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ABSTRACT

HETEROGENEOUS COMBUSTION OF CONDENSED PARTICLES IN TRANSITION REGIME

by Deniz Yildiz

A steady-state model of heterogeneous combustion for a spherical particle is developed accounting for the transition regime of heat and mass transfer. The model assumes formation of condensed products and reaction rate controlled by the transport of oxidizer to the particle surface. The model is based on the Fuchs' limiting sphere approach. Calculations are performed for combustion of zirconium particles of different sizes. Temperature and oxygen concentration profiles are calculated and compared to those predicted by the continuous medium transfer model. It is shown that for particles in the range from 100 nm up to 30 µm heat and mass transfer occur in transition regime. The predictions are also compared with the available experimental data.

For coarse particles, both predicted combustion temperatures and burn rates match respective experimental data when the reaction is assumed to produce zirconium-oxygen solution with an enthalpy of formation reduced compared to that of the stoichiometric ZrO₂. A weak effect of particle sizes on their burn times is predicted for small particles, in qualitative agreement with recent experiments. An implementation of time variability accounted for 30% change of particle diameter during particle burning for different particle diameter and the discrepancy is maintained. However, the model underestimates the burn times and overestimates the combustion temperatures for small particles. This discrepancy is likely associated with the finite reaction kinetics at the particle surface that must be accounted for in the future work.

In the heat transfer modeling, additional errors are predicted to be caused by an incorrectly assumed value of the thermal accommodation coefficient of gas molecules on the particle surface. The technique of finding the accommodation coefficient for small metal particles heated to high temperatures is developed and tested for the Zr - Ar system. The optical emission intensity decay times for micron-sized Zr particles heated and cooled in Ar are measured. The emission decay times are interpreted as cooling times. The cooling times are calculated using the two-layer Fuchs' model. The calculated and measured results are matched by adjusting the value of the thermal accommodation coefficient. Thermal accommodation coefficient is shown to be much smaller than unity; with an estimate of 0.005. It is likely to be changing as a function of the particle size for the $1 - 10 \,\mu$ m particles.

HETEROGENEOUS COMBUSTION OF CONDENSED PARTICLES IN TRANSITION REGIME

by Deniz Yildiz

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering

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May 2013

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APPROVAL PAGE

HETEROGENEOUS COMBUSTION OF CONDENSED PARTICLES IN TRANSITION REGIME

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To Love and to the *lineage*...

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CHAPTER 1

INTRODUCTION

Metal powders, such as Al, Mg, Zr, and Ti are widely used as fuel additives in propellants, explosives, and pyrotechnics. As dimensions of metal (and other fuel) particles become smaller, energy outputs from combustion processes increase due to increased reactive surface area. This results in finer metal particles to be more desired as additives in energetic formulations [1-3]. Therefore, the studies of the combustion of fine metal particles attract interest.

It is commonly accepted that for coarse particles combustion is controlled by mass transfer processes whereas for fine particles surface kinetics determine the burn rate. Transport processes in heterogeneous combustion of metal particles are usually assumed to be governed by Continuum Mechanics principles [4-7].

However, it is known that the combustion of metal particles with dimensions of 0.01-10 μ m differs from that of coarser particles. Literature and experiments lead to the conclusion that when the particle size reduces and becomes comparable to the surrounding gas molecules mean free path, the continuum mechanics approach loses its adequacy to explain the transport processes [6]. For the very small particles with dimensions less than 0.1 μ m, transport rates are governed by the free-molecular processes [8].

An intermediate combustion regime (transition regime) combining the limiting cases of continuum and free-molecular transport regimes, is required to understand and describe combustion of particles in 100 nm to 10 μ m size range. Zirconium is used in pyrolants or in propellants due to its high-reactivity with oxygen at high temperatures and its high density, giving rise to higher heat of combustion per unit

volume [9]. There have been studies conducted on understanding the combustion of zirconium metal [10-12]. These studies haven't considered the combustion characteristics of finer Zr particles. The current study will generate a steady-state and transient solution with quasi-steady approximation to the combustion of Zr particles in the transition regime centered on the two-layer model introduced by Fuchs [8].

Additionally, this work will conduct a study of the thermal accommodation coefficient, which accounts for the specular collisions of gas molecules with the Zr particle. The correlation of a cooling model based on the transition transport principles based on two-layer model with the experimental cooling times will reveal the knowledge of accommodation coefficients for more realistic models.

CHAPTER 2

TRANSITION COMBUSTION MODEL

2.1 Introduction

Heterogeneous particle combustion occurs in multiple practical situations, from oxidation of soot [13, 14] to combustion of coal [15, 16] to combustion of fine metal particles in propellants, explosives, and pyrotechnics, e.g., [1, 17-19]. It is commonly assumed that mass transfer controls the burn rate for coarse particles, and when the particle size decreases, the combustion becomes rate-limited by the surface reaction kinetics. The rate of mass transfer is usually assessed considering diffusion and convection in terms of conventional continuous media models. However, it is well-known that when the particle size decreases to become comparable to the gas molecule mean free path (i.e., when Knudsen number Kn increases), the heat and mass transfer processes are no longer described by the continuous model [4, 5, 7]. The transport occurs in the free-molecular regime for very small particles (typically less than 0.1 μ m) and so-called transition regime exists for particles in a broad range of sizes from 0.1 to $\sim 40 \ \mu m$ (the relevant particle size range shifts depending on pressure). The effect of an increased value of Kn has been extensively investigated for heat and mass transport processes individually; however, few treatments are available for the situations when both heat and mass transport occur simultaneously and when temperature and concentrations gradients are not small, which are typical for particle combustion.

An extensive review of different methods used to analyze the heat transfer in the transition regime is given in Ref. [5] where different methods are classified into three main approaches: approximate analytical techniques of solving the Boltzmann equation, interpolational approach leading to simple equations applicable in the conditions close to isothermal (or small concentration differences), and limiting-sphere or two-layer model, which is sometimes also referred as Fuchs' model [20]. Based on comparison with direct Monte-Carlo simulations [5, 21], it is concluded that the latter approach is preferable over any existing interpolation formulae. The two-layer Fuchs' approach is used here to model heterogeneous combustion of a metal particle burning in a transition regime. Specific calculations are performed for combustion of zirconium particles. The reactions are limited to formation of non-volatile products and results are compared with the experimental data published in the literature.

2.2 Physical Model

A steady-state model of heterogeneous combustion of a spherical fuel particle is considered as schematically illustrated in Fig. 2.1. The particle with radius r_p is placed in a gaseous environment consisting of an inert gas and an oxidizer. The oxidizer diffuses towards the particle where it reacts on its surface with the formation of a condensed product. Both fuel and product remain condensed, i.e., the model is limited to systems with nonvolatile metals and oxides. The focus of the present study is on the effect of heat and mass transport processes; the reaction occurring at the surface is assumed to be rapid, so that all the oxidizer reaching the particle surface is consumed. To simplify the analysis, only a single gas phase oxidizer and a single condensed product are considered. In the future, the model can be readily extended to describe multicomponent systems as well as systems with volatile fuels and products. The particle surrounding is separated into two distinct regions: inside and outside of the Knudsen (or Langmuir) layer with radius r_s and thickness $\delta = r_{\delta} - r_{p}$ of the order of one molecular mean free path [21]. Within the Knudsen layer, $r_{p} < r < r_{\delta}$, there is no collision between molecules and transport is described by molecular kinetics; outside of it, $r > r_{\delta}$, transport phenomena are described by the heat and mass transfer equations of continuum mechanics. The mass and energy fluxes in the two regions are matched at $r = r_{\delta}$. The environment temperature is assumed to be lower than the particle surface temperature, where the reaction occurs.



Figure 2.1 A two-layer model of particle combustion. A particle within the Knudsen layer considered in the present model.

A number of simplifying assumptions are used, as listed below.

a. The particle burns in a quiescent, infinite spherically symmetric gaseous environment. Influence of convection or thermophoretic effects is not considered.

- b. The combustion is treated as a steady-state process. The particle size and spatial distributions of temperature and concentrations of gaseous species remain constant.
- c. The particle temperature is uniform.
- d. The gas surrounding particle contains two components: oxidizer that reacts with the particle and an inert component.
- e. The transport of the oxidizer towards the particle is the rate-controlling process; the concentration of the oxidizer at the particle surface is zero.
- f. Values of gas mass diffusivity ρD , thermal conductivity, k, and heat capacity, c are fixed outside of the Knudsen layer. The effect of temperature on these values is accounted for by adjusting their values depending on the calculated temperature profiles. This adjustment is done using computational iterations as described below.
- g. The thermal accommodation coefficients for the gas molecules interacting with the particle surface are assumed to be equal to 1. In other words, each collision results in the complete energy transfer from gas to particle.
- h. If an oxidizer molecule impacts upon the particle surface, it always bonds to the particle chemically (reacts); in other words, the sticking coefficient is also assumed to be equal to 1.

Whereas the Knudsen layer thickness, δ , is known to be comparable to the mean free path of gas molecules, λ , different specific values are used by different authors. Fuchs considered a mass transfer problem of droplet evaporation and argued that thickness should be slightly larger than λ [8]. Young compared non-equilibrium heat transfer coefficients found from his model of droplet condensation/evaporation with the ones obtained from the solution of the

Boltzmann equation and found the best match at $\delta = 0.75\lambda$ [22, 23]. Wright [24] proposed a relation between δ and Knudsen number *Kn*. As pointed out in [25], Write's expression effectively gives $\delta \approx \lambda$ for a broad range of *Kn*. The effect of selected value of δ is considered for droplet evaporation – condensation problems [22, 23] and for high-temperature heat transfer [25]; the effect is found to be negligible for a wide range of Knudsen numbers corresponding to the transition transport regime. Thus, in this work it is simply assumed that $\delta = \lambda$, or:

$$r_{\delta} = r_{p} + \lambda \tag{2.1}$$

It is shown that for multicomponent transfer problems, the mean free path defined by collision of different molecules needs to be corrected compared to the mean free path in a single component gas only when the mass ratio of colliding molecules is either much smaller or much greater than one [26]. In the range of molecular mass ratios from 0.43 to 86, change of λ is less than 10%. Therefore, here the mean free path is taken for air at the temperature at the Knudsen layer interface, T_{δ} . The mean free path expression defined by McCoy and Cha [25, 27] applicable to both monatomic and polyatomic gases is used:

$$\lambda = \frac{k(T_{\delta})}{f(T_{\delta})p} [\gamma(T_{\delta}) - 1] \sqrt{\frac{\pi T_{\delta} M_{air}}{2R}}$$
(2.2)

where p is the pressure, $k(T_{\delta})$ - thermal conductivity, M_{air} is the molecular mass of air, γ is the specific heat ratio of gas, and $f(T_{\delta}) = [9\gamma(T_{\delta}) - 5]/4$ is the Eucken factor. All parameters in Eq. (2.2) are taken at the Knudsen layer interface.

2.3 Equations

2.3.1 External Region; r>r.

For a spherically symmetric steady flow, the radial component of the total mass flow rate \dot{m} is constant:

$$\frac{d\dot{m}}{dr} = 0 \tag{2.3}$$

where the mass flow rate can be expressed using the Stefan flow velocity, u, and gas density, ρ , as:

$$\dot{m} = 4\pi r^2 \rho u \tag{2.4}$$

The mass continuity is also valid for mass flow rates of individual gas species: oxidizer and inert components. Since the inert component is not absorbed by the particle surface, the total mass flow rate \dot{m} is just the mass flow rate of the oxidizer.

$$\dot{m} = \dot{m}Y_{ox} - 4\pi r^2 \rho D_{ox} \frac{dY_{ox}}{dr}$$
(2.5)

where Y_{ox} and D_{ox} are respectively mass fraction and the diffusion coefficient of the oxidizer molecules in the gas mixture. The energy conservation equation is:

$$\frac{dE}{dr} = 0 \tag{2.6}$$

where \dot{E} is the energy flow rate, that can be expressed using the enthalpy of an oxidizer, h_{ox} as:

$$\dot{E} = \dot{m}h_{ox}\left(T\right) - 4\pi r^2 k \frac{dT}{dr}$$
(2.7)

The boundary conditions are defined at infinity and at the Knudsen layer:

$$r \rightarrow r_{\infty}: Y_{ox} = Y_{ox,\infty}; T = T_{\infty}$$
 (2.8)

$$r = r_{\delta} : Y_{ox} = Y_{ox,\delta}; \dot{E} = \dot{m}h_{ox}\left(T_{\delta}\right) - 4\pi r_{\delta}^{2}k \left.\frac{dT}{dr}\right|_{\delta}; T = T_{\delta}$$
(2.9)

where T_{∞} and $Y_{ox,\infty}$ are respectively temperature and mass fraction of oxygen in the environment, T_{δ} and $Y_{ox,\delta}$ are respectively temperature and mass fraction of oxygen at the Knudsen layer boundary (unknown at the moment), and h_{ox} is the specific enthalpy of formation of the oxidizer.

Assuming a constant specific heat of oxidizer, c_{ox} , its enthalpy can be calculated as a function of temperature as:

$$h_{ox}\left(T\right) = h_{ox}\left(T_{\delta}\right) + c_{ox}\left(T - T_{\delta}\right)$$
(2.10)

The solution of Eqs. (2.3)-(2.7) with the boundary conditions (2.8), (2.9) is:

$$Y_{ox} = 1 - \left(1 - Y_{ox,\infty}\right) \left(-\frac{\dot{m}}{4\pi\rho D_{ox}r}\right)$$
(2.11)

$$T = T_{\infty} + \frac{q^c}{\dot{m}c_{ox}} \left\{ \exp\left(\frac{\dot{m}c_{ox}}{4\pi kr}\right) - \exp\left[\frac{\dot{m}c_{ox}}{4\pi k}\left(\frac{1}{r_{\delta}} - \frac{1}{r}\right)\right] \right\}$$
(2.12)

where the conductive heat flow through the Knudsen layer boundary is defined as

$$q^{c} = -4\pi r_{\delta}^{2} k \frac{dT}{dr} \Big|_{\delta}$$
(2.13)

Equations (2.11) and (2.12) suggest that the mass flow rate and temperature at the Knudsen layer interface are:

$$\dot{m} = 4\pi\rho D_{ox}r_{\delta} \ln\left(\frac{1-Y_{ox,\infty}}{1-Y_{ox,\delta}}\right)$$
(2.14)

$$T_{\delta} = T_{\infty} + \frac{q^{c}}{\dot{m}c_{ox}} \left\{ \exp\left(\frac{\dot{m}c_{ox}}{4\pi kr_{\delta}}\right) - 1 \right\}$$
(2.15)

2.3.2 Knudsen layer; r_p<r<r_s

Energy and mass fluxes in the Knudsen layer are calculated based on velocity distribution at the particle surface and Knudsen layer interface. One of the major difficulties in the problems with the bulk flow of masses and energies is the non-Maxwellian velocity distribution of molecules. Strictly speaking, accounting for Stefan flow requires solution of the Boltzmann equation. Previously, for similar evaporation-condensation problems, Stefan flow is often neglected, and Maxwell distribution is used. In ref. [28], Maxwell distribution with a superposed bulk flow component is utilized. Young introduced a model with the Grad distribution at the Knudsen layer interface [22, 23]. Later, Young's model is used in multicomponent droplet evaporation-condensation problem [29]. Here, the Young's approach is followed: half-Maxwellian and Grad velocity distributions are assumed at the particle surface and at the Knudsen layer interface, respectively. The model and respective assumptions are discussed in detail elsewhere [22]. The derivation of the equations is similar to that reported earlier [23, 26]; however, some changes are made to make the derivation suitable for the present problem (cf. Appendix A). The mass transfer of the oxidizer from the Knudsen layer towards the particle is:

$$\dot{m} = -\frac{p Y_{ox,\delta} M_{\delta}}{\left(\frac{1}{r_p^2} - \frac{1}{2r_{\delta}^2}\right)} \sqrt{\frac{8\pi}{RT_{\delta}M_{ox}}}$$
(2.16)

where p is pressure and M_{δ} is the equivalent molecular mass for a gas mixture at the Knudsen layer interface:

$$M_{\delta} = \frac{M_{ox}M_{in}}{(M_{in} - M_{ox})Y_{ox,\delta} + M_{ox}}$$
(2.17)

The energy flow rate from the particle to the Knudsen layer is

$$\dot{E} = \sqrt{\frac{8\pi}{RT_{\delta}}} r_{p}^{2} p M_{\delta} \sum_{i} \frac{Y_{i,\delta}}{\sqrt{M_{i}}} \left(\Delta h_{i} - \frac{R\left(T_{p} - T_{\delta}\right)}{2M_{i}} \right) + \left(1 - \frac{r_{p}^{2}}{2r_{\delta}^{2}}\right) \dot{m} \left(\Delta h_{ox} - \frac{RT_{p}}{2M_{ox}}\right) + \frac{r_{p}^{2}}{2r_{\delta}^{2}} \left\{ q^{c} + \dot{m} \left(1 - Y_{ox,\delta}\right) \left[h_{ox} \left(T_{\delta}\right) - h_{in} \left(T_{\delta}\right) - \frac{5}{2} \left(\frac{R}{M_{ox}} - \frac{R}{M_{in}}\right) T_{\delta} \right] \right\} + \dot{m} h_{ox} \left(T_{\delta}\right) \right)$$

$$(2.18)$$

where h_i is the specific enthalpy of a gas component *i* (*i*=inert, oxidizer), summation is performed over both gas components, and $\Delta h_i = h_i (T_p) - h_i (T_\delta)$.

Boundary conditions at the particle surface:

$$r = r_p : Y_{ox} = 0; \ \dot{E} = \dot{m} \left[h_{pr} \left(T_p \right) - h_f \left(T_p \right) \right] - 4\pi r_p^2 \varepsilon \sigma \left(T_p^4 - T_\infty^4 \right)$$
(2.19)

where h_{pr} is the enthalpy of product, ε is emissivity, and σ is the Stefan-Boltzmann constant. Note that h_{pr} is calculated for the mass of product generated when 1 kg of oxidizer is consumed. One can introduce the heat of reaction, Q (normalized per kg of oxidizer) as

$$Q(T) = -h_{pr}(T) + h_f(T) + h_{ox}(T)$$
(2.20)

where h_f is the enthalpy of fuel calculated for the mass of fuel consumed by 1 kg of oxidizer. Considering conservation of energy, the conductive heat flow over the Knudsen layer interface used in Eq. (2.12) is expressed as:

$$q^{c} = -\dot{m}Q\left(T_{p}\right) - \dot{m}\left[h_{ox}\left(T_{p}\right) - h_{ox}\left(T_{\delta}\right)\right] - 4\pi r_{p}^{2}e\sigma\left(T_{p}^{4} - T_{\infty}^{4}\right)$$
(2.21)

Note that Eq. (2.20) contains the difference of the oxidizer enthalpies at the particle surface and Knudsen layer temperatures. This is because the oxidizer molecules crossing the Knudsen layer are assumed to not experience any collisions until they strike the particle surface.

2.4 Parameters and Solution Procedure

Calculations are performed for combustion of zirconium particles in air at a temperature $T_{\infty} = 298 K$, with the air modeled as a mixture of oxygen, $Y_{ox,\infty} = 0.23$, and nitrogen that is treated as inert.

The equations in external region above assume constant gas properties. Variability of these properties with composition is neglected. The effect of temperature on thermal conductivity, heat capacity and mass diffusion ρD_{ox} is accounted for by using their values at a reference temperature T_{ref} , calculated as:

$$T_{ref} = T_{\delta} + f\left(T_{\infty} - T_{\delta}\right) \tag{2.22}$$

Eq. (2.22) is referred to as 1/3 rule [30, 31] or 1/2 rule [32] depending on whether $f = \frac{1}{3}$ or $f = \frac{1}{2}$. The value of $f = \frac{1}{3}$ is selected here based on a better match of the calculated burn time with the reported experimental data for large particles, which burn in a continuous regime.

Values of γ and thermal conductivity in the air are calculated using polynomial temperature dependence (in the range from 300K to 4000K) reported in [25]. The diffusion coefficient of oxygen is calculated using Chapman-Enskog kinetic theory [33]:

$$D(T) = D(T^*) \left(\frac{T}{T_{ref}}\right)^{3/2} \frac{\Omega_{D/T_{ref}}}{\Omega_{D/T}}$$
(2.23)

where $D(T^*)$ is the known value of the diffusion coefficient at a specific temperature T^* , $\Omega_{D/T}$ is the collision integral for diffusion which depends on dimensionless temperature $k_B T / \varepsilon_{O_2 - N_2}$ (k_B is the Boltzmann constant, and $\varepsilon_{O_2 - N_2}$ is the energy of intermolecular interaction of oxygen and nitrogen pairs). Parameter $\varepsilon_{O_2-N_2}$ is estimated through oxygen and nitrogen molecule interaction using the formula,

$$\varepsilon_{O_2 - N_2} = \left(\varepsilon_{O_2} \varepsilon_{N_2}\right)^{1/2} \tag{2.24}$$

with $\varepsilon_{O_2}/k_B = 113 K$ and $\varepsilon_{N_2}/k_B = 99.8 K$ [33]. The value of diffusion coefficient of oxygen in nitrogen $D(T^*)=0.208\times 10^{-4} \text{ m}^2/\text{s}$ for $T^*=298 K$ is used in Eq. (2.22) [34]. Values of heat capacities and enthalpies of each component are calculated using Shomate equations according to the NIST database [35].

The enthalpy of formation of products, h_{pr} in Eq. (2.19) affects the heat release in reaction and the resulting solution substantially. It is reported that liquid solution of oxygen in zirconium is produced when Zr particles burn in air [36, 37]. In calculations, two cases are considered: enthalpy of formation of products is assumed to be equal to the heat of oxygen dissolution in one case and to the enthalpy of formation of ZrO₂ (standard enthalpy of formation of 1097 kJ/mol varied as a function of temperature as reported in ref. [38]) in the other. The heat of dissolution of oxygen in liquid zirconium is estimated to be in the range 700-830 kJ/mol of zirconium [39]. A constant value of 700 kJ/mol is used here.

The final set of nonlinear algebraic equations contains four unknowns: \dot{m} , $Y_{ox,\delta}$, T_{δ} , T_{p} . It is solved using an iteration procedure provided by the MATLAB[©] standard function *fsolve* (with the default 'trust – region dogleg' algorithm). The values of unknown variables change in a wide range (e.g., the order of 10⁻⁹ kg/s and less for mass flow rate, and 10³ K for temperatures), leading to different variations for different quantities in each iteration, making the solution difficult.

To avoid this problem, all equations are solved in a normalized form. For example, the normalized form of Eq. (2.15) is:

$$\left[T_{\delta} - f\left(\dot{m}, Y_{ox,\delta}, T_{\delta}, T_{p}\right)\right] / T_{\delta} = 0$$
(2.15n)

To estimate the direction of gradient in each iteration, the analytical Jacobian of these equations is used, including the derivatives of all thermophysical properties with respect to unknowns. Together with the solution of the current model, the equations are solved for the fully continuous case obtained assuming $r_{\delta} = r_p$ in Eqs. (2.13) and (2.14). The numerical solution procedure can be summarized as follows:

1. The initial particle size is taken greater than 100 μ m and a problem without Knudsen layer (i.e., the continuous problem) is solved. This problem is simple and its resulting values are used to arrive at the initial approximation for the Knudsen layer problem, which should yield very similar values for large particles. The found values of \dot{m} and T_p serve as the initial approximation of the current model with the Knudsen layer. For the initial approximation, the value of T_{δ} is taken equal to T_p and the value of $Y_{ox,\infty}$ is set to a small number approaching zero (e.g., 10^{-4}).

2. The problem with Knudsen layer is solved iteratively for the same particle size as the continuous problem.

3. The particle size is reduced in small steps. For each reduced particle size, the problem is solved using solutions obtained for the previous larger particle size as the initial approximation. The specific rate by which the particle sizes can be reduced depends on the convergence of the numerical method. Generally,

reducing particle sizes by 1 μ m is observed to always result in converging solutions.

4. Steps 2 and 3 are repeated until the desired minimum particle size. The relative errors of the final solution for each particle size and each unknown variable are monitored to ensure that they are less than 10^{-6} (typical values are in the range from 10^{-7} to 10^{-12}).

2.5 Results and Discussion

Figure 2.2 represents particle temperatures calculated using different energetics of combustion process:

a) Heat release due to formation of ZrO₂ and

b) Heat release as a result of dissolution of oxygen in zirconium.



Figure 2.2 Particle temperature for particles of different diameters in calculated using two different energetics of combustion: formation of ZrO_2 and dissolution of oxygen in Zr.

High reaction heat in case of formation of ZrO_2 (case a) leads to temperatures that are much higher than the boiling point of ZrO_2 , 4573 K for fine particles. The boiling of products is not considered in the model, allowing the calculated temperatures to exceed the boiling point. However, even for coarse particles, e.g., 200 μ m diameter, the calculated temperatures exceed substantially the measured values reported in ref. [36]. The calculation using case b) gives temperatures below the boiling point of ZrO₂ for all particle sizes. It matches well the experimental data for coarse particles [36].



Figure 2.3 Temperature at the particle surface and Knudsen layer interface (a) and oxygen mass fraction (b) for various particle diameters. Continuous asymptotic solution valid for large particle diameters (Kn <<1) is shown with the dashed line.

Figure 2.3 shows computed temperatures and oxygen fraction at the Knudsen layer interface as a function of the particle diameter for the reaction forming a Zr-O solution. For the diameters decreasing below approximately 40 μ m, the reduced rates of heat and mass transfer in the Knudsen layer become noticeable and the oxygen fraction at the Knudsen layer interface increases, leading to a lower particle temperature. For reference, temperature calculated as a function of the particle size for a continuous model is also shown. The difference between the temperatures calculated from the continuous and transition regime transfer models becomes greater than 1000 K for particles less than 5 μ m.



Figure 2.4 Spatial profiles of temperature and oxygen concentration for a particle of 1 μ m diameter (Kn = 0.8).

Figure 2.4 illustrates the calculated spatial temperature and oxygen fraction profiles for a 1- μ m diameter Zr particle in the air. As for the calculations shown in Fig. 2.3, the heat release is defined by dissolution of oxygen in zirconium. For comparison, results of calculations using the continuous model are also shown. The oxygen fraction at the distance r_s (equal to one free molecular path) from the particle is significantly higher, while particle temperature about 1000 K lower than the value obtained in a continuous model. It is interesting to note how much lower both temperature and concentration gradients are for the current model compared to the continuous model at the Knudsen layer boundary. This clearly implies lower reaction and heat transfer rates, indicating that the particle is effectively isolated from the environment by the introduced Knudsen layer.

The variation of oxygen mass flow rate with particle diameter is represented in Fig. 2.5 (once again assuming that the reaction leads to the formation of the Zr-O solution). The asymptotic values for both continuous and free-molecular regimes are shown for comparison. The mass flow rate in a continuous regime is proportional to particle diameter d, while in the free molecular regime it becomes proportional to d^2 . It is clear from Fig. 2.5 that



Figure 2.5 Mass flow rate of oxygen for various particle diameters. The dashed lines show the solutions for continuous (Kn \ll 1) and free-molecular (Kn \gg 1) regimes

Predicted steady-state burn rates, \dot{m} , can be directly used to approximately predict the burn times of Zr particles:

$$t_b = \frac{\pi d^3 \rho_m}{6v \dot{m}} \tag{2.25}$$

where ρ_m is density of zirconium, and v is the stoichiometric coefficient. In calculations, the particle is assumed to be completely consumed when it absorbed enough oxygen to convert into ZrO₂, so $v = \frac{M_{Zr}}{M_{o_1}}$, where M_{O2} and M_{Zr} are

respectively molecular weights of oxygen and zirconium. This approach is expected to slightly under-estimate the burn times for the combustion scenario including formation of a saturated Zr-O solution with slightly less oxygen than in the stoichiometric ZrO_2 (followed by a fast transformation of the solution into ZrO_2 in an additional combustion step after a micro-explosion, as observed in respective particle combustion experiments [36, 40, 41]). Experiments on combustion of 2-25 μ m diameter Zr particles ignited by a CO₂ laser are reported in ref. [11]. The results of these experiments are shown in Fig. 2.6 along with earlier experimental data [36] for larger size particles. For fine particles, a very weak dependence of the burn time vs. particle diameter is observed.

Figure 2.6 also shows the burn times for particles of different sizes estimated using both transition transfer and continuous models. Both models result in the same burn times for coarse particles, which match nicely the experimental data. The difference between the two calculated burn time trends becomes noticeable for 20-µm particles and becomes significant for particles finer than 10 µm. The effect of particle size on burn time for fine particles is predicted to become weaker by the transition transfer model; however, the predicted burn times are still shorter than the experimental ones. The effect of particle size in experiments is also weaker than for the calculated curve. The observed discrepancy may indicate the importance of the surface reaction kinetics in addition to the heat and mass transfer rates in defining the particle burn rate. Indeed, if the reaction kinetics is comparable to the rate of oxygen transfer to the particle surface, the concentration of oxidizer at the particle surface may be greater than zero, affecting the entire obtained solution. Another indication of importance of the chemical reaction might be the fact that the maximum temperatures reported in Ref. [11] for fine powders are in the range 3100 - 3683K independent on the particle size, while the model for the diffusion limited process predicts higher temperatures, up to 4000 K for particles of 2 µm. The kinetics of surface reaction of zirconium with air is unknown. However, the present model can be readily modified to include an expression for the reaction kinetics with adjustable parameters. These parameters can be found by matching the predictions with experiments; thus unknown reaction kinetics for heterogeneously burning fuels can be established.



Figure 2.6 Burn time of Zr particles of various diameters. Experimental data [11, 36] and results of modeling. For comparison, results of both continuous solution (without Knudsen layer) and using the Knudsen layer approximation are shown.

Finally, the present calculations can also be compared with a different set of experiments, involving Zr-based alloys as reported in Ref. [42]. Particles are ejected from a Zr₃Hf foil. Combustion is recorded with a high-speed camera and velocities of ejected particles are measured by laser velocimetry. Two types of experiments are conducted using different methods of particle ejection: by mechanical impact of a steel bead on the foil, and by the laser ablation. The mass flow rates are calculated assuming the same heat release rate as in case of combustion of pure zirconium. To calculate burn times according to Eq. (2.24), the particle is assumed to have density and molar masse of a mixture of Zr and Hf in the molar ratio 3:1. Figure 2.7 shows comparison of the present calculated burn times with the experimental data. It is interesting that the calculated burn times match well with the burn times measured for the particles generated by the mechanical impact. Shorter burn times for the particles produced by laser ablation are likely associated with partial laser-assisted combustion for the latter experiments.



Figure 2.7 Comparison of computations with experimental data on burn times of Zr/Hf alloys [42].

2.6 Conclusions

A model describing heat and mass transfer for heterogeneously burning particles is developed capable of describing reaction rates for small particles, when their dimensions become comparable to the mean free path of the gas molecules. The model assumed that the combustion is rate limited by transport of oxidizer to the particle surface. The model is applied to establish combustion characteristics of Zr particles in air, assuming that the reaction products remain condensed. The predictions are compared with available experimental data. For coarse particles, both predicted combustion temperatures and burn rates match respective experimental data when the reaction is assumed to produce zirconium-oxygen solution rather than stoichiometric ZrO_2 . This is consistent with the Zr combustion mechanism proposed earlier based on the analyses of the compositions of particles quenched at different burn times [36, 37, 43]. A reduced effect of particle size on their burn time is predicted for small particles, in qualitative agreement with recent experiments [11]. However, the model underestimates the burn times and overestimates the combustion temperatures for small particles. This discrepancy is likely associated with the finite reaction kinetics at the particle surface.

CHAPTER 3

QUASI-STEADY TRANSITION COMBUSTION MODEL

3.1 Introduction

A steady-state model based on the two-layer Fuchs' approach studying the heat and mass transfer for heterogeneous combustion of metal particles is presented in the previous chapter in a range of particle sizes where the particle dimensions are comparable to the mean free path of gas molecules. The steady-state model of combustion considered is based mainly on the experimental temperature observations during combustion of metal particles, in particular, Zr and Ti particles.

At the same time, the parameters of the problem, and most importantly, the particle burning rate in the approximation of fast kinetics considered here, may change as the particle size is changing. The comparison of the experimental data and the steady-state model predictions exhibited that for coarse particles both combustion temperatures and burn rates are predicted with reasonable accuracy. However, this comparison suggested a discrepancy between calculations and experiments for small particles. It is possible that this discrepancy is arising from the finite reaction kinetics at the particle surface. However, it is also possible that taking into account an effect of changing particle size during combustion may improve the accuracy of the model.

The effect of changing particle size is addressed by the implementation of the effect of burn time modifying the steady-state model. In order to include the time domain, quasi-steady approximation is imposed on the current transient model. The quasi-steady approximation assumes that the boundary conditions defining the burn rate respond very slowly to the changing conditions in the combustion system. In other words, within each time step considered, combustion can be described using the steady-state model; however, the particle dimensions and respective boundary conditions are adjusted between the time steps.

3.2 Quasi-Steady Model

The quasi-steady model is constructed by applying the quasi-steady approximation of the current steady-state model presented in the previous chapter. Therefore, the steady-state model equations from Eq. 2.3 through Eq. 2.21 and assumptions are also applicable to the transient model. The quasi-steady approximation states that the time variability of boundary conditions of the system responds very slowly compared to the changing conditions arising from the combustion reaction. The quasi-steady enables us with the ability to discretize the time into small intervals. The differential equations expressing the temporal variability of the mass of fuel and of the particle radius are expressed as follows:

$$\frac{dm_F}{dt} = v\dot{m} \tag{3.1}$$

$$4\pi r_p^2 \frac{dr_p}{dt} = -\dot{m} \left(\frac{1+\nu}{\rho_{pr}} + \frac{\dot{m}_{pr}}{\dot{m}} - \frac{\nu}{\rho_F} \right)$$
(3.2)

With the initial condition:

$$t = t_0: r = r_{p0}, m_F = \frac{4}{3}\pi r_{p0}^3 \rho_F$$
(3.3)

The solution accounts for a continuous change in the particle size as it burns out. As a result, the heat and mass transfer rates calculated by the transition transport model are both affected. The process should stop due to the complete consumption of the fuel particle. The burn time is the moment when the fuel is completely reacted, i.e.

$$t = t_h : m_F = 0 \tag{3.4}$$

The expressions (3.1-3.3) are discretized in time domain and incorporated with the steady-state equations. The time is discretized into small intervals (with the time step of 1 μ s), and at each time step the steady-state solution for a given particle radius r_p is found using the numerical procedure described above. At the next time step, the corrections to the particle size according to equations (3.1-3.3) are made and the steady-state solution is obtained for this updated particle size. The calculations are performed until the condition (3.4) is satisfied.

3.3 Parameters and Procedure

The solution algorithm is based on the procedure of the steady-state solution except for the addition of iterative steps carrying out the numerical solution of the system in the time domain. The solution of the model is performed on the single Zr particle for cases with both boiling and non-boiling product species.

The solution of the model is conducted using a MATLAB[©] based program which utilizes the standard *fsolve* function. The size range taken into account is in the order of microns, leading to the values of other variables being in the orders of 10^{-9} or smaller; therefore, the normalization of the system of equations are required in the calculations. Since, the system of equation treated by the program is non-linear, the Jacobian matrix is provided.

The burn times are of the order of several milliseconds; therefore, the time of discretization is taken at the order of microseconds. In the calculation, a steadystate solution is found for each particle size in the desired range to obtain initial values for the entirety of the variable. The values of the variables obtained from the steady state solution serve as the initial value table for the transient solution. The steady-state iterations are embedded in every iterative step of the transient solution. In the steady-state solution, the initial metal particle size is taken around 100 and the continuous problem is solved. For this particle size the continuous transport model is expected to result in a good match with the experimental data. The results obtained from the continuous solution are used in providing the initial values of mass flow rate () and the particle temperature () that are required for the solution of the Knudsen Layer problem. The steady-state calculation performed in each iterative step of the transient solution as the particle size is decreasing.

The initial values of mass flow rate, particle temperature, Knudsen Layer temperature and the mass fraction of oxygen in the system are provided. In every iterative step of the steady-state calculation, the particle size is reduced and the results of the previous step are used as the initial values of the variables.

The transient solution is performed by marching in time, multiple iterations of the steady-state solution are performed; the results obtained from the steady-state solution in the previous interval of the time domain are taken and provided as initial values in the quasi-steady solution of the next time interval. The reduction in the particle size and the determination of the time-steps are subject to the convergence of the numerical solution. The reduction of the particle size by 1 leads to converging results in the steady-state solution discussed in Chapter 2. Similarly, it is concluded that taking time steps as microseconds resulted in converging solutions, although it leads to an increased computational time required.

The results of transient model calculations are presented in Figures 3.1a through 3.1d:



Figure 3.1 (a) Time variability of Particle Radius for the initial particle diameters of 20 μ m, 16 μ m, 12 μ m, 8 μ m and 4 μ m. (b) Time variability of Particle Surface Temperature for the initial particle diameters of 20 μ m, 16 μ m, 12 μ m, 8 μ m and 4 μ m. (c) Time variability of oxidizer mass flow rate for the initial particle diameters of 20 μ m, 16 μ m, 12 μ m, 8 μ m and 4 μ m. (d) Variation of burn times of particles of varying diameters obtained from the quasi-steady solution

Figure 3.1a depicts the time variability of the particle radius experiencing combustion in the transition model. The results are provided for the initial particle diameters of 20, 16, 12, 8 and 4 μ m. These dimensions are selected such that they are in the designated range of particle sizes corresponding to the transition transport regime. The particle radius is observed to increase as the combustion

proceeds because of replacement of zirconium with zirconium oxide. The particle radius increases approximately ~28.8% in the range.

Figure 3.1b illustrates change of the particle surface temperature with the progression of combustion over time for the initial particle diameters selected in the transition transport range. It is observed that the temperature of the particle surface decreases as the combustion proceeds. For the particles with initial diameters of 4, 8, 12, 16, and 20 μ m, the percentage decrease in the particle surface temperature during the burn time is predicted to be 0.49, 0.82, 1.34, 1.89, and 2.40, respectively. As the particle diameter increases, the decrease in the particle surface temperature increases.

Figure 3.1c provides the results of the change of mass flow rate of oxidizer over time during the particle combustion for the initial particle diameters in the transition transport regime. It is observed that mass flow rate increases over time. The percentage increase in mass flow rate of oxidizer for the sample particles with diameter 4μ m through 20µm respectively are 49.75, 45.85, 42,48, 39.57, and 37.12.

Figure 3.1d shows the variation of burn times of particles of varying diameters obtained from the quasi-steady solution of the transition transfer model. The plot illustrates the burn times for the particle diameters in the range from 250 nm to 20 μ m. The trend of increasing burn time with increasing particle size is comparable to steady-state solution, as illustrated in Figure 2.6. We know that for coarse particles continuous and transition transfer models predict similar burn times, which are in good agreement with the experimental data. Also, as previously stated, experiments reveal that for finer particles the effect of particle size on burn times becomes less significant. Therefore, finer particles are studied

in the quasi-steady solution to investigate the discrepancy between the experimental burn times to the shorter burn times predicted by the steady-state solution results. Although the quasi-steady model still does not constitute the reaction kinetics, involving time may suggest a more realistic burn time trend. However, the correction compared to the steady state solution is found to be rather small.

3.5 Conclusions

The effect of the change of a particle size during combustion on burn time is considered theoretically. It is shown that the particle diameter increases during combustion up to 30%. This leads to significant mass flow rate increase, about 50%, compared to steady state-burning model. At the same time, the experimental burn times remain several orders of magnitudes higher than those obtained in the model. Thus, the discrepancy of the model with the experimental data is likely to be explained by accounting for the reaction kinetics that is not taken into considered in the model. Since reaction kinetics has highly nonlinear dependence on temperature, the experimental method for determining the thermal accommodation coefficient must be developed accounting for the temperature dependence.

CHAPTER 4

THERMAL ACCOMMODATION COEFFICIENT

4.1 Introduction

The correct description of the heat transfer has a critical importance in modeling and understanding of combustion processes. As is shown in the previous chapter on the example of Zr particle combustion, combustion of particles having sizes about 10 micrometers and lower occurs in a transition regime, i.e. between the continuous regime and free-molecular regime. With decreasing particle size, the molecule-particle collision rate and energy exchange between gas molecules and the particle surface play increasingly more important role. However, the transition transport model applied to describe the particle combustion in the previous chapter did not match experimental data on burn times. Before the kinetic models that may limit the reaction rates are developed, the transport phenomena must be modeled accurately and validated for the transition transport situations, for which chemical reactions can be neglected.

For a chemically inert particle, it can be assumed that no adsorption (reaction) of gas occurs on the particle surface. The molecules colliding with the particle, are reflected away from the particle. Only a fraction of all reflected particles exchange energy with the particle surface, while the other fraction reflects specularly without exchange of energy with the particle. The total energy exchange between the particle surface and Knudsen layer interface is described using the thermal accommodation coefficient [44]:

$$\alpha = \frac{\dot{E}_i - \dot{E}_r}{\dot{E}_i - \dot{E}_p} \tag{4.1}$$

where E_i is the incident energy flux towards the particle per second, E_r - the energy flux per second carried away by reflected molecules, and E_p - the energy that the receding molecules would carry away from the particle if the mean energy per a molecule would be the same as the stream of gas issuing from a gas in equilibrium at the particle surface temperature. In general, thermal accommodation coefficient may depend on both surface and gas temperature as well as on mass and structure of interacting molecules, etc. In the previous chapter, the thermal accommodation coefficient is assumed to be equal to one for simplicity. This assumption will be tested and improved here.

The thermal accommodation coefficient has been extensively studied for different gas-solid systems and different temperatures, both theoretically and experimentally [45-50]. Most of that work, especially experimental, is performed for low temperatures, thus making the use of the obtained accommodation coefficients poorly suitable for the high-temperature, combustion applications. Recently, a very intensive activity has been taking place in studying accommodation coefficients of gases on soot and graphite at high temperatures by laser-induced incandescence technique [51-54]. Though not a universal rule, there are many cases when the accommodation coefficient decreases when the solid surface temperature increases. In [55] the upper limit of thermal accommodation coefficient of gas on a silica nanoparticle at high particle (2000-2250 K) and gas (2000 K) temperatures is estimated to be equal to 0.005. It is also proposed that the thermal accommodation coefficient is a function of the particle size [55] has an effect that might be of critical importance for the present effort aimed at development of combustion models for small particles.

The knowledge of accommodation coefficients at high temperatures and for particles of different sizes is necessary to properly model heat transfer processes and reaction kinetics in combustion of fine particles. Below, an experimental investigation of thermal accommodation coefficient for Ar on a fine zirconium particle surface at high temperatures is reported.

4.2 Experimental

4.2.1 Apparatus

The experimental setup, developed and used previously in metal particle combustion studies is used here for measuring coefficient of thermal accommodation of Ar to Zr particles at 1 atm. Spherical zirconium powder from Alfa Aesar with nominal size of 2-3 μ m is used. A brief description of the experimental apparatus with the details relevant to the current experiments is given below. A more detailed description of the setup and data processing can be found elsewhere [56-59].



Figure 4.1 Experimental setup and diagnostic

The setup as illustrated in Figure 4.1, consists of three main parts; a particle feeder for Zr powder, a laser scatter diagnostic for particle size measurements, and a particle heating detector system. The powder is suspended using am acoustically vibrating feeder, through which Ar is flowing at a flow rate of ~0.5 m/s and carrying the particles into the laser beams. Prior to the heating, Zr particles cross a beam of 30mW, 785 nm laser diode (Stocker-Yale, Lasiris), whose scatter signal is collected by PMT for particle size measurement purposes. The scatter laser diode ss focused with the internal optics to an elliptical spot approximately ~0.5×2 mm². After passing through the scatter laser observation area, the particles enter the focused CO₂ laser beam. The detection of the heated particle emission is performed using a fiber optic bundle, which is introduced to an array of three photomultiplier tubes (PMT, Hamamatsu C6270 AA3927). The signals collected from 700 nm, 800 nm, and 900 nm channels of PMT are used to detect the emission of the heated particle.

4.2.2 Data Processing

In order to determine the powder particle size distribution a commercial device is used, based on low-angle laser light scattering, Beckman-Coulter LS230. The particle size distribution obtained from the scattered 785 nm light pulses collected during the experimental procedure is compared with the size distribution determined by the commercial device. The comparison of these results is performed by adjusting the scaling factor. The result of matching two distributions is provided in Figure 4.2:



Figure 4.2 Comparison of particle size distribution obtained for the 2-3 µm Zr powder from the in situ laser scattering and using the commercial device (Coulter LS230)

Scattered light pulses and the pulses collected from heated incandescent particles are required to be correlated for further processing. The matching of the two pulse sequences is needed for determining the sizes of the particles corresponding to the individual heating peaks to be studied. Zirconium particles travel the distance separating two laser beams as explained above. The time required to travel this distance is taken into account when correlating the two sets of pulses. Although all particles are carried by the same argon flow, this time may vary slightly for different particle sizes due to differing individual particle velocity slip. In addition, the gas velocity might fluctuate during the experiment, resulting in different shift between the two pulse sequences for different data subsets. During the data processing, the time delay between two pulses is adjusted for different intervals of the data gathered to compensate for the variation of time particles traveled between two beams and to maximize the amount of matches between pulses. Though the laser heating occurs in Ar stream, and most particles exhibit heating – cooling emission profile, some of the particles are ignited. This happens most likely because due to small stream perturbations they are flowing too close to the edge of the stream or even are thrown out of the stream, so that they contact the air outside Ar stream. Therefore, the identification and differentiation of the heated particles from the particles experiencing combustion is required. Particles that are ignited and go through combustion and those that are just heated and cooled down in Ar, have different characteristic emission profiles, as shown in Figure 4.3. Heated particles, which do not experience combustion, have shorter emission light pulses and are represented by smooth curves showing their heating and cooling. The particles that ignited, have a plateau-like portion of the pulse and have a spike by the end of the pulse, well-known to represent micro-explosions of nearly fully combusted Zr particles [36, 43]. The differentiation between these two types of profiles is conducted visually and pulses showing ignition are removed from further analysis.



Figure 4.3 Typical emission intensity profiles collected by PMT (700 nm band pass filter) in case of particle (a) heating and (b) burning. In (a), the temperature cooling (decay) profile is shown with the solid line. The decay time t_d is the time between maximum intensity and 10% intensity threshold.

A part of the heating – cooling profile starting from the maximum intensity and ending when the intensity is reduced to 10% of its maximum, is identified as a temperature decay profile. The time between these two intensity values, decay time t_d , is found for each heating –cooling trace. Since each profile is matched with the corresponding particle size obtained from laser-scaterred light measurements, the decay time dependence on particle diameter is found.

Assuming that the PMT signal is proportional to the radiation emitted at a particular wavelength, experimental traces are modeled using the Planck's radiation energy distribution, i.e., at a temperature T in the wavelength interval $[\lambda - d\lambda, \lambda + d\lambda]$, the energy emitted by a particle per second is:

$$\frac{8\pi r_p^2 h c^2}{\lambda^5} \frac{d\lambda}{e^{\frac{hc}{\lambda k_B T}} - 1} = kI$$
(4.2)

where *I* is the signal level from a PMT filtered at the wavelength, λ , and *k* – is the proportionality factor.

Using Eq. (4.2), the relation between the maximum temperature inferred by the emission signal profile (Fig. 4.3) which serves as an initial temperature of the emission decay profile, T_i , and the final temperature of the cooling curve T_f (corresponding to the intensity reduced to 10% of its maximum value) is obtained as:

$$T_f = \frac{hc}{\lambda k_B} \ln^{-1} \left[1 + 10 \left(\exp\left(\frac{hc}{\lambda k_B T_i}\right) - 1 \right) \right]$$
(4.3)

The initial temperature of the cooling curve is expected to be in the range of 2000 - 4000 K based on previous experiments using laser-heated metal particles. It can be measured using color pyrometry; however, the accuracy of this

measurement is low. Instead, in the present analysis it is treated as a variable parameter of the problem and the sensitivity of the result to its variation within a reasonable range is determined. The final temperature obtained from Eq. (4.3) is used in the model of particle cooling as described below.

4.3 Cooling Model

The particle cooling is modeled using the Fuch's approach described in Chapter 1 in the quasi-steady heat transfer approximation, which assumes that characteristic time for particle cooling is much longer than the characteristic time of equilibration of molecular distribution near the particle. As follows from discussion in [60], the quasi-steady approximation is typically applicable to the conductive heat transfer problems between dense solid particles and gases with Kn = O(1). Then, the rate of change of particle temperature is defined by the energy flow towards the particle, \dot{E} , and radiation:

$$\frac{4}{3}\pi r_p^3 c_p \rho_p \frac{dT_p}{dt} = -\dot{E} - 4\pi r_p^2 \varepsilon \sigma \left(T_p^4 - T_\infty^4\right)$$
(4.4)

 c_p and ρ_p are the particle heat capacity and density, correspondingly. In the absence of Stefan flow for non-reactive particles, the local equilibrium Maxwellian distribution is considered both at the Knudsen layer and at the particle surface. Then the energy flow rate across the Knudsen layer can be obtained from Eq. (2.18) by accounting only for the gaseous component, Ar, setting $\dot{m} = 0$, and neglecting the term with the heat conductivity q_c :

$$\dot{E} = \alpha \sqrt{\frac{8\pi M}{RT_{\delta}}} r_p^2 p \left(c - \frac{R}{2M} \right) \left(T_p - T_{\delta} \right)$$
(4.5)

Heat capacity of noble gases, in particular, Ar, has a very weak temperature dependence (close to the theoretical value of monoatomic ideal gas 5/2R). A constant value of $c = 20.786 J / (mol \cdot K)$ is used in the calculations.

In a quiescent, infinite, continuous region, the only mechanism of heat transfer is conductivity, and the heat flow rate can be written as:

$$\dot{E} = 4\pi r_{\delta} \int_{T_{\infty}}^{T_{\delta}} k(T) dT$$
(4.6)

k(T) is the thermal conductivity of Ar. The values of thermal conductivity are calculated using the formulas reported in [61]. Equations (4.4-4.6) are solved numerically with the initial condition:

$$t = 0: T_p = T_i \tag{4.7}$$

 T_i is a variable parameter of the problem, and the condition for the time of decay defined as,

$$t = t_d : T_p = T_f \tag{4.8}$$

where T_f is found from Eq. (4.3) for a given, predetermined value of T_i .

The procedure for solving Eqs. (4.4)-(4.8) is as follows:

- 1. For a given temperature, T_i , find the value of T_f using Eq. (4.3).
- 2. Set t = 0 and the initial particle temperature, $T_p = T_i$.
- 3. Find the value of T_{δ} at the time step t from the algebraic equation

$$\alpha \sqrt{\frac{8\pi M}{RT_{\delta}}} r_p^2 p\left(c - \frac{R}{2M}\right) \left(T_p - T_{\delta}\right) - 4\pi r_{\delta} \int_{T_{\infty}}^{T_{\delta}} k\left(T\right) dT = 0$$
(4.9)

Equation (4.9) follows from continuity of energy flow, Eqs. (4.5), (4.6). A standard Matlab library function *fzero* is used to solve the equation. 4. Find the value of $T_p(t + \Delta t)$ for the next time step from the discretized version of Eq. (4.4). The explicit scheme is used in the current calculations.

5. If $T_p > T_f$, set $t = t + \Delta t$ go to the step 3, otherwise stop the calculations.

The precision of the found solution, cooling time t_f , depends on the time step $\Delta t \cdot \Delta t = 1 \mu s$ is used in the current calculations, which is about two orders of magnitude shorter than the experimental cooling times.

4.4 Results and Discussion

The calculations are performed for different values of T_i , in the range from 2000 up to 4000 K. The minimum value of 2000 K is selected here based on sensitivity of the PMT: for the signal to be distinguishable, i.e., above the noise level, the particle temperature should be higher than approximately 1800 K. According to Eq. (4.3), the initial temperature $T_i = 2000 K$ corresponds to $T_j = 1634 K$ which is just below the PMT sensitivity limit. The thermal accommodation coefficient is varied to find the closest fit of modeled decay times to experimental results. Since emissivity of the burning particles, in particular Zr particles, considered here, is not well-known, the effect of emissivity on decay times is also considered.

Figure 4.4 represents the experimental cooling times and the results of calculations for various temperatures and thermal accommodation, $\alpha = 1$. The emissivity, ε , is taken as 1 as well for these calculations. The maximum difference in cooling times for the range of initial temperatures from 2000 to 4000 K and corresponding particle sizes considered, is less than 20 µs, which is a relatively weak effect. Thus, the sensitivity of the predicted cooling time to the

initial temperature is low. For the purposes of the current work, estimation of thermal accommodation coefficient, results will be illustrated for the initial temperature of 2000 K.

An important conclusion that can be drawn from Fig. 4.4 is that the complete accommodation of gaseous molecules by the particle surface, i.e., $\alpha = 1$, cannot adequately describe the heat transfer processes: all the cooling times obtained using this value of thermal accommodation coefficient differ from experimental data by at least an order of magnitude. Therefore, accommodation coefficient value is much less than unity.



Figure 4.4 Cooling time vs. particle diameter: experimental data (points) and results of calculation (solid lines) for various initial temperatures. Thermal accommodation coefficient $\alpha = 1$, emissivity $\varepsilon = 1$.

Figure 4.5 illustrates the results for initial temperature at the cooling curve $T_i = 2000K$ and various thermal accommodation coefficients. The best fit of theoretical calculations with experimental results is obtained at $\alpha = 0.005$. At the same time, the experimental dependence of cooling times on particle diameter is still much weaker than predicted by the theoretical model. Although only results for $T_i=2000$ K are shown in Fig. 4.5, the slopes of the trendlines predicted for

different maximum temperatures are hardly affected by selection of the value of T_i . Thus a weak dependence of the cooling time on the particle diameter cannot be explained in the framework of the current model assuming constant accommodation coefficient (or emissivity, as discussed below) for particles of different dimensions. Note also that if larger particles are generally heated to lower temperatures than smaller particles, the effect of the particle size on its apparent cooling time would be effectively reduced, making the experimental data closer to the calculation. However, it is unlikely that the experimental trend would be matched well, based on a relatively weak effect of the initial temperature on the cooling time, as shown in Fig. 4.4.



Figure 4.5 Cooling time vs. particle diameter: experimental data (points) and results of calculation (solid lines) for various thermal accommodation coefficients. Initial temperature 2000 K, emissivity $\varepsilon = 1$.

Figure 4.6 illustrates the results of variation of emissivity for T=2000 K and $\alpha = 0.005$. The decrease of emissivity leads to an almost parallel shift of the decay time curve towards longer times.



Figure 4.6 Cooling time vs. particle diameter: experimental data (points) and results of calculation (solid lines) for various emissivities. Initial temperature 2000 K, thermal accommodation coefficient, $\alpha = 0.005$.

It is interesting that the closest fit with the experimental data is obtained for $\alpha = 0.005$, which is the upper limit reported in for silica nanoparticles accommodation coefficients at the same temperature range, around 2000 K [55].

Summarizing comparisons of calculations and experiments, it is noted that a discrepancy remains between the experimental decay times and those obtained from the model. Experimental cooling times are almost independent on the particle size for diameters less than 1 μ m.

Several explanations can be put forward that require further elaboration. First, the theoretical curves in Figs. (4.4) - (4.6) are plotted for constant initial temperature of the decay profile, which assumes that particles of different diameters are heated to the same temperature before the emission signal starts decaying. If we assume that smaller particles are heated by the laser to higher temperature, qualitatively, the decay time dependence in Figs. (4.4) - (4.6) would become closer to the experimental trend. Therefore, it would be desirable to obtain experimental temperature profiles for each particle, based on which the corresponding initial temperature for decay profile could be used in the model. Another possible factor of discrepancy could be the assumption of temperature independent accommodation coefficient in the model. Since temperature vs. time profiles during cooling for particles of different sizes is different, the dependence of accommodation coefficient on temperature would change the total decay time. The change of accommodation coefficient with the particle size, as well as dependence of the emissivity on the particle size, are also possible issues that need to be addressed to reduce the errors in the model.

Experimental data can also introduce some error. For example, as seen in Fig. 4.2, the fraction of very fine particles obtained by the laser-scattered light technique is slightly higher than in the distribution obtained by Coulter. Since Fig. 4.2 depicts volume fraction distribution, the difference in number size distribution can be significantly higher. Note also that this discrepancy exactly in the range of particle diameters affecting the experimental data most significantly, because of the respectively large numbers of fine particles. This issue can be resolved by using particles with narrower size distribution.

4.5 Conclusions

A method of experimentally identifying thermal accommodation coefficient for fine metal particles is developed and tested. A combination of in situ size measurements by laser scattering, and heating particles in a CO_2 laser is used to find the time of emission intensity decay for Zr particles of different diameters cooled in Ar atmosphere. By modeling the decay times using a two-layer Fuchs' model and comparing the results of modeling with the experimental data, a range of accommodation coefficient values is found that allowed to match the experimental data and calculations. It is shown that the thermal accommodation coefficient is much smaller than unity, consistently with recent literature reports [55]. At the same, a discrepancy between the theoretical results and experiments is observed: submicron size particles have a much weaker dependence of the decay time vs. diameter than predicted by the model. This discrepancy could not be interpreted assuming constant initial temperature, accommodation coefficient, and emissivity for particles of different diameters. Future experiments should address the effect of the above parameters, which should eventually be represented in the model

CHAPTER 5

CONCLUSIONS

A model of heat and mass transfer during heterogeneous combustion of small fuel particles is developed, applicable to a wide range of particle sizes, both coarse particles, for which combustion occurs in the diffusion-limited regime, and fine particles (of the order of several μm and less), for which the collisions of gas molecules with the particle surface is the rate-controlling process. The focus of this work is on transport properties during combustion of particles in the transition regime, when Knudsen number defined as a ratio of molecular mean free path over particle radius; predicted to be in the order of one. Therefore, infinitely fast chemical reaction kinetics is assumed.

As a model system, combustion of Zr in air is considered for the range of particle diameters from 1 μm to 200 μm . Theoretical combustion temperatures and burn times are compared with the data available from the literature. Initially, the complete energy accommodation of gas molecules to the particle surface is assumed. Combustion of large particles is successfully described by this model, in accord with the experimental data. For the small particles, diameters of order of several μm , the burn times are underestimated and particle temperatures overestimated compared to the experimental data.

The effect of changing particle size occurring during combustion on the temperature and rate of combustion of Zr particles in air is considered. The effect is found to be relatively weak and inadequate for resolving discrepancies between the model and experimental data. Although it is proposed that the main possible cause of these discrepancies is the assumption of infinitely fast heterogeneous

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kinetics, other factors, such as the value of thermal accommodation coefficient or particle emissivity, especially if they are particle size-dependent, could substantially affect the comparisons of the model and experiments.

One of the major outcomes of this model is a conclusion, which is often overlooked in combustion modeling, that starting from about $10\mu m$ and less, the continuous transport process model does not provide an adequate description of the heat and mass transfer processes between the gas and the particle. For this range of particle sizes, the collision of gas molecules with the particle surface, as well as energy exchange of molecules with the particle, i.e., thermal accommodation coefficient, become important. Since the kinetics of reaction is usually a thermally activated process and has highly nonlinear temperature dependence, the proper thermal accommodation coefficient values must be used in the combustion models.

The lack of data on accommodation coefficients at high temperatures, relevant to combustion processes, does not allow currently developing the quantitative models with finite chemical kinetics. Therefore, efforts are directed towards developing methods of finding the accommodation coefficients of various gas-condensed particle systems.

A technique combining the CO₂ laser heating and in situ laser-scattered particle sizing is used to find the cooling time of a metal particle of a given size in inert gaseous atmosphere. In particular, experiments are performed on laser heating and cooling Zr particles in the range of sizes of $0.5 - 5 \ \mu m$ in Ar. Applying the transition heat transfer model for small particles and varying the accommodation coefficient, the value of the coefficient that gives the best fit of the modeled cooling time to the experimental cooling time is found. The value of

accommodation coefficient of Ar to Zr is found to be about 0.005 which agrees with recent reports investigating the thermal accommodation coefficient for fine, high temperature particles [55].

A discrepancy between theoretical and experimental cooling times, and especially, between the predicted and observed effect of particle size on the cooling time, could not be removed in the framework of the present model. The experimental cooling time has a much weaker dependence on the particle diameter than that predicted by the model. Possible sources of errors are analyzed and some corrections to the experimental procedure as well as possible changes in the model are considered.

As a result of investigation conducted and described in this thesis, the following future studies can be proposed. First, the data on thermal accommodation coefficient values as a function of the particle size should be obtained. This is critical for developing realistic models of combustion of small condensed particles in gaseous atmospheres. The thermal accommodation coefficient can be obtained by heating particles by CO₂ laser in inert environment and allowing them to cool while recording the temperature traces using twochannel PMT. Direct measurements of the cooling particle's temperatures will allow modeling details of the cooling process. It is desirable to narrow down the particle size distribution, and achieve more accuracy in the in situ particle sizing. A possibility of the temperature effect on the accommodation coefficient as well as on emissivity should be considered and introduced into the model. It is not clear a priori how the temperature dependence of accommodation coefficient can be modeled, therefore it may be necessary to solve the inverse problem: find temperature dependence of accommodation coefficients by fitting modeled data to the experimental data.

After thermal accommodation coefficients in inert environments are found, the experiments on combustion of different metal-gas systems with different ratios of oxidizer-inert gas (e.g. Ar-O₂) in a gas mixture can be conducted, where inert gas serves as the bath gas and accounts for the major part of heat transfer in a particle-gas systems. The results of these experiments would be parameters of combustion, such as particle temperature and burn time for a wide range of particle diameters.

The model should be developed including chemical kinetics and as a general case, gasification of condensed phases, either condensed products or fuels. Using particle-size dependent thermal accommodation coefficients in inert gases, and results of combustion of condensed particles in inert gas-oxidizer mixture, the procedure for finding reaction kinetics can be developed, in future work.

APPENDIX A

ENERGY FLOW RATE ACROSS THE KNUDSEN LAYER

An expression for the mass flow rate with the Grad distribution at the Knudsen layer interface obtained in references [22, 23] is used without changes. Care should be exercised using this expression since it is obtained in the assumption of small dimensionless heat flow, the condition which for the case considered here, can be written as:

$$\left| \frac{\sqrt{2\pi} q_{ox} M_{ox}}{\sqrt{RT_{\delta}} p Y_{ox,\delta} M_{\delta}} \right| <<1$$
(A1)

where q_{ox} is the heat flux at the Knudsen layer interface transferred by oxygen molecules due to conduction q_{ox}^{c} and diffusion of enthalpy which, taking into account Eq.(2.5), is:

$$q_{ox} = q_{ox}^{c} + \dot{m} \left(1 - Y_{ox,\delta} \right) h_{ox} \left(T_{\delta} \right)$$
(A2)

The energy exchange rate between the particle surface and Knudsen layer interface is deduced in refs. [22, 23, 29] using two major assumptions: a) translational energy of molecules is uncorrelated to the internal energy (i.e. rotational and vibrational energies); b) the mass flow rate is sufficiently small so that:

$$\left|\frac{\dot{m}}{4\pi r^2 \sqrt{2}p} \sqrt{\frac{RT}{M_i}}\right| << 1 \tag{A3}$$

Then, in a general case of multi-component gas, the rate of energy transfer by the *i*-th component can be written as:

$$\dot{E}_{i} = \sqrt{\frac{8\pi}{RT_{\delta}}} r_{p}^{2} p M_{\delta} \frac{Y_{i,\delta}}{M_{i}} \left[\left(U_{i,p} - U_{i,\delta} \right) + \frac{2R}{M_{i}} \left(T_{p} - T_{\delta} \right) \right] + \left(1 - \frac{r_{p}^{2}}{2r_{\delta}^{2}} \right) \dot{m}_{i} \left(U_{i,p} + \frac{2RT_{p}}{M_{i}} \right) + \frac{r_{p}^{2}}{2r_{\delta}^{2}} \left\{ \frac{5RT_{\delta}}{2M_{i}} \dot{m}Y_{i,\delta} + q_{i} \right\}$$
(A4)

where $U_{i,p}$ and $U_{i,\delta}$ are the internal energies per mass (i.e. rotational and vibrational energy) of molecules of the *i*-th component at the particle surface and Knudsen layer interface, respectively, and q_i is the heat flux of the *i*-th component at the Knudsen layer interface, similar to Eq. (A2), which in general case is:

$$q_i = q_i^c + \left(\dot{m}_i - mY_{i,\delta}\right) h_i\left(T_{\delta}\right)$$
(A5)

The internal energy per mass of molecules of the *i*-th component can be written as

$$U_i(T) = h_i(T) - \frac{5}{2} \frac{RT}{M_i}$$
 (A6)

Substituting Eqs. (A5), (A6) into Eq. (A4), and performing summation over all gas components, the total energy flow rate can be obtained:

$$\dot{E} = -\sqrt{\frac{8\pi}{RT_{\delta}}} r_{p}^{2} p M_{\delta} \sum_{i} \frac{Y_{i,\delta}}{M_{i}} \left[\left(h_{i}(T_{p}) - h_{i}(T_{\delta}) \right) - \frac{R}{2M_{i}} \left(T_{p} - T_{\delta} \right) \right] + \left(1 - \frac{r_{p}^{2}}{2r_{\delta}^{2}} \right) \sum_{i} \dot{m}_{i} \left(\left(h_{i}(T_{p}) - h_{i}(T_{\delta}) \right) - \frac{RT_{p}}{2M_{i}} \right) + \frac{r_{p}^{2}}{2r_{\delta}^{2}} \sum_{i} \left\{ \left(\dot{m}_{i} - \dot{m}Y_{i,\delta} \right) \left(h_{i}(T_{\delta}) - \frac{5RT_{\delta}}{2M_{i}} \right) + q_{i}^{c} \right\} + \sum_{i} h_{i} \left(T_{\delta} \right)$$
(A7)

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