A SURFACE BURNING MODEL FOR MELT CAST TNT

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A two-stage thick-pyrolysis zone surface regression model was developed to describe the decomposition of homogeneous explosives, such as melt-cast TNT. In the first stage, pyrolysis starting at germ nuclei beneath the surface forms a porous structure. In the second stage, transformation to the gas phase is completed at the surface where the remaining solid explosive is exposed to the decomposition products. The resulting gases then chemically react in the flame zone above the surface and release their energy. The model qualitatively explains the anomalous behavior of melt cast TNT grains in closed-bomb tests.

INTRODUCTION

A significantly different behavior from that of rocket and gun propellants was observed in closed bomb tests of small melt-cast TNT grains (½" long and ¼" in diameter).[1] The closed bomb was equipped with a rupture disc that allowed rapid depressurization and interruption of burning. The extinguished grains were recovered in an evacuation chamber. The surface was examined using scanning electron microscopy. Subsurface burning features were examined by cold fracturing the grains.

The striking phenomenon that was revealed by the study is the extensive subsurface pyrolysis, resulting in a complex system of holes and tunnels interlaced throughout the recovered grains. Although the TNT grains were solid, the rate of pressurization was progressive (not regressive as expected), even more progressive than propellant grains containing several axial perfs. Unfortunately, because TNT is difficult to ignite, extended ignition delays were observed, the variation in behavior from grain to grain was significant, and the evolution of pressure was path dependent and irreproducible.

In previous work[2] a single-stage thick-pyrolysis zone surface regression model was developed by combining a traditional surface decomposition

model for propellants[3] with Avrami's nucleation and growth model for phase changes in solids.[4] The model qualitatively explains the unexpected appearance of holes and tunnels in TNT burnt in ARL's closed bomb. It also explains how the different mechanisms involved act in concert such as to compensate for the low number density of germ nuclei in melt-cast TNT. The surface temperature is significantly increased such that the resulting surface regression is only slightly slower than in composite propellants of comparable energy but incorporating much more germ nuclei. But some of the assumptions introduced into the model to simplify the solution procedure are difficult to justify. The two-stage pyrolysis model introduced in this paper removes the inconsistencies of the previous model.

TOPOLOGY OF PYROLYSIS

The holes and tunnels observed on the surface and deep within the TNT grains when the reaction was extinguished by rapid depressurization of the bomb in which they were burnt are reminiscent of those observed during the isothermal decomposition of energetic crystals.[5] Being homogeneous, if the temperature is uniform, the probability of a thermally induced phase change is mostly equal at all points. The transformation is therefore expected to start at micro-structural defects, inclusions, second-phase precursors, etc.,

where the free energy is locally higher than the surrounding "regular" points. These are the sites of "germ nuclei." They are randomly distributed throughout the bulk of the material, but only a few are thermally activated at a time. Once activated, a germ nucleus steadily grows in size resulting in a continuously expanding sphere, disc, or cube of the second phase. The process is usually called nucleation and growth. If the germ nuclei in a row are preferentially activated, the second phase is rod-shaped, and if it is gaseous, a hollow tunnel is formed.

In order to distinguish it from surface nucleation and growth which controls the advance of the transformation interface between two phases, the process described above will be referred to in this paper as bulk nucleation and growth. Even if the whole crystal is at the same, uniform temperature, the two processes are physically different. Whereas at the interface between two phases (in chemical decomposition, the burning surface) the germ nuclei are activated by diffusion of ions from the transformed phase, in bulk nucleation they are thermally activated, randomly, but in-situ. The parameters quantifying the two processes, for example the activation energy, are also different.

Both processes are capable of generating holes and tunnels. For example, if the elemental areas at the surface of the semi-infinite explosive illustrated in Fig. 1 are randomly activated, the growth of the second phase in a normal direction will generate the shown tunnels. Because they started at different times, even if the growth rate is the same, they penetrate to different depths. If the direction of growth is also random, a complex system of tunnels interlaced throughout the explosive is formed, not unlike that observed in melt-cast TNT grains burnt in ARL's closed-bomb tests.[1] The important feature to notice in this case is that the surface is not regressing. The solid explosive is solely consumed by the action of these tunnels, continuously boring through its bulk. Consumption is enhanced if the tunnels were radially expanding at the same time,

but it is not necessary for complete pyrolysis.

Bulk nucleation and growth can also lead to the formation of holes and tunnels as illustrated in Fig. 1. If a germ nucleus is activated before it is ingested by the growing second phase of a neighboring nucleus activated at an earlier time, the union of the resulting cubes (spheres, or discs) will be tunnel-shaped. Especially after the process has progressed for a while and the density of the already activated germ nuclei has increased.

As explained above, tunneling from the surface does not lead to surface regression, but it is also an inherently unsteady process. In this paper, surface regression was coupled to bulk nucleation and growth to formulate a physically consistent model for *steady* surface decomposition of homogenous explosives. Laminar surface regression can be introduced within the frame of surface nucleation and growth as a special case in which the whole surface is instantaneously activated, for example, if it is abundantly covered with germ nuclei. From each point on the surface pyrolysis radially grows at a finite rate. The union of the resulting hemispheres creates a front parallel to the surface that advances in the normal direction at the growth rate, thus in this case equal to the rate of regression. The same argument applies if the growth starts from small elemental areas at the surface instead of points, and proceeds in a normal direction.

SURFACE DECOMPOSITION MODEL

Figure 2 illustrates the basic features of the new model. Pyrolysis of the solid takes place in two stages. The first, due to bulk nucleation and growth in a relatively thick zone (in comparison to the flame) heated by thermal conduction from the surface, yields a porous structure. In the second stage similar to traditional surface regression,
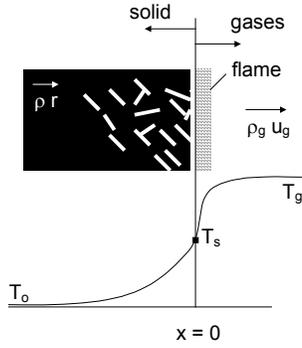

tunneling   surface regression
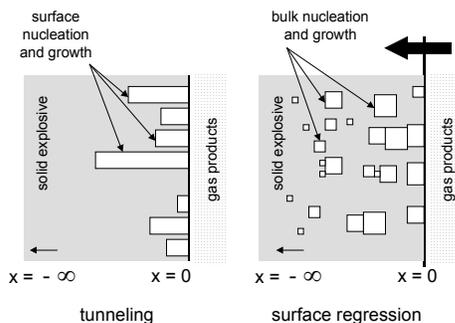
FIGURE 2. ELEMENTS OF SURFACE DECOMPSOSITION MODEL

pyrolysis of the remaining solid occurs within an infinitesimally thin layer at the surface. Exothermic chemical reactions are assumed to occur strictly in the gas phase, in the flame zone above the surface. A brief description of the governing equations is given below.

Avrami's Nucleation and Growth Model

Assuming an initial density of germ nuclei $\bar{N}$, and a probability of activation $\eta(T) = Z_c \exp(-E_c/RT)$, where the subscript c is used to designate the properties of the solid explosive, the rate of depletion of germ nuclei dN/dt can be expressed as the sum of two terms. The first, due to thermal activation $= -\eta N$. The second mechanism of depletion, due to the ingestion of germ nuclei (before they are activated) by the growing second phase $= -N/(1-V)\, dV/dt$, where V is the volume fraction of the second phase. Integrating, we get

$$N = \bar{N}\, e^{-\eta t}\,(1 - V) \qquad (1)$$

The group ηt was identified by Avrami as a scaled time of reaction τ. For example, if the temperature is increased such that $\eta(T)$ is doubled, we get similar results, but in half the time.

Assuming that the activated nuclei radially grow at a rate G(T), a nucleus that is activated at time θ will occupy at time t a volume $4/3\pi\, G^3(t - \theta)^3$. The number of nuclei activated between θ and $\theta + d\theta$ is $\eta N\, d\theta$. But a simple integration of the product of these two terms does not yield V(t) because some of the growing spheres overlap and will be counted more than once. The correct integral s[4]

$$\int_1^V \frac{dV}{1-V} = 6\sigma G^3 \bar{N} \int_0^t \eta\; e^{-\eta\theta}\,(t-\theta)^3\, d\theta \qquad (2)$$

yielding

$$-\log(1-V) = 6\sigma\left(\frac{G}{\eta}\right)^3 \bar{N}$$
$$\cdot\left[e^{-\tau} - 1 + \frac{\tau}{1!} - \frac{\tau^2}{2!} + \frac{\tau^3}{3!}\right] \qquad (3)$$

where the geometric factor σ was substituted for $4/3\,\pi$ to extend the validity of the equations to cases when the activated nuclei do not grow into spheres. For example, if the nuclei form cubes, $\sigma = 8$.

In addition to the scaled time $\tau \equiv \eta t$, Avrami also introduced the concept of "isokinetic range", defined as a temperature range within which $G/\eta = \alpha$ is a constant independent of temperature. The basis for this concept is that the physics controlling the growth of a nucleus are similar to those governing its activation. Thus only 3 seemingly temperature-independent factors determine the volume fraction: τ, α, and $\bar{N}$. Since $t = \tau/\eta$, the temperature just shortens or extends the time by a factor $\eta(T)$. Figure 3 is an example of the progress of decomposition with time at different temperatures as predicted by Eq. 3.

Energy Balance

With the exception of the bulk nucleation and growth stage, and the deviation in the rate of regression due to the porous structure at the surface, the new model is similar to traditional surface decomposition models for propellants.[3] Assuming that surface regression proceeds at constant speed r, the conservation equations in 1-D can be simplified by changing to a moving frame of reference such that the interface between solid and gases remains fixed with time at x = 0. Neglecting changes in pressure and kinetic energy, the energy equation can be further reduced to $\rho C_p\, dT/dt = \partial/\partial x\, (k\; \partial T/\partial x) + \omega Q$, where $d/dt = \partial/\partial t + u\, \partial/\partial x$, ρ denotes the density, u the velocity, C_p the specific heat, T the temperature, k the coefficient of thermal conduction, ω the rate of reaction per unit volume, and Q the heat released per unit mass. Under steady state conditions, $\partial/\partial t = 0$ yields

$$\rho C_p u \frac{dT}{dx} = \frac{d}{dx}\left(k(x)\frac{dT}{dx}\right) + \omega Q \qquad (4)$$

Assuming that pyrolysis of the explosive produces an intermediate gaseous second phase that reacts later in the flame zone, then $k(x) = k_c [1 - V(x)]$, where k_c is the coefficient of thermal conduction in the pristine solid phase. That is because gases are significantly less thermally
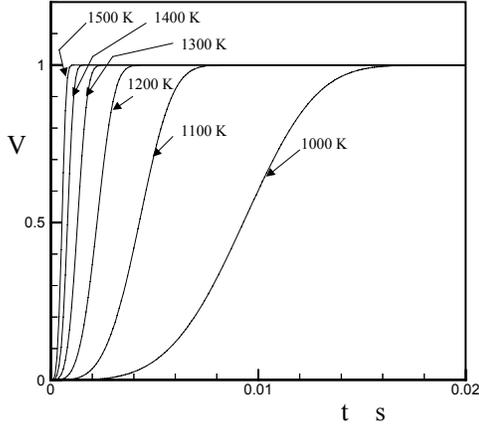
FIGURE 3. PROGRESS OF PYROLYSIS AT DIFFERENT TEMPERATURES

conductive than solids or liquids. At any location x, $(1-V)$ is equal to the fraction of the cross sectional area remaining in the solid phase. Assuming further that pyrolysis of the solid is energy neutral, neither endothermic nor exothermic, the solution of Eq. 4 for $-\infty < x < 0$, when $Q = 0$, $u = r$, and the boundary conditions $T(0) = T_s$ and $T(-\infty) = T_o$ are imposed is

$$\frac{T(x) - T_o}{T_s - T_o} = \exp\left(\frac{r}{\kappa}\int_0^x \frac{dx}{1 - V(x)}\right) \qquad (5)$$

T_s is the temperature at the surface, T_o the initial temperature, and the thermal diffusivity $\kappa \equiv k_c/\rho C_c$. If $V^* \equiv V(0)$ is the fraction of the second phase at the surface, the heat flux on the left side of $x = 0$

$$q_c = k_c\left(1 - V^*\right)\left(\frac{dT}{dx}\right)_{x = 0^-} = \rho\, r\, C_c\left(T_s - T_o\right) \qquad (6)$$

When applied to the gas phase extending from $x = 0$ to $+\infty$ and where all the chemical energy Q is assumed released, Eq. 1 yields a linear first order ODE of the flux $k_g\, dT/dx$, the solution of which at $x = 0$ is

$$q_g = k_g\left(\frac{dT}{dx}\right)_{x = 0^+} = \int_0^\infty \omega\, Q\, e^{-\frac{\rho_g u_g C_{pg}}{k_g}x}\, dx \qquad (7)$$

provided $\omega = \omega(x)$, instead of the more realistic dependence on temperature $\omega = \omega(T)$. A special case is obtained by assuming $\omega = $ constant $= \omega(T_g)$, where T_g is the adiabatic (maximum) flame temperature given by

$$T_g = T_o + \frac{Q}{C_{pg}} \qquad (8)$$

The subscript g is used to denote the properties of the gas phase. Similarly, ρ_g, u_g, C_{pg}, and k_g cannot be dependent on the temperature. However, such assumption is not unrealistic since in 1-D flows, steady state implies that the mass flux $\rho_g\, u_g = $ constant $= \rho\, r$ although each of ρ_g and u_g alone varies with x, and C_{pg}, k_g are not as sensitive to variations in temperature as $\omega(T)$ is. The coefficient of thermal conduction k_g does change with pressure p, but unlike detonations, the drop in pressure across deflagration waves is usually small. The pressure of the whole domain can significantly change, but that is a change with time, not x.

Assuming further that the flame is attached to the surface and is δ_f thick, and denoting by $\overline{\omega}$ the average rate of reaction, Eq. 4 can be integrated in closed form, yielding

$$q_g = k_g\left(\frac{dT}{dx}\right)_{x = 0^+} = \frac{k_g\overline{\omega}\, Q}{\rho\, r\, C_{pg}}\left[1 - e^{-\frac{\rho\, r\, C_{pg}}{k_g}\delta_f}\right] \qquad (9)$$

where q_g is the heat flux on the right side of $x = 0$ and ρr is already substituted for $\rho_g\, u_g$. For most gases, k_g is small, hence $\exp(-\rho r\, C_{pg}\,\delta_f / k_g) \ll 1$ and can be neglected in Eq. 9, thus rewritten as

$$q_g = k_g\left(\frac{dT}{dx}\right)_{x = 0^+} = \frac{k_g\overline{\omega}\, Q}{\rho\, r\, C_{pg}} \qquad (10)$$

Equating the heat fluxes on both sides of the interface, $x = 0^-$ and $x = 0^+$, we get

$$r = \sqrt{\frac{k_g\overline{\omega}\, Q}{\rho^2\, C_{pg}\, C_c\left(T_s - T_o\right)}} \qquad (11)$$

In Eq. 11 the dependence of surface regression on pressure is mainly introduced by $k_g(p)$ and $\overline{\omega}(p)$. The dependence of thermal conductivity k_g on pressure and temperature is tabulated for most gases in terms of their properties at the critical point. The rate of reaction in the gas phase $\overline{\omega}$ depends on the pressure via the concentration of the reactants. For example, if pyrolysis of the explosive generates two new species A and B that later react in the flame zone and produce C, then for the second order reaction $A + B = C$, $\overline{\omega} \equiv d[C]/dt = [A][B]Z_g\exp(-E_g/RT_g)$. In terms of the mass fractions Y_A and Y_B,

$$\overline{\omega} = Y_A Y_B \rho_g^2 Z_g\, e^{-\frac{E_g}{R\, T_g}}$$

$$= Y_A Y_B\left(\frac{p}{R_g\, T_g}\right)^2 Z_g\, e^{-\frac{E_g}{R\, T_g}} \qquad (12)$$

Since the flux of heat to the surface is mostly controlled by the maximum rate of energy release, $\omega(T_g)$ was already substituted for $\bar{\omega}$. For simplicity, the gas phase is assumed to obey the ideal equation of state $p_g = \rho_g R_g T_g$, but more complex equations can be used as well. The dependence of $\bar{\omega}$ on the pressure in this case is second order too.

In general, after substituting $k_g(p)$ and $\bar{\omega}(p)$, Eq. 11 can be written as

$$r = r(T_s, p) \tag{13}$$

Mass Balance

In traditional surface decomposition models pyrolysis of the solid is assumed to take place at the surface, i.e., at temperature T_s, hence in its simplest form,

$$r(T_s) = Z_{cs} e^{-\frac{E_{cs}}{R\,T_s}} \tag{14}$$

By eliminating T_s between Eqs. 13 and 14, we get $r(p)$, which can be usually fitted to an expression of the form ap^n. It is important to notice that in the resulting $r(p)$, r does not depend on p the same way $\sqrt{(\bar{\omega})}$ depends on p, because as implied by Eq. 14, T_s in Eq. 13 changes with r. Even if k_g is constant and $\bar{\omega} \sim p^2$, r does not change linearly with p.

SOLUTION PORCEDURE

Unlike traditional surface decomposition, in the new model pyrolysis starts deep in the solid. As the explosive material moves (rigid translation) towards the surface, the germ nuclei are activated at a rate equal to $\eta(T)$, then radially grow at a rate $G(T)$, in a manner similar to isothermal bulk decomposition, but here the temperature changes with location, i.e., $T = T(x)$.

Once $\alpha \equiv G/\eta$ and $\bar{N}$ are known, the scaled time τ^* needed to progress with pyrolysis up to a volume fraction V^* can be conveniently calculated from Eq. 3, independently of the temperature T hidden in $\tau \equiv \eta(T) t$. Specifically, the temperature path $T(x)$ affects the real time t, but not τ. If the temperature is constant, the real time $t^* = \tau^*/\eta(T)$, but since $T = T(x)$, t^* is evaluated from the integral equation

$$\int_0^{t^*} \frac{\eta(T)\,dt}{\tau^*} = \int_{-x^*}^0 \frac{\eta(T(x))\,dx}{\tau^*\,r} = 1 \tag{15}$$

where

$$\eta(T) = Z_c\, e^{-\frac{E_c}{RT}} \tag{16}$$

In the second integral of Eq. 15, dt has been replaced by dx/r, $t = t^*$ by $x = 0$, and $t = 0$ by $-x^*$, the depth of nucleation. The temperature $T(x)$ in the second integrand is given by Eq. 5, but it is unfortunately coupled to Eq. 3 via $[1-V(x)]$ in the denominator of the integrand.

The solution procedure is simplified by using the chain rule for differentiation

$$
\begin{aligned}
\frac{dT}{d\tau} &= \frac{dT}{dx}\frac{dx}{dt}\frac{dt}{d\tau} \\
&= \frac{r(T-T_o)}{\kappa(1-V)}\, r\, \frac{1}{\eta(T)}
\end{aligned}
\tag{17}
$$

The expression for dT/dx was obtained by integrating Eq. 4 ($Q = 0$) and applying the boundary condition $T = T_o$ and $dT/dx = 0$ at $x \to -\infty$. By separating the variables in Eq. 17 depending on T from those depending on τ and rearranging, we get

$$r^2 = \frac{\kappa \displaystyle\int_{T_o}^{T_s} \frac{\eta(T)}{T-T_o}\,dT}{\displaystyle\int_0^{\tau^*} \frac{1}{1-V(\tau)}\,d\tau} = f^n(T_s, V^*) \tag{18}$$

The apparent singularity in the numerator is not an issue because $\eta(T) \ll 1$ well before $T \to T_o$.

The next stage following bulk nucleation and growth is surface regression. But unlike simple regression described by Eq. 14, because the first stage yields to a porous structure, the rate will depend in addition on the porosity V^* at the surface. The surface exposed to the decomposition products is augmented by the total surface area of the spherical pores within a zone width equal to the incipient depth of penetration of these products.

Assuming all the germ nuclei have been already activated by the time the explosive material reaches the surface, and that all the pores are equal in size, the total surface area of the pores will be proportional to $\bar{N}^{1/3} V^{*2/3}$. Same for the incipient depth of penetration of the decomposition products proportional to the total cross sectional area of these pores. Thus a corrected version of Eq. 14 is written as

$$r\left(T_s, V^*\right) = \beta \ \overline{N}^{\frac{2}{3}} \ V^{*\frac{4}{3}} \ . \ Z_{cs} \ e^{-\frac{E_{cs}}{R\,T_s}} \qquad (19)$$

where β is an adjustable parameter.

The rate of surface regression r is an eigen value that is calculated by eliminating T_s and V^* between Eqs. 13, 18, and 19, yielding r(p).

EXAMPLE

For TNT ρ = 1.63 gm/cc and Q $\approx$ 1.0 kcal/gm. Assuming that α = 0.5, β = 5.0 x10^{-6} cm^2, Z_c = 5.0 x 10^5 cm/s, , Z_{cs} = 2.5 x 10^5 cm/s, $Z_g Y_A Y_B$ = 2.30 x 10^8 cm/s, $E_c = E_g$ = 17.0 Kcal/mole, E_{cs} = 9.70 Kcal/mole, $C_c = C_{pg}$ = 0.35 cal/gm K, R_g = 3 atm cc/gm K, κ = 0.01 cm^2/s, and k_g = 0.0001 cal/ cm s K, T_s, V^*, and r were calculated for three values of the initial density of germ nuclei, $\overline{N}$ = 10^3, 10^4, and 10^5 cc^{-1} for a range of pressures for 10 to 1000 atm.

Because 18 is an integral equation, eliminating T_s and V^* between Eqs. 11, 18, and 19 is done by iteration. At a given pressure p and surface porosity V^*, T_s is changed until the rate of regression r resulting from Eq. 11 is equal to the value predicted by Eq. 18. $\overline{\omega}$ in Eq. 11 is calculated using Eq. 12. η(T) and V(τ) in Eq. 18 are evaluated using Eqs. 16 and 3, respectively. Then V^* is changed until the rate r satisfying both Eqs. 11 and 18 is equal to the value of r resulting from Eq. 19.

Figures 4 to 6 show the variation in surface regression rate, temperature, and porosity at different pressures as the number density of germ
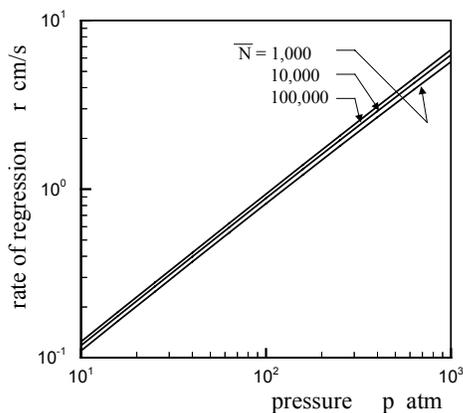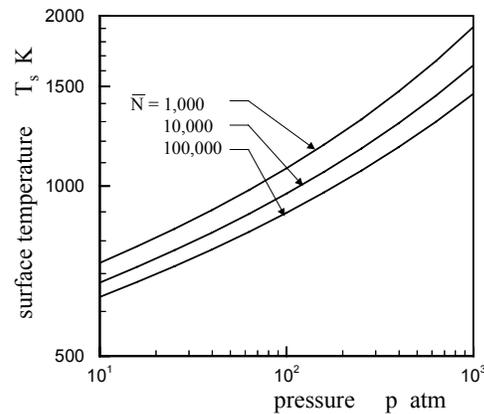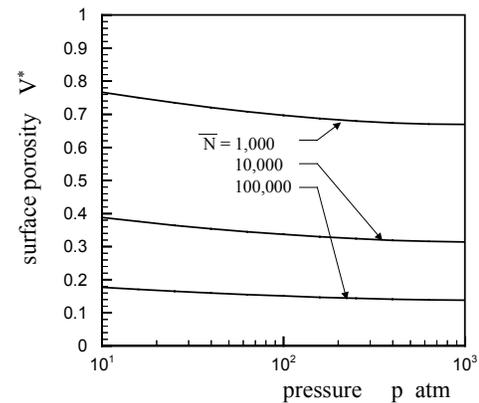

FIGURE 4. SURFACE REGRESSION

FIGURE 5. SURFACE TEMPERATURE

nuclei $\overline{N}$ is changed by one and two orders of magnitude. As illustrated in Fig. 4, the rate of regression r increases when $\overline{N}$ or p increases, but it is not sensitive to variations in $\overline{N}$. That is because the surface temperature increases as $\overline{N}$ decreases such as to compensate for the reduced number density of germ nuclei. As shown in Fig. 5, for every order of magnitude reduction in $\overline{N}$, the temperature at the surface increases by 50-100 K. The surface porosity on the other hand is significantly reduced as $\overline{N}$ is increased, as illustrated in Fig. 6.

ARL CLOSED-BOMB TESTS

The two-stage thick-pyrolysis zone surafce regression model described above takes into account the effects of nucleation and growth in the subsurface layer, but it still yields a regression rate that can be fitted to ap^n as illustrated in Fig. 4. On the other hand, the vivacity curve obtained in

ARL's closed bomb tests for melt cast solid TNT grains exhibits an anomalous behavior implying that a simple surface regression model with $r = ap^n$ is inadequate. Instead of being regressive, the burning of solid grains is more progressive than gun propellant grains containing a large number of perfs.[1]

One possible explanation is that the flame penetrated the tunnels interlaced throughout the TNT grains. When the sum of the external surface areas of all the grains is augmented by the additional surface area these tunnels expose, a traditional surface regression model with $r = ap^n$ may adequately describe the evolution of vivacity in the late time regime. The slow rate of

FIGURE 6. SURFACE POROSITY
decomposition in the early regime can be attributed to the delayed ignition of some of the grains. However, this does not explain how and why these tunnels were formed in the first place. In contrast, but yet recognizing that other mechanisms can be involved as well, the thick pyrolysis zone model can alone explain the observed behavior of melt cast TNT. However, it is important to examine first the validity of the steady state assumption.

The TNT grains used in ARL's tests were ½" long and ¼" in diameter. For steady surface burning, the onset of reaction is a few mm below the surface.[2] The depth of nucleation being of the same order of magnitude as the radius of the grain, surface decomposition cannot reach a steady state. An unsteady surface decomposition model is required to quantitatively replicate the evolution of vivacity obtained in ARL's closed bomb tests for melt cast TNT. Such models will be addressed in a future publication, but the objective of this work is to construct a simple model that can be used for larger, more practical systems, in which surface decomposition is bound to reach a steady state of regression. Nevertheless, based on the predictions of the steady state model, it is still possible to qualitatively explain the observed behavior of the melt cast TNT grains in these tests.

Black powder was used to ignite the TNT grains. Heat from the resulting products started raising the temperature of TNT, but as verified by the observed significant delays, even failure in igniting some of the grains, their surface did not start decomposing promptly. The delay can be attributed to the small density of germ nuclei in melt cast TNT. Thus, in the early regime, the rate of gas generation and in turn the rate of pressure

rise within the bomb was low because surface regression was slow to start. Before surface regression progressed to any significant degree, the bulk of the grain was already heated and pyrolysis was well on its way. This explains the extensive system of tunnels observed within the bulk of those TNT grains that were extinguished during the process of decomposition by rapid depressurization of the bomb. These grains were recovered in an evacuation chamber the walls of which were padded with a soft material. When combustion was not interrupted, subsequent decomposition in the tunnels already formed, combined with the decomposition taking place at the external surface of the grains then caused the quick rise in the rate of gas generation in the late time regime.

RADIATION AND MELTING

Two important mechanisms are conspicuously absent in the models presented in this paper – radiation and melting. A brief discussion of their effects is given next, but the details are postponed to a future publication.

Depending on the transparency of the cast TNT, radiation can penetrate and start pyrolysis (or photo-chemistry) deep beneath the surface. If TNT is optically thick and the coefficient of absorption uniform throughout, the radiation intensity will decay exponentially with depth. The resulting temperature profile will be similar to that produced by heat conduction. The analysis described above will be equally valid in explaining how the holes and tunnels observed in ARL's closed bomb tests were formed. If on the other hand the radiation energy is discretely absorbed at locations where microscopic defects or impurities already exist, the transformation to a second phase will likely become auto-catalytic. That is because the growth of the new phase will inevitably enhance radiation absorption at these locations. The formation of holes and tunnels is easier to explain in this case because the second phase is naturally limited to a number of discrete locations without having to invoke random nucleation as an underlying reason.

Because it melts at about 85°C, melting can also play a significant role in the chemical decomposition of TNT, whether it occurs on the surface or within the bulk of the material. But whereas a thin melted layer on the surface would react almost as quickly as it forms, if melting was substantial within the bulk of TNT, the holes and tunnels observed in ARL's closed bomb tests

would most likely have collapsed by the time the TNT was cold enough to solidify after burning was extinguished by rapid depressurization of the bomb.

CONCLUSIONS

A new model was developed to describe the steady surface decomposition of melt cast TNT. The model was built by combining the elements of a simple, traditional surface regression model with those of Avrami's nucleation and growth model successfully used to describe phase changes in solid materials, including the isothermal decomposition of energetic crystals. Unlike traditional surface decomposition, if thermal diffusion is faster than chemical decomposition, a relatively thick layer beneath the surface is steadily kept heated. This can be the result of an excessively large coefficient of thermal diffusivity, or because the number of germ nuclei from which the decomposition can grow is too small. The latter is likely to be the case in homogeneous materials, such as melt cast TNT.

Preliminary calculations carried out using the new model indicate that the rate of regression is slightly reduced when the density of the germ nuclei is one or two orders of magnitude smaller. That is because the surface temperature increases such as to compensate for the smaller number of germ nuclei at which pyrolysis can start. Because surface regression is slowed down, bulk nucleation and growth takes a more dominant role and the surface porosity is increased.

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