The mechanism of reaction of nitric acid and N_2O_4 with both aromatic and aliphatic compounds has been reviewed by Urbanski.[8] In the absence of N_2O_4, the only nitrating agent in nitric acid is NO_2^+ ion. It will attack the benzene ring of xylidine [Formula $C_6H_3.(CH_3)_2.NH_2$] at a position decided by the directive influence of the two $-CH_3$ and one $-NH_2$ groups already present in the molecule, to form a mononitro derivative. Further attack on the ring and formation of dinitro derivative along with production of heat will result in the cleavage of benzene ring, i.e., the ring after substitution will be unstable at the prevailing thermal environment. When N_2O_4 is present, there is the additional possibility of N_2O_4 directly attacking all the double bonds of the benzene ring making the whole system unstable. From the trend of the data it can be presumed that ignition delay with 100% N_2O_4 will be much less than that for 100% nitric acid, thus showing that attack by N_2O_4 is faster, taking less time to produce unstable compounds during the preignition phase.

In case of triethylamine [Formula: $(CH_3.CH_2)_3N$], the most probable position of attack by nitric acid is the nitrogen atom itself, because the three ethyl groups are directly linked to the electronegative element nitrogen and because of the electron releasing nature of the ethyl group, this nitrogen will be surrounded by a high electron density cloud thus facilitating the electrophillic attack. Once the NO_2 is attached to nitrogen, the three $-CH_2-$ of the ethyl groups will become active and will be susceptible to attack by nitric acid leading to the formation of unstable compounds and free radicals. When N_2O_4 is present, simultaneous attack on all ethyl groups and on the nitrogen atom is possible. The very considerable decrease in ignition delay in presence of small concentrations of N_2O_4 and the fact that larger concentrations of N_2O_4 do not produce further decrease in ignition delay, indicate that oxidative attack by N_2O_4 may be very vigorous and highly energetic. Small quantities of N_2O_4, therefore, are enough to start this attack, which can then be sustained by nitric acid alone under the prevalent thermal environment.

The chemical structure of UDMH [Formula: $NH_2.N(CH_3)_2$], is such that NO_2^+ ion can attack only the nitrogen atoms. The reactivity of methyl group with N_2O_4 is very low[9] and even when N_2O_4 is present, attack is mainly on nitrogen atoms. Hence, there is practically no difference in ignition delay with or without N_2O_4. The very small decrease in presence of N_2O_4 may be attributed to the slight increase in reactivity of $-CH_3$ in presence of N_2O_4.

From the preceding discussion, it is clear that the action of N_2O_4 depends on the chemical structure of the fuel, particularly on the positions of the various functional groups in its molecule. There are a number of other fuels which are hypergolic with nitric acid. It may be expected that because of its stronger action, presence of N_2O_4 in the acid will reduce the ignition delay in all cases. The quantitative effects, however, could be quite different, as shown in the present study and can best be determined only by experiment.

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Surface Reaction Model for Metal Particle Combustion

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Nomenclature

c, λ, D = heat capacity, thermal conductivity coefficient, binary diffusion coefficient
ρ, T = gas density and temperature
$\hat{T}$ = cT/L
L = specific heat of vaporization or sublimation
m = fuel consumption rate
M = $m/(4\pi r_s \rho D)$
r = radial distance
$\hat{r}$ = r/r_s
Q_1 = heat of reaction, per unit mass of fuel, to form gaseous products from gaseous reactants
Q_2 = heat of condensation for the products per unit mass of fuel
$\hat{Q}_1, \hat{Q}_2$ = $Q_1/L, Q_2/L$
Y = mass fraction
v_1 = stoichiometric mass ratio of oxidizer to fuel
O, s, ∞ = subscripts for oxidizer, particle surface, and infinity

Introduction

VARIOUS models have been postulated to describe the vapor-phase combustion of metal particles.[1,2] However under many situations this combustion mode does not always occur. For nonvolatile metals it is simply not favored. For volatile metals the absence of this burning mode maybe caused by the difficulty either in achieving ignition or in maintaining combustion in an ambient atmosphere of low temperature T_∞ and oxidizer concentration $Y_{O,\infty}$. Under these circumstances it has been observed that chemical reactions between fuel and oxidizer may take place on the particle surface.[3] We shall formulate in the following a surface reaction model in which the gas-phase diffusion of heat and species are the rate-limiting processes.

Formulation

The combustion process is assumed to be quasi-steady, isobaric, and spherically symmetric. Oxidizer gas diffuses from infinity to react stoichiometrically and completely with the fuel at the particle surface, producing either condensed oxides that reside on the surface or vaporized oxides that are transported to the ambient. The spherical particle, which can

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be in either the liquid or solid phase, is at a uniform temperature T_s. It is further assumed that the presence of condensed oxides on the particle surface in no way inhibits the successful consumption of the chemical reactants, implying these condensed oxides either exist in liquid phase such that they contract under surface tension and leave large part of surface exposed, or are sufficiently porous to the diffusion of the oxidizer gas if they are in the solid phase. Finally we assume that the thermal conductivity coefficients λ are constants, that the heat capacities c for the gas and condensed phases are constants and equal to each other, and that the Lewis number is unity.

The diffusion equation for the oxidizer gas can be written as

$$\nu_2 M Y_O - \hat{r}^2 dY_O/d\hat{r} = -\nu_1 M \tag{1}$$

where

$$\nu_2 = \sigma(1+\nu_1) - \nu_1 \tag{2}$$

and σ is equal to 1 or 0 when the oxides are formed in the gas phase and transported outward or in the condensed phase and reside on the surface.

Integrating Eq. (1) with the boundary condition that at $\hat{r} = 1$, $Y_O = 0$, we obtain

$$Y_O = (\nu_1/\nu_2)\{\exp[-\nu_2 M(\hat{r}^{-1} - 1)] - 1\} \tag{3}$$

Evaluating Eq. (3) at $Y_O(\infty) = Y_{O,\infty}$, the constant, nondimensionalized mass consumption rate can be found as

$$M = \nu_2{}^{-1} \ln[1 + (\nu_2/\nu_1) Y_{O,\infty}] \tag{4}$$

Putting Eq. (4) into Eq. (3), the radial distribution of the oxidizer gas can be expressed explicitly as

$$Y_O = (\nu_1/\nu_2)\{[1 + (\nu_2/\nu_1) Y_{O,\infty}]^{-(\hat{r}^{-1}-1)} - 1\} \tag{5}$$

The gas-phase energy equation can be written as

$$\nu_2 M(\hat{T} - \hat{T}_s) - \hat{r}^2 d\hat{T}/d\hat{r} = M\hat{Q} \tag{6}$$

where

$$\hat{Q} = \hat{Q}_1 + (1-\sigma)\hat{Q}_2 - 1 \tag{7}$$

Integrating Eq. (6) with the boundary condition that at $\hat{r} = 1$, $\hat{T} = \hat{T}_s$, and using Eq. (4), we obtain

$$\hat{T} = \hat{T}_s + (\hat{Q}/\nu_2)\{1 - [1 + (\nu_2/\nu_1) Y_{O,\infty}]^{-(\hat{r}^{-1}-1)}\} \tag{8}$$

The surface temperature $\hat{T}_s$ is found by evaluating Eq. (8) at $\hat{T}(\infty) = \hat{T}_\infty$

$$\hat{T}_s = \hat{T}_\infty + \hat{Q} Y_{O,\infty}/\nu_1 \tag{9}$$

Substituting Eq. (9) into Eq. (8), the radial distribution of temperature can be explicitly expressed as

$$\hat{T} = \hat{T}_\infty + (\hat{Q}/\nu_2)\{1 + (\nu_2/\nu_1) Y_{O,\infty}\}\{1 - [1 + (\nu_2/\nu_1) Y_{O,\infty}]^{-1/\hat{r}}\} \tag{10}$$

Equations (4, 5, 9 and 10) provide the complete solutions to the problem.

Discussions

The present model is expected to be applicable to an atmosphere satisfying the relation $\hat{T}_s < \hat{T}_b$, or

$$\hat{T}_b > \hat{T}_\infty + \hat{Q} Y_{O,\infty}/\nu_1 \tag{11}$$

where T_b is the boiling point of the metal. When the surface temperature reaches the boiling point, vaporization rate is greatly enhanced, therefore favoring vapor-phase combustion. It may be noted that the upper limit of this surface reaction model, as given by Eq. (11) with $T_b = T_s$, is just the flammability limit identified for the vapor-phase combustion model of Refs. 1 and 2.

The value σ assumes is to be determined in a consistent manner. If, for example, by assuming $\sigma = 1$ a value for T_s is obtained which is lower than the oxides' boiling point, then $\sigma = 0$ should be used. It is expected, however, that a unique value of σ exists for a given pair of reactants.

Finally we note that since the rate of supply of the oxidizer is specified independent of T_∞, and since the oxidizer reacts stoichiometrically with the fuel, the fuel burning rate M is found to be independent of T_∞.

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Inclusion of Transverse Shear Deformation in Finite Element Displacement Formulations

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INCLUDING transverse shear deformation in finite-element formulations is essential if the elements are used to model such components as thick plates, short beams, or sandwich panels consisting of soft cores and stiff face sheets. In a recent publication, Irons and Razzaque[1] presented an artificial, and in their own words "theoretically inadequate," method to include transverse shear in a plate-bending finite element as an afterthought. The stated justification for their somewhat complicated procedure is the idea put forth by Severn[2] that the usual finite-element technique of directly minimizing the strain energy is not applicable when transverse shear deformation is included.

It is the purpose of the present Note to demonstrate that a straightforward energy minimization does in fact yield the correct finite-element behavior when transverse shear effects are included and that additional finite-element grid point degrees of freedom are not required to treat these effects. Since the derivation in Ref. 1 have their basis in Ref. 2, many of the comments herein are directed at Ref. 2.

The stiffness matrix for a beam element with transverse shear deformation will be derived in this section in a similar fashion to Ref. 2 to illustrate the correct approach for a simple and familiar component. The general approach to plate elements is described in Refs. 3 and 4.

The normal displacement w in the element is the same as that used in Ref. 2, thus

$$w = a_0 + a_1 x + a_2 x^2 + a_3 x^3 \tag{1}$$

The relation between transverse shear strain γ, w', and θ is, from Fig. 1

$$w' = \theta + \gamma \tag{2}$$

Transverse shear strain γ, consistent with the cubic polynomial for w, is assumed to be independent of x, i.e.,

$$\gamma = b_0 \tag{3}$$

Moment equilibrium of an infinitesimal beam section yields

$$dM/dx - V = 0 \tag{4}$$

Note that the introduction of equilibrium equations in the formulation is formally equivalent to a constraint, since a dis-

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