PRODUCTION SCALE UP OF THE GRAPHNOL N PROCESS

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A raw petroleum coke base, fine grain graphite, Graphnol N3, is one of several developed on a laboratory scale by Oak Ridge National Laboratory for the U.S. Navy. The unique Graphnol materials exhibit high thermal shock resistance and very high strain-to-failure (elasticity) characteristics. Therefore, these graphites are particularly well-qualified for aerospace nosecone and leading edge applications. At Great Lakes Research Corporation (GLRC) the Graphnol N3 process has been modified and scaled-up under sponsorship of the Naval Surface Weapons Command.[1] The scale-up to 5øx9 inch production-size billets represented a volume increase of some eight times that of laboratory billets. This necessitated a corresponding increase in batch size and equipment capacities.

The distinctive process, as indicated in the accompanying flow chart, involved preliminary coke homogenization through blending and uniform heat treatment followed by close preliminary sizing of the raw petroleum coke filler with a maximum particle size of 120 mesh (125μ). Approximately twenty five percent of the minus 400 mesh (37μ) material is removed for graphitizing at 2500°C.

The graphitized fines are reblended with the original coke and combined with 30 medium (S.P. ca. 103°C) pitch in a solvent slurry operation. This "mix" then is heat treated to 325°C for one hour. All heat-treated material is remilled and combined with A-240 petroleum pitch and a plasticizing agent in a second solvent slurry operation. This "mix" is allowed to air dry before final milling and molding.

The material is molded at 100°C and 2000 psi and then allowed to cool under pressure to room temperature, before ejection.

Each green billet is loaded into a graphite-lined steel restraint. The billets are baked to 820°C in six days followed by pitch impregnation and rebake before graphitization to 3200°C.

During the scale-up of this process the following parameters were found to be critical: 1) the furnace oxygen level during heat treatment of the coke-pitch mixtures; 2) the particle size distribution at each milling step; 3) green density during molding; 4) the bake cycle to achieve desired baked density; 5) percent pitch pick-up as an indicator of both billet uniformity and proper baking off-fire temperature.

The ability to protect larger batches from oxidation during heat treatment of the coke-pitch mixes became an obvious first requirement to achieve the required green density. An oxygen level of less than 100 ppm is required during the heating of the mixes. Higher levels cause enough embrittlement of the pitch coating to greatly reduce compaction during molding. Mixes heat-treated within the control limit for oxygen produced densities of 1.41±.01 g/cc while oxidized mixes yielded green densities of 1.25 g/cc. Billets of marginal green density could be processed successfully through graphite only to exhibit high resistivity, indicative of previous oxidation. Modifications of the furnace design and of the techniques for oxygen analysis proved to be very successful in this regard.

Mix agglomeration, which had plagued previous scale-up attempts, occurs while preheating the mix for molding. A main objective during this contract was to eliminate the agglomeration in order to guarantee structural integrity and consistent within-billet properties. This has been accomplished by means of a cold mix-screening and precompacting step. The resulting cold compacts, although low density (1.10 g/cc), are easily handled and subsequently uniformly heated prior to final molding.

In order to maintain geometric uniformity and maximize baked density, each billet is baked in a separate graphite-lined steel restraint. The original, internally-threaded design was altered to include a set of external bolts which provided ease in assembly and disassembly of the units and prolonged the life of the shrink-fitted liners.

Studies of bake cycle parameters led to adoption of an eight day schedule employing heating rates of 10° per hour to 200°C, 4° per hour to 600°C and 6° per hour to an 820°C off-fire temperature. Cooldown rates of 50-70°C per hour, as obtained by cutting the furnace power at off-fire temperature, developed hoop stresses in the 5øx9 inch billets and caused linear splits on the surface. A controlled 6° per hour cooldown to 500°C followed by natural cooling at 20° per hour to 200°C yielded excellent billets. After the adoption of this cycle, no defects in the billets could be attributed to the baking step.

Large-scale graphitization at 3200°C of up to twelve 5øx9 inch billets per load was successfully accomplished with a 31 hour heating schedule. The off-fire temperature has not been finalized due to the fact that the slower rate and larger loads used in the scaled-up equipment led to longer cooldown periods and may provide conditions for overgraphitization. This over-graphitization could cause degradation of some properties.

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Table I

Non-Destructive Physical Test Results of Graphnol N3: 3øx3 and 5øx9 Inch Billets

Pc	Density g/cc	Resistivity ohm-cmx10^{-5} WG	AG	MOE psi x 10^{-6}
3øx3-1	1.785	710	960	0.97
-2	1.782	715	1015	0.96
-3	1.811	750	1060	1.09
-4	1.806	670	885	1.06
-5	1.776	640	885	0.96
-6	1.787	645	900	1.04
5øx9-1	1.774	620	900	0.90
-2	1.773	660	850	0.93
-3	1.790	620	890	0.96
-4	1.777	640	940	0.96
-5	1.773	660	900	1.00
-6	1.787	615	940	0.95

FLOW SHEET A
COKE PREPARATION

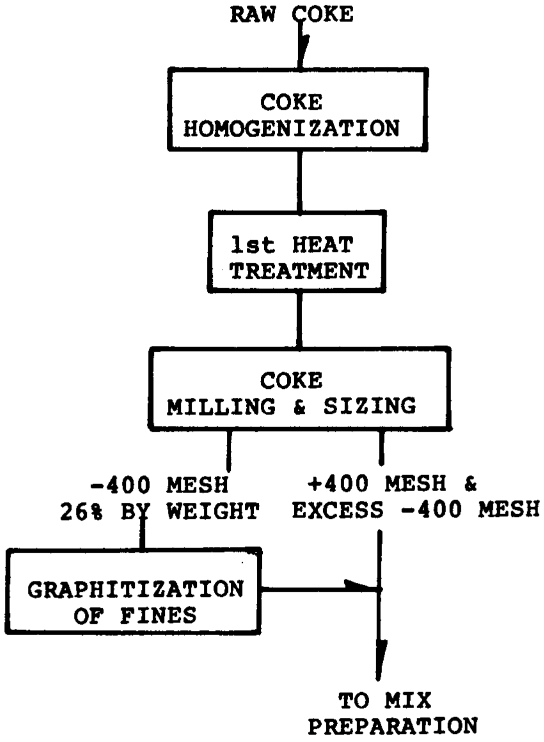

Table 1 shows initial non-destructive test comparisons between the 3øx3 and the 5øx9 inch billets produced at GLRC.

Further production work at the scaled-up level will allow for the optimization of process flow as well as for finalization of the specifications for the various process check points.

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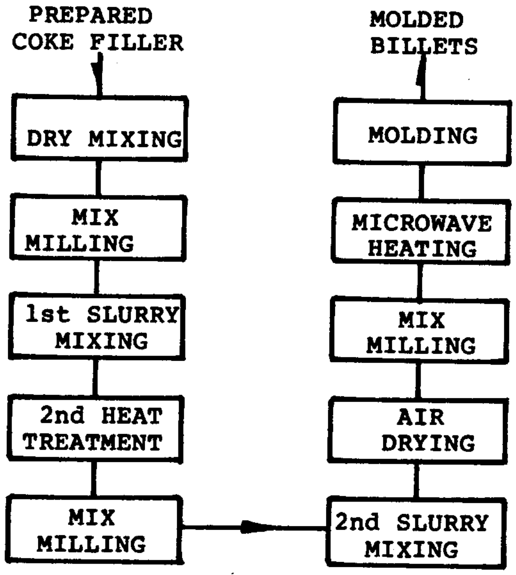
[1]Contract No. N-00197-76-C-0088

FLOW SHEET B
MIX PREPARATION AND MOLDING



FLOW SHEET C
HIGH TEMPERATURE PROCESSING