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METALLOGRAPHY OF PYROLYTIC CARBON COATED AND UNCOATED URANIUM CARBIDE SPHERES

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METALLURGY DIVISION

METALLOGRAPHY OF PYROLYTIC CARBON COATED AND UNCOATED URANIUM CARBIDE SPHERES

C. K. H. DuBose and R. J. Gray

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METALLOGRAPHY OF PYROLYTIC CARBON COATED AND UNCOATED URANIUM CARBIDE SPHERES

INTRODUCTION

Uranium carbide in a graphite matrix is being considered for use as a fuel in powering nuclear reactors with an all-ceramic core. There is specific interest at the present time in using coated fuel particles where the purpose of the coating may be threefold: (1) to promote ease of handling, especially for the phrophoric thorium-uranium carbides; (2) to retain fission products and therefore minimize contamination of the reactor coolant; and (3) to provide a reaction barrier between the carbide and the matrix material during fabrication and operation.

The metallography of arc-cast uranium carbide has been studied and reported by several laboratories;[1,2] however, very little has been presented on the variations of the microstructure and stoichiometry of uranium carbides produced as 0.01–0.02-in. spheres.

This report describes metallographic techniques which have been developed for examining coated and uncoated uranium carbide particles, both in the unsupported condition and as-fabricated in graphite matrices. The structural and compositional variations which can be found in various batches and within a given batch are presented, and the effects of various heat treatments on the particles and the coatings are described.

TECHNIQUES

Particle Morphology

Considerable information can be obtained from a morphological study of particles. Size, shape, porosity, and color depict uniformity of composition and can foretell its working characteristics if it is to be fabricated in a matrix material.

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[1]M. W. Mallet, A. F. Gerds, and D. A. Vaughn, Uranium Sesquicarbide, AECD-3060 (Jan. 31, 1950).

[2]R. J. Gray, W. C. Thurber, and C. K. H. DuBose, Preparation and Metallography of Arc-Melted Uranium Carbides, ORNL-2446 (Dec. 27, 1957).

Two techniques have been developed which permit particle studies on both a macro- and microscopic scale. The macroscopic technique, which is an examination at 25X-or-under magnification, provides a coverage of more particles with a good comparison of particle sizes. This technique uses oblique lighting with a backgound light as shown in Fig. 1. The microscopic technique employs a research metallograph with dark-field illumination, which is essentially a 360-deg oblique illumination (as shown in Fig. 2), to examine and photograph particles at magnifications up to 500X. Surface characteristics of the particles are more easily observed at this higher magnification. The results of both techniques will be presented later.

Mounting and Grinding

A technique had to be developed to permit median cross-sectional examinations of both the uncoated and coated spheres. These examinations were necessary for mensuration purposes and to observe variations in the microstructure of the uranium carbide spheres and the coating material, as well as any possible reaction products between the pyrolytic-carbon coating and the spheres.

The particle sizes of the uranium carbide spheres examined to date have ranged from 50 to 500 μ in diameter. The pyrolytic-carbon coatings have been approximately 100-μ thick.

Due to friability of the spheres, a specimen mounting technique must be chosen which does not damage the spheres. A room-temperature-setting epoxy resin[3] meets this requirement and provides good adherence for the spherical particles; however, spherical shapes are extremely difficult to retain in a mount if they are ground beyond a median plane. Added difficulties are encountered in retaining a coated sphere, for the uranium carbide sphere does not fit tightly in its coating of pyrolytic carbon, due possibly to differences in thermal expansions and shrinkage of these

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[3]Two epoxy resin products are satisfactory, "Araldite," manufactured by Ciba Products Corp., Fairlawn, N. J., and "Hysol-2105," manufactured by Hysol Corp., 322 Houghton Ave., Olean, N. Y.

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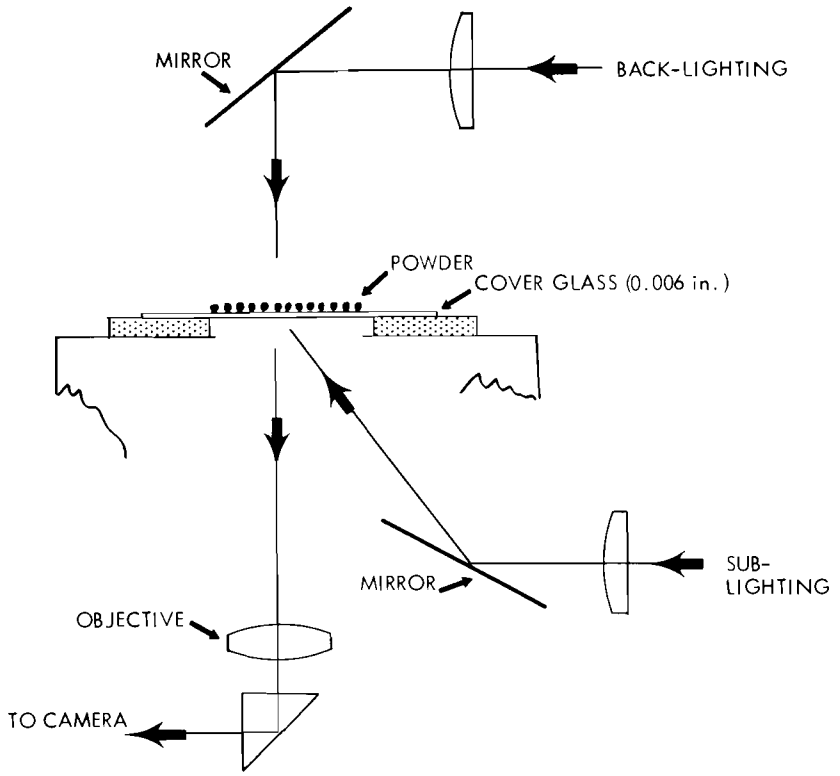

Fig. 1. Method for Photographing Spheres at Low Magnification by Oblique Illumination.

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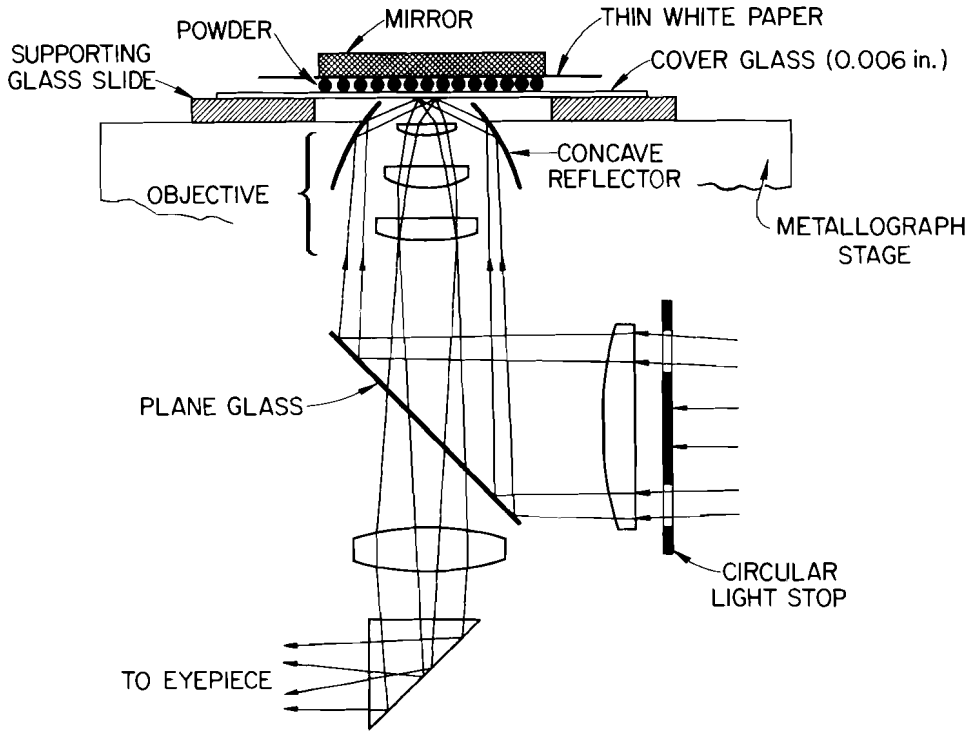

Fig. 2. Method for Photographing Spheres at High Magnification by Dark-Field Illumination.

two materials during the coating process. Therefore, great care must be exercised when grinding and polishing an object that is essentially a sphere within a sphere with only a mechanical bond at the interface. For mensuration purposes, the plane of examination must be sufficiently near the median plane to eliminate exaggerated thickness of the coating or false diameters of the spheres by being near the top or bottom of the sphere.

It was obvious that this problem required a mounting technique which would position the spheres at different levels in the specimen mount. If there could be some control of these different levels from the center to the outer edge of the specimen mount, a median plane of some of the spheres could be obtained in the preliminary grinding. By having a slight concave, rather than the customary flat, bottom mount, this control is achieved. To accomplish this, a mold is made by fusing one end of a 1.25-in.-diam Lucite ring with acetone to a thin sheet of acetate. Warpage of the thin acetate sheet occurs as the acetone dries. This warping effect produces an irregular, somewhat concave surface at the bottom of the mold. Enough spheres are sprinkled into the mold to cover the bottom with one layer; then the epoxy resin is added. Due to the higher specific gravity of the spheres, they stay at the bottom of the mold after the resin has been added. After the resin has cured, the acetate sheet at the bottom of the mold is stripped off, leaving the Lucite ring as part of the mount (see Fig. 3). The spheres can be considered to be positioned in a concentric-band fashion and at different levels with respect to the subsequent grinding operation.

The specimen is hand ground until the spheres near the outer edge of the mount have been ground beyond a median plane of the sphere or, in the case of coated spheres, until the uranium carbide spheres near the edge have fallen out of the pyrolytic-carbon coating. The specimen is then polished for examination. In a center-to-edge transverse of the specimen, an area can be found where a number of the spheres can be examined near a median plane.

With larger spheres, in the 400–500-μ range, the mid-cross section may be found before the spheres along the outer edge of the sample are completely ground away, although the carbide particle may fall out as the

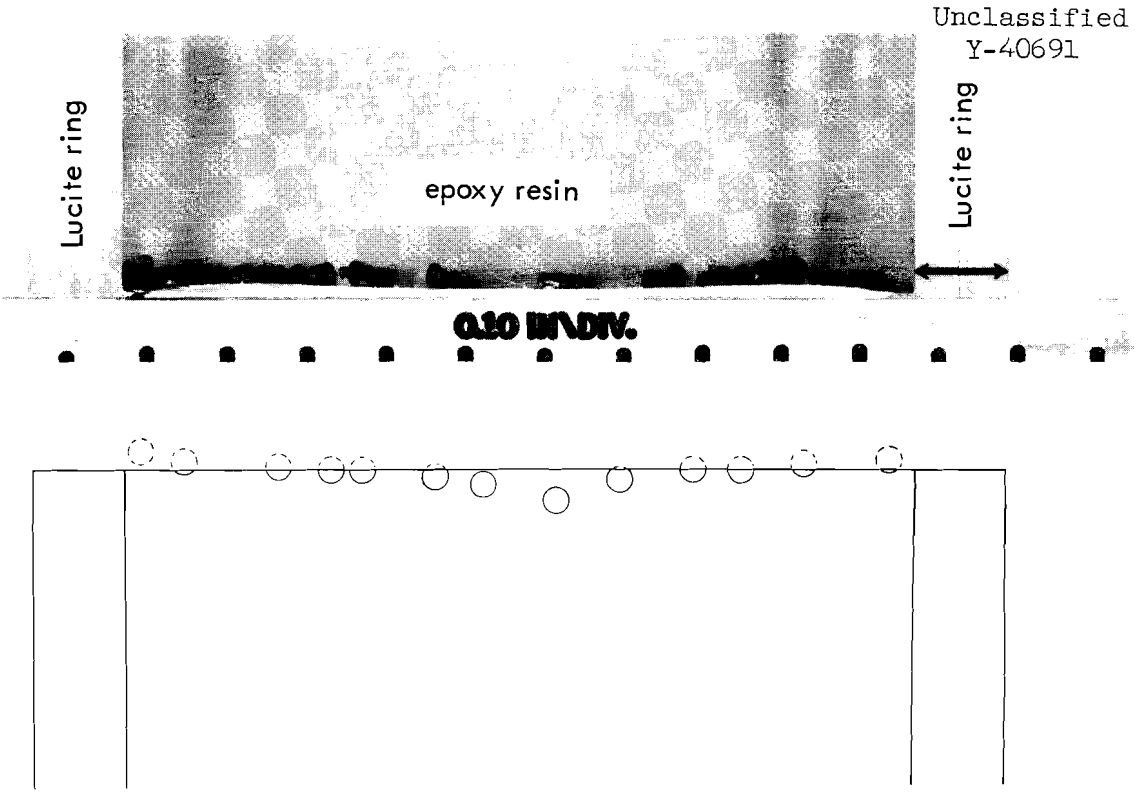

Fig. 3. Specimen Mounting Technique for Spheres. Top half of figure is a cross section of the metallographic mount, showing an irregular surface on the bottom; lower half of the figure is a mirror image sketch showing the cross section after the specimen has been polished.

midpoint of the sphere is passed. The grinding operation is done on 320-, 400-, and 600-grit silicon carbide papers using a water-free oil as the lubricant. Since the polishing operation does not appreciably change the plane obtained from the grinding papers, care must be exercised to be at the midsection of the spheres by the time grinding is completed.

For accurate data on the dimensions of coatings and core materials, several measurements should be taken on several spheres.

Polishing

Metallographic vibratory polishing[4-7] was employed to reduce, as much as possible, the rounding over of the carbide sphere-carbon coat interface. Due to the tendency for uranium carbide to hydrolyze, a completely water-free oil was used for the extended polishing time inherent with vibratory polishing. A silicone oil has been found to be satisfactory for this purpose.[8] Just enough silicone oil is mixed with the polishing abrasive alumina to form a paste-like slurry. For the 12-in. vibratory polisher, 10 g of alumina and 100 ml of oil are sufficient. Graphite has been found to assist the polishing in obtaining a surface suitable for microscopy in a single polishing step. The graphite is not added as a powder to the polishing compound, but a section of graphite is mounted as a sample and left polishing with the other samples for about an hour.

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[4]E. L. Long, Jr., and R. J. Gray, Preparation of Metallographic Specimens Through Vibratory Polishing, ORNL-2494 (June 13, 1958).

[5]E. L. Long, Jr., and R. J. Gray, "Better Metallographic Techniques... Polishing by Vibration," Metal Prog. 74, 145–48, 1958.

[6]E. L. Long, Jr., J. T. Meador, and R. J. Gray, "Experience with Vibratory Polishing and Design for Hot Cell Application," pp 79–89 in Symposium on the Preparation of Metallographic Specimens, Spec. Tech. Publ. No. 285, American Society for Testing Materials, Philadelphia, Pa., 1960.

[7]E. L. Long, Jr., and R. J. Gray, "Status of Vibratory Polishing at Oak Ridge National Laboratory," presented at the 15th AEC Metallography Group Meeting, Savannah River Laboratory, May 17–19, 1961.

[8]Dow Corning 702 Diffusion Pump Fluid.

The graphite sample is then removed, leaving the other samples to remain polishing. The samples, from which the following photomicrographs were taken, were all polished for 6 hr on a nylon cloth using a slurry of graphite-silicone oil with alpha alumina (Linde "A").

Etching

The etchant for the uranium carbide spheres consists of equal parts by volume of acetic acid, nitric acid, and water. The sample is immersed 10–15 sec for spheres composed principally of uranium monocarbide; however, the etching time should be lengthened to approximately 30 sec for spheres with a majority of uranium dicarbide. The microstructure of the pyrolytic-carbon coating is revealed satisfactorily in the as-polished condition with polarized light; therefore, an etchant for this material has not been found necessary. However, cathodic etching of pyrolytic carbon has been reported[9] and is also used for etch pitting for orientation studies.

Extraction of Reaction Products

An extraction technique was developed for the coated uranium carbide particles which was directly associated with the location of the reaction products and the microstructure. A better description is contained in the section on Identification of Reaction Products.[10]

Microradiography

Although a median cross-sectional examination is extremely informative, it leaves much to be desired in being able to establish accurate measurements as well as the geometry of the core and coating.

One approach to this problem is the use of microradiography. Due to the extreme differences in the density and corresponding x-ray absorption, the core and the coating should be resolved on a radiographic film.

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[9]Aram Tarpinian and G. E. Gozza, Etch Pits in Pyrolytic Graphite, WAL TR 130.5/1 (1960).

[10]Page 24 of this report.

Since high magnifications are important for the subsequent examination, only fine-grain emulsions are considered to be suitable. In addition, there must be sufficient contrast to detect any anomaly, such as a reaction product, between the pyrolytic-carbon coating and the core. Although internal voids or similar flaws would not be detected in the fuel core, considerable information could be gained from the coating and the interface by the use of low-voltage radiographic techniques.[11]

The Kodak Spectroscopic Plate type 649 GH was considered to be most suitable in meeting the requirements of resolving power, sharpness, and granularity. This plate has a resolving power to white light of approximately 1000 lines per millimeter. The developer recommended for this plate is D-19.

In a darkroom, a retaining ring of Lucite is positioned on the plate and the spheres are scattered one layer deep over the emulsion within the retaining ring. The x-ray exposures are made within the darkroom at 10 kv, 30 ma for 2 1/4 hr in a helium atmosphere. The plate and particles are located 45 in. from the x-ray target. After the plate is developed, considerable care must be exercised in cleaning and drying so any artifact will not interfere with high-magnification examinations and photomicrography.

Although the preliminary use of this technique has been satisfactory, additional development is under way in the choice of emulsions, exposures, and developers to obtain the best combination for revealing the most information.

MICROSCOPIC EXAMINATIONS

Morphology of Uncoated and Coated Uranium Carbide Spheres

The general appearance of the uranium carbide spheres shown by oblique illumination (see Fig. 1) is presented in Fig. 4. At this magnification (20X), the main interest is the size variation. A study of the

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[11] R. W. McClung, "Techniques for Low-Voltage Radiography," presented at the Annual Convention of the Society for Non-Destructive Testing, Detroit, Mich., October 20–27, 1961.

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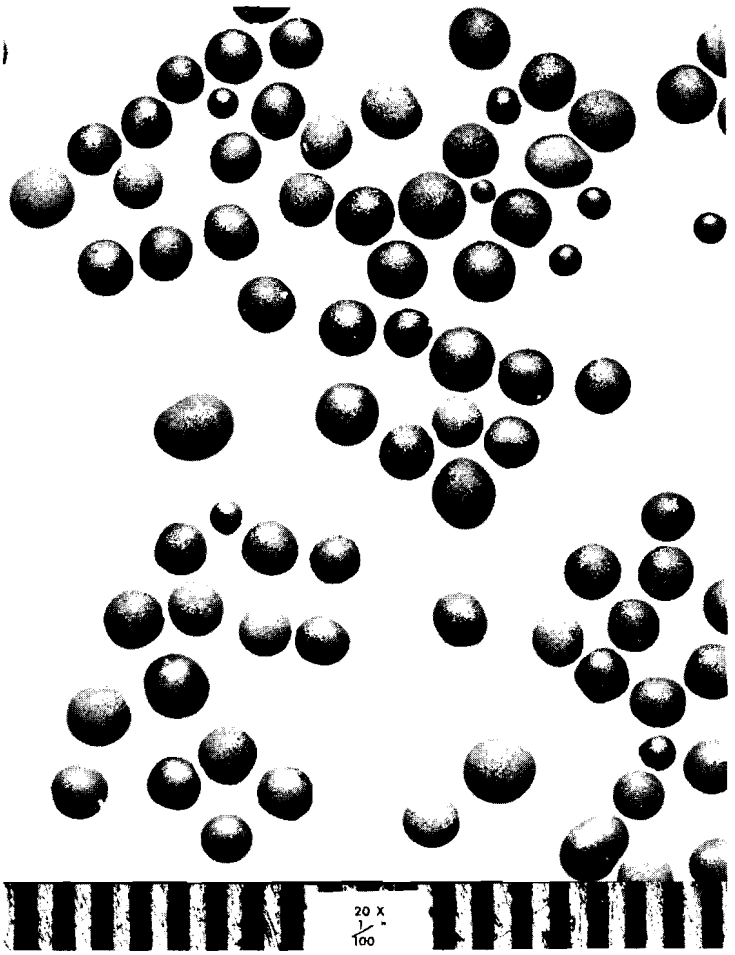

Fig. 4. Uncoated Uranium Carbide Spheres, Oblique Illumination.

outer surface morphology of the pyrolytic-coated spheres requires a higher magnification and dark-field illumination (see Fig. 2). Two morphological characteristics of coatings are shown in Figs. 5 and 6. The smooth-surface coatings were deposited at 1400–1500°C (Fig. 5) and the pebble-finish coatings were deposited at 1600–1700°C (Fig. 6). Only deposition temperatures were available from the vendor; however, deposition rates are also known to influence the microstructure of the graphite.[12]

Microstructure of Uncoated and Coated Uranium Carbide Spheres

A representative example of the microstructure of the fuel spheres observed in a median cross-sectional examination is presented in Fig. 7. Based on previous metallographic work[4] on uranium carbides, a majority of the spheres from several batches were estimated to have an average ratio of approximately 70% UC_2 and 30% UC. In every instance, a very small number of the spheres within the same batch did not fall within this composition range. Some spheres had a composition of 55% UC_2 and 45% UC; however, others contained 95% UC_2 and 5% UC. Deviations from stoichiometry were indicated by the presence of graphite flakes in varying amounts. Examples of these variations in stoichiometry of the carbide spheres and microstructural variations of the carbon coating will be shown later.

The microstructures of pyrolytic-carbon coatings examined to date have either of two characteristics: (1) multiple layers of "onion-ring" type structure or (2) columnar-grain type. These two types of structures have been produced by deposition temperatures of approximately 1400–1500°C and 1600–1700°C, respectively. As stated previously, only temperature conditions were known; other influential conditions, for example – deposition rates, were not available. Photomicrographs representing the two microstructural characteristics are shown in Fig. 8a and 8b. Examples of duplex pyrolytic-carbon coatings of onion-ring type with an outer coating of columnar-grain type microstructures

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[12]A. C. Secrest et al., "Carbon Coating Studies – Coated Particle Fuel Material," Progress Related to Civilian Applications During March 1961, BMI-1509 (Del.) p L-4 (April 1, 1961).

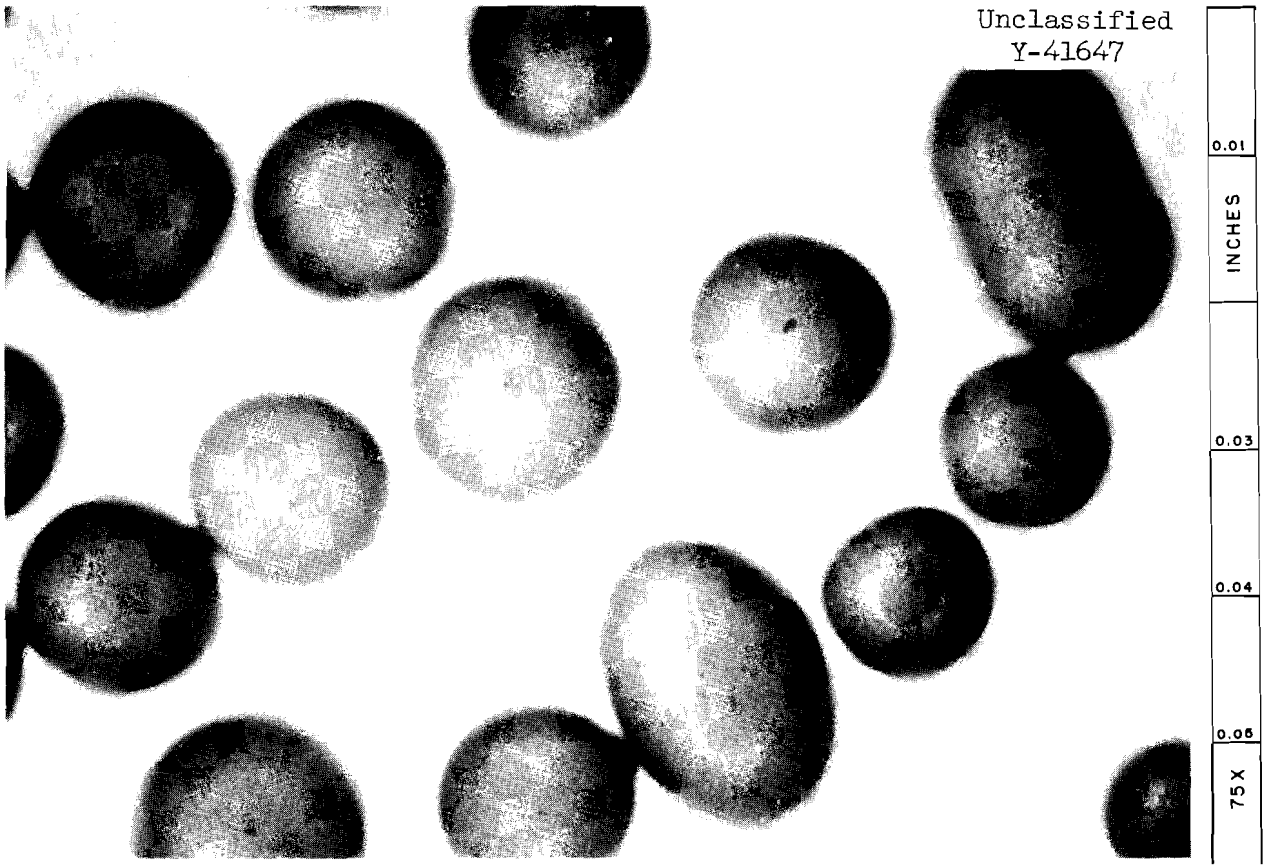


Fig. 5. Pyrolytic-Carbon Coated Uranium Carbide Spheres, Dark-Field Illumination. Representative of coatings after deposition from a carbonaceous vapor at 1400–1500°C.

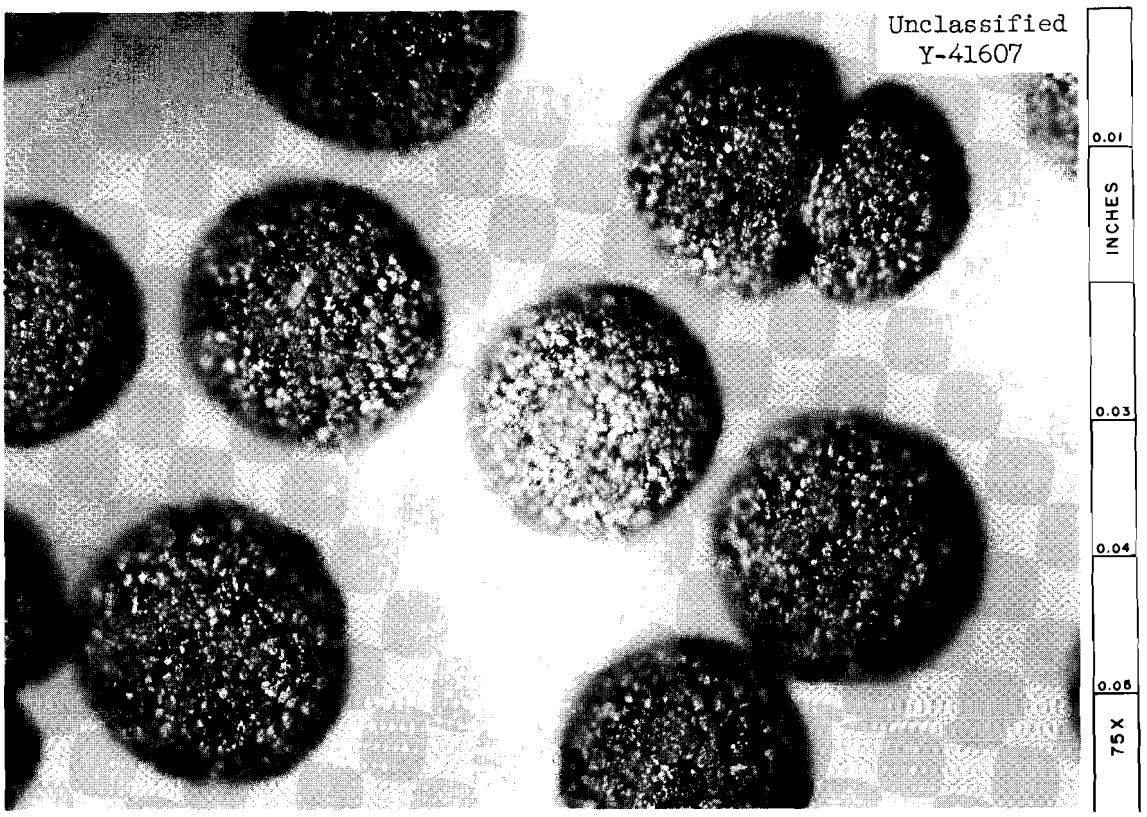
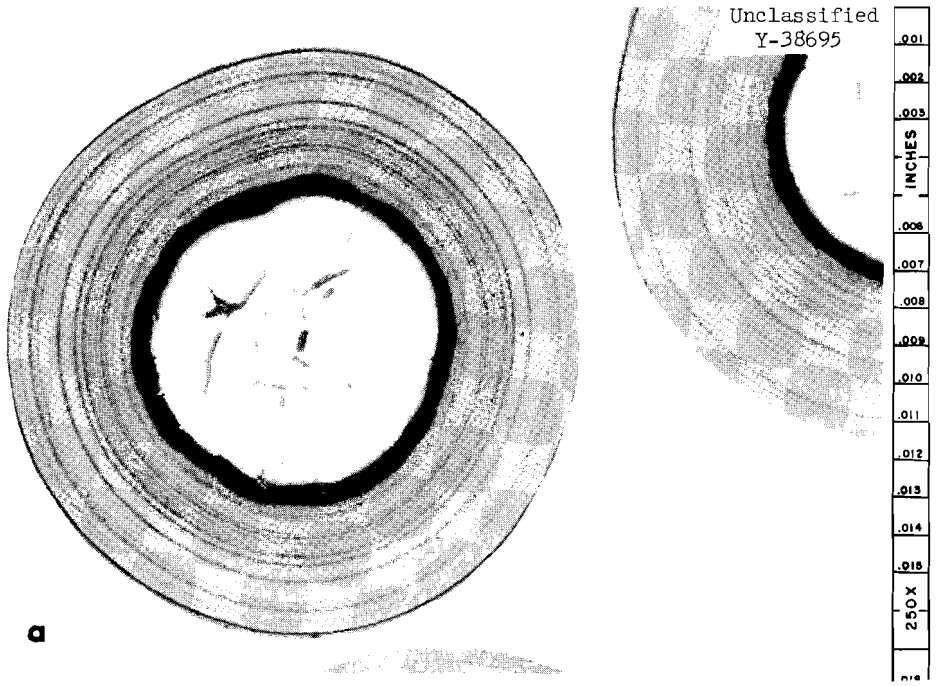


Fig. 6. Pyrolytic-Carbon Coated Uranium Carbide Spheres, Dark-Field Illumination. Representative of coatings after deposition from a carbonaceous vapor at 1600–1700°C.

Fig. 7. Microstructure of Uncoated Uranium Carbide Spheres. Etchant: CH_3COOH, HNO_3, H_2O 1:1:1.



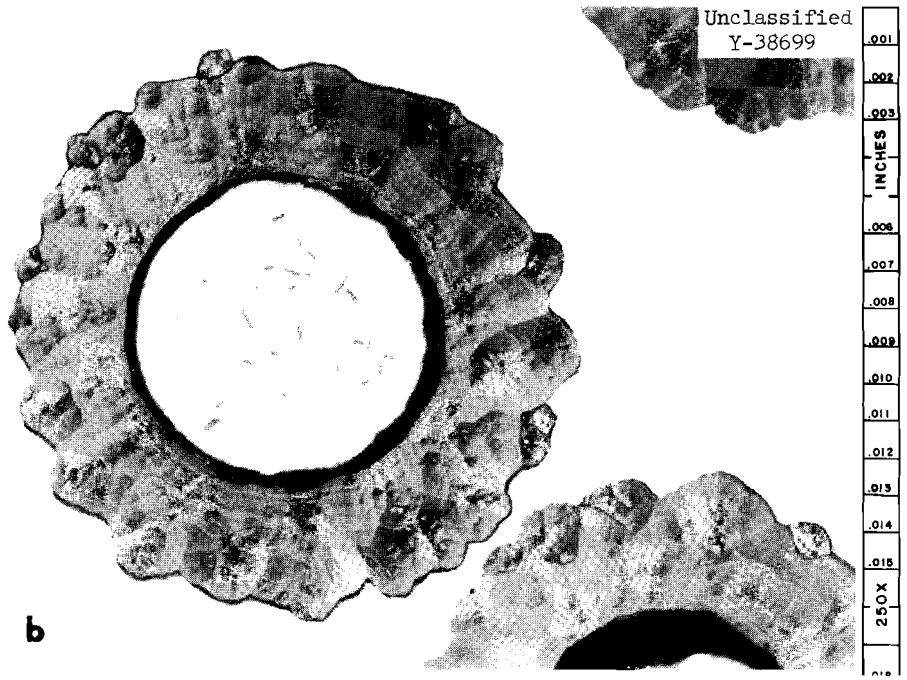


Fig. 8. Microstructure of Pyrolytic-Carbon Coated Uranium Carbide Spheres. (a) Pyrolytic coating representative of deposition at 1400–1500°C and (b) pyrolytic coating representative of depositions at 1600–1700°C. The gray constituent in the uranium carbides is graphite flakes. As polished. Bright field.

are shown in Fig. 9a and 9b. The duplex coating could be due to a change in flow rate and/or a temperature change of the carbonaceous vapor.

It was pointed out previously that there was some variation in the microstructure of the uranium carbide spheres. Variations were also present in the pyrolytic-carbon coatings. In some batches the microstructures of the coatings were uniform; however, in some cases variations were obvious within a single batch. Photomicrographs of these variations are shown as follows: Fig. 10 – noncircular "onion-ring" deposition which possibly could be due to nonuniform agitation of the carbide spheres in the carbonaceous vapor; Fig. 11 – effect of nonspherical carbide cores and "twin cores" (note "twin cores" in Fig. 6) and the subsequent effect on the deposition patterns; Fig. 12a and 12b – some of the carbide cores within a single batch contained an unidentified blue-gray precipitate, and other cores contained above average amounts of graphite flakes; Fig. 13a and 13b – variations in the ratio of UC_2 and UC within a single batch.

Dispersion and Fabrication of Spheres in Graphite

A primary objective of this study was to evaluate the integrity of the coated and uncoated fuel after dispersion and fabrication in a graphite body. Although reaction between the fuel and the graphite was anticipated, uncoated uranium carbide spheres were dispersed in the graphite (see Appendix, item 4) to obtain a comparison for the examination of subsequent fabrication procedures (see Fig. 14). Varying amounts of reaction with the graphite occurred, probably due to a reaction with an oxidizing gas which evolved from the binder of the graphite during the firing of the pellet. The reaction was more severe along the outer edge of the pellet than at the center as shown in Fig. 15a and 15b, respectively. The reaction product was extracted and identified by x-ray diffraction as UO_2.

Both types of pyrolytic-carbon coated uranium carbide spheres were fabricated in graphite and examined. The onion-ring type coated uranium carbide was fabricated in pellets with the shape of a right cylinder 3/4-in. diam x 1/4 in. high. The columnar-grain type coated uranium carbide was fabricated in graphite spheres approximately 2 in. in diameter.

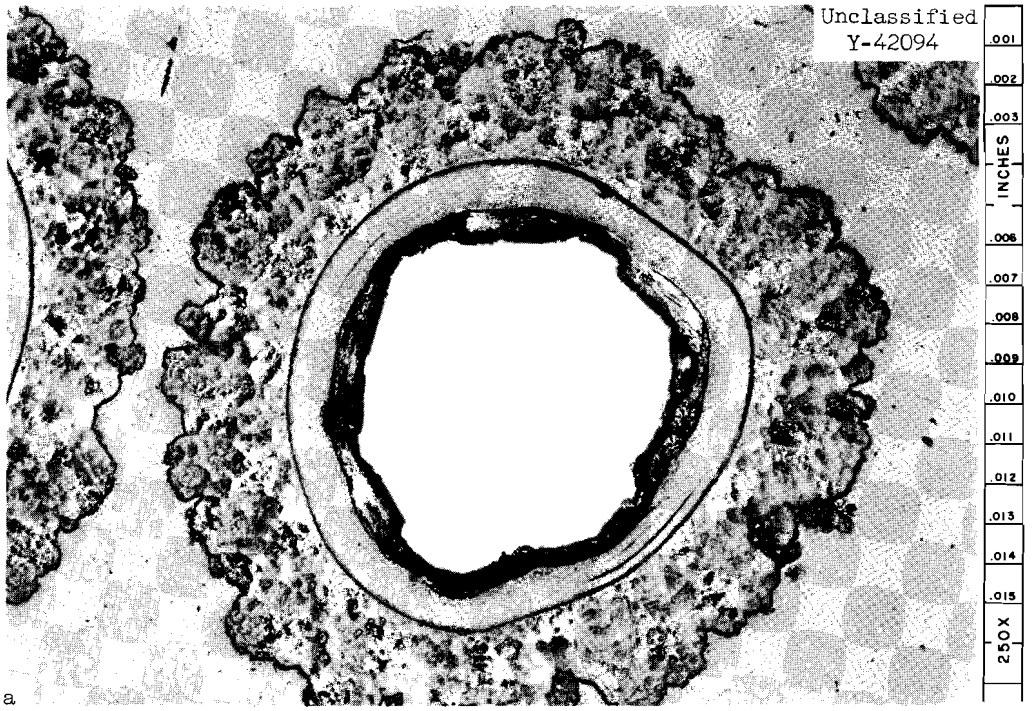


Fig. 9. Duplex-Type Coatings Showing an "Onion-Ring" Deposition with the Columnar-Type Structure as the Outer Coating. (a) Bright field (b) polarized light. As polished.

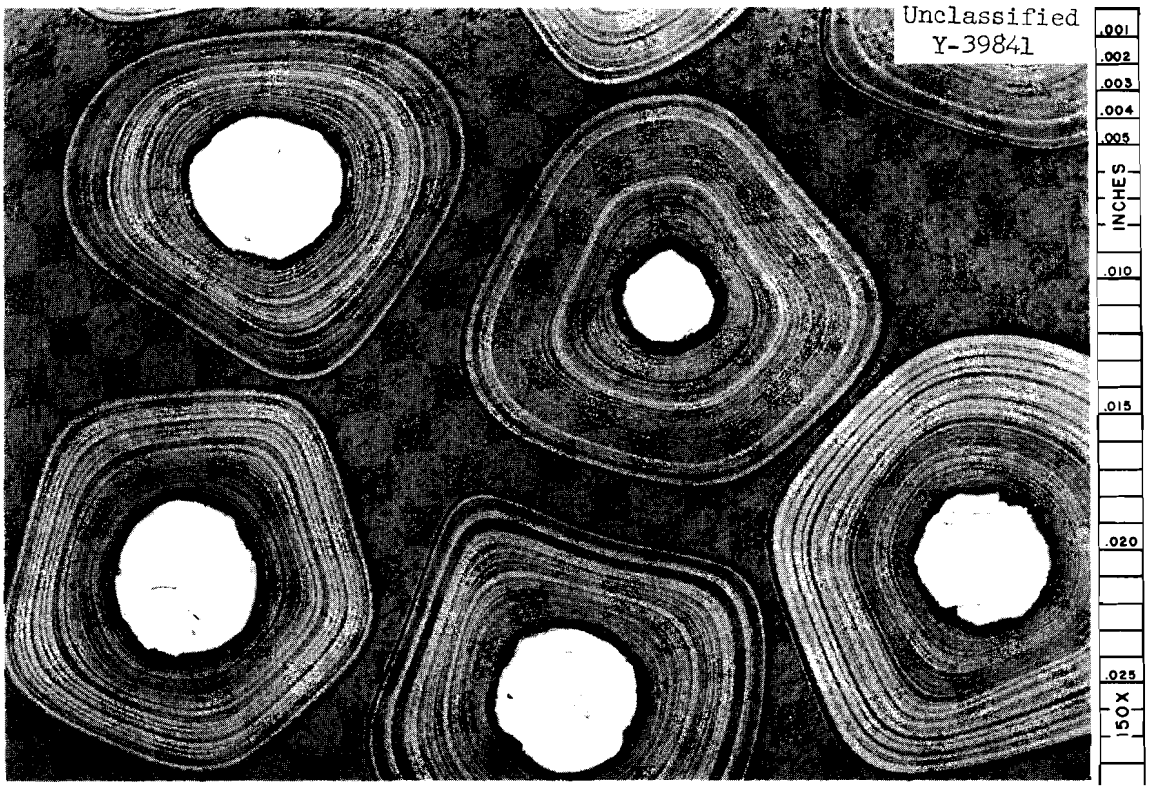


Fig. 10. Noncircular "Onion-Ring" Deposit. As polished. Bright field.

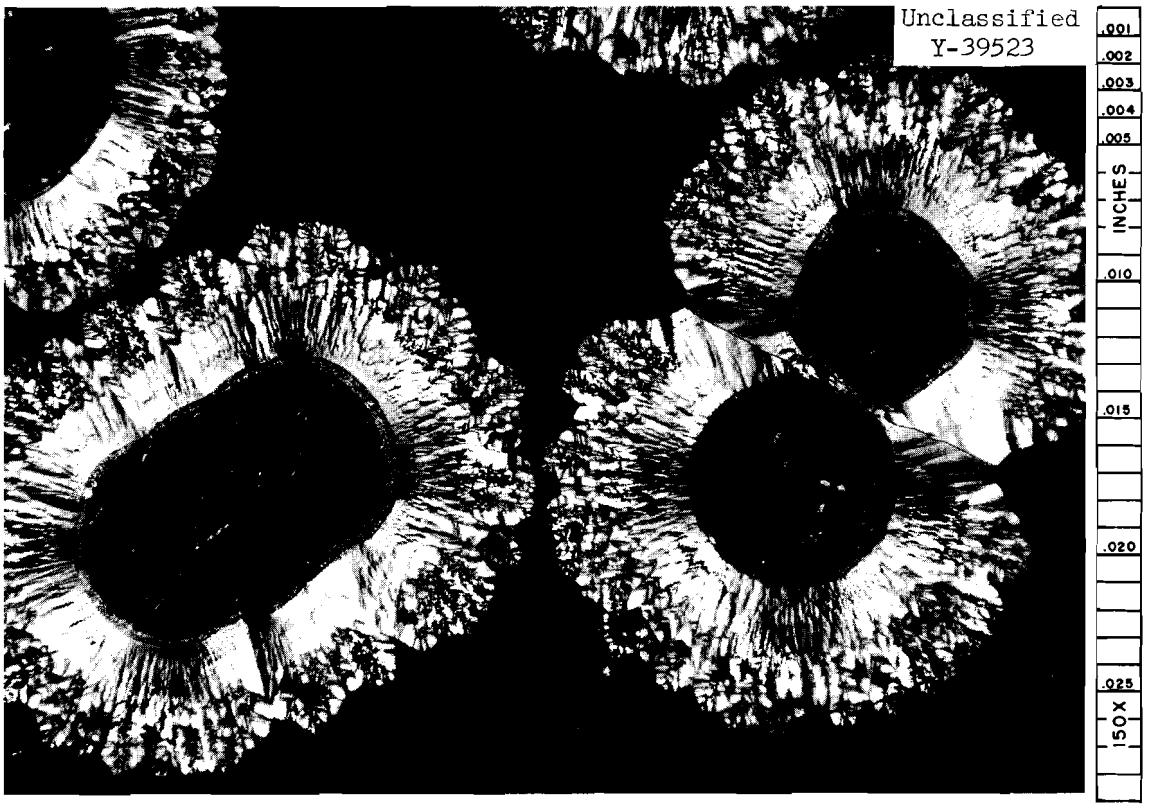


Fig. 11. Nonspherical Uranium Carbide Cores and "Twin Cores." As polished. Polarized light.

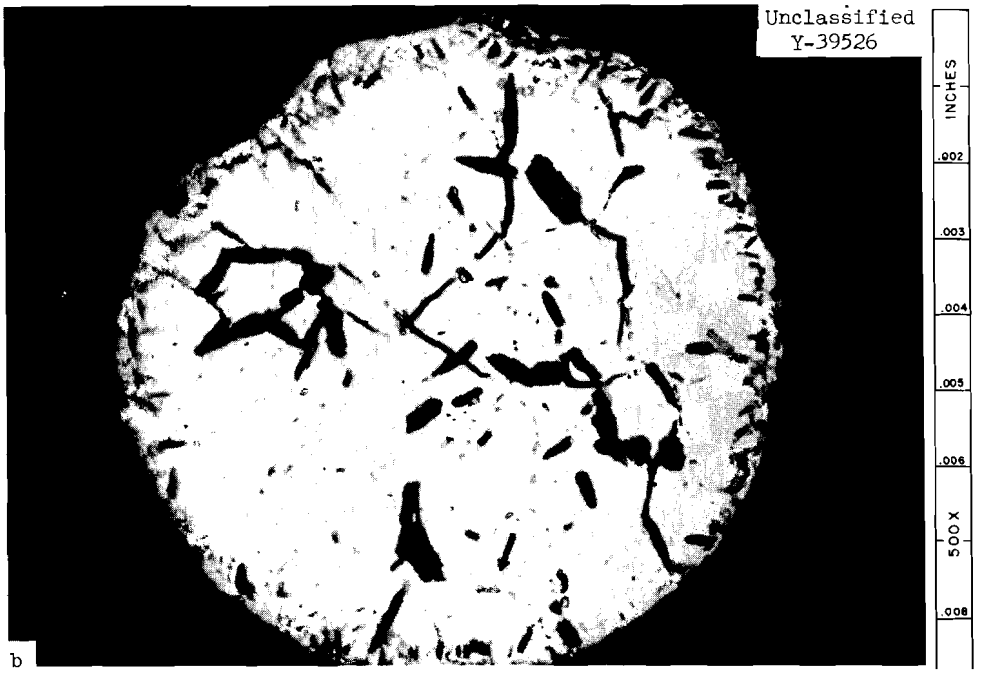


Fig. 12. Variations in the Amount of Graphite Flakes and Unidentified Blue Phase. Graphite flakes are dark gray. Unidentified phase is light gray (arrow). (a) Average amount of graphite flakes and above average amount of blue-gray phase and (b) above average amount of graphite flakes and average amount of blue-gray phase. As polished. Bright field.

Fig. 13. Variations in the Microstructure of Uranium Carbide Spheres. (a) 70% UC_2–30% UC and (b) 95% UC_2–5% UC. Etchant: CH_3COOH, HNO_3, H_2O 1:1:1.

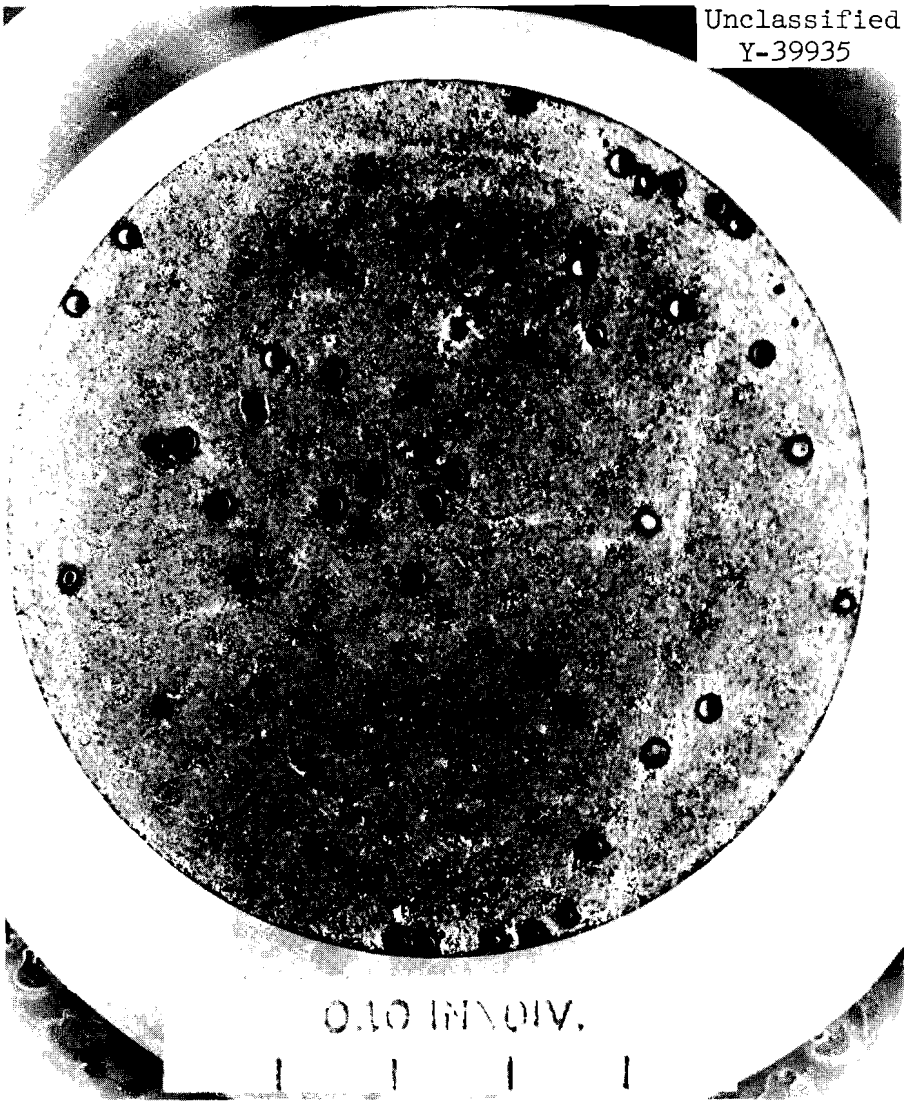
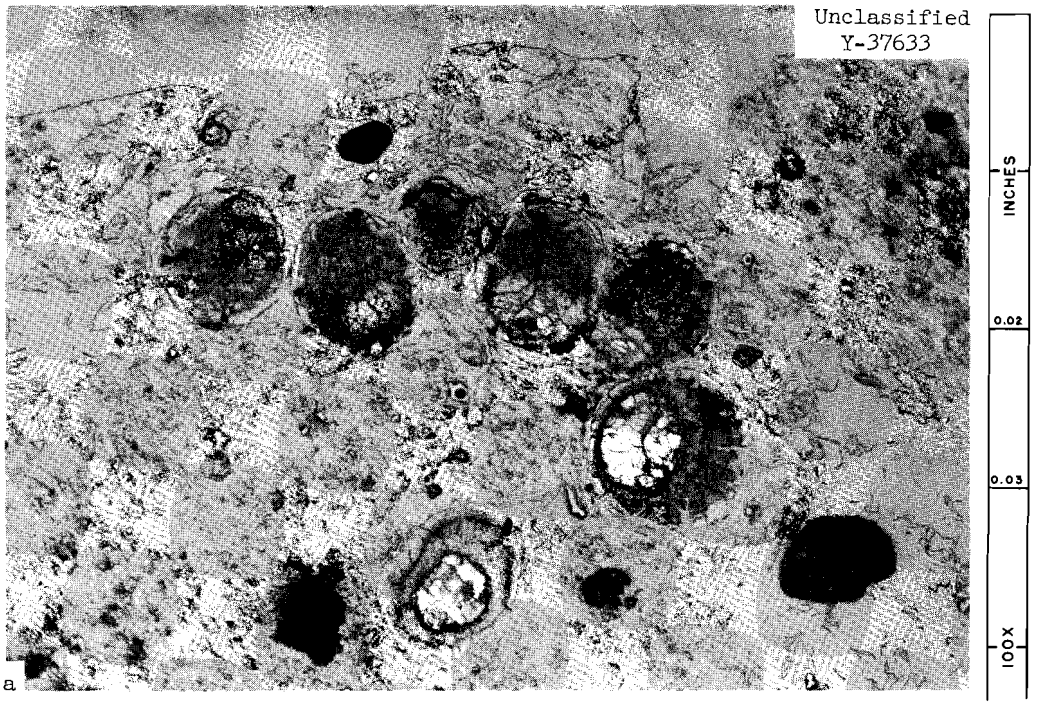


Fig. 14. Uranium Carbide Spheres Fabricated in a Graphite Pellet.



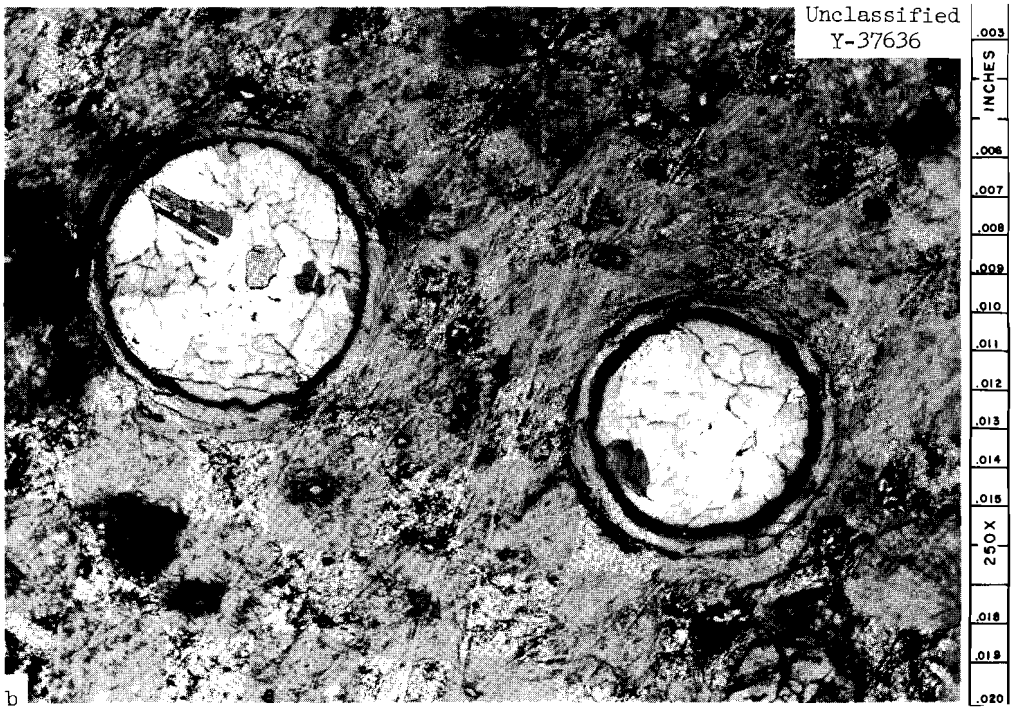


Fig. 15. Reaction of Uncoated Uranium Carbide Spheres with Graphite After Fabrication and Firing. (a) Near outer surface of pellet and (b) near center of pellet. Etchant: CH_3COOH, HNO_3, H_2O 1:1:1.

In making metallographic examinations of the graphite spheres and cylinders, it must be emphasized that direct comparisons of the stability of the two coating techniques are not valid in a postfabrication examination at this time because each type was fabricated in different graphite shapes and by different fabricators (see Appendix) and only results of the examination can be reported.

The onion-ring type coated uranium carbide appeared to withstand its particular fabrication treatment, as shown in Fig. 16. Since the coating maintained its integrity, there was no detectable evidence of any reaction with the graphite matrix.

The columnar-grain type coated uranium carbide, which was dispersed in a 2-in. sphere by another fabricator (see Appendix), did not withstand the fabrication and/or the firing treatment. If the pyrolytic carbon cracked, complete reaction of the uranium carbide core occurred, as shown in Fig. 17, probably with the gas evolved from the graphite and/or binder during the firing. The reaction product has been identified by x-ray techniques as $U_{0.88}O_{2.12}$. It is difficult to ascertain what caused the pyrolytic shell to rupture. It is quite possible that the shell may have been weakened by some fracturing during the blending with the graphite. Apparently the basal plane of the pyrolytic carbon fractures readily, as evident by the internal fractures which parallel the outer surface, as shown in Fig. 18.

Identification of Reaction Products

Detailed identifications of the reaction products are of prime importance since the spheres will be tested in a reactor and the origin of these products must be established prior to postirradiation examination. The form of the reaction products has varied from a minute 0.0005-in. layer at the interface of the uranium carbide sphere and its coating of pyrolytic carbon to a complete reaction of an entire carbide sphere in the graphite matrix. An ultrasonic chisel technique[13] was attempted but was

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[13]G. L. Kehl, H. Steinmetz, and W. J. McGonnagle, Metallurgia 55(329), 151, 1957.

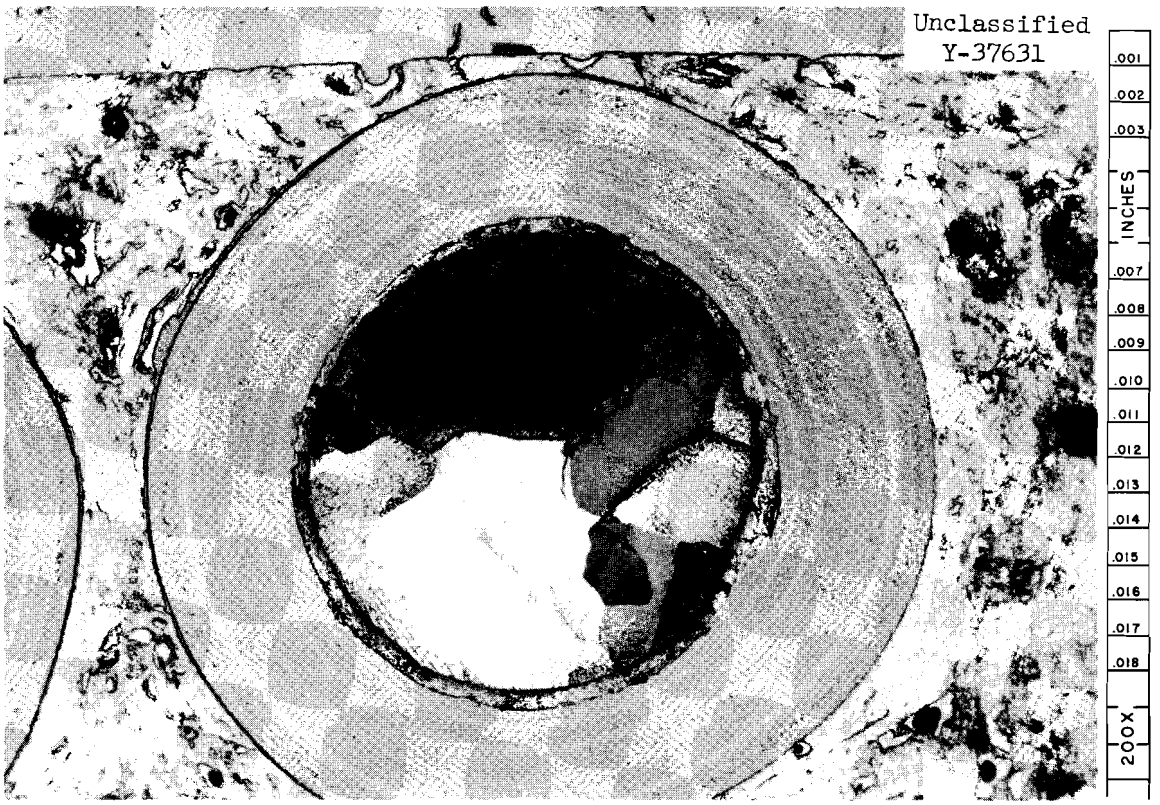

Fig. 16. "Onion-Ring" Type Pyrolytic-Carbon Coating on Uranium Carbide After Fabrication in Graphite. Etchant: CH_3COOH, HNO_3, H_2O 1:1:1.

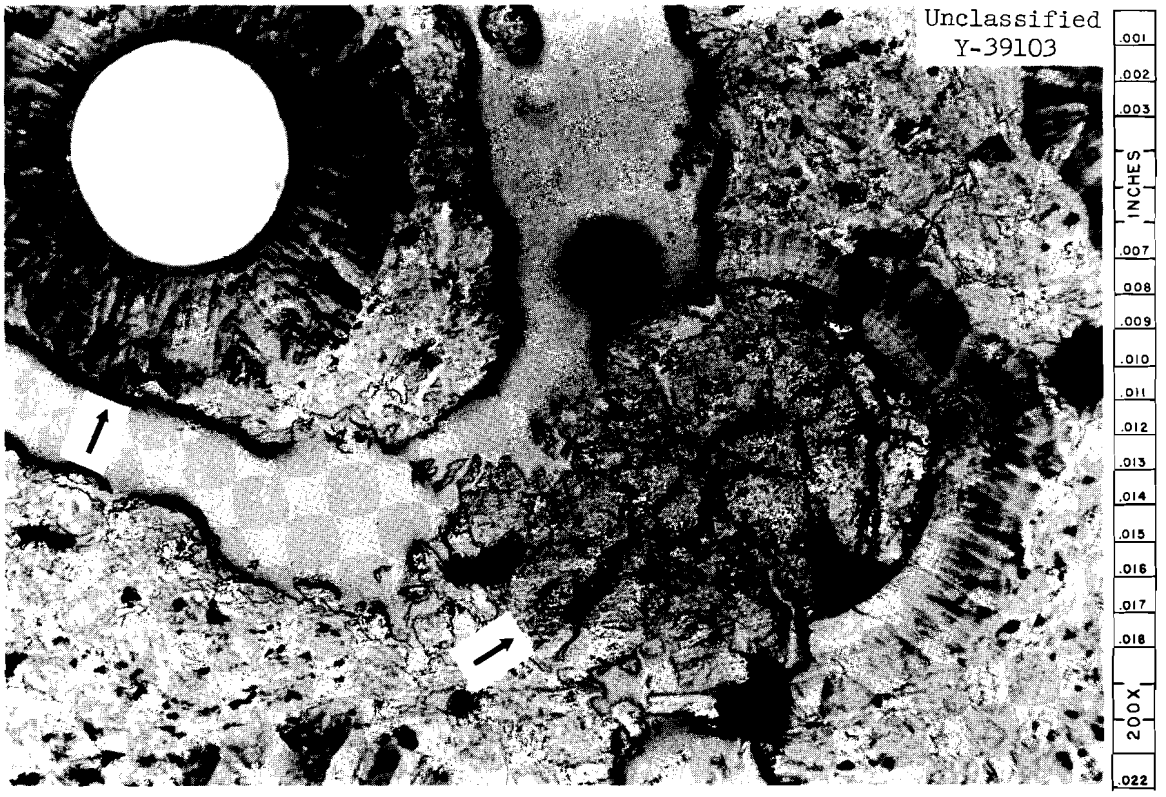

Fig. 17. Columnar-Type Pyrolytic-Carbon Coating on Uranium Carbide After Fabrication in Graphite. Arrows indicate sound sphere and sphere which shows rupturing of the pyrolytic-carbon shell and subsequent complete reaction of the fuel core. As polished.

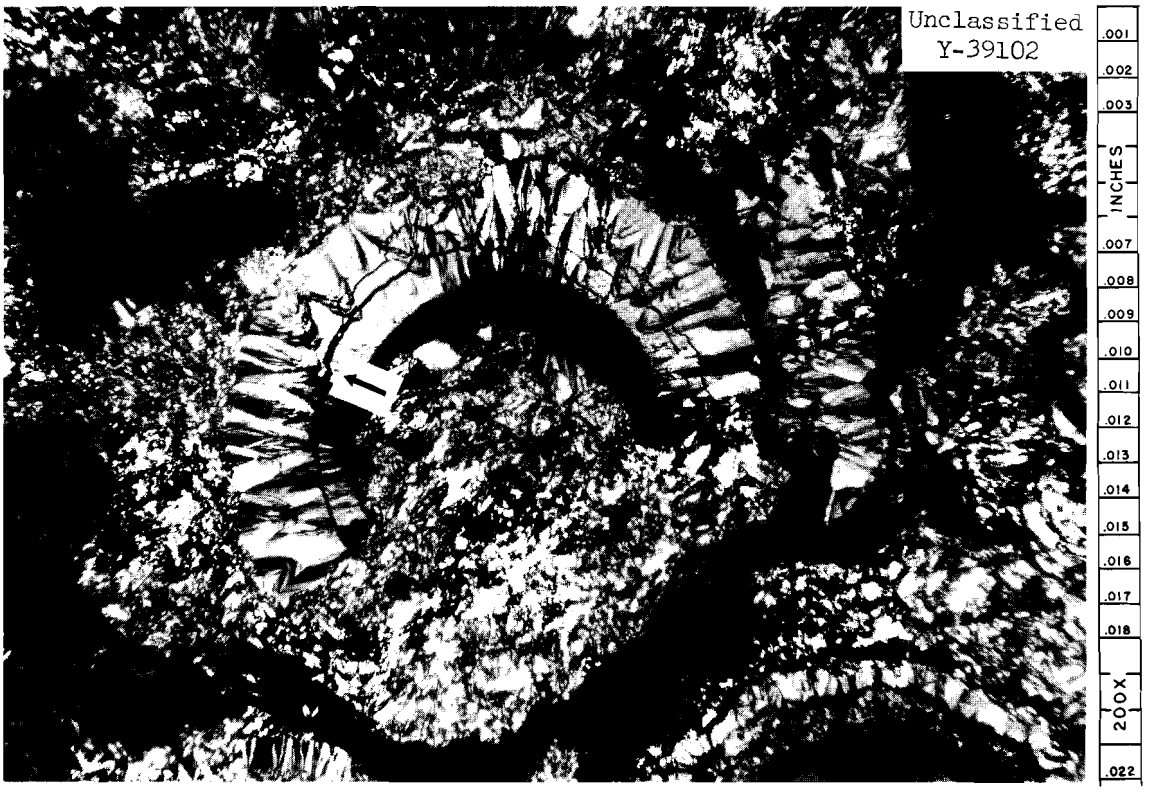

Fig. 18. Cracked-Open Pyrolytic-Carbon Shell in a Graphite Matrix. Note cracks along the basal plane of the pyrolytic carbon. As polished. Polarized light.

not satisfactory. This technique utilizes a miniature ultrasonic jack-hammer with a small chisel point that is positioned on the area in question by means of a microscope to produce microscopic fragments for x-ray identification. The heat generated by the friction between the chisel point and the specimen altered the composition of the fragments and another extraction technique was necessary.

If there was an abundance of reaction product, as was the usual case for uncoated uranium carbide after the fabrication in graphite, the product in question could be removed with a needle-point knife. The blade was manually maneuvered to dislodge minute volumes of the reaction product while the specimen was viewed at a magnification of 100X with a microscopic objective, having a working distance of 14 mm. The loosened reaction product was picked up on a glass fiber previously dipped in Vistanex[14] and the sample was ready for x-ray diffraction study.

To expose the layers found between the uranium carbide sphere and the pyrolytic-carbon coating for x-ray study, this hand technique was altered by pushing on one edge of the polished cross-section surface of the carbide sphere with the needle point until the sphere turned in its socket of pyrolytic carbon, as shown in Fig. 19. The layer was then picked off the side of the sphere with the glass fiber previously dipped in Vistanex.

Examination of the first coated particles representative of the onion-ring and columnar-grain type coatings revealed a very minute unidentified layer at the interface of the carbide sphere and the pyrolytic coating. As other samples were received and examined, it became increasingly evident that this layer was not limited to the first samples. Extraction and identification of this material were attempted repeatedly with confusing x-ray results. A request was made to the vendor for a sample of uncoated uranium carbide spheres. Metallographic examination of these uncoated spheres showed that there was a minute coating on all spheres before they were coated with pyrolytic carbon. X-ray studies of this material identified it as graphite. Returning to the x-ray patterns produced from the material previously extracted from between the carbide

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[14]Vistanex Adhesive, manufactured by Enjay Company, Inc., 15 W. 51st Street, New York, New York.

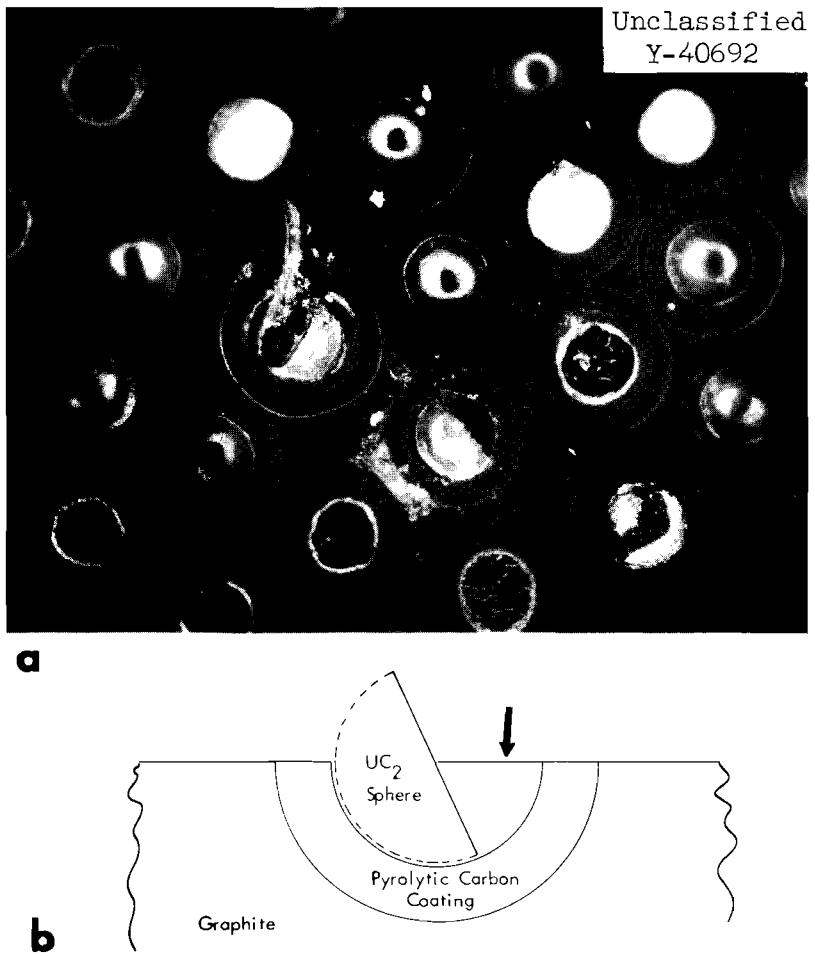

Fig. 19. Extraction Procedure. Method of obtaining a sample of the layor found at the interface of the UC-UC_2 sphere and the pyrolytic-carbon coating. (a) The UC-UC_2 sphere, after polishing down to its mid-cross section, is pushed on with a needle-point blade until it turns in its socket of pyrolytic carbon. The reaction layers are then picked up on a glass fiber off the side of the sphere for x-ray diffraction. Sketch (b) shows hemisphere turned in its socket of pyrolytic carbon.

sphere and its pyrolytic-carbon coating, a better interpretation was resolved. This material was composed primarily of graphite and a trace of UO_2. The graphite, being vulnerable to gaseous pickup, could have provided a source of oxygen which reacted with the uranium carbide during the heat treatment required for applying the pyrolytic-carbon coating, thus producing a slight amount of UO_2 (see Fig. 20).

Microradiography of Coated Spheres

Additional information on the relative morphology of the core and pyrolytic coatings of different spheres can be obtained from a microradiograph. The original exposure (1X) is shown in the inset of Fig. 21. In order to obtain the desired magnification, transmitted light photomicrographs can be made of the original exposure, as shown in Fig. 21 at 75X and in Fig. 22 at 300X. For these particular microradiographs, mixed sizes of spheres were chosen to evaluate the feasibility of microradiography. Due to the great differences in diameter, many of the small spheres lie under the larger spheres; however, there is sufficient contrast to resolve the individual spheres and coatings. The interface of the core and coating is relatively smooth in some of the spheres; however, other spheres exhibit a very irregular interface. This irregularity could be due to varying amounts of graphite and/or reaction between the core and coating, as shown in Fig. 20.

Low-voltage microradiography appears to be very promising for the measurement of core diameters, coating thicknesses, and for evaluating the cores and the integrity of the coatings.

Heat Treatment of Coated Spheres

On prolonged heat treatment of the as-fabricated spheres, considerable reaction at the carbide sphere-carbon coat interface takes place. Figure 23 shows spheres that were thermal cycled three times from 200 to 2170°C for a total of 3 hr. This interface-reaction product was extracted by the hand technique in the same manner described earlier and was identified by x-ray studies as UO_2. It appears that this product may be a continuation of the UO_2-graphite interface reaction described in the previous section. Another avenue of thought is that the UO_2 could be the result of a reaction of UC_2

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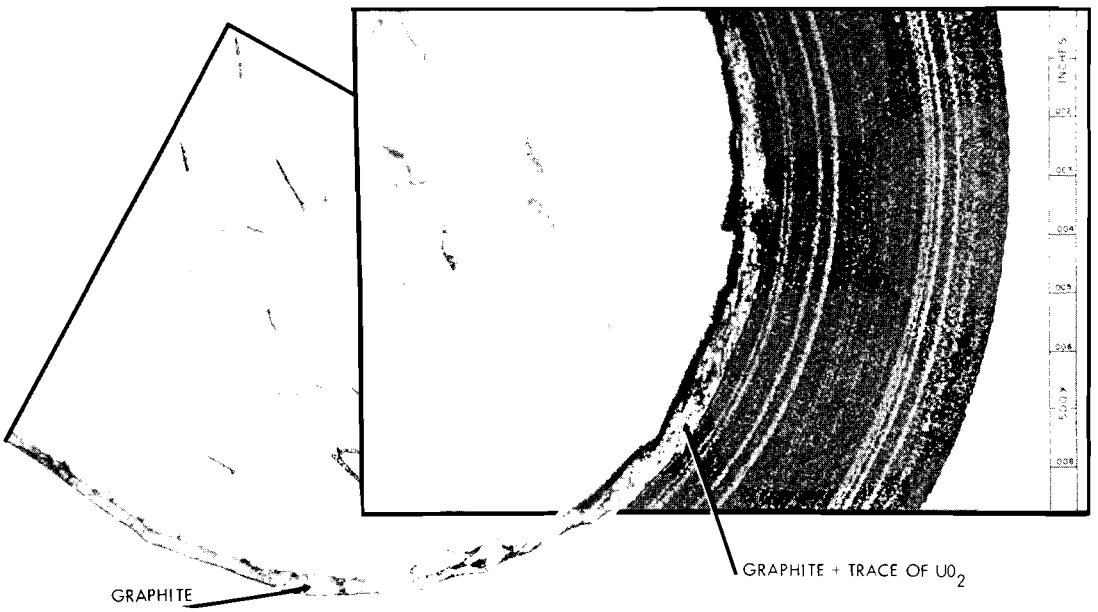

Fig. 20. Layer on $UC-UC_2$ Sphere Before and After It Was Coated with Pyrolytic Carbon. This layer on the uncoated $UC-UC_2$ sphere has been shown by x ray to be graphite. This same layer, after the pyrolytic-carbon coating has been added, has been identified as graphite and a trace of UO_2.

Fig. 21. Microradiographs of Pyrolytic-Carbon Coated Uranium Carbide Spheres. Mixed sizes are shown. The inset shows the original exposure (1X). Arrows indicate overlap of a larger sphere with a smaller sphere. X-ray exposure was 10 kv, 30 ma for 2 1/4 hr. 75X.

Fig. 22. Microradiographs of Pyrolytic-Carbon Coated Uranium Carbide Spheres. Same as Fig. 21 at higher magnification. Note the irregular interface indicating varying amounts of graphite and/or reaction between the core and coating, as shown in Fig. 20.

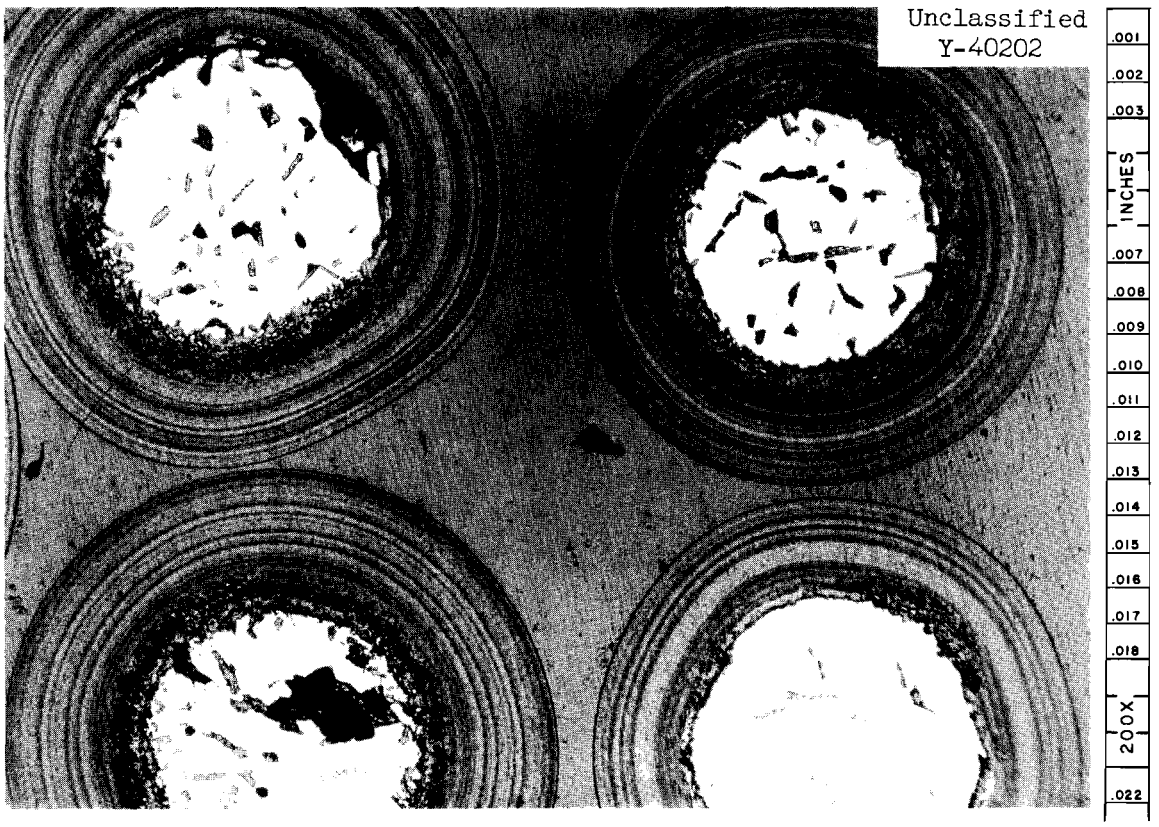

Fig. 23. "Onion-Ring" Coated Uranium Carbide Spheres After Heat Treatment. Reaction product at the interface of the UC-UC_2 sphere and pyrolytic-carbon coating is UO_2. As polished. Bright field.

with the atmosphere as follows: Fine UC_2 powder particles at the interface could have reacted with the atmosphere after the polished cross section had been prepared and exposed to room air to form UO_2. However, the authors have not, to date, observed the oxidation of uranium carbide, even in powder form, with the atmosphere to form UO_2 at room temperature.[15] Oxidation of uranium carbides, however, has been observed at higher temperatures.

Coated Spheres Prior to Irradiation

Irradiation tests of pyrolytic-carbon coated UC-UC_2 spheres are now under way in the Low-Intensity Test Reactor at the Oak Ridge National Laboratory. Prior to insertion in the reactor, these spheres were subjected to three thermal cycles between 200 and 1370°C to test the integrity of the pyrolytic-carbon coating, since the latter temperature would be the maximum temperature that would be attained in the irradiation capsule. For control purposes, random spheres were examined and no adverse effects from this cyclic heat treatment could be seen metallographically, as shown in Fig. 24. There was a noticeable difference in the appearance of the pyrolytic-carbon coating on these spheres which was in no way related to the cyclic heat treatment, but indicated some procedure alterations during the original deposition. Information from the vendor indicated that, after the first deposition period, the coating thickness was checked and found not to be thick enough. A rerun was started, stepping up the temperature and flow rate of the hydrocarbon gas. This change in deposition temperature and flow rate resulted in two different types of structure in the pyrolytic-carbon coating. This effect was also evident in Fig. 10.

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[15] R. J. Gray and C. K. H. DuBose, A Microscopic Study of the Effect of Moisture in the Air on Arc-Cast Uranium Monocarbide and Uranium Dicarbide at Room Temperature Over Extended Periods, ORNL-TM-56 (Nov. 20, 1961).

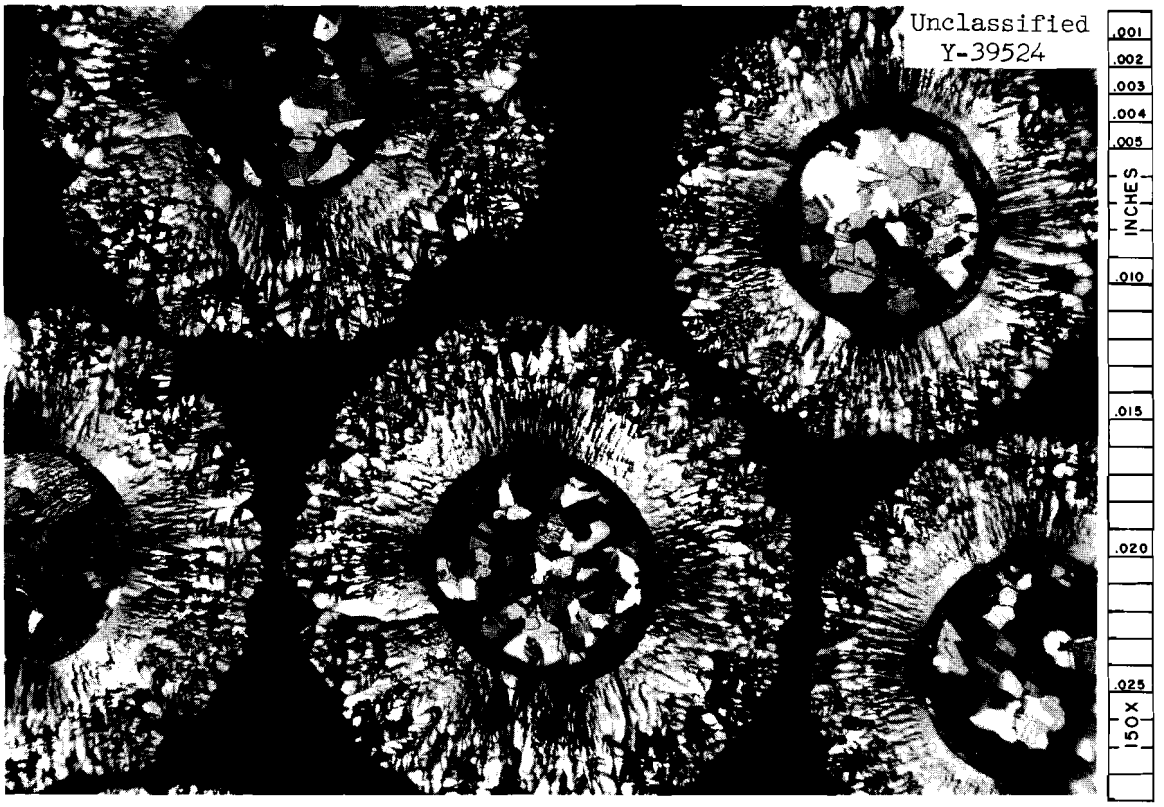

Fig. 24. Condition of Coated Fuel Particles After Thermal Cycling. These particles were subjected to a short-time thermal cycle between 200 and 1370°C. No adverse effects from this heat treatment could be seen metallographically. Note the two different types of structure in the pyrolytic-carbon coating, due to different temperatures and/or flow rate of deposition. Polarized light. Etchant: CH_3COOH, HNO_3, H_2O 1:1:1.

After irradiation to a burnup of 10 at. % of the U^{235}, the spheres will be removed from the reactor and hot-cell metallography will be performed. Comparisons will be made with the control spheres to determine irradiation effects.

ACKNOWLEDGMENT

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APPENDIX

	Material	Figure(s)	Manufacturer and/or Fabricator and Available Fabrication Information
1.	Uranium Carbide Spheres	4 and 7	Vendor A
2.	Natural Graphite	14, 15, and 16	Vendor B
3.	Binder	14, 15, and 16	Vendor C
4.	Fabrication of Uranium Carbide Spheres in a Graphite Pellet 3/4-in. diam x 1/4-in. high	14 and 15	Fabricated by Ceramics Group of Metallurgy and Ceramics Division, ORNL. The graphite, binder, and fuel were dry mixed in a V-blendor, cold pressed in a 3/4-in. die at 45 tsi, fired at a rate of 20°C/hr to 1000°C in argon, and cooled at a rate of 33 1/3°C/hr to room temperature
5.	Pyrolytic-Carbon Coating "Onion-Ring" type	5, 8a, 10, 16, and 23	Vendor A Deposited at 1400–1500°C
6.	Fabrication of "Onion-Ring" Coated Spheres in Graphite Pellet	16	Same procedure as item 4
7.	Pyrolytic-Carbon Coating "Columnar-Grain" Type	6, 8b, 11, 12, 13, 18, and 24	Vendor D Deposited at 1600–1700°C
8.	Fabrication of "Columnar-Grain" Type Coated Spheres in a 2-in.-diam Graphite Sphere	17 and 18	Vendor E Fabricated as a fuel cored graphite sphere, fired at approximately 1000°C
9.	Duplex-Type Pyrolytic-Carbon Coating and Sphere	9	Vendor F

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