into this sirup remained suspended. Samples of these suspensions could be slowly dried then ignited to BeO (in an inert atmosphere) without any loss of beryllium or oxidation of the UO_2 . The resulting material was a slightly porous glass of BeO enclosing the UO_2 particles, similar in appearance to the basic acetate preparation 14 Be-1.

2.2 Spherical Particles

Tiny spheres, 2-200 μ , of semiporous BeO , each sphere containing one to several UO_2 particles,** were produced by dispersing a sirupy solution of basic beryllium oxalate or formate containing UO_2 in an organic liquid, partially drying the dispersed spheres with an organic drying agent, removing them from the organic liquid followed by further drying and ignition to the oxide. The procedure that produced consistently good results was the following: Place 200 ml of toluene containing 5 w/v per cent of an organic wetting agent (e.g. Aerosol OT) and 1-6 vol % water in a baffled beaker with an agitator (Fig. 2). With the agitator rotating at 2000-3000 rpm, pour into the beaker 5-10 ml of the viscous beryllium solution containing the suspended UO_2 particles.*** When a satisfactory dispersion has been accomplished, pour about 200 ml of acetone into the mixture. For additional drying of the spheres, bubble anhydrous ammonia into the liquid with continued stirring until saturation with ammonia is evident. Stop the stirrer, remove the spheres, place in a desiccator,

*This 2/1 beryllium/acid ratio does not correspond to the composition of the beryllium compounds reported by Sidgwick (3), $\text{Be}_4\text{O}(\text{COOH})_6$ and $\text{Be}[\text{Be}(\text{C}_2\text{O}_4)_2]$, and the compounds were not volatile in further difference from the compounds reported by Sidgwick.

**In successful preparations all spheres observed contained some UO_2 . In general, the smaller the average sphere size the larger the proportion of spheres containing only one UO_2 particle.

*** UO_2/BeO weight ratios of 1/10 to 1/2.5 were used successfully; higher concentrations of UO_2 were not tried.

and evacuate. Leave them in the desiccator under vacuum 10-20 hr and then place them in an oven at 110-115°C for 1-2 hr, after which they may be ignited to BeO. Photomicrographs of preparations ignited at various temperatures 200° and higher may be seen in Fig. 3.

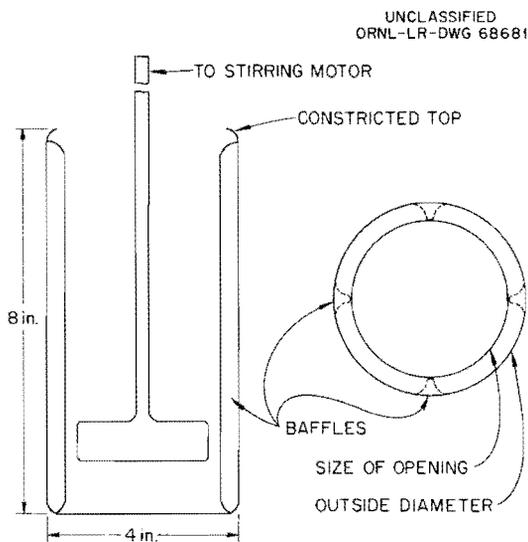


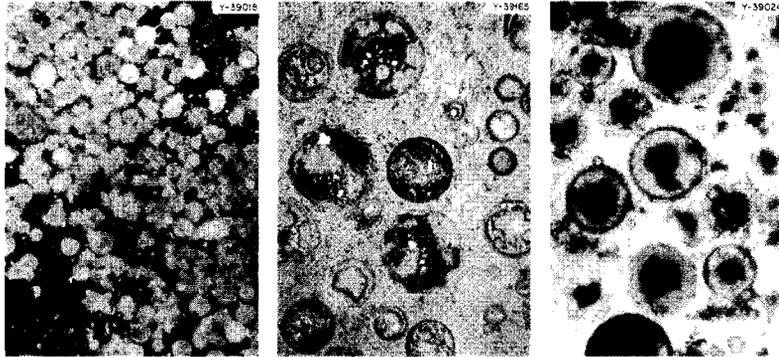
Fig. 2. Baffled Beaker Used in Preparing Dispersed Spheres.

2.3 Effects of Variables

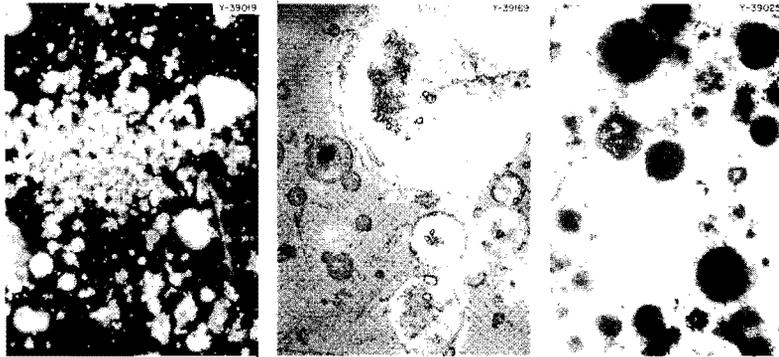
Qualitative observations of the variables indicated that the size of the particles produced depended most strongly on the turbulence produced during the dispersion, the viscosity of the beryllium solution, and the wetness of the organic phase. Smaller particles were produced by greater turbulence (doubling the impeller speed decreased the size of the spheres 50%), less viscous beryllium solution, and a wetter organic phase, the last two variables being somewhat interdependent. The best products (small spheres, easily dried, most UO₂ inside) resulted from high turbulence (5000 rpm) a viscous beryllium solution (about the viscosity of Karo white sirup ca. 10 M in Be), and an organic phase containing about 1 vol % water.* An increase in the total amount of water in the dispersion (beryllium solution plus aqueous phase) resulted in smaller particles, but too much water made drying of the particles difficult or impossible, and in some cases caused

*The 5 w/v percent Aerosol OT solution saturated with water contains about 7 vol % water at 25°C.

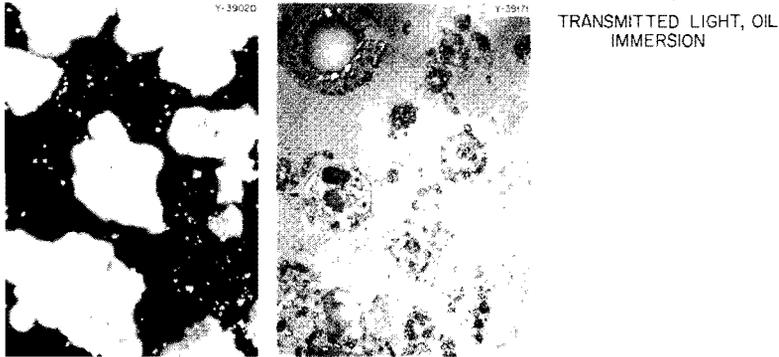
20 Be-2
UO₂ IN Be BASIC SALT SPHERES
OVEN DRIED AT 110-115 °C



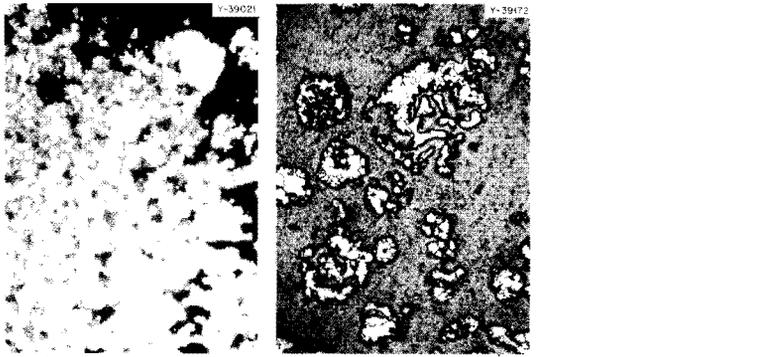
20 Be-3
THE ABOVE HEATED 2 hr AT
200°C IN ARGON



20 Be-4
THE ABOVE HEATED 3 hr AT
600°C IN ARGON



20 Be-5
THE ABOVE HEATED 8 hr AT
1300°C IN ARGON



DIRECT PHOTOGRAPH
DARK FIELD

POLISHED SECTION
BRIGHT FIELD

TRANSMITTED LIGHT, OIL
IMMERSION

Fig. 3. UO₂ in BeO from Basic Formate Sirup by Organic Dispersion Method.

the UO_2 particles to migrate to the outside surface of the beryllium salt sphere. The absolute minimum amount of water necessary in the organic phase was not determined, but some water was necessary. A completely dry 5% Aerosol OT solution in toluene was completely ineffective in dispersing the beryllium solution, as was toluene alone.

2.4 Drying

The beryllium compound spheres were dried in two stages: in the organic phase and after separation from the organic phase. Some drying in the organic phase was necessary to prevent their sticking together when agitation was stopped. When the spheres had been separated from the organic phase by filtration or centrifugation and decantation, the residual organic material was removed by washing the spheres with acetone. The acetone and residual water were removed by vacuum desiccation followed by oven drying. The dried beads showed no tendency to take up moisture from the air.

Slower drying of the beads appeared to produce a denser product. For example, the product of 16-20 hr standing in a vacuum desiccator followed by 1-2 hr in the drying oven was denser than that produced by 5-6 hr in the desiccator and 10-20 hr in the oven. Each step in drying was necessary, however, and there appeared to be a minimum treatment time for each step. If the spheres were insufficiently dried while dispersed, they stuck together when separated from the organic liquid; similarly, too short a drying time under vacuum (generally <2-3 hr, but dependent on previous drying) allowed sticking together in the oven, and spheres held in the oven <2 hr melted in the furnace.

2.5 Ignition

Spheres of the beryllium compound dried as described above retained their shape through ignitions at 600°C for 3 hr (20 Be-4, Fig. 3) and 1000°C for 8 hr, but began to show crystal growth with eventual destruction of the spherical shape at 1300°C (20 Be-5, Fig. 3). Since temperatures in the 800 to 1000°C region are probably required to ensure decomposition of all the organic acid radical present (Table 1), this range is probably optimum for igniting these materials. Ignitions were in all cases in an inert atmosphere to prevent oxidation of UO_2 to U_3O_8 .

2.6 Densification

The spheres produced as described above were solid but they appeared to be filled with small pores (Fig. 4), and a dye solution quickly penetrated to the interior. The UO_2

Y-39026

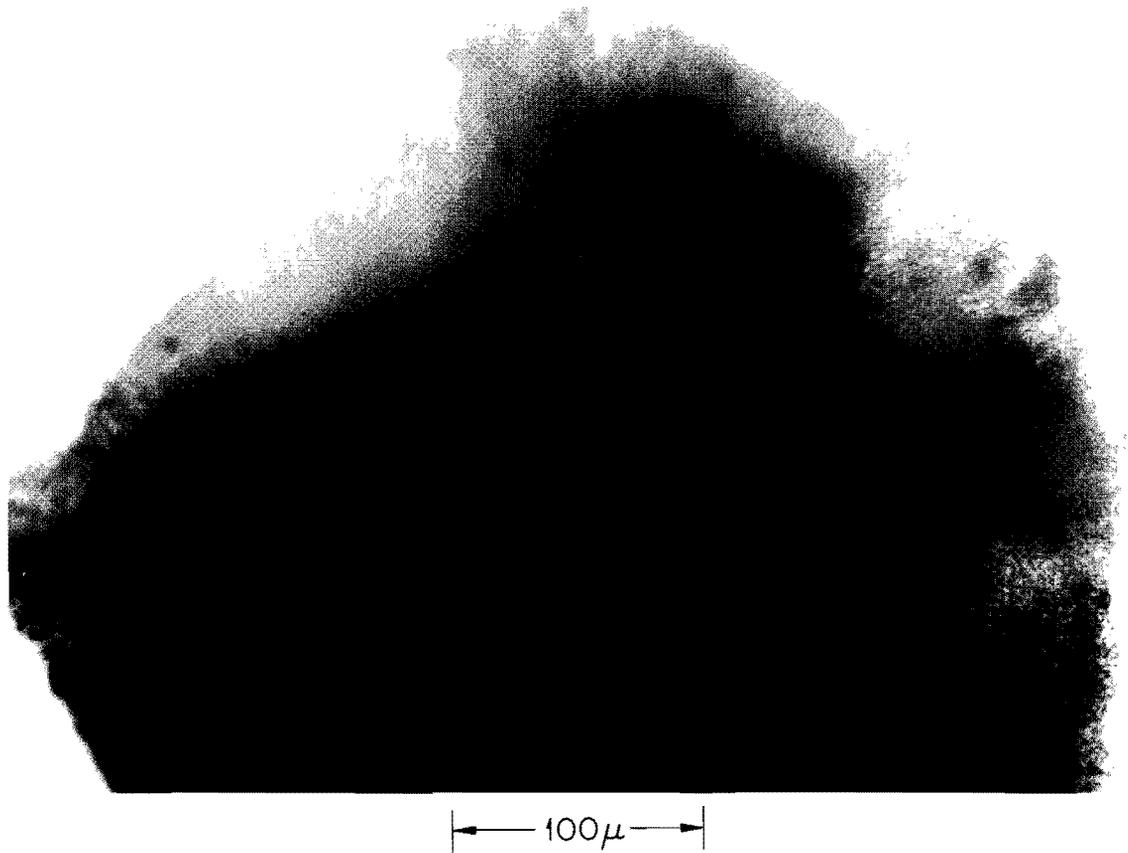


Fig. 4. Porous Nature of BeO from Basic Beryllium Formate.

Table 1. X-ray Diffraction Analysis of BeO-UO₂
Product from Beryllium Basic Formate

Prep	Ign. Temp, °C	Time, hr	Relative Line Intensities		Unknown*
			UO ₂	BeO	
20 Be-4	600	3	57	3	4
20 Be-4	1300	8	54	12	None detected

*A light element compound, probably a beryllium compound other than BeO.

enclosed in the spheres was therefore not protected from chemical attack. Leaching rates with nitric acid were similar to those found for the UO₂ trapped in flocculent BeO from hydroxide (Table 2, Sect. 3).

In several preliminary attempts to densify the porous BeO by fusion, one test gave fused beads (indicated by optical microscopy). This partial success is encouraging as an indication that a fusion method might be feasible. The furnace was a graphite tube, embedded in carbon black and protected inside by an argon atmosphere, which attained a temperature of 2500-2800°C (optical pyrometer) for a few minutes. The spheres were dropped through the tube at this temperature and collected in a water cooled cup. One attempt to fuse some of the BeO spheres in an arc image furnace by supporting them in a gas stream was not successful, probably because the residence time of each particle in the arc image was short.

Small quantities of two preparations melted on tungsten ribbon in an inert atmosphere gave a smooth melt, which formed transparent red-brown crystals on cooling. A metallographic section of the crystals suggested that the UO₂ may go into solution in the melted BeO, since the UO₂ appeared to be re-deposited as interstitial material in a matrix of BeO crystals (Fig. 5). If UO₂ does dissolve in melted BeO, densification of this material by fusion with retention of a BeO shell enclosing discrete UO₂ particles would be difficult. It might be accomplished by very rapid heating and cooling, e.g., by fusion by transport through a gas flame or plasma jet, or in other types of vertical tube furnaces.

3.0 SLURRY AND PRECIPITATION

The most obvious approaches to coating UO₂ particles with beryllium oxide from solutions or suspensions are slurring together finely divided BeO and UO₂ and precipitation of beryllium hydroxide or carbonate in a suspension of UO₂ particles. These two procedures, tried under various

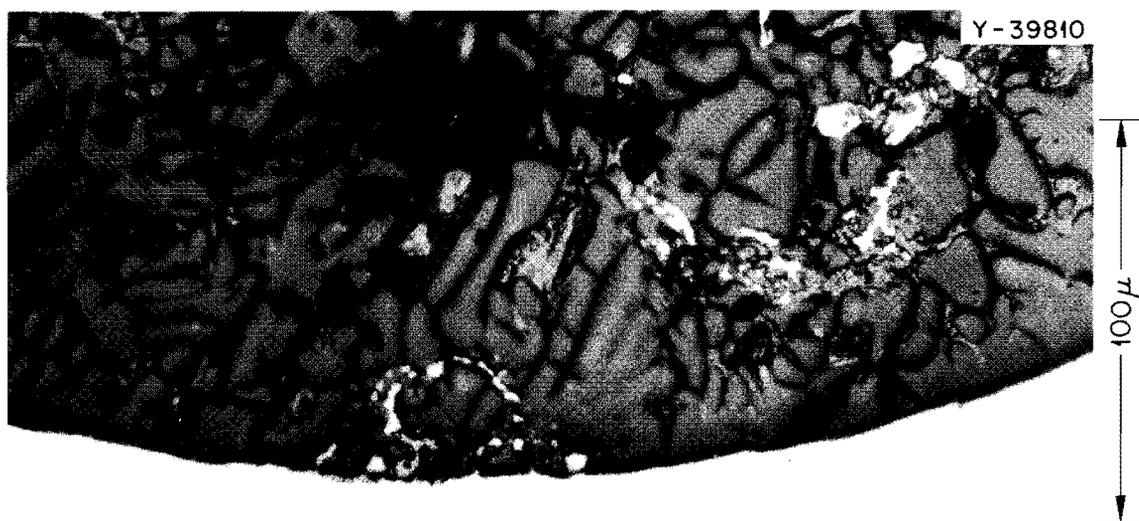


Fig. 5. Solidified Melt from BeO-UO₂ Sphere Preparation on Tungsten Ribbon.

conditions, did not produce any actual coating of the UO_2 particles (Table 2). The materials simply mixed or slurried together could be seen to separate. Photomicrographs of the precipitates (Fig. 6) indicated that the UO_2 was trapped inside a lattice of loose flocculent beryllium hydroxide (or carbonate) and remained there during firing of the beryllium compound to BeO . Individual UO_2 particles (white spots in bright-field photos) did not, however, appear to be surrounded by or enclosed in BeO .

The percentage uranium remaining after leaching of the dried solids indicated that the beryllium oxide apparently protected the UO_2 from chemical attack to some degree in some cases in spite of the fact that microscopic examination showed no coating. It should be pointed out, however, that the results of these leaching tests were very sensitive to the manner in which they were done. Prolonged leaching would always dissolve all the uranium.

4.0 REFERENCES

1. M. F. Browning et al., "Alumina Coating of UO_2 Shot by Hydrolysis of Aluminum Chloride Vapor," BMI-1471, (Oct. 25, 1960).
2. R. L. Hamner, ORNL Metals and Ceramics Division, private communication, May 1961.
3. N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, Oxford, Vol. I, pp 213-214 (1950).

Table 2. Coating Attempts by Slurrying and PrecipitationEach test^a involved 0.5 g of UO₂ particles

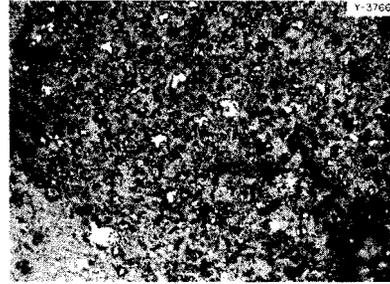
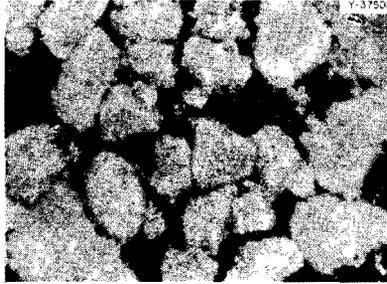
Materials (all plus 0.5 g UO ₂)	Treatment ^b	Product	
		Appearance	U, %
0.5 g BeO	Mixed powders fired	No change	0.1-4.0
0.5 g Be(OH) ₂	Mixed powders fired	No change	0.1-0.4
0.5 g BeO+10 ml H ₂ O	Slurried and fired	Gray lumps	0.8
0.5 g Be(OH) ₂ +10 ml H ₂ O	Slurried and fired	Gray lumps	1.7
0.5 g BeO+10 ml 0.01 N NaOH	Slurried and fired	Gray lumps	0.25
0.5 g Be(OH) ₂ +10 ml 0.01 N NaOH	Slurried and fired	Gray lumps	0.5
10 ml 2 M Be(NO ₃) ₂ + 10 ml 2 M (NH ₄) ₂ CO ₃	Precipitation	Gray lumps	0.5
100 ml 0.2 M Be(NO ₃) ₂ + 100 ml 0.2 M (NH ₄) ₂ CO ₃	Precipitation	Gray powder	0.9
1000 ml 0.02 M Be(NO ₃) ₂ + 1000 ml 0.02 M (NH ₄) ₂ CO ₃	Precipitation	Gray powder	0.7
40 ml 2 M Be(NO ₃) ₂ + 40 ml 4 M NH ₄ OH	Precipitation	Gray lumps	1.2
100 ml 0.8 M Be(NO ₃) ₂ + 100 ml 1.6 M NH ₄ OH	Precipitation	Gray powder	1.0
1000 ml 0.08 M Be(NO ₃) ₂ + 1000 ml 0.16 M NH ₄ OH	Precipitation	Gray powder	3.1
10 ml 2 M Be(NO ₃) ₂ + 10 ml 4 M NH ₄ OH	Precipitation	Gray lumps	24
100 ml 0.2 M Be(NO ₃) ₂ + 100 ml 0.4 M NH ₄ OH	Precipitation	Gray powder	17
1000 ml 0.02 M Be(NO ₃) ₂ + 1000 ml 0.04 M NH ₄ OH	Precipitation	Gray powder	26

^aMaterials:UO₂: <10-μ particles, from Y-12 Production.

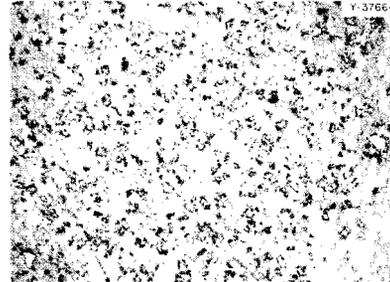
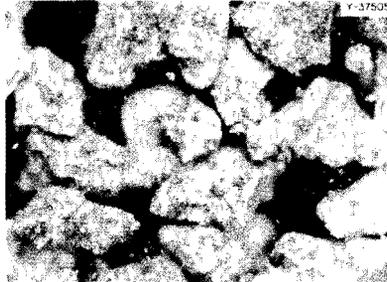
BeO: ceramic grade, high-fired sub-micron powder, Brush Beryllium Co., from R. L. Hamner, Ceramics Laboratory.

Be(OH)₂: Beryllium Corp. grade 1 powder, from L. R. Phillips, Y-12 Development.Be(NO₃)₂ solutions: Be(OH)₂ + HNO₃^bIn precipitation tests the UO₂ was stirred vigorously in the Be(NO₃)₂ solution during the addition of the precipitant, and after 10-20 min additional stirring, the gel was recovered by filtration and calcined 16-20 hr at 1100°C; the resulting solid was leached 20 min with 8 M HNO₃-13% H₂O₂, and the residue was dried and analyzed for uranium.

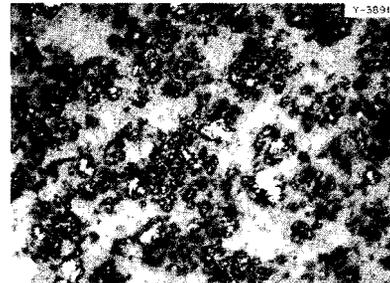
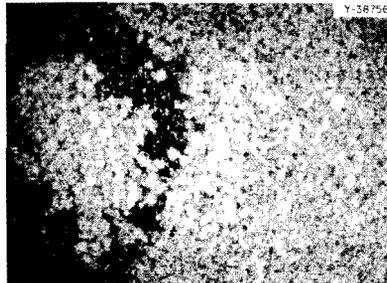
4 Be-3
0.5 g UO₂ SUSPENDED IN 1000 ml 0.02 M
Be(NO₃)₂ - 1000 ml 0.04 M NH₄OH
ADDED
FIRED 1100°C 16hr
wt RATIO UO₂/BeO = 1



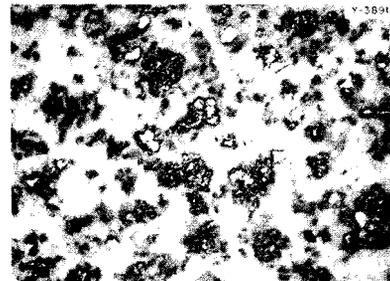
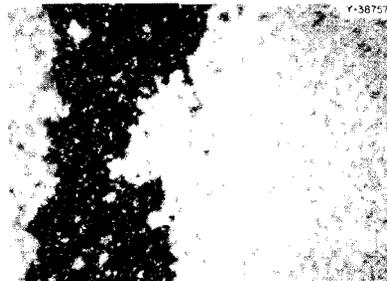
6 Be-3
AS ABOVE EXCEPT PRECIPITATED AS
BASIC CARBONATE



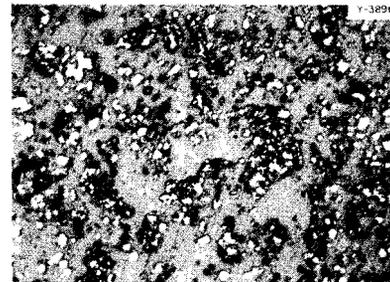
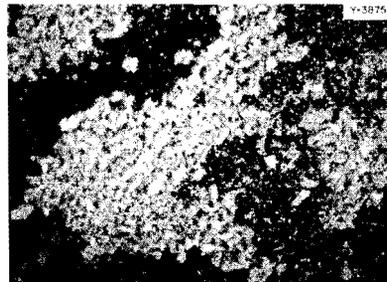
7 Be-1
0.5 g UO₂ SUSPENDED IN 1000 ml
0.01 M Be(NO₃)₂ - 1000 ml 0.02 M
NH₄OH ADDED - DRIED
FIRED 1000°C
THREE PRECIPITATIONS
wt RATIO UO₂/BeO = 1/15



7 Be-2
AS ABOVE EXCEPT UO₂ IN NH₄OH
Be(NO₃)₂ ADDED



11 Be
UO₂ SUSPENDED IN A SIRUP OF Be
BASIC NITRATE AND INJECTED
RAPIDLY INTO CONC NH₄OH FIRED
8hr AT 1300°C



1000 μ

DIRECT PHOTOGRAPH
DARK FIELD

100 μ

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BRIGHT FIELD

Fig. 6. Precipitation Tests.

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