APPARENT CATALYSIS OF GRAPHITIZATION.
IV. EFFECT OF TITANIUM

H. N. Murty,* D. L. Biederman** and E. A. Heintz***
Technical Department
Airco Speer Carbon-Graphite
P. O. Box 828
Niagara Falls, New York 14302

*Present Address: The Carborundum Co., Niagara Falls, N.Y.
**Present Address: Stauffer Chemical Co., Mt. Pleasant, Tenn.
***To whom all correspondence should be addressed.

Additions of titanium at the 5% (wgt.) level enhance the graphitization process to such an extent that a 2500°C heat treated catalyzed coke has a degree of graphitization equivalent to a 2700°C heat treated uncatalyzed coke.

Titanium appears to react with the less organized carbons by a reactive wetting process[1] in which some recrystallization of graphite is observed alongside of the titanium carbide formed during the heating process. In all cases, it is apparent that the catalyst reacts with the less-organized carbons[2] which tend to enhance their mobility and that of the catalyst[3,4] to enhance the graphitization process.

The cokes used in this study were typical of the graphite industry. Coke A was a premium rotary calcined petroleum coke; Coke B was a well-aligned vertically calcined petroleum coke while Coke C was a rotary calcined isotropic coke prepared from the mineral Gilsonite. All prior heat treatments, sizing of the cokes and x-ray diffraction data were performed as described previously.[5,6]

The titanium metal used was obtained from Alfa Products Division of Ventron Corporation as a -325 mesh powder with a minimum purity of 99% (wgt.). The desired amount of metal was added to the coke sample and intimately blended to ensure uniformity. To avoid segregation effects due to storage, each coke-metal sample was prepared and blended immediately prior to the heat treatment. Analysis of the one-hour, 2700°C heat treated samples before and after the heat treatment showed that no detectable amount of the titanium was lost during the heat treatment. In all cases, a level of 5% (wgt.) titanium powder was added to the cokes. Unadulterated samples were calcined in separate compartments at the same time in order to ensure constancy of heat treatment. Duplicate runs were performed at each temperature and the x-ray data, reported in Table I, for these runs never differed by more than 0.0006Å; averages are presented in Table I for Cokes A and B. Coke C behaves similarly.

TABLE I

Interlayer Spacing of Catalyzed and Uncatalyzed Cokes

Temperature (°C)	Interlayer Spacing ($c_t/2$, Å)			
	Coke A		Coke B	
	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
1600	3.4331	3.4357	3.4266	3.4305
1700	3.4253	--	3.4227	--
1800	3.4279	3.4243	3.4214	3.4253
1900	3.4240	3.4231	3.4214	3.4249
2000	3.4219	3.4208	3.4225	3.4208
2200	3.4090	3.4037	3.4101	3.4037
2300	3.3880	3.3851	3.3886	3.3851
2400	3.3815	--	3.3833	--
2500	3.3724	3.3650	3.3730	3.3656
2600	3.3700	--	3.3698	--
2700	3.3656	3.3582	3.3667	3.3599

The Mering and Maire[7] degree of graphitization for the same materials were calculated and showed that there is little, if any, catalysis of graphitization up to 2000°C, confirming the report of Whittaker and Fritz.[8] Above 2200°C there is a rapid decrease in interlayer spacing and rapid increase in the degree of graphitization for the titanium doped coke samples. Generally, the degree of graphitization for the catalyzed cokes at 2500°C is equivalent to the

degree of graphitization of the uncatalyzed cokes at 2700°C. It is interesting to note that the catalytic effect appears to proceed as Coke A > Coke B > Coke C, that is in the order of decreasing anisotropy. In other words the presence of titanium had the greatest catalytic effect on the most anisotropic coke.

Some recent work by Matthews and Jenkins[1] has shown that titanium metal shows definite signs of wetting graphite in the process of being heated to 2700°C. Once the graphite and titanium react, however, cubic particles of titanium carbide are visible on the surface as detected by stereoscan microscopy. Some re-crystallization of the graphite near the titanium carbide particles appears evident. One could tacitly assume that the (liquid) titanium metal reacts with those groups of carbon atoms which were not as highly developed as some of their neighbors. These could be considered to be analogous to those specific atoms which are thought to decelerate the graphitization process.[2] Since there is evidence for some recrystallization of graphite alongside the titanium carbide particles,[1] the conclusion could be made that the wetting by the titanium assisted in their further development. This view is quite consistent with the observation of others concerning the mobility and preferential removal of selected carbon atoms in the catalysis of graphitization.[2,3,4]

Marsh and Warburton have also recently reported the catalytic influence of titanium additions of up to 20% (wgt.) on three cokes of varying anisotropy.[9] They measured crystallite-height and -diameter and found some catalytic activity at temperatures as low as 1600°C but considerable enhancement of graphitization at 2700°C, especially for the most isotropic coke. They concluded that the most probable mechanism of catalysis involves dissolution with subsequent precipitation of graphite at increasing temperatures. Unfortunately, no interlayer spacing data is presented so no direct comparison of the increased degree of graphitization can be made with this work. Nonetheless, the importance of carbide formation and the structure of the initial carbon is stressed in the work of Marsh and Warburton[9] and confirmed by Matthews and Jenkins.[1]

In the present study, the useful liquid phase is very small, from 1675°C (melting point of titanium) to ca. 1900°C (formation of carbide). Reference to both the interlayer spacing and degree of graphitization data, as a function of heat treatment temperature, show that little, if any, catalysis occurs by titanium below 2000°C. However, at temperatures in excess of 2200°C con-

siderable catalysis occurs, again suggesting that the carbon atoms used in the formation of the carbide were those decelerating the graphitization process in the uncatalyzed cokes. Of significant practical interest in the manufacture of graphite, is the fact that if the carbides decompose (to the metal vapour and graphite), apparent graphitization occurs at a lower temperature than when the carbide exhibits high thermal stability.

Using the method reported earlier,[5,6] apparent activation energies (E_a) of the titanium catalyzed systems may be calculated. Using the parameter, g_0, defined previously as a kinetic function, the apparent activation energies may be calculated and are presented in Table II. The similarity of the catalyzed and uncatalyzed E_a values indicates that the mechanism of the graphitization process is, at least, similar in both cases, but the rate has certainly been increased as shown by the displacement of the lattice constant values listed in Table I.

TABLE II
Activation Energies (E_a) for the Catalyzed and Uncatalyzed Systems

Coke	E_a, Kcal/mole	
	Uncatalyzed[5]	Catalyzed With 5% (wgt.) TI
A	231	242
B	226	264
C	219	220

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