with $\bar{\delta}_{h_o}$ being evaluated utilizing Eq. (22) and the results of computations similar to those presented in Fig. 1.

Finally, the generalized definitions for each of the integral thicknesses employed here are compatible with the limiting case of axial boundary-layer flow over a needle. In this situation τ approaches infinity and each of the integrals reduces to the form of the following equation for displacement thickness

$$\delta^*_{\tau \gg l} = \left(\int_0^l (1 - \bar{\rho}\bar{u}) \, \mathrm{d}\eta^2 \right)^{1/2} \tag{24}$$

Acknowledgment

The author would like to acknowledge the very helpful critique provided by F.E.C. Culick.

References

[1]Scholkemeier, F.W., Die laminare Reibungsschicht an rottationssymmetrischen Körpern, *Archiv der Mathematik.*, Vol. 1, 1949, pp. 270-277.

[2]Kutateladze, S.S., Leont'ev, A.I., "Boundary Layers in Compressible Gases," translated by Spalding, D.B., Academic Press, New York, 1964.

[3]Schlichting, H., *Boundary Layer Theory*, 6th edition, McGraw-Hill, New York, 1968.

Effect of Crystallization Kinetics on Rocket Performance

Charles B. Henderson*
Atlantic Research Corporation, Alexandria, Va.

Nomenclature

A, n	= constants in crystallization velocity equation
C	= specific heat capacity per unit mass
d	= diameter
k	= thermal conductivity
M	= Mach number
(MW)	= molecular weight
P	= pressure
R	= universal gas law constant
Re	= Reynolds number
T	= temperature
V	= velocity of crystallization wave
γ	= ratio of specific heats
μ	= viscosity
ρ	= density

Subscripts

F	= fusion
g	= gas
M	= equilibrium melting
P	= particle
t	= throat

Introduction

THE performance at high expansion ratios of metal-containing solid rocket propellants is sensitive to the recovery of the latent heat of fusion of the metal oxides formed in the combustion products. The thermal radiation from the plumes of such rocket exhausts, as a consequence of its dependency on the temperature of the particulates, is also sensitive to the recovery of the latent heat of fusion. An ex-

tensive literature exists on the kinetics of nucleation and crystal growth in liquids. There has been very little application of this research, however, to the problems just described.

Review of Crystallization Kinetics

Both homogeneous nucleation and heterogeneous nucleation play a role in the fusion of a liquid droplet in a temperature-decreasing gas stream. The fusion process starts by homogeneous nucleation, that is by the spontaneous formation of molecular aggregates in an otherwise homogeneous liquid. Once the crystallization process has been initiated, fusion can also proceed by the process of heterogeneous nucleation in which the nuclei are formed at the interface between the liquid and the already-formed crystal phase.

From homogeneous nucleation theory[1,2] it may be inferred that the nucleation frequency is such a strong function of the temperature that it is permissible to define a homogeneous fusion temperature, T_F, which is a function only of the equilibrium fusion temperature, T_M. Above T_F, nuclei form too slowly to be of practical importance. Below T_F, nuclei form at exceedingly high rates. This inference has been confirmed experimentally; T_F has been found to be approximately $0.8 \, T_M$ for a wide variety of materials.[2-5] If only homogeneous nucleation is considered in solidification problems, the liquid is assumed to fuse at the temperature T_F, just as if it were an equilibrium thermodynamic melting temperature. This oversimplified approach has been previously used[6] in the prediction of rocket performance.

If a liquid melt were at uniform temperature, only homogeneous nucleation need be considered; this is not the case, however, with a liquid droplet in a temperature-decreasing gas stream. Fusion commences when the temperature at the outside of the drop reaches T_F. At this point, as discussed below, the temperature of that portion of the drop undergoing fusion increases, and homogeneous nucleation ceases to be of importance. Once homogeneous nucleation has provided a crystal phase, crystallization proceeds in a wavelike manner throughout the remainder of the liquid phase by the process of heterogeneous nucleation. An equation giving the linear velocity of the interface was derived by Hillig and Turnbull,[7] who modify a Volmer-type rate expression by assuming that only a fraction of the total sites on the crystal surface are available for molecular attachment; the number of sites is based on an assumption that crystallization occurs via a screw-dislocation mechanism. In the resulting expression, the velocity of the crystallization wave is proportional to the square of the supercooling; i.e., $V = A(T_M - T)^n$ where $n = 2$. A number of experimental investigators[7,8] have found that n is usually somewhat less than 2, namely 1.7-1.8.

Application of the crystallization velocity equation to a liquid drop in a temperature-decreasing gas stream leads to a rationalization of the phenomenon of recalescence in which, once crystallization has begun, the surface temperature of the drop rises as a consequence of the liberation of latent energy of fusion. This has been often detected experimentally by a sudden increase in the luminosity of the particle giving rise to the designation of spearpoint temperature, T_{sp}, to the maximum temperature achieved by the solidifying droplet.

The constants A and n in the wave velocity expression have been measured for zirconium oxide by Rosner and Epstein[8] who gave values of 0.72×10^{-4} cm/sec/$K^{1.8}$ and 1.8, respectively. No data have been found for aluminum oxide, but the theory of Hillig and Turnbull[1] suggests that the rates for the two oxides should be of the same order of magnitude.

Results and Discussion

The kinetics of crystallization presented previously have been applied to the rocket propellant exhaust by making one-dimensional calculations of a two-phase, nonreacting nozzle

Fig. 1   Particle and gas temperature profiles, in supersonic nozzles based on heterogeneous nucleation wave equation.
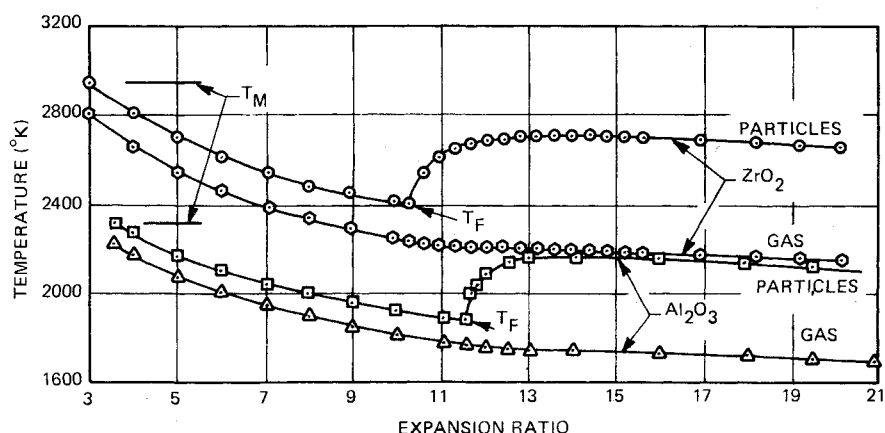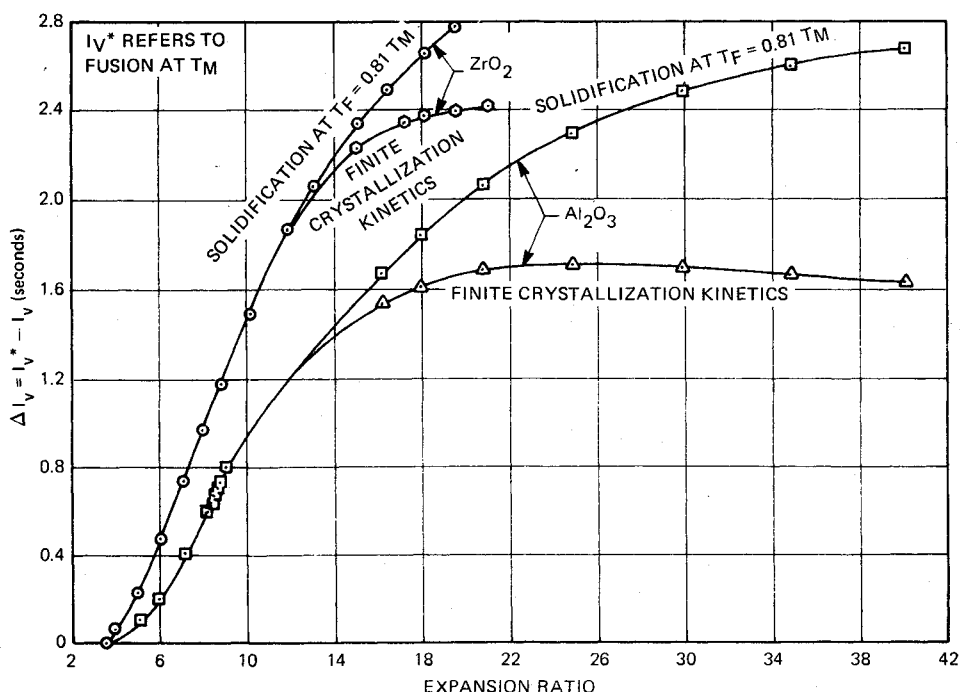

Fig. 2   Effect of finite crystallization rate on vacuum specific impulse.

flow in the supersonic portion of a nozzle using standard finite-difference techniques including the introduction of the crystallization wave equation. Particulate drag and heat-transfer data were those of Henderson[9] and Carlson and Hoglund,[10] respectively. Since the particulates in rocket exhaust are ordinarily less than 15 μm, an assumption of a uniform drop temperature introduces little error. The results of such calculations are shown in Figs. 1 and 2.

Figure 1 shows the temperature profiles, both condensed and gaseous, for two exhaust streams, one containing 50% by weight of 4 μm zirconium oxide droplets and the other 33% by weight of 4 μm aluminum oxide droplets. The wave

Table 1   Starting conditions for nozzle calculations

	ZrO_2 Exhaust	Al_2O_3 Exhaust
Throat diameter, cm	4.23	18
Molecular weight of gas	21.5	20
Ratio of specific heats of gas	1.25	1.23
Conditions at start of calculation		
Expansion ratio	3	3.47
Pressure, MPa	1.17	0.32
Gas velocity, m/sec	1880	2150
Particle velocity, m/sec	1580	2020
Gas temperature, K	2810	2235
Particle temperature, K	2950	2325

velocity expression measured for ZrO_2 was used in both flows. The calculations were started where $T_p = T_M$ since crystallization kinetics has no influence upstream of this condition. Other starting conditions – assumed to be "typical" – are listed in Table 1.

The calculations show that the particle temperature rises to the spearpoint temperature very rapidly after the fusion process begins but thereafter decreases only slightly as fusion proceeds to completion. Fusion is complete at expansion ratios of 21 and 23 for the ZrO_2 and Al_2O_3 flows, respectively. Figure 2 shows differences in vacuum specific impulse calculated for the two flows described above. In each case the reference I_v is one calculated assuming fusion at the equilibrium fusion temperature. Application of homogeneous nucleation theory (i.e., fusion at $T_F = .8T_M$) leads to too high an estimate of the performance loss. It is obvious that estimates of specific impulse made at one expansion ratio from observations made at a different expansion ratio can result in a significant error unless crystallization kinetics are taken into account. Since both the onset and the speed of crystallization are dependent on nozzle size (as shown further on) it is also obvious that the crystallization must be adequately treated in a determination of the effect of thrust level on specific impulse.

The degree to which T_{sp} falls short of the equilibrium fusion temperature is related to a number of parameters describing the two-phase flow, among which is the
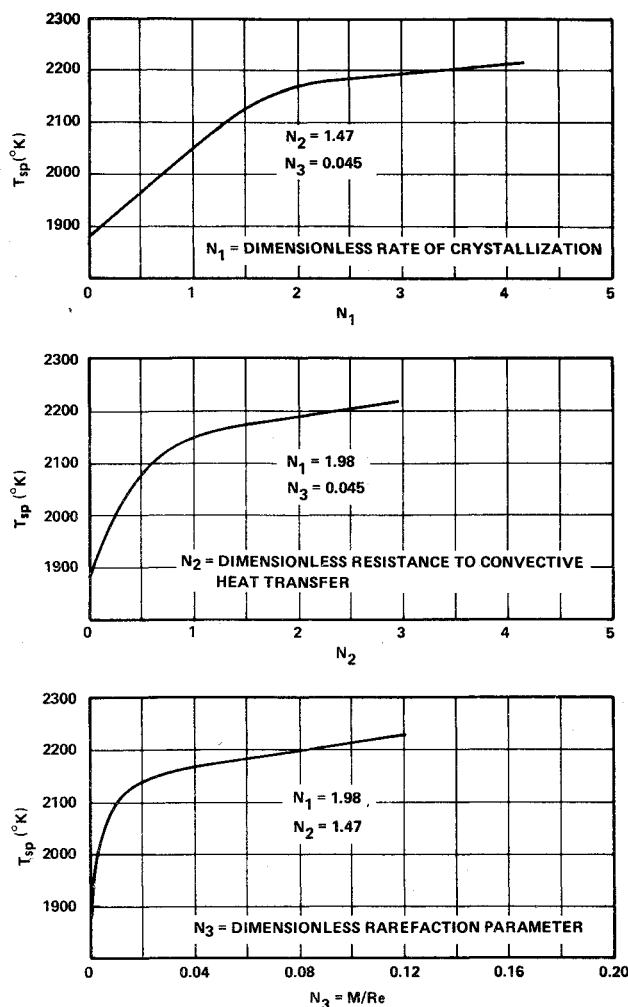
Fig. 3   Effects of dimensionless groups on spearpoint temperature.

crystallization wave speed. The relative importance of the more important parameters was determined by combining them into three dimensionless groups and determining their effect on T_{sp} by a series of parametric calculations similar to those described previously. The first of the three groups is the ratio of the time constant of the nozzle to the time constant for the kinetically limited fusion of the drop

$$N_1 = d_r \sqrt{\frac{(MW)_g}{RT_g}} \bigg/ \frac{d_p}{A(T_M - T_F)^n}$$

The second group is the ratio of the time constant for convective heat transfer to the particle to the time constant of the nozzle,

$$N_2 = \frac{(d^2 \rho c)_p}{k_g} \bigg/ d_r \sqrt{\frac{(MW)_g}{RT_g}}$$

The third group measures the degree of rarefaction of the flow:

$$N_3 = \frac{M}{Re} = \frac{\mu}{d_p P} \sqrt{\frac{RT}{(\gamma \cdot MW)_g}}$$

All three groups were calculated at the flow conditions corresponding to an expansion ratio of 3.5.

Results are shown in Fig. 3. Low spearpoint temperatures are associated with slow crystallization kinetics (low N_1), high convection rates (low N_2) and denser flows (low N_3). The N_3 interaction is a consequence of higher degree of convective coupling between gas and particulates at higher pressures

(i.e., higher Nusselt numbers). The significant difference in spearpoint temperatures can lead to significant variations in the thermal radiation calculated from exhaust plumes.

Since accurate predictions of performance and plume radiation require knowledge of the heterogeneous crystallization velocity, experimental data on oxides other than ZrO_2 would be extremely useful.

References

[1] Turnbull, D., "Phase Changes," Solid State Physics, Vol. 3, Seitz, F. and Turnbull, D., eds., Academic Press, N.Y., 1956, pp. 226-310.

[2] Buckle, E.R. and Ubbelohde, A.R., "Studies on the Freezing of Pure Liquids," Proceedings of the Royal Society, Vol. A259, 1961, pp. 325-340, Vol. A261, 1961, pp. 189-206.

[3] Turnbull, D. and Cech, R.E., "Microscopic Observation of the Solidification of Small Metal Droplets." Journal of Applied Physics, Vol. 21, Aug. 1950, pp. 804-810.

[4] Thomas, D.G. and Stavely, L.A.K., "A Study of the Supercooling of Some Molecular Liquids," Journal of the Chemical Society, (London) 1952, pp. 4569-4577.

[5] DeNordwall, H.J. and Stavely, L.A.K., "Further Studies of the Supercooling of Drops of Some Molecular Liquids," Journal of the Chemical Society, (London), 1954, pp. 224-227.

[6] Atlantic Research Corporation, Alexandria, Va., QPR No. 7, "Solid Propellant Research and Development-The Study of Multiphase Flow Through Rocket Nozzles," Contract Now-61-0687-c, ARPA Order No. 22-61, Dec. 1962, pp. 83-88.

[7] Hillig, W.B. and Turnbull, D., "Theory of Crystal Growth in Undercooled Pure Liquids," Journal of Chemical Physics, Vol. 24, April 1956, p. 914.

[8] Rosner, D.E. and Epstein, M., "Simultaneous Kinetic and Heat Transfer Limitations in the Crystallization of Highly Undercooled Melts," Chemical Engineering Sciences, Vol. 30, 1975, pp. 511-520.

[9] Henderson, C.B., "Drag Coefficients of Spheres in Continuum and Rarefied Flows," AIAA Journal, Vol. 14, June 1976, pp. 707-708.

[10] Carlson, D.J. and Hoglund, R.F., "Particle Drag and Heat Transfer in Rocket Nozzles," AIAA Journal, Vol. 2, Nov. 1964, pp. 1980-1984.

Comparative Performance of Chemical Lasers with Axisymmetric and Two-Dimensional Nozzles

Harold Mirels* and Walter R. Warren, Jr.†
The Aerospace Corporation,
El Segundo, California

Nomenclature

B	$= \sigma/\epsilon$
$[F]_0$	= initial atomic fluorine concentration, moles/cc
g	= local gain, $\sigma[n_u - n_\ell]$
I	= net local intensity
j	= 0, 1 for two-dimensional and axisymmetric nozzles, respectively
K_l	$= k_f/k_{cd}$
k_{cd}	= collisional deactivation rate (sec^{-1})
k_f	= forward pumping rate (sec^{-1})
N	= 1/2, 1 for laminar and turbulent mixing, respectively
P	= output power up to station x, Eq. (2a)
$\bar{P}$	= normalized output power up to station x, Eq. (2b)
$\bar{P}_e(j,N)$	= normalized net laser output power
p	= static pressure at nozzle exit