Isothermal CVI of Carbon:
Side Reaction Limitation of Production Infiltration Rates

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Introduction

The common perception regarding isothermal chemical vapor infiltration of carbon is that the process is intrinsically slow, and therefore undesirable. We demonstrate in this paper that while the commonly practiced process is slow, the limitations have little to do with intrinsic limitations of isothermal CVI, and more to do with control of unwanted side reactions in the gas phase.

Intrinsic CVI Limitations

Formal treatments of the isothermal CVI process have pointed out that the Thiele modulus, a dimensionless parameter derived from heterogeneous catalysis theory, is the best indicator of infiltration and deposition profiles for a reactive-diffusive process for which the deposition process is first order. The Thiele modulus is given by:

$$h_T = W \sqrt{\frac{k_s S_{V,0}}{D_{eff,o}}}$$

h_T = Thiele modulus
W = ½ thickness of material
k_s = first order reaction rate coefficient
$S_{V,o}$ = initial surface area per unit volume l
$D_{eff,o}$ = initial effective diffusivity of the gas

In a reaction environment containing only one reactive gas species, the Thiele modulus defines the eventual density gradient that can be achieved in the process. It is usually assumed that the generation of an undesirable density gradient limits the rate of infiltration, so that moderation of the rate constant, k_s, is required to obtain a part with a minimum of internal porosity at the time during processing that the surface porosity reaches zero (surface pore closure). This equation also demonstrates that similar density gradients in thin parts could be obtained at considerably higher rates. Decreasing W by a factor of two should allow an increase in the rate constant of a factor of four.

In practice, however, it has been found by commercial practitioners that these conditions cannot be used as a predictor of success. Even thin parts are found to be adversely affected by processing conditions more aggressive than those used for thick parts.

Side Reaction Limitations

Many authors have shown that there are a variety of carbonaceous species present in high temperature carbon CVI environments, and that each of these has its own effective deposition rate constant.

A very reactive gas would have a very high value for the Thiele modulus. This means that these species have a very high "sticking coefficient" and will likely deposit carbon on the first surface that they contact. These species do not have to be "droplets" as is often argued in droplet deposition models, they need only be reactive carbon containing molecules, likely only of the size order of simple aromatics. These species also do not have to be present in high concentrations. Thick deposits on the relatively small external surface area can be formed with a relatively small amount of carbon, so the reacting species need not be more than a minor constituent in the gas.

The creation of these species has to occur away from surfaces, since their precursors would be more likely to be removed from the gas stream the nearer they are to such surfaces. It is very likely, therefore, that the highest concentration of the precursors to these species is found in the open areas of industrial CVI furnace systems. The corollary to this is that in very small furnace systems, where distances to surfaces are never more than a few millimeters, the likelihood of the buildup of these species is considerably reduced.

Supporting evidence of this behavior is given by operators of commercial furnaces, who take great pains to avoid "sooting" conditions in the CVI furnace, which are more often encountered with either partial furnace loads or with materials being processed with low surface areas. In fact, most CVI conditions are chosen, for very practical reasons, to be as aggressive as possible while avoiding these sooting conditions. Since the formation of soot particles in the free gas stream is undoubtedly the end game in the formation of more and more reactive carbon species, the observation and practice of CVI is consistent with the

avoidance of these reactive side-species rather than the optimization of the infiltration rate of the CVI process.

Experimental

To demonstrate this effect, samples of a commercial product which are normally processed using 150 hours of CVI processing, were processed at the commercial process conditions in a small tube furnace, and compared with samples processed in the tube furnace at successively more aggressive conditions.

Figure 1 shows the mass of samples within a 2" ID tube furnace equipped with a mass balance to track mass during processing.
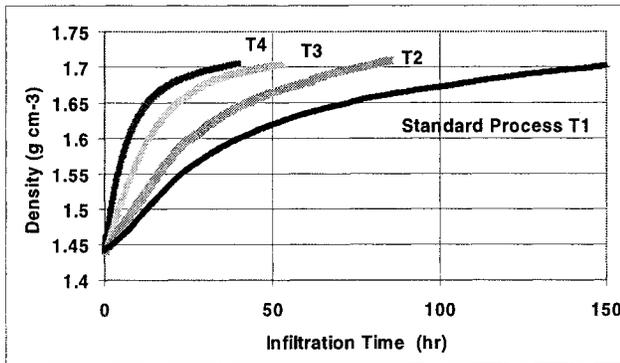

Figure 1. Mass gain curves for successively higher processing temperatures for test sample in a 2" tube reactor.

Normal processing temperature and three successively higher temperatures were used. Other process conditions were held constant. The material, which would be at risk for failing to densify above 1.65 g/cc if processed at a higher rate in the production environment, was successfully densified to that value within a time as low as 15 hours in the laboratory environment, with no indication of adverse density gradient or surface sealing.

Figure 2 shows another set of data where samples were processed in the laboratory at even more aggressive conditions. In this experiment, the thickness of carbon deposit on the surface per unit time was plotted vs. temperature. The sharp increase in coating thickness rate at 1100 °C indicates a very non-linear process for the onset of a more reactive species. The thickness deposition rate *inside* of the sample over this whole temperature range was below 0.1 microns per hour.

A production furnace system was loaded with a dummy load simulating the end of the normal CVI process, and the processing conditions varied over a wide range to establish the envelope of conditions, which would be characterized as "sooting".
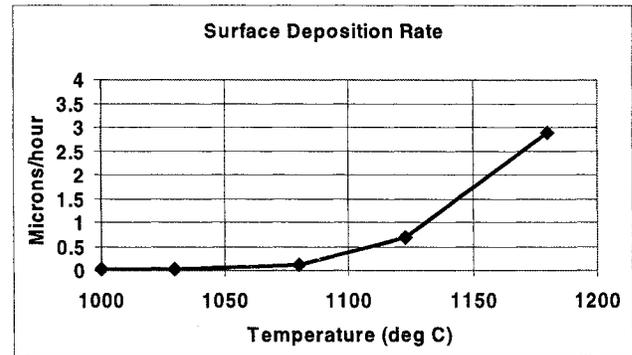

Figure 2. Surface thickness growth rate vs. process temperature in 2" reactor.

Figure 3 shows a plot of the sooting envelope found as a function of flow, pressure, and gas composition for a particular production furnace.
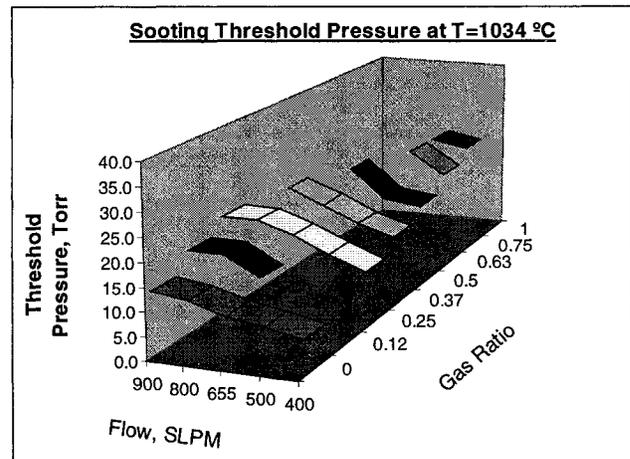

Figure 3. Sooting condition threshold pressures in a large batch furnace at a variety of processing conditions.

Simulations of the infiltration rates at points just below these sooting thresholds were used to establish limits to the infiltration rates which could be "practiced". Comparison of the limiting rates in the production furnace to the successful rates in the small tube furnace indicated that while the material itself could be successfully densified at higher rates, the sooting threshold in production would preclude the use of those rates.

Discussion and Conclusions

It is clear from this study, that considerably more attention should be paid to remedies for limiting the onset of side reactions in the gas phase. Such remedies would be capable of unlocking ranges of processing conditions, which, particularly for thin parts, could result in significant processing time reductions in the isothermal CVI process.