Puffing of Carbon Artifacts During Graphitization

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Introduction

It is well known that puffing, i.e. irreversible volumetric expansion of carbon artifacts during graphitization, is correlated to sulfur release from coke. Puffing decreases bulk density, strength, electrical and thermal conductivity, and can induce the formation of cracks. Graphite manufactures have a long experience in dealing with the puffing phenomenon /1/, and production parameters influencing puffing, e.g. sulfur content of coke, heating rate, grain size, calcination temperature, and puffing inhibitors have been studied extensively /2-8/.

The puffing effect is generally understood as being due to the spontaneous release of organic (basically thiophenic) sulfur from the carbon crystal structure, the pressure of the volatile sulfurous gases (elemental sulfur, polysulfur, and possibly H,S and CS,) being responsible for the volumetric expansion by creation of porosity between the crystal lamellae. However, as shown in a companion paper /9/, sulfur evolution of medium and high sulfur cokes starts at 1200 to 1300 °C leading to pre-puffing, i.e. creation of closed porosity without any macroscopic expansion of coke grains. The begin of puffing of coke grains and artifacts made thereof is observed at temperatures some 300 K higher, at 1500 to 1600 °C. It will be demonstrated here that puffing, i.e. macroscopic expansion of coke grains, can only start at pregraphitization temperatures, where the carbon structure softens due to crystal alignment in c-direction.

Experimental

Calcined petroleum cokes A, D, and F with low (0.19 %), medium (1.07 %) and high (1.53 %) sulfur content were processed under standard conditions (maximum grain size 1 mm, no puffing inhibitor added) to rods of diameter 70 mm. Details of coke properties are presented in table 1 and /9/. The extruded stock was backed to 1000 °C and finally heat treated to temperatures between 1200 and 3000 °C. The mechanical and electrical properties after heat treatment were determined by standard laboratory methods.

Results and Discussion

Dynamic Young's modulus (parallel and perpendicular to grain) and compressive strength of artifacts made from cokes A, D, and F are presented in figs. 1 and 2 as a function of heat treatment temperature. It is obvious that modulus and strength show a drastic decrease in the temperature range from 1000 to 2000 °C with a definite minimum at 2000 °C and some recovery at higher temperatures. Within a few hundred Kelvin around 1600 °C, modulus and strength fall from the high niveau of carbon to the low niveau of graphite.

This transition correlates well with the pregraphitization stage as described by A. Oberlin and coworkers from electron microscopy work /10-12/; crystal growth occurs first in c-direction (pregraphitization stage) and then in a-direction (graphitization). Pregraphitization takes place between 1500 and 2000 °C. By removal of interstitials, small mosaic elements about 10 A in size (aromatic layers with 4 to 10 rings, stacked by N = 2 to 3) become associated in an almost parallel alignment in the crystalite c-direction. N, the number of layers in stack, increases drastically, but L, does not change, since only interstitials are removed but not in-plane defects. In-plane defects disappear at temperatures above 2000 °C,
leading to a drastic growth of layer diameter $L$. The aromatic layers become stiff and perfect. At the same time, the $\pi$ electrons of the perfect lattice acquire a semimetallic character and the electrical resistivity decreases drastically.

It is obvious that puffing is associated with pregraphitization: a prerequisite for macroscopic expansion of carbon grains forced by sulfurous gases is a softening of the carbon lattice by crystal ordering in c-direction. Below 1500 to 1600 °C, the grain structure can resist the pressure of the volatile sulfurous gases to some extent and only microporosity develops without macroscopic expansion of the carbon grains (fig. 3).

Conclusions

It has been demonstrated that the two-stage graphitization process as observed by A. Oberlin and coworkers with electron microscopy methods can be seen clearly from artifact data: crystal c-axis growth, i.e. drastic increase of carbon layers in stack during pregraphitization stage (1500 to 2000 °C), is associated with transition of modulus and strength from the carbon to the graphite level. Puffing, i.e. macroscopic expansion of the carbon grain structure by outbursting sulfurous gases, is only possible after the begin of this transition. On the other hand, graphitization, i.e. growth of layer diameter $L$ by removal of inplane defects, takes place above 2000 °C and can be followed, e.g., by the decrease of electrical resistivity.

References

/11/ A. Oberlin, G. Terriere, J.L. Boulnier, Tanso, 80 (1975) 29; 83 (1075) 153.