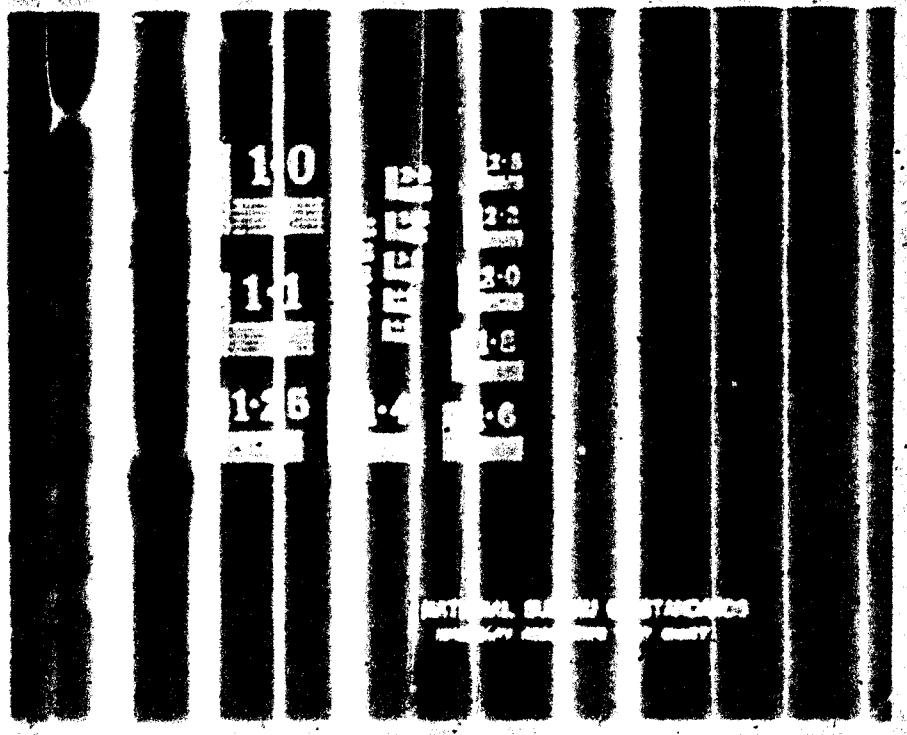

RESEARCH NOTE 25

BURNUP RATES OF POWDERS BEHIND A NORMAL SHOCK WAVE

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ABSTRACT

The burnup rate of teflon powders in a shock-heated argon bath has been studied with the use of a shock tube. The rate of disappearance of the ablating particles was monitored by measuring the absorption, at 2536Å, of CF_2, which is the end product in the (assumed) reaction

$$(\text{Teflon})_{\text{solid}} \xrightarrow[\text{vaporization}]{\text{depolymerization}} (C_2F_4)_{\text{gas}} \xrightarrow{\text{dissociation}} (CF_2)\ \text{gas}.$$

The data, which was obtained over the temperature interval of 1600-3100°K, was interpreted to deduce the thermal accommodation coefficient for argon/teflon collisions. The coefficient was found to be of order unity.

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1. INTRODUCTION

The development of a facility to ablate submicron-size particles in gases behind a normal shock wave has been described in References 1 to 3, and analyses of the dynamics of a particle in a shocked flow have been described in References 1, 2, and 4. As was discussed in Reference 4, the utility of a device for ablating powders of selected materials in a shocked flow is demonstrated only when it can be shown that the powders selected do, indeed, ablate in a time short compared to the characteristic testing time in the shock tube flow. In addition, for such a facility to be used to make chemical kinetics measurements, there is the further restriction that the powder ablation time must be short compared to all subsequent chemical reaction times in the gas phase.

Having demonstrated that it is possible to inject powders of selected materials uniformly and reproducibly into the driven section of a shock tube[5], it is necessary to then show that these powders burn up in a time that is short compared to experimental testing times, and is comparable to computed burnup times. In this Note, we discuss the measurement of burnup rates for teflon powders behind normal shock waves in argon, and deduce an average thermal accommodation coefficient from the data.

2. TECHNIQUE FOR PARTICLE BURNUP MEASUREMENT

In order to measure the disappearance rate of small particles in a shocked flow, it is necessary to either measure the rate of change of size of the particle directly, or indirectly, by measuring the absorption of a gaseous decomposition product of the particle. Light scattering techniques can be used to directly measure the rate of disappearance of a particle, based on the rate of change of scattered intensity. However, since the particles considered are in the Rayleigh scattering regime, the change in scattered intensity with particle size goes as the sixth power of the particle size. Therefore, for a change of only a factor of two in the particle size, the scattered intensity is lowered by almost two orders of magnitude. Since it was not possible to cover such a large dynamic range with the instrumentation available, we chose, instead, to measure the rate of disappearance of particles via a measurement of absorption of one of the gaseous decomposition products of the particle.

The material chosen for initial studies was teflon. Numerous studies of teflon have indicated that the initial decomposition product is the monomer, C_2F_4. Using this information, the rate of disappearance of teflon particles can be determined by measuring the absorption of C_2F_4, or any of its subsequent decomposition products.

The molecule CF_2 has been shown[6] to have an extensive system of many-headed bands in the spectral interval from approximately 2300Å to 5000Å. Modica[7] has determined the absorption coefficient of CF_2 at 2536Å over the temperature interval 1700 to

3700°K. He made this measurement by measuring the absorption of CF_2 behind shock waves in a mixture of gaseous C_2F_4, highly diluted in argon. The concentration of CF_2 was deduced from the known initial amount of C_2F_4, and the calcula. equilibrium of C_2F_4 and CF_2 at the equilibrium temperature behind the shock wave. With this technique, he showed that the absorption coefficient at 2536Å is nearly constant over the temperature interval measured.

Using the measured absorption of CF_2 at 2536Å to determine the amount of CF_2 present, Modica[7] subsequently measured the rate of dissociation of C_2F_4 to CF_2 over the temperature interval 1200 to 1800°K. This reaction takes the form

$$M + C_2F_4 \underset{k_{-M}}{\overset{k_M}{\rightleftharpoons}} M + CF_2 + CF_2, \qquad (1)$$

where M is any collision partner, and k_M, k_{-M} are the forward and reverse reaction rates, respectively. From Eq. (1), the rate of disappearance of C_2F_4 may be written as

$$\frac{d(C_2F_4)}{dt} = -k_M(M)(C_2F_4) + k_{-M}(M)(CF_2)^2, \qquad (2)$$

or, if the reverse reaction is ignored,

$$\frac{d(C_2F_4)}{dt} = -k_M(M)(C_2F_4). \qquad (3)$$

From the initial slope of the absorption curve behind the shock wave, Modica determined a second order rate constant for C_2F_4 dissociation in excess argon. Over the temperature interval covered, this reaction rate constant has the value

$$k_A = 7.82 \times 10^{15} T^{1/2} \exp\left(-\frac{55,690}{RT}\right), \text{cm}^3\text{-mole}^{-1}\text{-sec}^{-1}. \quad (4)$$

Using a similar technique, Modica[8] studied the CF_2 dissociation reaction in excess argon as given by

$$A + CF_2 \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} A + CF + F. \quad (5)$$

The observed data was interpreted by a second order mechanism (ignoring the reverse reaction) as

$$\frac{d(CF_2)}{dt} = -k_A(A)(CF_2), \quad (6)$$

yielding a reaction rate constant given by

$$k_A = 2.07 \times 10^{14} T^{1/2} \exp\left(-\frac{98,300}{RT}\right), \text{cm}^3\text{-mole}^{-1}\text{-sec}^{-1}. \quad (7)$$

In order to use CF_2 absorption as an indicator of the rate of disappearance of teflon particles in a shock-heated argon/teflon mixture, the following restrictions on test conditions are required:

a. The temperature and density behind the shock wave must be chosen so that the rate of disappearance of the particles is short compared to the available experimental testing time, but not shorter than the experimental resolution element.

b. The decomposition of C_2F_4 to CF_2 must be fast compared to the teflon particle burnup rate.

c. The temperature and density behind the shock wave must be such that the CF_2 formed from C_2F_4 dissociation does not substantially decompose to CF + F during the testing time.

d. The mass fraction of teflon powder in the shock heated argon must be small enough that the conditions behind the shock wave are not strongly influenced by the chemistry of burnup of the particles and subsequent gas phase decomposition.

Using the results of Reference 4, the calculated burnup times of 1 micron diameter teflon particles are shown in Fig. 1, and compared with computed[9] and measured experimental testing time for a shock tube with driven dimensions of 3 inch diameter and 15 feet length to the observation station. The teflon burnup time calculations were made with an assumed thermal accommodation coefficient equal to unity. The calculations were made for teflon in air, for which there was a substantial amount of experimental test time data available for the present facility. However, there would be no qualitative difference for argon, except that the experimental test time available would be somewhat larger. Since the calculated

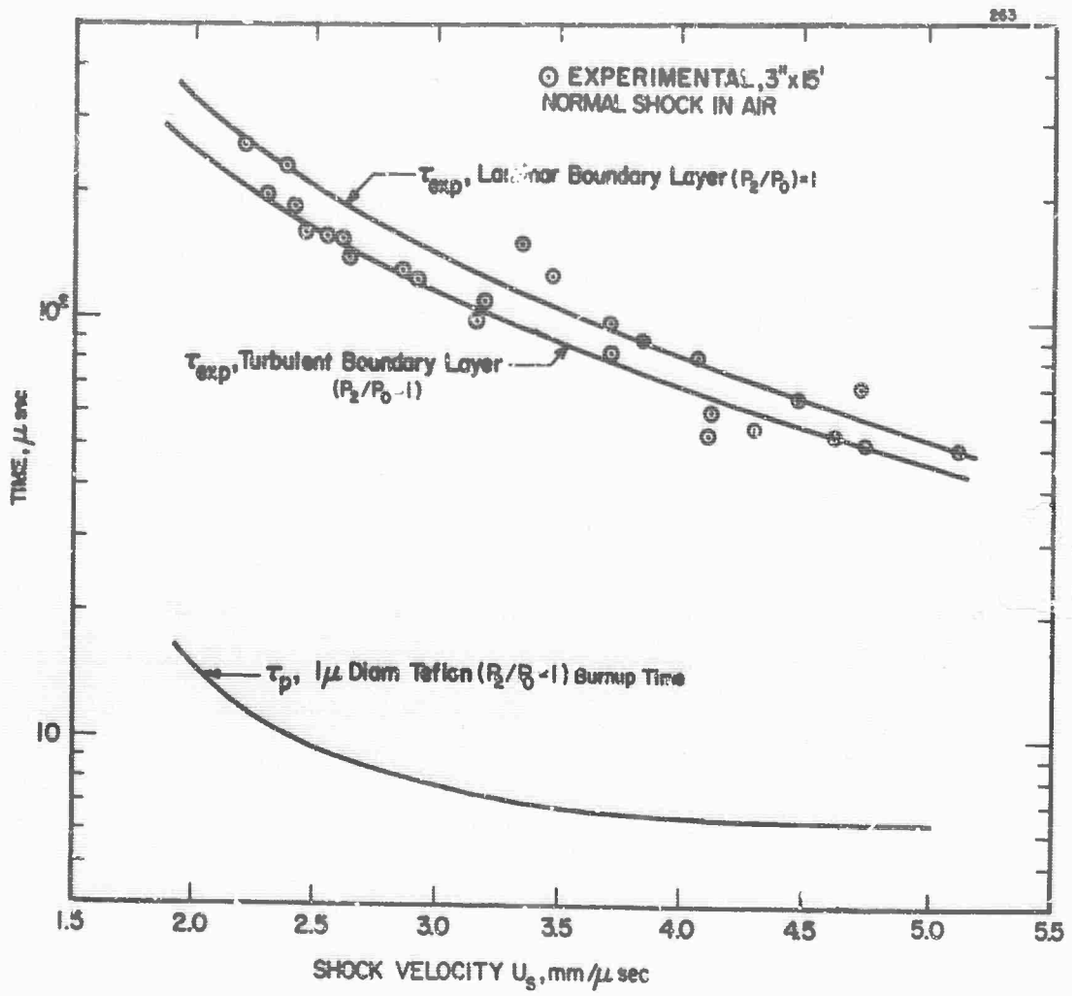

Fig. 1 Shock tube testing time and teflon powder burnup time versus shock velocity.

burnup time is approximately an order of magnitude smaller than the available experimental testing time, it is seen that criterion (a) above is satisfied.

If we integrate Eq. (3) and use the rate constant of Eq. (4), we find that the time required for the initial C_2F_4 concentration to be reduced to 1/e of its original value is given by

$$(t_{1/e})_{C_2F_4} = \frac{1}{k_A(A)} = \frac{1.28 \times 10^{-16} T^{-1/2} \exp\left(\frac{55,690}{RT}\right)}{(A)}. \qquad (8)$$

Similarly, if we integrate Eq. (6) and use the rate constant of Eq. (7), we find that the time required for the initial CF_2 concentration to be reduced to 1/e of its original value is given by

$$(t_{1/e})_{CF_2} = \frac{1}{k_A(A)} = \frac{4.84 \times 10^{-15} T^{-1/2} \exp\left(\frac{98,300}{RT}\right)}{(A)}. \qquad (9)$$

Equations (8) and (9) have been plotted in Fig. 2 for the range of conditions covered by our tests. It is seen from Fig. 2 that for the temperature interval from approximately 1750°K to 3000°K, the C_2F_4 concentration decays rapidly while the CF_2 concentration remains nearly unchanged. Therefore, criteria (b) and (c) above are satisfied.

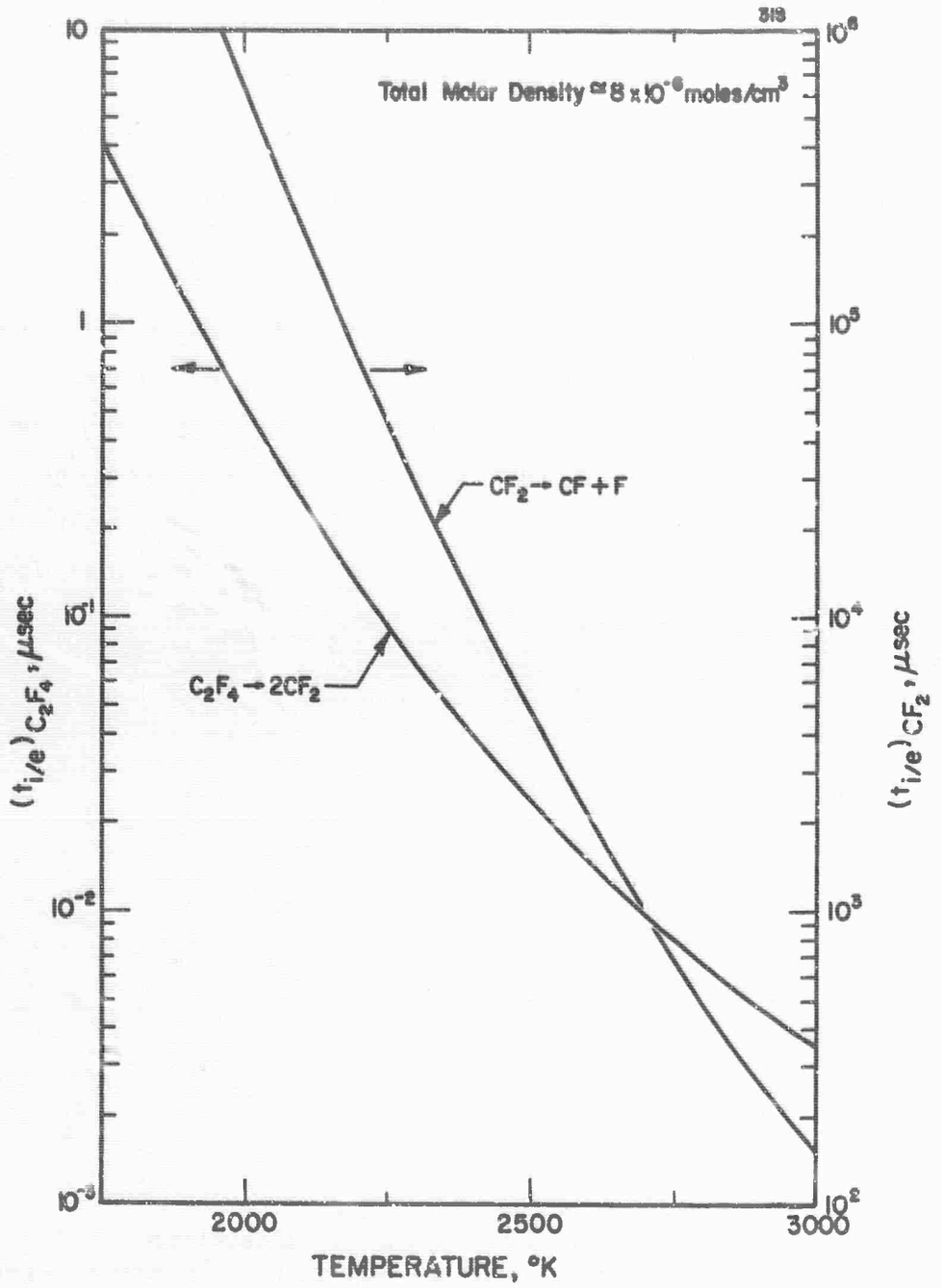

Fig. 2 Relaxation times for C_2F_4 and CF_2 behind normal shocks in argon.

An estimate* of the equilibrium temperature behind a shock wave in an argon-teflon mixture may be made by calculating the energy absorbed in vaporizing the teflon powder, and subsequently dissociating the C_2F_4 completely to CF_2. With a heat of vaporization of approximately 40 kcal per mole[4], and a dissociation energy of approximately 75 kcal per mole[7], the effective dissociation energy is approximately 115 kcal per mole. For the test conditions considered in these experiments, this results in a reduction in shocked gas temperature of approximately 150 to 350°K. Since the CF_2 absorption coefficient does not change substantially over the temperature interval covered[7], this reduction in temperature due to vaporization and dissociation would not alter the data interpretation. Therefore, criterion (d) above is satisfied.

*At the present time, a computer code is being developed which accounts for all of the momentum and energy transfer processes in a powder-laden gas. An initial report on this subject is presented in Reference 10.

3. EXPERIMENTAL PROCEDURE

We have run a series of 15 tests on teflon and argon in our shock tube. The temperature covered by these experiments ranged from approximately 1600°K to 3100°K behind the incident shock wave, as calculated for pure argon from the measured shock velocity. The initial driven pressure in the shock tube was kept constant at a value of 4 cm Hg, and the amount of teflon injected into the tube varied from 1/2 to 1-1/2 mole percent

The optical equipment and the test section of the shock tube used for these experiments is shown in Fig. 3. With the exception of the powder injection subsystem, the shock tube is of conventional design having driven section dimensions of 3 inch diameter by 18 foot length. The driving gas used for the experiments reported herein was helium. CF_2 absorption behind the incident shock wave in the argon/teflon mixture was monitored at a station 16-1/2 feet from the diaphragm, with the use of a Bausch and Lomb Model 5 monochromator (see Acknowledgment), utilizing a deuterium light source and a 1P28 photomultiplier detector. The windows and lenses used were quartz and quartz-fluoride combinations.

The general features of the absorption records obtained are shown in Fig. 4. The zero and 100 percent transmission traces were put on the film shortly before the teflon/argon mixture was admitted to the driven section of the shock tube. The teflon/argon transmission before shock arrival at the observation station does not coincide with the 100 percent transmission line, due to the scattering loss of light from the source by the teflon powder. A

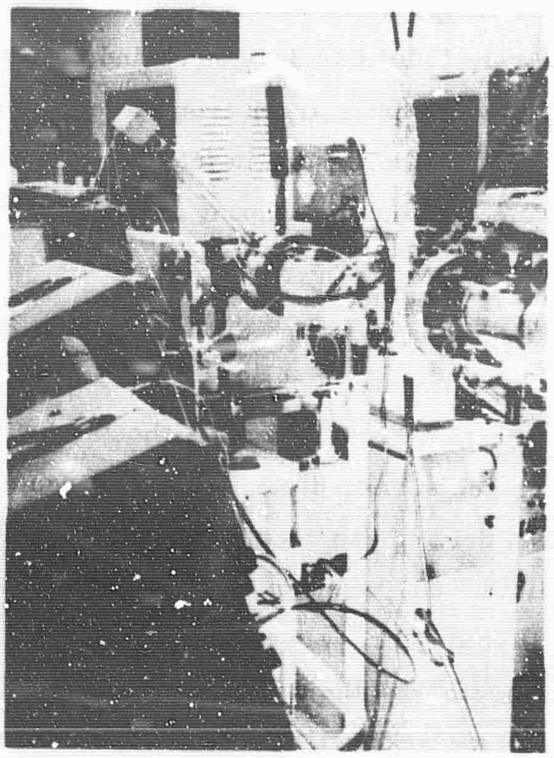

Fig. 3 View of the shock tube test section showing the grating monochromator (vertical).

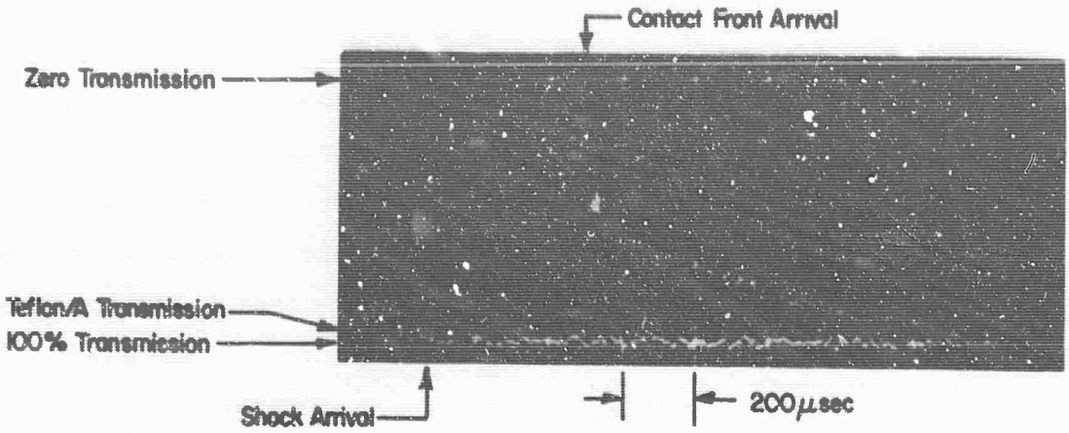

Fig. 4 CF_2 absorption record (Run No. 3). Total molar density = 8.1×10^{-6} moles/cm^3; teflon molar concentration = 5×10^{-8} moles/cm^3. Equilibrium temperature = 1980°K. Shock velocity = 1.44 mm/μsec.

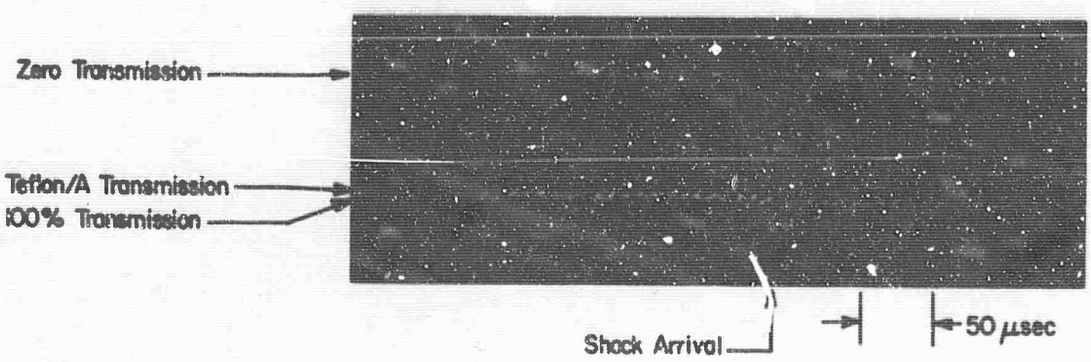

Fig. 5 CF_2 absorption record (Run No. 2). Total molar density = 7.9×10^{-6} moles/cm^3; teflon molar concentration = 7.9×10^{-8} moles/cm^3. Equilibrium temperature = 1930°K. Shock velocity = 1.42 mm/μsec.

rapid increase in CF_2 absorption is shown upon shock arrival, followed by a period of almost constant absorption, indicating the uniformity of the teflon powder concentration along the length of the driven section of the shock tube. The termination of testing time is indicated by the contact front arrival. The apparent noisiness of the signals arises from the fact that the cathode ray tube was blanked at a 100 kc rate with a time mark generator.

The details of the leading edge of an absorption record are shown more clearly in Fig. 5. The bright spots on the traces are timing marks at 10 μsec intervals. From a record such as that shown in Fig. 5, the burnup time is deduced to be that at which the absorption record attains a steady state value.

In both of the figures shown, the absorption is caused by CF_2 at a wavelength of 2536Å, and a spectral interval of approximately 10Å.

4. DATA INTERPRETATION

As has been shown in Reference 4, if the bulk of the material ablated from a particle comes off while the particle is at rest with respect to the shocked flow, then a simple expression for the particle burnup time may be deduced. This time is given by

$$t_p = \frac{2}{3}\frac{\gamma \rho_p}{\rho_\infty}\left(\frac{M_\infty}{U_\infty}\right)^3 \frac{[h_v + C_p(T_v - T_o)]\sqrt{\frac{\pi\gamma}{2}}}{\left(1 - \frac{T_v}{T_\infty}\right)}\left(\frac{a}{\alpha}\right) \times 4.185 \times 10^7 \text{, sec,} \tag{10}$$

where the appropriate quantities for teflon and argon are given by

γ = shocked gas specific heat ratio = 5/3

T_o = shocked gas initial temperature = 300°K

ρ_p = particle density = 2.2 g-cm^{-3}

h_v = particle heat of vaporization = 410 cal-g^{-1}

T_v = particle temperature of vaporization = 900°K

C_p = particle specific heat = 0.25 cal-g^{-1}-°K^{-1}

M_∞ = shocked gas Mach number

U_∞ = shocked gas velocity, cm-sec^{-1}

ρ_∞ = shocked gas density, g-cm^{-3}

T_∞ = shocked gas temperature, °K

a = initial particle radius, cm

α = thermal accommodation coefficient. (11)

Substituting the values of Eq. (11) into Eq. (10) gives

$$t_{teflon} = 9.25 \times 10^{10} \left(\frac{M_\infty}{U_\infty}\right)^3 \frac{1}{\rho_\infty \left(1 - \frac{900}{T_\infty}\right)} \left(\frac{a}{\alpha}\right), \text{ sec.} \qquad (12)$$

For a given set of experimental conditions, the burnup time calculated from Eq. (12) will scale linearly as the ratio (a/α). This time should then be equal to the experimentally measured burnup time, suitably adjusted for the difference between particle and laboratory time as is shown in

$$(t_{teflon})_{calculated} = \frac{\rho_\infty}{\rho_1} (t_{teflon})_{laboratory}, \qquad (13)$$

where (ρ_∞/ρ_1) is the density ratio across the shock wave.

From Eq. (13), it is seen that if the initial particle size, a, is accurately known, then the present measurements can be used to determine the thermal accommodation coefficient, α, as is shown in

$$\left(\frac{a}{\alpha}\right) = 1.08 \times 10^{-11} \left(\frac{\rho_\infty}{\rho_1}\right) \left(\frac{U_\infty}{M_\infty}\right)^3 \rho_\infty \left(1 - \frac{900}{T_\infty}\right) (t_{teflon})_{laboratory}, \text{cm.} \qquad (14)$$

Since the teflon powder used in the presently reported experiments did not have a single size but contained a distribution of particle sizes, it was decided to reduce the experimental data according to

Eq. (4), in order to deduce the ratio (a/α). It is seen from Fig. 6 that the average value of (a/α) for the data presented is approximately 2 to 2-1/2 microns.

An electron micrograph of the teflon powder used in the tests reported herein is shown in Fig. 7. The teflon powder used in obtaining the micrograph shown in Fig. 7 was taken from the shock tube after a normal injection into the shock tube (but without passing a shock wave through the mixture). Since each particle produces an amount of gaseous decomposition product that is proportional to the cube of the particle size, it is seen that the large particles dominate the rate of production of CF_2 and, hence, it is the burnup of the large particles which is principally measured by this technique.

From Fig. 7 it is seen that the larger particles, or agglomerates of smaller particles, fall in the size range of from 3 to 5 microns in diameter. This, then, leads us to conclude from the data shown in Figs. 6 and 7, that for the temperature and density range covered by the experiments reported herein, the thermal accommodation coefficient for argon collisions with teflon is nearly unity. Indeed, under no conditions could the accommodation coefficient be less than 0.1 since, in the powder used for these tests, no particles smaller than 0.2 micron were ever observed.

Since the magnitude of the thermal accommodation coefficient is the largest unknown in the computation of particle burnup times, its determination is exceedingly important for the ablation material/air chemistry program described in Reference 4. The fact that these initial measurements with teflon and argon yield a value of the accommodation coefficient of order unity is very encouraging.

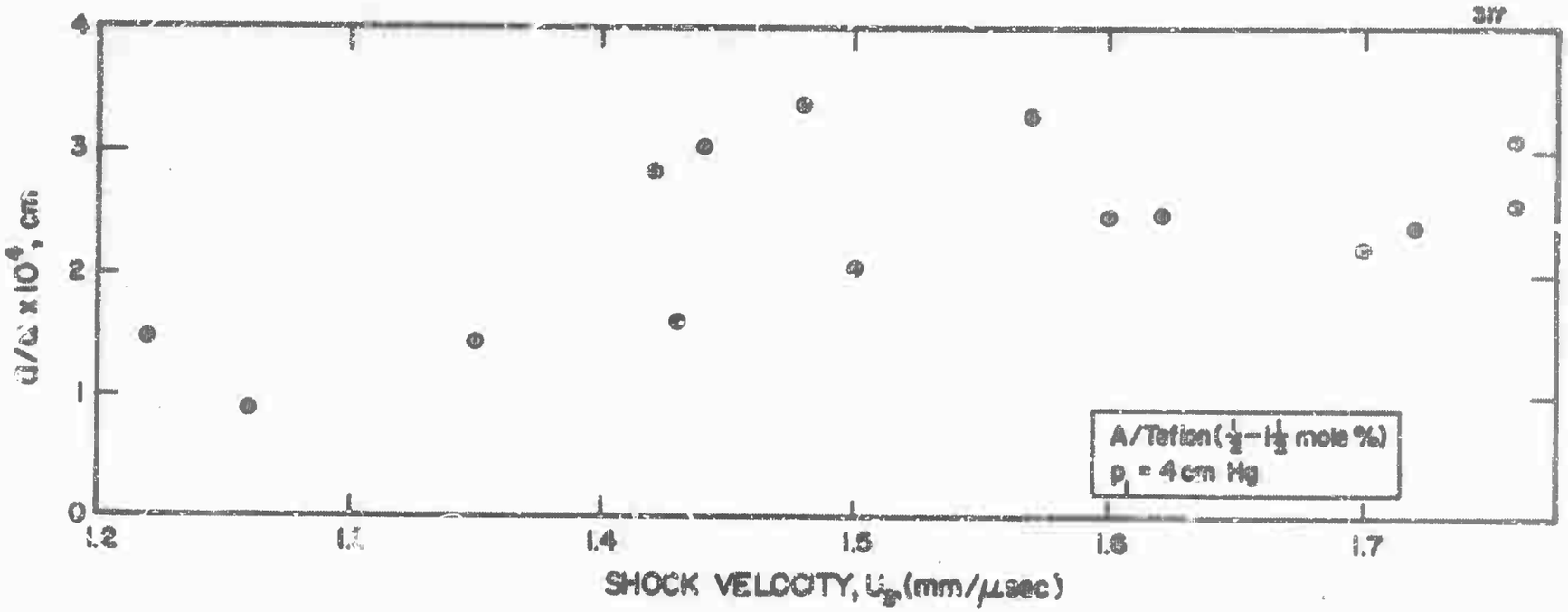

Fig. 6 Initial particle radius divided by the thermal accommodation coefficient as deduced from particle burnup records, as a function of shock velocity.

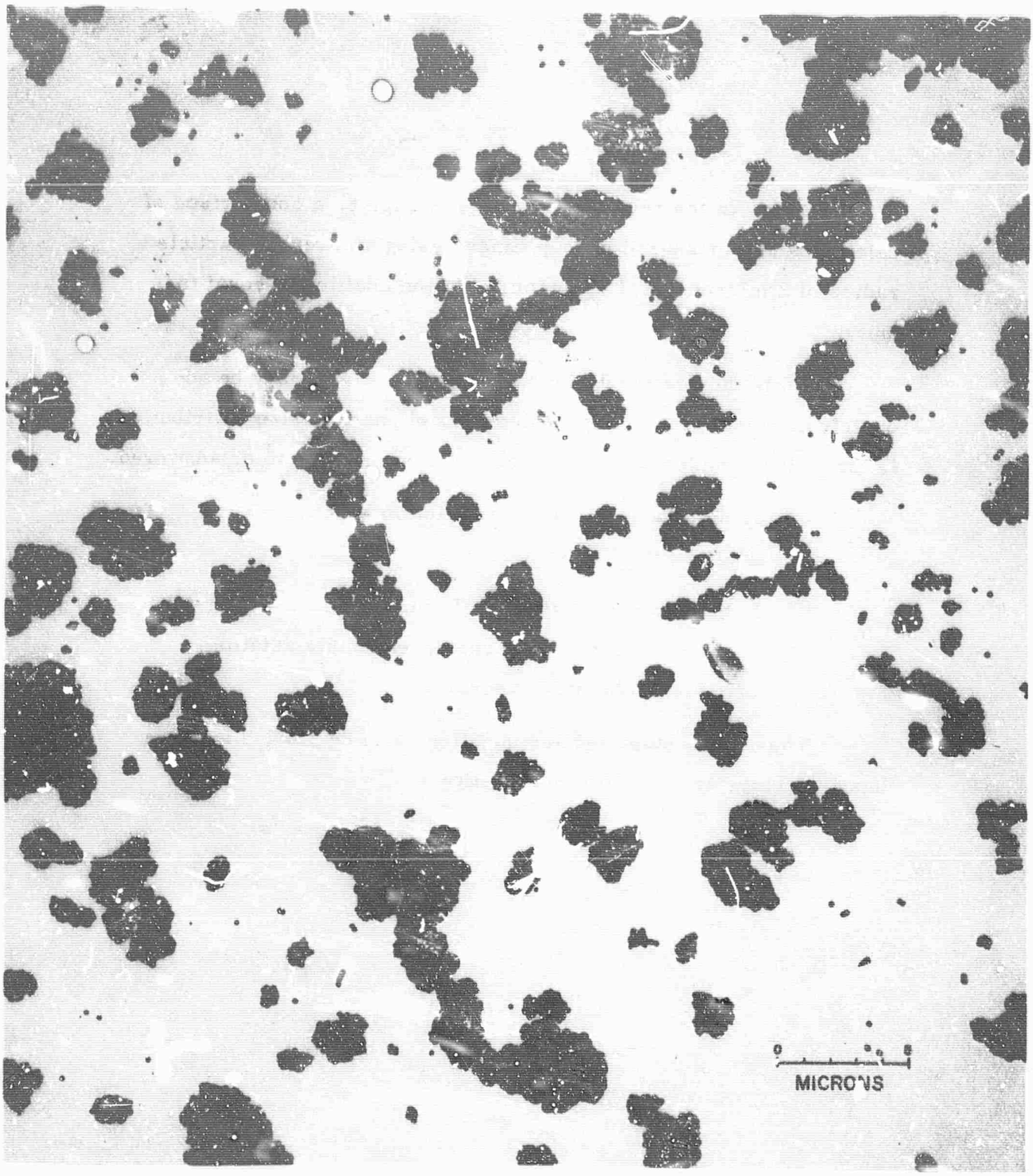

Fig. 7 Electron microscope picture of 1/2 micron teflon dust as obtained from the material in bulk. Magnification is 5000X. The white circles and extremely fine dots are imperfections in the mask on which the powder is dispersed. Note the scalloped edges on some large particles. These large particles are either agglomerations of small particles or relatively large pieces covered by small particles.

Based on the results, we show, in Fig. 8, a comparison of calculated and measured burnup times, using an average particle radius of 2 microns, and an accommodation coefficient equal to unity.

While the scatter in the data shown in Fig. 6 may be adequately accounted for by the randomness of particle size distributions in the teflon samples used, several questions remain to be answered.

a. Is there a systematic variation in accommodation coefficient with temperature?

b. Is the accommodation coefficient nearly unity for all of the materials to be considered in this ablation material chemistry program?

These, and other related questions will be studied in more detail in future studies with this facility.

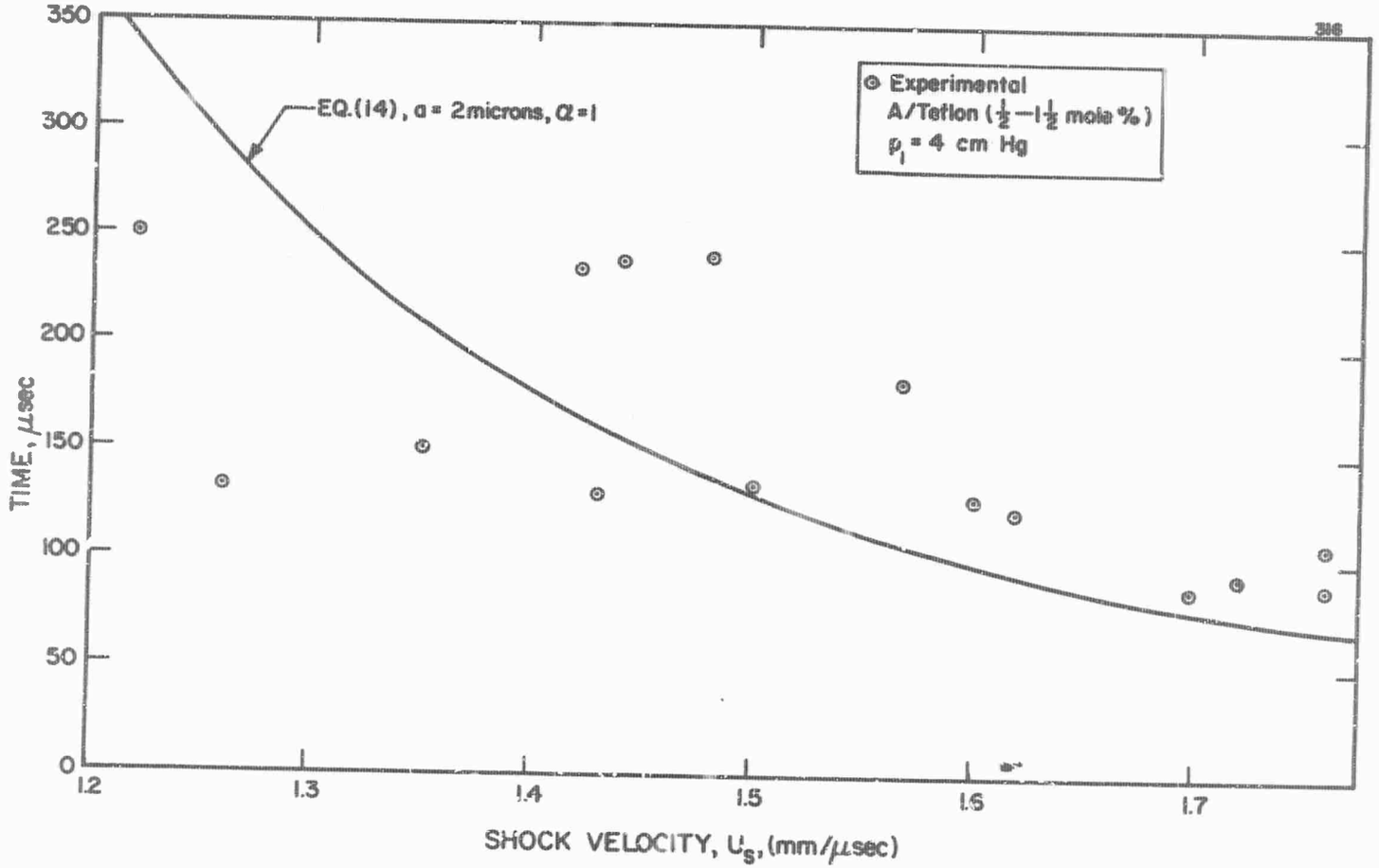

Fig. 8 Comparison of calculated and measured burnup rates, based on the thermal accommodation coefficient derived from Figs. 6 and 7.

REFERENCES

1. Hickman, R.S., "Progress on SAPAG Facility, I," Heliodyne Corporation Research Note 5, December (1962).

2. Hickman, R.S., "Progress on SAPAG Facility, II," Heliodyne Corporation Research Note 12, December (1963).

3. Hickman, R.S., Ory, H.A., and Tannenbaum, I.R., "Progress on SAPAG Facility, III," Heliodyne Corporation Research Note 15, June (1964).

4. Hooker, W.J., "A Summary of Calculations of Chemical and Fluid Dynamic Parameters in the SAPAG Facility," Heliodyne Corporation Research Note 17, June (1965).

5. Holden, R.R. and Hooker, W.J., "The Preparation and Injection of Teflon/Gas Dispersions for Shock Tube Investigations," Heliodyne Corporation Research Note 24, June (1965).

6. Laird, R.K., Andrews, E.B., and Barrow, R.F., "The Absorption Spectrum of CF_2," Trans. Faraday Soc., 46, 803-805, April (1950).

7. Modica, A.P. and LaGraff, J.E., "Thermal Decomposition of C_2F_4 Behind Shock Waves: I. Kinetics and Equilibria of the C_2F_4-CF_2 Reaction," Avco Corporation Technical Memorandum RAD-TM-65-3, January (1965).

8. Modica, A.P. and LaGraff, J.E., "Thermal Decomposition of C_2F_4 Behind Shock Waves: II. Kinetics and Equilibria of the $CF_2 = CF + F$ Reaction," Avco Corporation Technical Memorandum RAD-TM-65-4, January (1965).

9. Mirels, H., "Test Time in Low Pressure Shock Tubes," Aerospace Corporation Report No. TDR-169(3230-12)TN-5, December (1962), and Mirels, H., "Shock Tube Test Time Limitation Due to Turbulent Wall Boundary Layer," Aerospace Corporation Report No. TDR-169(3230-12)TR-3, May (1963).

10. Nayfeh, A.H., "Shock Wave Structure in a Dusty Ablating Gas," Heliodyne Corporation Research Note 23, June (1965).