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GRAPHITES FABRICATED FROM GREEN PETROLEUM PITCH COKES*

by

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INTRODUCTION

MASTER

Conventional graphite bodies are normally fabricated by combining carbonized or graphitized filler materials with hydrocarbon binders such as coal tar or petroleum pitches. During the subsequent heat treatment to produce the final graphite body, the filler undergoes little or no shrinkage, while pronounced shrinkage of the binder material occurs, resulting in a final product which contains a network of angular voids. This pore morphology obviously weakens the overall structure and its ability to withstand stressing.

The effect of pore morphology is particularly significant in obtaining graphites with structures yielding high mechanical integrity. These types of structures are very important in considering the resistance to differential crystallite growth during nuclear irradiation and to resisting the high strains produced by thermal stress or shock. Both types of problems can presumably be solved by strengthening the inter-particle boundaries and reducing the role of pore structures to act as

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stress risers. Thus, the desired structure is one having a monolithic character with the pore texture smaller or less angular than the pores inherently present in the coke structure.

One approach to obtain a monolithic-type structure with smaller or less angular pores is to employ green coke as the filler material. This approach offers at least two advantages. The first is that the coke particle still retains some chemical reactivity and will readily unite with the binder. Secondly, the volume shrinkage of the green coke filler more readily matches the binder shrinkage during pyrolysis. And, indeed, Kennedy and Eatherly^{1,2} have reported that graphite based on green cokes does have the necessary monolithic structural characteristics and does exhibit dramatic improvements in both irradiation and thermal shock resistance.

The search for fillers which result in graphites with low thermal expansion and high thermal conductivity (essential for thermal shock resistance) led to the use of highly acicular green cokes instead of isotropic cokes used for irradiation resistance. The purpose of this study was to determine the parameters involved in preparing high-quality acicular coke from a petroleum pitch and to compare the properties of graphites fabricated with the A-240-derived green cokes with properties of graphites fabricated using other conventional acicular cokes. Thus, acicular cokes were prepared from A-240 pitch under varying conditions, and bodies were fabricated using these cokes as fillers.

EXPERIMENTAL

The conventional acicular cokes were obtained from Union Carbide Corporation (UCC), Carbon Products Division, and Great Lakes Carbon Corporation (GLCC), while the A-240 pitch was a petroleum distillate fraction obtained from the Ashland Oil Company.

The experimental cokes were prepared by firing approximately 1800 g of A-240 pitch in carbon boats for 1 hr at 575, 600, 650, or 675°C under

an inert atmosphere. An additional filler was prepared by heating A-240 pitch at 425°C for 24 hr and an initial room temperature argon pressure of 2000 psi. The pressure-coked material was then fired at 500°C for 5 hr.

Appropriate quantities of the binder pitch (A-240) were dry mixed with the fillers and subsequently slurry blended using benzene until reasonably dry. After grinding to -120 mesh, the mix was warm molded at approximately 95°C at a pressure of 2000 psi. The 1.6-in.-diam blocks were cooled under pressure and placed in restraining holders. After carbonization to 1000°C on a controlled three-day cycle, the carbonized blocks were removed from the restraining holders and heated to 2800°C on a one-day cycle. The graphitized bodies were then machined for brittle ring and electrical resistivity specimens.

RESULTS AND DISCUSSION

Properties of the graphite fabricated from the conventional and A-240-derived cokes are listed in Table 1. As indicated in the table, properties such as electrical resistivity, fracture stress, etc., were directly dependent upon the final graphitized density, which was a direct function of the initial green density. In general, the initial green density increased with increasing binder content.

Properties of graphites fabricated with the UCC and GLCC fillers were quite similar, with the GLCC-derived graphites being slightly more anisotropic than the UCC-derived graphites. Properties of the graphites fabricated with the A-240-derived fillers were quite dependent upon the coke preparation temperature and, in general, exhibited a somewhat greater degree of anisotropy than graphites fabricated from either the GLCC or UCC fillers. Green densities of the A-240-derived filler bodies decreased significantly as the temperature at which the coke was prepared increased.

Table 1. Properties of Experimental Graphites

Sample Number	Filler Used ^a	A-240 Binder Content (pph)	Density, g/cm ³		Electrical Resistance ($\mu\Omega$ -cm)		Brittle Ring Results		
			Green	Graphite	Axial	Normal	σ_f	E	ϵ_f
							$\downarrow$ (psi)	$\downarrow$ (psi $\times 10^{-6}$)	$\downarrow$ (%)
1-74A4	UCC	12	1.18	1.63	2080	1200	4340	1.05	0.65
1-74B1	UCC	14	1.18	1.62	2000	1210	4370	1.00	0.71
1-74C4	UCC	16	1.23	1.69	1490	920	5310	1.14	0.74
1-76A4	GLCC	12	1.12	1.57	2300	1270	4100	1.04	0.64
1-76B4	GLCC	14	1.19	1.63	2020	1070	4830	1.11	0.68
1-76C1	GLCC	16	1.19	1.64	1810	1010	5220	1.13	0.74
1-78B1	A-575	10	1.17	1.61	1730	1110	3720	0.95	0.62
1-78C1	A-575	12	1.20	1.70	1690	920	6070	1.36	0.71
1-78D1	A-575	14	1.24	1.74	1550	830	7340	1.54	0.77
1-80A2	A-600	12	1.16	1.55	2000	1240	3660	0.84	0.63
1-80B2	A-600	14	1.21	1.62	1620	1080	4640	1.01	0.68
1-80C2	A-600	16	1.22	1.61	1750	1030	8710	0.93	0.73
1-82A2	A-650	12	1.10	1.41	2920	1370	1790	0.40	0.64
1-82B2	A-650	14	1.12	1.42	2650	1550	1690	0.41	0.55
1-82C3	A-650	16	1.15	1.48	2080	1290	2230	0.49	0.64
1-84C4	A-675	12	1.10	1.39	3110	--	1190	0.30	0.55
1-84D2	A-675	14	1.12	1.40	2620	1560	1560	0.39	0.58
1-84E1	A-675	16	1.15	1.47	2060	1290	2060	0.41	0.58
1-104A2	I-A240	12	1.22	1.63	1240	810	4490	0.99	0.72
1-104B3	I-A240	14	1.24	1.67	1090	740	5370	1.12	0.76
1-104C4	I-A240	16	1.28	1.66	980	670	5400	1.10	0.78

^aUCC filler obtained from Union Carbide Corporation.

GLCC filler obtained from Great Lakes Carbon Corporation.

A-xxx fillers prepared from Ashland Oil Company's A-240 pitch.

xxx denotes the heat-treatment temperature.

I-A240 filler prepared from pressure-coked A-240 pitch.

Specimens fabricated from the pressure-coked A-240 filler failed to attain graphite densities comparable to specimens fabricated with the A-575 filler, even though these specimens had similar green densities. Brittle ring results, as indicated in Table 1, were mainly a function of graphite density as noted for the other specimens. However, electrical resistivity values were significantly lower than expected and indicated a higher degree of isotropy than observed in any of the other specimens. This was probably a result of the pressure coking.

CONCLUSIONS

Graphites fabricated from A-240-derived green cokes show similar properties to graphites fabricated from high-quality acicular cokes. Graphite densities equal to or surpassing the densities of bodies fabricated using either the UCC or GLCC fillers were obtainable by the choice of the appropriate A-240 coke preparation temperature and the appropriate binder content. Though a greater degree of anisotropy was present in bodies fabricated from the A-240-derived cokes, reasonably isotropic bodies were prepared using fillers prepared by the heat treatment of pressure-coked A-240 pitch.

REFERENCES

1. C. R. Kennedy and W. P. Eatherly, *The Development of Thermal Shock Resistant Graphite*, paper presented at the 11th Biennial Conference on Carbon, Gatlinburg Meeting, June 4-8, 1973, CONF-730601, p. 131.
2. *Ibid.*, p. 304.