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MASTER

R. D. Reiswig
P. Wagner
C. M. Hollabaugh
R. W. White
J. A. O'Rourke
K. V. Davidson
D. H. Schell

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

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BEHAVIOR OF LASL-MADE GRAPHITE, ZrC, AND ZrC-CONTAINING COATED PARTICLES IN IRRADIATION TESTS HT-28 AND HT-29

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ABSTRACT

Three types of materials, extruded graphite, hot-pressed ZrC, and particles with ZrC coatings, were irradiated in Oak Ridge National Laboratory High Fluence Isotope Reactor Irradiation tests HT-28 and HT-29. The ZrC seemed unaffected. The graphite changed in dimensions, x-ray diffraction parameters, and thermal conductivity. The four types of coated particles tested all resisted the irradiation well, except one set of particles with double-graded C-ZrC-C coats. Overall, the results were considered encouraging for use of ZrC and extruded graphite fuel matrices.

INTRODUCTION

Materials of interest for advanced fuels work at Los Alamos Scientific Laboratory (LASL) have been tested in the High-Fluence Isotope Reactor (HFIR) in experiments HT-28 and HT-29.[1] This report summarizes the materials tested and the results of the postirradiation examination.

The High Temperature Fuels Technology for Nuclear Process Heat program at LASL is directed toward identifying nuclear fuels that can withstand higher processing temperatures and operate at higher temperatures in gas-cooled reactors than fuels now in use. The rationale and technology developed during the program have been described in several publications.[2-5]

The first reactor tests of LASL-made materials were run in Oak Ridge National Laboratory (ORNL) HFIR[6] experiments HT-28 and HT-29. These tests were made to provide fast-neutron irradiation stability data on the materials intended for use in the LASL program. Because the information sought was preliminary and the tests were basically screening tests, the irradiations were performed in the HFIR target position, HT. Hot-pressed ZrC, extruded graphite, and coated particles with inert kernels were irradiated. The postirradiation examination results for each type of material are discussed separately.

ZIRCONIUM CARBIDE

The ZrC samples were made by hot pressing the powdered carbides at 3000 K and 100-MN/cm^2 pressure using a graphite die. The billets were then repurified by heating in vacuum. Two samples were irradiated in HT-28 as follows.

In capsule position 1-A at 900°C, 4.3×10^{21} n cm^{-2} (E > 0.18 MeV),

In capsule position 14-A at 1250°C, 7.7×10^{21} n cm^{-2} (E > 0.18 MeV).

This material was contaminated and was not returned to LASL. ORNL reported no observable damage or dimensional changes.

GRAPHITE

Extruded graphites heat treated at 1800 and 2200°C were irradiated in HT-28. Lot 5508-AA was made from 85 parts M-3 graphite flour and 15 parts Thermax with 0.2 g/cm^3 of wood flour added. The green mix was made using Varcum, a polyfurfuryl alcohol binder, and was extruded through a 12.7-mm- (1/2-in.-) diam die. Lot 5508-AA-2 was given a final heat treatment at 1800°C; these samples were 2.5 mm thick. Lot 5508-AA-2-3 was given a final heat treatment at 2200°C; these samples were 10 mm in diameter by 2.5 mm thick. The nominal density of this extrusion lot was 1.76 g/cm^3.

The dimensional changes in the graphite are listed in Table I. Table II lists x-ray diffraction parameters measured before and after the irradiation. There were no observable changes in the graphite microstructure, and no cracks or porosity growth were noted. Figure 1 shows the 5508-AA-2-3 (2200°C heat treatment) graphite as-prepared and after irradiation.

Changes in thermal conductivity, λ, of the two extruded graphites due to irradiation in the HT-29 test have been determined. Thermal diffusivities, α, were measured parallel to the extrusion axis at 300 K on archival and irradiated (at 900°C) samples of both graphites. Thermal conductivities were calculated using

$$\lambda = \alpha \rho C_p .$$

Postirradiation densities, ρ, were computed from original densities and dimensional changes after irradiation; the heat capacity of graphite was used for C_p.

The λ data are displayed in Fig. 2. The thermal conductivities drop off with irradiation and seem to reach saturation at about 20% of the original value where λ is near 15 $W\,m^{-1}K^{-1}$. The figure also shows the advantages of higher heat treatment temperature. Recognizing that the curves have only three points, it looks as though higher λ values resulting from the higher heat treatment temperature keep λ at an elevated value throughout most of the irradiation and it approaches 15 W $m^{-1}K^{-1}$ only after full HTGR fluence is reached. Price[7] has pointed out that λ decreases further at lower irradiation temperatures. Higher temperature irradiation tests should yield higher postirradiation thermal conductivities.

TABLE I

DIMENSIONAL CHANGES IN LASL GRAPHITES IRRADIATED IN HT-29

Material	Position in Reactor[a]	Fluence (n/cm^2)	Original Dimensions (cm)	Postirradiation Dimensions (cm)	% Change	Orientation wrt c-axis
Lot 5508-AA-2	1A	4.8×10^{21}	ℓ = 0.701	ℓ = 0.683	−2.5	∥
			w = 0.706	w = 0.693	−1.8	∥
			h = 0.261	h = 0.255	−2.0	⊥
Lot 5508-AA-2	14-A	9.7×10^{21}	ℓ = 0.704	ℓ = 0.714	+1	∥
			w = 0.704	w = 0.713	+1	∥
			h = 0.264	h = 0.251	−5.3	⊥
Lot 5508-AA-2-3 2200°C heat treatment	52-A	4.8×10^{21}	diam = 0.950	diam = 0.940	−2.8	∥
			h = 0.259	h = 0.256	−1.2	⊥
Lot 5508-AA-2-3 2200°C heat treatment	39-A	9.7×10^{21}	diam = 0.950	diam = 0.960	+1	∥
			h = 0.258	h = 0.244	−5.1	⊥

[a] Temperature at all positions used was 900°C.

TABLE II

X-RAY DIFFRACTION PARAMETERS OF GRAPHITES IRRADIATED IN HT-29

Material	Position in Reactor	Irradiation Temp (°C)	Fluence[b] ($n\,cm^{-2}$)	Effective Crystallite Height L_c(Å)	Effective d_{002} (Å)	Effective a(Å)	(110)[c] Breadth	Bacon Anisotropy Factor	Remarks
5508 AA-2 (1800°C)[a]	---	---	0	332	3.362	2.461	0.43		Composite
				342	3.36				Crystalline component
				66	3.43				Noncrystalline component
	1-A	900	4.8×10^{21}	183	3.370	2.459	0.59		
	14-A	900	9.7×10^{21}	95	3.375	2.458	0.74		
5508 AA-2-3 (2200°C)[a]	---	---	0	290	3.363	2.461	0.43	1.437	Composite
				370	3.36				Crystalline component
				121	3.42				Noncrystalline component
	52-A	900	4.8×10^{21}	169	3.369	2.459	0.60		
	39-A	900	9.7×10^{21}	93	3.374	2.457	0.89	1.282	

[a]Heat treatment temperature.
[b]$E > 0.18$ MeV.
[c]Increasing value is measure of increasing basal plane disorder.

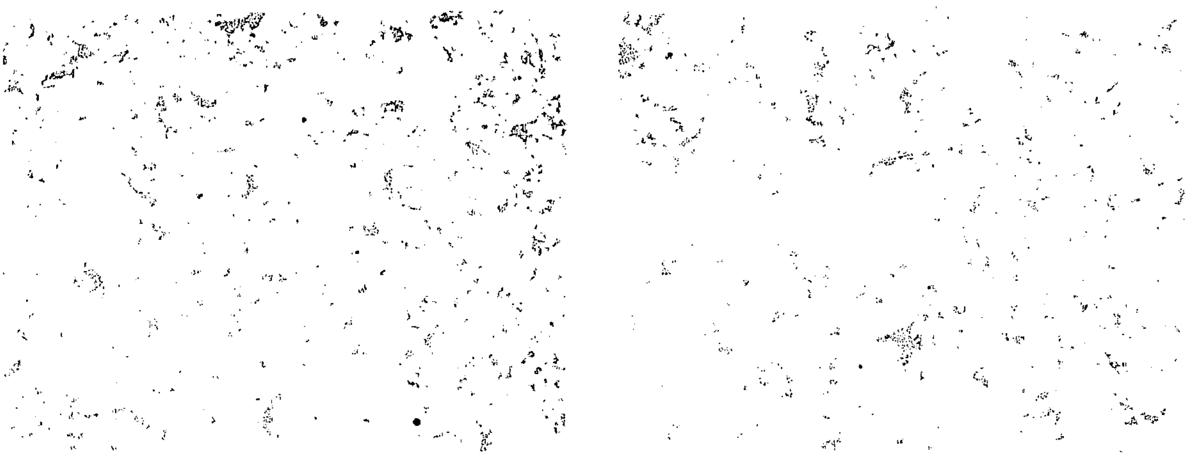

Fig. 1.
Microstructure of 5508-AA-3-2 graphite irradiated in HT-29. Left: As-prepared (2200°C heat treatment). Right: After 900°C, 9.7×10^{21} n cm^{-21} irradiation. 50X.

COATED PARTICLES

Four types of LASL-made coated particles were tested in HT-28 and HT-29. All had carbon kernels, and they were tested to determine their stability at high temperature and fluence. These particles were made as follows.

Run 1435:

Carbon kernel with a mean diameter of 192 μm (12)* and density of 1.48 g/cm^3. The buffer coat was

Numbers in parentheses are standard deviations of the mean.

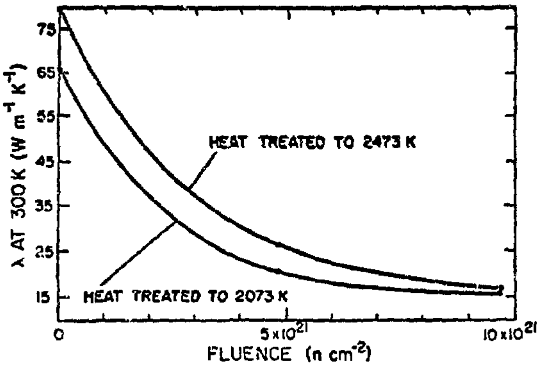

Fig. 2.
Radiation vs thermal conductivity of two graphites (measured parallel to extrusion axis).

93 μm (7) thick with a density of 1.18 g/cm^3. It was deposited at a maximum temperature* of 1400 K using a 99% C_2H_2 − 1% Ar coating gas. The inner low-temperature isotropic (iLTI) pyrolytic carbon coating was 28 μm (3) thick with a density of 2.0 g/cm^3. It was deposited at a maximum temperature of 1750 K using a 29% C_3H_6 − 71% Ar coating gas. The outermost layer on these particles was ZrC, 24 μm (2) thick with a calculated density of 6.4 g/cm^3 (~97% of theoretical). It was deposited at a maximum temperature of 1725 K using 8.6% $ZrCl_4$-0.6% CH_4-74% H_2-16.8% Ar coating gas.

Run 1436:

These were TRISO particles. To some of the particles from run 1435, an outer LTI (oLTI) was added. This coating was 35 μm (7) thick with a density of 1.80 g/cm^3. It was deposited at a maximum temperature of 1775 K using an 18% C_3H_6-82% Ar coating gas.

Run 1450:

These particles contained the same kernel and buffer substrate as those in runs 1435 and 1436. They had an additional coating that started out as a pure LTI. Zirconium carbide was added, and the pyrolytic carbon content was diminished gradually until pure ZrC was deposited, giving a coating graded from iLTI to ZrC. The maximum temperature was 1670 K. The LTI was deposited from a 22% C_3H_6-78% Ar gas mixture. Zirconium chloride and hydrogen were added, and the C_3H_6 was decreased until the outermost ZrC layer was deposited from a 1% C_3H_6-3% $ZrCl_4$-15% H_2-81% Ar gas mixture. The innermost part of the graded coat looks like pyrolytic carbon under the microscope. It was 18 μm (3) thick; the outermost part was 22 μm (4) thick.

Run 1452

These particles had the same kernel and buffer substrate used for runs 1435, 1436, and 1450. Added to this was a double-graded coat that started out as pure LTI, 23 μm (4) thick. It was then graded to ZrC, a pure ZrC layer, and then ZrC graded to pure LTI. The maximum temperature was 1670 K, and the coats were deposited as follows.

Inner Graded Coat. Started with 22% C_3H_6-78% Ar. Added $ZrCl_4$ and H_2 and decreased C_3H_6 gradually until final gas composition was 1% C_3H_6-4% $ZrCl_4$-20% H_2-75% Ar.

Pure ZrC. Switched from C_3H_6 to CH_4 and coated with 0.6% CH_4-3.4% $ZrCl_4$-18% H_2-78% Ar gas.

Outer Graded Coat. Switched back to C_3H_6 and started coating using 1% C_3H_6-4% $ZrCl_4$-18% H_2-77% Ar gas mixture. Increased C_3H_6 gradually until concentration was about 8%. Then switched to 21% C_3H_6-79% Ar gas mixture for outermost pure LTI. The inner graded coat was 35 μm (2) thick, the ZrC was 7 μm (0.1) thick, and the outermost graded coat was 35 μm (2) thick. The oLTI was 7 μm (0.8) thick. All particles were heated for 3.6 ks (1 h) at 2075 K in vacuum as an initial preirradiation preparation.

Table III lists the particles tested, the reactor test, the capsule position, irradiation test temperature, and total fluence. Also listed is the crushing strength ratio. Metallography and crushing strength tests were run when there were enough particles. In general, the strength increased with irradiation.

The TRISO-type particles from Runs 1435 and 1436 were undamaged. Irradiated particles from Run 1435 looked no different from the as-prepared particles; however, microscopy of the outer ZrC coat showed evidence of chemical attack (Fig. 3). Examination of other particles from Run 1435 showed similar evidence of reaction, but to a lesser extent. We conclude qualitatively that some oxidation occurred at the ZrC surface. Whether or not other particles with ZrC surfaces were affected is speculative. Figures 4-6 are photomicrographs of typical non-irradiated and irradiated particles from these runs.

All the coated particles from Run 1450 survived. They are shown in Figs. 7-11. A few of the irradiated particles had small radial cracks through the outermost ZrC layer. Most notable was the development

*There is an axial temperature gradient in the fluidized bed coating furnace. Temperature maxima are quoted.

TABLE III

IRRADIATION TEST CONDITIONS AND CRUSHING STRENGTHS

LASL Coating Run No.	Reactor Test	Capsule Position	Temp (°C)	Fluence (n cm^{-2} × 10^{21})	Crushing Strength Ratio[a]
1435	HT-28	ES-1	900	3.5	1.11
1435	HT-29	MS-1	900	9.4	1.64
1436	HT-28	ES-2	900	3.5	1.38
1436	HT-29	MS-2	900	9.4	1.64
1450	HT-29	ES-1	900	4.4	1.75
1450	HT-29	EL-1	900	9.0	1.67
1450	HT-29	ML-1	900	10.7	1.82
1450	HT-28	MS-1	1250	7.5	1.65
1452	HT-29	ES-2	900	4.4	0.99
1452	HT-29	EL-2	900	9.0	---
1452	HT-29	ML-2	900	10.7	---
1452	HT-28	MS-2	1250	7.5	---

[a] Postirradiation strength/preirradiation strength.

Fig. 3.
Coated particle from Run 1435 after 3.5 ×10^{21} n cm^{-2} at 900°C showing reaction at outer surface of ZrC. 1000X.

of preferred orientation as evidenced by the polarized light activity in the innermost layer of the graded coat. This can be seen in Figs. 8-11, photomicrographs made using polarized (polars at 85°) light. This orientation suggests a volume expansion in the carbon-rich ZrC-C layer. Because particles with ZrC-doped LTI's are being irradiated in on-going tests, we will examine this hypothesis further.

Figures 12-16 show coated particles from Run 1452. Survival percentages were as follows.

After 4.4 × 10^{21} n/cm^2 at 900°C, 100% (Fig. 13),

After 9 × 10^{21} n/cm^2 at 900°C, 100% (Fig. 14).,

After 10.7 × 10^{21} n/cm^2 at 900°C, about 95% (Fig. 15),

After 7.5 × 10^{21} n/cm^2 at 1250°C, about 20% (Fig. 16).

The particles in Fig. 13 show no preferred orientation under polarized light; however, many of the particles show circumferential cracks at the junction of the ZrC and the graded coat. The greater fluence experienced by the particles shown in Fig. 15 has generated a preferred orientation and has led to some radial cracking in the outer graded coats. Part of the outer coat of one particle was separated from the ZrC. The other particles looked good. The particles in Fig. 16 have undergone the most dramatic changes of any tested. Only about 20% of the particles recovered had intact outer coats, 70% had no

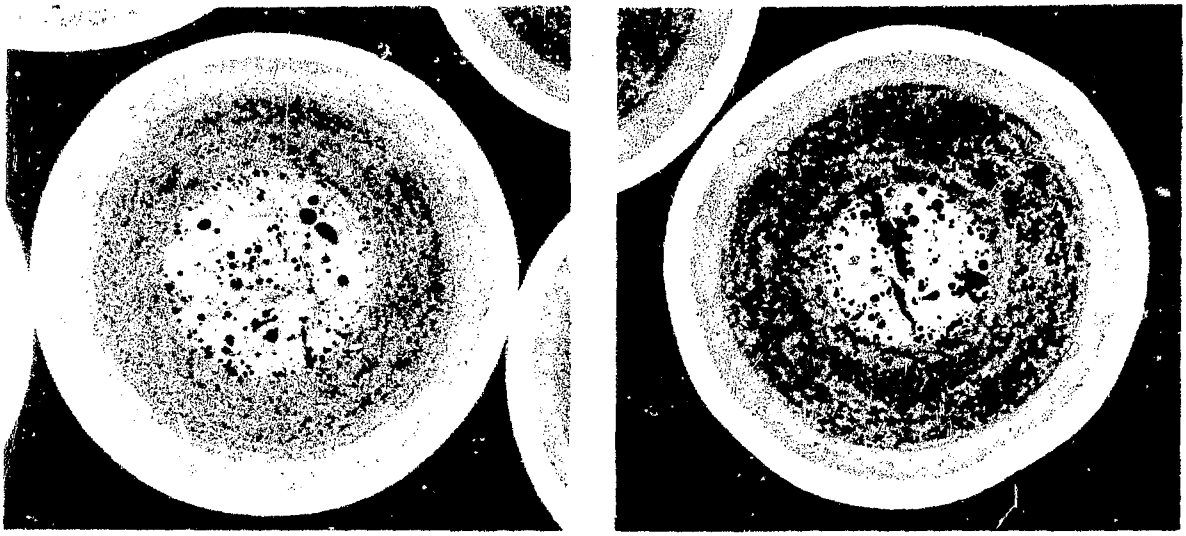

Fig. 4.
Coated particles from Run 1435. Left: As prepared. Right: After 900°C, 9.4 $\times 10^{21}$ n cm^{-2} irradiation. 150X.

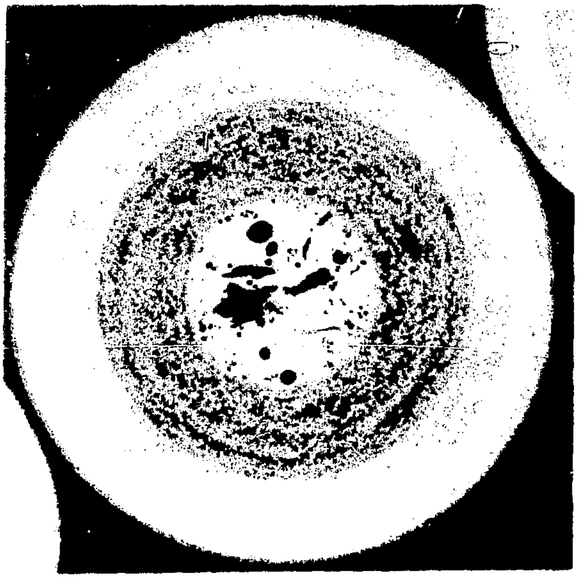

Fig. 5.
Coated particle from Run 1436 after 3.5 $\times$ 10^{21} n cm^{-2} at 900°C. Bright field. 150X.

outermost graded coat at all, and 10% had ruptured ZrC coats as well as broken outer coats. The intact particles showed preferred orientation in the inner and outer carbon-rich layers of the ZrC-C. As-made, these particles were like those shown in Fig. 7, the only difference being addition of the outer graded coat. The two sets of particles were in adjoining positions in the test capsule and they should have undergone very similar irradiations. Just why Run 1452 seems so different from Run 1450 in irradiation behavior is a puzzle. Perhaps further data on the particles with graded coats now being irradiated will help explain these phenomena.

STATISTICS OF PARTICLE COATING THICKNESS CHANGES

The LASL Statistical Services Group has analyzed the statistics of the measurements required to identify particle coating thickness changes caused by irradiation. The analysis took the form of tables of coefficients of variation of the mean (coating thickness), detectable changes, and number of measurements needed to detect the change. For example, in the TRISO configuration, the outer coating is 35 μm thick. If the coefficient of variation of the mean is 10%, 40 measurements would be required to identify a 1-μm change in coating thickness with 95% confidence. Too few particles from HT-28 and HT-29 were obtainable to permit meaningful measurement of coating thickness changes due to irradiation.

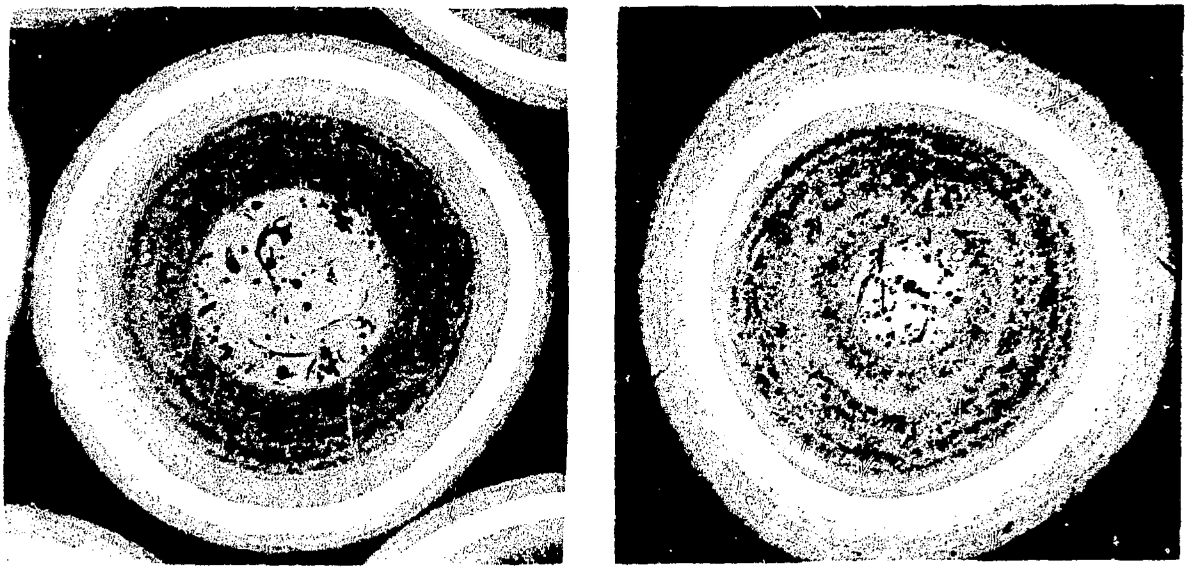

Fig. 6.
Coated particles from Run 1436. Left: As prepared. Right: After 900°C, 9.4 $\times 10^{21}$ n cm^{-2} irradiation. 150X.

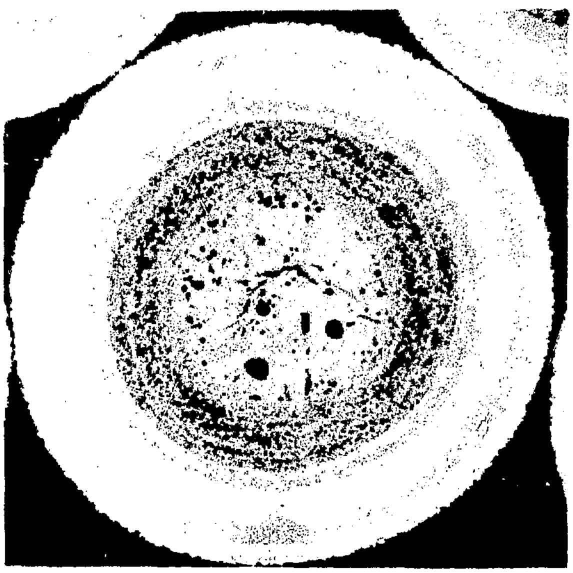

Fig. 7.
Coated particles from Run 1450. As prepared. 150X.

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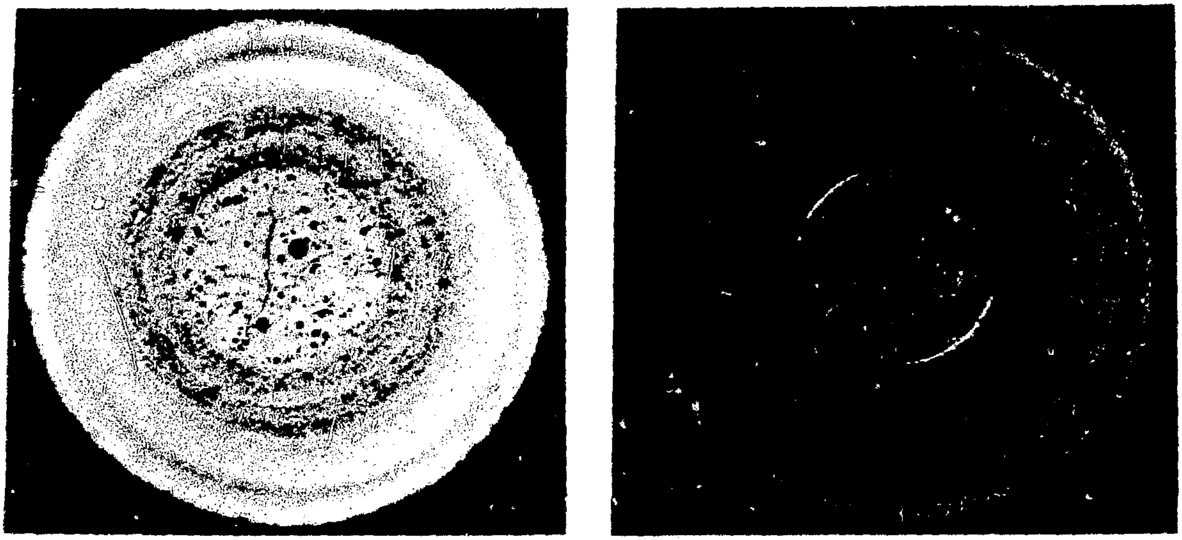

Fig. 8.
Coated particles from Run 1450 after 4.4 × 10^{21} n cm^{-2} at 900°C. Left: Bright field. Right: Polarized light, preferred orientation barely detectable. 150X.

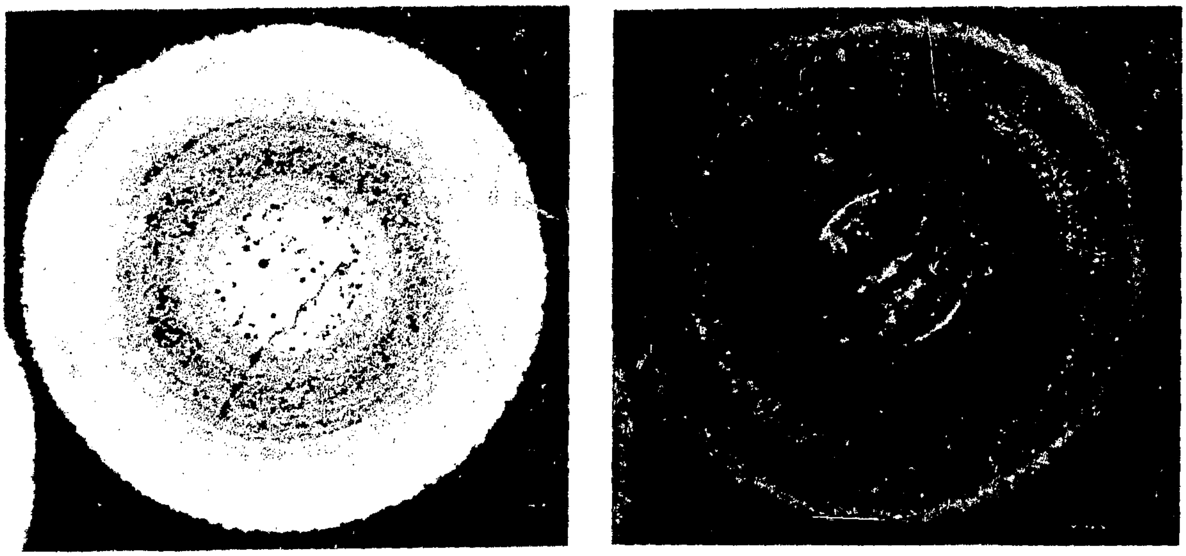

Fig. 9.
Coated particles from Run 1450 after 9.0 × 10^{21} n cm^{-2} at 900°C. Left: Bright field. Right: Polarized light showing preferred orientation. 150X.

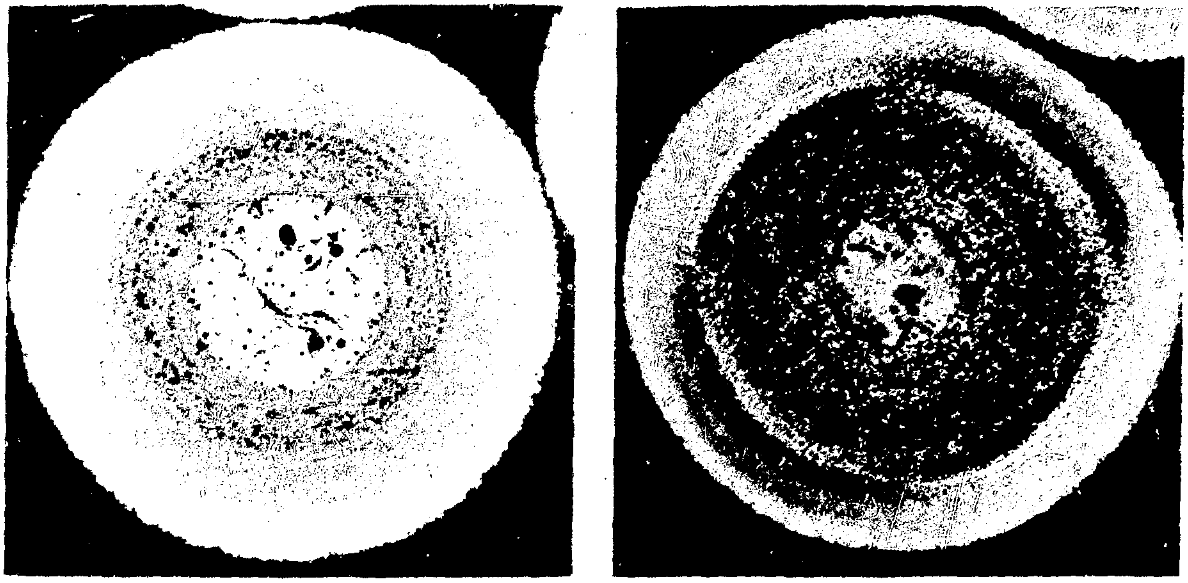

Fig. 10.
Coated particles from Run 1450 after 10.7 × 10^{21} n cm^{-2} at 900°C. Left: Bright field. Right: Polarized light showing preferred orientation. 150X.

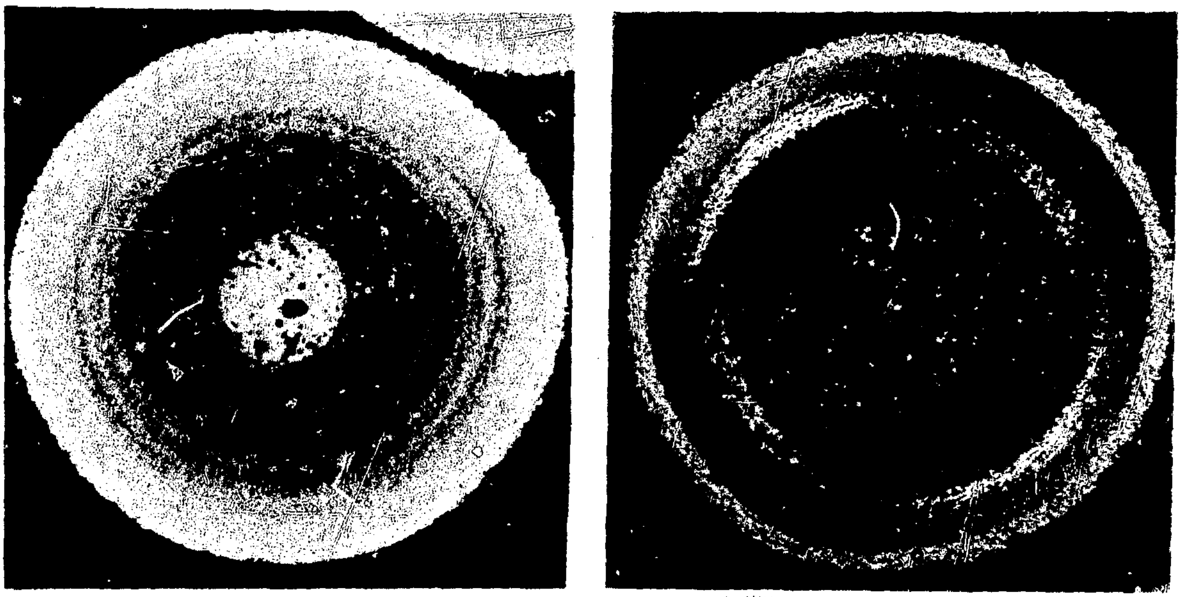

Fig. 11.
Coated particles from Run 1450 after 7.5 × 10^{21} n cm^{-2} at 1250°C. Left: Bright field. Right: Polarized light showing preferred orientation. 150X.

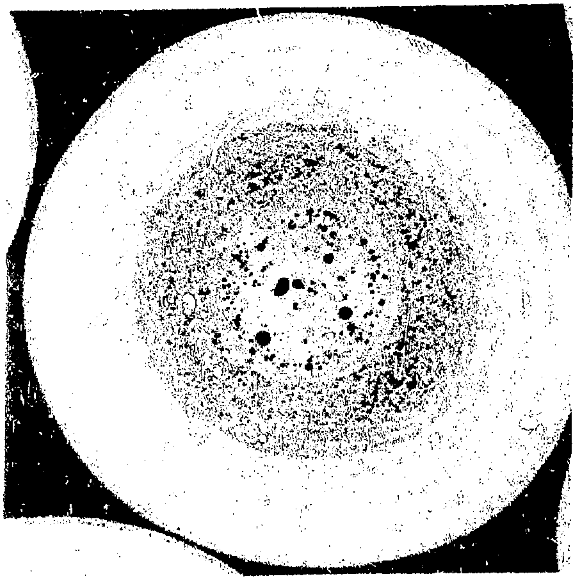

Fig. 12.
Coated particles from Run 1452 as prepared. 150X.

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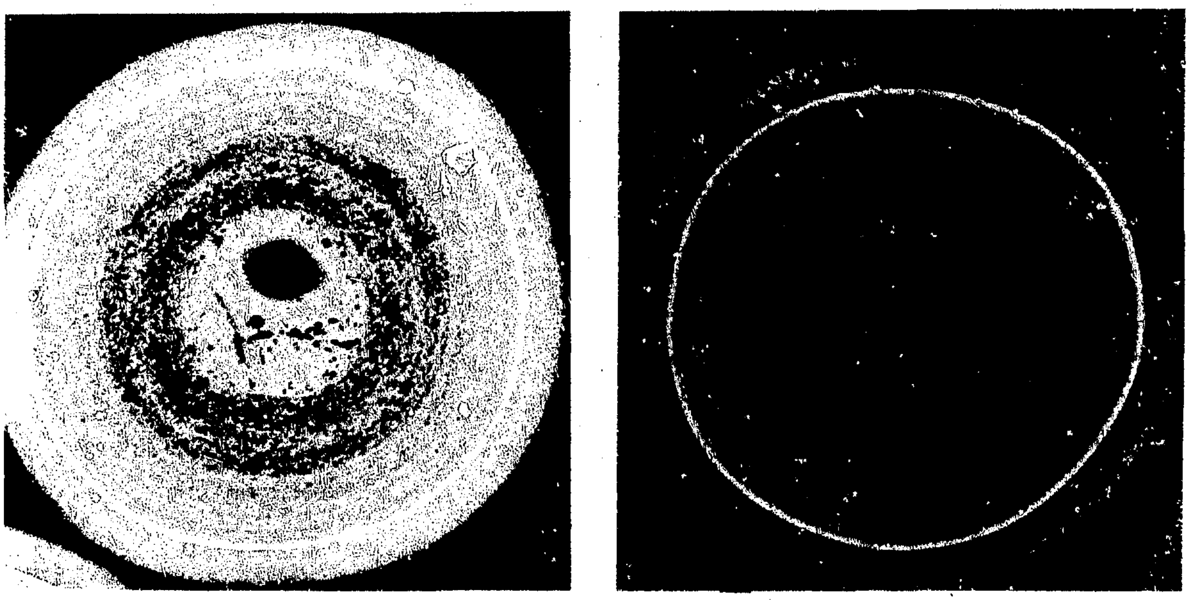


Fig. 13.
Coated particles from Run 1452 after 4.4 × 10^{21} n cm^{-2} at 900°C. Left: Bright field. Right: Polarized light showing preferred orientation. 150X.

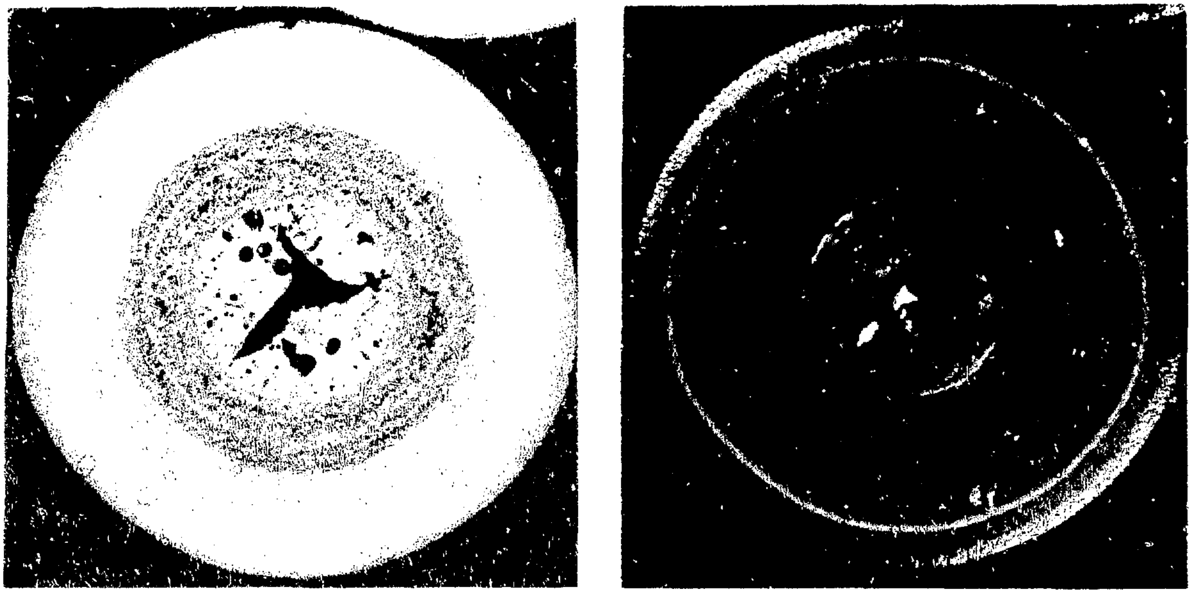


Fig. 14.
Coated particles from Run 1452 after 9.0 × 10^{21} n cm^{-2} at 900°C. Left: Bright field. Right: Polarized light showing preferred orientation. 150X.

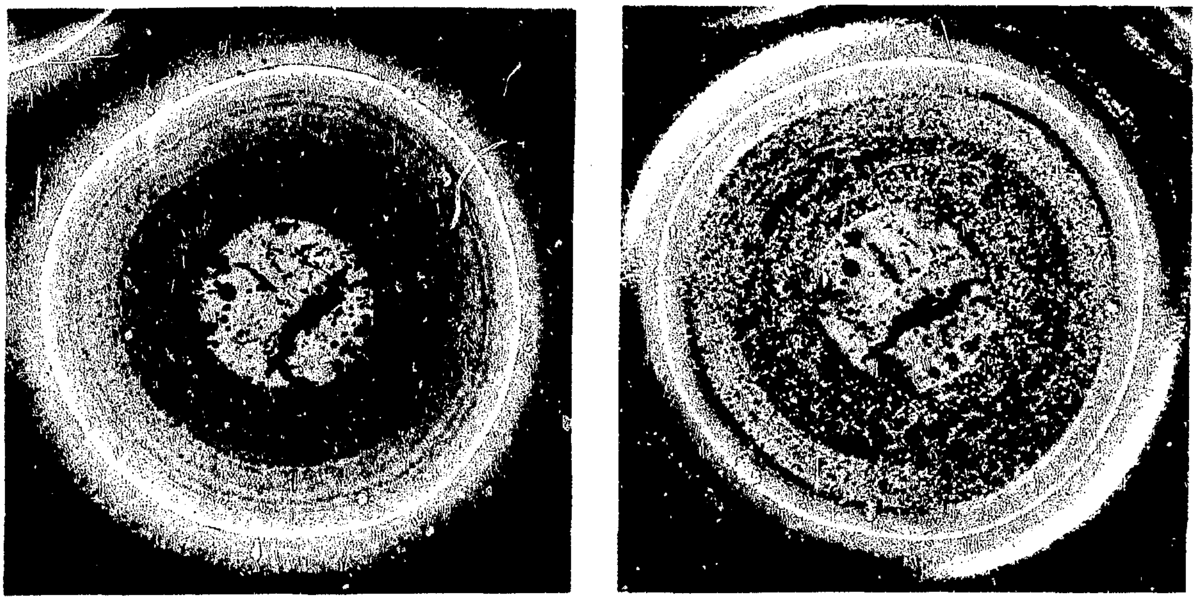
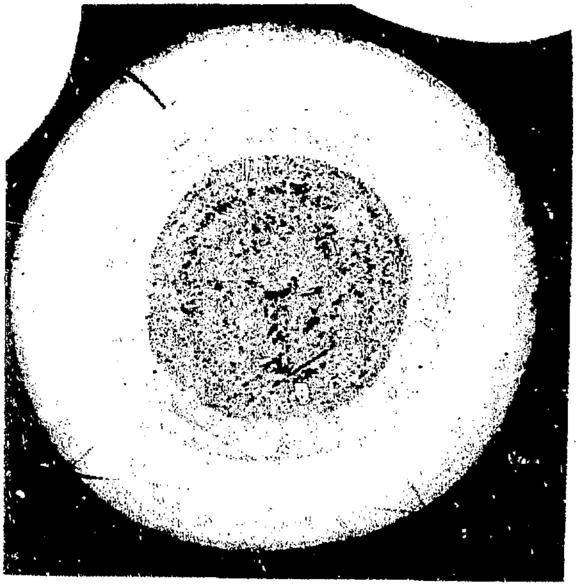
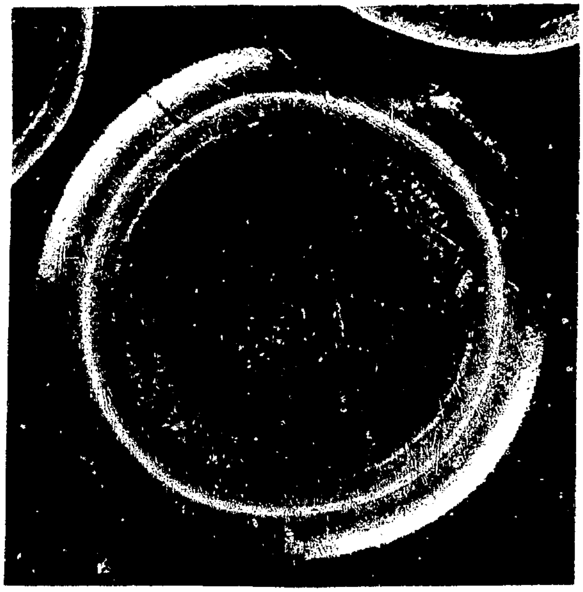


Fig. 15.
Coated particles from Run 1452 after 10.7 × 10^{21} n cm^{-2} at 900°C. Left: Bright field. Right: Polarized light showing preferred orientation. 150X.

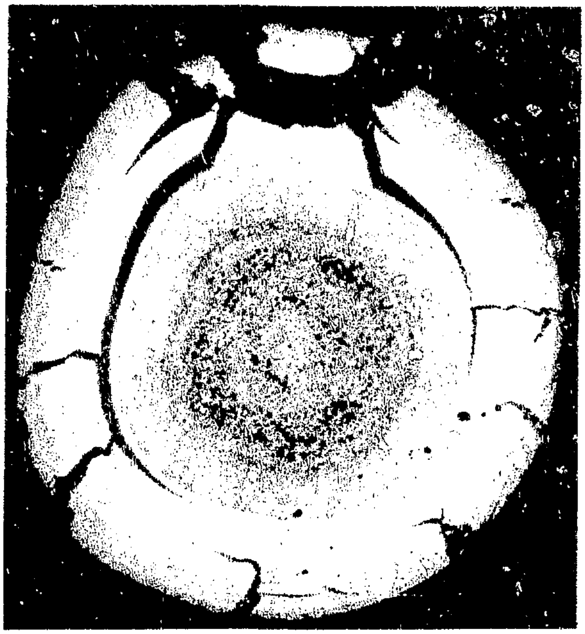


Bright field. About 20% survived test in this condition.



Polarized light showing preferred orientation.

Particle with outermost coat stripped (70%).



Particle with severely cracked coat (10%).

Fig. 16.

Coated particles from Run 1452 after 7.5×10^{21} n cm^{-2} at 1250°C. 150X.