

CARBON MICROSTRUCTURAL DEVELOPMENT AT HIGH PRESSURES

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Introduction

In recent years there has been a continually increasing interest in the effect of pressure on the chemistry and kinetics of various organic compounds during pyrolysis and carbonization (1,2,3). Corresponding interest in the development and formation of mesophase carbon from various organic compounds has also been reported (4,5,6). The formation of mesophase has been shown to be a key process in the transformation or organic liquids to graphitizable carbon. The importance of heating rate, composition, and pressure in the development of mesophase has been demonstrated but a real understanding of methods for controlling and maintaining this phase have not yet been developed. Pressure has been shown to have a pronounced effect on carbonization mechanisms but the lack of control or lack of understanding of how to control the mesophase development under pressure has lead to only small scale laboratory experiments relating to these effects.

Experiments to-date have not emphasized the relationship between carbonization effects and pressure methods. These techniques have included conventional hot pressing in heated dies, low pressure (less than 1000 psi) standard gas autoclaving and high pressures gas processing (greater than 10,000 psi). The behavior of any organic compound during carbonization will be dependent on the method in which pressure is applied. The carbon yield will be effected by the specific technique used but more importantly, the microstructural development of the carbon during decomposition of the organic compound will be significantly affected. The extent of mesophase coalescence and gas-phase bubble percolation and related carbon morphology are dependent on the specific pressurization method and not merely the pressure at which carbonization has been performed.

Pressure Processing Description

Within the past ten years the hot isostatic pressing (HIP) process has been developed into an efficient fabrication technique for producing unique powder metallurgy components and more recently in densifying high performance 3D carbon-carbon composites for strategic missile nose tip and rocket nozzle throat applications (7,8). The process developed to densify and carbonize porous woven carbon fiber preforms has been identified as high pressure impregnation/carbonization (HiPIC). The process essentially involves the carbonization of liquid pitch impregnated preforms at temperature of 650 C and pressures of 15,000 psi in sealed steel containers. The typical carbonization cycle is illustrated in Figure 1. Performing the pyrolysis and carbonization in vacuum sealed metal cans significantly retards the bubble nucleation characteristics of the gaseous decomposition products and reduces

the coalescing tendencies of the mesophase. The solubility of gaseous decomposition products is significantly increased and the kinetics of carbonization are retarded. The microstructural development of the carbon solid is therefore directly related to the sequences which occur within the processing containers and the ability of the container to remain sealed.

Experiments at Battelle Columbus Laboratories identified that a significant increase in temperature occurs within 15-inch diameter by 20-inch long processing containers when the cans fail to remain sealed during carbonization (9). Temperatures within these pitch-filled containers raised from approximately 520 C to over 800 C in several minutes time while carbonizing at 15,000 psi. This "exotherm" effect is apparently due to either increased heats of reaction within the pitch liquid after the container failed due to pressure build-up from decomposition gases or to an actual exotherm which occurred as the result of carbonization which caused a large gaseous decomposition effect which in turn caused the container to fail. It is proposed that the "exotherm" was caused by the failure of the container which in turn increased the decomposition and carbonization reactions in the pressurized pitch. The microstructural development of the carbon solid from the liquid pitch will be dependent on the type of processing container, open or sealed can, and the pressure and temperature parameters during carbonization in the 400 to 600 C range.

The carbonization of pitch impregnants while at pressures of 15,000 psi has produced a high density, fine porosity carbon not attainable by conventional techniques. Other advantages include (1) over 90 weight percent carbon (coke) yields from coal tar pitch, (2) short processing cycle times in attaining high density carbon (graphite) materials, and (3) refined microstructured carbons (graphites). The process is still being developed and little fundamental research work has been performed in understanding the chemistry and kinetics which are occurring.

Discussions of Results

The microstructure, and properties, of carbon-carbon composites and bulk graphites are dependent on the specific methods used in carbonizing organic precursors. The ability of a process to control and reduce mesophase coalescence is dependent upon reducing bubble nucleation and gaseous decomposition products in a liquid organic during carbonization. Not only can a unique fine-grained isotropic carbon (graphite) be produced if this condition is controlled but a fine pore structure, homogeneous bulk solid is produced. Process economic or processing time may also be significantly improved. Numerous

unique microstructural carbons (graphites) have been observed during the development of the HiPIC process.

Highly graphitizable carbons have been produced utilizing HiPIC processing of coal tar pitch materials. Coke yields always exceed 90 weight percent and the microstructural character of the carbon (graphite) solid is dependent on certain conditions during processing such as when can failure time, impregnant composition, carbonization pressure and the presence of substrate surfaces. The characteristics of the excess coke (carbon) surrounding the C/C materials is different than the microstructure of the carbon within the fiber preform at the pore interstices. The fiber surfaces appear to modify the nucleating characteristics of the carbon but the extent to which this can be controlled is not known. The microstructural characteristics of carbon formed outside of the fiber preforms is illustrated in Figure 2. Although both the fine-grained and coarser structures possess the same bulk

porosity, the inherent microstructure is considerably different. The difference in microstructure is caused by the time at which the container fails and thermal fluctuations within the cans. Some of the most interesting microstructures have been observed in large pores within the coke mass surrounding the preforms. Suspended mesophase concentrations have been observed along one side of numerous pores, as illustrated in Figures 3 and 4, while adjacent areas show mesophase coalescing into a solid surface structure. The use of higher carbonization pressures may develop a more stable mesophase microstructure by eliminating or retarding can failure and maintaining mesophase stability without coalescence through the liquid/solid carbonization range. The hot isostatic carbonization of organic precursors does allow for unique control of carbon microstructures and products in large production size capabilities. Further development of this process is expected to produce unique carbon-bar materials of unusual quality.

References

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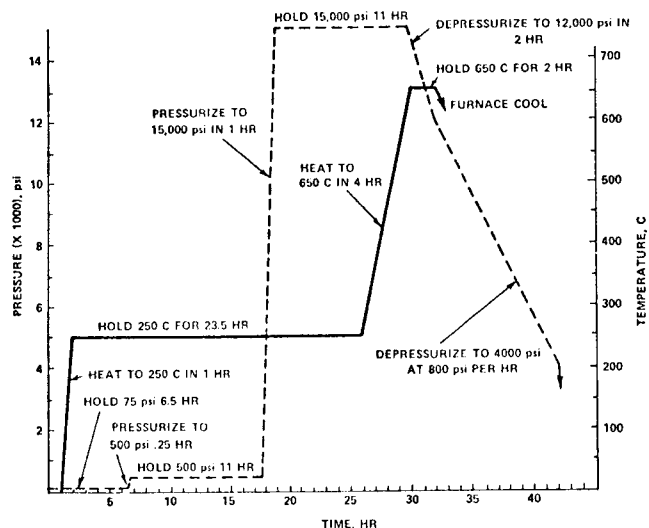


FIG. 1. HiPIC PROCESSING CYCLE

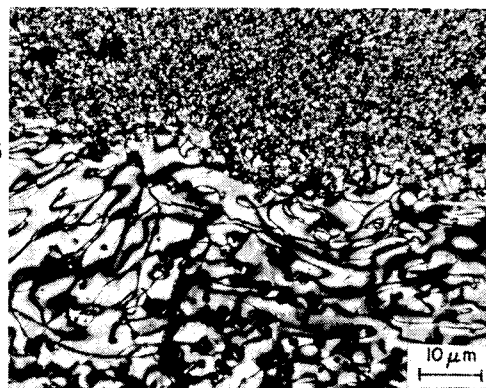


FIG. 2. HiPIC CARBON MICROSTRUCTURES

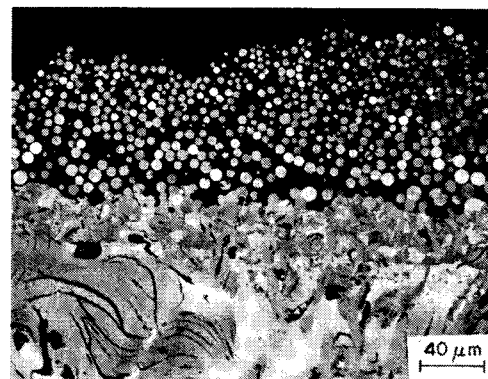


FIG. 3. HiPIC MESOPHASE DEVELOPMENT

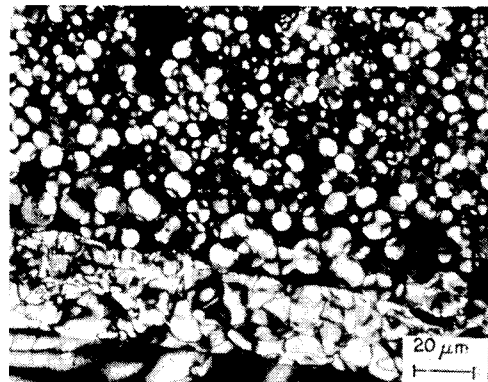


FIG. 4. HiPIC MESOPHASE, POLARIZED LIGHT