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HOT-WORKING OF GRAPHITE FOR GRAPHITE-MATRIX
NUCLEAR FUELS

by

J. L. White and R. J. Price

July 17, 1964

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DIVISION OF
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ABSTRACT

Hot-working reduces the porosity of artificial graphites. The possibility of using hot-working in the fabrication of graphite-matrix fuel bodies for nuclear application was investigated by compressing specimens of fuel-matrix graphite, both with and without a dispersion of ZrC particles, in the temperature range 2350° to 2950°C . Studies were made of the effects of changing the temperature and strain of hot-working, and the pitch content and method of fabrication of the starting material, on the deformation during hot-working and the properties of the hot-worked material. The activation energy for flow during hot-working was about 200 kcal/mole for matrix graphite either with or without ZrC particles present, but the deformation rates at a given temperature and strain were much higher with the carbide particles present. The most striking results of hot-working were the production of a strong preferred orientation and an increase in density in all the samples. Except in the case of bodies containing ZrC particles, hot-working also sharply reduced the permeability of the samples, especially when the initial pitch content was high. The favorable properties of hot-worked graphite of high initial pitch content and its behavior during hot-working make this material the most promising candidate for the further development of hot-worked nuclear fuel-matrix graphite.

INTRODUCTION

The porosity and permeability to fission products of nuclear graphites prepared by conventional processes pose serious limitations on their use in certain graphite-matrix fuel bodies.⁽¹⁾ A process of hot-working is attractive as a means of closing the pores, thereby increasing the density and reducing the permeability of the graphite matrix. In addition, hot-working imparts a strong preferred orientation and therefore may be used to improve the thermal conductivity in certain directions. The purpose of this investigation was to examine the hot-working characteristics of typical fuel-matrix graphites with and without carbide particles representative of the fuel particles and to measure the properties of the resulting materials.

The range of material and process variables which might apply to the hot-working of a fuel-matrix graphite is large, and the information available on hot-working graphite⁽²⁾⁽³⁾ is limited. Consequently, the present work started by examining the hot-working of a typical fuel-matrix graphite⁽¹⁾ and proceeded to the selective exploration of variables, such as the hot-working temperature, hot-working strain, pitch content, and method of preparation of the starting material (i. e., molding or extrusion).

The presence of carbide fuel particles in the graphite matrix introduces further considerations. First, the hot-working process must not disrupt the fuel carbide particles, since particle breakup would increase fission recoil damage to the matrix graphite.⁽¹⁾ Second, the hot-working must be done below the temperature where eutectic reactions between the fuel carbide and the graphite matrix occur (2450°C for the UC₂-graphite eutectic⁽⁴⁾). The possibility of hot-working a graphite-carbide composite in spite of these limitations was therefore examined. Particles of ZrC were chosen as a representative carbide phase for dispersion in the graphite matrix because of the refractoriness of ZrC and its potential value as an alloying addition for fuel carbides.

HOT-WORKING APPARATUS

Hot-working was accomplished by compressive deformation at temperatures between 2300° and 3000°C in a simple high-temperature compressive creep machine (see Fig. 1). It was necessary to pay particular attention to the temperature distribution and to the alignment of the rams in order to obtain large plastic strains without fracture or nonuniform deformation. The plastic flow of graphite is very sensitive to temperature,⁽⁵⁾ and uniform temperature within the specimen is desirable to obtain homogeneous deformation. Because graphite is the only practicable structural material for the high-temperature components, the distributions of stress and temperature within the graphite ram heads were designed to minimize deformation in the heads, despite the work-hardening of the graphite specimen.

Flexibility in heating conditions was attained by the use of cylindrical graphite heaters whose cross section could be varied to attain various heating profiles. The heater life was improved by using several heated shields; above about 2600°C it was found desirable to pass an additional heating current directly through the specimen. Compressive loads up to 10,000 lb were applied by a hydraulic jack acting on the lower water-cooled copper ram. The load was held constant to $\pm 5\%$. The standard hot-working specimen was 1 in. in diameter by 2 in. long.

The hot-working runs were normally made with an argon atmosphere to repress volatilization. In the later stages of the work, an automatic temperature-control system was added; optimum performance was achieved with the total radiation pyrometer sighted directly on the specimen.

DEFORMATION DURING HOT-WORKING

The investigations were based on the hot-pressed, graphite-matrix fuel body developed for the High-temperature Gas-cooled Reactor (HTGR).⁽¹⁾ This fuel body uses a graphite matrix prepared with 90 wt-% graphitized

Fig. 1--Schematic diagram of hot-working device

petroleum coke and 10 wt-% pitch binder. The compact is carbonized under compression at 800°C and fired at 1850°C in vacuum. The investigations also included exploratory studies on hot-pressed and extruded bodies prepared with higher pitch contents. The four materials whose hot-working characteristics were studied were prepared with graphitized petroleum coke filler (GP-38, average particle size $20\ \mu$) and a conventional pitch binder (Barrett No. 30). The following fabrication methods and formulations were used:

1. Hot-pressed matrix graphite prepared with 10 wt-% pitch.
2. Hot-pressed matrix graphite prepared with 10 wt-% pitch and containing 22 vol-% ZrC particles (average size $\sim 80\ \mu$).
3. Hot-pressed matrix graphite prepared with 25 wt-% pitch.
4. Extruded matrix graphite prepared with 25 wt-% pitch.

Comparison specimens were prepared for property measurements by annealing without load at hot-working temperatures for times of the order of those used for hot-working.

The initial studies were made with the matrix graphite prepared with 10 wt-% pitch. A series of specimens without ZrC particles were hot-worked at temperatures from 2300°C to 3000°C , the upper limit being determined by the vaporization of graphite. A second series of specimens containing ZrC particles were hot-worked at temperatures from 2300°C to 2800°C , the upper limit in this case being determined by the ZrC-graphite eutectic (approximately $2835^{\circ}\text{C}^{(6)}$).

Two typical hot-working curves of compressive strain versus time are shown in Fig. 2. Since the deformation was measured by ram displacement, a small fraction of the observed displacement consists of deformation in the load train. The temperatures indicated are representative of specific locations on the specimens and consist of averages of observations over the period of hot-working. No attempt was made to correct for departure from black-body conditions. The platen design shown in Fig. 1 was chosen because it resulted in little or no specimen barrelling.

Fig. 2--Hot-working curves of matrix graphite prepared with 10 wt-% pitch, with and without the addition of 22 vol-% ZrC particles; nominal stress 6300 $\pm$ 300 psi

Plots of deformation rates at three strain levels as a function of temperature are shown in Figs. 3 and 4. The plots of the logarithms of the deformation rate versus the reciprocal temperature give reasonably well-defined straight lines whose slopes correspond to activation energies of about 200 kcal/mole. Strain rates in the specimens containing ZrC particles were about three times higher than in the pure graphite specimens at the same temperature and strain level, although the activation energies for flow were not significantly different.

In order to confirm the observations of increased plasticity in carbide-bearing graphite bodies, a differential hot-working experiment was conducted. Disks of matrix graphite and ZrC-bearing matrix graphite, prepared by identical processes of hot-pressing and annealing, were stacked alternately to make a composite hot-working specimen.

The results of compressing such a specimen at approximately 2500°C are illustrated in Fig. 5, where the greater barrelling of the ZrC-bearing disks is evident. The average deformation was 21% for the matrix graphite and 33% for the ZrC-bearing matrix graphite, which is in acceptable agreement with the hot-working curves given in Fig. 2. A similar differential deformation experiment was performed at 2540°C in which the deformation of a disk of hot-pressed and sintered ZrC was compared with the deformations of disks of matrix graphite and ZrC-bearing graphite. The ZrC showed a higher compressive strain (30%) than either the ZrC-bearing graphite (average strain, 29%) or the matrix graphite (19%).

The hot-working curves show that the strain rate decreases rapidly with increasing strain. In order to reach strain levels of the order of 70% true strain, it was necessary to use hot-working temperatures of 2800°C or higher to complete the deformation within a reasonable period.

Hot-working runs on hot-pressed specimens prepared with higher pitch content (25 wt-%) showed that the deformation rates were not appreciably affected by the change in pitch content. However, these specimens showed a markedly lower tendency to fracture during hot-working. Since the creep

Fig. 3--Deformation rates of matrix graphite (10 wt-% pitch) at three nominal strain levels as a function of temperature

Fig. 4--Deformation rates of matrix graphite (10 wt-% pitch) containing 22 vol-% ZrC particles as a function of temperature

Fig. 5--Hot-worked composite specimen used in differential deformation experiment performed at 2500°C ; disks were initially of same thickness; top, middle, and bottom disks are matrix graphite, and second and fourth disks are matrix graphite containing 22 vol-% ZrC particles

rate is sensitive to the applied stress, the higher pitch content therefore allows higher working loads to be applied, resulting in faster deformation with less risk of fracture.

Hot-working increases the preferred orientation already present in hot-pressed graphite. In order to investigate graphite with a different orientation texture, extruded graphite specimens were hot-worked in compression parallel to the extrusion axis. These specimens tended to fracture at relatively low loads or to deform nonuniformly. The tendency to fracture was greatest at the outset of hot-working, and the fracture surfaces tended to run parallel to the extrusion axis. This behavior suggests that the preferred orientation of an extruded rod renders it unstable in respect to compressive deformation along the extrusion axis.

Representative photomicrographs of matrix graphite before and after hot-working at temperatures near 2600°C and to true strains of the order of 35% are shown in Figs. 6 and 7. Qualitative observations of the preferred orientation by means of the sensitive-tint technique revealed a strong increase in the preferred orientation as well as the pore closure indicated in Figs. 6 and 7.

The X-ray diffraction technique developed by Bacon⁽⁷⁾ was used to obtain quantitative measurements of the preferred orientations existing in several representative hot-pressed and hot-worked specimens. The results, expressed as plots of $I(\phi)$ versus ϕ , where ϕ is the angle between the hot-working direction and the direction in which the intensity of c-axes, $I(\phi)$, is being measured, are shown in Figs. 8 through 10. Hot-working in the same direction as the original hot-pressing direction sharpens the preferred orientation, although the intensity curves always have a pronounced "tail," $I(\phi)$ remaining at 0.02 to 0.1 as ϕ approaches 90° . Thus, even after extensive hot-working, an appreciable fraction of the crystallites have their c-axes oriented perpendicular to the hot-working direction. Comparisons of the preferred orientation curves suggest that the texture depends on the hot-working strain but not on the temperature. In the as-pressed condition,

M-2501-2-1

150×

M-2502-2-3

150×

Fig. 6--Photomicrographs (bright-field illumination) of annealed matrix graphite (top) and matrix graphite hot-worked in compression at 2575°C to a strain of 38% (bottom) (longitudinal sections)

M-2504-2-2

150×

M-2505-2-2

150×

Fig. 7--Photomicrographs (bright-field illumination) of matrix graphite containing ZrC particles, as-annealed (top) and as hot-worked in compression at 2575°C to a strain of 37% (bottom) (longitudinal sections)

Fig. 8--Preferred orientation curves for matrix graphite (a) as hot-pressed, then annealed at 2500°C; (b) hot-worked 28% at 2500°C

Fig. 9--Preferred orientation curves for matrix graphite hot-worked
 (a) 30% at 2810°C and (b) 64% at 2850°C

Fig. 10--Preferred orientation curves for matrix graphite containing ZrC particles (a) as hot-pressed, then annealed at 1850°C; (b) hot-worked 30% at 2415°C

before hot-working, the matrix graphite containing ZrC particles possesses a more strongly oriented texture than the matrix graphite alone; this difference is decreased by hot-working.

PROPERTIES OF HOT-WORKED MATERIAL

Measurements of some physical properties relevant to nuclear applications were made on test specimens cut from the hot-worked and annealed reference specimens. Densities were obtained by weighing machined cylinders. The pore spectra were determined by conventional mercury porosimetry; typical curves are shown in Fig. 11. Measurements of the directional properties--thermal expansion, electrical resistivity, compressive strength, and helium permeability--were made on specimens cut both parallel and perpendicular to the direction of hot-working. The thermal expansion was measured between 22^o and 1000^o C in a Leitz dilatometer; some representative expansion curves are shown in Fig. 12.

The physical properties of conventional fuel-matrix graphite prepared with 10 wt-% pitch are given in Tables 1 and 2 for various hot-working temperatures. The values are given for a strain level of 35% true compressive strain, which is attainable with little risk of fracture or nonuniform deformation. In general, each value represents the average of two to four measurements on similar specimens.

The porosity shows a sharp decrease when specimens are hot-worked; the characteristic pore size, i. e., that corresponding to the maximum slope on curves such as Fig. 11, becomes lower. The results for helium permeability and compressive strength showed considerable scatter; however, a tendency toward lower strengths at higher hot-working temperatures was noticeable.

Matrix graphite containing ZrC particles had lower strength and higher permeability than matrix graphite without ZrC particles, and the effects of hot-working on physical properties were smaller. In the case

Fig. 11--Typical porosity curves, determined by mercury porosimetry, for annealed and hot-worked fuel-matrix graphites

Fig. 12--Typical curves for thermal expansion of hot-worked fuel-matrix graphite (solid and open symbols refer to measurements made parallel and perpendicular, respectively, to direction of hot-working)

Table 1

PHYSICAL PROPERTIES OF HOT-WORKED AND ANNEALED MATRIX
 GRAPHITE PREPARED WITH 10 WT-% PITCH
 (Parallel and Perpendicular to Direction of Compression
 during Hot-working)

Property	Average Annealing Temperature (°C)			Average Hot-working Temperature (°C)					
	1850	2500	2800	2430	2510	2600	2710	2810	2910
True compressive strain, % (avg.)	0	0	0	27	33	36	34	35	38
Density, g/cm ³ (avg.)	1.81	1.79	1.75	1.92	1.93	1.92	1.88	1.91	1.88
Porosity, d > 0.086 μ , % (avg.)	12.8	13.4	15.0	7.9	7.6	7.6	10.2	8.1	9.2
Characteristic pore size, μ	0.40	0.41	0.45	0.24	0.24	0.24	0.30	0.22	0.27
Mean coefficient of thermal expansion, (25° to 1000°C), °C ⁻¹ × 10 ⁶									
Parallel	9.3	7.5	6.9	12.6	14.9	14.5	12.6	14.6	----
Perpendicular	3.1	2.9	3.8	1.6	2.0	2.0	1.7	1.8	----
Electrical resistivity, (ohm-cm) × 10 ³									
Parallel	3.2	2.9	2.6	4.5	4.7	4.0	4.9	7.4	----
Perpendicular	1.2	1.2	1.3	1.0	0.9	1.0	1.1	1.0	1.0
Helium permeability, (cm ² /sec) × 10 ³									
Parallel	3.8	3.4	4.5	1.1	0.6	1.2	1.6	0.7	2.0
Perpendicular	5.0	5.3	6.4	2.0	1.6	1.3	4.4	2.4	3.3
Compressive strength, psi									
Parallel	8140	6430	5840	7380	6490	6510	5070	5900	5960
Perpendicular	7410	5450	5220	4960	5050	3710	3450	3890	3080

Table 2

PHYSICAL PROPERTIES OF HOT-WORKED AND ANNEALED MATRIX
GRAPHITE (10 WT-% PITCH) CONTAINING ZrC PARTICLES

Property	Average Annealing Temperature (°C)		Average Hot-working Temperature (°C)				
	1850	2650	2420	2520	2600	2720	2740
True compressive strain, % (avg.)	0	0	35	36	35	42	39
Porosity, d > 0.086 μ , %	14.1	14.8	9.0	9.2	10.7	11.1	11.4
Characteristic pore size, μ	0.64	0.63	0.40	0.44	0.44	0.46	0.47
Density, g/cm ³	----	2.56	2.65	2.69	2.65	2.64	2.70
Mean coefficient of thermal expansion, (25° to 1000°C), °C ⁻¹ × 10 ⁶							
Parallel	7.4	6.6	10.0	9.7	10.9	9.9	9.8
Perpendicular	2.7	3.8	3.6	3.7	4.0	3.8	3.7
Helium permeability, (cm ² /sec) × 10 ³							
Parallel	13	36	18	47	41	36	47
Perpendicular	28	59	12	57	68	98	143
Compressive strength, psi							
Parallel	6430	5280	5150	5080	4010	3480	3460
Perpendicular	5290	4610	4590	3330	3070	2320	2850

of permeability and compressive strength, the changes were negligible or adverse.

In order to investigate which of the material and process variables of hot-working might be changed to produce improved physical properties, it was assumed that the temperature of hot-working was not a significant variable, and attention was restricted to the matrix graphite without carbide particles. Representative results of investigations of the effects of hot-working strain, pitch content, and preferred orientation in the starting material are given in Tables 3, 4, and 5.

No significant improvements in the properties of graphite prepared with 10 wt-% pitch were found by going to true strains of greater than 50%. However, higher pitch content in the hot-pressed starting material led to substantial improvements in the physical properties and a reduction in the incidence of fracture during hot-working. Although the higher pitch content causes a greater porosity and permeability in the starting material, the hot-worked materials showed low porosity and permeabilities of less than 10^{-4} cm²/sec in the most favorable orientation. These hot-worked graphites also showed a greater anisotropy in their properties compared with the 10 wt-% pitch bodies. For example, hot-working increased the compressive strength in the parallel direction while reducing it in the perpendicular direction.

The properties of extruded matrix graphite prepared with 25 wt-% pitch also showed substantial improvement after hot-working, but the absolute values were inferior to those obtained by hot-working the high-pitch, hot-pressed matrix graphite.

DISCUSSION

Two significant features of the hot-working process are the strong orienting influence acting on the graphite crystallites and the pore-closing action, which is accompanied by densification. These effects are observed micrographically and by direct measurement. The high degree of preferred

Table 3

PHYSICAL PROPERTIES OF HOT-WORKED
AND ANNEALED MATRIX GRAPHITE
(Hot-pressed Bodies Prepared with 10 wt-% Pitch) ;

Property	Annealing Temp. (°C)	Finishing Temperature in Hot-working (°C)			
	2800	2810	2710	2900	2900
True compressive strain, %	0	35	49	66	78
Density, g/cm ³	1.75	1.91	1.98	1.96	1.99
Porosity, d > 0.086 μ , %	15.0	8.1	6.9	6.9	7.1
Characteristic pore size, μ	0.45	0.22	0.18	0.17	0.19
Mean coefficient of thermal expansion (25° to 1000°C), °C ⁻¹ × 10 ⁶					
Parallel	6.9	14.6	14.5	14.8	----
Perpendicular	3.8	1.8	0.85	0.83	0.55
Helium permeability, (cm ² /sec) × 10 ³					
Parallel	4.5	0.65	----	1.6	0.43
Perpendicular	6.4	2.4	18.4	5.4	----
Compressive strength, psi					
Parallel	5840	5960	6100	4900	4030
Perpendicular	5220	3080	2850	2435	1800

Table 4
 PHYSICAL PROPERTIES OF HOT-WORKED
 AND ANNEALED MATRIX GRAPHITE
 (Hot-pressed Bodies Prepared with 25 wt-% Pitch)

Property	Annealing Temp. (°C)	Finishing Temperature in Hot-working (°C)	
	2800	2940	2900
True compressive strain, %	0	67	82
Density, g/cm ³	1.76	2.05	1.94
Porosity, $d > 0.086 \mu$, %	15.9	4.2	1.9
Characteristic pore size, μ	0.5	0.13	0.12
Mean coefficient of thermal expansion (25° to 1000°C) °C ⁻¹ × 10 ⁶			
Parallel	5.3	----	17.0
Perpendicular	2.0	----	0.49
Helium permeability, (cm ² /sec) × 10 ³			
Parallel	271	0.013	0.093
Perpendicular	450	3.4	1.5
Compressive strength, psi			
Parallel	6,920	11,430	8,560
Perpendicular	7,220	4,890	4,330

Table 5
 PHYSICAL PROPERTIES OF HOT-WORKED AND ANNEALED
 MATRIX GRAPHITE
 (Extruded bodies prepared with 25 wt-% pitch)

Property	Annealing Temp. (°C)	Finishing Temperature in Hot-working (°C)		
	2800	2700	2880	2900
True compressive strain, %	0	36	45	75
Density, g/cm ³	1.56	1.77	1.80	1.86
Porosity, d > 0.086 μ, %	27.4	11.8	12.6	12.2
Characteristic pore size, μ	1.0	0.31	0.29	0.28
Mean coefficient of thermal expansion (25° to 1000°C) °C ⁻¹ × 10 ⁶				
Parallel	0.93	4.4	4.7	13.4
Perpendicular	4.6	----	3.5	2.8
Helium permeability, (cm ² /sec) × 10 ³				
Parallel	207	21.2	9.2	4.0
Perpendicular	118	25.8	14.5	10.2
Compressive strength, psi				
Parallel	4240	3650	3470	4630
Perpendicular	3650	2470	2940	3070

orientation that can be attained is exemplified by the thermal expansion curves of Fig. 12; the negative thermal expansion typical of the graphite single crystal in the a-direction can be achieved by hot-working hot-pressed bodies to about 40% compressive strain. The fact that the property anisotropy characteristic of an extruded body can be converted to that representative of a molded sample suggests that, providing care is taken to avoid fracture, the hot-working process could be employed to produce preselected orientation textures in graphitic bodies. For example, a completely isotropic body might be made by this method.

As regards further investigations of the hot-working of graphite, it is clear from the present work that the more favorable starting materials are hot-pressed bodies prepared with a high pitch content. The reduced fracture risk of higher-pitch bodies is particularly useful in the hot-working of carbide-containing bodies where eutectic reactions severely limit the maximum hot-working temperatures, since higher stresses can be applied in order to attain reasonable hot-working strains within acceptable time periods. The fine-grained nature of graphitized pitch suggests that improvements in the hot-working characteristics and in the resulting properties of the hot-worked bodies may be related to grain size. It should be noted that the pitch originally used in preparing the hot-pressed bodies is essentially fully graphitized before hot-working; furthermore, no significant change in the rate of hot-working was observed when the original pitch content was increased from 10 wt-% to 25 wt-%. Further studies to optimize the properties of hot-worked fuel-matrix graphite should therefore consider variations in the grain size of the filler material as well as in the pitch content.

The necessity of temperature uniformity to obtain uniform deformation probably results from the high activation energy for flow in polycrystalline graphite at high temperature. The fact that the creep rate decreases rapidly with strain favors uniform deformation but also provides a practical limit to the hot-working strains that can be obtained in the lower temperature

ranges, e. g., below 2500°C. Fortunately, the present work indicates that the major portion of the improvement in properties is obtained at strain levels below about 50%.

The present work shows that the presence of ZrC particles increases the strain rate in a fuel-matrix graphite during hot-working without greatly affecting the activation energy for flow. It is not clear whether this increased plasticity is caused simply by the relative softness of the ZrC at hot-working temperatures or by a more fundamental effect on the mechanisms of plastic flow in graphite. For example, it is well known that many metals and metal carbides cause catalytic recrystallization in graphite, and it is possible that such recrystallization during deformation could result in "superplasticity" of the graphite matrix. Alternatively, if high-temperature flow in graphite is due to the stress-aided flow of point defects (Nabarro-Herring creep), the carbide-graphite interfaces could act as good sources and sinks for the defects and thus increase the deformation rate.

The relatively poor physical properties of hot-worked ZrC-graphite composites observed in the present investigation indicate that more work is necessary in exploring carbide particle size, pitch content, and preliminary heat-treatment before this enhanced plasticity of ZrC-bearing graphite can be profitably employed in the hot-working of fuel-matrix graphites.

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