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HIGH-TEMPERATURE COMPATIBILITY OF Al_2O_3 -,
BeO-, AND METAL-COATED UO_2 PARTICLES
WITH GRAPHITE AND COKE

by

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HIGH-TEMPERATURE COMPATIBILITY OF Al_2O_3 -, BeO -, AND METAL-COATED UO_2 PARTICLES WITH GRAPHITE AND COKE

Arnold F. Gerds and Allison K. Smalley

The compatibility of carbon and graphite matrices with UO_2 particles coated with Al_2O_3 , BeO , nickel, niobium, and nickel-chromium alloy has been investigated at several temperatures up to 3000 F in flowing helium. Two different carbonaceous fillers and binders were used. As expected, the 2 to 8- μ metal coatings were badly damaged by reaction with carbon at temperatures as low as 1700 F. Both oxide coatings were completely destroyed after 6 hr at 3000 F. Considerable reaction between the matrices and Al_2O_3 and BeO coatings occurred during 1000 hr at 2500 F. Coating damage was more severe in surface particles than in particles located inside the specimens. The graphite filler and pitch binder combination used in this study was less reactive than combinations containing coke filler or resin binder.

INTRODUCTION

Uranium dioxide particles, individually coated with a dense ceramic oxide and dispersed in a graphite matrix, may have several important advantages in high-temperature fuel-element applications. Among these are fission-gas retention and prevention of UO_2 oxidation and uranium migration. One factor limiting the use of these two coatings at very high temperatures is their reactivity with the graphite matrix. Based on fragmentary information from kinetic studies reported in the literature, Al_2O_3 and BeO are expected to react with carbon at some temperature less than 3000 F. Of these two oxides BeO is more stable. Reported threshold temperatures vary over a wide range, reflecting the importance of raw materials, carbon-oxide contact, and environmental atmosphere on the reaction kinetics. One of the important reactions is reduction of the oxide with the formation of carbide and, possibly, free metal. Diffusion undoubtedly plays a dominant role in the reaction kinetics. With the oxide coating in contact with both carbon and UO_2 , the reaction mechanism is complex.

This report describes the results of heating Al_2O_3 - and BeO -coated UO_2 particles at 2500 and 3000 F, and nickel-, niobium-, and nickel-chromium-coated UO_2 particles at 1700 and 2500 F, in graphite matrices in helium. The purpose of the work was to determine the gross behavior of the coatings at low temperatures where little coating deterioration would be expected and at high temperatures where extensive coating deterioration would be expected.

The work reported here was carried out in support of fuel-element development programs for several sites. The Al_2O_3 -coated UO_2 and metal-coated UO_2 were investigated as part of the Pebble-Bed Reactor fuel-element evaluation program for Sanderson & Porter.

MATERIALS

Sintered Oxide Coatings

A ceramic process for producing sintered Al_2O_3 and BeO coatings has been described in the literature.⁽¹⁾ In this process a sinterable BeO or Al_2O_3 powder is sprayed and dusted onto relatively coarse (20 mesh) unsintered UO_2 particles as they are being tumbled. The coatings then are compacted on the particles hydrostatically, using a noncompacting filler powder which transmits the pressure to the particles but prevents them from bonding to each other. The compacted granules are sintered for 1 hr at 2800 F in hydrogen. Thick, dense coatings ranging from 200 to 600 μ have been prepared by this process. As shown in Figure 1, the UO_2 particle fits loosely in the oxide shell.

Vapor-Deposited Oxide Coatings

Alumina-coated UO_2 also has been prepared at Battelle by a vapor-deposition process.⁽²⁾ The coating is applied by hydrolizing Al_2Cl_6 in a fluidized bed of the UO_2 particles at about 1800 F. The coating is dense and adheres tightly to the UO_2 particles. Typical coatings of vapor-deposited Al_2O_3 on UO_2 are shown in Figure 2.

Metal-Coated UO_2

Uranium dioxide particles (minus 100 plus 140 mesh) coated with 2 to 8 μ of nickel, niobium, and nickel-chromium alloy were supplied by a commercial vendor. A vapor-deposition method was employed, although the details of the coating process are not known. The as-received particles are shown in Figure 3.

Carbonaceous Fillers and Binders

Two graphite fillers, reactor-grade AGOT graphite and petroleum coke, and two binders, medium-hard coal-tar pitch and a thermosetting resin, were used to make the specimens for the compatibility studies. In most of the studies, the specimens were made with the graphite filler and pitch binder. The resin binder, BV-1600, contained a phenolformaldehyde base.

EXPERIMENTAL PROCEDURE

Graphite specimens containing UO_2 particles with sintered oxide coatings or with metal coatings were prepared by placing a layer of coated particles in a steel die

(1) References at end.

50X

As Polished

N62238

a. 300 to 500- μ Al_2O_3 Coating

50X

As Polished

N62230

b. 200 to 600- μ BeO CoatingFIGURE 1. SINTERED OXIDE COATINGS ON UO_2 PARTICLES

100X

As Polished

N65246

a. 20- μ Coating

100X

As Polished

N65245

b. 40 to 60- μ CoatingFIGURE 2. VAPOR-DEPOSITED Al_2O_3 COATINGS ON UO_2 PARTICLES

250X

As Polished

N61005

a. Nickel Coating

250X

As Polished

N61007

b. Nickel-Chromium Coating

250X

As Polished

N61006

c. Niobium Coating

FIGURE 3. VAPOR-DEPOSITED METAL COATINGS ON UO_2 PARTICLES

The coatings ranged from 2 to 8μ thick on the minus 100 plus 140-mesh UO_2 . Details of the coating process were not given by the commercial supplier.

partially filled with a powdered mixture of graphite or coke and binder. More of the mixture was added, and the powders were compacted at 24,000 psi. These compacts were about 1/2 in. in diameter and 3/4 in. high. The green compacts were heated slowly to 1700 F in a CO-CO₂ atmosphere, generated from residual air in the system, and then soaked at 1700 F for 4 hr. This prebake released volatile constituents in the binder and increased the strength of the compacts.

Specimens containing vapor-deposited Al₂O₃-coated UO₂ were prepared by a commercial graphite supplier from 200-mesh AGOT graphite filler and coal-tar pitch binder. These compacts were prebaked at 2300 F.

In the 2500 F study, the prebaked specimens were placed in separate holes drilled in a split graphite block and heated in flowing helium by a Globar resistance furnace. The helium used was dried by passing it through a dry ice-acetone trap. After an initial purge, the furnace was brought to temperature. Specimens were removed at 168, 500, and 1000 hr after allowing the furnace to cool to room temperature.

Some of the oxide-coated particles were heated in a graphite crucible at 3000 F for 6 hr in a high-frequency induction furnace with a graphite susceptor. For these experiments, the furnace tube first was evacuated and then filled with dry helium to atmospheric pressure. Specimens were cooled to room temperature with the furnace in the presence of helium.

The specimens were sectioned after heat treatment, mounted in an epoxy resin, and examined metallographically. Metallographic techniques have been described previously. (3)

RESULTS

Metal-Coated UO₂ Particles

The metal-coated particles in specimens prebaked 4 hr at 1700 F are shown in Figure 4. All three coatings deteriorated badly, exposing the fuel cores. It is evident that the nickel and nickel-chromium alloy both agglomerated into metallic masses. Two metallic phases were present in each mass. Somewhat less agglomeration occurred in the nickel-chromium alloy than in the nickel. The alloy still covered part of the individual fuel particles.

The niobium coating was altered to a series of small gray particles that were probably niobium carbide. Little change in the UO₂ particles occurred in any of the three specimens.

A duplicate set of prebaked specimens was heated at 2500 F in helium for 168 hr. In all cases the reaction was more extensive than in the prebaked specimens.

A summary of the results is presented in Table 1.

250X

As Polished

N61974

250X

As Polished

N61972

250X

As Polished

N61975

a. Nickel Coating

b. Nickel-Chromium Coating

c. Niobium Coating

FIGURE 4. VAPOR-DEPOSITED METAL COATINGS ON UO_2 PARTICLES DISPERSED IN AGOT GRAPHITE AFTER 4 HR AT 1700 F

Melting apparently occurred in the nickel- and nickel-chromium-coated particles while the niobium coating reacted during the exposure to form, presumably, a carbide. Coal-tar pitch was employed as a binder in preparing the specimens.

TABLE 1. SUMMARY OF RESULTS FROM METALLOGRAPHIC EXAMINATIONS OF METAL-COATED UO_2 PARTICLES
DISPERSED IN AGOT GRAPHITE^(a) AND HEATED AT 1700 AND 2500 F

Specimen Condition	Nickel-Coated UO_2	Nickel-Chromium-Coated UO_2	Niobium-Coated UO_2
As-received particles	Coating 2 to 8 μ thick and tightly adherent UO_2 particles generally spherical but porous and cracked UO_2 particles 100 to 120 μ in diameter	Coating 2 to 8 μ thick and tightly adherent UO_2 particles generally spherical but quite porous and fragmented UO_2 particles 100 to 160 μ in diameter	Coating 1 to 3 μ thick and generally nonadherent to particles UO_2 particles generally spherical but quite porous and fragmented Niobium filled some cracks in UO_2 particles UO_2 particles 100 to 180 μ in diameter
Prebaked at 1700 F for 4 hr	Particles retained shapes but free of coatings Coating agglomerated into two-phase metallic mass	Particles retained their shapes and many still retained some semblance of their coating A small amount of coating apparently melted and agglomerated into two-phase mass	Particles unchanged in shape or appearance Coating reduced to series of small, porous gray particles which appeared not to adhere to larger UO_2 particles
Heated at 2500 F for 168 hr	Most particles appeared to have lost their shapes and dissolved into the nickel, forming a metallic mass consisting of three distinct phases Much interaction evident among particles, coating and graphite	Many particles lost their shapes and dissolved into the nickel-chromium alloy, forming two or three phase mass A few particles retained their integrity but even these showed evidence of a metallic reaction product	Most particles retained their integrity but some were badly fragmented Coating between particles a tan, metallic color, nonadherent, to UO_2 particles and appeared as series of small, porous, discontinuous particles Some porous UO_2 particles contained small light gray or metallic inclusions

(a) Coal-tar pitch was used as a binder.

It is of interest to compare the results obtained with nickel coatings with those reported⁽⁴⁾ earlier in a compatibility study in which sandwiches containing graphite in contact with nickel-plated stainless steel were studied. After heating these sandwiches at 1850 F for 250 hr, carbon was found to have diffused through the 2.5-mil nickel plate, forming carbides in the underlying stainless steel.

The mechanism by which melting of the nickel and nickel-chromium alloy covering the UO_2 particles occurred was considered on the basis of the known thermodynamics data. No satisfactory process could be deduced to explain what appeared to be a rather complex and perhaps multistep reaction.

It has been reported⁽⁴⁾ that carbon diffusion through chromium is much slower than carbon diffusion through nickel. In view of this, it would be expected that less carbon would diffuse through the nickel-chromium alloy coating investigated in this work than through the nickel coating. The data support this view (see Figure 4).

Al_2O_3 -Coated UO_2

Most of the work with the Al_2O_3 -coated material was done with vapor-deposited coatings. Unless otherwise stated, the photomicrographs discussed below show structures deep inside the graphite specimens.

Vapor-Deposited Coating

The appearance of the prebaked vapor-deposited Al_2O_3 -coated UO_2 particles is shown in Figure 5. Two coating thicknesses, 20 and 40 to 60 μ , were investigated. The photomicrographs show that no reaction occurred between the Al_2O_3 and the graphite matrix during prebaking. At 2300 F cracks and voids were evident in the UO_2 particles. The coatings were dense and contained few voids. The coatings adhered tightly to the UO_2 , and only small voids were evident at the Al_2O_3 -graphite interfaces.

Heating the coated particles in the graphite matrices for 168 hr at 2500 F in helium produced only slight reaction at the Al_2O_3 -graphite interface (Figure 6). In the photomicrographs presented in Figure 6 this reaction is evidenced by the larger gap between the matrix and the coating and a rounding off of the knobs on the coating. The UO_2 particles were cracked. This may have resulted from thermal shock occurring when the specimens were heated and cooled. Slight reductions in the thickness of the Al_2O_3 coatings were observed also.

Figure 7 shows photomicrographs of the particles heated at 2500 F for 500 hr. The coatings remained continuous, but reaction between the Al_2O_3 and the graphite was clearly evident.

It was observed that particles near the surfaces of specimens heated for 500 hr or longer and directly exposed to the flowing helium atmosphere frequently lost their coatings. An example of a UO_2 particle initially covered with a 20- μ coating and located near the surface of the graphite matrix is shown in Figure 8. The photomicrograph at 50X shows several particles adjacent to the surface that are free of coating. The smooth light-gray material surrounding these particles is the mounting resin.

50X

As Polished

N67296

250X

As Polished

N67295

a. 20- μ Coating

50X

As Polished

N67291

250X

As Polished

N67292

b. 40 to 60- μ Coating

FIGURE 5. VAPOR-DEPOSITED Al_2O_3 COATING ON UO_2 PARTICLES EMBEDDED IN AGOT GRAPHITE AFTER PREBAKING AT 2300 F

The coatings showed good adherence to the UO_2 particles. There are small voids at the Al_2O_3 -graphite interface but no evidence of a reaction. Coal-tar pitch was employed as the binder in preparing the specimens.

50X

As Polished

N67301

250X

As Polished

N67302

a. 20- μ Coating

50X

As Polished

N67297

250X

As Polished

N67298

b. 40 to 60- μ Coating

FIGURE 6. UO_2 PARTICLES WITH VAPOR-DEPOSITED Al_2O_3 COATING EMBEDDED IN AGOT GRAPHITE AND HEATED 168 HR AT 2500 F

Slight reductions in coating thickness and voids at Al_2O_3 -graphite interface seem to indicate some reaction occurred during exposure. Coal-tar pitch was employed as a binder in these specimens; prebaking was at 2300 F.

50X

As Polished

N67855

250X

As Polished

N67856

a. 20- μ Coating

50X

As Polished

N67853

250X

As Polished

N67854

b. 40 to 60- μ Coating

FIGURE 7. EFFECT OF 500-HR EXPOSURE AT 2500 F ON UO_2 PARTICLES COATED WITH VAPOR-DEPOSITED Al_2O_3 AND DISPERSED IN AGOT GRAPHITE

Reaction between Al_2O_3 and graphite is clearly evident. Specimens were prepared with a binder of coal-tar pitch and were prebaked at 2300 F.

50X

As Polished

N70558

250X

As Polished

N70557

FIGURE 8. DESTRUCTION OF 20- μ VAPOR-DEPOSITED Al_2O_3 COATING ON UO_2 PARTICLE NEAR SURFACE OF AGOT GRAPHITE SPECIMEN HEATED AT 2500 F FOR 500 HR

The apparent metallic phase in UO_2 particle in lower photomicrograph is UO_xC_{1-x} . The gray material surrounding the particle in lower photomicrograph is the mounting resin which filled a void produced by reaction during exposure. Coal-tar pitch was used as a binder in preparing this specimen; prebaking was at 2300 F.

No simple mechanism to explain the loss of Al_2O_3 coatings from UO_2 particles at the surface of compacts exposed to the helium atmosphere has been found. However, one likely factor appears to be the role played by oxidation on reduction of impurities and components in the furnace assembly as well as in the helium flowing stream. Such components include the graphite setter and air, metallic, or organic impurities in it as well as in the compacted specimens, the Mullito furnace tube and thermocouple-protection tube, and small amounts of gaseous impurities in the helium. In a flowing furnace atmosphere, these gaseous impurities could become significant during the course of a heating for 500 hr or longer.

The metallic-appearing phase, clearly shown in Figure 8 at 250X at the edges of the gray UO_2 particle, is $\text{UO}_x\text{C}_{1-x}$, which has been reported in the literature.⁽⁶⁾ This phase was not found in particles deep within this specimen. The existence of the phase was verified by extracting a particle predominantly composed of the metallic phase and analyzing it by X-ray diffraction techniques. The formation of $\text{UO}_x\text{C}_{1-x}$ by reaction of Al_2O_3 -coated UO_2 particles with graphite appears to take place by a two-step process: (1) reaction of the Al_2O_3 coatings with graphite, resulting in the removal of the Al_2O_3 , and (2) reaction of the resulting uncoated UO_2 particles with graphite.

The compounds UC, UO, and UN all are NaCl-type cubic structures with lattice parameters of 4.962, 4.920, and 4.890 Å, respectively. Thus, carbon, oxygen, and nitrogen atoms can replace each other interchangeably in the lattice, and these changes can be detected by shifts in lattice parameter. The value of "x" in $\text{UO}_x\text{C}_{1-x}$ is believed to be about 0.5.

The Al_2O_3 -coated UO_2 particles, heated in graphite at 2500 F for 1000 hr, showed more extensive reaction than those heated for shorter times (Figure 9). In the specimen with particles having a 20- μ coating, the Al_2O_3 became extremely thin in some areas. The UO_2 particles contained a few very small areas of the metallic-appearing phase, $\text{UO}_x\text{C}_{1-x}$. Particles near the surface of this specimen (not shown) were substantially converted to $\text{UO}_x\text{C}_{1-x}$ and were free of the Al_2O_3 coating. As is evident in Figure 9, the thicker (40 to 60 μ) coating protected the UO_2 much better than the 20- μ coating.

Sintered Coatings

The sintered Al_2O_3 -coated particles showed no reaction with the two types of graphite matrices after prebaking for 4 hr at 1700 F (Figure 10). A void existed between the UO_2 and the Al_2O_3 , as well as between the coatings and the graphite the particles were similar in appearance to the as-produced particles in Figure 1.

There was no evidence of reaction between the coated particles and graphite after heated at 2500 F for 168 hr.

Heating the coated particles at 2500 F for 1000 hr in a coke matrix produced decidedly more reaction than in similarly heated particles in a reactor-grade graphite matrix. Figure 11 shows photomicrographs of particles in both matrices. In the graphite matrix, the Al_2O_3 was slightly changed and small voids appeared in boundaries of the small grains. The UO_2 contained a few light-etching particles near the Al_2O_3 interface. These particles are indicated by arrows in the photomicrograph (Figure 11b).

a. 20- μ Coating b. 40 to 60- μ Coating

FIGURE 9. EFFECT OF 1000-HR EXPOSURE AT 2500 F ON UO₂ PARTICLES COATED WITH VAPOR-DEPOSITED Al₂O₃ AND EMBEDDED IN AGOT GRAPHITE

Extensive reaction at Al₂O₃-graphite interface occurred, particularly with the 20- μ coating. This specimen was prepared with a coal-tar pitch binder and was prebaked at 2300 F.

50X

As Polished

N62663

a. Coke Matrix

50X

As Polished

N62235

b. Graphite Matrix

FIGURE 10. UO_2 PARTICLES WITH SINTERED Al_2O_3 COATINGS EMBEDDED IN COKE AND AGOT GRAPHITE AFTER PREBAKING AT 1700 F

There are voids at the UO_2 - Al_2O_3 and Al_2O_3 -matrix interfaces but there is no evidence of a reaction between the coating and matrix. Coal-tar pitch was used as a binder in the preparation of both specimens.

50X

As Polished

N64886

250X

As Polished

N64885

a. Coke Matrix

50X

As Polished

N64882

250X

As Polished

N64881

b. Graphite Matrix

FIGURE 11. EFFECT OF 1000-HR EXPOSURE AT 2500 F ON UO_2 PARTICLES COATED WITH SINTERED Al_2O_3 AND EMBEDDED IN COKE AND AGOT GRAPHITE MATRICES

More severe reaction occurred in the particles embedded in the coke than with graphite matrix. The Al_2O_3 coating was almost completely destroyed. A few light-etching particles were found in the UO_2 in the graphite-matrix specimen (indicated by arrows in lower right photomicrograph) but no other reaction was noted. Both specimens were prepared with coal-tar pitch binder and were prebaked at 1700 F.

No evidence of eutectic formation, incipient melting, or other interaction was noted. The Al_2O_3 coating was almost completely destroyed in the coke matrix. The clear gray material that surrounds the particle shown at 50X in Figure 11a, is the epoxy mounting resin containing a few small residual pieces of Al_2O_3 . The Al_2O_3 has a darker gray and rougher appearance. A considerable amount of a light-etching phase can be seen at 250X next to the original Al_2O_3 interface and also as small metallic particles within the UO_2 . This phase may be $\text{UO}_x\text{C}_{1-x}$.

A few experiments were made in which the AGOT graphite filler was bonded with the resin binder instead of coal-tar pitch. The Al_2O_3 -coated UO_2 particles heated in contact with resin-bonded AGOT graphite completely lost their coatings after 1000 hr at 2500 F. A typical particle is shown in Figure 12. Metallographic mounting resin appears as the dark gray material surrounding the UO_2 in Figure 12. A considerable amount of the metallic-appearing phase is found in the UO_2 particle which was initially adjacent to the Al_2O_3 . This phase is believed to be $\text{UO}_x\text{C}_{1-x}$. Resin-bonded graphite appears to react more rapidly with Al_2O_3 -coated UO_2 particles than does pitch-bonded graphite.

Figure 13 shows the results of heating Al_2O_3 -coated UO_2 in graphite and coke at 3000 F for 6 hr. The coating was completely destroyed in the AGOT graphite matrix. A metallic shell was all that was left of an Al_2O_3 -coated particle after this 6-hr heat treatment. The photomicrograph showing the coated particle in coke (Figure 13a) is not typical. It was difficult to find particles in this specimen. Undoubtedly, most of the particles disintegrated. In the photomicrographs shown, the coarse-grained rim of the particle in the coke appears metallic in reflected white light. Based on its appearance, this reaction product is believed to be $\text{UO}_x\text{C}_{1-x}$. No evidence of the Al_2O_3 coating can be seen on this particle. The core resembles UO_2 in color but contains a second phase clearly visible at 250X.

BeO-Coated UO_2

The study of BeO-coated UO_2 was limited to material having a sintered coating.

Results of a 1000-hr heating at 2500 F in coke and graphite are shown in Figure 14. In the microstructures shown (Figure 14b), the grain size of the BeO is coarser than before the heating, but no reaction is noticeable at the graphite-BeO or the BeO- UO_2 interface. However, some reaction can be observed between the coating and the coke matrix. The presence of the metallic particles in grain boundaries⁴ in the BeO is evidence that some diffusion occurred. It can also be noted at 50X that the UO_2 adjacent to the BeO has a much rougher appearance than that in the center of the UO_2 particle. A small amount of a dark-gray phase also can be seen at 250X in the UO_2 adjacent to the BeO at the top of the photomicrograph (Figure 14a).

Figure 15 shows BeO-coated UO_2 particles in coke and graphite after heating at 3000 F for 6 hr. In the typical microstructures shown very extensive reaction can be observed with both matrices, causing severe damage to the coatings. In the graphite matrix (Figure 15b), the dark gray and roughly spherical particles, in what appears originally to have been UO_2 , resemble BeO in color. An unidentified metallic phase can be noted in the BeO grain boundaries in the photomicrograph at 250X. With the exception of this phase, the BeO still retained its characteristic dark-gray appearance. In the coke matrix, the entire particle lost its integrity, apparently reacting with the BeO and

50X

As Polished

N64879

250X

As Polished

N64880

FIGURE 12. EFFECT OF 1000-HR EXPOSURE AT 2500 F ON UO_2 PARTICLES WITH SINTERED Al_2O_3 COATING AND EMBEDDED IN AGOT GRAPHITE MATRIX PREPARED WITH RESIN BINDER

More reaction is evident here than occurred with coal tar-pitch bonded graphite. Apparent metallic phase in UO_2 is believed to be $\text{UO}_x\text{C}_{1-x}$. The gray material surrounding the particle in the top photomicrograph is mounting resin which has filled void space produced by reaction during exposure.

50X

As Polished

N71202

250X

As Polished

N71203

a. Coke Matrix

50X

As Polished

N62218

250X

As Polished

N62217

b. AGOT Graphite Matrix

FIGURE 13. EFFECT OF 6-HR EXPOSURE AT 3000 F ON UO₂ PARTICLES HAVING SINTERED Al₂O₃ COATINGS AND EMBEDDED IN COKE OR GRAPHITE MATRICES

White phase surrounding particle in the coke matrix is believed to be UO_xC_{1-x}. Notice also the two-phase structure of the UO₂. Nearly all of the particles and coatings were completely disintegrated in the coke matrix following the exposure. The coatings were almost completely destroyed in the graphite matrix. Only an apparent metallic shell remains in the microstructure shown in the photomicrographs. Coal-tar pitch was employed as a binder in both specimens; prebaking was at 1700 F.

50X

As Polished

N64883

250X

As Polished

N64884

a. Coke Matrix

50X

As Polished

N64878

250X

As Polished

N64877

b. AGOT Graphite Matrix

FIGURE 14. EFFECT OF 1000-HR EXPOSURE AT 2500 F ON BeO-COATED UO_2 PARTICLES EMBEDDED IN COKE AND AGOT GRAPHITE MATRICES

Some reaction occurred in the particle in the coke matrix. The surface of the UO_2 is roughened and a small amount of second-phase material is visible. The presence of a metallic phase in the grain boundaries of the BeO (top right photomicrograph) indicates that some diffusion occurred. While the grain size of the particle appears coarser, there is no evidence of a reaction in the graphite matrix.

a. Coke Matrix

b. AGOT Graphite Matrix

FIGURE 15. EFFECT OF 6-HR EXPOSURE AT 3000 F ON BeO-COATED UO_2 PARTICLES EMBEDDED IN COKE AND AGOT GRAPHITE MATRICES

Extensive reactions occurred in both specimens. In the coke matrix apparently the entire particle reacted with the BeO and carbon to form molten phases. The dark hourglass band visible in the upper right photomicrograph is the remainder of the BeO coating. In the graphite-matrix specimen extensive interdiffusion of the BeO and UO_2 occurred, and the various phases visible in the photomicrographs have not been identified.

TABLE 2. SUMMARY OF THE RESULTS FROM THE METALLOGRAPHIC EXAMINATION OF OXIDE-COATED UO_2 PARTICLES DISPERSED IN AGOT GRAPHITE^(a) AND HEAT TREATED AT 1700, 2500, AND 3000 F

Specimen Condition	UO_2 With Sintered Al_2O_3 Coating	UO_2 With Sintered BeO Coating	UO_2 With Vapor-Deposited Al_2O_3 Coating	
			20- μ Coating	40- μ Coating
As-received particles	Coating 300 to 500 μ thick and contains some porosity Particles generally angular and porous Voids ranging from 40 to 200 μ wide noted between UO_2 particles and coating	Coating 200 to 600 μ thick and somewhat porous Particles angular and contained small tan-gray inclusions Voids up to 60 μ wide existed between particles and coating	Coating 15 to 20 μ thick, dense, and tightly adherent A few voids evident in coating on some particles UO_2 particles generally spherical but somewhat porous and cracked UO_2 particles ranged in diameter from about 75 to 160 μ	Coating 30 to 60 μ thick, dense, and tightly adherent UO_2 particles generally spherical and range in diameter from about 80 to 160 μ Voids and cracks evident in UO_2 particles
Prebaked ^(b)	No reaction evident between particles and coating or coating and graphite Appearance and shape of particles unchanged	No reaction evident between particle and coating or between coating and graphite Particles contained small, tan-gray inclusions	No reaction evident between particle and coating or coating and graphite Appearance and shape of particle unchanged Alumina coating 16 to 20 μ thick	Particles retained their shapes and did not appear to react with coating No reaction evident between graphite and coating Coating ranged from 32 to 36 μ in thickness
Heated at 2500 F for 168 hr in helium after prebake	No reaction evident between particles and coating or coating and graphite Appearance and shape of particles unchanged	No evidence of reaction between particle and coating or coating and graphite Appearance and shape of particles unchanged	Coating appeared slightly thinner and free of spikes (thickness ranged from 12 to 18 μ) Slight void evident at coating-graphite interface No reaction product evident in particle	Coating ranged from 28 to 32 μ in thickness on particles in core of compact Slight void evident at coating-graphite interface Some particles quite cracked and fragmented No reaction product evident in particles
Heated at 2500 F for 500 hr in helium after prebake	Not tested	Not tested	Coating on particles in core 8 to 16 μ thick and appeared ragged at graphite interface Sizable void at coating-graphite interface Particles near surface exposed to helium almost devoid of coating and contained metallic reaction product, probably $\text{UC}_x\text{O}_{1-x}$	Coatings range from 20 to 32 μ in thickness in core Sizable void at coating-graphite interface Many particles contain cracks and voids Particles near surface exposed to helium almost devoid of coating and contained metallic reaction product, probably $\text{UC}_x\text{O}_{1-x}$
Heated at 2500 F for 1000 hr in helium after prebake	Coating contained voids which appeared to be in grain boundaries A few small metallic areas detected in particles adjacent to coatings Appearance and shape of particles otherwise unchanged	No reaction evident between particle and coating or coating and graphite Particles retained their original shape and appearance	Coating on particles in core 4 to 11 μ thick and ragged at graphite interface Sizable void at coating-graphite interface Some particles near surface exposed to helium devoid of coating and contained metallic reaction product, probably $\text{UC}_x\text{O}_{1-x}$	Particles near surface exposed to helium almost devoid of coating and contained metallic reaction product, probably $\text{UC}_x\text{O}_{1-x}$ Coating on particles in core of compact 15 to 30 μ thick Voids evident at coating-graphite interface
Heated at 3000 F for 6 hr in helium after prebake	Particles completely lost their integrity Only a metallic-appearing shell remained where coated particle had been in graphite matrix	Extensive reaction between particle and coating which appeared to cause melting and distortion of particles At least three phases evident in particles Metallic phase noted in grain boundaries of coating	Not tested	Not tested

(a) Coal-tar pitch was employed as a binder.

(b) All vapor-deposited-coated particles in graphite were prebaked at 2300 F; particles with sintered coatings dispersed in graphite were prebaked at 1700 F.

the carbon to form molten phases. Only the rather thin, hourglass-shaped, dark-gray band, clearly shown at 250X in Figure 15a, remained from the BeO cladding.

The Al_2O_3 and BeO results with graphite matrices are summarized in Table 2.

CONCLUSIONS

The following conclusions may be drawn from this investigation of coated UO_2 particles:

- (1) Thin coatings of nickel, niobium, and nickel-chromium alloy are readily destroyed when heated in graphite matrices at 1700 F or higher.
- (2) Coatings of Al_2O_3 react with graphite matrices at temperatures of 2500 F and higher. Although detailed studies of many of the parameters affecting this reaction have not been made, it is likely that long-time service of Al_2O_3 -coated UO_2 will be restricted to temperatures lower than 2500 F.
- (3) Coatings of BeO are more compatible with graphite than Al_2O_3 coatings at temperatures between 2500 F and 3000 F. However, no quantitative data for this comparison were obtained in the present study.
- (4) Coke is a more reactive carbonaceous matrix than graphite.
- (5) Graphite matrices in which the binder is a phenol-formaldehyde resin react more readily with the two oxide coatings than graphite matrices in which the binder is coal-tar pitch.

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