LOW-PERMEABILITY GRAPHITE : A STUDY OF SELECTED ORGANIC IMPREGNANTS

ABSTRACT

A commercial extruded fine grain graphite, having a permeability in the region of 1.10^{-2} cms^2/sec, has been processed to yield a wholly carbonaceous material having a uniform permeability to dry air below 1.10^{-6} cms^2/sec, throughout a wall thickness of 1cm. The development of a reliable and consistent process demands that the pore structure of the material, at all stages of processing, be characterised more fully than is possible using the mercury porosimeter and the gas-flow properties alone.
The introduction of carbon into the pore network may be accomplished by the pyrolysis in situ of a wide range of organic materials; however there are correspondingly wide differences in the properties of the treated material into which a given amount of carbon has been introduced, which arise mainly from the pyrolysis characteristics of the impregnant. The residual char may vary considerably in apparent density, it may be microporous, it may or may not be graphitisable, it may conform to the pore wall or shrink away, it may be deposited preferentially in large voids or at constrictions, or it may even be non-uniform in macroscopic distribution. In reducing the permeability of a given material, an ideal process will first reduce the size of those internal voids which exceed the maximum access pore diameter as revealed by the mercury porosimeter, and thereafter reduce the pore network more-or-less uniformly until the desired permeability has been attained.
The latitude which exists in regard to departures from this ideal is inversely related to the permeability required; low-permeability treatments are therefore particularly exacting.
Acrylonitrile, when used as an impregnant with a suitable free-radical initiator, exhibits polymerisation characteristics which reflect the geometry of the pore network; at any given initiator concentration there is a minimum pore size in which polymerisation can be initiated.
The experimental facts suggest that the pore walls rapidly adsorb the free radicals released by the dissociation of the initiator, until the internal surface has become saturated; thereafter, if the local supply of initiator has not been exhausted, polymerisation will commence.
Thus acrylonitrile is able to see beyond the flow-controlling constrictions which limit the information furnished by the mercury porosimeter, and can discriminate between networks which appear identical by the usual criteria of permeability, porosimetry and surface area, but in fact possess different void-size distributions. This additional characterisation of the pore network increases the total information to the point where consistent and comprehensive explanations can be offered for the modus operandi of the four selected impregnants. Fortunately there turns out to be few points of similarity between these four impregnants, each one of which has distinctive characteristics.

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It is found that acrylonitrile, used as an impregnant for permeability reduction, is appropriate for the initial treatments of coarse-grain graphite in large sizes and that it is also appropriate to the final stages of low-permeability treatments, with certain reservations on the pore structure which can be processed.
It is also shown that furfuryl alcohol selectively attacks the finer pores and can be most effectively used for this purpose provided that the pore network is one which remains incompletely filled ($\sim 85\%$ max.) by simple immersion of the specimen.
Furfuraldehyde-aniline is a valuable impregnant for the medium pore region (roughly 10 - 0.5μ), the carbon residue from which undergoes a particularly high shrinkage on graphitisation. Where the pore geometry is appropriate, it is possible to accomplish strategic blocking with this impregnant, which being effected after complete elimination of volatiles is a feasible short-cut to reducing the accessible void volume.
Finally, trichlorethylene-modified acrylonitrile is found to be very different from straight acrylonitrile, and is virtually foolproof as an impregnant for difficult materials. It resembles pitch in its ability to fill large voids with little effect on the flow-controlling constrictions, but does not suffer from exudation or inhomogeneous distribution, is highly penetrating, may be used repetitively, and remains effective to permeabilities of about 1.10^{-6} cms^2/sec.
Although none of the other impregnants can be used repetitively on EYX60 certain mixed treatments are satisfactory. In the light of retrospective understanding, however, better mixed treatments could probably be devised.
Many examples are given of the changes in permeability and pore structure brought about by various impregnation sequences.

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