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Pulsed laser annealing of carbon black

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ABSTRACT

Laser heating was used to study the rates and trajectories of carbon black during the earliest stages of annealing. A commercial carbon black, Regal 250 (R250 Cabot Corporation) was heated with a Q-switched Nd:YAG laser and a continuous wave CO_2 laser. Structural transformations were observed with transmission electron microscopy. Micrographs were processed with in-house codes for the purpose of extracting distributions of fringe length, tortuosity (curvature), and number of lamellae per stack. Time-temperature-histories with nanosecond temporal resolution and temperature reproducibility within tens of degrees Celsius were determined by spectrally resolving the laser induced incandescence signal and applying multi-wavelength pyrometry. The Nd:YAG laser fluences include: 25, 50, 100, 200, 300, and 550 mJ/cm^2. The maximum observed temperature ranged from 2400 °C to the C_2 sublimation temperature of 4180 °C. The CO_2 laser was used to collect a series of isothermal (2600 °C) heat treatments versus time (100 ms–20 s). Laser heated samples are compared against R250 annealed in a furnace at 2600 °C. The material transformation trajectory of Nd:YAG laser heated R250 was different than the traditional furnace heating. The traditional furnace annealing pathway is followed for CO_2 laser heating as based upon equivalent end structures.

1. Introduction

Thermal annealing of carbon has been occurring since at least the earliest natural conversion of carbon feedstocks to graphite in the Earth's crust and upper mantel. The carbon industry had its beginning circa 1800, when Sir Humphry Davy produced an electric arc with electrodes produced from carbonized wood [1]. Carbon heat treatment has been extensively evaluated with an emphasis on identifying the structural transformation dependence with Heat-Treatment-Temperature (HTT). A detailed quantification of HTT and resulting material annealing was provided by Oberlin in 1984 [2]. In the same year, Marsh and Crawford [3] published their findings in agreement with Oberlin's now well-known work. The 4 stages outlined in Oberlin's HTT diagram (temperature dependent) are believed to be separated by "very rapid" transitions [2]. Just how rapid remains unknown.

The insightful work of Oberlin [2] was based on thermodynamics alone (temperature) and the kinetics were not identified. Little attention has been directed towards the kinetics of carbon material annealing [4]. Many studies on structural changes during heat treatment only provide HTT, without providing the time at temperature [2,3,5,6]. There are considerable experimental challenges in determining the kinetics of solid-state reactions above 2000 °C, specifically achieving short time durations at temperature. The ideal kinetic study of carbon annealing would be made in situ under isothermal conditions. Such measurements are technically feasible using in situ X-ray diffraction (XRD) as demonstrated by Fitzer and Weisenburger [7]. However, such measurements at elevated temperatures are plagued by the c-axis thermal expansion [8]. The d_{002} spacing increases by nearly 10% when heated to 2500 °C, whereas the decrease in spacing due to graphitization (measured at ambient temperature) is only about 2% [8]. A more serious complication, one that likely cannot be accounted for, rendering in situ XRD measurements not useful for kinetic studies is that the c-axis thermal expansion coefficient is a function of carbon crystalline perfection (not easily removed as structure and thermal expansion data is required) [8].

Due to the unknown material properties at elevated temperatures, the next option is a series of isothermal heat treatments versus time. The ideal heat treatment would heat the sample to the desired temperature instantaneously, remain constant for a desired duration, with instantaneous cooling to the ambient temperature [8]. Such a heating scheme is not possible but can be approximated

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by either direct resistive (Joule) heating [9] or by rapid sample insertion into preheated graphitization furnaces [8,10]. Furnace heating is limited to time scales no less than several minutes due to slow heating rates. On this time scale, the only material transformation that is rate restricted is the layer plane spacing reduction. These rates with respect to temperature are known for these time scales (several minutes, minimum) [4,8,10–13]. Shim and Hurt [14] examined the oxidation reactivity reduction of coal char on the timescales relevant to pulverized coal-fired systems. They designed a direct heating apparatus capable of heating coal to 2400 °C at a ramp rate of 1.1×10^3 °C/s. The rapid heating results showed that coal char annealing steps are incomplete after 2 s of annealing at 2400 °C. This is an exciting observation as much of the annealing transformation rate can be systematically studied at this time scale (seconds).

Lasers can heat carbon materials to graphitization temperature within nanoseconds (ns) to milliseconds (ms), depending upon the laser source. On these extremely short time scales, the extent of material transformation is kinetically limited by time at temperature. Therefore, laser heating can be used to study the rates and trajectories of carbons during the earliest stages of annealing. Carbon analysis remains challenging as average properties by XRD and Raman are limited in elucidating structural transformations. A more insightful technique is needed to visualize carbon structure.

A heat treated carbon black was used by Heidenreich et al. [15] in 1968 for testing the resolving power of a transmission electron microscope. This sample was selected because of the: known layer plane spacing of 3.4 Å (measured by XRD), stability under the electron beam, and it is inherently thin. They were successful in resolving the 3.4 Å layer plane spacing. Carbon blacks fall under the non-graphitizable category since they have turbostratic spacing of 3.44 Å even after heat treatment up to 3000 °C. Their non-graphitizability is likely due to the geometry of the primary particle. As the lamellae flatten out and grow they are constrained to join at high angles forming closed shell polyhedrons. Thus, carbon black is a good test specimen for laser annealing as lamellae growth and rearrangements reach a state of thermodynamic equilibrium upon the formation of a multifaceted polyhedron with layer spacing of 3.44 Å. The time scale for the conversion of turbostratic to graphite layer spacing from graphitizable carbons are well known. Thus, carbon black can be used to isolate the early rapid annealing stages from the subsequent kinetically limited graphitization stage.

2. Experimental

2.1. Material selection

A commercial carbon black, Regal 250 (R250) was provided by Cabot Corporation and used as the test specimen. Carbon black imposes natural geometric constraints in that primary particles are spherical nanoparticles and aggregate morphology is a collection of primary particles. Primary particles of R250 typically have a diameter in the range of 30–60 nm as was observed with TEM. At this size scale they behave as volumetric absorbers of both 1064 nm and 10.6 μm laser light and thus undergo uniform heating. The semi-separated nature of the primary particles enables easy observation of nanostructure material transformation as such change is largely restricted to the primary particles' interior.

2.2. Heat-treatment

Samples were heat treated with control over the heating rate and duration with 2 different lasers: a Q-switched Nd:YAG laser and a continuous wave CO_2 laser. The heating was extremely rapid followed by fast cooling. The laser excitation energy is dissipated to internal heat on a sub-nanosecond timescale, far faster than other heat transfer timescales involved in the process [16]. Therefore, laser irradiation is equivalent to heat addition in the absence of ablation and/or vaporization. Laser heated R250 is compared to traditional furnace heated R250.

2.2.1. Furnace

Furnace heat treatment was performed under argon in a Centorr Vacuum Industries series 45 graphitization furnace. The furnace was heated at a rate of 25 °C a minute until the desired temperature and held for an hour. The maximum achievable temperature was 2600 °C.

2.2.2. Nd:YAG laser

Although the Continuum Surelite-III Nd:YAG laser is equipped with harmonic generators, only 1064 nm laser light was used in this study. Shorter wavelengths were not utilized to avoid inducing spectral interferences such as fluorescence or phosphorescence when measuring the laser induced incandescence (LII) signal [17]. Shorter wavelengths are also more likely to cause material ablation, which is undesired given the focus here upon thermal annealing [18,19]. The 1064 nm laser light also has the advantage of increased Rayleigh range as compared to shorter wavelengths. For laser heating to occur uniformly, the Rayleigh size regime ($\pi d/\lambda < 0.3$) must be satisfied. For 1064 nm laser light the Rayleigh range is approximately 102 nm. When this criterion is satisfied, absorption occurs volumetrically and the sample is uniformly heated. The primary particle diameter of R250 is ~45 nm and thus the primary particles are in the Rayleigh range.

The laser beam diameter is 9 mm and was not expanded or focused. The Nd:YAG laser pulse width is fixed at ~8 ns. The experimental control variable is the laser energy, measured in energy per unit area of the beam (laser fluence). For the purpose of fixing experimental timing and providing beam reproducibility, a fixed lamp voltage was used. The corresponding delay from trigger to laser pulse was 70 ns. The pulse jitter was less than 2 ns shot to shot. The shot to shot pulse energy varied by <5%.

An experimental schematic is shown in Fig. 1. Laser fluence was varied by partial beam rejection with the use of partially reflective mirrors that were easily moved in and out of the optical path. Fine tuning the fluence was achieved by passing the beam through a homemade variable attenuator, comprised of 2 quartz plates mounted on counter-rotating plates. The counter-rotation of the 2 plates acts to cancel beam walk. Prior to striking the sample the wings of the beam are clipped off by a 5 mm diameter aperture. Following the aperture, a ground glass diffuser is used to convert the Gaussian beam into a top-hat-like beam for the purpose of providing uniform spatial heating. The uniform illumination after passage through the ground glass diffuser is displayed by the burn pattern compared to a burn pattern without passage through the ground glass diffuser (Fig. 1). The sample chamber is shown in Fig. 1. The beam is transmitted through a quartz window. The sample is heated directly on lacey carbon TEM grids. The grids are held in a steel sample holder with recessed holes. Heating was performed under argon at atmospheric pressure.

2.2.3. CO_2 laser

The R250 was heated with a 250 Watt Synrad Firestar series F201 continuous wave CO_2 laser. The predominant laser light emitted from a CO_2 laser is 10.6 μm. The laser was made to pulse by turning on and off the radio frequency amplifier, controlled with a pulse generator. The delay between trigger and pulse is a constant 100 μs (μs) due to the rise and fall time of the lasing medium. The output beam diameter is 4 mm. The CO_2 sample chamber is