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Cover *Hot metal is charged into argon-oxygen-decarburization (AOD) furnace at Watervliet, N.Y. Works of Allegheny Ludlum Steel. A larger AOD furnace is under construction at Brackenridge (PA.) Works. It will feed the planned continuous casting facility for increased production of stainless, electrical and other specialty steels. The AOD process is particularly effective in conserving chromium.*

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Fracture and Thermal Shock of Polycrystalline Electrode Graphites

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Part I: Properties of Electrode Graphites

The unique thermal, electrical, and mechanical properties of polycrystalline graphite have resulted in its widespread utilization as steelplant furnace electrodes. In addition similar graphite anodes are used in production of magnesium, caustic soda, potash, chlorine, and sodium chlorate. Graphite molds and crucibles for metallurgical applications, and applications in the nuclear field also comprise a substantial market (1). The aforementioned properties give graphite excellent thermal shock resistance (2), which along with its relatively low cost, characterizes polycrystalline graphite as an extremely versatile material.

In the specific application as steelplant furnace electrodes, large extruded polycrystalline graphite logs, often as large as 110 in. in length and 28 in. in diameter, are subjected to rapid temperature changes and oxidizing conditions which can cause degradation of the electrode and subsequent thermal shock damage. A potential method for the evaluation of electrodes for these applications is the calculation of theoretically derived thermal shock damage resistance parameters which are based on ex-

perimentally measurable physical and mechanical properties such as the elastic modulus, the coefficient of thermal expansion, the fracture strength, and the fracture surface energy. These thermal shock damage resistance parameters have proven useful in other refractory material evaluations, for they have been demonstrated to directly relate to results of the A.S.T.M. panel spalling test for thermal shock damage of refractories (3, 4).

It is the purpose of this article to present experimental data for the physical properties of several different extruded polycrystalline electrode graphites. Then, after subjecting these graphites to severe thermal shocks, an attempt will be made to correlate their damage resistance parameters with their performance and with their properties.

Electrodes for Steelmelting Furnaces, Review of the Art

Electric furnace steelmaking is a rapidly expanding metallurgical process utilized for the production of quality steels. Sharp (5) reviews the fundamentals of the process. He describes electric-arc steelmelting

as an efficient melting method in which the heat is generated by three single-phase arcs between extruded graphite electrodes and the metal charge. Virtually no contamination of the steel melt results, provided that the impurities in the graphite electrodes are kept low through the manufacturer's judicious choice of the coal tar pitch and petroleum coke raw materials, and well-controlled graphitization process. Since about twelve pounds of graphite electrode are consumed per ton of steel, the 27 million tons of electric furnace steel produced in the United States in 1973 (6) required about 160,000 tons of graphite electrodes.

Blackman (7) has discussed electric furnace steelmelting electrodes in detail. These graphite electrodes are manufactured from combinations of various petroleum cokes and coal tar pitches, whose choice is based upon cost and availability; but, moreover, for the consideration of the final thermal, electrical, and mechanical property requirements of the electrodes. Conventional graphite forming processes have been discussed in detail by Liggett (1) and by Austin (8). Only highlights of Liggett's article will be reviewed here.

The aforementioned raw materials may be classified as "filler" and "binder" constituents of the electrode. The "filler" is commonly a petroleum coke, made by the delayed coking process employing a low sulphur crude oil. Pitch cokes, and cokes derived from shale oil, asphalts, and bitumens may also be used; however, their utilization is severely restricted by their availability. As it is obtained from the refinery, "green coke" has been exposed to a thermal treatment of only about 450°C to 500°C; consequently it usually still contains up

to 15% volatiles. During later crystallite development, there is an accompanying volumetric shrinkage that results in a real density increase of about 30%. Therefore, a calcination process is necessary to pre-shrink this coke. This thermal treatment is carried out between 1200°C and 1300°C, generally in a rotary kiln. Next, the material is subjected to a combination of grinding, pulverizing, and sizing operations to reduce the coke particles. A screen size range of -3 to +100 mesh is typical for the filler coke particles used in the fabrication of large electrodes.

The second constituent of electrode graphites is the "binder". Its purpose is to plasticize the coke particles for ease of forming into the desired shapes and sizes. It must also carbonize thoroughly to minimize any further dimensional changes and prevent any degradation during the later stages of processing. For these and economic reasons, materials derived from coal tar pitches have traditionally proven to be the most suitable binders for electrode grade graphites.

Following the separate preparation of the filler and binder materials, the two are combined in a kneader-type mixer at about 120°C to insure adequate plasticity of the mix. It is essential to the final mechanical, thermal, and electrical properties of the electrodes that sufficient binder is employed, as well as adequate heat during subsequent extrusion to exclude most of the air from the interstices between the particles. For extruded direct-arc steelmelting electrodes, a "recipe" of 30 parts of pitch binder mixed with 100 parts of coke is typical. The extrusion is conducted at about 100°C at pressures varying from 400 psi to 8000 psi, depending

on the electrode diameter and the specific processing characteristics of the individual mix.

The formed electrodes are then "baked". In this process, the coal tar pitch is converted to coke, which serves to connect the filler particles and increase the strength of the electrode. Baking cycle temperatures reach about 950°C so that a considerable amount of volatiles is evolved. The extremely important baking cycle involves nearly 10 days of heating at only 4°C/hour. It is concluded with an equal number of days for cooling in the batch-type baking kiln. During this processing step, about 35% of the binder and about 15% of the green body weight is lost and the thermoplastic binder becomes sufficiently rigid to stabilize the body shape. The electrode now contains about 20% porosity.

To reduce this pore content, the electrode may be impregnated with additional coal tar pitch prior to graphitization. After sealing in an evacuated autoclave the electrodes are covered with a bath of molten pitch or a similar material, which is then forced under pressure into the pores. Impregnation, interspersed with baking, may be repeated a number of times; however, significant porosity decreases and substantial property enhancement are generally not realized after the second impregnation.

At this point, the electrode is a baked carbon. It is very brittle, hard, and possesses only moderate electrical and thermal conductivities. In order to improve these properties to the level necessary for utilization as a steelmaking electrode, a crystalline transformation, or conversion, is required to develop artificial graphite or electrographite. During the graphitization process, the temperature of

the baked carbon is slowly raised from room temperature to about 3000°C over a ten day period. Acheson graphitizing ovens are usually employed, wherein the baked carbon is electrically resistance heated. Electric currents up to 100,000 amps at 35 to 200 volts are utilized. Following graphitization, the material is polycrystalline and possesses high electrical and thermal conductivities, good resistance to thermal shock, and a low coefficient of thermal expansion. Increase of strength with temperature, easy machinability and improved oxidation resistance are additional desirable properties that help to render graphitized electrodes a good choice for steelmaking applications.

Properties of Electrode Graphites

To understand the thermal shock behavior of extruded electrode graphites, it is necessary to investigate several physical properties of electrodes, including: density, thermal expansion, elastic modulus, strength, and the fracture surface energy. In addition, it is of interest to investigate both "Regular" and "Premium" grades of electrodes. These two electrode classes generally reflect their nomenclature, each having its own characteristic raw materials and proces-

Table I Densities of Electrode Graphites†

Grade	Density (g/cc)
"Regular"	
R1	1.68 ± .01
R2	1.66 ± .01
R3	1.62 ± .02
"Premium"	
P1	1.72 ± .01
P2	1.71 ± .01
P3	1.72 ± .01
P4	1.69 ± .01
P5	1.66 ± .02

†The electrodes are products of Airco Speer Carbon-Graphite. The R prefix designates a Regular electrode, while the P prefix signifies a Premium grade throughout this article.

sing, the exact details of which are proprietary.

Density

Table I lists the densities of several of the grades studied. For comparison, the true density of the ideal graphite crystal is 2.268 g/cc. It is apparent that the "Premium" grade is generally denser.

Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) is an essential factor for many graphite applications. It is particularly useful as an indication of the degree of macroscopic anisotropy present in extruded electrode graphite. It is well known that the thermal expansion anisotropy of the graphite crystal is high. It is about twenty times different in directions parallel and perpendicular to the graphite basal plane (9), that is $1.5 \times 10^{-6}/^{\circ}\text{C}$ and $28.3 \times 10^{-6}/^{\circ}\text{C}$, respectively, over the range of 15°C to 800°C . This high anisotropy in the graphite crystallite will be reflected, more or less, in the thermal expansion anisotropy in the polycrystalline graphite electrode. The degree depends upon the extent of crystallite alignment and the magnitude of pore volume between crystallites, which in turn affects the extent to which crystallite expansion can be accommodated without resulting in significant over-all expansion of the electrode. If the crystallites in a given electrode tend to be preferentially oriented with their basal planes parallel to the electrode axis, then smaller expansion will be observed along the electrode length than in the radial direction. Typically "Regular" grades have a transverse (radial direction) thermal expansion coefficient of about $2.9 \times 10^{-6}/^{\circ}\text{C}$; while "Premium" grades have slightly lower values, about $2.7 \times$

$10^{-6}/^{\circ}\text{C}$. In the longitudinal direction both grades have a CTE of only about $2.0 \times 10^{-6}/^{\circ}\text{C}$.

Sampling

All specimens examined were rectangular bars 1 in. x 1 in. x 3 in. long. They were cut from 24 in. diameter electrodes and are designated either transverse or longitudinal specimens, depending upon whether their long dimension was perpendicular or parallel to the extrusion axis of the electrode. Generally thirty specimens were cut from an electrode in each direction and measurements were made on each specimen. Full details on the techniques used to make the various measurements are given elsewhere (10).

Table II Flexural Strengths of Electrode Graphites

Grade		Strength (psi)	
		Transverse	Longitudinal
R2	"Regular"	840 ± 100	960 ± 60
R3		950 ± 70	1300 ± 250
P2	"Premium"	1530 ± 50	1800 ± 100
P3		1850 ± 90	2480 ± 120
P4		1280 ± 110	1440 ± 45
P5		1470 ± 120	1820 ± 70
P6		1530 ± 35	1850 ± 60

Flexural Strength

Table II summarizes flexural strength values on selected samples. As expected, because of some preferred orientation in each electrode, bars cut in the longitudinal direction show higher values than those cut in the transverse direction. Table III summarizes elastic

Table III Elastic Moduli of Electrode Graphites
Moduli (psi) x 10⁶

Grade	Transverse	Longitudinal	Anis. Ratio
R1	0.66	0.70	1.06
R2	0.55	0.86	1.56
R3	0.51	0.86	1.69
P1	0.80	1.37	1.71
P2	1.09	1.02	0.94
P3	1.35	1.09	0.81
P4	0.60	1.16	1.93
P5	0.64	1.10	1.72

modulus values measured using a resonance technique. For comparison, with values given in Table III, elastic modulus values for the single crystal graphite have been reported as 0.33×10^6 psi and 150×10^6 psi in directions perpendicular and parallel to the basal plane (11). As with flexural strength, higher values are expected for the longitudinal samples. That this correspondence was not found for two of the "Premium" electrode grades is interesting, but not fully understood at this time. No effect on mechanical properties was found insofar as the radial location in the electrodes from where the specimens were cut.

Fracture Surface Energy

Fracture surface energy (12), defined as the energy required for the creation of a unit area of new surface by crack propagation, was estimated using both the work-of-fracture (WOF) and the notched beam (NB) techniques. Values are summarized in Table IV. The notched-beam test is generally accepted as a measure of the fracture energy $\gamma_{(NB)}$ required for crack initiation. A large spread exists in the anisotropy of $\gamma_{(NB)}$ values. The largest anisotropy ratios of 1.76 and 2.02 are present in grades R4 and P3 respectively. Anisotropy ratios near one are found for sam-

ples R2, R3, P4, and P5. Graphite grades which possess the smallest anisotropy ratios for the energy required for crack initiation are seen to exhibit the highest anisotropy ratios of elastic moduli (Table III).

Fracture Toughness Vs. Flexural Strength

Fig. 1 presents a comparison of the fracture toughness, K_{IC} , calculated from $\gamma_{(NB)}$ values as described elsewhere (12), with flexural strengths for six electrode graphites. Although there is some scatter, flexural strength increases with increasing $\gamma_{(NB)}$ for both specimen orientations. Thus, if the manufacturer understands the raw materials and processing parameters necessary to increase fracture toughness or fracture surface energy, flexural strength increases may also be realized.

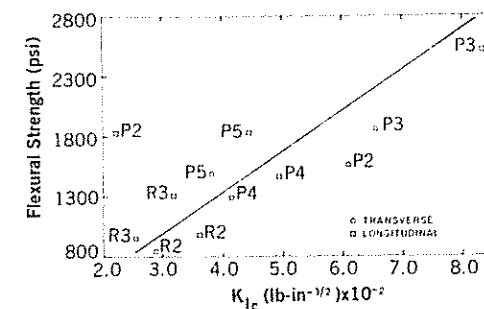


Fig. 1. Flexural strength versus fracture toughness of electrode graphites.

Table IV Fracture Surface Energies of Electrode Graphites
Fracture Surface Energies (ergs/cm²)

Grades	Transverse Samples			Longitudinal Samples		
	WOF	NB	γ (WOF)	WOF	NB	γ (WOF)
			γ (NB)			γ (NB)
R1	155,600 ± 10,000	—	—	213,500 ± 12,800	—	—
R2	127,800 ± 16,700	13,300 ± 1,700	9.6	137,700 ± 22,700	13,100 ± 2,300	10.5
R3	225,000 ± 32,700	11,200 ± 2,600	20.1	271,900 ± 64,900	10,300 ± 3,300	26.4
R4	—	26,600 ± 2,300	—	—	46,800 ± 3,400	—
P2	174,300 ± 12,900	29,900 ± 2,700	5.8	205,000 ± 19,600	42,800 ± 4,300	4.8
P3	166,400 ± 8,300	27,800 ± 2,400	6.0	215,100 ± 12,800	56,000 ± 3,900	3.8
P4	135,600 ± 13,900	24,900 ± 4,400	5.5	186,600 ± 48,600	18,400 ± 2,300	10.1
P5	315,700 ± 45,100	19,800 ± 2,700	15.9	405,300 ± 101,400	15,700 ± 2,500	25.8

Fracture Surface Energy (γ_{WOF} and γ_{NB})

Fracture surface energies as measured by the work-of-fracture technique (γ_{WOF}) for both the "Regular" and "Premium" electrode grades are also shown in Table IV. All work-of-fracture values are substantially greater for the longitudinal than for the transverse samples. Higher values for the longitudinal orientation can be explained by the additional energy required for the crack front to propagate predominately perpendicularly to the oriented graphite crystallites. In addition to the energy consumed traversing the binder phase and large numbers of pores, the majority of the total energy absorbed by the specimen is consumed by interactions between the crack front groups of crystallites. Anisotropy ratios vary from 1.08 for grade R2 to 1.38 for grades R1 and P4. Fracture surface energy values, as measured by the work-of-fracture technique, can also be controlled by the electrode manufacturer by varying the baking cycle, extrusion pressure, and raw materials. An optimization of this energy should result in an increase in the thermal shock damage resistance of electrode graphites.

Table IV also presents values for the ratios of γ_{WOF} to γ_{NB} , measured at room temperature, for both transverse and longitudinal samples. For transverse samples, this ratio varies from 5.8 to 20.1. For longitudinal samples, a much larger variation in $\gamma_{\text{WOF}}/\gamma_{\text{NB}}$ exists between grades; that is, it ranges between 3.8 for grade P3 to 26.4 for grade R3. The largest anisotropy in $\gamma_{\text{WOF}}/\gamma_{\text{NB}}$ is found for grades R3 and P5 for both the transverse and longitudinal samples. It is apparent that a propagating crack front transverses a more tortuous path in these two grades than in the other graphite grades examined.

Mechanical property measurements on polycrystalline electrode graphite reflect primarily the extent of crystallite alignment and the nature of the porosity in the artifact. It is apparent that by a judicious choice of raw materials and processing parameters, the manufacturer can produce a wide range of electrode properties.

Thermal Shock Characteristics

Thermal shock characteristics of regular and premium grade graphites, as determined from single and multiple quenches of graphites into liquid nitrogen (-196°C), will be presented in next concluding part.

References

1. Liggett, L. M., "Carbon-Baked and Graphitized Products Manufacture", *Ency. of Chem. Tech.*, Vol. 4, 158-202 (1964).
2. Shobert, E. I., II, "Carbon and Graphite", *Modern Materials*, Vol. 4, 37-38 (1964).
3. Nakayama, J. and Ishizuka, M., "Experimental Evidence for Thermal Shock Resistance", *Amer. Cer. Soc. Bull.*, 45, (7), 666-669 (1966).
4. Treusch, A., "Thermal Shock of Fireclay Refractories", M.S. Thesis, The Pennsylvania State University, p. 85, (1973).
5. Sharp, J. D., "Electric Steelmaking", C. R. C. Press, 9-19 (1967).
6. McNanus, G., "Scrap Prices Stir Up Activity in Direct Reduction", *Iron Age*, April 1, 213 (13), 45-56 (1974).
7. Blackman, L. C. F., "Modern Aspects of Graphite Technology", Academic Press, 45-59 (1970).
8. Austin, A. E., "Crystal Structure Properties of Carbon Blacks", Third Conference of Industrial Carbon and Graphite, 389-394 Pergamon Press, (1959).
9. Ubbelohde, A. R. and Lewis, F. A., "Graphite and Its Crystal Compounds", Oxford Press, p. 50, (1950).
10. Hollenbeck, T. M., M. S. Thesis on "Fracture and Thermal Shock of Polycrystalline Electrode Graphites", The Pennsylvania State University, 1975.
11. Kaae, J. L., "The Effect of Annealing on the Microstructures and the Mechanical Properties of Poorly Crystalline Isotropic Pyrolytic Carbons", *Carbon*, 10 (6), 691-699 (1972).
12. Wachtman, J. B., Jr., "Highlights of Progress in the Science of Fracture of Ceramics and Glass", *J. Am. Cer. Soc.*, 57, (12), 509-519 (1974).

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Cover *Gas-fired radiant tubes, in covers which lower over roller conveyors, provide means for controlling temperature to enable slow, uniform cooling of rod coils as they are conveyed to final water wash cooling and inspection. The radiant tube covers, shown framed by the yellow railing and walkway, are in three lines (two shown) of this continuous rod mill. This capability of closely controlling microstructure, regardless of the steel type being processed, allows the development of desired rod properties - particularly a high degree of ductility. (See article on page 8.)*



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