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Research Article

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The Soret Effect in Laser Chemical Vapor Deposited Carbon Fibers

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Abstract

Laser Chemical Vapor Deposition (LCVD) is the process by which free standing fibers additively deposit from the gas-to-solid phase under a laser focal point. In this letter, we address how the mixing of disparate molecular weight precursors facilitate changes in the growth and fiber structure using the Soret effect. The Soret effect causes lighter particles to migrate to warmer regions and heavier particles to migrate to cooler regions in a reaction. Using ethylene mixed with helium, the reaction rate, temperature, activation energy, and morphology for a series of carbon fibers are compared. It was found that the onset of the Soret effect bypasses specific growth regimes, reduces the extent of graphitization, and creates morphological variations within the fiber core. These results highlight the potential use of the Soret effect as a new means of tailoring LCVD fiber processing.

Keywords: Laser Chemical Vapor Deposition, Soret Effect, Carbon Fiber, Growth Regimes, Hydrocarbon Deposition

Introduction

Laser chemical vapor deposition (LCVD) is a technique by which materials deposit directly from the gas-to-solid phase under the focal point of a laser [1-5]. During this deposition a Soret effect has been proposed to occur which can have a dramatic influence on the deposited fiber structure. The Soret effect is the tendency of lighter particles to migrate to higher temperature regions then heavier particles which move to cooler regions in the reaction zone. Since LCVD can deposit materials from a precursor gas, mixing of such gases leads to compounds such as boronitrides and transition metal carbides. Hence, understanding this gas mixing is critical to the
processing characteristics in how final fibers form. For example, the buildup of lighter particles such as hydrogen from the dissociation and deposition from a hydrocarbon is postulated to create a barrier around the reaction zone that alters how the hydrocarbon molecule must then diffuse through to reach the fiber tip [6]. The formation of such a barrier increases the energy required to sustain the reaction and reduce the reaction rate. Maxwell et al. proposed this Soret effect in the deposition of carbon fibers as a cause in the change of the activation energy between different hydrocarbon gases [7]. Cook and Thompson furthered this claim in the deposition of carbon fibers from alkane hydrocarbons where a proposed gaseous barrier influenced the fiber morphology, microstructure and mechanical strength [6]. While the Soret effect is established in traditional CVD [8], and has been speculated to exist in LCVD, arguably, there has not been a definitive LCVD study to concretely demonstrate its presence in the control of mixed gas chemistries. Here we propose to mix helium (He) with ethylene (C2H4) to form carbon fibers, where He, being the lighter weight molecule, will exacerbate the proposed Soret effect.

**Experimental**

The carbon fibers were grown in a spherical pressure vessel with a 10 W ytterbium laser with a wavelength of 1070 nm. The fiber growth rate is tracked using a digital camera with the temperature of the reaction zone monitored by a multi-wavelength pyrometer. Further details of the experimental set-up can be found in reference [9]. The concentration of the alkene C2H4 is fixed at 4 bar whereupon 2 additional bars of He is added for a total pressure of 6 bar. Additionally, the concentration of C2H4 was reduced to 2 bar with 2 bar of He added for a total pressure of 4 bar. Both gas mixtures are compared to a control deposit of only C2H4 at 4 bar and 6 bar. In all cases,
the gases were not flowed but statically filled; any gas movement during deposition is created from natural convection created by the temperature gradient.

**Growth Regimes**

When depositing C₂H₄ between 2 to 6 bar, the fibers exhibit two different growth regimes, which are Surface-Reaction-Kinetically (SRK) limited and Mass Transport (MT) limited [9], with the growth regime being a function of the laser power and reaction rate. SRK behavior is nominally at lower temperatures and follows the Arrhenius equation

\[ r = A_r \times \exp \left( -\frac{E_a}{R \times T} \right) \times [B]^n \] (2)

where \( r \) is the growth rate, \( A_r \) is a rate constant, \( E_a \) is the activation energy, \( R \) is the gas constant, \( T \) is the absolute temperature, \( B \) is the molar concentration, and \( n \) is the reaction order [9]. For the MT regime, at a sufficient temperature and growth rate, a boundary layer forms from the zero-slip condition at the fiber-gas interface because of the high convective flow. With this gaseous barrier, the precursor must diffuse through it to continue fiber growth making it diffusion limited. In either growth regime, if the temperature is sufficiently high, gas phase nucleation (GPN) initiates and the precursor molecules dissociate forming a solid phase as ‘dust’ particulates rather than solely depositing on the fiber surface. While GPN not a growth regime, it does stagnant and even deceases the fiber deposition since the precursor is no longer fully contributing to the fiber growth.

**Results and Discussion**

In Figure 1, for the pure C₂H₄ precursor, two distinct growth regimes appear for both pressures. The first regime being SRK limited and occurs from approximately 725 to 800°C at 4 bar and 710 to 730°C at 6 bar. Using equation (1), the activation energy is 50.4 kJ/mol (for both
pressures). As the temperature further increases, a sharp drop in the growth rate occurs for \( \text{C}_2\text{H}_4 \) followed by an increase and then stagnation of the growth rate. This drop is caused by the diffusion barrier created in the MT regime and the stagnation is the onset of GPN.

\[ \text{Fig. 1. Deposition rate as a function of reaction temperature for pure C}_2\text{H}_4 \ [9] \text{ and C}_2\text{H}_4 \text{ with the addition of He gas.} \]

With the addition of 2 bar He, both 4 bar and 6 bar total pressure reveal different growth rates. In both cases, there is no drop but an increase and then stagnation of the growth rate. Hence, the reaction still behaves according to the Arrhenius relationship, or, in other words, it is still within the SRK regime with the stagnation then being GPN and the MT regime has been bypassed. The activation of the \( \text{C}_2\text{H}_4 + \text{He} \) gas mixtures is 131 kJ/mol, with this higher activation energy manifesting itself into a slower rise in growth rate with increasing temperature.

If lighter particles stay in and around the reaction zone because of the increase temperature, then the heavier hydrocarbon molecules are forced out of the central region of the reaction zone. In this case, the He particles, with a molecular weight of 4.00 g/mol [10], form a barrier around the reaction with the \( \text{C}_2\text{H}_4 \) molecules, 28.05 g/mol [11], located in the surrounding region. This differential in the gas profile is depicted in Figure 2. The other notable difference in the mixed gas
reaction is absence of the MT regime. Instead, the reaction remains in the SRK regime for the entirety of the test range. The Soret effect created by the extra He prevents the reaction from achieving a sufficient growth rate for C$_2$H$_4$ to transition to MT. This highlights how the Soret effect, *i.e.*, gas mixing, manipulates the growth regimes for LCVD fibers and even match growth regimes from other precursors, such as the alkane hydrocarbons [6] that bypass the MT regime at these pressures and temperatures.

![Fig. 2. LCVD schematic illustrating the buildup of He particles around the reaction zone creating a barrier that the hydrocarbon must go through to reach the fiber surface. Figure adapted from [6].](image)

This growth behavior for C$_2$H$_4$ + He now more closely follows the reaction of C$_2$H$_6$ [6] plotted in Figure 3. In the deposition of carbon from a C$_2$H$_6$ precursor, Cook and Thompson suggested one of the causes for the slower deposition rise for the alkane C$_2$H$_6$ as compared to alkene C$_2$H$_4$ was the Soret effect. This Soret effect would be brought on by the buildup of an abundance of lighter hydrocarbons and/or hydrogen around the reaction zone during the decomposition of C$_2$H$_6$. Since C$_2$H$_6$ has a greater content of hydrogen (compared to C$_2$H$_4$), this would likely increase the
hydrogen concentration around the reaction zone thereby slowing the rate. While this was speculated at that time, the similar growth rate profile of \( \text{C}_2\text{H}_4 + \text{He} \), which now has a comparable number of lighter particles compared to the greater amount of hydrogen in \( \text{C}_2\text{H}_6 \) proves that the Soret effect is indeed a contributor in deposition behavior across these different LCVD precursors. The shift in the growth rates between the \( \text{C}_2\text{H}_4 + \text{He} \) at 4 bar and 6 bar is simply a result of the change in concentration of the hydrocarbon that alters the deposition rate [9, 12, 13].

**Fig. 3.** Deposition rate at 6 bar as a function of reaction temperature for \( \text{C}_2\text{H}_4 \) with the addition of \( \text{He} \) gas and pure \( \text{C}_2\text{H}_6 \) [6].

To understand the influence of the Soret effect on fiber structure, SEM micrographs for the \( \text{C}_2\text{H}_4 + \text{He} \) at 6 bar are shown in Figure 4. The first notable observation is the core-shell structure characteristic of the SRK regime [6, 9, 12] with its formation previously discussed in detail by Longtin *et al.* [14]. The core shell observation at the start of the fiber growth as well as in the stagnant region of growth, Figure 1, clearly indicates that the fiber retains the SRK growth characteristics throughout the entirety of the temperature range investigated. The notable difference between the two fibers is the core region. For the higher temperature fiber, a clear divot
is identified in the center of the fiber (with an arrow to guide the eye). This divot is absent in the low temperature fiber.

![F1 and F2 Fiber Cross-Sections](image)

**Fig. 4.** Fractured fiber cross-section for pure C\textsubscript{2}H\textsubscript{4} (left) and C\textsubscript{2}H\textsubscript{4} with the addition of He gas.

Another notable difference is the nodularity in the core portion of the fiber, with the higher temperature fiber having a higher degree of nodularity. Cook and Thompson reported that an increase in nodularity results in a fiber that is less graphitized [12]. Hence, the increased nodularity in the center of the higher temperature fiber indicates a less graphitized region that tracks with the location of the divot.

Finally, we note that both fibers have a parabolic fracture surface, except at the divot region of the higher temperature fiber. This parabolic fracture shape is a result of the fiber deposition characteristics formed under the Gaussian distribution of the laser beam [14]. When the fiber fractures under tension, the weak Van der Waals forces between the graphitic planes fail and the fracture surface mimics the parabolic shape. Collectively, the nodular structure as well as the divot in the fracture surface leads one to realize that the center region is structurally different. Noting that the Soret effect is a function of temperature, the formation of these features in the high
temperature fiber indicates that the Soret effect is now more dominate during fiber deposition. This too can be gleaned in the growth rate curves of Figure 1, where at the lowest temperature, the growth rates between $C_2H_4$ (4 bar) and $C_2H_4 + \text{He}$ (6 bar) are nearly identical in value. As the temperature increases, the growth rates diverge because the Soret effect is becoming ever more prevalent with increasing temperature.

Since the reaction will have the highest temperature at the center of the fiber because of the laser’s Gaussian profile, the diffusion barrier created by the He molecules will be the greatest in this region once a sufficient temperature is reached. This combined with a higher growth rate lead to the hydrocarbon molecules having a reduced resident time in the reaction at the fiber center resulting in this region of the deposit to become less graphitized or, alternatively, more nodular. With the He build up at the fiber center, the carbon deposition in the center lags as compared to the outer regions of the fiber, where the He concentration is less, causing the precursor to diffuse through this Soret barrier, Figure 2. The lack of either the divot or nodular morphology at the lower temperature condition, even though the He content is present, confirms that the Soret effect influence requires a sufficient temperature to be reached.

**Conclusion**

In this letter, the influence of the Soret effect is isolated by a mixture of He gas with $C_2H_4$ at different temperatures. The addition of the He gas, which is nearly 7x lower in molecular weight than the hydrocarbon, allows it to converge in the higher temperature region of the LCVD reaction. The addition of He enables the growth regimes to be manipulated with the $C_2H_4 + \text{He}$ bypassing the MT regime and mirroring another type of hydrocarbon (alkane) precursor. Furthermore, the Soret effect changes the characteristics of the carbon fiber structure by reducing the extent of
graphitization as well as the formation of a divot in the fiber’s fracture surface center. The extent of the Soret effect is controlled by the deposition temperature, where an increase in temperature furthers its influence. Collectively, the Soret effect’s ability to regulate the fiber structure through altering the deposition characteristics offers LCVD potentially new routes to tailor fiber properties through mixing of different types of precursors as well as the temperatures by which these mixed gases deposit.

Declaration of Competing Interest
The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CAC, KF and GBT conceptualized the experiment; CAC and KF performed the experiment methodology and formal analysis. CAC provided the original draft. GBT assisted in reviewing and editing the draft, supervision, and funding acquisition.

Data Availability
Data will be made available upon request.

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