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Flame temperature effect on the transition between soot and graphitic carbon products in premixed stagnation flames

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Abstract: Particulate carbon is known to exist in a wide range of forms, some of which exhibit properties that are desirable for emerging technologies. For example, graphitic carbon is widely integrated into energy storage devices due to its charge storage capacity and inherent electrical conductivity. The effect of flame temperature on the structure of carbon products formed in premixed stagnation flames is assessed in this work. Namely, the progression of carbon products from amorphous soot to more ordered carbon structures is examined by tracking the evolution of Raman spectra as a function of flame temperature and time. The stagnation flames are modeled in a pseudo-1D formulation to precisely quantify the temperature-time relationship in the carbon growth region. Raman spectra for carbon formed in all flames consisted of Raman Shifts representing the D and G band close to 1350 and 1600 cm-1, respectively. The relative intensity of the two bands changed as a function of flame temperature and the trend can be interpreted as indicating larger graphitic regions on carbon particles formed at higher flame temperatures. The observations made here provide insight into carbon formation in flames that is useful for soot theory / modeling and flame synthesis processes.

Keywords: Flame Synthesis, Carbon, Nanoparticle, Soot

1. Introduction

Besides being a problematic by-product of combustion processes, carbon, in its many forms, can also be the desired end-product from flames. There are similarities between nuisance soot and more useful graphititc forms of carbon. These similarities have been invoked to describe soot reactivity by referring to experiments [1] on graphite. In addition, soot growth and ageing is regularly described by the degree of graphitization in the carbon structure. Dobbins and co-workers [2, 3] were the first to draw upon classical works on carbonization (see e.g., [4, 5]) to describe the evolution of so-called precursor particles (also known as nascent soot in more recent works [6-8]) to mature soot. For producing useful carbon materials, relatively high flame temperatures are important for achieving carbonization and uniform growth conditions are necessary to obtain precisely controlled properties. The essential commodity known as carbon black is produced industrially using flames operating at the aforementioned conditions.

In this work, the range of flame conditions leading to less-desirable soot formation and more valuable graphitic carbon will be demonstrated. Stretch-stabilized premixed flames will be used because the stabilization mechanism allows for a pseudo one-dimensional flame without significant heat loss [9]. These flame characteristics will enable particle formation under uniform growth conditions with temperatures approaching 2500K. Raman Spectroscopy will serve as a diagnostic for the presence of sp^2 bonded carbon. The raman spectra of amorphous, crystalline and

nano-scale carbon have been extensively studied. Soot structural details have also been investigated in raman spectroscopy studies [7, 10-14]. Boehman and co-workers incorporated analysis of the Raman spectra for laboratory [13] and Diesel engine [14] soot to examine soot reactivity and carbon structure. Russo and Ciajolo carried out a systematic Raman study on soot from premixed flames and parsed out subtle differences in soot structure resulting from fuel structure and flame conditions [12].

Empirical [15] and theoretical [16] works showing the relationship between XRD derived crystallite size and the ratio of prominent bands in the Raman spectra marked the beginning of numerous XRD and Raman studies as complimentary carbon diagnostics. XRD peaks attributed to (002), (10) and (110) have been reported for both soot and carbon black [14]. Graphite and turbostratic carbon are known to have one major XRD peak attributed to (002) [17]. In this work, Raman analysis will be carried out to isolate the effect of flame temperature on the carbon products formed in premixed flames. The relatively high-temperature that is accessible in premixed stretch-stabilized flames is expected to allow for observation of higher ordered carbon structure relative to carbon products obtained at lower flame temperatures.

2. Experimental

The experimental setup, summarized in Fig. 1, consists of a burner with an aerodynamically shaped nozzle and a stagnation / deposition surface. The stabilization mechanism of the premixed flames studied herein requires flow stagnation to set the kinematic balance between the local flame speed and normal flow velocity immediately upstream of the flame surface [9]. Microscope slides were placed flush with the surface for deposition of carbon aerosol formed in the flame. The aerodynamic shape of the burner nozzle body is designed to achieve plug flow at the burner exit (1.43 cm nozzle exit diameter). The standing distance between the flame and stagnation / deposition surface, L_s, may be varied by changing the unburned gas flow rate. The gas temperature at the nozzle exit, T_n, was measured with an uncoated fine-wire (125 μm wire diameter) Pt-Rh thermocouple placed near the centerline of the flow. The temperature at the stagnation surface, T_s, was measured by a type-K thermocouple (0.2 cm wire diameter). The gas temperature at the nozzle exit was determined to be T_n = 340 K; and the stagnation surface temperature was T_s = 385 K. Numerical sensitivity calculations show that within the uncertainty values quoted the flame structure exhibits little sensitivity towards the boundary temperature variations.

The carbon structure of the flame products was analyzed by Raman spectroscopy for a series of premixed ethylene flames. The flame diluent was alternated between nitrogen and argon to expand the range of acceptable flame temperatures. The unburned gas composition and cold gas velocity are summarized in Table 1 for each flame. The examined flames range from relatively high velocity flames approaching the limit where stretch-induced flame extinction processes occur to low velocity flames approaching the flashback limit.

A modified OPPDIF computation [18] based on USC Mech II [19] was used to calculate the temperature, velocity and species profiles. The boundary conditions were given by the measured temperatures at the nozzle exit and the stagnation surface/sampling probe. The OPPDIF code invokes the pseudo one-dimensional formulation introduced by Kee, Smooke and co-workers [20, 21]. Plug flow is designated at the burner boundary and non-slip conditions are assumed at the

stagnation surface boundary. For particles formed in the flame, the finite residence time is determined by considering the thermophoretic velocity which is driven by the significant temperature gradient, $\partial T/\partial x$, at the stagnation plate. The thermophoretic velocity was calculated numerically and added to the total velocity. The residence time of the soot particles is defined as the time interval for the particle (or precursors) to traverse from the calculated location of the peak flame temperature to the location of the stagnation probe. The carbon flame products were analyzed by Raman Spectroscopy. A Thermo Nicolet DXR Raman Microscope (Thermo Scientific) with a 532 nm laser was used. The laser power was 5 mW and changes to the spectra and sample occurred over the sampling period.

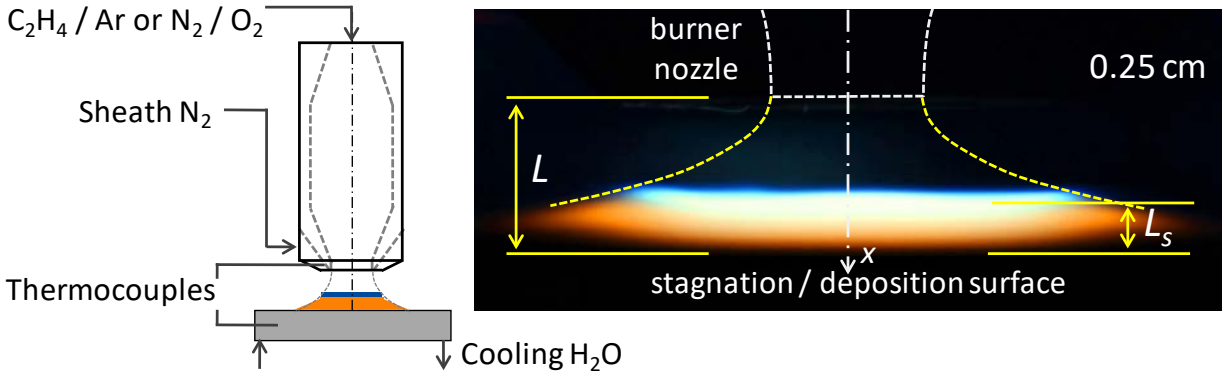

Figure 1: Experimental setup for carbon synthesis and deposition in premixed stagnation flames.

Table 1. Flame parameters[a]

	time, t_p (ms)	$T_{f,max}$ (K)	Velocity, v_0 (cm/s)	Standing distance, L_s (cm)	Separation distance, L (cm)
			15.2 % C_2H_4 / 18.5 % O_2 / 66.2 % N_2		
1	18	1790	20.6	0.48	1.0
2	25	1750	12.0	0.65	1.0
			21.1 % C_2H_4 / 25.3 % O_2 / 53.5 % N_2		
3	6	2125	43.6	0.71	1.0
4	23	2070	43.6	1.85	2.6
			14.9 % C_2H_4 / 17.9 % O_2 / 67.1 % Ar		
5	28	2070	40.4	1.75	2.6
			16.4 % C_2H_4 / 19.7 % O_2 / 63.8 % Ar		
6	19	2150	61.9	1.56	2.6
			19.2 % C_2H_4 / 23.0 % O_2 / 57.8 % Ar		
7	14	2270	71.1	1.62	2.6

3. Results and Discussion

The Raman spectra for the flame-formed carbon showed peaks in the vicinity of known Raman Shifts for the D and G bands. The intensities of the broad peaks close to 1350 and 1600 cm^{-1} were compared for each flame condition. The relative intensity of these bands has been attributed to the change in aromatic layer size [15] and the area of aromatic domains [22]. For the 1775 K maximum

flame temperature condition (shown in Fig. 2), there was very little effect of growth time on the Raman spectra. The spectra for flame-formed carbon at the 2100 K is shown in Fig. 3 for two growth times. The intensity of the non-graphite Raman shift at 1300 cm-1 is the same as the graphite peak at 6 ms and gets becomes larger than the graphite peak at 23ms growth time. The spectra for flame-formed carbon for a series of flame temperatures at comparable growth times is shown in Fig. 4. The relative intensity of the non-graphite peak also becomes larger than the graphite peak as the flame temperature approaches 2300 K. Ferrari and Roberston [22] showed that the relative intensity of the D and G bands is proportional to the area of graphitic regions on the carbon surface if the crystallite size is smaller than 2 nm. The estimated characteristic length of the graphitic crystallite region, La, based on the formation of Ferrari and Robertson is shown in Fig. 5. Under this regime, the crystallite region of the flame-formed carbon approaches 1.9 nm for particles formed at 2270 K maximum flame temperature.

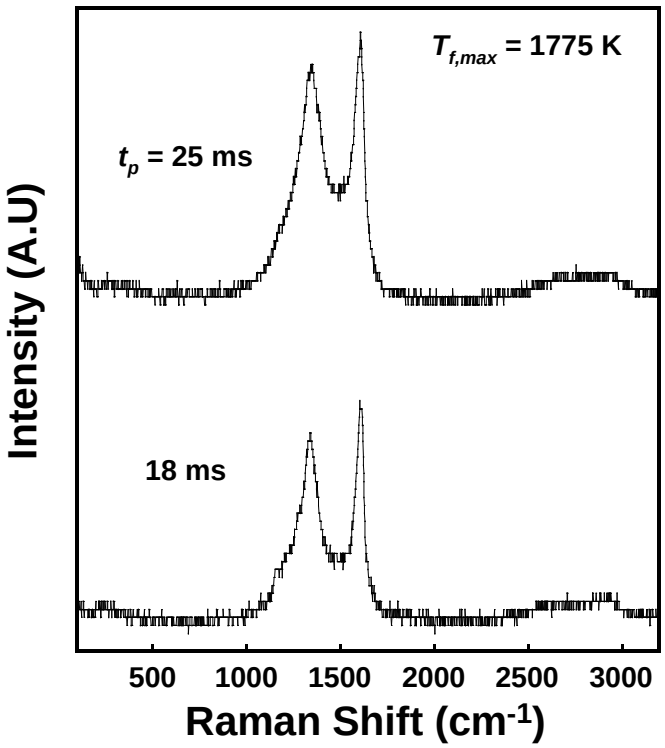

Figure 2: Raman spectra of highly ordered pyrolytic graphite (left) and as-deposited carbon films

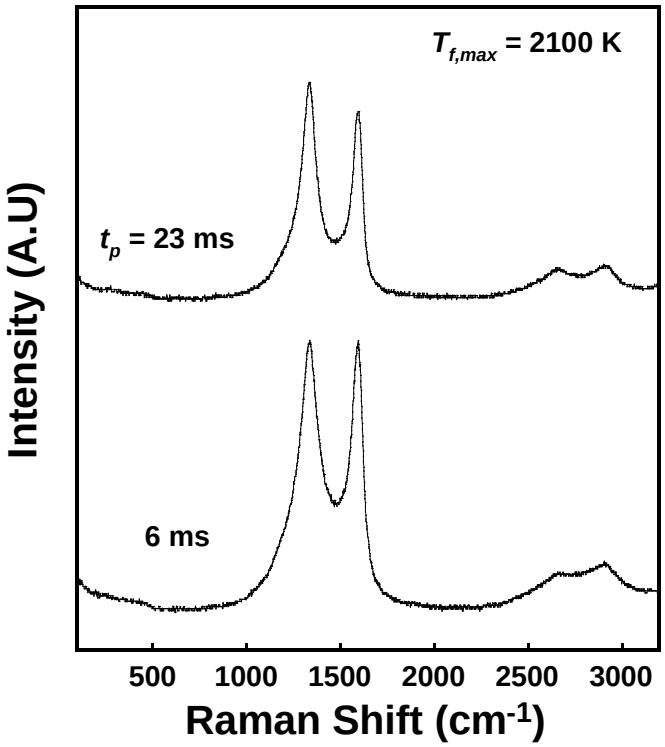

Figure 3: Raman spectra of highly ordered pyrolytic graphite (left) and as-deposited carbon films

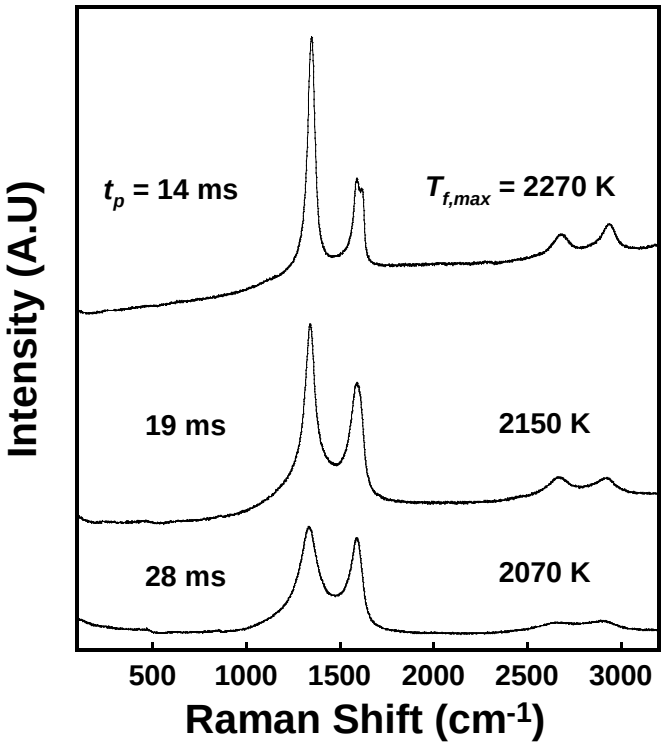

Figure 4: Raman spectra of highly ordered pyrolytic graphite (left) and as-deposited carbon films

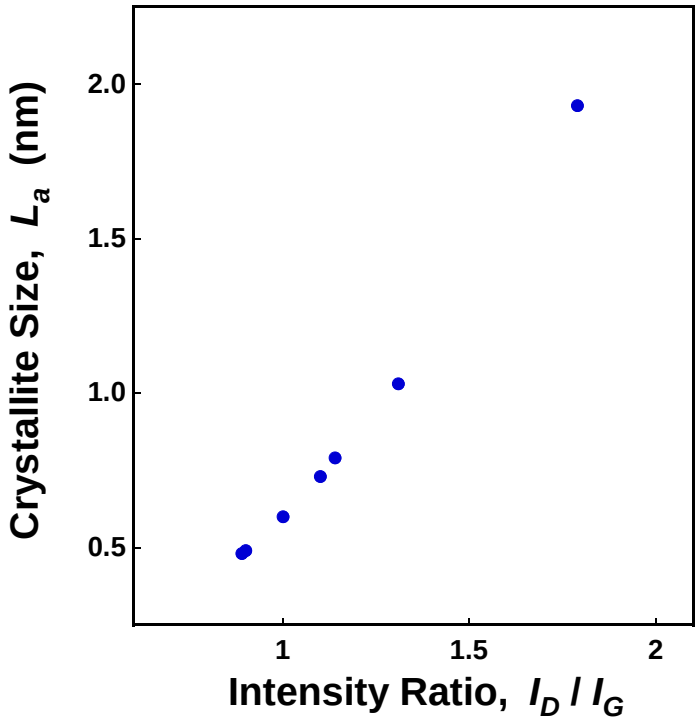

Figure 5: Raman spectra of highly ordered pyrolytic graphite (left) and as-deposited carbon films

4. Conclusion

The effect of flame temperature on the structure of carbon products formed in premixed stagnation flames is assessed in this work. Namely, the progression of carbon products from amorphous soot to more ordered carbon structures is examined by tracking the evolution of Raman spectra as a function of flame temperature and time. Raman spectra for carbon formed in all flames consisted of Raman Shifts representing the D and G band close to 1350 and 1600 cm-1, respectively. The relative intensity of the two bands changed as a function of flame temperature and the trend can be interpreted as indicating larger graphitic regions on carbon particles formed at higher flame temperatures.

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