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Nanoparticle production in arc generated fireballs of granular silicon powder

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Recently we observed buoyant fireballs by arc igniting silicon that drift in air for several seconds and postulated that the low aggregate density was attributed to the formation of a network of nanoparticles that must completely surround the burning silicon core, trapping the heated vapor generated as a result of particle combustion [Ito \textit{et al.} Phys Rev E \textbf{80}, 067401 (2009)]. In this paper, we describe the capturing of several of these fireballs in flight, and have characterized their nanostructure by high resolution microscopy. The nanoparticle network is found to have an unusually high porosity ($> 99\%$), suggesting that this arc-ignition of silicon can be a novel method of producing ultra-porous silica. While we confirm the presence of a nanoparticle network within the fireballs, the extension of this mechanism to the production of ball lightning during atmospheric lightning strikes in nature is still the subject of ongoing debate. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [doi:10.1063/1.3681283]

I. INTRODUCTION

According to some surveys,\textsuperscript{1–3} sightings of ball lightning, i.e., the reported appearance of buoyant fireballs lasting for several seconds, is almost always concomitant with natural lightning events. The vast majority of these sightings are reported to have occurred during thunderstorms, and nearly 80\% of ball lightning was seen to occur right after flashes of lightning, most of which were to the ground. It has been widely believed that ball lightning is initiated by natural lightning strikes.

In laboratory experiments, two types of luminous objects have been produced that behave in ways similar to those reported for ball lightning. One is those sustained by using external energy sources (such as microwaves)\textsuperscript{4–7} to generate plasmas in ambient air, and the other are those sustained by the release of internal potential energy (such as chemical oxidation reactions).\textsuperscript{8–11} In this paper we discuss the production of fireballs that we attribute to the latter, from combusting granular silicon powder made buoyant with the formation of a surrounding coalescing cloud of oxide nanoparticles.

In a previous paper, Abrahamson and Dinniss\textsuperscript{8} suggested that ball lightning may be caused by a strike of natural lightning against the ground, ejecting filamentary nanometer-scale networks of Si, SiO or SiC, which release more heat following self-sustaining exothermic oxidation reactions\textsuperscript{12} that can produce luminous emission. While such structures can be easily convected in air, luminous objects were not reproduced in the laboratory. Using an arc discharge between an electrode and a silicon wafer, Paiva \textit{et al.}\textsuperscript{9} produced long-lived silicon fireballs (reminiscent of welder’s sparks) that had features resembling those of ball lightning. Similar experiments by Stephan and Massey\textsuperscript{10} indicated that these fireballs have a Planck radiation distribution characterized by a temperature in the range of 2800–3400 K, suggesting that these fireballs are sustained by combustion with the...
surrounding air. Recently, our studies of the dynamic behavior in air of similar fireballs produced by arc discharges over granular silicon powder\textsuperscript{11} indicate that fireballs can be generated to have an apparent density close to that of standard air, causing them to be buoyant for several seconds. This buoyancy is rather peculiar, since the combusting silicon particle and any of its solid oxide products have a density that greatly exceeds that of air. To explain its buoyancy, we proposed in Ref. 11 that the combustion process ignited by the arc discharge produced a relatively stable and high porosity oxide “nanoforest” that completely surrounds the burning silicon core. We suggested that the heated vapor products are trapped by the surrounding nanostructure, producing the observed buoyant flight. At the time of these studies, we had not experimentally confirmed the presence of such a nanostructure in the millimeter-sized luminous balls. This paper is to report on new findings as a result of the quenching and capturing of the particles during flight. While this report further confirms that the nano-structured silicon-based luminous balls can be easily convected by a gentle breeze, making them a plausible candidate for the ball lightning events seen in nature, it does not experimentally answer the remaining question of how such silicon-based structures form from natural soil, the primary constituent of which is SiO$_2$, during natural lightning strikes.\textsuperscript{8}

II. EXPERIMENTS

The approach used to produce the fireballs is described schematically in Fig. 1. The approach used here is similar to that of our previous study\textsuperscript{11} and prior experiments\textsuperscript{9,10} with the exception of either a superimposed upward draft of 1.3 m/s to draw the fireballs into an 8 cm inner-diameter vertical acrylic wind tunnel to confine particle flight and facilitate video recording, or a substrate for capturing the fireballs to investigate their microscopic structure.

The arc discharge is initiated by detaching the electrodes with $\sim$100 A current flow. The anode is a 99.99\% purity graphite rod with a diameter of 5 mm and the cathode is a 99.5\% purity graphite plate immersed in granular silicon powder. The arc discharge duration is approximately 0.5 s. The silicon grains, approximately 0.5 - 1 mm in characteristic size, are produced from a ground P-doped silicon wafer ($< 0.02 \ \Omega \text{cm}, 0.5 \text{ mm thickness}$). No attempt was made to characterize the initial silicon grain size distribution, and the results appeared to be independent of the ground samples used. Heated and melted silicon induced by the arc discharge ignites into fireballs that are monitored or captured.

The fireballs entering the vertical acrylic wind tunnel are recorded by a conventional video camera. For particle capture, fireballs are allowed to strike silicon substrates positioned on the floor during downward trajectories (in the absence of an upwards imposed flow). The trajectory of the fireballs are recorded by a conventional video camera (Fig. 2 (enhanced)) to confirm the position of the quenched particle as it strikes the substrate. We also employ the gated CCD camera to capture detailed images from which we can estimate the apparent diameter just prior to quenching and capture of the same particle studied by an optical microscope and a field emission scanning electron microscope (FE-SEM). Micro Raman analysis is also performed on the captured fireballs, but these particles are quenched on a copper substrate to avoid the strong background Raman signal associated with the silicon substrate.

III. RESULTS AND DISCUSSION

Figure 3 (enhanced) shows a sequence of video frame recordings of the fireballs in the vertical tunnel. We can see from this figure, that the fireballs are easily carried by the flow because of their low apparent density, which can range from 1 -20 kg/m$^3$ (see Fig. 4(a)).\textsuperscript{11} The density is estimated from its buoyancy at zero velocity, as described in detail in Ref. 11. As also proposed in Ref. 11 and supported by the nanostructure confirmation below, we believe that the heated vapor products are trapped by the surrounding nanostructure, resulting in such low apparent density. The fireballs attain an initial upwards velocity due to the recoil from the energy deposited by the arc discharge while decelerating due to gravity. After a short period (0.2-0.5 s), they experience an upwards acceleration as their apparent densities decrease and are easily carried by the upward draft. The “apparent particle diameter,” against which the density is compared to in Fig. 4(a), is obtained in flight using a gated
charged coupled device (CCD) camera from the size of the luminous region.\textsuperscript{11} The relationship between this measure of the particle’s size, and the overall “gross” diameter (diameter of the entire oxide nanostructure), and silicon “core” diameter, as determined from microscopy of captured particles (described in more detail below) is shown in Figs. 4(b) and 4(c), respectively. The proposed mechanism for the formation of the surrounding nanoparticle network is illustrated in Fig. 4(d).

The microstructure of such fireballs were investigated after quenching and capturing the particles on silicon wafer substrates. Examples of low resolution optical microscope images of two typical particles are shown in Figs. 5(a) and 5(j). In all of the quenched and captured particles, we see a spherical core surrounded by a hazy region that is found to be made up of a complex nanostructure as revealed by higher resolution SEM analysis.

From Fig. 4(b) we see that the apparent diameters are consistently greater than the diameters determined from microscopic analysis by about 60%, likely due to the finite pixel resolution and charge spill-over to adjacent pixels for signals close to saturation. In this paper, we use the physical diameter determined from microscopic studies of captured particles to ascertain the diameter of the
fireballs. Fig. 4(c) indicates that there is a strong correlation between the overall particle diameter (defined by the hazy region in the optical microscope image) and the diameter of the core. Both the optical as well as the high-resolution SEM images of Fig. 5 suggest that the hazy region is a network of nanoparticles that surround the silicon core. From spectroscopic Raman analysis of the captured droplet we have confirmed that the core is comprised predominantly of Si, exhibiting a strong Raman shift at 520 cm$^{-1}$. Unfortunately, low signal to noise precluded analytical characterization of the solid nanoparticle network in the hazy region. Closer inspection of the SEM images indicates that the particle size increases in an outward direction towards the outer region of the nanostructure (e.g. Figs. 5(b)–5(e)), although the most outer edge (Fig. 5(f)) is found to have only relatively small nanoparticles.

The mechanism proposed for the growth of this surrounding nanoparticle network is illustrated in Fig. 4(d). During arc ignition, the silicon grains melt, and oxidation with surrounding air results in strong core heating and in the vaporization of silicon monoxide ($\text{SiO}_\text{(g)}$). $\text{SiO}_\text{(g)}$ clustering occurs as this vapor expands and reacts with additional molecular oxygen to form $\text{SiO}_2\text{(s)}$. We expect $\text{SiO}$ to be the primary vapor products in the reaction between the silicon core and surrounding oxygen since its evaporation temperature is $\sim$2150 K, i.e., much lower than that of silicon dioxide ($\sim$2500 K). Diffusion (both concentration and temperature-driven) leads to the outward transport of the clusters, which grow in size during this transit as heterogeneous reactions occur on the particle surfaces due to the continued supply of $\text{SiO}_\text{(g)}$ and $\text{O}_2$, and agglomerate to form the aggregated...
FIG. 3. Video frames (from left to right, top to bottom) of luminous silicon fireballs in an upward 1.3 m/s flow taken by a conventional video camera at 30 fps. The values shown in the bottom of the figure is the time in seconds. Each image has a size of 1 m × 0.1 m. Note: there are wall image reflections giving the appearance of several particles at any single vertical position. This is apparent in the later frames (0.8-1.2 s) when there is only a single particle in the field of view (enhanced online). [URL: http://dx.doi.org/10.1063/1.3681283.2].

FIG. 4. (a) Nominal density and (b) gross diameter as functions of the apparent diameter by a CCD camera, (c) gross diameter as a function of the core diameter, and (d) the proposed mechanism for nanoparticle network growth. The continued growth via clustering and oxidation can elevate the nanoparticle temperatures to above melting limits, resulting in their spherical morphology and the further promotion of particle aggregation (Fig. 5(d) and 5(e)). The nanoparticles within the network can reach sizes in excess of 200 nm. Interestingly, we find that when the captured particles have smaller cores (Figs. 5(j)–5(r)), there are no such large spherical particles even at comparable distances from the core (Fig. 5(d) vs. 5(m)). We attribute this to the lower evaporative SiO$_2$ flux associated with particles of smaller core. The lower outward flux is still capable of nucleating smaller particles, which results in the finer nanoparticle network seen at the outer edge (Fig. 5(f) and Fig. 5(n)).
It is noteworthy that with some fireballs, we see trails on the substrates (Figs. 5(g)–5(i) and 5(o)–5(r)), which are consistent with the white smoke trails apparent in the videos of the fireballs in flight (you can see these smoke trails in the Fig. 2 (enhanced)). From the SEM analysis of the quenched trail (Figs. 5(i), 5(q), and 5(r)), we find that the nanostructure resembles the structure seen near the outer ridge of the network (Figs. 5(e), 5(m), and 5(n)). We believe that the smoke trail
seen during flight is the consequence of the separation of these nanoparticles from the fireball. From Fig. 4(c), we see that the overall nanoparticle network size is determined by the size of the molten silicon core, essentially independent of the time of capture. The dependency of the relation between the core and the network sizes is also supported by the fact that the nominal density is largely determined by the fireball size (Fig. 4(a)). In other words, the size and structure of the surrounding nanoparticle network is limited by the vapor flux from the molten silicon core, which is determined by its surface area (size) - a finding that should be validated by simulations of particle combustion, vapor product transport, nanoparticle nucleation and growth, and the diffusion of the nanoparticles, which may be strongly driven by temperature gradients.

These data afford an opportunity to estimate the volume-fraction porosity of the nanoparticle network that surrounds the silicon core. The volume-fraction porosity, \( P \), is determined from:

\[
P = 1 - \left( \frac{\bar{\rho}V - \rho_{Si}V_c}{\rho_{SiO_2}(V - V_c)} \right)
\]

Here, \( \bar{\rho} \), \( \rho_{Si} \), and \( \rho_{SiO_2} \), are the measured average (nominal) density (Fig. 4(a)), liquid silicon, and silica, density respectively. \( V \) and \( V_c \) are the overall particle and core volumes respectively (determined from microscopy: \( V - V_c \) represents the volume of the porous region). Note that in using this equation, we assume that the vapor density within the pore is much less than the density of the \( SiO_2 \) nanoparticles comprising the network surrounding the molten core. For a fireball of 1.7 mm diameter (0.2 mm diameter molten silicon core) of measured density of 8 kg/m\(^3\), we estimate a porosity of 99.7%. Smaller fireballs, e.g., those of about 1.2 mm in diameter with 60 \( \mu \)m diameter core are expected to have an average density similar to that of standard air (1.29 kg/m\(^3\)) and a porosity of 99.95%. While the values are estimated from properties determined “in flight” and following capture, these volume-fraction porosities seem to be comparable to the high porosities reported for silica aerogels.\(^{13} \) This provides support for the original proposal that the dynamics can be explained by the presence of a surrounding “nanoforest” in the buoyant fireballs. However, the release of hot reaction products during oxidation in flight may have some effect on the particle flight, and should be considered in future analysis of particle dynamics. Our findings also suggest that this arc discharge process may afford a new opportunity for large-scale production of ultra-porous silica.

IV. SUMMARY

We describe the capturing of fireballs generated by arc discharges in granular silicon, and have characterized their nanostructure by high resolution microscopy. The nanoparticle network is found to have an unusually high porosity (> 99%), resulting in the nominal density of the fireballs which is low enough to be carried by a gentle upward wind as demonstrated with the vertical wind tunnel. The high porosity suggests that this arc-ignition of silicon can be a method of producing ultra-porous silica.

While we confirm the presence of a nanoparticle network within the fireballs,\(^{8,9} \) as growing from the molten silicon core suggested in our previous paper,\(^{11} \) the extension of this mechanism to the production of ball lightning during atmospheric lightning strikes in nature is still the subject of ongoing debate.

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