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D

where Δr_j represents the bin size. Integrating
we obtain

$$\frac{dN_j}{dt} = -F_{j+1} + F_j + J_j + \frac{N_j}{\rho} \frac{d\rho}{dt}$$

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NUCLEATION OF COPPER DURING SUPERSONIC EXPANSION

by

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SUMMARY

Nucleation of copper vapor during gas expansion in a supersonic nozzle is investigated. Time scales for nucleation delay and supersaturation doubling are considered in establishing the need for non-steady state nucleation theory. A population balance model is constructed for tracking the size spectrum of stable clusters formed from self nucleation and exposed to supersaturated gas. It is found that at average cooling rates exceeding 10^7 K/s, copper vapor exists in a highly nonequilibrium concentration at the nozzle exit. Copper condensation is severely limited by the nucleation kinetics and the available residence time. It is influenced by the monomer concentration and the nozzle exit pressure and temperature. The size spectrum of stable clusters is dominated by small clusters containing fewer than fifteen molecules. Nucleation persists throughout the expansion process because of the inability of the vapor condensation processes to relieve supersaturation buildup due to rapid gas cooling. Nucleation rate is sensitive to the surface energy of the clusters corresponding to the critical size. Monte-Carlo simulations of admissible cluster configurations are recommended for determining statistically-averaged surface energies of clusters containing two-to-twenty molecules.

1.0 INTRODUCTION

High-enthalpy arc heaters are being considered as a means of providing simulated test gas in ground test facilities for hypersonic propulsion systems. Erosion of copper electrodes in smaller arc heaters has been observed and is of concern. From the standpoint of characterizing the test environment, it is important to estimate the concentration of copper contaminant in the gas stream and to determine the behavior of copper vapor as the arc-heated gas is expanded in a supersonic nozzle to simulated engine conditions. This report analyzes the condensation behavior of copper vapor during the expansion process.

A typical ground simulation of flight Mach number 15 involves heating air at 46 atm stagnation pressure to 2840 K and rapidly expanding the hot gas to Mach 3.5 in a supersonic nozzle. At nozzle exit, the static gas temperature is 1000 K, and the static pressure is 0.5 atm. From past experience with electrode loss in a laboratory arc heater, the expected range of mole fraction of copper in the gas phase is 10-100 ppm. Corresponding to the higher estimate, the partial pressure of copper at nozzle exit is 5.1 Pa. As a comparison, the saturation pressure of copper over the bulk at 1000 K is 2.5×10^{-6} Pa and implies a supersaturation ratio of 2×10^6 for copper vapor. At this level of supersaturation, vapor species is susceptible to spontaneous nucleation. The purpose of this investigation is to follow the evolution of stable copper clusters formed from the homogeneous nucleation process.

Although steady-state nucleation theory is often used to describe cluster formation, its validity must be questioned in light of the rapid gas cooling rate in the nozzle. There are two relevant time scales: nucleation delay time and the supersaturation doubling time. The nucleation delay time refers to the incubation time to achieve steady-state cluster distribution at given supersaturation. It can be shown that

$$\tau_n = \frac{1}{4} \left(\frac{2\pi m}{kT} \right)^{1/2} \frac{4\pi\sigma}{P_v (\ln S)^2} \quad (1)$$

where S denotes the supersaturation, P_v the partial pressure, σ the surface energy, T the gas temperature, m the mass of a molecule, and k the Boltzmann constant (Kanne-Dannetschek and Stauffer, 1981). The nucleation delay time alone is the appropriate time scale for an isothermal process. For a non-isothermal process, a second time scale for change in state points can be established by following the change in supersaturation ratio. From the definition of supersaturation, $S = P_v/P_s$ where P_s is the saturation pressure,

$$\frac{1}{S} \frac{dS}{dT} = \frac{1}{P} \frac{dP}{dT} - \frac{1}{P_s} \frac{dP_s}{dT}. \quad (2)$$

One can define the supersaturation doubling time τ_s as the time required for a 100% change in supersaturation, i.e., $\Delta S/S = 1$. Thus

$$\tau_s = \frac{1}{\left(\frac{1}{P} \frac{dP}{dT} - \frac{1}{P_s} \frac{dP_s}{dT} \right) \frac{dT}{dt}} \quad (3)$$

For the steady-state nucleation theory to be valid, τ_n must be much smaller than τ_s . Figure 1 shows the relative magnitudes of τ_s and τ_n for an isentropic expansion in a nozzle from a reservoir with stagnation pressure of 46 atm and 2840 K stagnation temperature. The nucleation delay time is seen to be larger than the supersaturation doubling time for copper concentration less than 100 ppm and gas cooling rate faster than 10^6 K/s. As noted earlier, the expected range of copper concentration in the arc-heated gas stream is 10-100 ppm. A representative value for gas residence time in the supersonic nozzle flow is 0.1 ms which gives an average cooling rate of 2×10^7 K/s. Thus, we need to pursue a non-steady state formulation of nucleation theory.

A 'critical cooling rate' can be identified from Eqs. (1) and (2) at which $\tau_s = \tau_n$. Figure 2 displays the calculated critical cooling rate as a function of nozzle exit Mach number and copper concentration. The results reinforce the need for pursuing the non-steady state nucleation theory.

2.0 THEORY

Non-steady state nucleation has been formulated in literature using the liquid drop model, molecular dynamics simulation (Lippman, Schieve and Canestaro, 1984) and chemical kinetics model (Bauer and Frurip, 1977). Of the three approaches, the liquid drop formulation is the simplest and is adopted in this work. It presumes that cluster growth is governed by a series of bimolecular addition reactions and neglects cluster-cluster and three-body reactions. The latter assumption is inapplicable for the initial dimerization and, perhaps, larger clusters such as trimers which must involve a third body. The chemical kinetics models do not invoke this restrictive assumption, but suffer from the difficulties associated with estimating rate constants for bimolecular and trimolecular reactions. The molecular dynamics simulations incur tedious statistical calculations that require knowledge of force constants which are usually not available.

Fig. 1. Time Scales for Nucleation Delay and Supersaturation Doubling

Fig. 2. Critical Cooling Rate

The main interest in this study is not confined to nucleation kinetics, but extends to the disposition of stable clusters formed from self nucleation. For this reason, a population balance model is constructed to track the evolution of the size spectrum of the stable clusters entrained and exposed to the supersaturated gas in the nozzle flow field.

2.1 NON-STEADY STATE NUCLEATION THEORY

The kinetics of cluster growth may be represented as a series of stepwise elementary reactions between the clusters and the monomers (Abraham, 1974).

The forward reaction denotes an accretion process involving combination between an (i-1)mer and a monomer (A_1) to form an i-mer (A_i). The reverse reaction denotes an evaporative loss of a monomer from an i-mer. The net flow between A_{i-1} and A_i is

$$I_{i-1} = C_{i-1}A_{i-1} - E_iA_i \quad (5)$$

where C_{i-1} is the rate at which molecules (monomers) condense on the clusters A_{i-1} , and E_i is the rate at which molecules evaporate from the cluster A_i . Following a similar argument, the net flow between the clusters A_i and A_{i+1} in the population is

$$I_i = C_iA_i - E_{i+1}A_{i+1} \quad (6)$$

In the foregoing kinetic scheme, a cluster A_i may be formed by monomer accretion to A_{i-1} or by evaporation of a monomer from A_{i+1} . It decays by monomer accretion to A_i or by monomer loss from A_i . Thus, the master equation for A_i is

$$\frac{dA_i}{dt} = I_i - I_{i-1} + \frac{A_i}{\rho} \frac{d\rho}{dt} \quad (7)$$

An expression for the condensation rate can be developed by representing the cluster A_i as a spherical aggregate of i molecules with an equivalent radius of $r_i = i^{1/3}r_0$, where $r_0 = (3m/4\pi\rho_c)^{1/3}$, and ρ_c is the condensate density. The hard sphere cross-sectional area for collision between an i-mer and a monomer is $\pi(r_i + r_0)^2$. From the kinetic theory of gases, the average relative velocity between A_i and A_1 is $(8kT/\pi\hat{m}_i)^{1/2}$ where $\hat{m}_i$, the reduced mass, is equal to $(i/1+i)m$. Let α_i represent the accommodation coefficient,

that is, the fraction of molecules striking the cluster that stick. Then, it follows that

$$C_i = \alpha_i \beta_i i^{2/3} A_1 \quad (8)$$

where

$$\beta_i = (1 + 1/i^{1/3})^2 (1 + 1/i)^{1/2} (kT/2\pi m)^{1/2} 4\pi (3m/4\pi\rho_c)^{2/3}. \quad (9)$$

An expression for the evaporation rate can be developed from the principle of microscopic reversibility. Accordingly,

$$E_i = (A_{i-1}^e / A_i^e) C_{i-1} \quad (10)$$

where the superscript e denotes the equilibrium value. The classical liquid-drop theory of thermodynamics of cluster formation relates the equilibrium concentration of the imers to the macroscopic volume and surface free energies. According to the classical thermodynamics,

$$A_i^e = A_1^e \exp(i \ln S - \mu i^{2/3}) \quad (11)$$

where A_1^e is the concentration of monomers in equilibrium with bulk, S is supersaturation (A_1/A_1^e) and μ is related to the surface energy of the cluster (σ) as

$$\mu = 4\pi \left(\frac{3m}{4\pi\rho_c} \right)^{2/3} \frac{\sigma}{kT}. \quad (12)$$

A critical size i^* can be identified as the number of molecules in the cluster present in smallest concentration.

$$i^* = (2\mu/3 \ln S)^3 \quad (13)$$

Relative to the critical size, conventionally defined as the nucleus, E_i displays the following functional behavior.

$$E_i > C_i \quad \text{for } i < i^*$$

$$E_i = C_i \quad \text{for } i = i^*$$

$$E_i < C_i \quad \text{for } i > i^* \quad (14)$$

Many numerical solutions to the master equation, (Eq. 7), have been reported in literature for an isothermal gas ($dp/dt = 0$). These are generally based on the assumption that the steady-state concentration of small clusters (for example, 19-molecule clusters in Courtney, 1962) is established rapidly and is equal to the equilibrium concentration. We need to relax these assumptions since our interest is in rapid gas expansion, cooling rate greater than 10^5 K/s, leading to $S \gg 10^3$ and i^* as small as 2-3. Thus, we seek, a direct solution to Eq. (7) for all $i \geq 2$ by posing it as a set of stiff ordinary differential equations and solving by an implicit method in the GEAR package (Hindmarsh, 1972).

2.2 STABLE CLUSTER POPULATION

We determine the size distribution of the stable clusters $i \geq i^*$ from the population balance equation.

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r} (\dot{r}n) = J\delta(r - r^*) + \frac{n}{\rho} \frac{\partial \rho}{\partial t} + \left(\frac{\delta n}{\delta t} \right)_{\text{coll}} \quad (15)$$

In the foregoing, $n(r,t)$ is the distribution function, r is the cluster size, r^* is the critical radius corresponding to a nucleus of i^* molecules, J is the nucleation rate, and $(\delta n / \delta t)_{\text{coll}}$ refers to the rate of change of n due to agglomeration of clusters. Consistent with the nucleation theory, the agglomeration term is dropped because the residence time of interest is of the order of milliseconds only. We identify the nucleation rate J with the current I_{i^*} determined from the solution of the master equation, Eq. (7).

From kinetic theory of gases, the following expression for growth rate $\dot{r}$ in the free-molecular limit can be derived upon accounting for the relative thermal motion between the monomers and the clusters, and the Kelvin effect.

$$\dot{r} = \alpha_i \left(1 + \frac{1}{i^{1/3}}\right)^2 \left(1 + \frac{1}{i}\right)^{1/2} \frac{P_v(1 - S^{r^*/r-1})}{\rho_c(2\pi mkT)^{1/2}} \quad (16)$$

where P_v is the partial pressure of the monomers.

Equation (15) can be transformed into an ordinary differential equation by replacing the continuous function n with a discrete number density function N_j .

$$N_j = \int_{r_{j-\Delta r}^{j/2}}^{r_{j+\Delta r}^{j/2}} n \, dr \quad (17)$$

where Δr_j represents the bin size. Integrating Eq. (15) over discrete bins, we obtain

$$\frac{dN_j}{dt} = -F_{j+1} + F_j + J_j + \frac{N_j}{\rho} \frac{d\rho}{dt} \quad (18)$$

where

$$F_j = \dot{r}_{j-1/2} \left| \frac{N_{j-1}}{\Delta r_{j-1}}, \frac{N_j}{\Delta r_j} \right| \quad (19)$$

An upwinding convention applies to Eq. (19): the first term inside the bracket is used if the multiplier is positive and the second if the multiplier is negative. Equation (18) represents a set of coupled ordinary differential equations and can be solved by the same technique as for the master equation, Eq. (7).

2.3 MONOMER CONCENTRATION

The depletion in monomer concentration due to the formation of stable clusters and condensation on the stable clusters is governed by the following conservation equation.

$$\frac{dA_1}{dt} = \frac{A_1}{\rho} \frac{d\rho}{dt} + \sum_j \frac{4}{3} \pi r_j^3 \frac{\rho_c}{m} \left[\frac{N_j}{\rho} \frac{d\rho}{dt} - \frac{dN_j}{dt} \right] \quad (20)$$

Equations (7), (18) and (20) represent a set of coupled, stiff ordinary differential equations and were solved numerically by the GEAR's backward-differencing implicit scheme.

3.0 RESULTS AND DISCUSSION

The foregoing cluster evolution model has been applied to isentropic gas expansion ($\gamma = 1.3$) in the diverging portion of a supersonic nozzle with 8.5° half angle and 3.81 cm throat diameter. The reservoir conditions and the nozzle length are determined from the specified exit Mach number, gas pressure and gas temperature.

The vapor pressure of copper (and copper oxide) is calculated from the JANAF thermodynamic data for ideal gas and condensed states (Chase et al., 1985). Table 1 lists the reference values of surface energy, copper concentration and nozzle exit conditions around which sensitivity calculations have been performed.

Table 1. Reference Data

	σ	P_e	T_e	M_e	Mole Fraction	ρ_c
Cu	0.8 N/m	0.5 atm	1000 K	3.5	100 ppm	8,920 kg/m ³
CuO	0.6 N/m	0.5 atm	1000 K	3.5	100 ppm	6,400 kg/m ³

3.1 CLUSTER DYNAMICS

For purpose of illustration, one calculation was performed for an isothermal gas at 1200 K and 1 atm. The concentration of copper is taken as 2 ppm which corresponds to a supersaturation of 138. For the master equation, the imposed initial condition is $A_i = 0$ for all $i > 1$. In this exercise, the population balance equation is disregarded.

Figure 3 depicts the transient variation in cluster concentration and its approach to the steady-state distribution in 10 ms. At steady state,

$$I_i = I_{i+1} \quad \text{for all } i$$

and the cluster current is constant and independent of cluster size. Also included is the equilibrium distribution of the clusters, defined as

$$I_i = 0 \quad \text{for all } i.$$

The equilibrium distribution has a marked minimum at $i = i^*$. For $i < i^*$, the steady-state distribution is coincident with the equilibrium distribution. Note also the rapid approach of dimer to the equilibrium value which constitutes the basis of equilibrium assumption for small clusters in many non-steady nucleation analyses.

3.2 SENSITIVITY TO SURFACE ENERGY

The liquid drop model assumes a constant value of specific surface energy regardless of the cluster size. This value is customarily equated to the bulk

Fig. 3. Cluster Dynamics

surface tension. Monte Carlo simulations of cluster configurations, however, reveal surface energy to be a fraction of the cluster size particularly for small clusters containing fewer than 10-20 molecules. For simple molecules like Ar, the statistically averaged surface energy of ten-atom clusters has been calculated to be about 20% less than that of the bulk. The surface tension of metals is temperature dependent and generally lies in the range 1-1.4 N/m. Copper has a surface tension of 1.2 N/m at its melting point. Since we are potentially interested in clusters as small as dimers and trimers, we choose a smaller value (0.8 N/m) as the reference and conduct a sensitivity study on cluster distribution as a function of σ .

Figure 4 depicts the calculated number density distribution of stable clusters at nozzle exit as a function of σ . These calculations are based on the gas dynamic conditions determined from Table 1 reference data. The flow residence time (τ_r) in the diverging section is 0.138 ms. The condensation time, defined as the residence time in which S is greater than 1, is 0.094 ms. It was found sufficient to consider up to 30-atom clusters in the non-steady nucleation model. The population balance equation was solved using twenty unequal size bins.

The calculated stable cluster size distribution is dominated by the small clusters, i.e., dimers and trimers. The number density decreases with cluster size and surface energy. The slight upturn in the last size bin should be regarded as a numerical aberration attributed to the finite limit in the maximum cluster size considered. The extent of condensation is limited by the available residence time in the nozzle and is a strong function of surface energy. For the three values of σ considered, the calculated amount of copper condensed was 0.10% for $\sigma = 1$ N/m, 0.30% for $\sigma = 0.8$ N/m and 29.81% for $\sigma = 0.6$ N/m. In each case, the rise in supersaturation because of the drop in temperature from gas expansion is not compensated by the ensuing homogeneous nucleation and condensation. There is a resultant monotonic increase in supersaturation along the flow direction. At nozzle exit, magnitude of S exceeding 10^6 has been calculated.

Figure 5 depicts the rise in supersaturation ratio with gas expansion. As S increases, the critical cluster size i^* decreases in accordance with Eq. (13), and the nucleation process accelerates. At $S = \exp(2^{2/3} \mu/3)$, the critical cluster size reduces to a dimer. Above this value of supersaturation, i^* becomes independent of S , and the nucleation rate levels off. At this point, J becomes a function of monomer concentration only and is independent of the supersaturation level.

With reference to Eqs. (15) and (20), vapor depletion occurs by two

Fig. 4. Sensitivity of Stable Cluster Size Spectrum to Surface Energy ($T_e = 1000 \text{ K}$, $P_e = 0.5 \text{ atm}$, $M_e = 3.5$, $X_i = 100 \text{ ppm}$)

Fig. 5. Variation of Supersaturation Ratio and Nucleation Rate During the Expansion Process ($T_e = 1000 \text{ K}$, $P_e = 0.5 \text{ atm}$, $M_e = 3.5$, $X_i = 100 \text{ ppm}$, $\sigma = 0.8 \text{ N/m}$)

processes: homogeneous nucleation to form embryos/nuclei and vapor condensation on the embryos. In clean gases, the homogeneous nucleation process forms embryos and provides sites for vapor condensation. In general, even though homogeneous nucleation is the initiator, much of the mass transfer occurs through vapor condensation on the embryos. The relative amounts of condensation by the two processes can be calculated from the following equations.

$$\Delta\rho_v \text{ (nucleation)} = \int \frac{4}{3} \pi r^3 \rho_c J \, dt$$

$$\Delta\rho_v \text{ (condensation)} = \iint 4\pi r^2 \rho_c n \, dr \, dt$$

As mentioned above, during the supersonic expansion S was calculated to increase along the flow direction. In the short residence time expansion process, J was persistently large so that nucleation dominated over the condensation process. This is also evident in the declining number density with cluster size seen in Fig. 4.

3.3 SENSITIVITY TO MONOMER CONCENTRATION

Figure 6 depicts the dependence of cluster size distribution at nozzle exit on initial copper vapor concentration. At low mole fraction, the number density decreases rapidly with cluster size. At 100 ppm, larger clusters begin to appear in the size distribution. When the initial concentration is increased to 200 ppm, the cluster distribution tends to become uniform with a small internal peak at 15-molecule size. As mentioned earlier, cluster segregation in the last size bin is an artifact of the numerical scheme and would disappear if larger clusters were included in the simulation.

Table 2 quantifies the cluster distribution in terms of the fraction of vapor condensed in the nozzle, and relative number density (A_{99}/A_2), concentration (ρ_{99}/ρ_2) and surface area (S_{99}/S_2) of 99-molecule clusters to dimers.

Table 2. Sensitivity to Monomer Concentration

X_1 , ppm	% Condensed	A_{99}/A_2	ρ_{99}/ρ_2	S_{99}/S_2
50	0.08	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$
100	0.30	2.75×10^{-5}	1.36×10^{-3}	3.7×10^{-4}
200	2.85	0.031	1.54	0.420

Fig. 6. Effect of Monomer Concentration on Formation of Stable Clusters
 $(T_e = 1000 \text{ K}, P_e = 0.5 \text{ atm}, M_e = 3.5, \sigma = 0.3 \text{ N/m})$

3.4 SENSITIVITY TO EXIT TEMPERATURE

Figure 7 displays the effect of nozzle exit temperature on the size distribution of the stable clusters. The nozzle exit pressure and Mach number are held constant in this set of calculations. The change in nozzle exit temperature is accomplished by varying the reservoir temperature. As the exit temperature is raised, lower levels of supersaturation are attained, and the flow residence time (τ_c) in which $S > 1$ decreases. Thus, the amount of condensation is strongly dependent on the nozzle exit temperature. The cluster distribution parameters as a function of T_e are summarized in Table 3.

Table 3. Sensitivity to Nozzle Exit Temperature

T_e , K	τ_r , ms	τ_c , ms	% Condensed	A_{99}/A_2	ρ_{99}/ρ_2	S_{99}/S_2
800	0.155	0.142	16.30	0.022	1.10	0.30
1000	0.138	0.094	0.30	2.75×10^{-5}	1.36×10^{-3}	3.71×10^{-4}
1200	0.127	0.052	0.08	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$

3.5 SENSITIVITY TO EXIT PRESSURE

Figure 8 compares the stable cluster size distribution at two nozzle exit pressures, 0.5 and 1 atm. The exit pressure is assumed to be controlled by the reservoir pressure. All other conditions are held constant, i.e., $T_e = 1000$ K, $M_e = 3.5$, $X_1 = 100$ ppm and $\sigma = 0.8$ N/m. Under this set of conditions, S varies directly as P_e . The resulting increase in the concentration of the large clusters is shown graphically in Fig. 8 and summarized in Table 4.

Table 4. Sensitivity to Nozzle Exit Pressure

P_e , atm	τ_c , ms	% Condensed	A_{99}/A_2	ρ_{99}/ρ_2	S_{99}/S_2
0.5	0.094	0.30	2.75×10^{-5}	1.36×10^{-3}	3.71×10^{-4}
1.0	0.100	2.93	0.031	1.55	0.421

Fig. 7. Effect of Nozzle Exit Temperature on Formation of Stable Clusters
($P_e = 0.5$ atm, $M_e = 3.5$, $X_i = 100$ ppm, $\sigma = 0.8$ N/m)

Fig. 8. Effect of Nozzle Exit Pressure on Formation of Stable Clusters
($T_e = 1000$ K, $M_e = 3.5$, $X_i = 100$ ppm, $\sigma = 0.8$ N/m)

3.6 SENSITIVITY TO EXIT MACH NUMBER

A set of calculations was done in which the nozzle exit Mach number was varied by changing the reservoir conditions but holding the exit pressure at 0.5 atm and temperature at 1000 K. As depicted in Fig. 9, the calculated size distribution of stable clusters is only mildly sensitive to the nozzle exit Mach number varied in this manner. Table 5 shows the fractional increase in copper vapor condensed as the Mach number is changed from 3 to 4.

Table 5. Sensitivity to Exit Mach Number

M_e	τ_r , ms	% Condensed
3.0	0.103	0.27
3.5	0.138	0.30
4.0	0.178	0.47

3.7 COPPER OXIDE CONDENSATION

Equilibrium thermodynamic calculations suggest that copper which exists as metallic vapor in the arc heater can combine with oxygen to form CuO during nozzle expansion. A chemical kinetic barrier, however, may prevent oxidation of copper in a time scale of 0.1 ms. The pertinent chemical rate constants are not available to permit a definitive assessment of the oxidation possibility. In order to assess the effect of oxide formation on copper nucleation, we disregard the possible chemical kinetic barrier. With this assumption, JANAF Gibbs free energy data alone can be employed to determine the saturation pressure of copper oxide.

The surface tension of metal oxides is generally lower than that of the metals and lies in the range 0.3-0.8 N/m. Within this range of σ , Figure 10 displays the calculated size distribution of stable CuO clusters at the nozzle exit. The results generally show the same trend as observed previously in Fig. 4 for copper clusters. Table 6 lists the distribution parameters. A noteworthy feature is that almost complete condensation of CuO is calculated for $\sigma = 0.4$ N/m. The distribution is heavily populated by clusters smaller than fifteen-molecule aggregates. On a concentration basis ($\rho_i = iA_i$), ρ_i is almost a constant for $i < 20$.

Fig. 9. Effect of Nozzle Exit Mach Number on Formation of Stable Clusters ($T_e = 1000$ K, $P_e = 0.5$ atm, $X_i = 100$ ppm, $\sigma = 0.8$ N/m)

Fig. 10. CuO Condensation ($T_e = 1000$ K, $P_e = 0.5$ atm, $M_e = 3.5$, $X_i = 100$ ppm)

Table 6. CuO Cluster Distribution Parameters

σ , N/m	% Condensed	A_{gg}/A_2	ρ_{gg}/ρ_2	S_{gg}/S_2
0.4	97.36	8.95×10^{-4}	0.044	0.012
0.6	39.45	3.27×10^{-4}	0.016	4.41×10^{-3}
0.8	$<10^{-3}$	7.13×10^{-4}	0.035	9.61×10^{-3}

4.0 CONCLUSIONS AND RECOMMENDATIONS

A non-steady nucleation theory based on the liquid drop model has been used to investigate the condensation behavior of copper vapor during supersonic expansion in a nozzle. The expansion process is characterized by a residence time of the order of 0.1 ms from nozzle throat to exit and by an average gas cooling rate exceeding 10^7 K/s. Little attention is paid to the subsonic flow in the converging section where the gas is highly superheated. The principal conclusions from this investigation are summarized below.

a) At the nozzle exit, copper vapor exists in a highly nonequilibrium state, $S \gg 10^6$. This is an outcome of the inability of homogeneous nucleation and vapor condensation processes to relieve supersaturation buildup due to rapid gas cooling. Consequently S increases monotonically along the flow direction.

b) Since high levels of S are attained and maintained, the nucleation process persists at an ever-increasing rate. Much of the mass transfer is associated with the formation of the embryos with a small contribution from vapor condensation on the sites provided by the embryos. Thus, the size spectrum of the stable clusters is dominated by small clusters containing fewer than fifteen molecules.

c) Because of the short residence time in the nozzle, the amount of vapor condensation is limited by nucleation kinetics and can be much smaller than that determined from thermodynamic equilibrium. The extent of condensation is found to be sensitive to the copper vapor concentration at the inlet, and the nozzle exit pressure and temperature. Nucleation is expected to continue into the engine test section downstream of the nozzle. The calculation of stable cluster size evolution needs to be extended up to and perhaps beyond the ignition point in the combustor section.

d) One source of uncertainty in the nucleation theory is the cluster surface energy. It is known to be smaller than the bulk liquid surface tension and to depend upon the cluster size. We recommend Monte-Carlo simulations of cluster configurations from which statistically-averaged surface energy can be deduced.

e) For small clusters, the condensate density can be much smaller than the bulk material density. This is particularly true for clusters containing 2-15 atoms which dominate the calculated size spectra. We recommend Monte-Carlo simulation of cluster configuration statistics to determine the size dependence of cluster density. We note from Eqs. (12) and (13) that the embryo size i^* is directly proportional to σ^3/ρ_c^2 . At steady state the nucleation rate is exponentially dependent on i^* . Thus nucleation kinetics is extremely sensitive to σ and ρ_c .

f) Finally, the calculated critical size of the embryos is smaller than the range in which the liquid drop model is normally used. Therefore, experimental data are needed to validate the nucleation theory applied to a rapid expansion process with cooling rate exceeding 10^7 K/s.

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