JOURNAL OF PROPULSION AND POWER
Vol. 11, No. 6, November–December 1995

Ignition of Boron Particles Coated by a Thin Titanium Film

Valery Rosenband,* Benveniste Natan,† and Alon Gany‡
Technion—Israel Institute of Technology, Haifa 32000, Israel

A theoretical model for the ignition of titanium-coated boron particles in dry air has been developed. In general, the results indicate reduction in ignition time due to a high heating rate of the particle resulting from the reactions of titanium with both boron and oxygen and the deterioration of the protective properties of the coating layers due to mechanical stresses. However, ignition strongly depends on the titanium coating thickness and the ambient temperature.

Nomenclature

a = constant described in Eq. (19)
c_p = specific heat
$\bar{c}_p$ = mean specific heat of the composite particle
D_{ij} = diffusivity
f, φ, ψ = fractions of titanium, titanium oxide, and boron in the liquid phases, respectively
K = mass transfer coefficient
$\bar{K}$ = effective mass transfer coefficient
(l) = liquid
M_i = molecular weight of the i species
Nu, Nu_D = heat and mass transfer Nusselt numbers
p = pressure
p_i^0 = vapor pressure of the i species
p_i^{0*} = equilibrium pressure of vapors above flat surface
$\dot{Q}_{G,i}$ = heating rate of the particle due to the generation of the i species
$\dot{Q}_S$ = heating rate of the particle by convection and radiation
$\dot{Q}_{V,i}$ = cooling rate of the particle due to vaporization of the i species
$q_{\mathrm{B_2O_3}}$ = heat release of the reaction $2\mathrm{B} + 3/2\mathrm{O_2} \rightarrow \mathrm{B_2O_3}(l)$
$q_{\mathrm{TiB_2}}$ = heat release of the reaction $\mathrm{Ti}(s) + 2\mathrm{B}(s) \rightarrow \mathrm{TiB_2}(s)$
$q_{\mathrm{TiO_2}(s)}$ = heat release of the reaction $\mathrm{Ti}(s) + \mathrm{O_2} \rightarrow \mathrm{TiO_2}(s)$
R = current radius of the composite particle
$R_{G,i}$ = mass generation rate per unit area of the i species
$R_{V,i}$ = mass evaporation rate per unit area of the i species
R_u = universal gas constant
R_0 = initial radius of the composite particle
r_0 = initial radius of boron particle
r_1, r_2 = radii of a hollow sphere
(s) = solid
T = particle temperature
T_{RAD} = surrounding radiation temperature
T_0 = ambient gas temperature
x = the thickness of the evaporated layer of $\mathrm{TiO_2}$
y = the thickness of the evaporated layer of $\mathrm{B_2O_3}$
α = evaporation coefficient of the liquid titanium oxide
β_i = volume fraction of the i species in coated particles
$\gamma_{\mathrm{TiO_2}}$ = surface tension coefficient of the liquid titanium oxide
Δ = interference
$\Delta H_{m,i}$ = heat of fusion of the i species
$\Delta H_{v,i}$ = heat of vaporization of the i species
δ_i = thickness of the layer of the i species
δ_0 = initial thickness of titanium film
ε = particle emissivity
$\varepsilon_{\mathrm{por}}$ = porosity of solid layer
$\kappa_{\mathrm{B_{23}O}}$ = ratio of the volume of boron-oxide to that of boron consumed in its formation
$\kappa_{\mathrm{TiO_2}}$, $\kappa_{\mathrm{TiB_2}}$ = ratios of the volumes of the titanium-oxide and diboride to those of titanium consumed in their formation, respectively
$\kappa'_{\mathrm{TiB_2}}$ = ratio of the volume of titanium diboride to the boron consumed in its formation
λ = parameter in Eq. (30)
μ = Poisson ratio
ν_i = Hertz–Knudsen impingement factor of the i species
ρ = density
$\bar{\rho}$ = mean density of the composite particle
σ = Stefan–Boltzmann constant
$\sigma_{\mathrm{eq},i}$ = equivalent stress of the i species
$\sigma_{\mathrm{lim},i}$ = ultimate strength of the i species
σ_r, σ_τ, σ_φ = stress tensor components
τ = tortuosity of pores

Introduction

THE use of boron as an additive in the polymeric fuel of solid fuel ramjets and ducted rockets, or as a major ingredient in slurry fuels, may provide a significant increase in the energetic performance of the motor due to the high heat of combustion of boron in air. However, the ignition of boron particles in oxidizing environments is very difficult because of the boron-oxide layer that covers the particles and slows down the oxidation reaction. As a result, boron particles often exhibit poor combustion efficiency.[1,2]

The combination of boron with titanium that reacts exothermically has been considered as a possible variant for boron combustion intensification in rocket and ramjet engines.[3,4] The coating of the boron particle with a thin layer of titanium may contribute in speeding-up the ignition process by two ways:

1) The heating rate of the particle increases due to the reactions of titanium with both boron and oxygen.

Received Feb. 25, 1994; revision received Nov. 11, 1994; accepted for publication Nov. 14, 1994.

*Research Fellow, Faculty of Aerospace Engineering.

†Research and Teaching Associate, Faculty of Aerospace Engineering. Senior Member AIAA.

‡Associate Professor, Faculty of Aerospace Engineering. Associate Fellow AIAA.

2) Mechanical stresses that develop in the TiO_2 and TiB_2 layers may cause their disruption, transforming them to nonprotective films for oxidation of titanium or boron.

A similar situation was studied by King.[3] However, in his work the B-Ti reaction was not considered. Moreover, King assumed an initial boron-oxide layer at the B-Ti interface. Such a layer should not exist in titanium-coated boron particles.

The objective of this research is to model and investigate the ignition processes of a boron particle initially covered by a thin titanium film. In principle, the model developed can be applicable for the ignition of various metal particles, initially plated by other materials, in a hot oxidizing medium.

Theoretical Analysis

A schematic description of the model is presented in Fig. 1. For the problem considered, the following assumptions are made:

1) Uniform temperature within the particle (for typical heating rates of the order of 5 × 10^5 K/s, the temperature difference between the surface and the center of a 10-μm particle will be only about 4 deg).

2) Interaction of the titanium with oxygen takes place as a result of diffusion of oxygen through the TiO_2 layer, while that of titanium with boron results from diffusion of boron through the TiB_2 layer.[5,6]

3) Oxygen and boron do not dissolve in titanium. They react completely at the interface with Ti generating new compounds, TiO_2 and TiB_2, respectively. As a consequence, oxygen begins to react with boron only after complete consumption of the titanium. Oxygen diffuses through the TiO_2 and TiB_2 layers, forming B_2O_3 upon encountering the boron. The present model is based on King's model and it is assumed that when the B_2O_3 layer is formed, the reaction between boron and oxygen proceeds at the B/B_2O_3 interface.[7,9] According to Glassman et al.,[10] boron diffuses through the liquid B_2O_3 and the reaction between oxygen and boron occurs at the outer edge of the boron-oxide layer. However, since in the present case, the B_2O_3 formation is mainly limited by the diffusion of oxygen through the TiO_2 and TiB_2 layers, the location of the B/O_2 reaction becomes less significant.

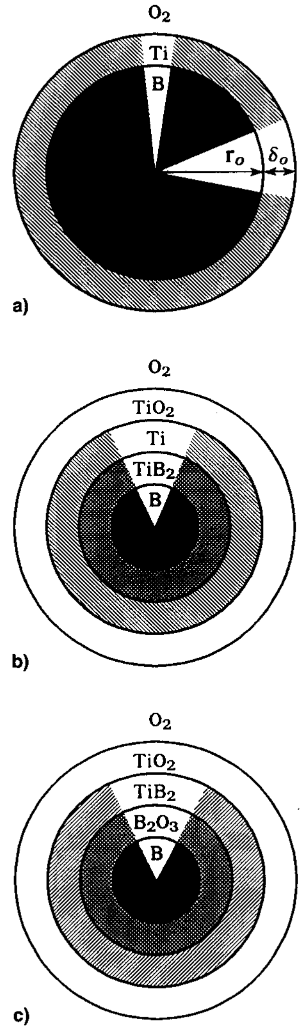

Fig. 1 Schematic description of the model: a) initial situation, b) first oxidation stage, and c) second oxidation stage.

4) Reaction between TiB_2 and O_2 is not considered. In general, the oxidation rate of TiB_2 is extremely low. Moreover, since the rate of generation of TiB_2 is very low, the resulting layer of TiB_2 is rather thin (~0.01 μm) and the heat that may be produced by the TiB_2/O_2 reaction is negligible.

5) The TiO_2 and TiB_2 films are assumed to be compact and protective, and so the rate of the process is limited by the diffusion of the reactants across them.

6) It is assumed that in the initial stage, the boron particle is coated by a thin titanium film and no B_2O_3 exists between boron and titanium. In general, boron particles are covered with a thin boron-oxide layer due to the immediate reaction of boron with ambient air. However, a new process to produce pure titanium-coated boron particles has been developed by AeroChem Research Laboratories.[11] The process involves separate reactions of sodium with boron trichloride and titanium tetrachloride, and finally, titanium gas coats the boron particles.

7) It is assumed that when mechanical stresses exceed the ultimate strength of the TiO_2 and TiB_2 films, these films are disrupted. As a result, the diffusion velocities across the films increase sharply.

Under these assumptions, the particle ignition process occurs in two successive stages. During the first stage (Fig. 1b) the titanium layer is consumed in parallel by the reactions with oxygen and boron that take place simultaneously. At the second stage of the process (Fig. 1c), after complete consumption of the titanium, oxidation of the boron begins. The thermodynamical data of the ingredients involved in the ignition process are presented in Table 1. All the data presented in this article are in SI units.

Within a temperature range of up to 3000 K the following processes are considered: melting and vaporization of B_2O_3; melting of B, Ti, and TiO_2; and vaporization of TiO_2. The polymorphic transfer $Ti(\alpha) \rightarrow Ti(\beta)$ at 1155 K is neglected, since the heating effect of this transfer is very small (about 4 MJ/kg-mol ≈ 0.08 MJ/kg).

Heating or cooling of the particle results from convective or radiative interactions with the surroundings. Additional heating contribution is due to the exothermic reactions between titanium and oxygen, titanium and boron, as well as boron with oxygen. On the other hand, the endothermic evaporation processes of titanium-oxide and boron-oxide extract energy from the particle.

The heating rates of the particle due to the various reactions are described by the following relations:

Titanium with oxygen ($Ti + O_2 \rightarrow TiO_2$):

$$\dot{Q}_{G,TiO_2} = q_{TiO_2} \cdot R_{G,TiO_2} \cdot 4\pi(R - \delta_{TiO_2})^2 \tag{1}$$

Titanium with boron ($Ti + 2B \rightarrow TiB_2$):

$$\dot{Q}_{G,TiB_2} = q_{TiB_2} \cdot R_{G,TiB_2} \cdot 4\pi(r_0 + \delta_{TiB_2})^2 \tag{2}$$

Boron with oxygen ($2B + 3/2O_2 \rightarrow B_2O_3$):

$$\dot{Q}_{G,B_2O_3} = q_{B_2O_3} \cdot R_{G,B_2O_3} \cdot 4\pi(r_0 - \delta_{B_2O_3} - y)^2 \tag{3}$$

Table 1 Some thermochemical data of the components involved in the B/Ti/O_2 system

Substances	T_m, K	T_b, K	Molecular weight	ΔH^0_m, MJ/kg	ΔH^0_v, MJ/kg
B	2450	3931	10.8	2.09	——
Ti	1933	3591	47.9	0.39	8.88
TiB_2	3193	——	69.5	1.44	——
TiO_2	2143	3200	79.90	0.84	7.53
B_2O_3	723	2316	69.78	0.32	5.26

The cooling rates of the particle due to vaporization of the oxides are given by

$$\dot{Q}_{V,\mathrm{TiO_2}} = \Delta H_{v,\mathrm{TiO_2}} \cdot R_{V,\mathrm{TiO_2}} \cdot 4\pi R^2 \tag{4}$$

$$\dot{Q}_{V,\mathrm{B_2O_3}} = \Delta H_{v,\mathrm{B_2O_3}} \cdot R_{V,\mathrm{B_2O_3}} \cdot 4\pi (r_0 - y)^2 \tag{5}$$

The heating rate of the particle by convection and radiation from the surroundings is given by

$$\dot{Q}_S = [(kNu/2R)(T_0 - T) + \varepsilon\sigma(T^4_{\mathrm{RAD}} - T^4)]4\pi R^2 \tag{6}$$

During the particle ignition stage, the surrounding gas contains only small amounts of three (or more) atom molecules (H_2O, B_2O_3, and TiO_2). Since diatomic molecules (O_2 and N_2) have no emissivity and absorptivity, they are, in fact, transparent for radiation. Therefore, in Eq. (6) the radiative heat exchange of the particle with the surrounding gas is not considered, and only radiation exchange with external walls is taken into account.

The total heating rate of the particle is given by

$$\dot{Q}_T = a(\dot{Q}_{G,\mathrm{TiO_2}} + \dot{Q}_{G,\mathrm{TiB_2}}) + (1 - a)(\dot{Q}_{G,\mathrm{B_2O_3}} - \dot{Q}_{V,\mathrm{B_2O_3}}) - \dot{Q}_{V,\mathrm{TiO_2}} + \dot{Q}_S \tag{7}$$

where $a = 1$ represents the first stage of the ignition process and $a = 0$ the second one.

The heat balance equation for the particle at various temperatures and states are described by

For $T < 1933$ K, $1933 \text{ K} < T < 2143$ K, $2143 \text{ K} < T < 2450$ K and $2450 \text{ K} < T < 3000$ K

$$\frac{4}{3}\pi R^3 \bar{\rho} \bar{c}_p \frac{dT}{dt} = \dot{Q}_T \tag{8}$$

For $T = 1933$ K

$$0 \le f \le 1, \quad \varphi = \psi = 0 \quad \text{if} \quad a = 1$$

$$f = 1, \quad \varphi = \psi = 0 \quad \text{if} \quad a = 0$$

$$\frac{4\pi}{3}[(R - \delta_{\mathrm{TiO_2}})^3 - (r_0 + \delta_{\mathrm{TiB_2}})^3]\rho_{\mathrm{Ti}}\Delta H_{m,\mathrm{Ti}} \cdot \frac{df}{dt} = \dot{Q}_T \tag{9}$$

For $T = 2143$ K

$$f = 1, \quad 0 \le \varphi \le 1, \quad \psi = 0$$

$$\frac{4\pi}{3}[R^3 - (R - \delta_{\mathrm{TiO_2}})^3]\rho_{\mathrm{TiO_2}}\Delta H_{m,\mathrm{TiO_2}} \cdot \frac{d\varphi}{dt} = \dot{Q}_T \tag{10}$$

For $T = 2450$ K

$$f = \varphi = 1, \quad 0 \le \psi \le 1$$

$$4\pi \left[\frac{r_0^3}{3} - \frac{r_0^2 \delta_{\mathrm{TiB_2}}}{\kappa'_{\mathrm{TiB_2}}} - \frac{(r_0 - \delta_{\mathrm{B_2O_3}} - y)^2}{\kappa_{\mathrm{B_2O_3}}}(\delta_{\mathrm{B_2O_3}} + y)\right] \cdot \rho_{\mathrm{B}} \cdot \Delta H_{m,\mathrm{B}} \frac{d\psi}{dt} = \dot{Q}_T \tag{11}$$

where

$$R_0 = r_0 + \delta_0 \tag{12}$$

$$R = R_0 - x \tag{13}$$

The rates of change of the thickness of the various layers are described by

$$\frac{d\delta_{\mathrm{TiO_2}}}{dt} = \frac{(aR_{G,\mathrm{TiO_2}} - R_{V,\mathrm{TiO_2}})}{\rho_{\mathrm{TiO_2}}} \tag{14}$$

$$\frac{d\delta_{\mathrm{TiB_2}}}{dt} = \frac{aR_{G,\mathrm{TiB_2}}}{\rho_{\mathrm{TiB_2}}} \tag{15}$$

$$\frac{d\delta_{\mathrm{B_2O_3}}}{dt} = (1 - a)\frac{(R_{G,\mathrm{B_2O_3}} - R_{V,\mathrm{B_2O_3}})}{\rho_{\mathrm{B_2O_3}}} \tag{16}$$

In order to calculate the thickness of the TiO_2 (and the B_2O_3) layers, the mass of the gaseous oxides that has been removed due to vaporization has to be considered. An imaginary layer of thickness x (and y for B_2O_3) is defined for this purpose, as the mass rate of vaporization divided by the liquid density since the remaining layer is in the liquid phase:

$$\frac{dx}{dt} = \frac{R_{V,\mathrm{TiO_2}}}{\rho_{\mathrm{TiO_2}}} \tag{17}$$

$$\frac{dy}{dt} = (1 - a)\frac{R_{V,\mathrm{B_2O_3}}}{\rho_{\mathrm{B_2O_3}}} \tag{18}$$

The coefficient a, which indicates whether titanium has been consumed, is calculated by

$$a = \begin{cases} 1 & \text{if} \quad \dfrac{(\delta_{\mathrm{TiO_2}} + x)}{\kappa_{\mathrm{TiO_2}}} + \dfrac{\delta_{\mathrm{TiB_2}}}{\kappa_{\mathrm{TiB_2}}} < \delta_0 \\ 0 & \text{if} \quad \dfrac{(\delta_{\mathrm{TiO_2}} + x)}{\kappa_{\mathrm{TiO_2}}} + \dfrac{\delta_{\mathrm{TiB_2}}}{\kappa_{\mathrm{TiB_2}}} \ge \delta_0 \end{cases} \tag{19}$$

$$\bar{\rho} = \sum \rho_i \beta_i \tag{20}$$

$$\bar{c}_p = \sum \frac{\rho_i}{\bar{\rho}} c_{p_i} \beta_i \tag{21}$$

$$\beta_{\mathrm{TiO_2}} = 3(R_0 - \delta_{\mathrm{TiO_2}} - x)^2 \delta_{\mathrm{TiO_2}} / R^3 \tag{22}$$

$$\beta_{\mathrm{TiB_2}} = 3r_0^2 \delta_{\mathrm{TiB_2}} / R^3 \tag{23}$$

$$\beta_{\mathrm{Ti}} = 3(r_0 + \delta_{\mathrm{TiB_2}})^2 \left[\delta_0 - \frac{(\delta_{\mathrm{TiO_2}} + x)}{\kappa_{\mathrm{TiO_2}}} - \frac{\delta_{\mathrm{TiB_2}}}{\kappa_{\mathrm{TiB_2}}}\right] \Big/ R^3 \tag{24}$$

$$\beta_{\mathrm{B_2O_3}} = 3(r_0 - \delta_{\mathrm{B_2O_3}} - y)^2 \delta_{\mathrm{B_2O_3}} / R^3 \tag{25}$$

$$\beta_{\mathrm{B}} = 3\left[\frac{r_0^3}{3} - \frac{r_0^2 \delta_{\mathrm{TiB_2}}}{\kappa'_{\mathrm{TiB_2}}} - \frac{(r_0 - \delta_{\mathrm{B_2O_3}} - y)^2}{\kappa_{\mathrm{B_2O_3}}} \delta_{\mathrm{B_2O_3}}\right] \Big/ R^3 \tag{26}$$

Eqs. (20) and (21) express the average value of the density and specific heat of the composite particle based on the additive contribution of the different components according to their mass fractions.

The generated flux of TiO_2 depends on the rate of diffusion of O_2 through the solid or liquid TiO_2 film, and it is described by

$$R_{G,\mathrm{TiO_2}} = \frac{M_{\mathrm{TiO_2}} D_{\mathrm{O_2,TiO_2}} p_{\mathrm{O_2}}}{R_u T_0 \delta_{\mathrm{TiO_2}}} \tag{27}$$

For temperatures below the melting point of TiO_2, the TiO_2 film may be disrupted due to mechanical stresses. In such a case, a new film is produced between the old one and the titanium layer, and the thickness of this new film is used in Eq. (27) for the generation rate calculation.

The vaporization of TiO_2 is not very essential, since the boiling temperature of titanium oxide is about 3200 K. Nevertheless, the mass flux of vaporized TiO_2 is given by

$$\begin{aligned} R_{V,\mathrm{TiO_2}} &= M_{\mathrm{TiO_2}} \alpha \nu_{\mathrm{TiO_2}} (p^0_{\mathrm{TiO_2}} - p_{\mathrm{TiO_2,surf}}) \\ &= M_{\mathrm{TiO_2}} K_{\mathrm{TiO_2}} (p_{\mathrm{TiO_2,surf}} - p_{\mathrm{TiO_2},\infty}) \end{aligned} \tag{28}$$

If $K >> \alpha\nu$, then vapors of titanium oxide are very quickly lead away from the surface to the surrounding gas, and vaporization proceeds in a kinetic regime. On the contrary, if $K << \alpha\nu$, then vapor diffusion is the slower process and will determine the vaporization rate.

The Hertz–Knudsen impingement factor ν_i is given by

$$\nu_i = (2\pi R_u T M_i)^{-1/2} \tag{29}$$

The mass transfer coefficient K_i is given by

$$K_i = \frac{D_{i,\mathrm{N_2}}}{R_u T \lambda_i} \tag{30}$$

where diffusion through air can be represented by $D_{i,\mathrm{N_2}}$, and where $\lambda_{\mathrm{TiO_2}}$ in this case is

$$\lambda_{\mathrm{TiO_2}} = 2R/Nu_D \tag{31}$$

Since the TiO_2 vaporization process may proceed both through diffusion- and kinetic-controlled regimes, the following expression for $R_{\mathrm{TiO_2}}$ is obtained:

$$R_{V,\mathrm{TiO_2}} = \frac{M_{\mathrm{TiO_2}} \alpha \nu p^{0*}_{\mathrm{TiO_2}}}{[1 + (\alpha\nu/K)]} \exp \frac{2\gamma_{\mathrm{TiO_2}} M_{\mathrm{TiO_2}}}{\rho_{\mathrm{TiO_2}} R_u T R} \tag{32}$$

taking into account additional Laplace pressure associated with the surface curvature of the particle. Here, the vapor pressure of TiO_2, namely, $p^{0*}_{\mathrm{TiO_2}}$, is determined by the equation[12]:

$$\log p^{0*}_{\mathrm{TiO_2}} = 14.376 - (30{,}060/T) \tag{33}$$

The rate of generation of TiB_2 (per unit area) is controlled by the diffusion rate of boron through TiB_2, hence,

$$R_{G,\mathrm{TiB_2}} = \frac{M_{\mathrm{TiB_2}}}{2M_{\mathrm{B}}} \frac{\rho_{\mathrm{B}}}{\rho_{\mathrm{TiB_2}}} \frac{D_{\mathrm{B,TiB_2}}}{\delta_{\mathrm{TiB_2}}} \tag{34}$$

At the second stage of the ignition process, when the titanium layer has been consumed, oxygen diffuses through the TiO_2 (liquid or solid), TiB_2 and B_2O_3 layers to react with boron. These layers are considered as series resistances, and the mass flux of generated B_2O_3 is given by

$$R_{G,\mathrm{B_2O_3}} = \frac{2}{3} M_{\mathrm{B_2O_3}} \frac{p_{\mathrm{O_2}}}{R_u T_0} \cdot \left(\frac{\delta_{\mathrm{TiO_2}}}{D_{\mathrm{O_2,TiO_2}}} + \frac{\delta_{\mathrm{TiB_2}}}{D_{\mathrm{O_2,TiB_2}}} + \frac{\delta_{\mathrm{B_2O_3}}}{D_{\mathrm{O_2,B_2O_3}}} \right)^{-1} \tag{35}$$

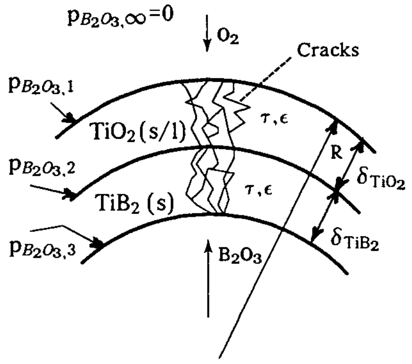

Fig. 2 Vaporization mechanism of B_2O_3.

As regards the removal of B_2O_3, the kinetic and diffusion limitations in the TiB_2 and TiO_2 layers as well as in the freestream are considered as series resistances (Fig. 2), and the mass flux of vaporized B_2O_3 is described by

$$\begin{aligned} R_{V,\mathrm{B_2O_3}} &= M_{\mathrm{B_2O_3}} \alpha \nu_{\mathrm{B_2O_3}} (p^0_{\mathrm{B_2O_3}} - p_{\mathrm{B_2O_3,3}}) \\ &= K_2 (p_{\mathrm{B_2O_3,3}} - p_{\mathrm{B_2O_3,2}}) \\ &= K_1 (p_{\mathrm{B_2O_3,2}} - p_{\mathrm{B_2O_3,1}}) \\ &= K_0 (p_{\mathrm{B_2O_3,1}} - p_{\mathrm{B_2O_3},\infty}) \end{aligned} \tag{36}$$

The partial pressures of the boron-oxide at the interfaces of the various layers are shown in Fig. 2, and K_i is calculated by Eq. (30). The relations described in Eq. (36) produce the solution for $R_{V,\mathrm{B_2O_3}}$, assuming that $p_{\mathrm{B_2O_3}}$ in the freestream is negligible:

$$R_{V,\mathrm{B_2O_3}} = \frac{M_{\mathrm{B_2O_3}} \alpha \nu_{\mathrm{B_2O_3}} p^0_{\mathrm{B_2O_3}}}{1 + (\alpha \nu_{\mathrm{B_2O_3}}/\bar{K})} \tag{37}$$

where $\bar{K}$ is given by

$$\bar{K} = \left(\frac{1}{K_0} + \frac{1}{K_1} + \frac{1}{K_2} \right)^{-1} = \frac{D_{\mathrm{O_2,B_2O_3}}}{R_u T} (\lambda_0 + \lambda_1 + \lambda_2)^{-1} \tag{38}$$

and the parameters λ are

$$\lambda_0 = 2R/Nu_D \tag{39}$$

$$\lambda_1(s) = \delta_{\mathrm{TiO_2}} \tau / \varepsilon_{\mathrm{por}} \tag{40}$$

$$\lambda_2(l) = \delta_{\mathrm{TiO_2}} \cdot D_{\mathrm{O_2,B_2O_3}} / D_{\mathrm{B_2O_3,TiO_2}} \tag{41}$$

$$\lambda_2(s) = \delta_{\mathrm{TiB_2}} \tau / \varepsilon_{\mathrm{por}} \tag{42}$$

τ is the tortuosity of pores ($\tau = 3$), and $\varepsilon_{\mathrm{por}}$ is the porosity of the solid layer ($\varepsilon_{\mathrm{por}} = 0.1$).

The boron-oxide vapor pressure is given by[9]

$$p^0_{\mathrm{B_2O_3}} = 1.53 \times 10^{13} \exp(-44{,}000/T) \tag{43}$$

The diffusivities are calculated by employing various models from the literature. For the calculation of the diffusion of a gas through a liquid layer the Wilke correlation[13] is employed, and the following formulas are used:

$$D_{\mathrm{O_2,TiO_2}}(l) = 1.9 \times 10^{-10} T \exp(-1.38 \times 10^8/R_u T) \tag{44}$$

$$D_{\mathrm{O_2,B_2O_3}}(l) = 9.7 \times 10^{-10} T \exp(-1.5 \times 10^8/R_u T) \tag{45}$$

$$D_{B_2O_3,TiO_2}(l) = 1.24 \times 10^{-10} T \exp(-1.36 \times 10^8/R_u T) \quad (46)$$

For the calculation of the diffusivity of a gas through a gas the solid-bodies model[14] is employed, and the various formulas are

$$D_{TiO_2,N_2} = 2.89 \times 10^{-4} T^{3/2}/p \quad (47)$$

$$D_{B_2O_3,N_2} = 1.96 \times 10^{-4} T^{3/2}/p \quad (48)$$

The diffusivities of a gas through a solid are given by[15-17]

$$D_{O_2,TiO_2}(s) = 2 \times 10^{-7} \exp(-2.5 \times 10^8/R_u T) \quad (49)$$

$$D_{O_2,TiB_2}(s) = 4.8 \times 10^{-5} \exp(-3.83 \times 10^8/R_u T) \quad (50)$$

The diffusivity of B through $TiB_2(s)$ is given by[18]

$$D_{B,TiB_2}(s) = 7 \times 10^{-4} \exp(-3.99 \times 10^8/R_u T) \quad (51)$$

During the heating process of the particle, mechanical stresses appear in the interfaces and may cause disruption of the various layers. The main reasons for the appearance of these stresses are 1) the difference in thermal expansion coefficients of the phases, 2) the difference in bulk densities of the initial substances and final reaction products, and 3) the change in density of the material upon melting.

The mechanical stresses in the present multilayer system are calculated by employing the thermal stress model in a multilayer composite particle.[19] According to this model the stress applied on the k layer of a multilayer particle is given by

$$\begin{aligned}\sigma_{t,k} = & -\sum_{i=1}^{k-1}\left(\frac{2\Delta_i/R}{\frac{R}{\delta_i}\frac{1-\mu_i}{E_i}+\frac{R}{\delta_{i+1}}\frac{1-\mu_{i+1}}{E_{i+1}}}\right) \\ & +\sum_{i=k}^{n-1}\left[\frac{\Delta_i/R}{\sum_{j=k}^{i}\left(\frac{\delta_j}{\delta_i}\frac{1-\mu_i}{E_i}+\frac{\delta_j}{\delta_{i+1}}\frac{1-\mu_{i+1}}{E_{i+1}}\right)}\right] \\ & +\frac{\Delta_n/R}{\sum_{j=1}^{n}\left(\frac{\delta_j}{\delta_n}\frac{1-\mu_n}{E_n}+\frac{2\delta_i}{R}\frac{1-2\mu_c}{E_c}\right)} \end{aligned} \quad (52)$$

where Δ is the interference between two successive layers.

When the stress exceeds its limiting value, the solid layer is disrupted.

Ignition of the particle is achieved when all the following criteria are fulfilled: 1) titanium has been completely consumed, 2) boron-oxide is generated, 3) boron-oxide evaporates at a rate that exceeds its generation rate, and 4) boron-oxide thickness becomes zero. If the particle reaches the boiling temperature of B_2O_3 (2450 K), the pressure buildup inside the layers causes a complete disruptive blowoff of the protective layers and ignition occurs.

Numerical Solution

The problem consists of 10 ordinary differential equations: one equation for the particle temperature [Eq. (8)]; three equations for the Ti, TiO_2, and B_2O_3 molten fractions [Eqs. (9), (10), and (11), respectively]; two equations for the thickness of the TiB_2 and B_2O_3 layers [Eqs. (15) and (16)]; two equations for the evaporated TiO_2 and B_2O_3 [Eqs. (17) and (18)]; and two equations for the thickness of the protective and nonprotective TiO_2 layers [Eq. (14)]. Equation (14) is used for the calculation of the total thickness of the TiO_2 layer. However, after the breakup of the layer, a new layer starts to form around the particle and for the calculation of the rate of generation of TiO_2 (R_{G,TiO_2}) only the thickness of the new (protective) layer is considered. So actually, Eq. (14) is used for the calculation of two layers.

In order to avoid numerical complications due to the stiffness of the system, the two stages were treated separately and the number of differential equations for each stage was reduced. Moreover, since the evaporated TiO_2 was found to be negligible, $R_{V,TiO2}$ was set to zero and Eq. (17) was not solved. The thermal equations [Eqs. (8–11)], were solved one at a time according to the thermal status of the particle, hence, the number of equations for each stage was reduced to four.

The equations were solved by the Runge–Kutta method. The time step required for convergence of the system was 0.5 μs with a numerical tolerance of 10^{-8}.

Results and Discussion

The aim of this research was to investigate theoretically the ignition behavior of titanium-coated boron particles. For this purpose a parametric investigation was conducted to evaluate the effect of the titanium coating thickness (0.1–1 μm) and the surrounding temperature (1400–2000 K) on the ignition time of various diameter particles (5–20 μm).

The surrounding radiation temperature as well as the initial particle temperature were assumed to be 300 K.

The initial thickness of the titanium layer affects significantly the ignition behavior of the particle. The results indicate the existence of a critical initial titanium thickness, below which the particle cannot ignite. [It is important to note that for sufficiently high surroundings temperature (~2000 K), no titanium coating is required at all.] For a demonstration of the importance of the initial Ti coating thickness, the temperature history of a 10-μ-diam particle with different Ti coating thickness is presented in Fig. 3. The critical Ti thickness of such a particle is $\delta_0 = 0.064$ μm. As shown in Fig. 3, the particle temperature increases rapidly at approximately 0.3 ms. At this point the particle temperature is about 1300 K and the mechanical stresses cause disruption of the still solid TiO_2 film. A new protective TiO_2 layer is then formed between the now unprotective TiO_2 and the Ti layers as shown in Fig. 4. This layer breaks immediately due to the mechanical stresses, and this phenomenon repeats itself continuously until the TiO_2 melts at 2143 K. The result of this continuous generation of a new protective layer and its disruption is the oxidation of titanium at a much higher rate, and consequently, an acceleration of the particle temperature increase (at $t \simeq 0.3$ ms), as shown in Fig. 3. At some time all the titanium will be consumed and oxygen will diffuse through the TiO_2,

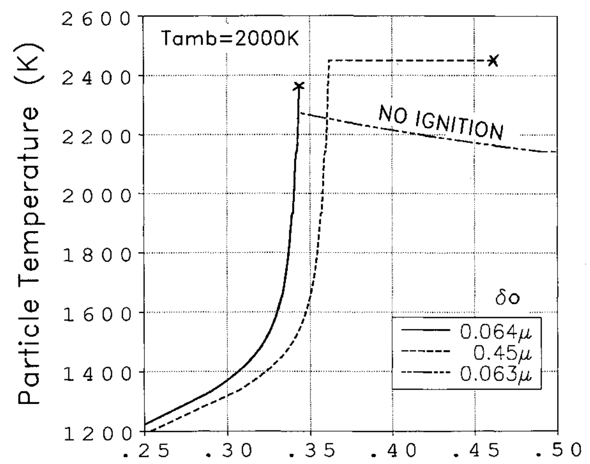

Fig. 3 Particle temperature history.

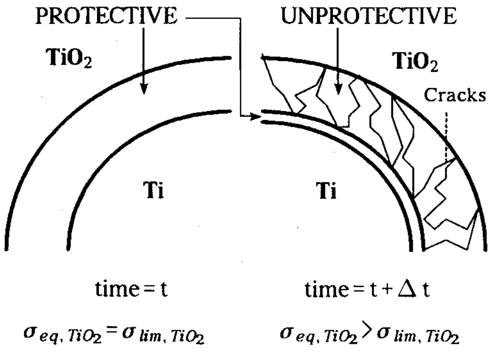

Fig. 4 Titanium oxidation mechanism.

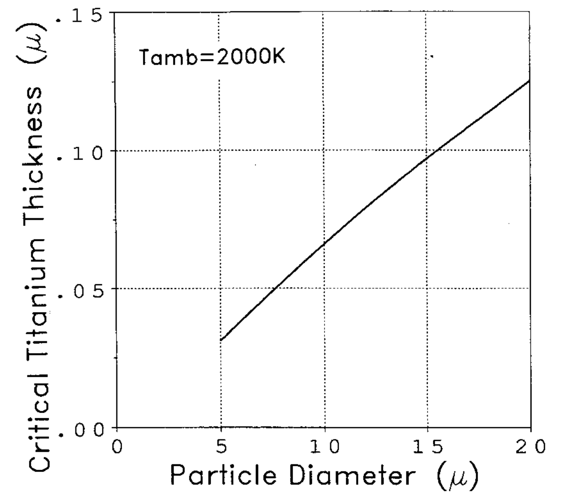

Fig. 5 Critical initial titanium thickness, for various particle sizes.

TiB_2, and B_2O_3 (initially zero) layers and will react with boron. The rate of diffusion of both O_2 and B_2O_3 through liquid TiO_2 increases with temperature [Eqs. (44) and (46)]. However, the three successive layers (TiO_2, TiB_2, and B_2O_3) produce a serious limitation for the oxidation of boron. Hence, if the particle temperature is not high enough, the amount of oxygen that reaches the boron may not be sufficient to provide the heat lost to the surroundings and for further temperature increase. If the initial Ti coating thickness is below the critical value, Ti is consumed before the particle reaches a critical temperature necessary for ignition. This temperature was found to be 2320 K, which is also the boiling temperature of B_2O_3. At this temperature the rate of vaporization of B_2O_3 exceeds the rate of generation, and the particle ignites (Fig. 3, δ_0 = 0.064 μm). Such a situation does not take place for a thinner Ti layer and the particle extinguishes (Fig. 3, δ_0 = 0.063 μm). If the initial Ti thickness is above the critical one, the particle temperature increases up to 2450 K and remains constant until Ti is consumed and the particle ignites. The critical initial titanium thickness as a function of the particle size is presented in Fig. 5 for particle sizes up to 20 μm.

It seems that the minimum initial titanium thickness necessary for particle ignition increases almost linearly with the particle diameter. However, for particle diameters of 5–20 μm and surrounding temperature of 2000 K, the titanium to boron mass ratio is almost constant, about 7.6%. The critical titanium thickness increases somewhat with decreasing the ambient temperature to 1400 K. Nevertheless, the important conclusion is that the critical titanium mass for most cases is about 8% of the boron mass.

The ignition time of particles of various sizes as a function of the initial titanium thickness for an ambient temperature of 2000 K is presented in Fig. 6. The ignition time increases with increasing the initial titanium thickness above the critical value. This indicates that by coating the particle with a mass of titanium above the required critical mass (8%), the performance of the motor may decrease, not only because of the much lower heat of combustion of titanium compared to that of boron, but also due to the increase of ignition time of the particles.

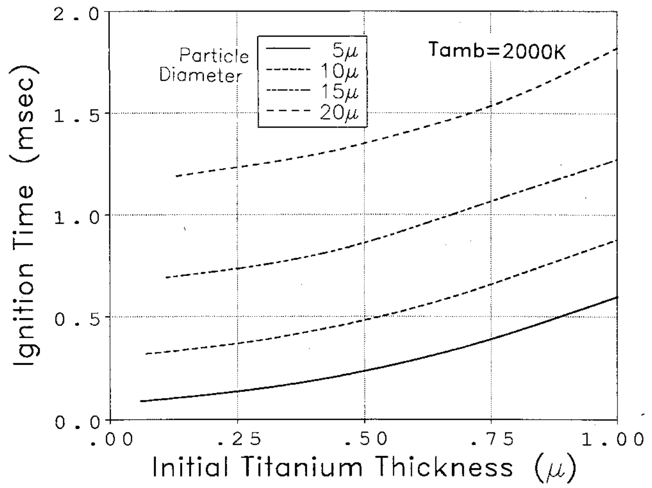

Fig. 6 Ignition time dependence on initial titanium thickness, for various particle sizes.

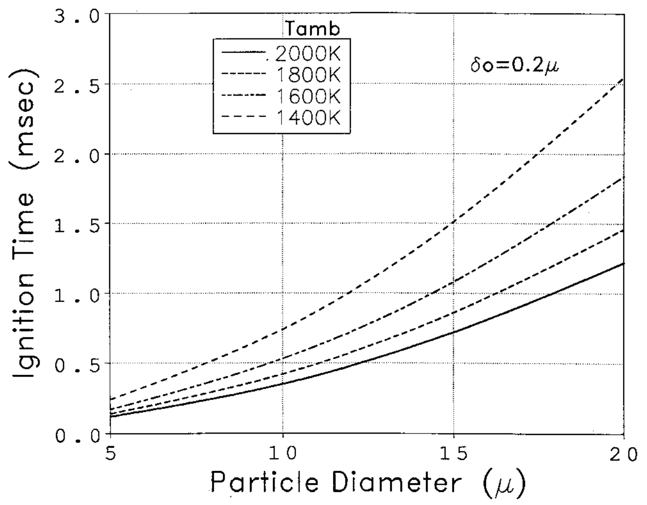

Fig. 7 Ignition time vs particle size for different surrounding temperatures.

The ignition time of particles having a titanium coating of 0.2-μm initial thickness vs the particle diameter for various ambient temperatures, is presented in Fig. 7. In contrast to uncoated boron particles that require ambient temperatures of approximately 2000 K, the titanium-coated particles can ignite even at temperatures of 1400 K. This is due to the oxidation of titanium that speeds up the particle heating and promotes the ignition process.

Concluding Remarks

A theoretical model for the ignition of titanium-coated boron particles is presented. The model includes the reactions of titanium and boron with each other as well as with oxygen and accounts for the mechanical stresses that develop in the various layers as a result of their different thermal expansion.

The results indicate the existence of a critical titanium mass, approximately 8% of the boron particle mass, necessary for ignition of the particle. Below that critical titanium mass the coated particle does not ignite at ambient temperature up to 2000 K, whereas a pure boron particle could ignite. On the other hand, titanium mass larger than the critical value causes longer ignition delay times. In general, the titanium coating promotes the ignition process even at low ambient temperatures (down to 1400 K).

Acknowledgments

This research was supported by the Ministry of Science and Technology, the Center for Absorption in Science of the Ministry of Immigrant Absorption, State of Israel, and the Wolfson Charitable Trust Program for the Absorption of Immigrant Scientists.

References

[1]Natan, B., and Gany, A., "Ignition and Combustion of Boron Particles in the Flowfield of a Solid Fuel Ramjet," *Journal of Propulsion and Power*, Vol. 7, No. 1, 1991, pp. 37–43.

[2]Natan, B., and Gany, A., "Effects of Bypass Air on Boron Combustion in Solid Fuel Ramjets," *Journal of Propulsion and Power*, Vol. 9, No. 1, 1993, pp. 155–157.

[3]King, M. K., "Review of Studies of Boron Ignition and Combustion Phenomena at Atlantic Research Corp. over the Past Decade," *Combustion of Boron-Based Solid Propellants and Solid Fuels*, edited by K. K. Kuo and R. Pein, CRC and Begell House, Boca Raton, FL, 1993, pp. 1–80.

[4]Gany, A., "Combustion of Boron Containing Fuels in Sold Fuel Ramjets," *Combustion of Boron-Based Solid Propellants and Solid Fuels*, edited by K. K. Kuo and R. Pein, CRC and Begell House, Boca Raton, FL, 1993, pp. 91–112.

[5]Kofstad, P., *High Temperature Oxidation of Metals*, Wiley, New York, 1966.

[6]*Composite Materials*, edited by D. M. Carpinos, Naukov Dumka, Kiev, 1985 (in Russian).

[7]King, M. K., "Boron Ignition and Combustion in Air-Augmented Rocket Afterburners," *Combustion Science and Technology*, Vol. 5, 1972, pp. 155–164.

[8]Messe, R. A., and Skifstad, J. G., "Ignition and Global Combustion Models for Clouds of Boron Particles," *AIAA Journal*, Vol. 12, No. 1, 1974, pp. 71–77.

[9]King, M. K., "Boron Particle Ignition in Hot Gas Streams," *Combustion Science and Technology*, Vol. 8, 1974, pp. 255–273.

[10]Glassman, I., Williams, F. A., and Antaki, P., "A Physical and Chemical Interpretation of Boron Particle Combustion," *20th Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1984, pp. 2057–2064.

[11]Calcote, H. F., Gill, R. J., Berman, C. H., and Felder, W., "Production of Pure Titanium Coated Boron Particles," Abstracts of the Second International Symposium on Special Topics in Chemical Propulsion: Combustion of Boron-Based Solid Propellants and Solid Fuels, Lampoldshausen, Germany, March 1991.

[12]*The Oxide Handbook*, edited by G. V. Samsonov, IEI/Plenum, New York, London, 1973.

[13]Geankopolis, C. J., *Transport Processes and Unit Operations*, Allyn and Bacon, Boston, 1983.

[14]Hirschfelder, J. O., *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.

[15]Wagner, S., and Yost, W., *Diffusion in Solids, Liquids, Gases*, Academic, New York, 1952.

[16]Andrievsky, A. R., and Spivak, I. I., *Strength of Refractory Materials and Compounds*, Metallurgia, Cheljabinsk, 1989 (in Russian).

[17]Kubaschewski, O., and Hopkins, B., *Oxidation of Metals and Alloys*, Butterworths, London, 1962.

[18]Hardt, A. P., and Phung, P. V., "Propagation of Gasless Reactions in Solids—I. Analytical Study of Exothermic Intermetallic Reaction Rates," *Combustion and Flame*, Vol. 21, No. 1, 1973, pp. 77–79.

[19]Natan, B., Rosenband, V., and Gany, A., "Thermal Stress Model in a Multilayer Composite Particle," Faculty of Aerospace Eng., Technion, Israel Institute of Technology, TAE Rept. 696, Haifa, Israel, Nov. 1993.