PRODUCTION OF LARGE ITEMS OF HOLLOW WARE OF GLASSY POLYMERIC CARBON WITH UNIFORM WALL THICKNESS USING SPRAY TECHNIQUE*

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INTRODUCTION

Radio frequency induction heating in the crucible wall permits improved thermal control of the melt solid interface shape in Bridgman-Stockbarger crystal growth. This in turn will improve compositional uniformity and crystallinity. The crucible must: be refractory to withstand the semiconductor melt temperatures, have material strength to withstand the internal vapor pressure of the melt constituents [1], be chemically inert to materials being grown, be sealed because the volatility of the constituents, and be electrically conducting to serve as a rf susceptor. The only likely crucible material is glassy polymeric carbon (GPC), studied since the 1960's. A detailed review of past research on fabrication and characterization of GPC is found in Reference 2.

Production of large scale GPC hollow ware is an enhancement of prototype techniques developed at Alabama A&M University [3]. We make GPC hollow ware precursors by repeated spraying of thin layers ($\approx 5\mu m$) of thermoset phenolic resin onto a hot rotating mandrel. The heat gels the phenolic resin on the mandrel. The precursor gel is further cured and hardened at a temperature below the melting point of the mandrel. The mandrel is then melted for removal and to initiate post curing of the phenolic precursor. Pyrolization and carbonization of the resin forms the glassy polymeric carbon ware. The resin is known to contract, become electrically conductive, and gain in mechanical strength upon pyrolization and carbonization into GPC.

The prototype technique produced only small artifacts primarily due to technical difficulties which are the subject of this paper. GPC contraction measurements are discussed along with room temperature mechanical and electrical characterization of GPC samples heat treated between 1270 and 2770 K.

EXPERIMENTAL

Production of GPC hollow ware begins with the casting of a mandrel onto a tubular steel liner. Bi-Sn eutectic was chosen as the mandrel material because its melting temperature was conveniently between the initial gelling temperature and the post curing temperature of the resin. A 1.2 meter long, 15.8 mm diameter mandrel split mold was designed to eliminate leakage at the large hydrostatic pressure encountered. Initially air bubbles were trapped on the mold during solidification. The trapping of air was apparent from craters on the surface of the cast. A long wire coil under compression is inserted into the heated mold prior to filling with the melt. The coil is pulled through the melt to scrape away any air bubbles and the mold is "topped up" with melt to replace the volume of the released air. The mandrel is cooled, removed from the mold, and polished to a smooth surface.

Our crucible generation station was built from a glass blower's lathe. A schematic of the station is shown in Figure 1. The non-rotating internal heater cartridge was developed with assistance of the Thermal Corporation (Huntsville, AL) to provide uniform linear power density. The mandrel is heated to the gelling temperature and sprayed automatically with many thin layers of resin to reach the a desired thickness ($\approx$ 2 mm). Sample thickness is limited to < 5 mm due to excessive diffusion driven heat treatment time. The eutectic mandrel is then carefully melted from the resin precursor with support to maintain crucible shape. The precursor samples were pyrolized to 1270 K and carbonized up to 2770 K in the High Temperature Furnace at the university. Heating profiles were developed for both processes to minimize thermal shock to the crucible.

After heat treatment to 1270 K, several GPC crucibles were cut into short samples using a diamond saw. Samples were characterized for mass loss and geometric shrinkage. A Kelvin double bridge was used to determine the room temperature electrical resistivity. Hoop stress analysis equipment was developed using wound constantan wire strain gauges for measurement of the hoop strength and stiffness. Stress analysis was performed to determine stress, strain, Young's modulus, and ultimate hoop strength. The system was calibrated by tests on Inconel 600 samples. These measurements were within 5% of handbook values for yield strength and Young's modulus.

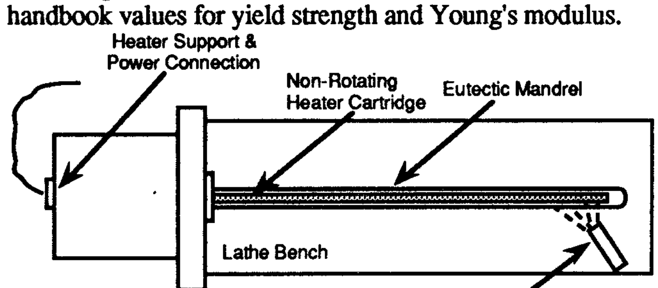

Figure 1 - Crucible Generation Lathe Schematic

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RESULTS AND DISCUSSION

Experimental results were compared to measurements of GPC properties in reference 2 for samples produced by other techniques.

Resin samples had approximately 10-15 % mass loss through the initial post-cure stage. Pyrolization to 1270 K yielded mass losses of ≈ 45 %. Negligible mass loss of less than 1-2 % was observed between 1270 and 2770 K. The mass loss was compared to mass loss test of GPC from Phenol-hexamine based resins [2]. The mass loss measurements were approximately the same as those shown for GPC from a Phenol to hexamine ratio of 6:1.

Linear shrinkage was measured for samples heat treated between 1270 and 2770 K. Again, little contraction occurred above 1270 K. Total linear shrinkage was approximately 18-19 % and these values are within 5 % of reported by Jenkins and Kawamura [2].

The electrical resistivity of polymeric carbon drops over 10 orders of magnitude from the cured resin to the GPC form. Electrical resistivity was measured at room temperature as a function of heat treatment temperature (HTT). The electrical resistivity is ≈ 7×10^{-2} Ω-mm for HTT of 1270 K and ≈ 3×10^{-2} Ω-mm for HTT of 2770 K. These resistivity values are compared to results from Jenkins and Kawamura in Figure 2.

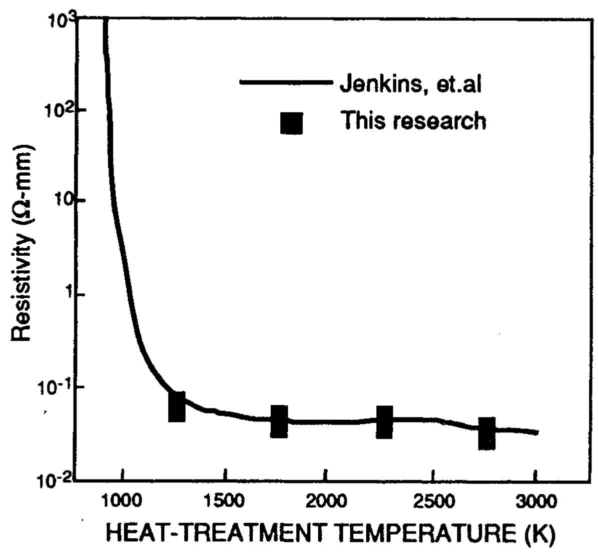

Figure 2 - GPC resistivity vs. heat treatment temperature

The mechanical properties of GPC were measured at room temperature for samples with HTT of 1270 K to 2770 K. All samples exhibit characteristic hoop failure initiating at the center. The ultimate hoop strength revealed scatter plot characteristic of brittle fracture. Samples failing at lower stress had fractures beginning at only a few points. Samples failing at the highest stress show fracture starting at all points around the hoop of maximum stress. Hoop strength varied between 25 and 90 MPa for the 1270 K samples. The strength of the 2770 K samples had values between 40 and 80 MPa. Samples treated at 1770 and 2270 K had hoop strengths of 25 to 30 MPa. The maximum ultimate strength of bulk GPC was found by Fitzer and Schafer [4] to be 150 MPa.

Our strain gauge allowed determination of Young's modulus. Samples showing the largest hoop strength exhibited some yielding before rupture. Young's moduli for this research are compared in Figure 3 with Jenkins and Kawamura [2]. The curve marked "glassy carbon" is bulk isotropic material. The "high modulus" carbon fibre had preferred orientation. The "Swansea Fibre" contained an isotropic core surrounded by textured carbon. Our research closely matches the "Swansea fibre" indicating some preferred hoop orientation. Laue diffraction will be used to further investigate the hoop structure.

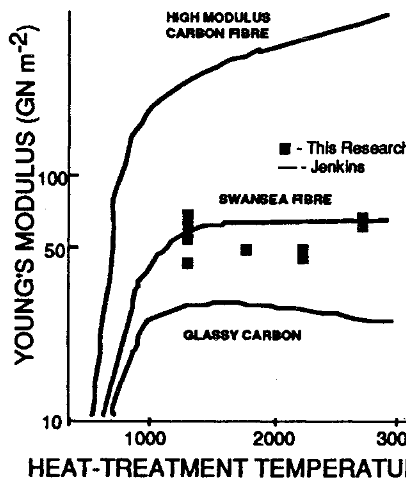

Figure 3 - GPC modulus vs. heat treatment temperature

CONCLUSIONS

Large crucibles, 0.6-.7 m long with 12.7 mm ID, of GPC with open or closed ends have been made by a multiple step process developed at Alabama A&M University. The size of carbon ware is limited primarily by the heat treatment equipment. Material shrinkage, electrical properties, and mechanical properties have been compared to past research. All measurements, except the Young's modulus, yielded results as expected. The Young's modulus anomaly requires additional research.

REFERENCES

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