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High-Temperature LDV Seed Particle Development

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PROJECT SUMMARY

The purpose of this research was to demonstrate the feasibility of developing a method for making monodisperse, unagglomerated spherical particles greater than 50 nm in diameter. This objective was achieved. Carbonaceous particles were made by pyrolyzing ethylene with a pulsed CO_2 laser, thereby creating a non-equilibrium mixture of carbon, hydrogen, hydrocarbon vapors, and unpyrolyzed ethylene. Via a complex series of reactions, the carbon and hydrocarbon vapors quickly condensed into the spherical particles. By cooling and dispersing them in a supersonic expansion immediately after their creation, the hot newly-formed spheres were prevented from colliding and coalescing, thus preventing the problem of agglomeration which has plagued other investigators studying laser-stimulated particle formation. The cold particles could be left suspended in the residual gases indefinitely without agglomerating. Their uniform sizes and unagglomerated nature were visualized by collecting the particles on filters that were subsequently examined using electron microscopy. It was found the mean particle size can be coarsely controlled by varying the initial ethylene pressure, and can be finely controlled by varying the fluence (energy/unit area) with which the laser irradiates the gas.

The motivating application for this research was to manufacture particles that could be used as Laser Doppler Velocimetry (LDV) seeds in high-temperature high-speed flows. Though the particles made in this program will not evaporate until heated to about 3000K, and thus could serve as LDV seeds in some applications, they are not ideal when the hot atmosphere is also oxidizing. In that situation, ceramic materials would be preferable. Research performed elsewhere has demonstrated that selected ceramic materials can be manufactured by laser pyrolysis of appropriate supply gases. We anticipate that, when the same gases are used in conjunction with our innovative rapid cooling technique, unagglomerated spherical ceramic particles can be made with little difficulty. Such particles would also be valuable to manufacturers of ceramic or abrasive products, and this technique may find its greatest commercial potential in those areas.

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1. INTRODUCTION

Measurement of gas flow velocities within propulsion system components is critical to the advancement of aerospace technology. Because of the high gas temperatures involved (~2000 C), usual wind tunnel measurement techniques, in particular Laser Doppler Velocimetry (LDV), are unsuitable. LDV fails primarily because it requires the use of seed particles within the flow to scatter light which is used to determine the particle, and thus the gas, velocity. Seed particles that have been used in the past are unable to withstand the high temperatures of interest, and are often too large to accurately track velocity gradients in the flowfield or too aspherical to scatter light uniformly.

This report describes a successful Phase I SBIR program in which an innovative method has been demonstrated for potentially manufacturing large quantities of particles that are suitable for LDV measurements in high-temperature high-speed flows. In this small-scale feasibility study, carbon spheres, typically 100 to 150 nm in diameter, were made by pyrolyzing ethylene with a pulsed CO_2 laser beam and allowing the decomposition products to condense. By manufacturing the spheres in a rapidly-expanding gas flow, they were cooled and hardened without suffering interparticle collisions. The result, unlike carbon-black or soot, was a high concentration of individual, non-agglomerated particles. We expect that, by similarly pyrolyzing other gases or gas mixtures, this process can yield a multitude of different particle compositions that can be selected as required to suit specific applications.

1.1 Background

To employ LDV for measuring the gas flow velocity of hot supersonic or hypersonic flows, the seed particles must meet several stringent requirements. They should be small enough to accurately follow local flow accelerations, typically limiting the particle diameter to a maximum of 0.5 microns. However, they must not be so small that the light scattered from the laser source is insufficient to give a good signal-to-noise ratio, requiring a theoretical minimum particle diameter of approximately 0.05 microns (though, in some applications, they must be considerably larger). So that the scattered intensity from different particles is sufficiently uniform to remain within the detectability limits of the electro-optic transducer, the seeds should be approximately spherical and monodisperse. In addition, the particles must be able to withstand temperatures of several thousand degrees for periods up to one second without losing a significant fraction of their mass. Since the time required for thermally insulating materials of 0.1 micron diameter to equilibrate with their environment is typically 10^{-8}s, and is shorter for thermal conductors and smaller diameters, the particles must be made of a material which neither evaporates nor reacts with its surroundings at the ambient temperature.

These criteria may be compared with the capabilities of commercially available particle generators marketed for LDV applications.[1] Three techniques are generally used: atomization, dispersion of solids, and evaporation/condensation. Atomization is typically able to generate only rather large (10 to 15 micron), polydisperse liquid spheres. Smaller solid particles can be made by atomizing a solution of the particle material in water and subsequently evaporating the water, but they remain both polydisperse and aspherical. Solid particles injected directly into the flow tend to agglomerate, and are difficult to feed at a constant rate. Dispersion of solids is therefore not a good solution to the problem at hand.

The evaporation/condensation technique is able to produce both small and monodisperse particles, but has been used only with fairly volatile liquids. In this process, oil droplets are generated by atomization and then heated to evaporation. Due to impurities in the oil, residual particulates are left suspended in the oil vapor. The vapor is subsequently cooled, and the particulates act as condensation nuclei. Once this <u>heterogeneous</u> nucleation process begins, it proceeds until all of the oil vapor has condensed, or more precisely, until the local vapor pressure has diminished to its equilibrium value. If the nucleation process is forced to begin on all of the particles at the same time, by rapid cooling for example, then they all grow to approximately the same size, yielding a very monodisperse aerosol. A recent variation of this technique, used to improve the stability and reproducibility of particle sizes, is to seed the oil vapor with externally provided salt nuclei[2], providing a constant number density of nucleation sites and therefore a constant number density of condensed particles having uniform sizes.

A similar process for generating monodisperse aerosols, which does not rely on the presence of residual or externally provided condensation sites, is <u>homogeneous</u> condensation of a vapor. Simply described, homogeneous condensation occurs when it is energetically favorable for randomly formed clusters of condensible molecules to grow by absorbing additional molecules rather than evaporate. These favorable conditions occur when the cluster size is greater than some "critical" value determined by the supersaturation ratio (i.e., the ratio of the vapor pressure of the condensing species to its equilibrium vapor pressure at the same temperature) and the temperature.

The usual method for triggering homogeneous condensation is to generate a condensable vapor by evaporating a liquid, and subsequently cool the vapor by expanding it. As the vapor cools, a point is reached where the rate of critical cluster formation increases so rapidly with decreasing temperature that there appears to be a specific nucleation "onset" temperature. As in heterogeneous condensation, once it begins in earnest, the condensation process continues until the local vapor pressure is reduced to its equilibrium value, resulting in a large number density (typically 10^{12} cm^{-3}) of highly uniform, spherical particles. The number density of nuclei can be controlled to a limited extent by altering the cooling rate, and the final particle size controlled by the initial vapor concentration.

Very early methods of seeding flows, such as smoke or carbon black injection, made use of a similar process but lost popularity because of difficulties in obtaining uniform, sufficiently small particles. Carbon black is created by rapidly combining into particulates molecules of carbon or carbon radical vapors, generated by burning or pyrolyzing a hydrocarbon in an oxygen-poor environment.[3] The resulting carbon vapor apparently condenses into spherical particles but, because they remain hot and sticky for several milliseconds after they form, the spheres suffer many interparticle collisions and agglomerate into chains or clumps, as shown in electron-microphotographs of carbon black particles in Figures 1a and 1b.[4,5] Each "particle" appears to comprise a large number of nearly monodisperse, 50 nm diameter spheres which have aggregated to form an irregular size and shape. These large, irregular particles are unsuitable for LDV seeding.

Because of its low vaporization rate, carbon is a potentially suitable material for use as an LDV seed material in a non-oxidizing heated environment. However, until now, there had been no method available for making monodisperse, submicron spheres of carbon or any other heat resistant material. In this program, a method for preventing agglomeration of condensed carbon particles was developed and demonstrated.

1.2 Agglomeration Mechanisms

In addition to its role in carbon black formation, agglomeration is now known to be one of the fundamental processes in the formation of soot.[5,6] It has also been observed in a process described by Haggerty and Cannon[7] for using lasers to manufacture ceramic powders. In that technique, a continuous wave (CW) CO_2 laser is employed to controllably heat a gas or mixture of gases to a temperature at which its constituents decompose. This pyrolysis yields a hot mixture of vapors, some components having high vapor pressures and others having very low vapor pressures. (An example is provided in Subsection 2.1 below.) The low-vapor pressure products condense rapidly, yielding submicron-sized, monodisperse, spherical particles. However, as shown in Figure 2, it is clear that even these particles agglomerate. As with carbon black, it is believed that agglomeration occurs because the particles remain hot for a few tens of milliseconds after their formation and suffer many interparticle collisions during that period.

Following the calculations of Haggerty and Cannon, the frequency with which a spherical particle suffers collisions is estimated through simple Brownian dynamics to be:

$$f = 8NkT/3\eta$$

where N is the number concentration of particles, T the temperature, η the viscosity of the gas in which the particles are embedded, and k is the Boltzmann constant. In one example of their ceramic production experiments, where silicon particles were formed after laser-supplied heat pyrolyzed silane (SiH_4), values of $N = 8.2 \times 10^{11}$ cm^{-3}, $\eta = 3 \times 10^{-4}$ poise, and $T = 1100$ K were
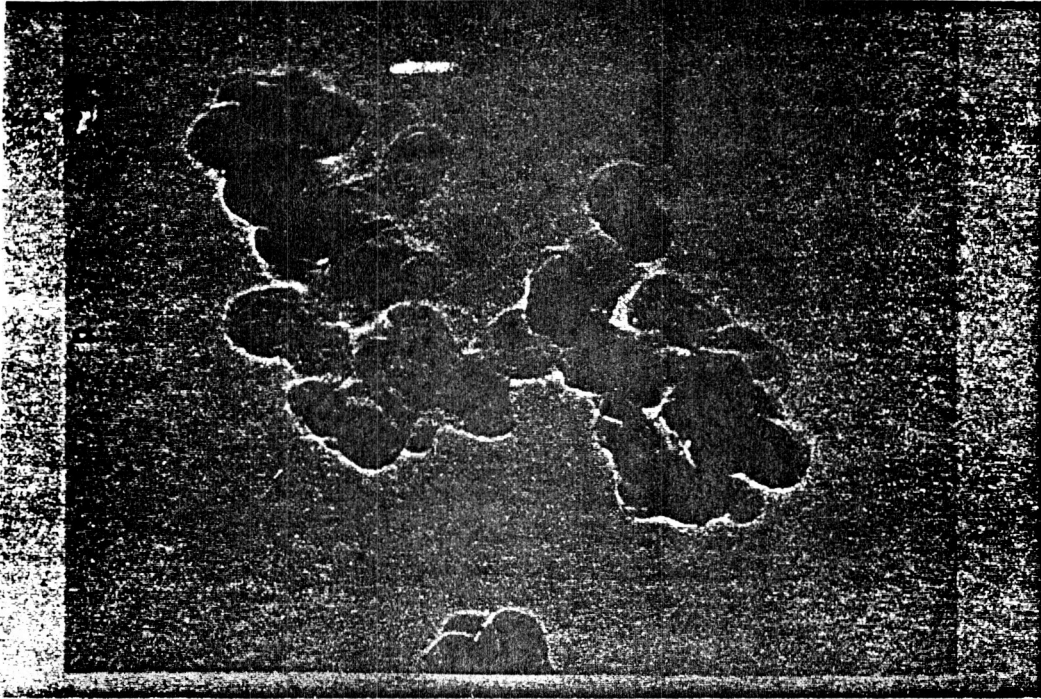
a. Low magnification showing agglomeration of smaller particles
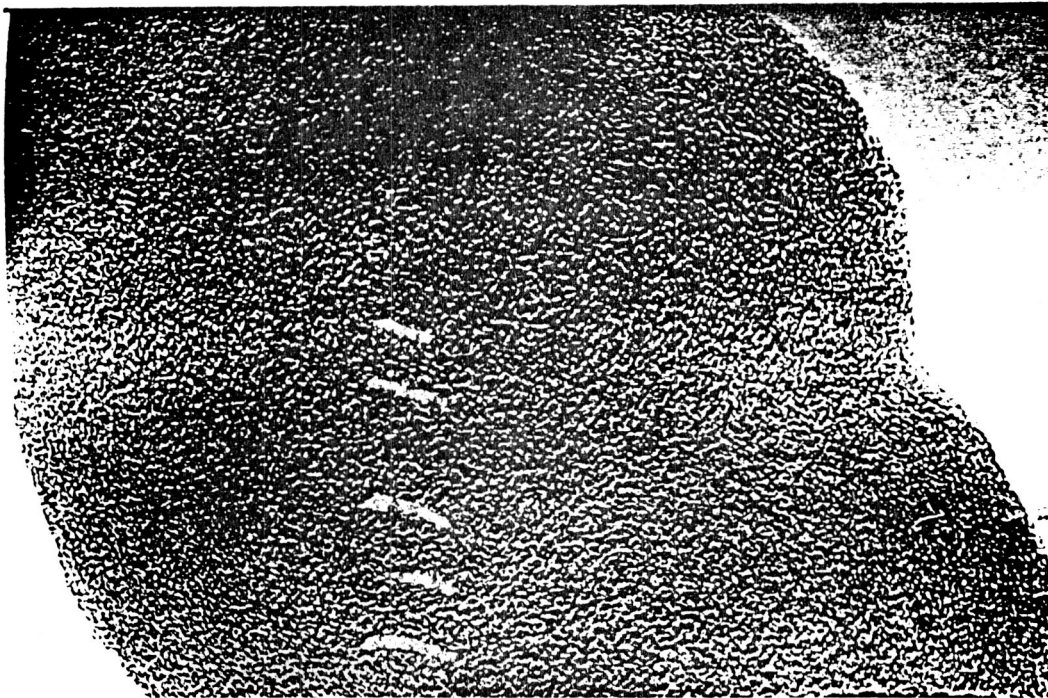
b. High magnification showing lack of structure at particle interface

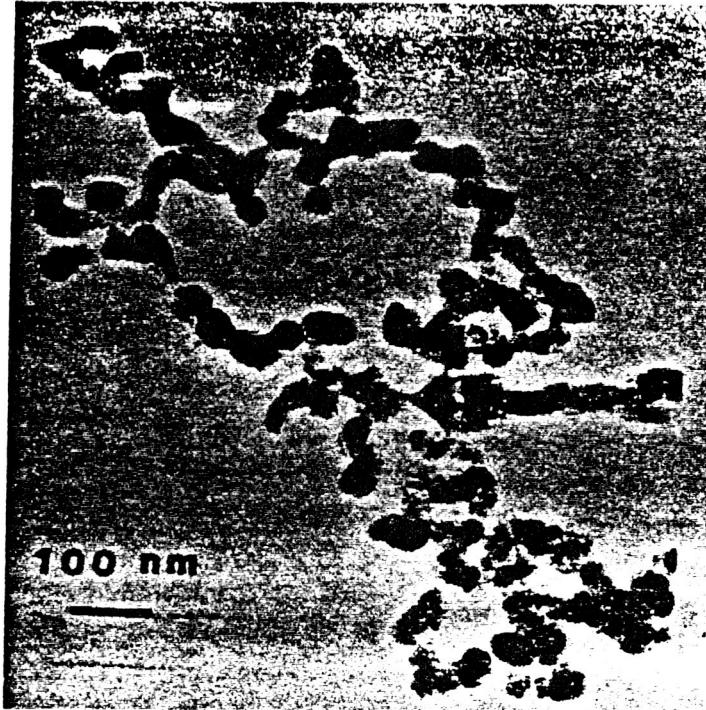Figure 1. – Electron migrographs of carbon black (from Ref. 4).

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Figure 2. – Transmission electron micrograph of silicon powder particles manufactured by the laser heating technique (from Ref. 8).

calculated, giving a collision frequency of 1100 s^{-1}, or about one collision per millisecond.

This collision time may be compared with the time required for the particles to form. Again following Haggerty and Cannon, the silicon particles of 43.5 nm diameter, having masses of 9.9×10^{-17}g, were created from a vapor having an initial density of 6.8×10^{-5} g/cm^3. The volume of vapor depleted to form each particle can be considered to be a sphere of 1.38×10^{-4} cm diameter. Assuming that the condensation process occurs at a rate limited only by gas phase diffusion, the order of magnitude time required to deplete a sphere of radius r is given by

$$t \sim r^2/6D$$

where D is the diffusion coefficient. Kinetic theory yields

$$D = 1/3 \; \lambda c$$

where

$$\lambda = \frac{1}{\sqrt{2}\,\pi d^2} \; \frac{kT}{P} \qquad \text{is the mean free path,}$$

and

$$c = \left(\frac{N_o kT}{\pi M}\right)^{1/2}$$ is the average molecular velocity,

where

        d = molecular diameter
        k = Boltzmann's constant
      N_o = Avogadro's number
        P = pressure
       M = molecular weight
and T = temperature.

Using $d = 4.2\text{Å}$, $P = 0.2$ atm, $M = 32$ g/mole, and $T = 1100$ K yields $t \sim 2 \times 10^{-10}$s for formation of the initial spherical particles. Although this calculation is, at best, a rough approximation of the actual diffusion process, and it is likely that this number will differ by several orders of magnitude for condensation of different species or under different conditions, it indicates that the time required to condense the initial spherical particles is typically a few orders of magnitude less than the average time between interparticle collisions.

1.3 Agglomeration Prevention Hypothesis

Though the precise mechanisms causing the particles stick upon collision are poorly understood, it appears that, when liquids condense, a combination of low surface tension and low viscosity enhances cohesion and subsequent coalescence of particles. There is evidence[5] suggesting that at high temperatures the particles comprising carbon blacks are actually viscous droplets of tar in which these mechanisms play an important role. These effects are reduced at lower temperatures, so that particle sticking becomes increasingly unlikely as the temperature of the particles decreases. As a result, we hypothesized that agglomeration in production of carbon black and ceramic powders could be avoided by dispersing and cooling the particles before they collide. Such individual particles, when injected into a flowfield, would be suitable for many LDV seeding applications. The primary objective of this Phase I effort was then to test that hypothesis.

As described below, the test was successful. In Section 2, the procedures used to manufacture and analyze the unagglomerated particles are described in detail, while the results are reported in Section 3.

2. PARTICLE MANUFACTURING PROCEDURE

2.1 Overview

In summary form, the procedure used to manufacture the unagglomerated particles was to condense them from ethylene gas that was pyrolyzed with a pulsed CO_2 laser. During a 100 to 200 µs interval after the pyrolysis, which was short compared to the mean time between interparticle collisions, the gas containing the newly formed spherical particles was expanded supersonically. Because this expansion cooled the particles to a temperature below their adherence temperature, the monodisperse spheres maintained their individuality.

The apparatus used in these experiments consisted of three major components, each of which is described in detail in Subsection 2.2: 1) The CO_2 laser used for pyrolyzing the gas; 2) A pulsed supersonic nozzle used for expansion and cooling; and 3) A particle detection and collection diagnostic. The configuration of the components is illustrated in Figure 3. The ethylene gas was fed from a supply tank into a 10 liter plenum that served as a reservoir for the nozzle. In some particle making experiments, the average gas flow rate through the nozzle was very slow, while in other
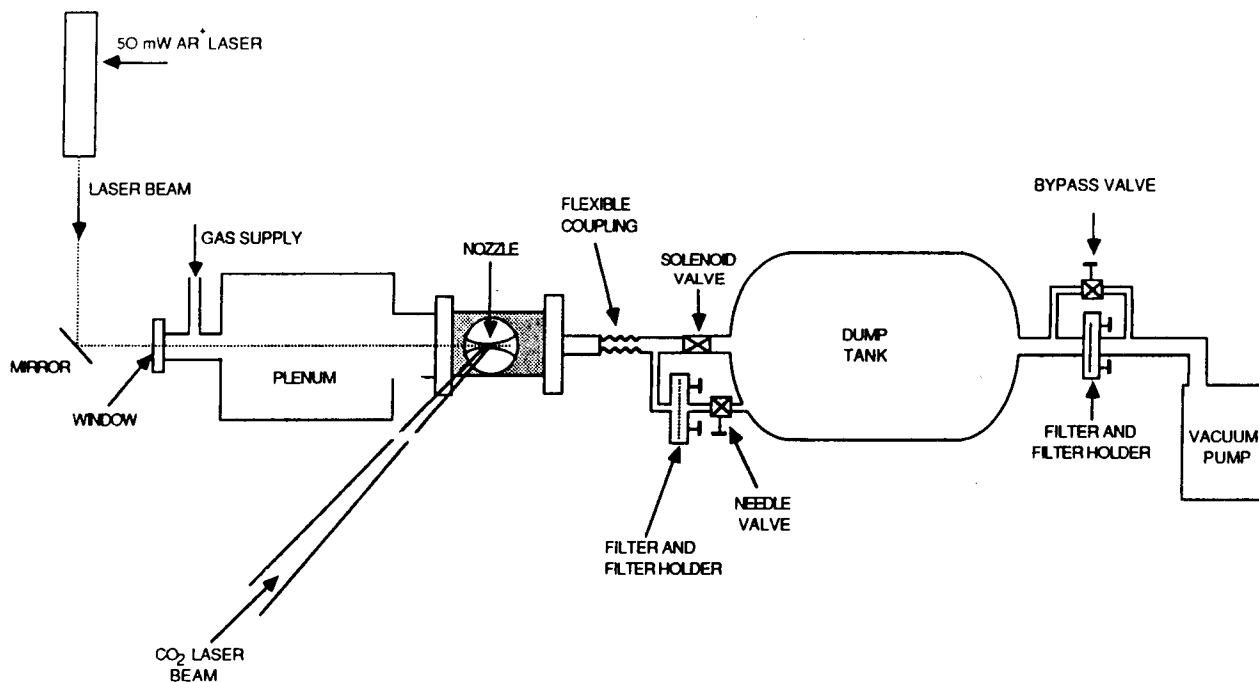

Figure 3. – Apparatus used to produce carbon particles.

experiments a steady supersonic flow was established prior to pyrolysis. Thus, the flow through the nozzle was controlled by two valves which separated the nozzle from an evacuated dump tank: a large solenoid valve was used to establish supersonic flow, while a small needle valve was used to regulate the slow flow. Steady supersonic flow conditions were established in the nozzle within about 100 ms after opening the solenoid valve, and the flow could be maintained for about another 100 ms before the plenum pressure dropped significantly.
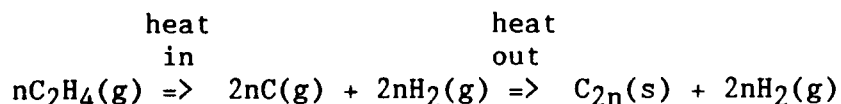
As illustrated in Figure 4, the 10 cm long and 1.25 cm wide nozzle was comprised of two identical nozzle blocks enclosed by parallel flat walls. Its throat was 5 mm high and the exit opening 21 mm high, providing an exhaust velocity of Mach 3. The CO_2 laser beam was transmitted into the nozzle orthogonal to the flow direction through a 50 mm diameter sodium chloride window embedded in the nozzle wall surrounding the area around and downstream of the throat. The beam was directed into the nozzle by a series of mirrors, the last of which was concave. The intensity (power/unit area) or fluence (energy/unit area) of the beam as it entered the nozzle was determined by the separation between the concave focusing mirror and the salt window.
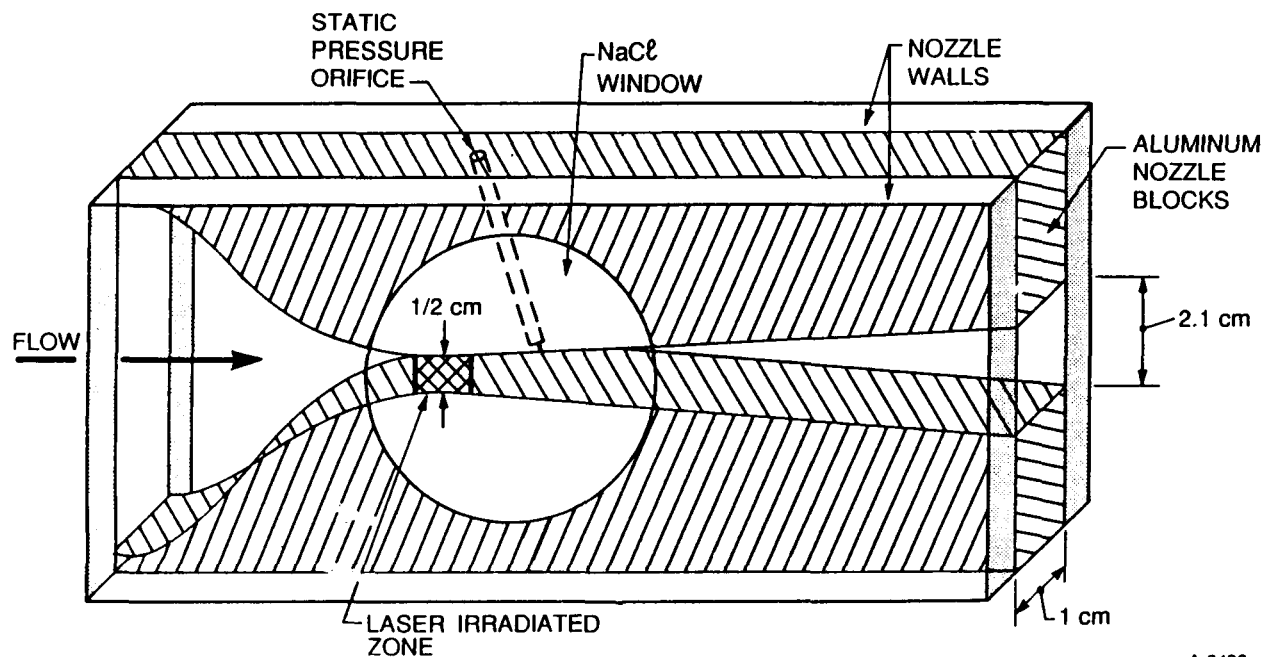
Figure 4. - Schematic illustration of nozzle. The area irradiated by the pulsed CO_2 laser is also shown.

Carbon particles were manufactured by filling the plenum and nozzle with ethylene gas, and then decomposing the gas with a pulse from the CO_2 laser, allowing the resultant carbon vapors to condense. The overall reaction may be summarized by the equation:

$$\overset{\text{heat}}{\underset{\text{in}}{}}\qquad\qquad\overset{\text{heat}}{\underset{\text{out}}{}}$$

$$nC_2H_4(g) \Rightarrow 2nC(g) + 2nH_2(g) \Rightarrow C_{2n}(s) + 2nH_2(g)$$

Ethylene was chosen for these Phase I studies because it is an excellent absorber of the 10.6 μm radiation provided by the CO_2 laser, and it is relatively safe compared to some other possible gases.

To prevent the particles from agglomerating, the residual gas containing the particles (a mixture of hydrogen and unpyrolyzed ethylene) was quickly expanded and cooled using either of two methods - a blast wave expansion caused directly by the local heating resulting from the absorption of laser energy, or combination of blast wave plus a steady supersonic expansion through the nozzle. After completing the expansion, the gases were exhausted from the system through Nuclepore ® filters, which captured the particles. The filters were subsequently analyzed by scanning electron microscopy (SEM). Particle size distributions were determined from the resulting micrographs, and the effects of various system parameters on these distributions were studied.

A visible wavelength argon-ion laser beam directed down the axis of the nozzle served as a quick diagnostic for determining whether or not particles were made after each laser pulse. Using the blast wave expansion method, the presence of particles was confirmed by visually observing light scattered from the beam.

In the following subsections, each of these system components and the experimental procedure are described in detail.

2.2 Components

2.2.1 CO_2 laser and laser interaction theory. - The first step in the particle manufacturing process was to heat the ethylene gas to a temperature where a substantial fraction of it is pyrolyzed. Heating was achieved by irradiating the gas with a laser. A pulsed CO_2 laser was used in this work, as opposed to a CW CO_2 laser used in the ceramic particle manufacturing experiments reported by Haggerty and Cannon.[7] The motivation behind this choice of laser is found in the following theoretical discussion of the laser beam's interaction with the gas.

As illustrated in Figure 5, when the laser beam propagates through the gas, its intensity (power/unit area), or in the case of a pulsed laser its fluence (energy/ unit area), decreases exponentially with distance according to Beer's law
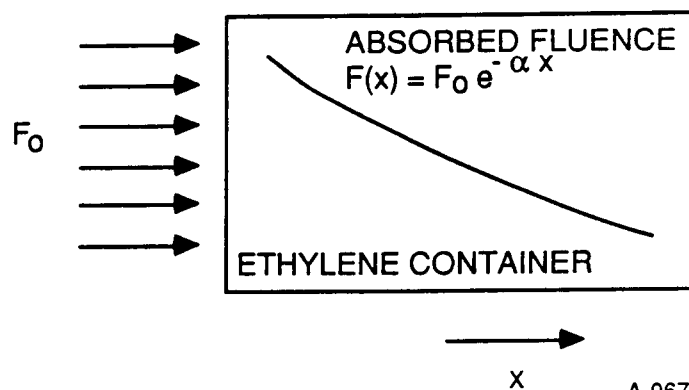
Figure 5. - Exponential decrease of laser fluence as the beam propagates through the gas.

ABSORBED FLUENCE

$$F(x) = F_0 e^{-\alpha x}$$

ETHYLENE CONTAINER

F_0

x A-9674

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$$F(x) = F_0 \exp(-\alpha x) \qquad (1)$$

where F_0 is the laser fluence before entering the gas, α is the absorption coefficient, and x is the depth from the nozzle window into the gas. Assuming that the absorption coefficient is roughly proportional to the number density, n, of the gas, then

$$\alpha = n\alpha_0 = (\rho/m)\alpha_0 \qquad (2)$$

where α_0 is a constant, ρ is the mass density, and m is the molecular weight. The energy absorbed per unit volume of gas is simply equal to the local change in fluence, given by

$$Q(x) = - dF(x)/dx = \alpha F_0 \exp(-\alpha x) \qquad (3)$$

or,

$$Q(x) = (\alpha_0 \rho/m) F_0 \exp(-\alpha_0 \rho x/m) \quad . \qquad (4)$$

This absorbed energy heats the gas, raising its temperature by an amount

$$\Delta T = Q(x)/\rho c_p \qquad (5)$$

where c_p is the specific heat, or

$$\Delta T = (\alpha_0/m c_p) F_0 \exp(-\alpha_0 \rho x/m) \quad . \qquad (6)$$

In a typical Haggerty and Cannon experiment, a continuous wave CO_2 laser was used to heat silane to about 1100 K. As in the present work, the gas flowed transversely to the laser beam, but at a velocity of only 570 cm/s. In the region traversed by the gas, the laser was focused to provide a Gaussian intensity profile described by the equation

$$I(r) = I_0 \exp[-2(r/r_0)2] \qquad (7)$$

where r is the radial position coordinate, I_0 is the maximum intensity found at the center of the beam ($r=0$), and r_0 is the so-called $1/e^2$ beam radius. A differential g~ element passing through the laser beam experienced an intensity which appeared to change with time. The resulting fluence experienced by the gas is the temporally integrated intensity

$$F = \int_\infty I(t)dt \qquad (8)$$

or, in the gas's moving frame of reference, $t = r/u$ so that

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$$F = (1/u) \int_{\infty}^{-\infty} I(r)dr \quad . \tag{9}$$

Recognizing that the laser power is given by

$$P = 2\pi \int_{\infty}^{-\infty} I(r)r \, dr = \frac{1}{2} \pi r_o^2 I_o \quad . \tag{10}$$

Equation (9) yields

$$F = \sqrt{\frac{2}{\pi}} \, (P/ur_o) \quad . \tag{11}$$

Since the Haggerty and Cannon 150W laser was focused to a $1/e^2$ radius of 0.35 cm, providing a peak intensity of 760 W/cm^2, the fluence experienced by the gas was about 0.7 J/cm^2, which, given the absorption properties of silane, was sufficient to raise the gas to the pyrolysis temperature.

The objective of the present work was to terminate the heating of the gas and cool the condensed particles as quickly as possible after pyrolysis. The cooling was accomplished using a supersonic expansion, either one associated with a blast wave triggered by rapidly depositing a large amount of energy in a small volume of gas or one created by expanding the gas through a nozzle into an evacuated dump tank. A CW laser could not have been a suitable heating source for either type of expansion. Because blast waves are created by rapid, local deposition of energy, they cannot be generated by a CW laser. The heated gas would simply flow slowly out of the laser beam by convection. Furthermore, the gas velocities achieved using the supersonic flow method exceeded 300 to 500 m/s, roughly 100 times faster than Haggerty and Cannon! Equation (11) indicates that a 15 kW CW laser would have been needed to provide the required fluence when using the same optical configuration. Such a large laser is hardly practical for making LDV seed particles! Because of these considerations, a _pulsed_ laser, which intermittently provides over 5 MW of power, was used in these experiments. The device was a Lumonics Model K-103 CO_2 TEA laser, capable of generating 15J per pulse at a wavelength of 10.6 μm. The pulse duration was about 2.5 μs, with 60 percent of the energy contained in an initial 300 ns spike.

As shown in Figure 6, the laser was directed into the nozzle using a pair of flat and concave mirrors. The 760 mm focal length concave mirror was used to control the fluence at the salt window. Due to the short duration of the laser pulse, the gas moved little while being irradiated so that in Eq. (6) the appropriate value for the fluence was simply equal to the (constant) energy emitted by the laser in each pulse divided by the area of the beam. By changing the distance between the focusing mirror and the nozzle's entrance window, the size of the beam where it intercepted the window
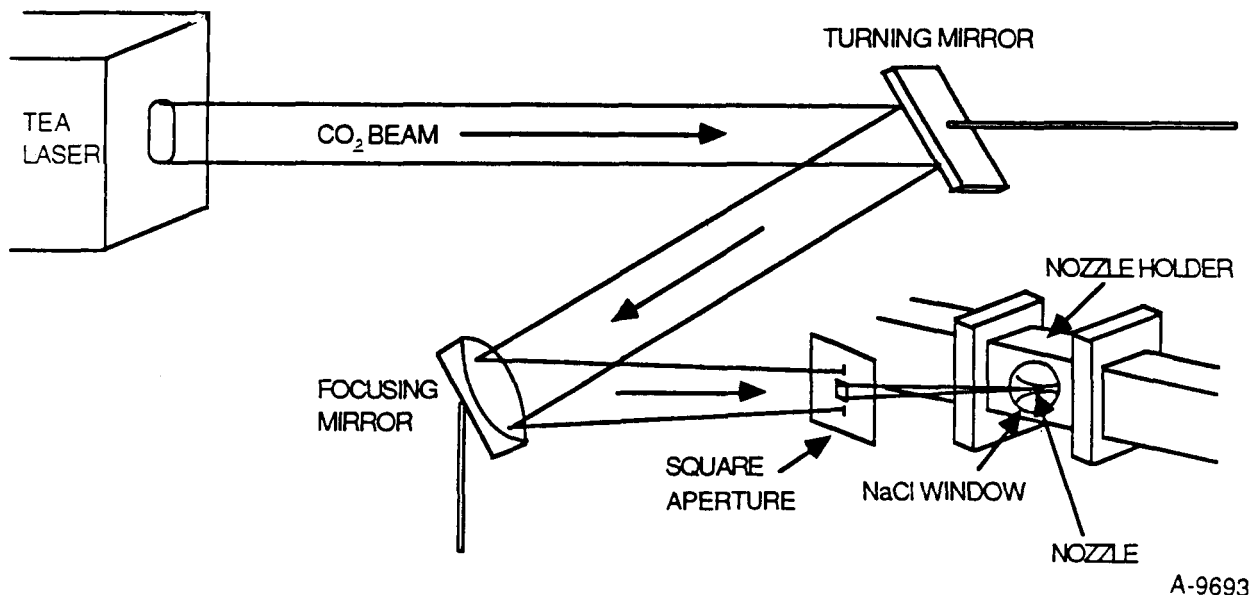
Figure 6. - Optics used to direct and focus the laser beam.

was altered as desired to control the fluence. After selecting the fluence, the actual area irradiated was further reduced to about 6 mm x 6 mm by placing an aperture in the beam's path. This prevented the beam from striking and damaging the nozzle blocks.

Since ethylene, not silane, was heated in this work, the fluence required to achieve pyrolysis was somewhat different than that used by Haggerty and Cannon. As stated above, ethylene, like silane, is an excellent absorber of the CO_2 laser radiation. The absorption coefficient, α_0, of the ethylene was calculated from published values of $\alpha = 1.09$ cm^{-1} at p = 1 atm and T = 300 K.[9] Using the ideal gas law, the mass density of ethylene under these conditions is

$$\rho = p/RT = 1.14 \times 10^{-3} \text{ g/cm}^3 \tag{12}$$

which, combined with Eq. (7) and m = 28 g/mole determines α_0 = 26,800 cm^2/mole. Inserting this value and $c_p = 1.59$ J/g-K into Eq. (11), gives the temperature rise as a function of depth as

$$\Delta T \quad 602 \text{ (cm}^2\text{-K/J) } F_0 \exp(-\alpha x) \quad . \tag{13}$$

The temperature rise as a function of fluence at x = 0 is plotted in Figure 7, where it is seen that, to raise the temperature to 1100 K, a fluence of about 1.4 J/cm^2, or roughly twice that used by Haggerty and Cannon, was needed.

Note that the heating of the gas throughout the nozzle's depth would be uniform only if $\alpha x \ll 1$. However, in these experiments $\alpha x \sim 1$. The resulting non-uniform heating may have led to variations in the density of pyrolyzed vapor products, causing some polydispersion of the particles. (This can

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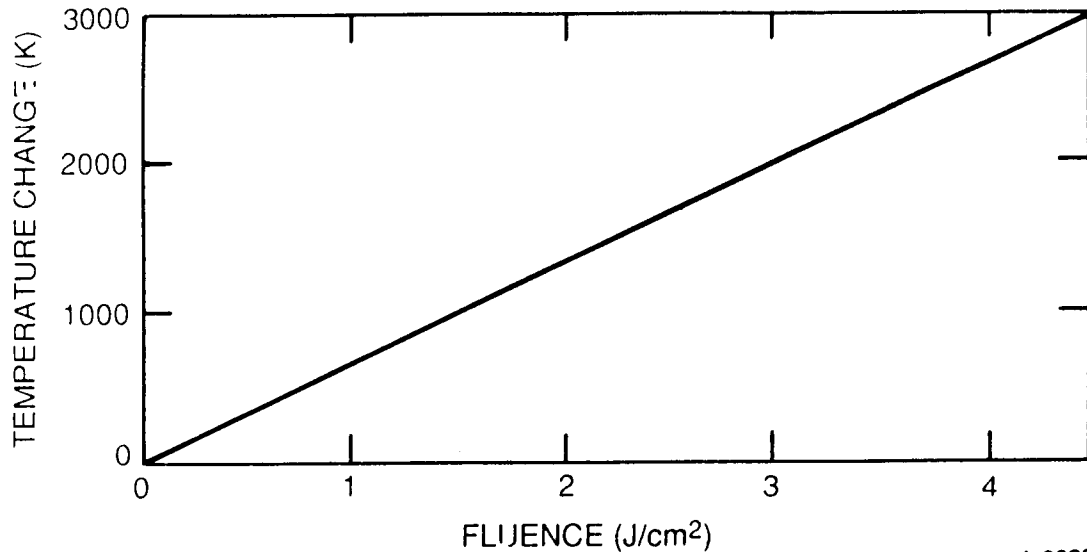
Figure 7. - Temperature rise as a function of fluence of x = 0.

explain some of the observations discussed later.) Furthermore, the
absorption coefficient changes dramatically when pyrolysis occurs, rendering
the calculations imprecise for x > 0. To pyrolyze the gas in depth, fluences
as high as 3 J/cm^2 were used.

2.2.2 <u>Supersonic expansion</u>. - The essential innovation in this work was
to prevent particles that condense after the gas pyrolyzed from agglomerating
by rapidly expanding and cooling the residual gas. The expansion was
accomplished by either a steady supersonic flow through a nozzle or by a
supersonic blast wave. As discussed in Subsection 2.2.3 below, the blast wave
method was preferable in this Phase I program because it facilitated
diagnosing the presence or absence or particles. However, the steady
expansion was the method that had originally been proposed, and may ultimately
prove to be preferable because of the control over particle size that it may
offer. Both techniques are described below. The steady expansion process is
discussed first.

a) Supersonic nozzle flow. - The general features of flow through a
supersonic nozzle are illustrated in Figure 8. From the high pressure side of
the nozzle the gas flows first through a contraction and then into an expand-
ing region which exhausts into low pressure. The changing characteristics of
the gas as it flows down the length of the nozzle are well known,[10] assuming
that the flow remains isentropic. At the junction of the contraction and the
expansion, called the nozzle throat, the flow velocity is equal to the local
speed of sound, Mach 1. Away from the throat, the local Mach number,
velocity, temperature, gas density and pressure are determined by the ratio of
the local cross-sectional area to the area of the throat. By knowing the
nozzle geometry and any one of these flow parameters at any point in the flow,
all of the other parameters can be calculated everywhere within the nozzle.

In the steady supersonic expansion method, the ethylene was decomposed
and carbon particles condensed near the sonic throat of the nozzle shown in
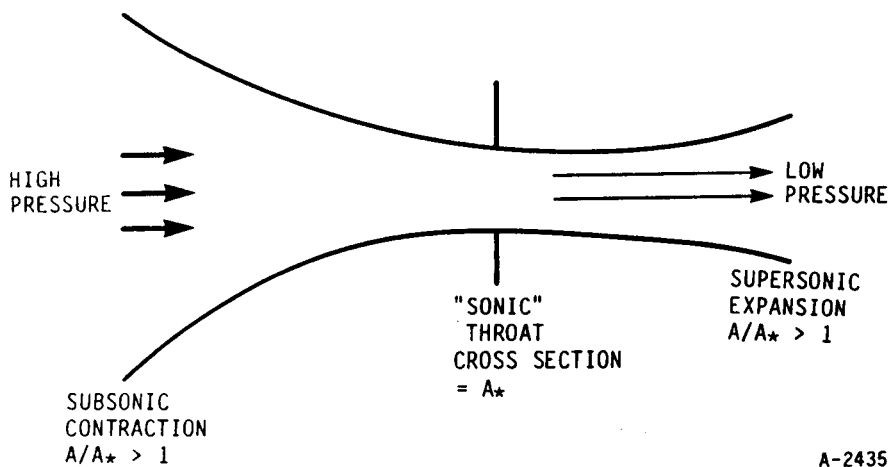
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Figure 8. - General features of gas flow
through a supersonic nozzle.

the laser heating and latent heat of condensation are ignored, the gas
temperature and density at the nozzle exit decreased to 43 and 12 percent,
respectively, of their values at the condensation point, and the typical gas
velocity between the throat and the exit of the nozzle was greater than
500 m/s. The time required for the gas to travel and cool between the nozzle
throat and its exit was therefore roughly 200 μs. Assuming that the average
probability of interparticle collisions during this time period decreased
linearly with distance along the nozzle, it had a value of approximately 21/40
of that at the nozzle throat, giving about 500 collisions per second, or 2 ms
per collision. Since particle collisions are random, the probability of
collision in the interval t is given by[11]

$$P(t) = 1 - e^{-Rt}$$

where R is the average collision rate. Inserting $R = 500$ s^{-1} and $t = 0.2s$
gives $P = 0.09$. Thus, fewer than one particle in ten should have suffered a
collision during the expansion process. The fraction of particles which
formed clusters of two could therefore be at most only a few percent.
Furthermore, because the particles cooled nearly as quickly as the gas, the
probability of sticking upon collision is even smaller. Thus, it was expected
that this expansion would prevent particle agglomeration, and, as discussed in
Section 3 below, appears to have functioned much as expected.

Unfortunately, early in this effort, we had intended to use the impact
probe illustrated in Figure 9 to capture the particles as they were swept into
the dump tank. Furthermore, as described below, prior to subjecting the
impact probe to SEM analysis we had intended to confirm that particles were,
in fact, being made by observing, either visually or with a linear Reticon
array, light scattered from the flow system's 50 mW Ar^+ laser. However, upon
operating the apparatus, it quickly became obvious that the particles were
being swept out of the nozzle too quickly for the available scattering
diagnostic to observe anything. Furthermore, because the particle sizes were
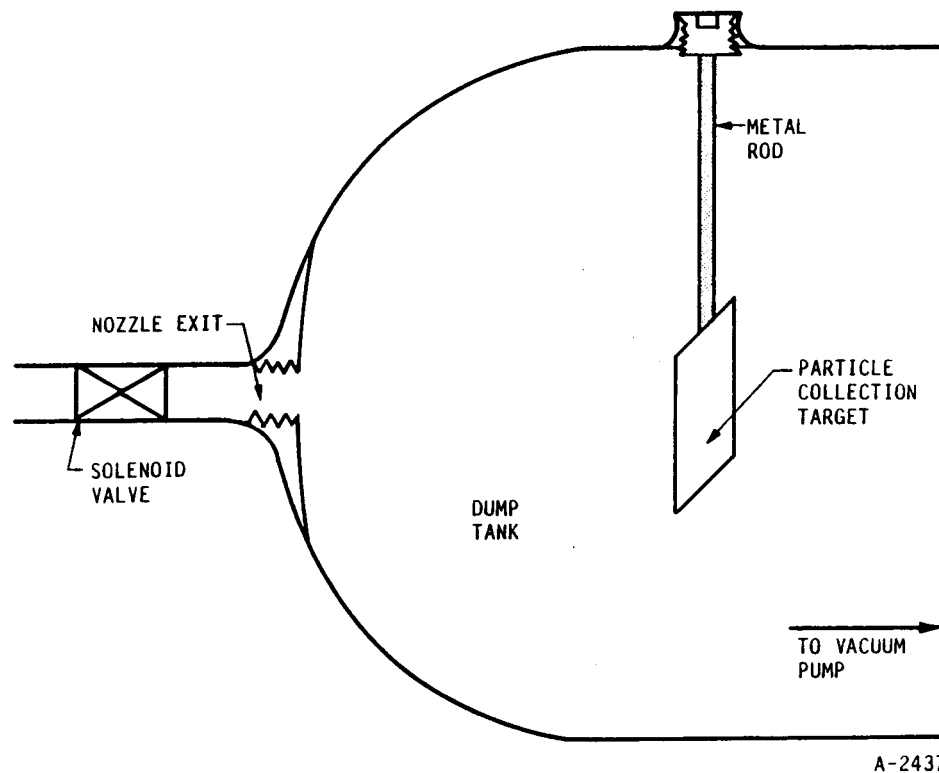
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Figure 9. - Schematic illustration proposed method of gathering particles
after their growth.

selected to be small enough to accurately follow the flow, they were swept
with the flow around the impact probe and no particles were collected. Later
in the program we found that particles could be captured by slowly exhausting
the dump tank through a filter, but we first explored alternative methods of
demonstrating that particles were being made. The most successful alternative
was the blast wave expansion method, discussed next.

b) Blast wave expansion. - A convincing demonstration that the laser
heating technique did indeed decompose ethylene and result in formation of
solid particles was achieved by rapidly heating, with the pulsed CO_2 laser, a
small volume of stagnant gas. Furthermore, it was found that, because the
localized heating raised the gas pressure as well as the temperature, it
caused a radial supersonic flow of gas away from the heated region in the form
of a shock front, as illustrated in Figure 10. This shock front was, in
essence, a blast wave. The gas enclosed by the front, along with the embedded
particles, cooled adiabatically as it expanded. Blast wave scaling laws[12]
indicate that the pressure and temperature within the shocked region decayed
to ambient after expanding to a radius of about 5 cm in a period of about
150 ms. Thus, particles manufactured in the nozzle using the pulsed laser
heating technique but with the supersonic flow turned off were cooled and
dispersed as rapidly as those made with the flow operating! Furthermore,
after the blast wave had subsided, the cold particles remained stationary

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LASER - HEATED
ZONE

GAS FLOW
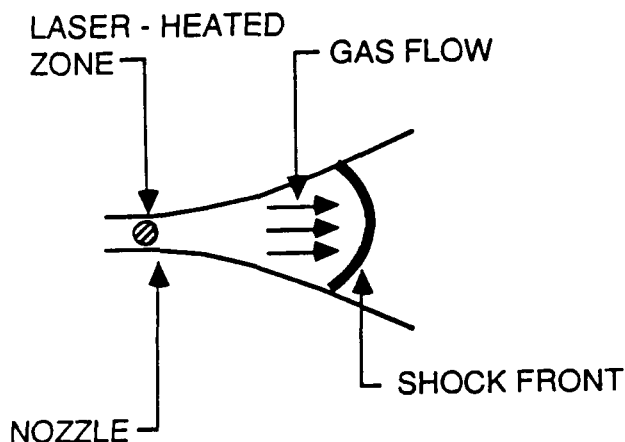
SHOCK FRONT

NOZZLE

A-9675

Figure 10. - Radial flow away from localized heated region in the form of a shock front.

within the 5 cm radius region and light scattered from them was easy to observe, as discussed next.

2.2.3 Particle detection and collection. - Two techniques were used to observe the particles. As mentioned above, a light scattering diagnostic was used to detect the particles during their production, while filters were used to capture the particles for subsequent study.

a) Light scattering. - To determine that particles were being made during any particular run, light scattering from an argon-ion (Ar^+) laser beam directed down the axis of the nozzle was used. The laser was an American Laser Corp. 50 mW air-cooled device. Its beam was directed into the flow apparatus, as illustrated in Figure 3, through a window located upstream of the plenum. The beam within the nozzle was essentially invisible to the naked eye when no particles were present. However, when the particles were present, they isotropically scattered enough light to make the beam clearly visible. Therefore, when the Ar^+ beam could be seen, particles were being produced. However, as mentioned previously, this technique could only be used with the blast wave expansion method. When using the supersonic flow, the particles were swept out of the nozzle too quickly to be seen with the human eye or with the Reticon array that was available for measuring the scattered light intensity as a function of position in the nozzle. For this reason, most of the particle manufacturing runs employed the blast wave expansion method.
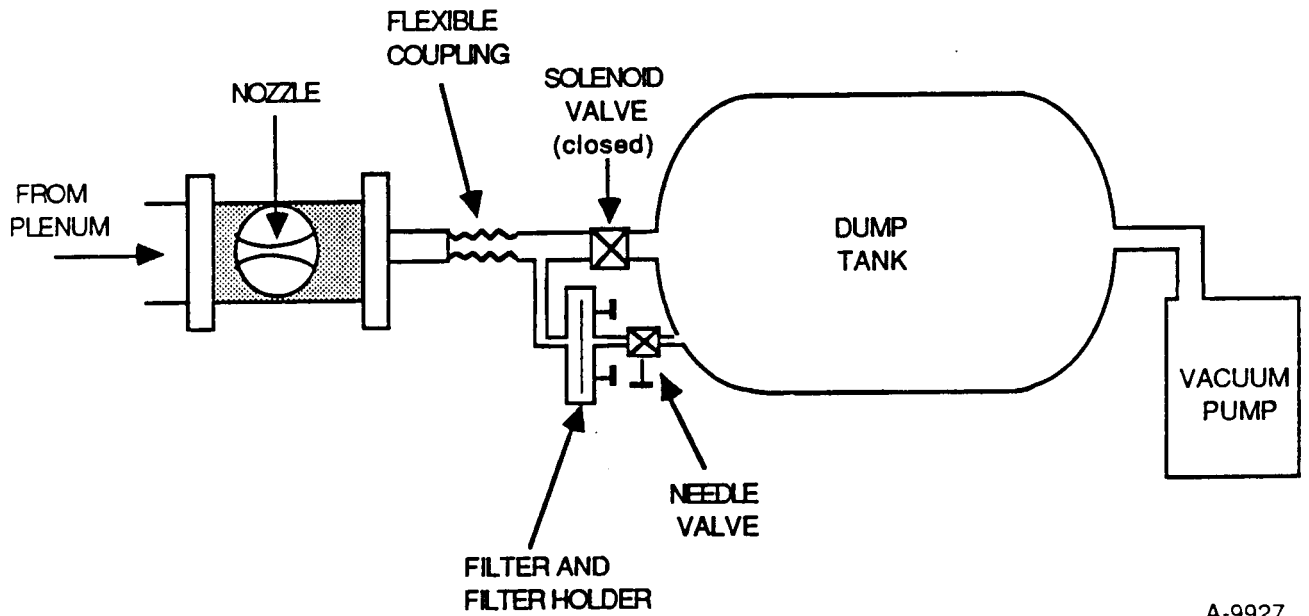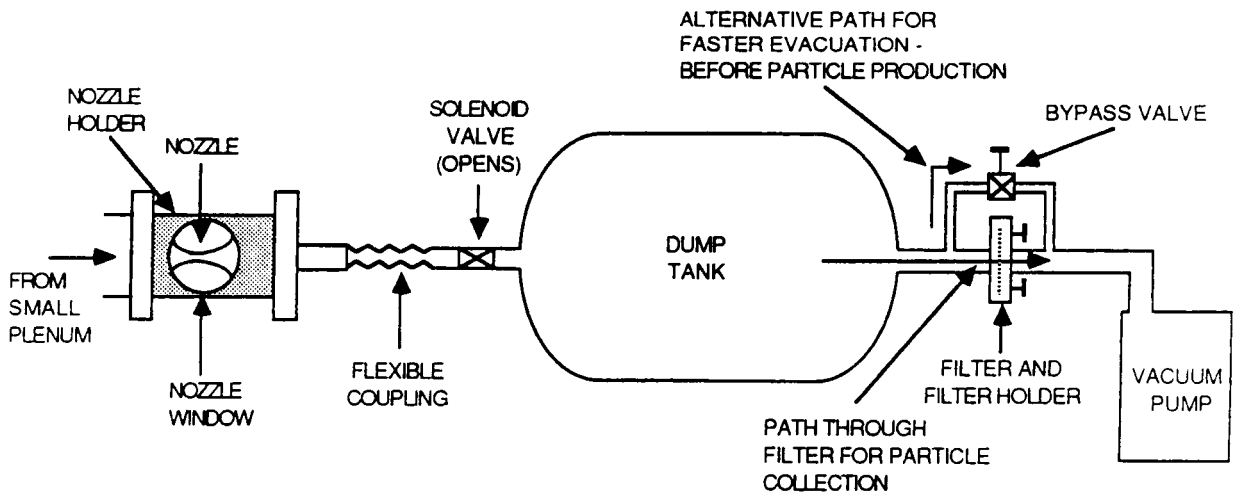
b) Particle collection. - The most important diagnostic was a direct measurement, with the aid of scanning electron-microscopy, of the particle size distributions resulting from different combinations of experimental parameters. To perform the SEM, the particles first had to be captured. Several particle capture techniques were tried without success until it was found that Nuclepore Ⓡ filters could be used for this purpose. These filters are thin pieces of plastic pierced with numerous holes that can be specified to be no larger than 15 nm in diameter. The holes allowed the gas to pass (albeit slowly) while blocking the particles. Because particle diameters were expected to be greater than 50 nm, the majority of experiments used filters with 30 nm holes.

As shown in Figures 11a and 11b, the filter was located differently for the two expansion methods. When the blast wave method was used, the filter was placed between the nozzle and the dump tank. The gas was forced through the filter by the pressure differential between the nozzle (typically operated

Figure 11a. - Apparatus configured for blast wave expansion.

Figure 11b. - Apparatus configured for supersonic expansion.

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at 20.4 psi) and the evacuated dump tank. For the supersonic expansion method, the filter was placed between the dump tank and the vacuum pump. Prior to each run, the dump tank was evacuated through the bypass valve shown in Figure 11b. When the solenoid valve was opened and the laser fired, gases and particles filled the dump tank, which was then slowly evacuated through the filter. The particles remained suspended within the tank for as long as there was sufficient pressure to inhibit their settling to the bottom. Thus, most of the particles were drawn onto the filter and captured.

Since the filters are not electrically conductive, they were gold coated to enable SEM analysis. The coating and the analysis was performed at the Massachusetts Institute of Technology's Material Science Department. A Jeob Scanning/Transmission Electron Microscope (STEM) was used to obtain high-resolution electron-micrographs of the filters and particles.

2.3 Particle Manufacturing and Data Analysis Procedure Summary

The previous sections described the details of the particle manufacturing system and the motivation behind the procedures which were used to create the particles. Those procedures are summarized by the following sequences:

2.3.1 Blast wave expansion method. -

1. The laser optics were configured to provide the desired fluence at the nozzle window;

2. A Nuclepore filter with desired pore sizes was inserted into filter holder;

3. The plenum and nozzle were filled with ethylene to the desired pressure;

4. The needle valve between the filter and the dump tank was opened to establish a slow but steady flow of ethylene. The valve was adjusted so that the flow was just fast enough to move the particles out of the nozzle and refill it with fresh ethylene in the time between laser pulses;

5. The CO_2 laser was fired repetitively at 0.5 Hz for the desired duration; light scattered from the Ar^+ laser was observed visually or recorded on videotape.

6. The filter was removed from its holder, labeled, and stored in a clean container.

7. An operational parameter (filter pore size, fluence, pressure, or run duration) was varied and the procedure repeated.

2.3.2 Supersonic nozzle expansion method. -

1. The laser optics were configured to provide the desired fluence at the nozzle window;

2. A Nuclepore filter with desired pore sizes was inserted into filter holder;

3. The plenum and nozzle were filled with ethylene to the desired pressure. The dump tank was completely evacuated through the bypass valve.

4. The supersonic flow was started by opening the solenoid valve in front of the dump tank, thereby changing the pressure profile in the nozzle. Steady flow conditions were established 100 ms after opening the valve;

5. The CO_2 laser was fired once;

6. The dump tank was slowly evacuated through the filter;

7. Steps 3-6 were repeated as desired;

8. The filter was removed from its holder, labeled, and stored in a clean container.

9. An operational parameter (filter pore size, fluence, pressure, or run duration) was varied and the procedure repeated.

2.3.3 Data analysis procedure. -

After collecting particles under a number of different conditions, a 3 mm x 3 mm segment was cut from each filter. The segments were gold coated, and photographed using SEM at a magnification of 15kX or greater. The sizes of the particles observed on the micrographs were measured using a hand-held ruler. The precision of particle size measurements was limited by the 0.25 mm resolution of the ruler to approximately 9 nm at 30kX magnification and 17 nm at 15kX magnification. For each run, histograms of particle size distributions were plotted. Average particle sizes, uncertainties in that average resulting from the lack of precision, and standard deviations around the average, corresponding to the width of the size distribution curve, were also calculated.

3. RESULTS

Data from six experiments, each with one parameter altered compared to a standard run, were collected and fully analyzed. Table 1 summarizes the experiments and the results. The electron-micrographs from each of the six runs are reproduced along with the particle size distribution histograms in Figures 12 through 17. Brief descriptions of each run follow.

TABLE 1. - TEST MATRIX

Run No.	Fluence (J/cm^2)	Ethylene Pressure (psi)	Run Time (min)	No. of Laser Shots	Supersonic Flow?	Average Particle Diameter (nm)	Standard Deviation (nm)
1	0	20.4	10	0	No	None	–
2	3	20.4	10	150	No	146	42
3	1.3	20.4	10	150	No	129	20
4	3	17.6	10	150	No	<79	>39
5	3	20.4	120	1800	No	?	?
6	3	20.4	–	12	Yes	<50	>24

Run 1 - Blank Sample

The purpose of this run was to examine a blank filter, and determine that the particles found on the filters in subsequent runs were due to the decomposition of the ethylene, and not some other source. Ethylene gas, at a pressure of 20.4 psi, flowed through a 30 nm pore filter for 10 min. The CO_2 laser was not fired.

In Figure 12, the 30 nm pores appear as distinct small black spots. As expected, no particles were observed except for two pieces of dust that were found after a great deal of searching. The larger dust particle measures about 500 nm.

Run 2 - Standard Sample

This run was designated the standard. In all subsequent runs, one parameter was varied in comparison to those used here.

The SEM for this run is shown at a magnification of 30kX in Figure 13a. The larger, white spots are the carbon particles, while the small, black spots are the 30 nm filter pores. The black shadows around the particles are due to secondary electrons striking the surface at an angle, creating shadows

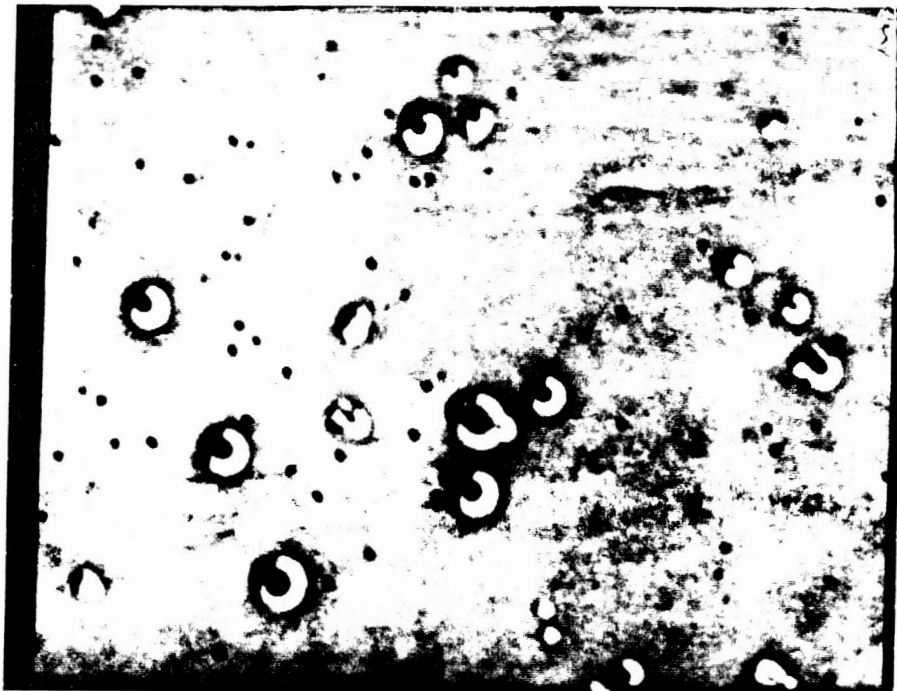Figure 12. - SEM of Nuclepore filter with two dust particles.
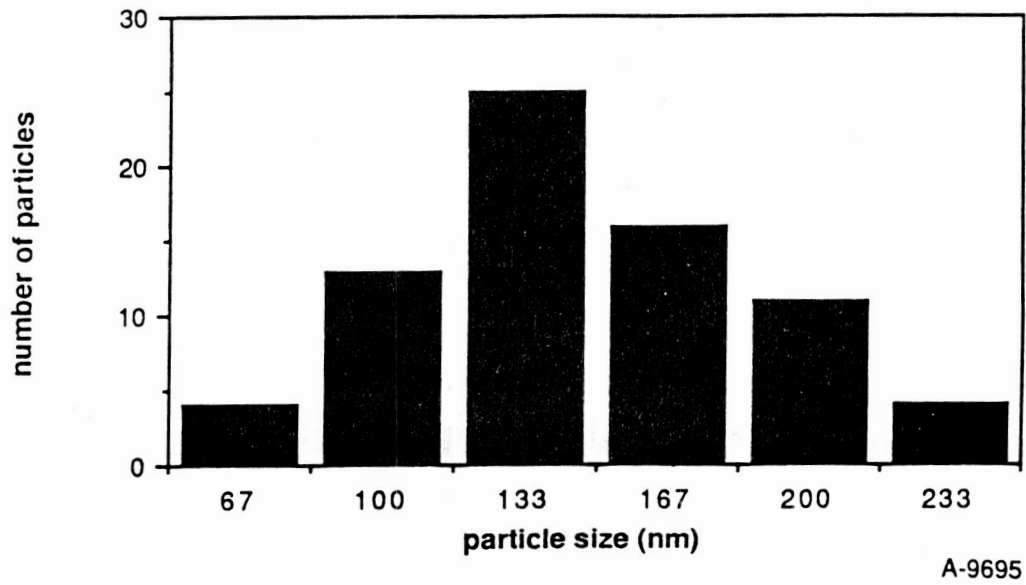

Figure 13a. - SEM of standard run.

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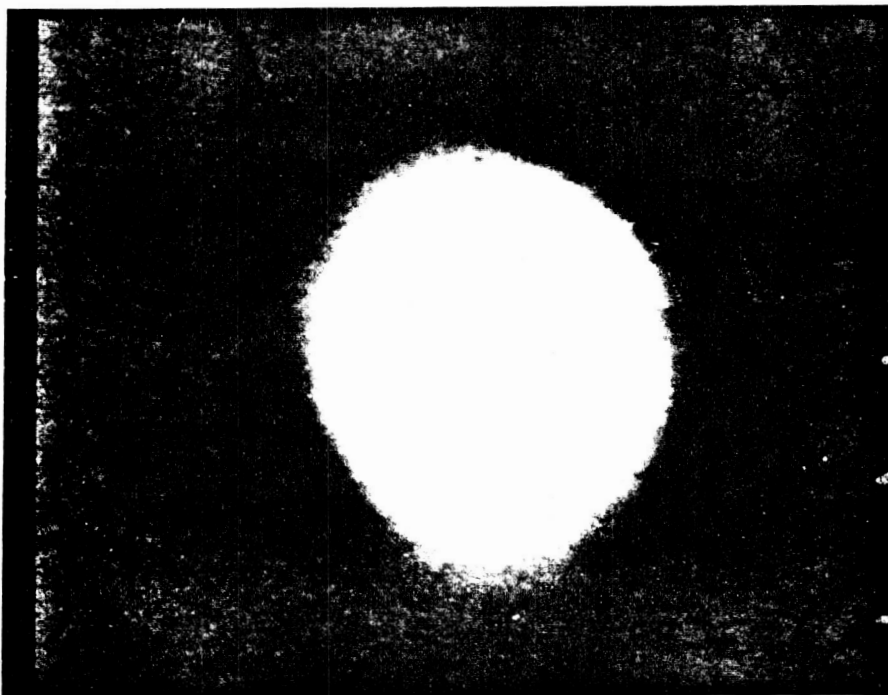Figure 13b. – Standard run particle size distribution.

Figure 13c. – High magnification SEM of carbon particle.

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around anything raised above the filter surface. Figure 13b shows the measured distribution of the particle sizes.

Figure 13c is a high-magnification (300kX) electron-micrograph of a 150 nm diameter particle made in this run. There is no unusual structure, and no evidence of any agglomeration.

Run 3 - Reduced Fluence Sample

Figures 14a and 14b show the results of this run, performed at reduced fluence compared to the standard. There is a slight decrease in the both mean particle diameter and the standard deviation. The mean diameter reduction is probably due to a decrease in the density of condensable vapor initially formed by the laser pyrolysis. The improved monodispersity may result from the decrease in the fluence gradient across the width of the nozzle, resulting in increased uniformity of the initial vapor distribution, as discussed in Subsection 2.2.1. Thus, it appears that by altering the laser fluence the particle size distribution can be finely adjusted.

The photo also appears to show a slight increase in the amount of agglomeration among the particles. Since the fluence was lower, the localized heating and the resulting blast wave was weaker than the standard. As a result, the rate of expansion and cooling was diminished, allowing more time for interparticle collisions that result in sticking.

Run 4 - Reduced Pressure Sample

Particles manufactured in this run, using a reduced pressure compared to the standard, are shown in Figure 15a. The rather small decrease in pressure resulted in a surprisingly large reduction in the mean particle size, as seen in Figure 15b. The decrease in diameter is most likely due to a combination of the reduction in the amount of decomposed vapor available to form the particles and an increase in the number density of particles formed after the decomposition. The particle number density is determined primarily by the supersaturation ratio that is established immediately after irradiating the ethylene. The decreased initial pressure changed both the temperature achieved by irradiation and the vapor pressure of condensable carbon, thus altering the supersaturation ratio. If the supersaturation was increased by this process, the number density was also increased. However, since the total vapor density was decreased, each particle had less mass available for its growth, resulting in smaller particles. Thus, it appears that the initial pressure provides a coarse control over the particle size distribution.

Note that the average size and standard deviation of the particles calculated from the histogram of Figure 15b may not be accurate. It appears that some captured particles are smaller than the 30 nm filter pore size, and it can be assumed that others passed through the filter and were not counted.

Figure 14a. - SEM of reduced fluence run.
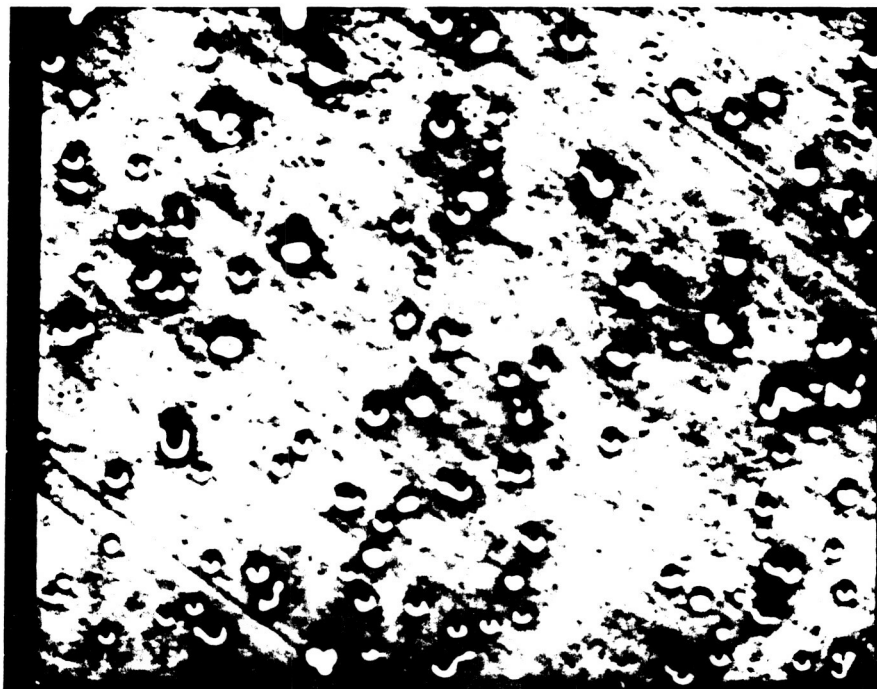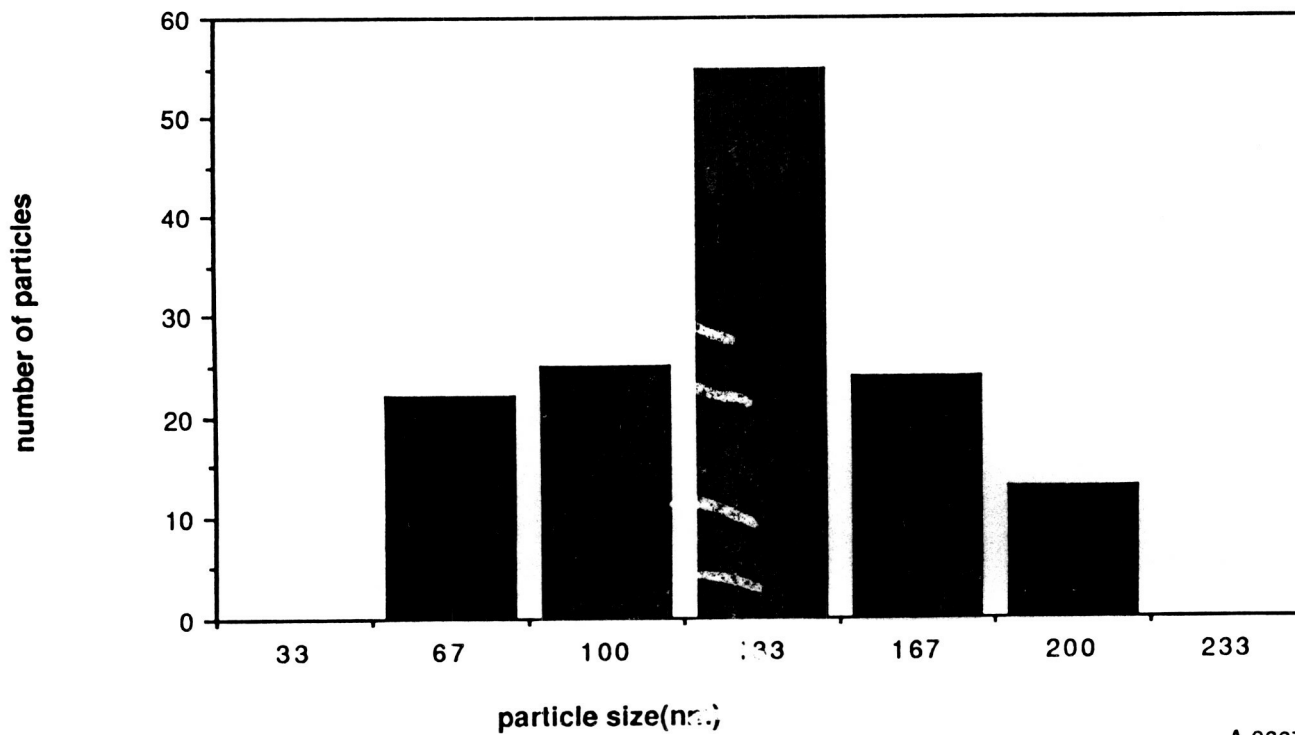

particle size(nm.)

A-9697

Figure 14b. - Reduced fluence particle size distribution.

24
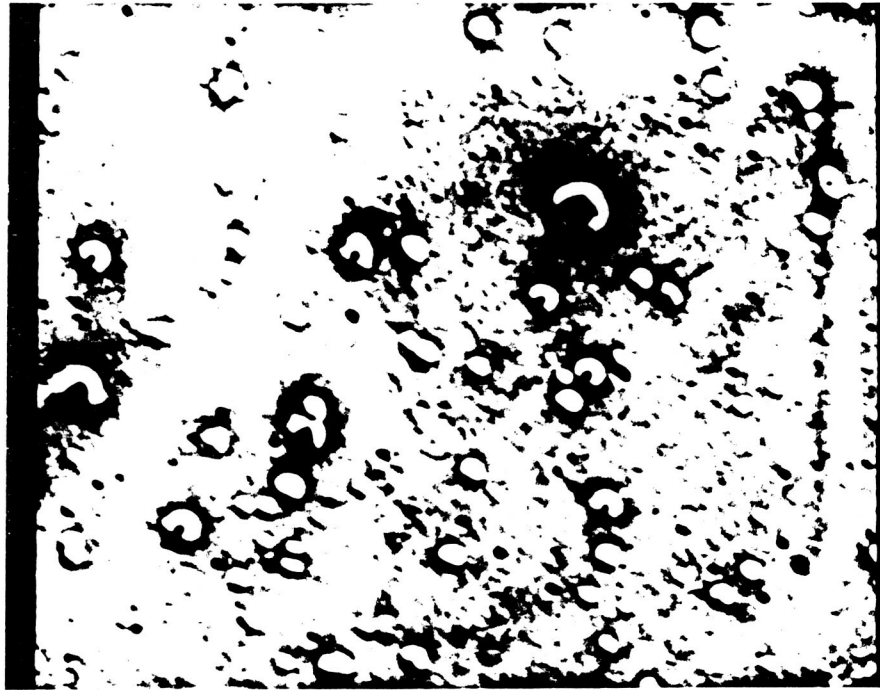
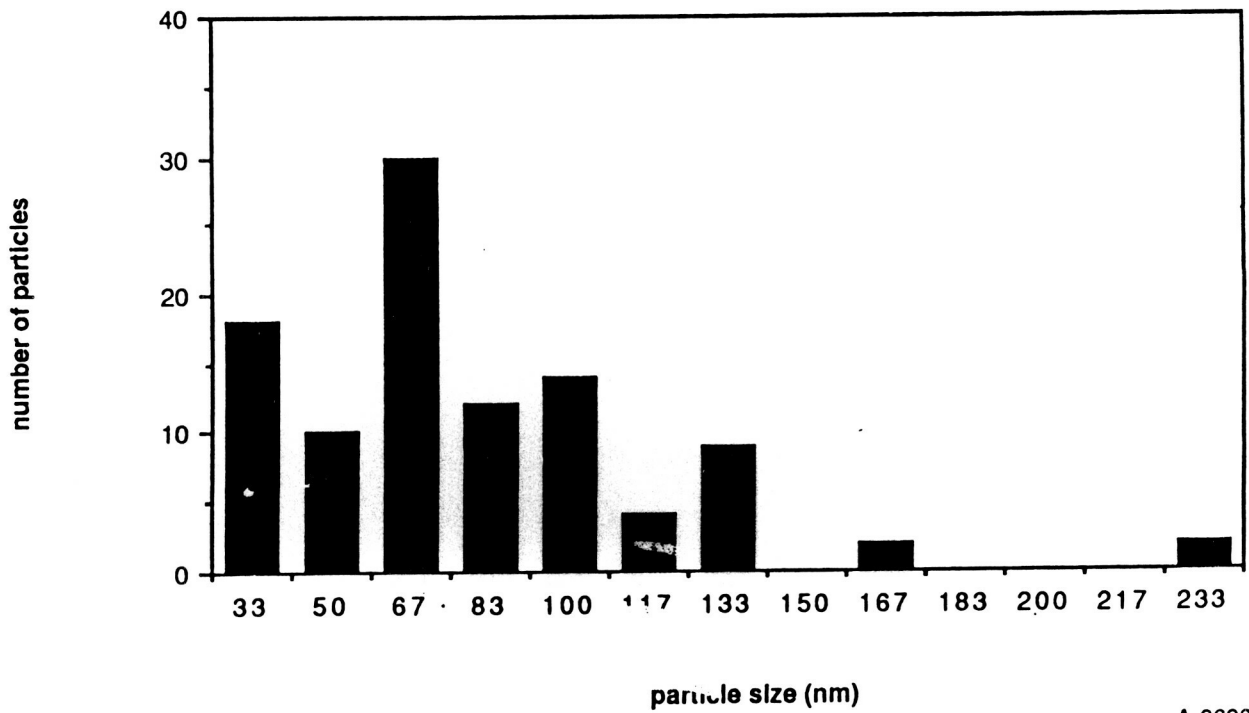Figure 15a. - SEM of reduced pressure run.

particle size (nm)

A-9698

Figure 15b. - Reduced pressure particle size distribution.

Run 5 - Long Duration Sample

This run was identical to the standard, but particles were collected for two hours rather than ten minutes. The electron-micrograph of the filter, at 30kX magnification, is shown in Figure 16. There is a clear increase in the number of particles, as well as a great deal of agglomeration. The increase of agglomeration suggests that particle pairs seen on other micrographs may have clumped on the filter rather than in the gas flow.

The particles on this picture were too concentrated to accurately measure their sizes. Thus, there is no corresponding size histogram.
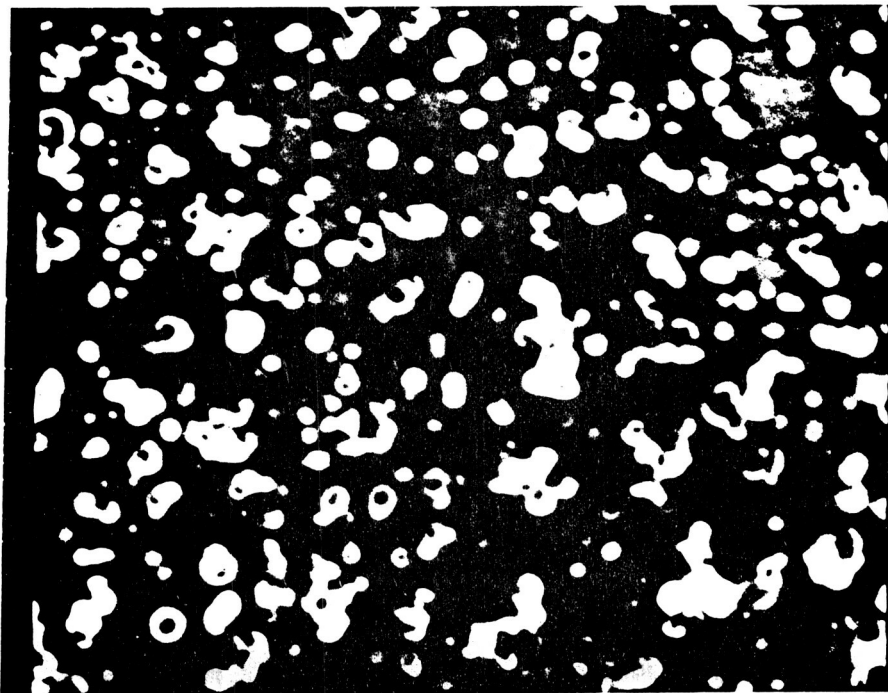
Figure 16. - Set of long duration run.

Run 6 - Supersonic Nozzle Sample

This final sample was obtained using the supersonic nozzle method of expansion and cooling. As shown in Figures 17a and 17b, this method produced the smallest average particle sizes of all. The large decrease in size is probably a result of the pressure drop from 20.4 psi in the plenum to about 10 psi at the nozzle throat. As in Run 4, the pressure reduction leads to a decrease in the available condensable vapor density and a change in the particle number density. The histogram of particle sizes in this case indicates that either the size distribution is strongly skewed to the smaller diameters, or that many small particles were lost by passage through the filter.

Figure 17a. — SEM of particles manufactured using the supersonic expansion method.

A-9699

Figure 17b. — Size distribution of particles made using supersonic expansion method.
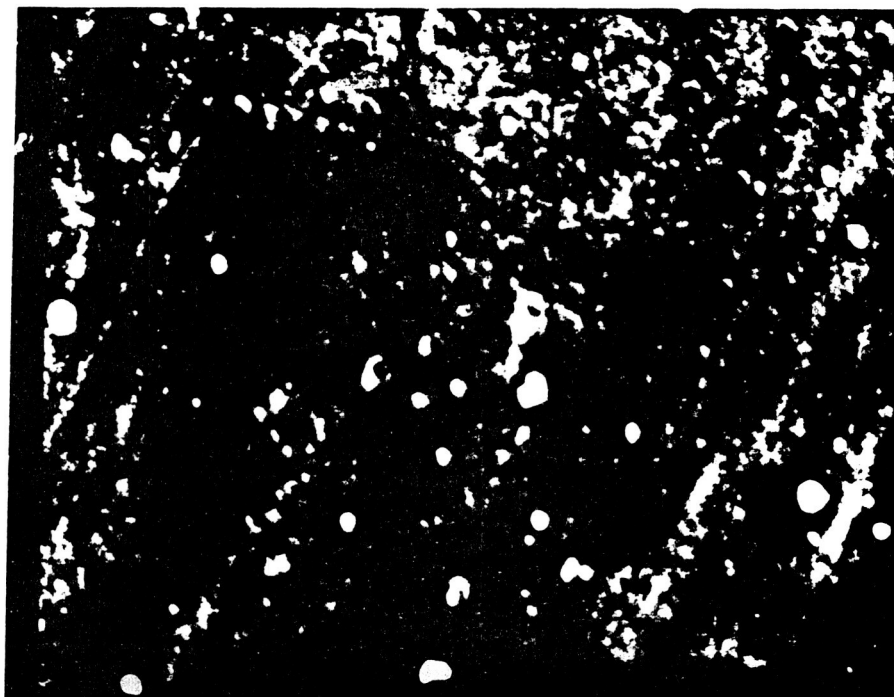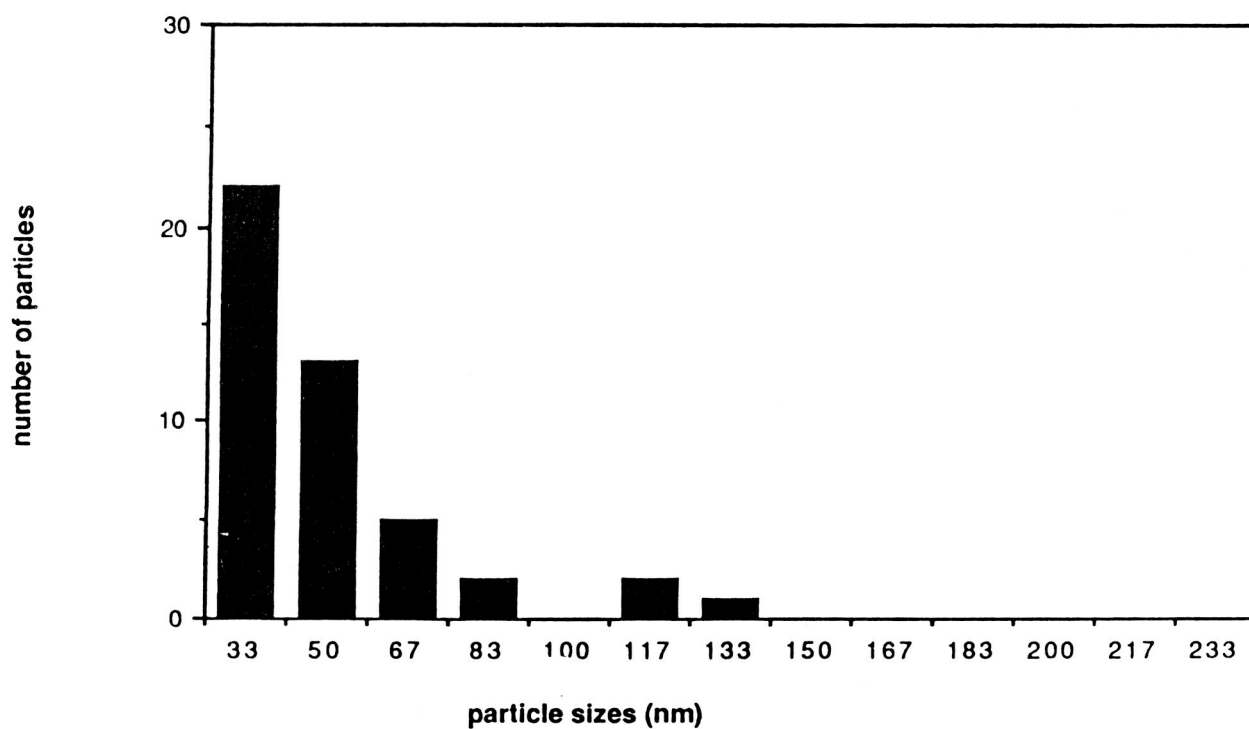
4. SUMMARY AND CONCLUSION

In this small Phase I program, we achieved our objectives by demonstrating that nearly monodisperse unagglomerated spherical 50 to 150 nm diameter solid carbon particles can be made by pyrolyzing ethylene with a pulsed CO_2 laser, allowing the low vapor pressure products to condense, and then rapidly expanding and cooling the condensed particles. We have shown that the mean particle size can be coarsely controlled by varying the initial gas pressure, and can be finely controlled by varying the laser fluence. The particles can be left suspended in a gas indefinitely and thereby remain unagglomerated. They can thus be used for LDV seeding simply by injecting this particle-laden gas into the flowfield of interest.

Much work remains to be done before a versatile high-temperature LDV seeding apparatus evolves from this effort. Though we have shown the feasibility of making monodisperse particles able to withstand heat, carbon particles are not ideal when the hot atmosphere is also oxidizing. In that situation, ceramic materials such as refractory oxides would be preferable. As discussed in Section 2 above, the materials science community has used a similar technique to manufacture a variety of ceramic materials, but they have not overcome the problem of agglomeration. We expect that, by using the same pyrolysis products as those researchers, combined with our rapid cooling technique, unagglomerated ceramic particles can be made with little difficulty.

Another problem which remains to be addressed is that, in some situations, the 150 nm particles made here may not be large enough to scatter sufficient incident laser light to overcome the inherent background noise in an LDV experiment. Though we have demonstrated an ability to control particle size, we have hardly begun to study the limitations of the technique or the degree of control that might be offered by variations of the manufacturing process. It is possible, in fact likely, that by using other optical configurations, nozzle shapes, types of gas mixtures, and initial pressures that the particle chemistry and size distributions can be virtually altered at will and thereby selected to suit specific applications. The particles can be pumped directly into the plenum supplying the flow to be seeded and dispersed by turbulent fluctuations. We hope to have the opportunity to explore these possibilities in a Phase II program which would lead to a usable LDV seeding apparatus.

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Project Manager, Richard Seasholtz, Instrumentation and Control Technology Division, NASA Lewis Research Center.

16. Abstract

The purpose of this research was to demonstrate the feasibility of developing a method for making monodisperse, unagglomerated spherical particles greater than 50 nm in diameter. This objective was achieved. Carbonaceous particles were made by pyrolyzing ethylene with a pulsed CO_2 laser, thereby creating a non-equilibrium mixture of carbon, hydrogen, hydrocarbon vapors, and unpyrolyzed ethylene. Via a complex series of reactions, the carbon and hydrocarbon vapors quickly condensed into the spherical particles. By cooling and dispersing them in a supersonic expansion immediately after their creation, the hot newly-formed spheres were prevented from colliding and coalescing, thus preventing the problem of agglomeration which as plagued other investigators studying laser-stimulated particle formation. The cold particles could be left suspended in the residual gases indefinitely without agglomerating. Their uniform sizes and unagglomerated nature were visualized by collecting the particles on filters that were subsequently examined using electron microscopy. It was found the mean particle size can be coarsely controlled by varying the initial ethylene pressure, and can be finely controlled by varying the fluence (energy/unit area) with which the laser irradiates the gas. The motivating application for this research was to manufacture particles that could be used as Laser Doppler Velocimetry (LDV) seeds in high-temperature high-speed flows. Though the particles made in this program will not evaporate until heated to about 3000K, and thus could serve as LDV seeds in some applications, they are not ideal when the hot atmosphere is also oxidizing. In that situation, ceramic materials would be preferable. Research performed elsewhere has demonstrated that selected ceramic materials can be manufactured by laser pyrolysis of appropriate supply gases. We anticipate that, when the same gases are used in conjunction with our innovative rapid cooling technique, unagglomerated spherical ceramic particles can be made with little difficulty. Such particles would also be valuable to manufacturers of ceramic or abrasive products, and this technique may find its greatest commercial potential in those areas.

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