POSTER

OPTIMIZATION OF THE IRON III CHLORIDE INTERCALATION OF GRAPHITE FIBERS

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INTRODUCTION

Intercalated graphite fibers have been proposed for several applications where high strength, low density, and at least moderately high electrical conductivity are required[1]. Before these fibers could be utilized, production methods must be scaled up from laboratory scale to production scale. Some intercalation reactions, such as those with bromine, appear to be remarkably insensitive to reaction conditions[2], but others, such as ferric chloride ($FeCl_3$) are not so forgiving.

$FeCl_3$ intercalated graphite has been produced under a variety of conditions, utilizing a variety of host graphites. In this study a response surface methodology (RSM) was utilized in an attempt to optimize the conditions to make low electrical resistivity P-100 graphite fibers. The strategy of RSM is to vary the process conditions in small increments in a statistically guided manner to move the process from an initial region of operation to a region of optimum operating condition. A laboratory optimization will guide the scale-up of this reaction.

EXPERIMENTAL

Thornel P-100 fibers purchased from Amoco were selected for this study because of their availability and ease of intercalation. $FeCl_3$ was purchased from Fisher and recrystallized once under vacuum. Experiments used 5.3 mg of fiber and 8-16 mg of $FeCl_3$ in 10 mm diameter pyrex tubes about 14 cm long sealed under vacuum.

After the intercalation runs, the vials were broken open and 12 fibers were mounted on resistance measurement plates using silver paint. Four-point resistivity measurements were made as described elsewhere[3]. The remainder of the fibers were stored in a vacuum desiccator with a $CaSO_4$ dessicant, to minimize their degradation due to water vapor[4].

The conditions varied were intercalation time and temperature, and the monitored variable was electrical resistivity. An initial time and temperature was selected using the literature and the results of preliminary experiments. Experiments with time and temperature lying at the four corners of a cube and four experiments at the center point in the time-temperature space were first run.

The resistivities of 12 fibers were measured for each experiment in order to judge fiber to fiber reproducibility within a chemical environment. The center point experiments were run four times to judge reproducibility. A regression to a second order response surface was calculated and analyzed using the SAS statistical package. Response surfaces were calculated and used to set the center point of the next experimental series.

A second set of experiments sought to move the process area to one closer to the optimum. A line was drawn in parameter space that followed the original surface from its lowest data point along the path of steepest descent. A series of incremental experiments following that line were run until the average resistivity began to rise again.

The third set of experiments was set up like the first, except that it was centered along the minimum point from the second set. In addition, a third variable was added, the difference in temperature between intercalate zone and the graphite zone of the tube furnace. This temperature difference was 25 °C in the first two experiments, but was allowed to be 15 or 35 °C in the third experimental set.

To verify the intercalation, x-ray diffraction patterns using filtered $Mo_{K\alpha}$ radiation were measured using bundles of several hundred fibers on a Huber Precession Camera mounted on a Rigaku RU-200 rotating anode generator.

RESULTS AND DISCUSSION

Regression to a response surface of the first set of experiments yielded a best fit resistivity dependence of time (t), in hours, and temperature (T), in °C of:

$$\rho = -26.57t^2 + 391.1t - .000903tT + 1.538T - 1798$$

The t^2 dependence was statistically significant, but the errors on the rest of the parameters (t, tT, T and intercept) make their usefulness suspect. The spread in the resistivity values is attributable to the intercalation being nearly binary in its interaction. Either intercalation occurs, resulting in resistivity from 10 - 35 $\mu\Omega$-cm, or it does not, resulting in resistivity from 200 - 300 $\mu\Omega$-cm.

Unlike the bromine system, there are some fibers which are either partially intercalated or intercalated at high stage number, but the large difference between pristine and intercalated fiber resistivity inhibits the analysis.

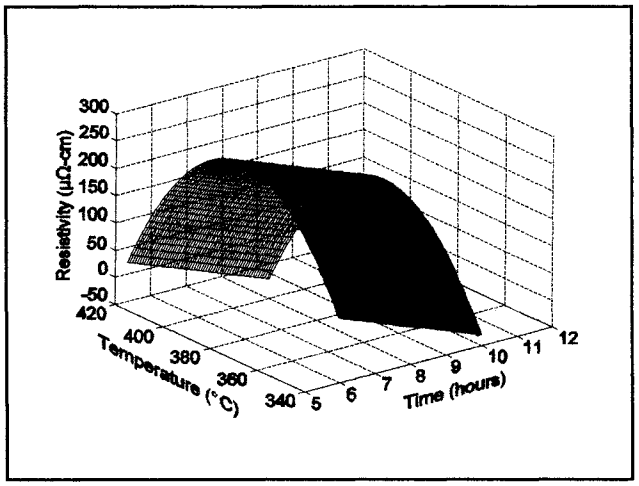

Figure 1 -- Resistivity response surface calculated after the first suite of experiments.

A plot of the response surface (Fig 1) was used to determine the steepest descent off of the lowest resistivity data point, 10 hours at 370 °C. This lead to incrementing the time by 2 hr, and the temperature by -4 °C. This analysis showed that over the range of 350 - 370 °C, the resistivity was independent of the temperature. The time dependence appeared to be quadratic, but small over the time range of 12 - 20 hours. The minimum occurred at about 15.25 hours, but was fairly broad.

The third experimental box design was built around the point 16 hr, 358 °C, and a temperature difference between the graphite and the intercalate of 25 °C. Over this range of variables, resistivity values were distributed nearly randomly, with F ratios (deviation due to parameter/deviation due to random error) just over 2. This was taken to be convergence.

X-ray diffraction data were measured to confirm that the resistivity was indeed a fair measure of the $FeCl_3$ intercalation of P-100 fibers. Figures 2-4 show the precession diffraction pattern of pristine P-100, high, and low resistivity intercalated fibers respectively. It can be seen that the low resistivity fibers show an ordered stage 2 structure, whereas the high resistivity fibers do not.

CONCLUSIONS

A statistical design of experiments was used to optimize the formation of $FeCl_3$ intercalation compounds with P-100 graphite fibers. A body-centered cubic design, followed by a steepest descent, followed by a second body-centered cubic design yielded the optimum region using only 26 experiments. The optimum region covers roughly temperatures from 350 - 365 °C, $T_{P\text{-}100}$-T_{interc} of 20 - 35 °C, and a time ranging from 14 - 18 hr. X-ray diffraction verified that those fibers with the lowest resistivity were also those with the most ordered staging.

ACKNOWLEDGEMENTS

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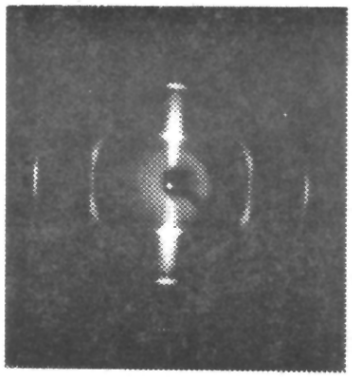

Figure 2 -- Precession XRD of pristine P-100 fiber.

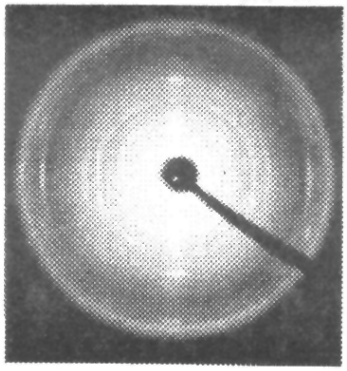

Figure 3 -- Precession XRD of high ρ P-100+$FeCl_3$.

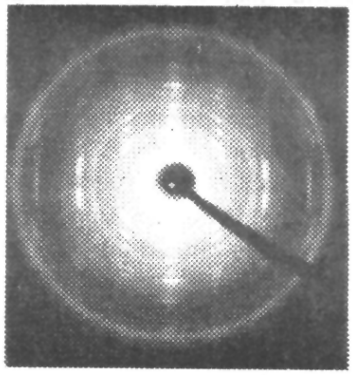

Figure 4 -- Precession XRD of low ρ P-100+$FeCl_3$.