



Metal-based nanoenergetic materials: Synthesis, properties, and applications



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ABSTRACT

Metal particles are attractive candidate fuels for various propulsion and energy-conversion applications, primarily due to their high energy densities. Micron-sized particles present several drawbacks, such as high ignition temperatures and particle agglomeration, resulting in low energy-release rates. Nanoparticles, on the other hand, are quite attractive due to their unique and favorable properties, which are attributed to their high specific surface area and excess energy of surface atoms. As a result, there is a growing interest in employing metal nanoparticles in propulsion and energy-conversion systems. The present work provides a comprehensive review of the advances made over the past few decades in the areas of synthesis, properties, and applications of metal-based energetic nanomaterials. An overview of existing methods to synthesize nanomaterials is first provided. Novel approaches to passivate metal nanoparticles are also discussed. The physicochemical properties of metal nanoparticles are then examined in detail. Low-temperature oxidation processes, and ignition and combustion of metal nanoparticles are investigated. The burning behaviors of different energetic material formulations with metal nanoparticles such as particle-laden dust clouds, solid propellants, liquid fuels and propellants, thermite materials, and inter-metallic systems are reviewed. Finally, deficiencies and uncertainties in our understanding of the field are identified, and directions for future work are suggested.

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1. Introduction

Energetic materials release large amounts of chemical energy quickly in the form of heat during combustion. In monomolecular energetic materials, fuel and oxidizer groups are present within a single molecule and the reaction rate is thus controlled by breaking and formation of chemical bonds (chemical kinetics) [1]. The energy densities of monomolecular energetic materials are, however, limited [1]. This can be attributed to chemical stability requirements and limitations on the physical density of materials [2]. Composite energetic materials, on the other hand, are synthesized by physical mixing of fuel and oxidizer particles. Fig. 1 shows a composite energetic nanomaterial consisting of aluminum and molybdenum trioxide (MoO_3) particles [3]. The nano-aluminum particles are spherical in shape and have an average diameter of 80 nm, while the MoO_3 particles are sheet-like particles with a length of 1 μm and thickness of 20 nm. The solid propellant employed in the U.S. Space Shuttle solid rocket boosters is another example of a composite energetic material. It consists of

ammonium perchlorate crystals and aluminum particles in a polymer binder [4]. The overall reaction rate of composite energetic materials is typically controlled by mass diffusion, since the fuel and oxidizer particles are separate entities [1]. The resulting rates of energy release are lower than the corresponding values that could be attained in a kinetically-controlled process [1].

The energy density of conventional energetic materials can be substantially increased by the addition of metal particles. Fig. 2 shows enthalpies of combustion of monomolecular energetic materials and metals in pure oxygen under stoichiometric conditions. On a volumetric basis, the enthalpy of combustion of metals is as high as 138 kJ/cm^3 , substantially greater than those of monomolecular compounds ($\sim 10\text{--}30\text{ kJ}/\text{cm}^3$). One of the most energetic, beryllium, is seldom used, due to its extreme toxicity, relative scarcity, and high cost [5]. Among the elements listed here, boron has the highest volumetric energy density of 138 kJ/cm^3 . Ignition of boron particles is, however, significantly delayed by the presence of an oxide (B_2O_3) layer [6–8]. The ignition temperatures of boron particles in oxygenated environments vary in the range of 1500–1950 K, regardless of

Nomenclature

a	distance between energy barrier maximum and adjacent minimum
A	surface area, pre-exponential constant, Hamaker constant
B	mass transfer number
c	speed of light in vacuum, molecular speed
C	concentration
CE	cohesive energy
C_p	constant-pressure specific heat
C_v	constant-volume specific heat
D	diffusivity
D_0	pre-exponential factor
Da	Damkohler number
d_{ag}	agglomerate diameter
D_f	fractal dimension
D_p	particle diameter
E	energy, activation energy, electric field
E_A	activation energy
f	fraction of exposed core area, fraction of surface atoms in the particle
G_c	critical Gibbs free energy for nucleation
g	acceleration due to gravity
H	enthalpy
h	atomic diameter, heat transfer coefficient, oxide layer thickness
h_f	enthalpy of formation
h_{fg}	enthalpy of vaporization
h_m	enthalpy of melting
H_R	enthalpy of reaction
$\hbar$	Planck's constant
i	stoichiometric fuel-oxidizer mass ratio
I	radiation intensity, nucleation rate
I_{sp}	specific impulse
J	diffusion flux
K	bulk modulus
k	rate constant
k_B	Boltzmann constant
LE	lattice energy
m	mass
$\dot{m}$	rate of mass change/consumption
M	molecular weight
MEC	minimum explosion concentration
MW	molecular weight
N	number density of molecules
n	entrainment index, number of ions per unit area
p	pressure
p_L	Laplace pressure
q	charge, heat of oxidation
Q	heat, heating rate
$\dot{Q}$	heat transfer rate
R	radius, gas constant
r_b	burning rate
R_c	core radius
R_p	particle radius
S	entropy
S_L	laminar flame speed
T	temperature
T_m	melting temperature
t	time
t_b	burning time
u_p	particle velocity
V	volume, Mott potential
W	energy barrier

X	mole fraction, reaction conversion factor
X_{eff}	effective oxidizer mole fraction
Y	mass fraction
<i>Greek</i>	
$\dot{\omega}$	rate constant
ρ	density
σ	surface tension, stress, Stefan-Boltzmann constant
ν	molar volume, attempt frequency
ε	emissivity
ω	frequency
$\dot{\omega}$	reaction rate
δ	oxide layer thickness, surface layer thickness
λ	thermal conductivity
α	accommodation coefficient, thermal diffusivity
γ	adiabatic constant
θ	Debye temperature, degree of superheating
β	heating rate, burning rate constant, normalized energy barrier
Ω	volume per displaced ion
α_m	magnetic permeability
ϕ	sticking probability
<i>Subscript</i>	
a	ambient
ad	adiabatic
ag	aggregate
am	amorphous
b	boiling, bulk material, black body
c	core, combustion
$chem$	chemical
$cond$	conduction
cr	critical
$diff$	diffusion
eff	effective
F	fuel
f	flame, formation
ign	ignition
in	internal
$init$	initial
l	liquid
$loss$	heat loss
lw	liquid water
m	melt, mixture
min	minimum
O	oxidizer
ox	oxidation
p	particle
$poly$	polymorphic phase changes
R	reaction
r	radial
rad	radiation
ref	reference
s	solid, surface
sur	surroundings
tr	polymorphic phase transformation
u	unburned
vap	vaporization
vol	volatilization
w	wall
wv	water vapor
<i>Superscript</i>	
b	bulk

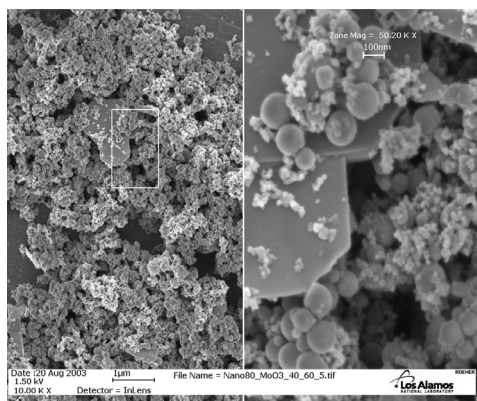


Fig. 1. High magnification scanning electron microscopy (SEM) image of nanocomposite consisting of aluminum and molybdenum trioxide (MoO_3) particles (reprinted from [3] with permission of Elsevier).

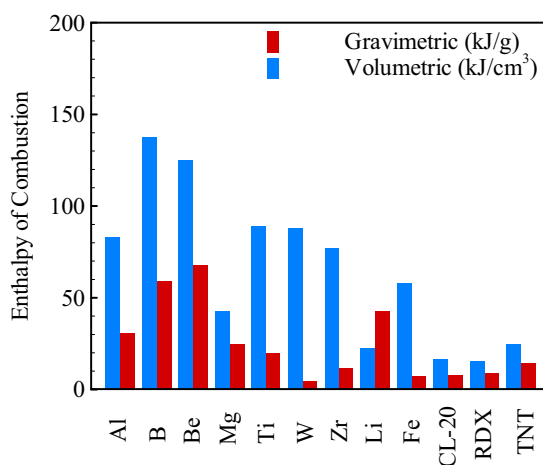


Fig. 2. Volumetric and gravimetric enthalpies of combustion of metals and monomolecular energetic materials in pure oxygen at stoichiometric conditions.

particle size [6,8]. In certain cases, energy release is significantly diminished in hydrogen-containing gases by the formation of metastable HBO_2 species [7]. These difficulties of ignition and combustion have limited the utilization of boron in practical applications, but novel passivation materials and approaches are being considered to enhance the combustion characteristics of boron particles. Bellott et al. [9], for example, employed halogen based passivation materials and studied the oxidation of 10–150 nm boron particles using thermogravimetric analysis at a heating rate of $10^\circ\text{C}/\text{min}$. The combustion efficiency of fluorine-coated boron particles was estimated to be $\sim 75\%$, greater than that of conventional boron particles ($\sim 50\%$) [10].

Aluminum is the most abundant metal in the Earth's crust and is relatively safe to use [4]. Aluminum particles can be used in space [4] and underwater [11] propulsion, explosions [12], pyrotechnics [13], and hydrogen generation applications [14]. One of the main issues concerning micron-sized aluminum (Al) particles is their high ignition temperatures [15]. Micron-sized and larger Al particles ignite at temperatures as high as 2350 K [15], and this high ignition temperature contributes to lower energy-release rates in various practical applications. Another important issue is particle agglomeration [16,17], which lowers the performance by as much as 10% [5]. As micron-sized Al particles ignite at higher temperatures, particles tend to coalesce and agglomerate on the propellant surface in a solid rocket motor [18]. The presence of agglomerates results in two-phase flow losses, as they slow the velocity of the flow, and fail to fully transfer the thermal energy of the flow [5].

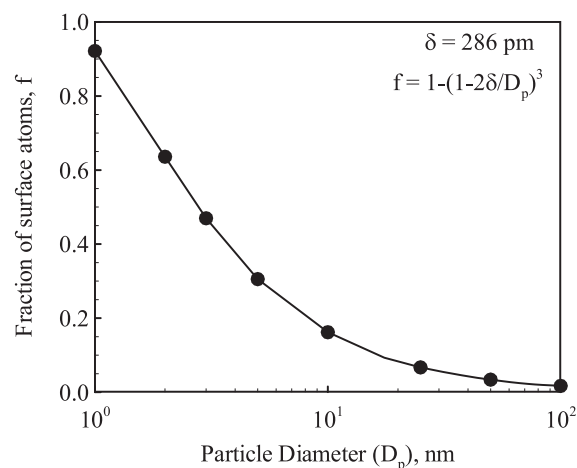


Fig. 3. Effect of particle size on the fraction of atoms on the surface layer of an aluminum particle.

Nanoparticles have recently attracted considerable attention due to their unique and favorable physicochemical properties, as compared with their micron-sized counterparts [19]. For example, bulk gold is a well-known inert material. If the diameter of gold particles is reduced to 1–5 nm, they exhibit excellent catalytic properties [20]. The physicochemical properties of nanoparticles are size dependent. For example, the melting temperature of nano-aluminum particles decreases with decreasing particle size, from about 930 K at 10 nm to 673 K at 3 nm [21]. A qualitatively similar trend is observed for the ignition temperature of aluminum particles. It decreases with decreasing particle size, from a value as high as 2350 K at 100 μm to ~ 1000 K at 100 nm [15].

The unique behavior of nanoparticles can be partly attributed to the presence of a large number of atoms on the surface and the excess energy associated with these surface atoms. Fig. 3 shows the effect of particle size on the fraction of atoms in the surface layer of aluminum particles. The fraction of atoms in the surface layer of the particle, f , can be calculated using the following equation [22]:

$$f = 1 - \left(1 - \frac{2\delta}{D_p}\right)^3, \quad (1)$$

where D_p is the particle diameter and δ the thickness of the surface layer. The surface layer thickness can be taken to be equal to the atomic diameter of aluminum (286 pm). The fraction of surface atoms in the particle increases from 0.17 to 16%, when the particle size decreases from 1 μm to 10 nm. The surface atoms have lower coordination numbers and greater energies than the atoms in the interior regions of the particle. As a result, properties of the particle are size dependent at nano-scales.

Although aluminum nanoparticles tend to have lower ignition temperatures than their micron-sized counterparts, the problem of sintering and aggregation persists due to solid-state diffusion and/or viscous flow [23]. Furthermore, the high specific surface area of nanoparticles ($\sim 10\text{--}50\text{ m}^2/\text{g}$) can result in high propellant viscosity [24] and poor mechanical strength [25]. These can decrease propellant density, produce erratic combustion, or even cause motor failure [26]. For these reasons, nanoaluminum particles are not currently used in practical solid propellants.

Use of metal nanoparticles in practical applications is also inhibited by low active metal content. Metal particles are covered by a passivating oxide layer; for aluminum, the oxide layer thickness is in the range of 2–4 nm [27]. Fig. 4 shows the effect of particle size on the mass fraction of the oxide layer in an aluminum particle. The oxide layer thickness is taken to be 3 nm. The mass fraction of the oxide layer increases with decreasing particle size, reaching a

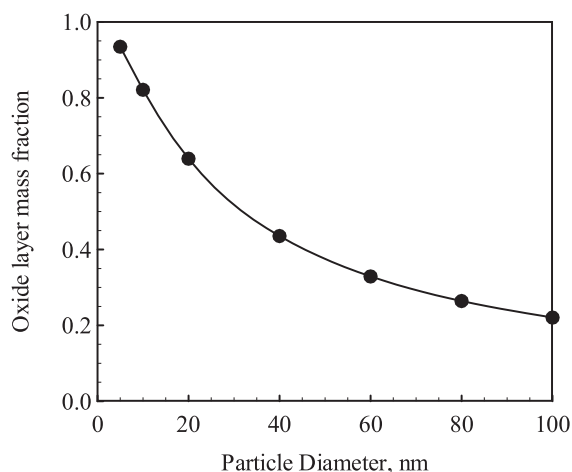


Fig. 4. Effect of particle size on the mass fraction of the oxide layer in nanoaluminum particles.

value of about 50% of the particle mass at 38 nm, and the particle energy density is substantially diminished. Attempts to enhance the aluminum content of nano-aluminum particles have met with mixed results. For example, replacement of the alumina layer with nickel coating increases the active aluminum content of nano-aluminum particles by only about 4% [28]. Other materials such as perfluoroalkyl carboxylic acids [29,30] and oleic and stearic acids [31] have also been considered to enhance the energetics of nanoaluminum particles.

It should be noted that although nanoparticles, in theory, promise good energy release rates, they pose serious safety issues during particle synthesis, handling, and storage. Nascent metal nanoparticles are pyrophoric and can ignite spontaneously when exposed to an oxidizing gas at room temperature [22]. For micron-sized and larger particles, oxidation reactions typically result in the formation of a stable 2–4 nm thick oxide layer [32]. At nano-scales, the heat release due to chemical reactions could be sufficient to ignite particles due to their low volumetric heat capacity. For example, nascent aluminum particles with diameters lower than a critical value are predicted to be pyrophoric, and theoretical analysis suggests that the critical particle size varies in the range of 10–100 nm [22,33,34]. Great care must therefore be taken when handling metal nanoparticles.

The potential benefits of nanomaterials have not yet been completely realized. As mentioned in the context of aluminum, nanoparticles aggregate significantly before and during combustion [35]. Although the initial powder may consist of nano-sized particles, aggregates have lower specific surface area and diminish the reactivity of the powder. The conventional method of preparing composite energetic materials consists of physical mixing of fuel and oxidizer particles by hand or by sonication. Fig. 5 shows a scanning electron micrograph of aggregates of nano-sized Al and CuO particles prepared using the sonication method [36]. It is apparent that the mixture consists of aggregates that lack uniformity in size and shape, with diffusion length scales on the order of few microns [36]. Recent advances in molecular self-assembly, supramolecular chemistry, and synthesis techniques that link nano and macro-scale structures are likely to pave the way for advanced next-generation nano-engineered energetic materials. These materials will have higher energy density, improved chemical responsiveness, better controlled energy and mass generation rates, enhanced reliability and reproducibility, reduced sensitivity and enhanced safety, and increased storage life.

Recent advances in the fabrication and use of metal-based nano-energetic materials, and the prospect of further progress in the field in the near future, demand a comprehensive review of the literature.

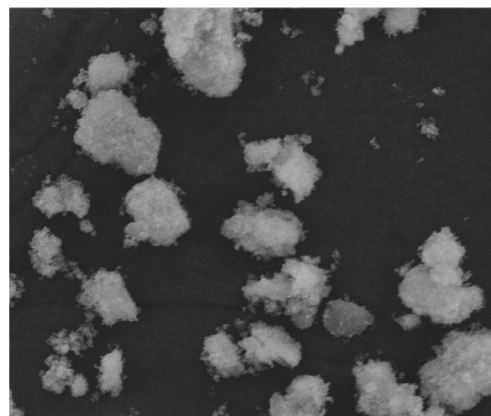


Fig. 5. Scanning electron micrograph of aggregates of aluminum and CuO nanoparticles prepared using the sonication method (reprinted from [36] with permission of American Chemical Society).

Previous reviews on the subject have tended to focus on specific aspects or issues. In these reviews, more emphasis was placed on subjects such as classical theories and applications [37], manufacturing processes and nanocomposite energetic materials [38], ignition mechanisms [39], combustion of nano-aluminum particles [40], and the role of nanoenergetics in MEMS [41]. Tremendous progress has been made in the past decade, however.

The overall aim of the present study is therefore to conduct an up-to-date comprehensive review and compile and discuss findings pertaining to the synthesis, properties, and applications of metal-based nanoenergetic materials. Isolated metal nanoparticles and powders and energetic material formulations based on metal nanoparticles including particle laden dust clouds, liquid fuels, solid and liquid propellants, thermite, and intermetallic systems are discussed. The work is organized into 15 sections. Section 2 provides an overview of techniques employed to synthesize nanomaterials. Novel approaches for passivating metal particles are discussed in Section 3. Section 4 reviews the physicochemical properties of metal nanoparticles. Sections 5 and 6 concern low-temperature oxidation processes and the pyrophoricity of metal nanoparticles, respectively. Sections 7 and 8 address respectively the ignition and combustion behaviors of metal nanoparticles. The burning behaviors of different energetic material formulations based on metal nanoparticles including particle-laden dust clouds, liquid fuels and propellants, particle and liquid oxidizer systems, solid propellants, thermites, and inter-metallic systems are reviewed in Sections 9–14, respectively. Conclusions and directions for future work are provided in Section 15.

2. Material synthesis

Material synthesis involves manufacture of nascent metal particles and passivation in a well-controlled oxidizing environment. Passivation ensures stability and preserves the active metal content of the particles. If possible, the manufacturing process should meet the following requirements: (1) applicability to a variety of materials (including metals and oxides); (2) ability to produce a wide and controllable range of particle sizes; (3) absence of impurities; (4) prevention of spontaneous reactions and agglomeration; (5) high level of productivity and economy; and (6) reproducibility. For laboratory studies, micron-sized particulates are manufactured by punch pressing of foils [42] and mechanical chopping of wires [43]; the resulting particles are ignited using a laser beam. Micro-arc discharge [44] and the plasma-jet technique [45] have also been employed to create molten metal droplets from a consumable electrode. In inert gas atomization, the molten metal stream is atomized by the impingement of an inert carrier gas. The resulting droplets condense to form solid particles. Particles produced using this technique has been

employed in a number of research works [46,47]. Note that in most studies, commercially available powders were employed. Manufacture of metal nanoparticles is an active research field and progress is expected in the near future. Commonly used methods of manufacturing nanoparticles are electric explosion of wires, inert gas condensation, flame synthesis, wet chemistry methods, and mechanical milling.

2.1. Electric explosion of wires

Ultrafine powders were first produced using electric explosion of wires by Abrams for radioactive aerosols [48]. The process was later applied to metals [49–60], alloys and inter-metallic compounds [61–64] and oxides [50,59,65,66]. In this technique, the wire explodes under the action of large current density. Fig. 6 shows the schematic of the experimental setup [67]. The capacitor battery is first charged from the power source. The wire driving mechanism feeds the wire into the gap between electrodes. When the wire reaches the high-voltage electrode, the commutator operates and electric discharge occurs. The energy density in the wire exceeds the binding energy of the material and the wire explodes and releases a mixture of superheated vapor and boiling droplets into the ambient gas. The expansion of vapor and collision with ambient gas molecules cools the vapor, providing conditions for homogeneous nucleation of the solid phase. Inert gas is typically used to synthesize powders of metals and inter-metallic compounds, while chemically active gas such as oxygen is employed for oxides, carbides, and nitrides. The metal clusters coalesce and condense to form nano-sized particles, which are collected on the walls of the vessel. The particles are then passivated in a well-controlled oxidizing environment [31,54,55,68]. Electric explosion of wires has also been performed in liquid medium [58,69,70]. A notable advantage of exploding wires in a liquid medium is that the formation of micron-sized particles is suppressed due to the higher energy density, sufficient volume expansion, and faster cooling of the particles [58].

In the electric explosion process, the key parameters of concern are the energy density [52,53,71,72], pressure [50,57,59,60,73], gas environment [57], and wire radius [74]. Fig. 7 shows the effect of energy density on the size of particles produced by the electric explosion method [53]. For low energy densities, particle size is strongly dependent on energy density. This has been attributed to the transition between mechanisms of particle formation

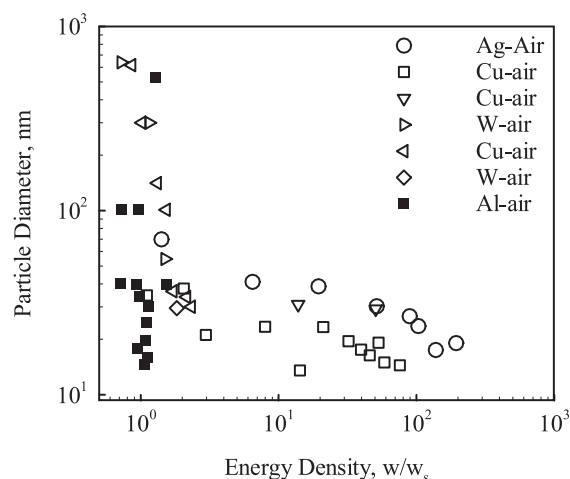


Fig. 7. Effect of energy density on particle size for electric explosion method (w_s is the sublimation energy of the material) (adapted from [53] with permission of Wiley).

mechanism, from liquid droplet to condensation nuclei (ions) mechanism [53]. The energy density, however, exerts a much weaker effect on the particle size for energy densities greater than the sublimation energy of the wire. In this regime, particles are formed only on the condensation nuclei, which are typically ions [53]. An increase in energy density results in an increase in number of ions and expansion velocity, thus resulting in smaller particle sizes [53]. Smaller particles can also be obtained by decreasing the gas pressure [50,57,59,60,73]. A lower pressure facilitates higher expansion velocity and fewer collisions (which are necessary for the growth of nuclei), thereby decreasing the particle size [75]. Particles tend to have a more spherical shape when they are formed at higher pressures [60].

Particle characteristics also depend on the type of ambient gas. Fig. 8 shows transmission electron microscopy (TEM) images of nanoaluminum particles produced in three different ambient gases and at different pressures [57]. Particles produced in nitrogen are highly irregular in shape, but the particles are spherical when formed in argon and helium environments. Although particle size decreases with decreasing pressure in argon, the situation is different for helium and nitrogen. It is speculated that gas thermal conductivity could influence size distribution as well. These phenomena are not properly understood and needs further investigation. The ambient gas also influences the content of particles [57]. The active aluminum content is diminished, for example, in a nitrogen environment due to the formation of aluminum nitride. The electric explosion process features high production rates and efficiency, with limited environmental contamination [75]. The particle size, however, typically ranges from a few nanometers to microns [76]. Achieving a narrow particle size distribution remains a major challenge.

2.2. Vaporization-condensation method

One of the most straightforward and simplest ways to synthesize nanoparticles is the vaporization-condensation method [77–80]. The approach is to achieve supersaturation by vaporizing the bulk material and cooling the resulting vapors by expansion, mixing with cooler gas, or by heat transfer. The resulting conditions favor the nucleation of the solid phase. Fig. 9 shows a schematic of the experimental setup of the inert gas condensation method [81]. The powder processing chamber is evacuated to a very low pressure ($\sim 10^{-4}$ mbar) and refilled with an inert gas. The metal wire is then fed onto the evaporator, which is a Joule-heated tungsten boat. The evaporator vaporizes the metal and vapors are carried by the inert gas flow into the chamber, where they condense to form

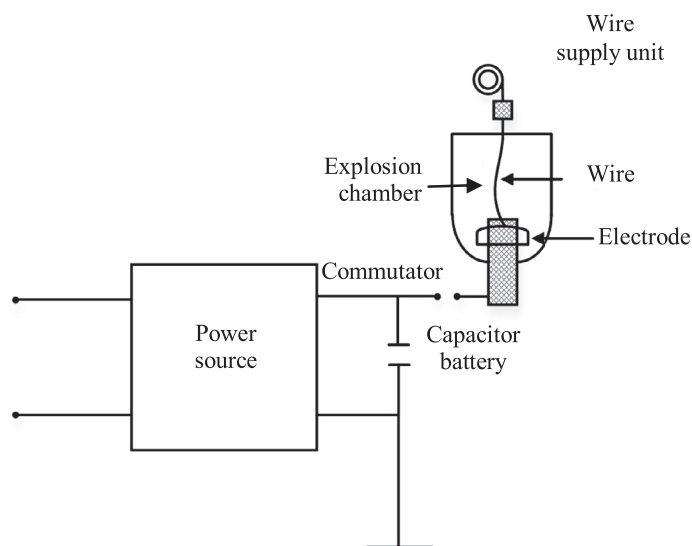


Fig. 6. Schematic of experimental setup for producing nano particles using electric explosion technique (adapted from [67]).

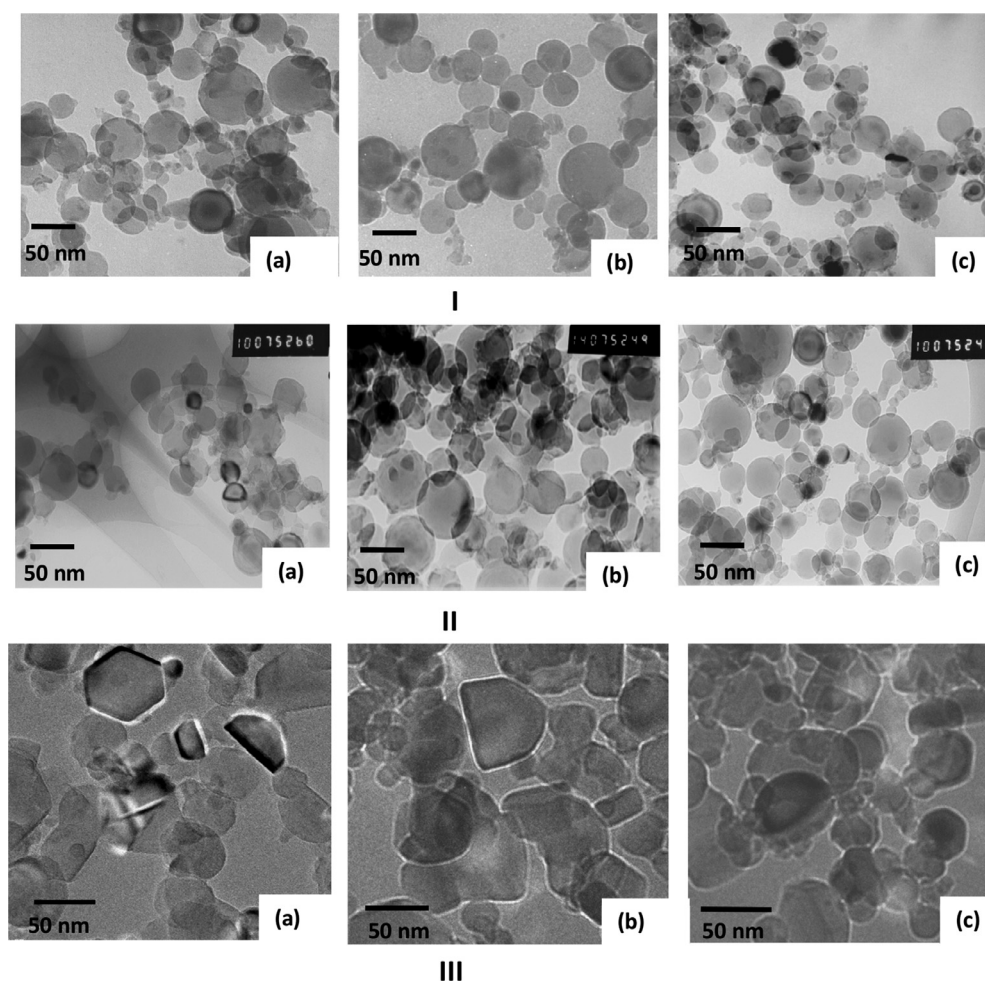


Fig. 8. Nanoaluminum particles manufactured by electric explosion method in (I) helium; (II) argon; (III) nitrogen environments at three different pressures of (a) 0.025 MPa; (b) 0.05 MPa; (c) 0.1 MPa (reprinted from [57] with permission of Elsevier).

nanoparticles. The particles are collected thermophoretically using a filter tube.

The formation and growth of particles in vaporization-condensation has been the focus of a number of theoretical studies [82–88]. Smaller particles can generally be obtained by lowering the pressure and molecular weight of the gas [78,81–83,86]. If the pressure is

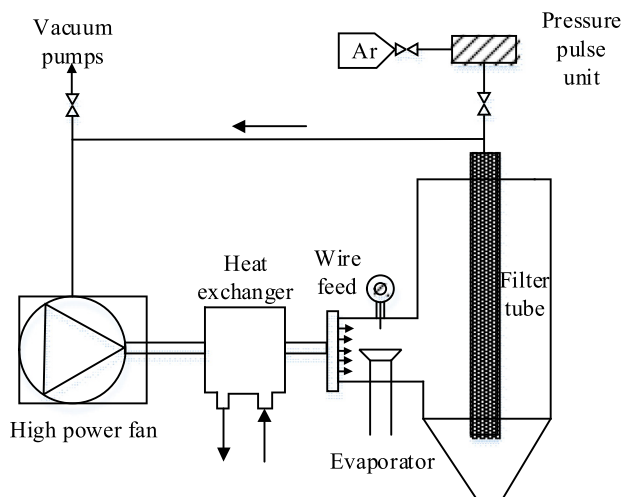


Fig. 9. Schematic of the experimental setup of the inert gas condensation technique (adapted from [81] with permission of Elsevier).

lowered, the vapor diffuses away from the evaporator and nucleation zones become more spread out [89]. This prevents particle growth by coagulation. Similarly, lighter inert gas atoms are less effective in confining the metal vapor and take away less momentum and energy from metal atoms during collisions [89], and so produce smaller particles. Other methods to lower particle size include increasing the cooling rate [82], adding oxygen [81], decreasing the wire feed rate [81], and imposing a forced convective flow on the inert gas [90,91]. Passivation is accomplished in oxygen gas and/or liquid solutions [92].

Powders of metal oxides can be synthesized by oxidizing metal particles produced by the conventional vaporization-condensation method [93–95] or by performing vaporization-condensation in a chemically active gas [96]. Note that materials with low boiling temperatures can be vaporized in a crucible or an oven. The temperature limits of oven or crucible material can restrict direct vaporization of high boiling point materials. More sophisticated techniques, such as inductive heating [97–99], laser heating/ablation [100–109], arc discharge [103,110], and sputtering [111–113] can be employed. While laser ablation is the process of removing material from a solid by irradiating it with a laser beam, sputtering involves bombarding the target material with high-velocity ions or atoms of an inert gas.

A notable adaptation of the conventional vaporization-condensation technique is the chemical vapor condensation (CVC) method, where the evaporative source is replaced by a chemical source [114–117]. This process combines rapid thermal decomposition and expansion of a precursor/carrier gas stream in a hot tubular reactor/

furnace with rapid condensation of the product particle species on a cold substrate [114]. This method, however, has some drawbacks, including incomplete heat transfer to precursor molecules, deposition of clusters on the furnace wall, and impurity entrainment from reactor walls [115,116]. This issue can be avoided by using the combustion flame chemical vapor condensation (CF-CVC) method [115]. In this method, precursor molecules are pyrolyzed by the flame, which is located outside the combustor [115]. Aggregation effects can be minimized by optimizing process parameters [118].

A wide range of materials can be produced by inert gas condensation [89]. Furthermore, the particle size distribution can be controlled by altering process parameters [89]. One of the major drawbacks of inert gas condensation is, however, particle agglomeration [89]. Van der Waals forces caused by temporally varying charge distribution in particles result in agglomeration. Cost is another issue, as the entire process needs to be carried out in ultra-high vacuum conditions [89]. Furthermore, it is not always easy to scale up this process, so the amount of powders produced per batch may be limited [89].

2.3. Flame synthesis

Flame synthesis is a one-step process with no moving parts and machinery [119–122]. The resulting powders are highly pure, since the flame acts as a self-purifying environment by driving out volatile impurities [119]. Flame synthesis is typically used to synthesize metal oxides, due to the oxidizing nature of the flame environment [116,123,124], although metal powders have also been produced [125–127]. The process can be scaled up easily and can thus offer high production rates [119]. Calcote and Felder [128], for example, obtained silicon particles at a rate of 1.5 kg/hr in a rocket motor combustor. In this method, the precursor material (such as SiCl_4 for producing SiO_2 nanoparticles) is injected into the burner as a gas, liquid droplet, or solid particle. The precursor vaporizes due to the energy supplied by the flame. The vapors decompose and react to form molecular clusters, which eventually grow by coagulation and/or surface reactions and form nano-sized particles. The resulting aerosol stream leaves the high temperature region and cools down to sufficiently low temperatures for particle collection.

Fig. 10 shows a schematic of some of the commonly used burner configurations [121]. Premixed flame [116,129,130], co-flow diffusion flame [124,125,131,132], counter-flow diffusion flame [133,134], and spray flame [123,135–140] burners are typically employed. Coarser particles are obtained by increasing the collision frequency of precursor molecules and providing energy to drive the growth of the particles. This can be accomplished by increasing the flame temperature and precursor concentration and by enhanced mixing of fuel and precursor streams [124]. In spray burners, the precursor is injected in the form of a spray of liquid droplets into the thermal zone. Inside the thermal zone, the solvent evaporates and reactions occur within each particle to form a product particle. The main advantage of this method is that multi-component materials can be synthesized [136], as solutions of different metal salts can be mixed and aerosolized into the reaction zone. Particle size can be controlled by modulating the flow rate and oxidizer composition [135].

One of the main challenges of the flame synthesis method is particle agglomeration [125], although mitigation has been attempted. Dufaux and Axelbaum [125] condensed sodium chloride (NaCl) on particles using a sodium co-flow flame in order to minimize agglomeration. The coating was then removed by washing with water and sublimating at 800 °C in vacuum. Other strategies for reducing particle size in the flame synthesis process include using dopants [141], applying an electric field [142,143], laser irradiation [144], blowing of cold inert gas and nozzle-quenching [145,146]. When an electric field is applied across the flame, ionic wind is generated across the

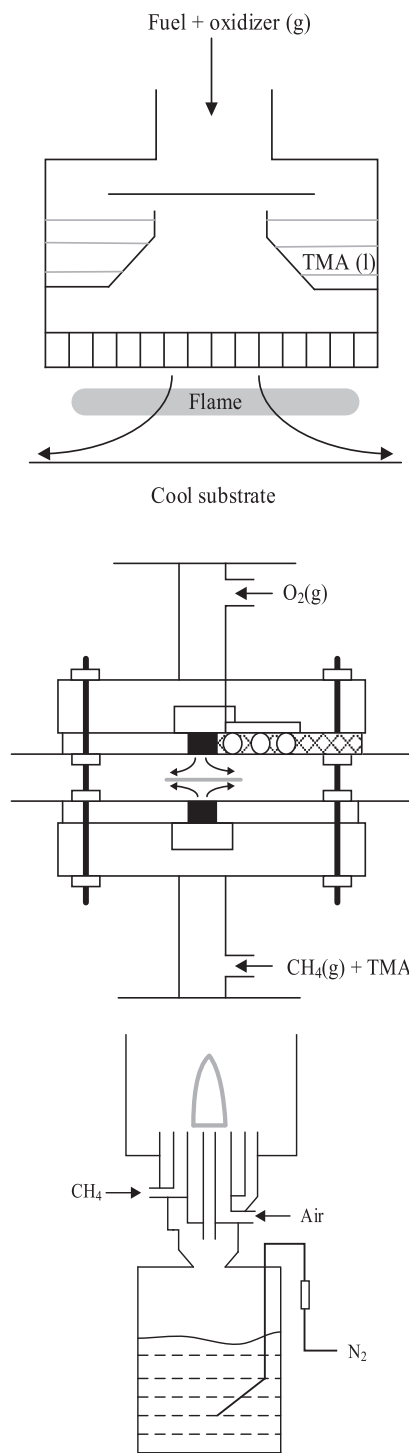


Fig. 10. Schematic of burners used for nanoparticle synthesis: (a) premixed flat flame burner; (b) counterflow diffusion flame burner; (c) multiannulus coflow diffusion flame burner (adapted from [121] with permission of ACS).

flame, decreasing the flame height, increasing the flame cooling rate [143], and resulting in shorter particle residence time at high temperatures [142]. Furthermore, charging of the particles results in electrostatic repulsion and dispersion. These effects result in reduced coagulation rates [142]. Similarly, the presence of dopants results in the formation of interstitial solid solutions, which decrease the sintering rate of particles [141]. Although laser irradiation enhances the sintering rate, it produces spherical particles which have lower collision cross sections and growth rates [144].

2.4. Wet-chemistry methods

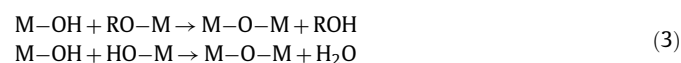
Wet-chemistry involves chemical reactions in liquids that in turn result in the formation of a solid phase [147]. The process begins with the nucleation of the first few molecules of the solid phase, followed by the growth of solid crystals, which is a thermodynamically favored process due to the decrease in the specific surface energy. The wet-chemistry method is a well-developed synthesis method that can yield uniform and controlled particle shape and size distribution [148,149]. It has been employed to synthesize nanoparticles of metals [28,149–153] and oxides [1,154–158] and core-shell structured particles [28,29,159–161]. Wet-chemistry methods are attractive due to the inherent safety of handling nanoparticles in a liquid medium [162], but the process is more of an art than a science and it features numerous additional steps, including filtration, washing, and drying.

One common solution method used to synthesize metal nanoparticles is decomposition of a suitable precursor material [28,29,150,151,159]. Nanoaluminum particles have been synthesized by decomposing alane-adducts in a xylene solvent containing a titanium catalyst [150]. Effective adduct species were reported to be trialkyl amines, tetramethylethylenediamine, aromatic amines, and ethers. The catalyst was added before or after heating the alane adduct solution. (Alternatively, the alane adduct can be added to a preheated catalyst solution). The particles were then separated from the solution by filtration or cannulation of the solvent. Passivation was achieved by exposing the solution to air or by controlled admission of air to the dried powder. Highly uniform particles were obtained; the particle size can be varied in the range of 65–500 nm by adjusting the catalyst concentration and adduct species. Alternative synthetic routes have also been explored. One such method is the reaction of aluminum acetylacetonate with lithium aluminum hydride in mesitylene solution to produce aluminum nanoparticles with carbonaceous residue that passivated the powder [163].

Another important wet-chemistry method is the sol-gel process [1,147,154,156,157,164,165], which is mainly used to synthesize metal-oxide nanoparticles. A reactive metal precursor such as metal alkoxide (M-OR) is used. In the first step, the precursor is hydrolyzed with water, resulting in a creation of sol (solid particles in a solution)



The second step involves condensation and gelation of the sol due to polycondensation reactions. This results in a dramatic increase in the viscosity of the solution.



The gel is a rigid three-dimensional network of polymeric molecules surrounded by the solvent. Polycondensation reactions continue until the gel is completely formed. The gel structure is reinforced by contraction of the gel matrix and expulsion of the solution. The gel is then dried by removing liquids and it is converted into a micro-porous structure. Calcination is performed to dehydrate the gel and form crystalline metal oxide nanoparticles. One of the main advantages of the sol-gel method is the high purity and uniform nanostructure achievable at low temperatures [166].

Other important wet chemistry approaches are micro-emulsion [167–170], microwave-assisted wet-chemistry [171], and sonochemical methods [155,160,172,173]. Micro-emulsions involve thermodynamically stable isotropic dispersion of two immiscible liquids consisting of nanosized domains of one liquid in the other, stabilized by an interfacial film of surface active molecules [174]. Two different micro-emulsions with reactants are forced together in a reactor, producing mixing of reactants. Note that there is a limited amount of reactant in each droplet [174,175]. As a result, the process has the ability to restrict reactions to these “nanoreactors” of miscelles

[174,175]. This process is by its nature capable of yielding fine and monodispersed particles [175], and it is useful for large-scale production of nanoparticles using relatively simple and inexpensive hardware [176].

In sonochemical methods, ultrasonic waves are used to create cavities in liquids [176]. The acoustic cavitation process generates a transient localized hot zone with extremely high temperature and pressure gradients [176]. Such changes in temperature and pressure assist the destruction of the precursor and formation of nanoparticles [176]. This technique can be used to produce large volumes of materials for industrial applications [176]. Aluminum nanoparticles capped with an organic shell have been synthesized using sonochemical-assisted thermal decomposition of alane adduct species [160]. Alane adduct and titanium isopropoxide catalyst were first added to a solution of dodecane and oleic acid. The solution was transferred to a sonication flask and placed in a nitrogen-filled glove bag encompassing the sonication instrument. The instrument consisted of a solid titanium horn operated at 20 kHz. The solution was sonicated for 7.5 min at an amplitude of 37%. The bulk reaction solution reached a maximum temperature of 70 °C and produced a black solution that precipitated, yielding grayish-black powder. The powder was recovered by evaporating the solvent under vacuum, and washing repeatedly with hexane. The powder consisted of particles with average sizes of either 5 or 30 nm, capped with an organic shell. Green chemistry methods have also been recently considered to minimize waste and utilize environmentally benign solvents and renewable materials [177].

2.5. Mechanical attrition

Mechanical attrition, one of the oldest and simplest methods available, is a top-down approach to the synthesis of nanomaterials [178]. Nanoparticles are formed in a mechanical device, generally known as mill, in which energy is imparted to feedstock to effect a reduction in particle size. The resulting powders may consist of particles of diameters less than 100 nm. In certain cases, the crystallite (grain) size after milling is between 1 and 10 nm. Such materials are called nanocrystalline materials. Fig. 11 shows a schematic of an attrition ball mill [179]. The powder is placed in a stationary tank with the grinding medium. The feedstock particles, agitated by the shaft rotating at a high speed, are crushed during media-media and media-wall collisions. Brittle materials tend to fracture under mechanical stress, whereas ductile and malleable materials can

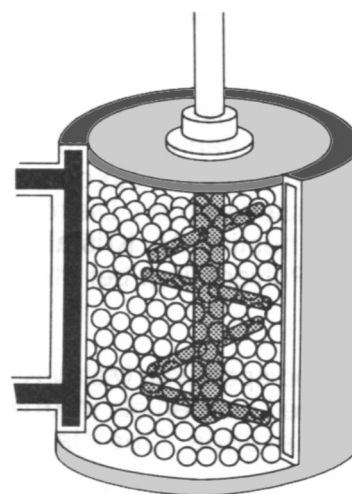


Fig. 11. Schematic of an attrition ball mill (reprinted from [179] with permission of Elsevier).

undergo plastic deformation. The kinetics of the milling process depends on the amount of energy transferred from the grinding medium to the powder. Dense materials such as steel and tungsten carbide are preferred for the grinding media [180]. Size reduction by fracturing is counteracted by cold welding, which tends to result in particle aggregation and fusion. Nanocrystalline aluminum powders have been synthesized by milling of micron-sized aluminum particles in oxygen, hydrogen, and argon environments using hardened steel balls [181]. The grain size and composition was dependent on the milling time and ambient gas. Longer milling times resulted in finer grains. Note, however, that prolonged milling may abrade the grinding medium and contaminate particles.

Nanoparticles typically form agglomerates during the gas-phase milling process, although particle agglomeration can be minimized by conducting the milling in a liquid medium [179]. Air-stable boron nanoparticles have been synthesized using high-energy ball milling in a liquid medium [182]. Commercial boron particles of diameter 800 nm were employed as feedstock. Milling was carried using a tungsten carbide milling jar and 1/8 inch diameter balls. About 2 g of boron was milled with ~15 mL of hexane added to prevent caking, thereby reducing the milling time. To generate ligand-protected boron nanoparticles, 1 mL of oleic acid was added to the boron/hexane mixture prior to milling. Milling was performed in a nitrogen environment. After milling, all samples were slowly brought into contact with oxygen. Prior to analysis, excess oleic acid was removed, although the ligand coating on the particles was preserved. The washed particles were readily dispersed in hexane or other hydrocarbon by ultrasonication, with mild centrifugation to remove any remaining aggregates. The particle size distribution was very narrow; the peak size was ~43 nm and no particles were detected outside the range of 35–60 nm. Furthermore, x-ray photoelectron spectroscopy (XPS) suggested complete protection against oxidation in air for ligand-coated particles.

Conventional mechanical milling is not always very efficient for ductile and malleable materials, since particles are not readily fractured and cold welding is quite efficient [183]. In the reactant-assisted mechanochemical method [183], liquid reagents are used to enhance reactions and improve milling efficiency. Reactant-assisted milling has been used to generate nanoparticles of aluminum, iron, and copper in a number of reagents/solvents [183]. Improved nanoparticle production using the reactant-assisted mechanochemical method has been attributed to binding of reagent/solvent on the metal surface, which lowers the surface free energy as cracks propagate and reducing cold welding [183]. The size distribution of particles has been attributed to the balance between wear processes that spall or abrade particles from media surfaces, and cold welding, which tends to build up larger particles and reattach particles to the media surfaces. Particle size reduction can also be achieved in reactive gases, as surface functionalization reduces surface free energy and tendency towards cold welding [184].

2.6. Cluster synthesis

Although metal particles have high energy densities, their rate of energy release is lower than in monomolecular energetic materials. The reactivity of metal particles can be enhanced by decreasing the particle size to nanometer scale, but nanoparticles are easily oxidized, due to their high specific surface area. An ideal metal-based energetic material consists of uniformly dispersed, extremely small, unoxidized metal clusters. Clusters are also of great interest to nanoenergetics as they provide a platform for the synthesis of novel energetic nanomaterials [185]. Clusters offer the exciting prospect of serving as building blocks for the “bottom-up” synthesis of new materials, whose desired properties may be tailored through the selection of size and composition.

The reactivity of clusters depends strongly on size [186]. For example, aluminum cluster anions containing 13, 23, and 27 atoms are unreactive in oxygen, while most other clusters are reactive [186]. This phenomenon is attributed to the differences in the electron shell configurations of clusters. Clusters with closed shells are typically stable, as predicted by the jellium shell model [187]. Note that cluster properties can be tuned by the addition or removal of one or more atoms [188]. For example, replacing an Al atom in the Al₁₃ cluster with a carbon atom leads to 40 electrons and a closed shell, thereby resulting in a stable and inert cluster [188].

Clusters could also be designed to have the desired properties of one or more of the elements in the periodic table [185]. The electronic structure of the Al₁₃ cluster resembles that of a halogen atom, so it was speculated that the Al₁₃ cluster has properties similar to those of a halogen atom. This hypothesis was supported by theoretical calculations, which suggested that electron affinities of the Al₁₃ cluster and chlorine atom are similar [188]. The Al₁₃ cluster is thus referred to as “superhalogen” [185]. Experimental evidence came from chemical reaction studies of halogenated aluminum clusters [189,190].

It is apparent that clusters could mimic one or more properties of a different element in the periodic table, and they are typically regarded as “super atoms” [185]. This gave rise to the concept of a three-dimensional periodic table of cluster elements, and the prospect of using clusters as the building blocks of new nanoscale materials with tailored properties [185]. The approach involves three synergistic steps: (1) identification of the potential building blocks through experiments on size-selected clusters in the gas phase; (2) investigation of the energetic and chemical stability of the cluster motifs through compositional energy diagrams based on first-principle based theoretical investigations. This information, along with experiments in step 1, enables identification of feasible units and pathways to their assembly; (3) synthetic chemical approaches designed to assemble desired cluster blocks using the information derived in previous steps, or cluster assembly via direct deposition [185]. The major difficulty in forming cluster-assembled materials is that clusters are generally metastable and in many cases have a tendency to coalesce [185]. The clusters must be isolated by passivation with organic ligands, insertion into cages, or deposition on surfaces [185].

Stable aluminum-based clusters have been synthesized from aluminum monohalides [191]. The equilibrium between liquid metal and gaseous mono- and trihalides, in the case of the aluminum-chlorine system, is given by [191]



Entropy arguments suggest that the equilibrium of the reaction shifts in favor of the gaseous monochloride with increasing temperature and decreasing pressure [191]. To ensure ease of handling and a continuous stream of aluminum monochloride (AlCl), a flow of hydrogen chloride (HCl) gas over aluminum is normally used [191]. Fig. 12 shows a schematic of the experimental setup used to produce aluminum clusters [191]. At the center of the vacuum chamber (pressure ~0.1 mbar), there is a high-temperature reactor containing molten aluminum in several graphite chambers heated to around 1000 °C. AlCl vapors are generated by the flow of HCl gas through graphite chambers containing a pool of liquid aluminum. Under these conditions, there is more than 20-fold excess of AlCl over AlCl₃



To prevent aggregation of AlCl species, toluene solvent is typically used. The AlCl molecules are then condensed with solvent on the walls of the stainless steel vessel, cooled to –196 °C. When the solid solvent mixture melts at about –100 °C, a deep red solution of

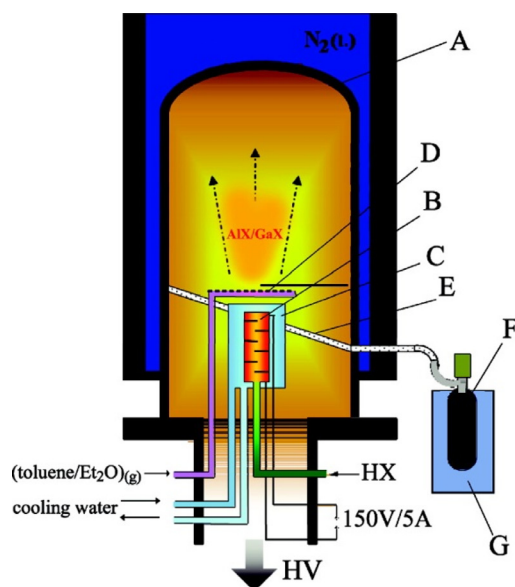
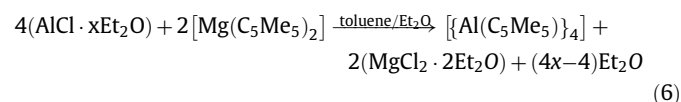


Fig. 12. Schematic of the co-condensation apparatus (A = stainless steel vessel; B = Al in the graphite cell with resistance heating; C = cooling shield; D = solvent input (toluene); E = drainage channel; F = Schlenk line; G = Dewar with dry ice; HX = hydrogen halide gas; HV = high vacuum (reprinted from [191] with permission of American Chemical Society).

the monohalide is usually obtained, which can be stored at temperatures of -78°C for several months. The solubilized metastable monohalide subsequently disproportionates, according to Eq. 4, in the temperature range of -40 to 50°C .

Dohmeier et al. [192] synthesized the first compound of monovalent aluminum stable at room temperature by treatment of this AlCl solution with $[\text{Mg}(\text{C}_5\text{Me}_5)_2]$



The resulting yellow crystals of $(\eta^5\text{-pentamethylcyclopentadienyl})\text{-aluminum}$ (I), referred to as Al_4Cp^*_4 , was the first Al(I) compound that was stable under normal conditions. The energetics of tetrameric aluminum (I) compound has been investigated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) [193]. The DSC trace suggested an exotherm at 117°C followed by a steady rising exotherm, indicating good reactivity as compared with micron and nano-aluminum powders. This was attributed to combustion of Cp^* ligands, followed by slow combustion of aluminum. Note that the initial decomposition temperature of 117°C is also lower than that of currently available CHNP explosives, PETN (163°C). The material, however, was not air stable enough to be considered as a replacement for aluminum particles. The enthalpy of combustion was $11.5 \text{ kcal}/\text{cm}^3$, about 60% of that of pure aluminum. A similar approach can be used to synthesize other metalloid clusters, such as the Al_{77} cluster, which is stabilized by 20 organic ligands [194].

Other cluster materials of concern are nickel-aluminum [193], aluminum hydride [195], boron-aluminum hydride [196], and magnesium-aluminum [197] clusters. Such clusters have been synthesized using the pulsed arc cluster ionization source (PACIS) process [195]. A discharge was triggered between a copper anode and a sample cathode and the sample was vaporized. Hydrogen gas was back-filled into the discharging region, where the hydrogen gas partially dissociated and aluminum and/or boron vaporized. Helium gas flushed the plasma mix down a flow tube, where it reacted, cooled, and formed clusters. Future studies must attempt to produce stable

metal-based clusters for next-generation propulsion and explosion applications.

3. Novel passivation materials

Metal particles are covered by a passivating oxide layer, whose thickness is in the nanometer range [7,8,27,198]. Passivation can be carried out after the nascent metallic particles are synthesized. The powder is typically placed in a constant-temperature box filled with argon and air [68]. To facilitate controlled particle oxidation, the concentration of air in the gas is taken to be small ($< 0.1 \text{ vol.}\%$). Note that metal oxide is an inert material and it does not react with oxidizing gas. As mentioned before, the presence of the oxide layer substantially diminishes the energy content of the particles at nano-scales. Alternative coating materials might enhance the energy content, improve reactivity, and/or reduce particle agglomeration [199]. For example, nickel coating reduces the agglomerate size in a composite solid propellant environment by about 40% [199]. This may be attributed to the reduction in ignition delay and temperature of aluminum particles due to intermetallic reactions [200]. An ideal coating material will maximize both energy content and shelf life, while ensuring ease of ignition without affecting the sensitivity characteristics. In the past, a variety of novel coating materials such as metals and organic materials have been considered. These are discussed below.

3.1. Metallic coatings

Metals are attractive coating materials since they can enhance the energy content of the particles. Aluminum particles passivated with metallic coatings have been synthesized using the wet-chemistry method [28], electric explosion process [201], and electroplating [202]. Foley et al. [28] synthesized nano-aluminum particles passivated with palladium, silver, gold, and nickel. The particle size was roughly 150 nm. Nascent aluminum particles were first slurried with dimethyl ether. In a separate flask, acetylacetonate of metals was dissolved in dimethyl ether. The resulting solution was added to the stirred aluminum slurry and allowed to react for 12 hours. The powder was then allowed to settle and the solvent was decanted. The resulting solid was washed with dimethyl ether and dried. The powder was passivated in air and the resulting particles contained both aluminum and transition metal oxides. Nickel was most efficient in protecting the active aluminum content; nickel-coated aluminum particles had about 4% more active aluminum than other particles. It was reported that more enhancements are expected for finer particles.

Nickel-coated aluminum nanoparticles have also been synthesized by electric explosion of Al-Ni composite wires in an argon environment [201]. The particle size was 237 nm. Results suggested that the nickel-coated aluminum powder has no superior reactivity properties compared to conventional aluminum powder. For example, the onset temperature of oxidation was about 565°C , comparable to that of conventional Al powder. Furthermore, the active aluminum content of the powder was only 53%. Note that electric explosion did not allow for precise control of particle size and resulted in the formation of coarse and fine particles. Boron-coated aluminum powders were also synthesized in the study. The aluminum content of boron-coated aluminum powder was comparable to that of alumina-coated aluminum powder [201]. The combustion enthalpy, however, increased from 5465 to 6232 kJ/kg, when the boron coating was substituted for the alumina counterpart. This is attributed to the high energy density of boron particles. From an energy perspective, boron-coated aluminum particles are thus attractive for propulsion and energy-conversion applications.

3.2. Organic material coatings

Organic materials are attractive candidate materials for passivation, as they can burn in many practical oxidizing environments and contribute to the overall energy release. Furthermore, they typically react and decompose at lower temperatures, thereby enhancing the reactivity of metal nanoparticles [203]. Another advantage of organic coatings is that they result in better processability of powders [204]. The extremely high surface area of Al nanopowders poses many processing difficulties in solid propellants, as the binder and plasticizer become incapable of wetting all of the solids. In this regard, organic-coated Al nanopowders show better compatibility than inorganic-coated Al nanopowders [204].

Aluminum nanoparticles passivated with carbon have been synthesized using both laser heating/ablation [205,203] and arc discharge [205,110]. Park et al. [205], for example, produced carbon-coated particles using the laser ablation or DC-arc discharge methods in an argon-ethylene gas flow. The particle size was about 80 nm and the thickness of the carbon coating was 1–3 nm. Fig. 13 shows TEM images of carbon-coated aluminum nanopowders [205]. The coating was found to be stable at temperatures lower than 700 °C and oxidized at about 800 °C. The latter value corresponds roughly to the oxidation temperature of carbon (or soot) particles. Carbon-coated aluminum particles were also synthesized by Ermoline et al. [110] using the microarc discharge process. A very narrow size

distribution was obtained; the geometrical mean size was 22.7 nm and standard deviation was 1.35 nm. Another important achievement was that the thickness of carbon coating was only ~1 nm.

Guo et al. [203] synthesized carbon-coated nanoaluminum particles by laser heating bulk aluminum and introducing methane gas into the chamber. The particle size was in the range of 28–50 nm. Results of thermal analysis revealed that the carbon-coated aluminum powder has a lower oxidation onset temperature (495 °C) and a lower peak temperature (556 °C), where the maximum exotherm occurs, compared to the conventional nanoaluminum powder. Furthermore, the enthalpy change of carbon-coated aluminum powder was 3.54 J/g, greater than that of conventional powder (2.76 J/g). These studies suggest that carbon coating is an effective route to increase the reactivity and energy-content of aluminum nanoparticles.

More complex organic compounds, such as perfluoroalkyl carboxylic acids have also been considered [29]. Carboxylic acids, in general, are known to have strong affinity to aluminum metal surfaces [152]. A major advantage of fluorine-based passivation agents is the high enthalpy of aluminum-fluorine reaction; the adiabatic flame temperature is about 4400 K, greater than the counterpart in the aluminum-oxygen system (4000 K). Aluminum powders coated with perfluoroalkyl compounds were synthesized using the wet-chemistry method [29]. A diethyl ether (DEE) solution of an alane adduct species was stirred in an argon-filled glove box. Titanium isopropoxide solution was added rapidly using a syringe and stirred for five minutes. A solution of perfluoroalkyl carboxylic acid in diethyl ether was then added drop-wise to the reaction flask. The resulting solid material was washed in diethyl ether and dried. Fig. 13b shows transmission electron microscopy (TEM) images of nano-aluminum particles passivated with perfluoroalkyl carboxylic acid [29]. The core size was estimated to be ~5 nm, so the active aluminum content was only 15.4% by mass. Attempts to control particle size by varying temperature, catalyst/alane ratio, and other methods were unsuccessful. Furthermore, reduction of the amount of carboxylic acid resulted in an extremely pyrophoric material. Further improvements in the passivation process will be necessary to synthesize larger particles with greater active aluminum content.

In a more recent study [152], two different alanes ($\text{H}_3\text{AlN}[(\text{CH}_3)_2\text{C}_2\text{H}_5]$ and $\text{H}_3\text{AlN}[(\text{C}_4\text{H}_8)(\text{CH}_3)]$) and a number of passivation agents were considered. Results suggested that non-fluorinated carboxylic acid was less effective than fluorinated counterparts in protecting aluminum particles from surface oxidation. The passivation agent plays the dual roles of trapping aluminum particles to keep them nanoscale during the alane decomposition and protecting the aluminum nanoparticles postproduction from surface oxidation [152]. An appropriate balance between the rate of alane decomposition and the timing in the introduction of the passivation agent into the reaction mixture is critical to obtain the desired product mixes and/or morphologies [152]. Further information on the rates of alane decomposition reactions could be valuable to the controlled and predictable production of stable and dispersed aluminum nanoparticles.

Other organic passivating materials such as oleic and stearic acids have also been considered [201,160,161,173]. For oleic acids, studies suggest that the organic layer was transparent to oxygen gas, so that an internal oxide layer was able to form, as shown in Fig. 14 [201]. The active aluminum content in the powder was thus as low as 45%. A similar observation was made by Fernando et al. [160] for nanoaluminum particles passivated by oleic acid. The organic layer acted as an oxygen source for the oxidation and passivation of aluminum. About 40% of the sample mass was active aluminum, 35% was organic coating, and 25% was organic-provided aluminum oxide layer. Alternative capping materials such as alkyl-substituted epoxides have also been considered [159,206]. Particles with diameters on the order of 20 nm are produced. The epoxide reagent polymerized on the particle surface to produce polyether. Although the organic layer is oxygen rich, the produced nanoparticles had low

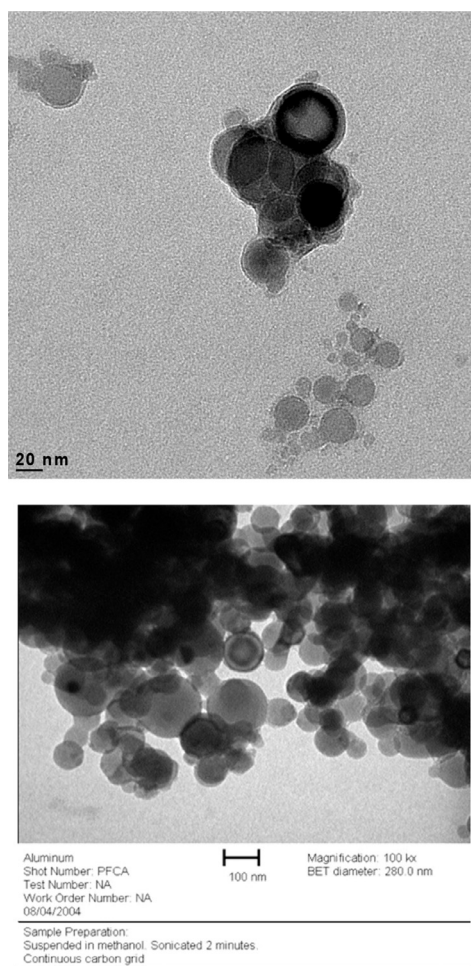


Fig. 13. Transmission electron microscopy (TEM) images of aluminum nanoparticles coated with (a) carbon (reprinted from [205] with permission of Springer); (b) perfluoroalkyl carboxylic acid (reprinted from [29] with permission of American Chemical Society).

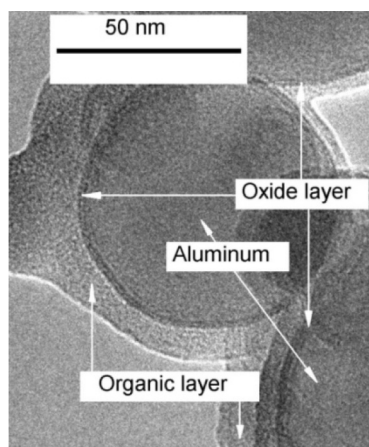


Fig. 14. Transmission electron microscopy (TEM) image of aluminum nanoparticle passivated with oleic acid showing the oxide layer formation due to unprotective oxide layer (reprinted from [201] with permission of Wiley).

oxide content. The active aluminum content was 96%, substantially higher than that of conventional aluminum powder of same size (31%).

Nano-aluminum particles have also been passivated with hydroxyl-terminated polybutadiene (HTPB) [204], which is typically used as a binder in solid rocket propellant because of its very low glass transition temperature, low viscosity and high combustion enthalpy. The powder was stored for 2 years in an ambient environment and then tested. The DSC signal of HTPB-coated powder attained its peak value at a relatively low temperature of 554 °C. Furthermore, the enthalpy change was 3.87 kJ/g, greater than that of conventional powder. These studies demonstrate the multiple benefits of using organic materials to passivate aluminum nanopowder.

Studies on novel passivation materials for other metallic particles are limited. Nano-boron particles have been passivated with bromine and fluorine in an attempt to increase the combustion efficiency [9]. Boron nanoparticles were first produced by gas phase pyrolysis of decaborane ($B_{10}H_{14}$). The particle size was 10–150 nm. The nascent boron particles were then treated with bromine and XeF_2 to obtain boron particles passivated with bromine and fluorine, respectively. The combustion efficiency of fluorine-coated boron particles was reported to be ~75%, greater than that of conventional boron particles (~50%) [10]. Oleic acid has also been used to passivate boron nanoparticles [182].

4. Physicochemical properties

As mentioned in Section 1, the properties of nanoparticles are size dependent and differ substantially from those of bulk materials, owing to the high specific surface area and excess energy of surface atoms. This applies to a variety of properties, such as melting and boiling points, enthalpy of combustion, emissivity, and so forth. For certain properties in some materials, deviations from bulk value become substantial for particles smaller than 10 nm, but for others, deviations are not negligible even for particle sizes as high as 100 nm. In any case, the properties of bulk materials cannot always be used to accurately predict the ignition and combustion behaviors of nanoparticles. As a result, experimental and numerical analyses are required to determine the unique properties of nanoparticles. In this section, the size dependence of nanoparticle properties is described and the underlying processes and mechanisms are discussed.

4.1. Melting temperature

Melting temperature is of primary concern in any consideration of the ignition and combustion of metal-based energetic nanomaterials. For example, it is proposed that melting of the aluminum core and oxide layer plays an important role in the ignition of aluminum nanoparticles [15,207]. Melting also promotes reactivity of thermite [208] and inter-metallic systems [200]. As a result, understanding the melting behavior of metal nanoparticles is of paramount importance. Table 1 shows the melting temperatures of bulk metals and their oxides. Metals typically melt at temperatures lower than those of their respective oxides. An exception is boron; the melting point of boron is 2349 K, significantly greater than that of boron trioxide (723 K).

The melting temperatures of nanoparticles can be calculated using molecular dynamics (MD) simulations. It is, however, important to first determine if the potential function can accurately predict the melting temperatures of the bulk. An unrealistic potential function often leads to erroneous predictions. Bulk materials can be modeled by imposing periodic boundary conditions in all three spatial directions. Fig. 15 shows variations of the thermodynamic and structural properties of bulk aluminum with temperature. Atomic interactions are captured using an embedded atom potential in order to treat the physics of metallic bonding. Melting is observed at a temperature of 1250 K, at which point sharp variations occur in the potential energy and translational-order parameter. Note that the temperature at which melting occurs is about 18% greater than the experimental value, due to the absence of nucleation sites [209]. To facilitate better agreement with experimental data, free-surface boundary conditions can be imposed in one of the directions [210]. For example, this approach was adopted to calculate the melting temperature of bulk alumina using a three-body interatomic poten-

Table 1
Melting temperature of metals and their oxides.

Metal	Melting point, K	Metal oxide	Melting point, K
Al	933	Al_2O_3	2350
B	2349	B_2O_3	723
Be	1560	BeO	2820
Fe	1811	FeO	1650
Li	453	Li_2O	1843
Mg	923	MgO	3125
Si	1687	SiO_2	1873
Zr	2128	ZrO_2	2988
Ti	1941	Ti_3O_5	2033

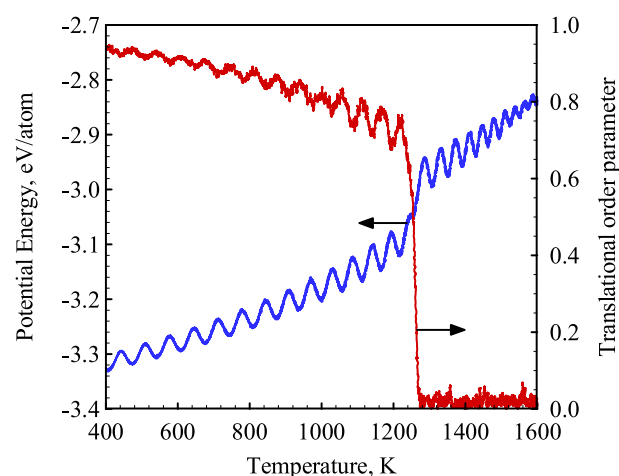


Fig. 15. Variations of thermodynamic and structural properties with temperature during melting of surface-free bulk aluminum; molecular dynamics simulations with the embedded-atom potential.

tial [210]. When periodic boundary conditions were imposed in all three directions, the crystal melted at 2700 K, which is substantially greater than the experimental value of 2350 K. Melting occurred at 2500 K when a free-surface boundary condition was imposed along the (001) crystallographic direction.

Melting temperatures and enthalpy of melting of nanoparticles are substantially lower than those of bulk materials. Most of the studies have considered aluminum and more studies on melting of nanoparticles of other energetic materials are needed. Fig. 16 shows the effect of particle size on the melting temperature and enthalpy of melting of aluminum particles [211]. Results of MD simulations [21,211,212] and, experimental [181,213] and theoretical studies [214] are shown. At melting point, equilibrium persists between the solid and liquid phases of the material. For temperatures greater than the melting point, the Gibbs free energy of the liquid phase is lower than that of the solid phase, and a spontaneous phase transformation is triggered. The excess energy of surface atoms alters the Gibbs free energy and reduces the melting temperature. As the fraction of surface atoms in the particle is a function of particle size, melting temperature is a size-dependent property. Note that the melting temperature of aluminum particles is as low as 473 K at a particle size of 2 nm. For smaller particles, melting was characterized by fluctuations in the potential energy, a phenomenon referred to as dynamic melting [215]. The particle oscillates between liquid and solid phases over a temperature range of 450–475 K.

The melting point depression can be calculated using the Gibbs–Thompson equation [214], which addresses the effect of interfacial energy on equilibrium properties. The size-dependence of melting

temperature, according to the Gibbs–Thompson theory, is given by

$$T_m = T_m^b - \left(\frac{2T_m^b \sigma_{sl}}{h_m^b \rho_p R_p} \right) \quad (7)$$

where T_m is the melting temperature, σ_{sl} the solid–liquid interfacial energy, h_m the latent heat of melting, ρ_p the particle density, and R_p the particle radius. The superscript b refers to the bulk material. The following equation is also frequently used to characterize the size dependence of the melting temperature of metal particles [216,217]:

$$\frac{T_m}{T_m^b} = \exp\left(-\frac{\alpha-1}{R_p/R_0-1}\right), \quad (8)$$

$$\alpha = \frac{2S_m^b}{3R} + 1, \quad (9)$$

$$R_0 = 3h. \quad (10)$$

Here, S_m is the melting entropy, R the gas constant, and h the atomic diameter. More sophisticated models, which couple phase-field theory to material mechanics, are also available [218–221].

The latent heat of melting exhibits a qualitatively similar trend. It decreases from 10.43 to 1.69 kJ/mol, when the particle size decreases from 40 to 13 nm. Predictions are in reasonably good agreement with experimental data [181]. An equation for the size dependence of the latent heat of melting has been proposed [216,217]:

$$\frac{h_m}{h_m^b} = \frac{T_m}{T_m^b} \left[1 - \frac{1}{(R_p/R_0-1)} \right], \quad (11)$$

where $R_0 = 0.9492$ nm for aluminum.

Predictions from the MD simulations differ from the experimental data. A number of factors may account for these discrepancies. In the experiments, particle melting was studied using differential scanning calorimetry (DSC) and thin-film DSC apparatus, with heating rates on the order of 1 and 10^5 K/s, respectively [181,213]. These are orders of magnitude lower than the heating rate employed in the MD simulations ($\sim 10^{13}$ K/s). Note that the Gibbs–Thompson theory corresponds to equilibrium melting point, while ultrafast heating typically results in non-equilibrium conditions. Furthermore, experiments considered passivated particles, whereas the MD simulations dealt with nascent particles. The melting temperatures of passivated particles could be different from those of their nascent counterparts due to pressure buildup and epitaxial interfacial structure [222]. Note finally that the measured melting temperatures of Eckert et al. [181] and Lai et al. [213] are not the same, perhaps because of differences in the heating rate and/or the powder synthesis method. Lai et al.'s particles were prepared using the gas-phase condensation method, whereas Eckert et al. employed the mechanical attrition technique. In the following sections, an attempt is made to elucidate the effects of heating rate, defects, and particle encapsulation on the melting of metal particles.

4.1.1. Effect of heating rate

Heating rate is an important parameter that affects melting dynamics. Melting temperature is typically measured using differential scanning calorimetry or laser heating methods. In conventional DSC studies, the heating rate is on the order of 1 K/s [223]. Heating rates of $\sim 10^5$ K/s can be achieved using a thin film differential scanning nano-calorimeter [213]. Other techniques that are associated with high heating rates include laser and shock heating [224]. In molecular dynamics simulations, the particle is heated at a rate of 10^{13} K/s, orders of magnitude greater than those in most practical systems. As a result, the effect of heating rate on the melting dynamics of nanoparticles must be considered.

The effect of heating rate on melting has been recently studied [222]. It is well known that in nanoparticles melting typically begins

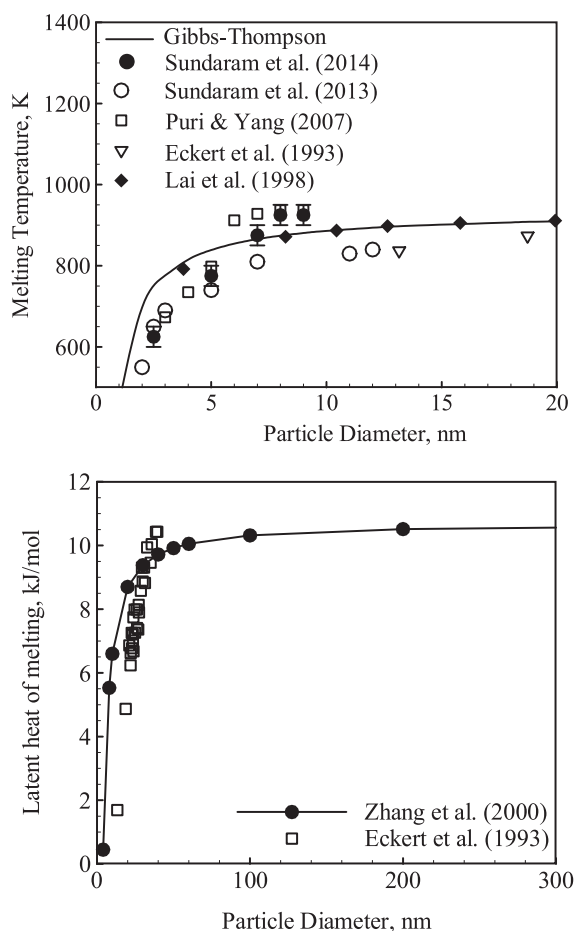


Fig. 16. Effect of particle size on (a) melting temperature (adapted from [211] with permission of Springer) and (b) enthalpy of melting of aluminum particles.

at the free surface and the melting front propagates to the interior regions of the core. This is referred to as heterogeneous melting. Under some conditions, heterogeneous nucleation can be prevented and melting occurs by catastrophic homogeneous melting of the whole system [222]. This is the case for low-dimensional materials and nanoparticles passivated by suitable high-melting point materials in such a manner that interfacial nucleation is prevented. In these cases, melting typically occurs at temperatures substantially greater than the thermodynamic melting temperature and the phenomenon is referred to as superheating. The degree of superheating is dependent on heating rate and a maximum limit is believed to be about 20% for aluminum [222], which is consistent with MD simulation results for surface-free bulk aluminum [212].

Luo and Ahrens [225] conducted a systematic study to determine the effect of heating rate on degree of superheating based on homogeneous nucleation theory. The steady-state nucleation rate is expressed as follows [225]:

$$I = M(m, T) \exp\left(-\frac{\Delta G_c}{k_B T}\right), \quad (12)$$

where M is a function of material properties (m) and temperature (T), ΔG_c is the critical Gibbs free energy for nucleation, and k_B the Boltzmann constant. Considering a spherical liquid nucleus of critical radius within a superheated crystal lattice, the critical Gibbs free energy for nucleation is expressed as [225]

$$\Delta G_c = \frac{16\pi\sigma_{sl}^3}{3\Delta G_{sl}^2}, \quad (13)$$

where σ_{sl} is the solid-liquid interfacial energy, ΔG_{sl} the Gibbs free energy difference per unit volume between solid and liquid state, approximated as follows:

$$\Delta G_{sl} \approx \Delta H_m(T - T_m)/T_m, \quad (14)$$

where ΔH_m is the enthalpy of melting, and T_m the melting temperature. The degree of superheating, $\theta = T/T_m - 1$, is thus a strong function of the energy barrier, β , which is a material-dependent property [225]

$$\beta = \frac{16\pi\sigma_{sl}^3}{3h_m^2 k_B T_m}. \quad (15)$$

Assuming that the probability x for a given amount of parent phase containing new phase is the same for both undercooling and superheating cases, the degree of superheating was estimated for different cases. The following equation was obtained empirically for the degree of superheating [225]:

$$\beta = A(Q)(1 + \theta)\theta^2. \quad (16)$$

The parameter A has values of 60 and 31 at heating rates of 1 and 10^{12} K/s, respectively. It represents the time scale characteristic of nucleation at different heating rates. The degree of superheating was found to increase with increasing heating rate, from ~15% at 1 K/s to 20% at 10^{12} K/s. Note that these are within the maximum superheating limits and agree with the MD simulation results at comparable heating rates.

An important question is whether superheating is also of concern for heterogeneous melting. For bare metal particles, there is no passivation layer that prevents heterogeneous melting of the particles. Results of MD simulations do indicate that heating rate is of concern to heterogeneous melting dynamics of metal particles. Fig. 17 shows the potential energy of bare aluminum nanoparticles during melting for different heating rates [212]. At a higher heating rate, melting occurs over a broader range of temperatures. Note that the heating rates considered are in the range of 10^{12} – 10^{14} K/s, achievable in MD simulations. A similar result was obtained by Shibuta and Suzuki [226] for solidification of molybdenum particles. The particle size was 6 nm and the number of atoms was 6750. Fig. 18(a) shows the

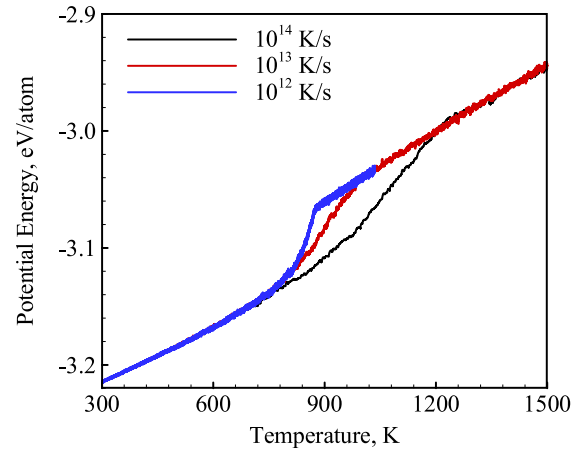


Fig. 17. Potential energy of aluminum nanoparticles as a function of temperature showing heterogeneous melting of aluminum nanoparticles at different heating rates; MD simulations with embedded atom potential (reprinted from [212] with permission of American Chemical Society).

potential energy of Mo particles as a function of temperature for various cooling rates [226]. For cooling rates lower than 5×10^{11} K/s, solidification is complete at their respective onset temperature. Solidification occurs over a much broader range of temperatures at higher cooling rates. Fig. 18(b) shows the onset and offset temperatures of solidification as a function of cooling rate [226]. The onset and offset temperatures decrease with increasing cooling rate and

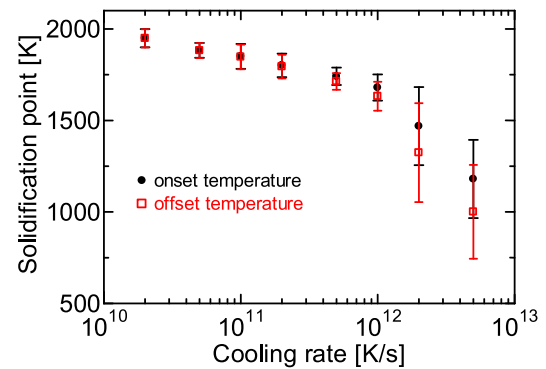
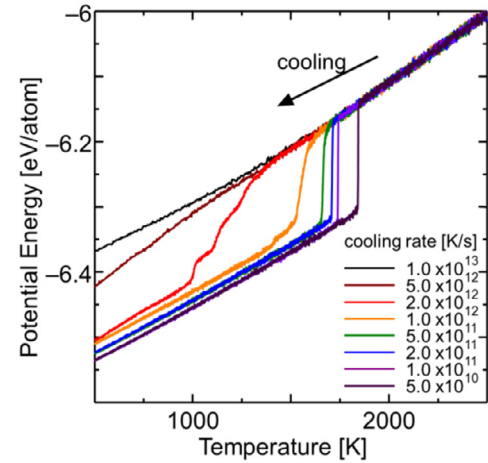


Fig. 18. MD simulation results showing (a) potential energy per atom for a 6750-atom Mo nanoparticle as a function of temperature during cooling at various cooling rates; (b) onset and offset temperatures during solidification of Mo particles as a function of cooling rate (reprinted from [226] with permission of Elsevier).

the difference between offset and onset temperatures increases with increasing cooling rate. More recent studies also indicate a pronounced effect of heating rate on the melting of bare aluminum particles for heating rates greater than 10^{12} K/s, but negligible effect for heating rates lower than 10^{11} K/s [221].

4.1.2. Effect of defects

Particles may have defects in the form of cracks, voids, and grain boundaries and these could affect the melting temperature of nanoparticles [209]. For instance, defects such as voids and surfaces could provide sites for nucleation of liquid phase. Puri and Yang [227] conducted molecular dynamics simulations and investigated mechanisms associated with defect nucleated melting. Fig. 19 shows the temporal evolution of particle density during melting of a 5.5-nm nascent aluminum particle with voids of different sizes [227]. For a defect-free particle, melting begins at the outer surface and propagates to interior regions of the particle. In a particle with a void, on the other hand, melting occurs simultaneously at the void and particle surface. Note that a void size of 8.2 nm^3 results in structural instability and collapse of the crystal. Fig. 20 shows the effect of void size on the melting temperature of a 5.5 nm nascent aluminum particle [227]. The melting temperature remains constant for void volumes smaller than 1 nm^3 , but decreases with further increase in the void volume. For void volumes exceeding 8 nm^3 , the particle is unable to withstand the destabilizing forces associated with the void

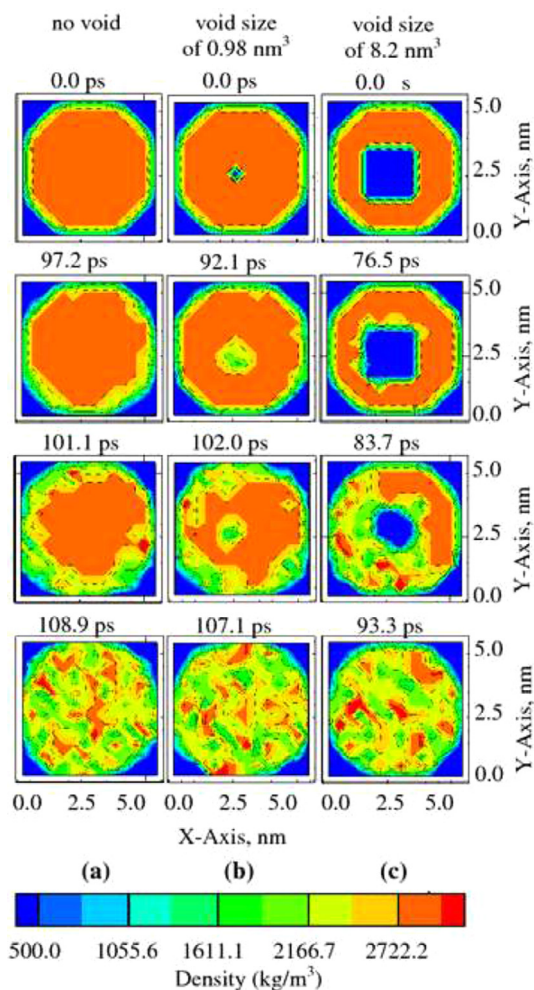


Fig. 19. Temporal evolution of particle density for a nascent 5.5-nm aluminum particle: (a) without defect; (b) with a void size of 0.98 nm^3 ; (c) with a large void size of 8.2 nm^3 ; MD simulations with glue potential (reprinted from [227] with permission of Springer).

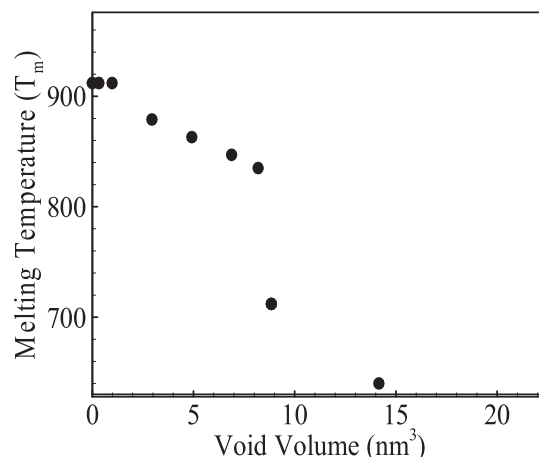


Fig. 20. Effect of void size on melting temperature of a 5.5 nm nascent aluminum particle; MD simulations with glue potential (reprinted from [227] with permission of Springer).

and the crystal collapses abruptly at 700 K. Voids could thus exert a significant effect on melting dynamics of metal nanoparticles.

4.1.3. Effect of passivation layer

The oxide layer covering metal nanoparticles could exert a significant effect on the melting point, so the predicted melting temperatures of nascent metal nanoparticles cannot be compared with experimental data, which are obtained for passivated nanoparticles. The effect of oxide layer on the melting temperature of metal particles must therefore be understood. Puri and Yang [207] conducted molecular dynamics simulations and calculated melting temperatures of passivated nano-aluminum particles. Fig. 21 shows the effect of particle size on the melting temperatures of aluminum core and oxide shell [207]. The oxide layer thickness is 1 nm. The melting temperature of the aluminum core increases with increasing core diameter, from about 650 K at 5 nm to 900 K at 10 nm. These values are approximately equal to melting temperatures of nascent aluminum particles predicted by MD simulations. These results suggest that the oxide layer exerts a negligible effect on the melting temperature of the aluminum core. Note, however, that the melting temperatures of the oxide shell vary in the range of 950–1200 K, substantially lower than the bulk value of 2350 K. It is important to also note that the Streitz–Mintmire potential has not been shown to reproduce melting temperatures of alumina, so the melting points determined from these MD simulations may not be very accurate.

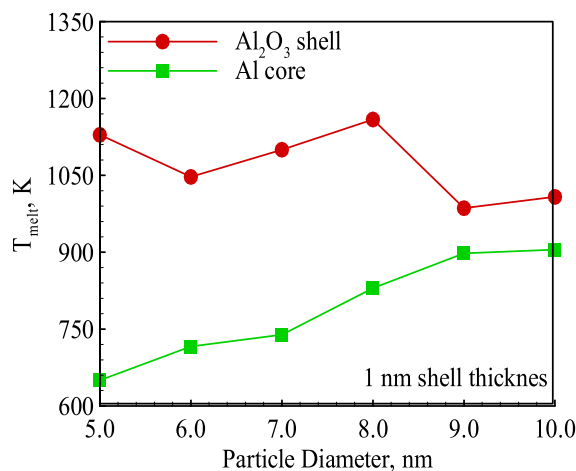


Fig. 21. Effect of particle size on melting temperatures of aluminum core and alumina shell; shell thickness is 1 nm; MD simulations with Streitz–Mintmire potential (reprinted from [207] with permission of Springer).

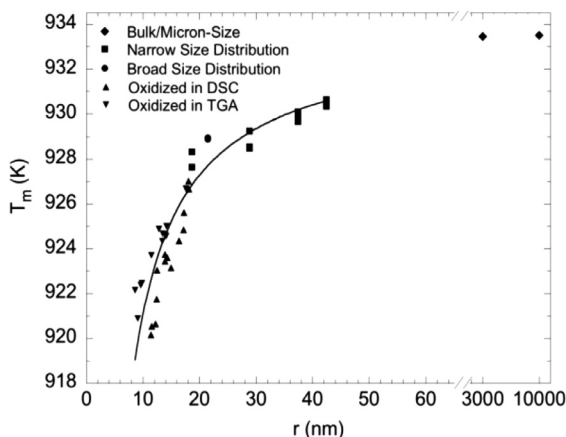


Fig. 22. Effect of particle size on melting temperature of passivated aluminum nanoparticles obtained using differential scanning calorimetry. Solid lines is the Gibbs–Thompson curve fit with solid-liquid surface tension of 68 mJ/m², lower than 90–150 mJ/m² found in the literature (reprinted from [228] with permission of Elsevier).

Experimental studies, on the other hand, suggest that the oxide layer exerts a significant effect on the melting temperatures of aluminum particles [214,228]. Fig. 22 shows the effect of particle size on the melting temperature of passivated aluminum particles (as measured using DSC) [228]. The oxide layer thickness is in the range of about 3–5 nm. The solid line in the figure represents the fit to the Gibbs-Thompson equation. As can be seen, the measured melting temperatures are well represented by the curve-fit, but for a solid-liquid interfacial energy of 68 mJ/m², which is lower than the values available in the literature (90–150 mJ/m²) [228]. The disparity was attributed to pressure buildup in the aluminum core due to the cage-like effect imposed by the oxide shell. The buildup of pressure results in elevated melting temperatures. When the melting temperatures were corrected to account for the pressure effect, the resulting solid-liquid interfacial energy was found to be 101 mJ/m², which is in better agreement with the data in the literature.

In another study [214], effect of oxide shell on melting point depression of aluminum nanoparticles was studied by intentionally damaging the oxide layers. The particle size varied in the range of 17 nm–12 μm and the oxide layer thickness was in the range of 1.7–4.1 nm. To create imperfections in the oxide layer, particles were damaged mechanically by placing them between two cylindrical pistons. A vertical load was applied to the powder with the single acting cylinder of the press. Fig. 23 shows the melting temperatures of passivated aluminum particles with damaged and undamaged oxide layers [214]. Results appear to suggest that the melting

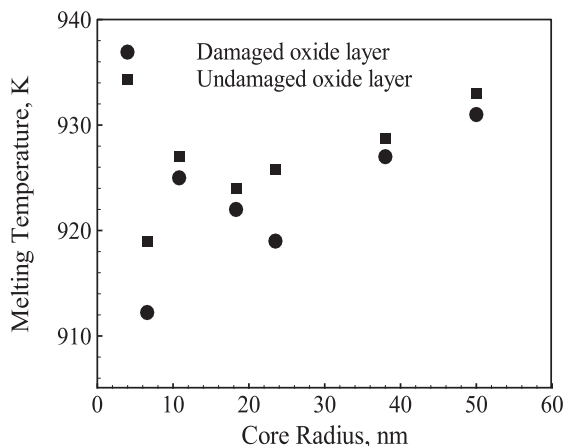


Fig. 23. Melting temperature of passivated nano-aluminum particles with damaged and undamaged oxide layers obtained using differential scanning calorimetry (adapted from [214] with permission from American Chemical Society).

temperatures of aluminum particles with undamaged oxide layers are greater than those of particles with damaged oxide layers, perhaps because of the buildup of compressive stresses in the aluminum core. This observation substantiates the theory that pressure buildup could affect the melting temperature of the aluminum core.

The melting temperature and pressure buildup are related by the Clausius–Clapeyron equation [214]

$$\Delta p = \Delta T \frac{h_m^b}{T_m^b} \left[\frac{\rho_s \rho_l}{\rho_s - \rho_l} \right], \quad (17)$$

where Δp is the pressure buildup and ΔT the melting temperature difference. The subscripts *s* and *l* refer to solid and liquid, respectively. For core pressures in the range of 0.1–1 GPa, the melting temperature difference varies between 10 and 100 K. Note that the uncertainties associated with data points in Fig. 23 are not fully known and differences in melting temperatures are not very substantial. Recent theoretical studies, however, do support the argument that the oxide layer exerts a significant pressure effect on melting temperature of aluminum nanoparticles [221].

The interfacial structure is also of concern with respect to the melting temperature of the core [222]. Fig. 24 shows the effect of particle size on the melting temperature of indium particles [229]. Lead and indium nanoparticles embedded in an aluminum matrix were synthesized using ball milling and melt spinning techniques [230,231]. Particle diameters varied in the range of 5–45 nm. Melting behaviors were studied using differential scanning calorimetry at a heating rate of 10 °C/min. An incoherent interface was observed in the ball milled particles, whereas a semi-coherent interface was present for melt-spun particles. For ball-milled samples, the melting temperature decreased with decreasing particle size. An opposite trend was observed for melt-spun particles and the temperatures were substantially greater than the bulk value (156.6 °C). It can be concluded that the nature of the core-shell interface has a tremendous impact on the melting temperature of nanoparticles.

The interface also affects the nucleation process and melting mechanism [222]. Molecular dynamics simulations of melting of nickel-coated silver nanoparticles suggest that nucleation occurred homogeneously when there was no lattice mismatch [229]. If there was lattice mismatch, nucleation occurred at the defective interfacial region. A similar scenario was observed for nickel-coated nano-aluminum particles [212]. Fig. 25 shows snapshots of an 8 nm nickel-coated aluminum particle colored by thermal displacement of atoms [212]. Nucleation occurs at the Al–Ni interface and the melting front propagates to the interior regions of the particle.

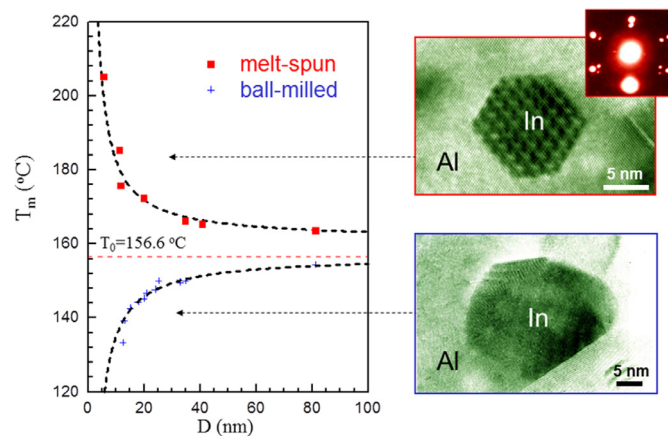


Fig. 24. Variation of melting temperature with particle size for indium nanoparticles embedded in an aluminum matrix for melt-spun and ball-milled samples (reprinted from [229] with permission of Elsevier).

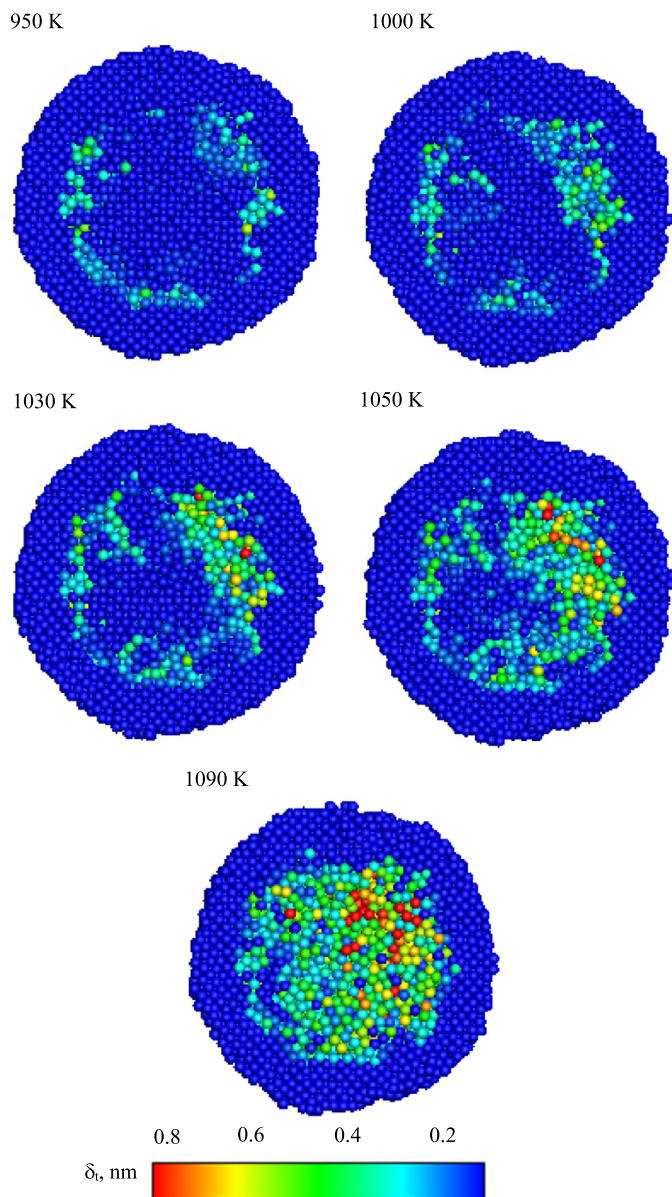


Fig. 25. Interfacial melt nucleation in nickel-coated aluminum particle; MD simulations with core diameter 6 nm and shell thickness 1 nm (reprinted from [212] with permission of American Chemical Society). (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

4.1.4. Melting temperature of passivation layer

The melting temperature of the passivation layer plays an important role in ignition and combustion of metal-based energetic nanomaterials, including conventional [207] and Ni-coated Al nanoparticles [212]. In ignition analysis of aluminum particles [22,34], particle ignition is associated with melting of the oxide layer, and the corresponding melting point is taken to be the bulk melting temperature of the oxide layer (~2350 K). It is well known that the thickness of the passivation layer is typically in the nanometer range and hence its melting point could be size dependent and lower than the corresponding bulk value. The phenomenon of melting point depression of nano-scale passivation layers may have important implications for ignition temperatures and mechanisms.

Fig. 26 shows the effect of shell thickness on the melting temperatures of the aluminum core and alumina shell [207]. Results were obtained using MD simulations. The melting temperature of the oxide shell increases with increasing shell thickness, from about 1130 K at 0.5 nm to 1300 K at 2 nm. Note that the melting

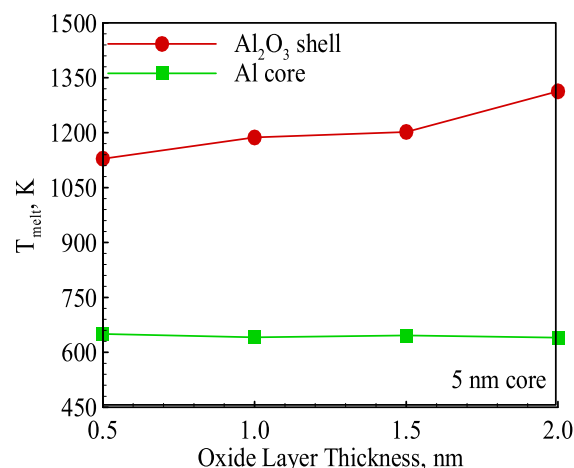


Fig. 26. Effect of shell thickness on melting temperatures of aluminum core and oxide shell; MD simulations with Streitz–Mintmire potential (reprinted from [207] with permission of Springer).

temperature of the aluminum core is independent of shell thickness. The particle sizes considered in the study are of the order of 10 nm and caution must be exercised before generalizing the result. Furthermore, the Streitz–Mintmire potential, used in the study, has not been proven to reproduce the bulk melting point of the oxide layer.

The equilibrium melting point depression of protective aluminum oxide films has been studied using Zhao and Jiang's model for thin films [232]

$$\frac{T_m}{T_m^b} = \exp\left(-\frac{\alpha-1}{D/2h-1}\right), \quad (18)$$

$$\alpha = \frac{2C_{p,m}}{3R} + 1, \quad (19)$$

where $C_{p,m}$ is the heat capacity difference between liquid and solid phases at the melting point. Fig. 27 shows the melting temperature of the oxide shell as a function of shell thickness [232]. For a shell thickness of 3–5 nm, the melting temperature is lower than the bulk value by 200–400 K. MD simulations indicate a similar trend for nickel and aluminum shells in Ni/Al core-shell structured particles, as shown in Fig. 28 [211,212]. The melting temperature of the nickel shell increases from 1325 K at 1 nm to 1580 K at 3 nm. Note that the result obtained for planar thin films cannot be directly used for spherical passivation layers over aluminum nanoparticles. Further studies, using more realistic models and potential functions, are

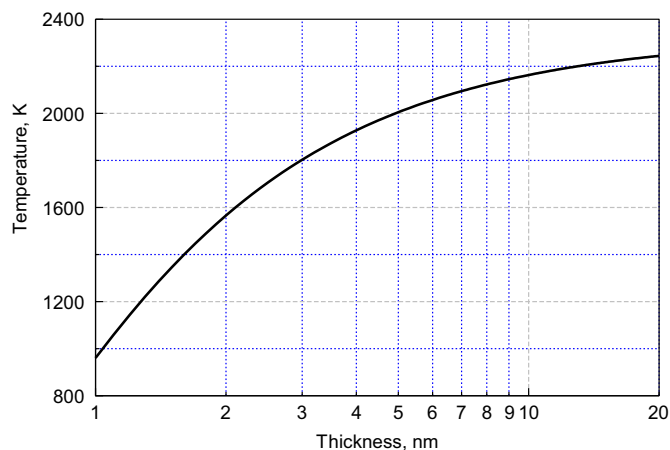


Fig. 27. Effect of film thickness on the melting temperature of alumina (Al_2O_3) film; Zhao and Jiang's model (reprinted from [232] with permission of Elsevier).

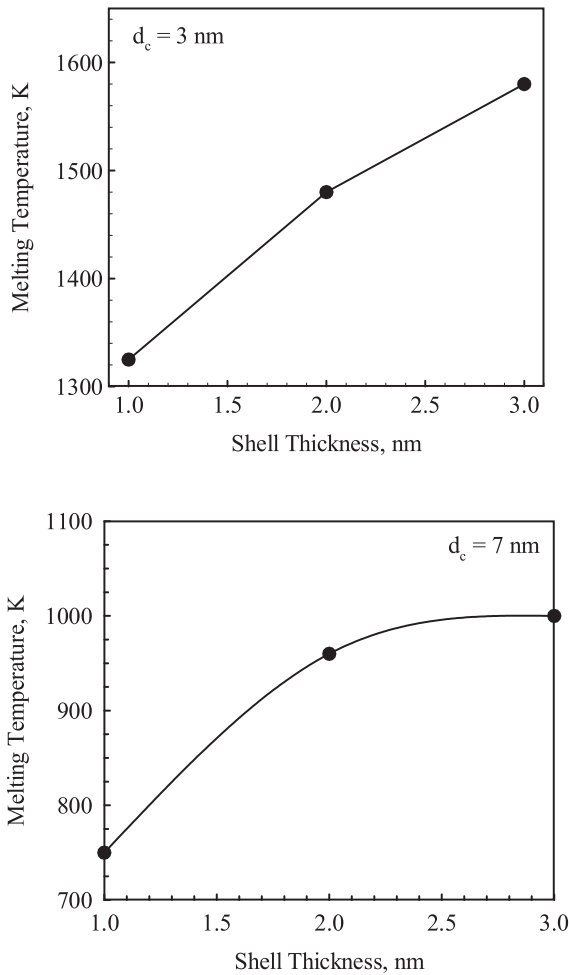


Fig. 28. Effect of shell thickness on the melting temperature of (a) nickel (b) aluminum shells in Al/Ni core-shell structured particles; MD simulations with embedded atom potentials (reprinted from [211,212] with permissions from American Chemical Society and Springer, respectively).

necessary to determine the effect of shell thickness and particle size on melting point of the passivation layer covering spherical metal nanoparticles. In any case, melting point depression of nano-scale passivation layers must be given its due importance in the analysis of ignition and combustion of metal particles.

4.2. Boiling temperature

Boiling temperature is also important in the study of the combustion of metal particles. Vapor-phase combustion can typically occur when the adiabatic flame temperature is greater than the boiling temperature of the particle. As a result, knowledge of metal boiling points under different conditions is essential to ascertain the mode of combustion. Boiling temperatures of metal nanoparticles that are substantially different from those of the bulk materials could have important implications on the possibility of vapor-phase combustion for metal nanoparticles. Table 2 shows the boiling temperatures of metals and their oxides at 1 atm pressure. The boiling temperatures of metals are typically lower than those of their respective oxides. Notable exceptions are boron, silicon, and zirconium.

The size dependence of the boiling temperature of aluminum particles has been characterized by treating the size effect of vapor pressure [22]. The vapor pressure of aluminum near the surface of a spherical aluminum particle, p_D , is given by [82]

$$p_D = p_0 \exp\left(\frac{4\sigma\nu_1}{k_B T D_p}\right), \quad (20)$$

Table 2

Boiling temperatures of metals and their oxides.

Metal	Boiling point, K	Metal oxide	Boiling point, K
Al	2791	Al ₂ O ₃	4000
B	4139	B ₂ O ₃	2340
Be	2741	BeO	4200
Fe	3133	FeO	3400
Li	1620	Li ₂ O	2710
Mg	1366	MgO	3430
Si	3173	SiO ₂	2860
Zr	4703	ZrO ₂	4280
Ti	3560	Ti ₂ O ₃	4000

where D_p is the particle diameter and ν the molar volume. The surface tension, σ , and vapor pressure of aluminum over a flat surface, p_0 , are given by [233,234]:

$$\sigma = 948 - 0.202T, \quad (21)$$

$$p_0 = p \exp\left(13.07 - \frac{36373}{T}\right). \quad (22)$$

Eqs. (20)–(22) were solved iteratively to calculate boiling temperatures of aluminum particles as a function of the particle size. Fig. 29 shows the calculated boiling temperatures for three different pressures, 0.5, 1.0, and 2.0 atm [22]. The boiling temperature is substantially lower than the bulk value only for particle diameters lower than 10 nm.

The effect of surface tension on the boiling temperature must also be considered. Surface tension can increase the pressure inside the particle, thereby elevating the boiling temperature. For a spherical particle, the Laplace pressure, p_L , is given by [235]

$$p_L = p_a + 2\frac{\sigma}{R_p}, \quad (23)$$

where p_a is the pressure of the ambient gas, in this case 1 bar. Fig. 30 shows the Laplace pressure and boiling temperature of aluminum as a function of pressure for different particle sizes [235]. The boiling temperature is the temperature corresponding to the point of intersection of the two curves. For example, the boiling temperature of a 100 nm Al particle is ~3700 K, which is substantially greater than the bulk value of 2740 K. Note that the Laplace pressure effect is more significant than the size dependence described by Eqs. (20–22). The net result is that the boiling temperatures of metal nanoparticles are predicted to be substantially greater than those of the bulk materials. Note that this effect is important even for particles with diameters on the order of 100 nm. This has important implications for the combustion mode of metal nanoparticles; the high boiling point implies that surface reactions could play a critical role during

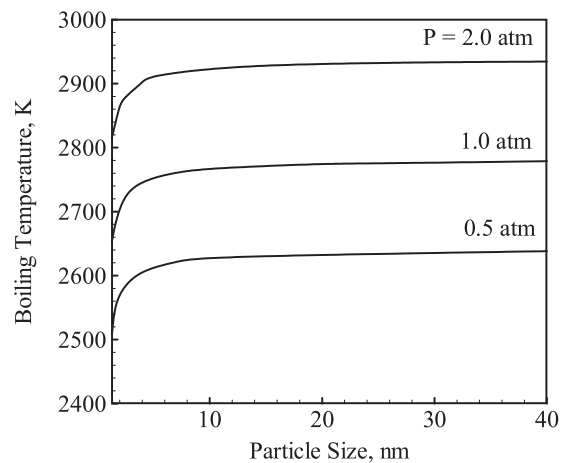


Fig. 29. Effect of particle size on the boiling temperature of aluminum nanoparticles; theoretical calculations (reprinted from [22] with permission of Elsevier).

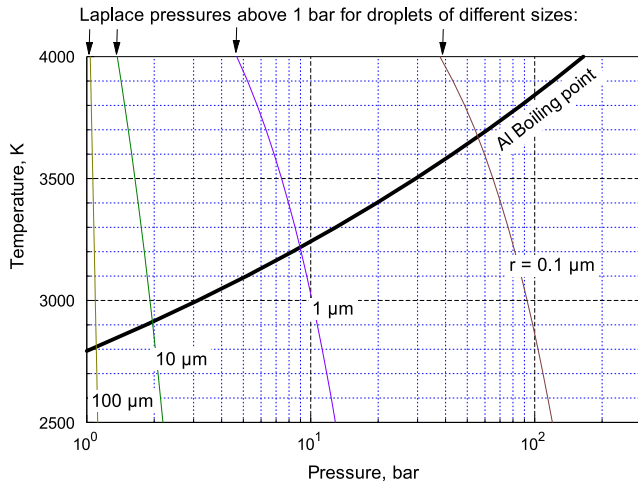


Fig. 30. Boiling temperature of aluminum as a function of pressure (black line) and Laplace pressure for different particle sizes (colored lines) showing the effect of surface tension on boiling point; theoretical calculations (reprinted from [235] with permission of Elsevier). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

combustion of metal nanoparticles. Experimental evidence of boiling point elevation of metal nanoparticles is however required.

4.3. Enthalpy of combustion

The enthalpy of combustion of aluminum particles is yet another important property of concern. The aluminum-oxygen reaction is given by



The enthalpy of combustion of bulk aluminum in pure oxygen is -1675 kJ/mol [236]. The size dependence of enthalpy of combustion of aluminum particles has been studied theoretically [237]. The analysis considered the size dependencies of the cohesive energy of aluminum and lattice energy of aluminum oxide. Two different cases were considered. In the first case, aluminum nanoparticles react to form aluminum oxide nanoparticles, whereas in the second case, aluminum nanoparticles react to form oxide agglomerates. For the first case, the thermodynamic energy balance can be written as [237]:

$$\Delta H_{R,1} = \Delta H_{R,bulk} + \Delta LE_{OX} - 2\Delta CE_{Al}, \quad (25)$$

where ΔLE_{OX} is the difference between the lattice energies of bulk and nano-alumina, while ΔCE_{Al} the difference between the cohesive energies of bulk and nano aluminum. For the second case, the energy balance is given by [237]

$$\Delta H_{R,2} = \Delta H_{R,bulk} - 2\Delta CE_{Al}. \quad (26)$$

Fig. 31 shows the effect of particle size on enthalpy of combustion of aluminum particles [237]. For isolated particles, the enthalpy of combustion decreases with decreasing particle size. Predictions can be used to obtain a closed-form expression for the enthalpy of combustion of isolated aluminum particles in oxygen [22]

$$H_R = -1690 + \frac{865.1}{D_p^{0.87}}, \quad (27)$$

where H_R is the heat of reaction in kJ/mol and D_p the particle size in nm. The observed size dependence of the combustion enthalpy is due to the fact that the particle size exerts a stronger effect on the lattice energy of alumina than on the cohesive energy of aluminum [237]. When particle agglomeration is considered, the lattice energy of alumina can be taken to be approximately equal to the corresponding bulk value [237]. As a result, reactions are more exothermic for smaller particles and the

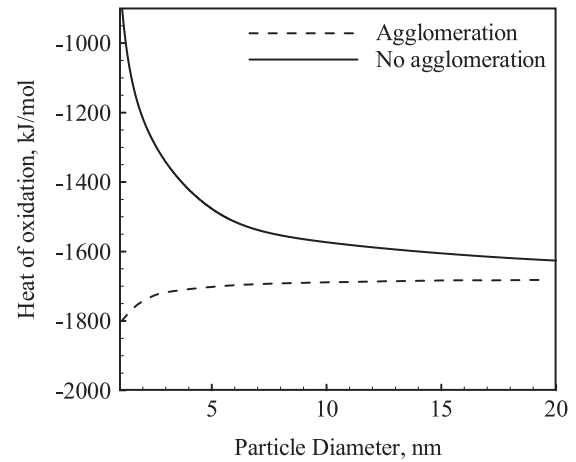


Fig. 31. Effect of particle size on enthalpy of combustion of aluminum particles obtained using thermodynamic energy balance (adapted from [237] with permission of Elsevier).

enthalpy of combustion is greater than the bulk value. This is a rather surprising effect of agglomeration for ultrafine particles. Note that the deviations from the bulk value are substantially only for particles smaller than 10 nm. It must be noted that the above results are solely based on theoretical analysis. Experimental studies will be necessary to verify the predicted size dependence of enthalpy of combustion.

4.4. Emissivity

To model ignition and combustion of metal particles, radiation heat transfer between particles and ambient gas must be accounted for. In most of the previous studies on aluminum combustion, radiation heat transfer between metal nanoparticles and ambient gases has been modeled using the Stefan-Boltzmann law [236]

$$\dot{Q}_{rad} = \varepsilon \sigma A (T_p^4 - T_a^4), \quad (28)$$

where ε is the emissivity, σ the Stefan-Boltzmann constant, and A the particle surface area. The subscripts p and a refer to the particle and ambient gas, respectively. The particle emissivity is treated as a constant and its value is chosen to be on the order of 0.1 [34]. For nanoparticles, the particle size is lower than the wavelength of thermal radiation and the particle emissivity is significantly lower than the bulk value [238].

The following expression was derived for the radiation intensity of metal nanoparticles by considering the magnetic dipole contributions [238]:

$$I = \frac{16R_p^3 k_B^5 J}{3c^3 \hbar^4} T^5, \quad (29)$$

$$J(p) = \int_0^\infty \alpha''_m(p\sqrt{x}) \frac{x^4}{e^x - 1} dx \quad (30)$$

$$p = \frac{R_p}{c} \sqrt{\frac{2\pi\sigma k_B T}{\hbar}}, \quad (31)$$

$$x = \frac{\hbar\omega}{k_B T}, \quad (32)$$

where I is the radiation intensity, c the speed of light in vacuum, $\hbar$ the Planck's constant, α''_m the magnetic permeability, and ω the frequency. For nanoparticles, the radiation intensity is proportional to the fifth power of temperature. The particle emissivity can be expressed as [238]

$$\varepsilon = \frac{I}{I_b} = \frac{80R_p k_B T J}{\pi^3 c \hbar}. \quad (33)$$

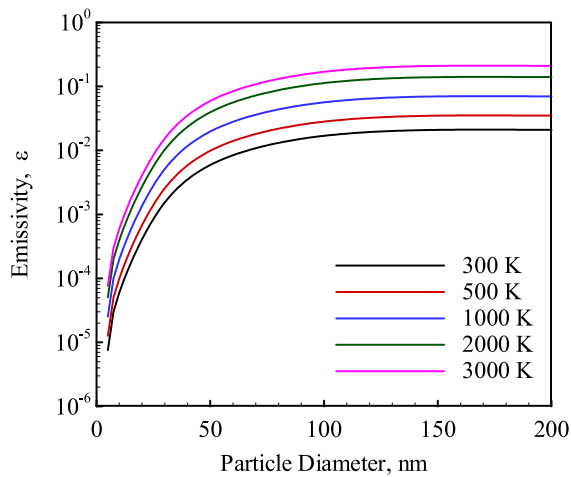


Fig. 32. Effect of particle size on emissivity of aluminum nanoparticles; analysis considered magnetic-dipole contribution but ignored electric dipole contribution, which is important at high temperatures (reprinted from [22] with permission of Elsevier).

Fig. 32 shows the effect of particle size on the emissivity of aluminum particles for different temperatures [22]. The particle emissivity is orders of magnitude lower than the bulk value; for a particle size of 20 nm and temperature of 300 K, the emissivity is $\sim 10^{-4}$, substantially lower than the bulk value of 0.02. Furthermore, emissivity is a strong function of temperature. It is important to note that the magnetic dipole approximation is strictly valid only for far-infrared and longer wavelengths (corresponding to low temperatures). In practical combustion systems, the temperature range of concern is as high as 3000 K. As a result, the electric dipole contribution must be treated. When electric and magnetic dipole contributions are considered, at a fixed temperature, the emissivity attains its maximum value when the particle radius is $1/2\pi$ times the wavelength of the peak thermal radiation as given by Wien's law [239]. This suggests that there is non-monotonic reduction in emissivity with decreasing particle size, contradicting the predictions of the magnetic dipole theory.

Experimental studies have also been conducted to measure the emissivity of alumina particles, and these experiments have shed some light on the spectral nature of emissivity and effects of temperature and optical depth of dust clouds. Lynch et al. [240] conducted heterogeneous shock tube experiments to measure the emissivity of alumina particles in an inert environment as a function of temperature (2000–3500 K), wavelength (0.55–0.95 μm), and particle diameter (50 nm–10 μm). The dependence of spectral emissivity on wavelength was expressed in the following form: $\varepsilon_\lambda = a \lambda^n$, where the exponent, n , was a function of temperature. For micro-sized alumina particles, emissivity decreased with increasing wavelength at low temperatures, but followed an opposite trend at higher temperatures. The exponent n thus increased from -1.4 to 0.5 , when temperature increased from 2500 to 3500 K. A roughly gray behavior was observed at about 3000 K. For alumina nanoparticles, emissivity exhibited a stronger spectral dependence. At 2678 K, n was approximately -1.2 but reached as high as 2.1 at 3052 K. For both cases, the emissivity was a strongly dependent on temperature.

In a subsequent study [241], measurements were made using the same shock tube setup, but for optically thin alumina particle clouds, and focusing on the effects of temperature and wavelength on emissivity. The emissivity was found to be weakly dependent on temperature over the temperature range of 2700–3500 K. The exponent in the emissivity-wavelength relationship was -1.4 and -1.2 for micro- and nano-alumina particles, respectively. This is not in agreement with the results obtained in the previous study [240]. The disparity was attributed to the sensitivity of optical depth of the cloud

to particle concentration at high temperatures. Efforts were made to measure emissivity of alumina nanoparticles at even lower temperatures. The exponent n decreased from -1.446 at 2368 K to -2.449 at 1801 K. This was attributed to the melting of the oxide layer at 2300 K. In general, optical depth had a significant effect on the wavelength dependence of emissivity of micron-sized alumina particles, while a relatively weak effect was observed with more spread for nanoparticles.

It is apparent that emissivity is dependent on various factors, including particle size, temperature, wavelength, and phase of the material. These can be considered to treat radiation heat transfer between metal nanoparticles and ambient gases more accurately. Also, the application of the classical Stefan-Boltzmann law with a constant emissivity value corresponding to the bulk material may lead to significant errors. Further studies will be necessary to fully understand the dependence of emissivity and absorptivity on particle size, wavelength, and temperature over a broad range of conditions.

5. Low-temperature oxidation of metal nanoparticles

Low temperature oxidation of metals has been the subject of research since the early 1900 s. Here, temperatures of concern are significantly lower than the ignition temperature of particles. Although these reactions and mechanisms may influence the overall ignition delay, they are not responsible for particle ignition. They may, however, have important implications for the shelf life and safety characteristics of particles. Oxidation of nascent particles involves formation and growth of a monomolecular oxide layer. For passivated particles, oxidation results in the growth of the existing oxide layer. In general, the mechanism of low temperature oxidation of metal nanoparticles depends on the particle temperature and the properties of the metal and oxide layer. The formation of the oxide monolayer is a quick process; however, the mechanistic details are not well understood. The oxidizer molecules diffuse and collide and adsorb on the particle surface. Once the oxide monolayer is established, the growth rate is largely dependent on the properties of the oxide layer and temperature.

Table 3 lists some important low temperature oxidation mechanisms. The linear oxidation law means that the oxide layer thickness grows linearly with time. This implies that the growth rate of the oxide layer is constant and the newly established oxide layer does not affect the growth rate. This is typically the case for particles with porous and/or cracked oxide layers [242]. In such cases, chemical kinetics controls the rate of oxidation of particles. The logarithmic law is typically applicable for low temperatures and thin intact oxide layers [243,244]. Here, the oxide layer thickness is a logarithmic function of time. Mass diffusion across the oxide layer is the rate-controlling process and the major driving force is the electric field across the oxide layer [245]. For thicker oxide layers and higher temperatures, particle oxidation may follow the parabolic law [103,243]. In this case, the major driving force for mass diffusion is the presence of concentration gradients. In the following sections, mechanisms governing oxidation of metals and kinetics of oxidation under different conditions are discussed in detail.

Table 3
Low temperature oxidation mechanisms of metals.

Oxidation law	Rate equation	Remarks
Linear	$\delta = k_l t$	Porous or cracked oxide layers
Parabolic	$\delta^2 = k_p t + c$	Thick and integral oxide layers and high temperatures
Logarithmic	$\delta = k_e \log (At + c)$ $\delta^{-1} = k_e \log (At + c)$	Thin oxide layers and low temperatures

5.1. Planar substrates

The oxidation of bare metallic substrates at near room temperature was first studied by Cabrera and Mott [245]. An initial fast oxidation stage, in which the oxide layer forms and grows rapidly, is followed by an abrupt and drastic reduction of the growth rate. They advanced a theory of low temperature oxidation of metals with passivated surfaces. The Cabrera-Mott theory corresponds to the logarithmic growth rate law. Fig. 33 shows a schematic of the electric field across the oxide layer of the particle, illustrating the Cabrera-Mott oxidation mechanism [22]. The oxidizer gas molecules are adsorbed on the particle surface. The metal electrons traverse through the oxide layer to ionize the adsorbed oxidizer atoms, creating an electric field between the metal-oxide and oxide-oxidizer interfaces. The presence of the electric field promotes mass diffusion across the oxide layer. The growth of the oxide layer on a planar substrate is given by [245]

$$\frac{d\delta}{dt} = \Omega n \nu \exp\left(-\frac{W}{k_B T}\right) \exp\left(\frac{qaE}{k_B T}\right), \quad (34)$$

where δ is the shell thickness and t the time. The model parameters are volume of oxide formed per cation (Ω), number of cations per unit area that jumps across the interface (n), attempt frequency for cation jump (ν), cation charge (q), distance ($2a$), energy barrier (W), and electric field (E). The volume of oxide per cation is calculated from the density of the oxide layer and the attempt frequency is commonly taken as 10^{12} s^{-1} [246]. Parameters q , a , and n may be known *a priori* or can be determined experimentally. The electric field can be expressed as:

$$E = -\frac{V}{\delta}, \quad (35)$$

where V is the Mott potential (V). Note that the diffusion process and oxide layer growth weakens the electric field and the growth rate slows down. The Mott–Cabrera model thus corresponds to the logarithmic growth rate law.

Jeurgens et al. [246] systematically studied the oxidation mechanism of pure aluminum substrates. The substrates were heated to temperatures in the range of 373–773 K and exposed to pure oxygen gas at a partial pressure of $1.33 \times 10^{-4} \text{ Pa}$. Exposure times varied in the range of 100–15,000 s. Fig. 34 shows the temporal evolution of the oxide layer thickness for different substrate temperatures. For temperatures up to 573 K, the oxide layer thickness attains a limiting value. This is consistent with the findings of Cabrera and Mott [245]. At higher temperatures, the growth of the oxide layer is not arrested and a limiting thickness is not attained. The initial fast oxidation process was attributed to electric-field controlled interstitial outward diffusion of Al cations. At the end of the initial fast oxidation stage, the electron tunnel current became effectively zero. As a result of

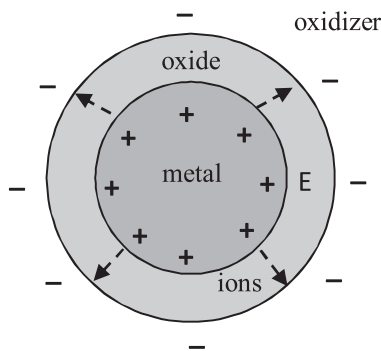


Fig. 33. Electric field across the oxide layer in a spherical nano-particle surrounded by oxidizer molecules (+ positive charge, – negative charge) according to the Mott–Cabrera mechanism (reprinted from [22] with permission of Elsevier).

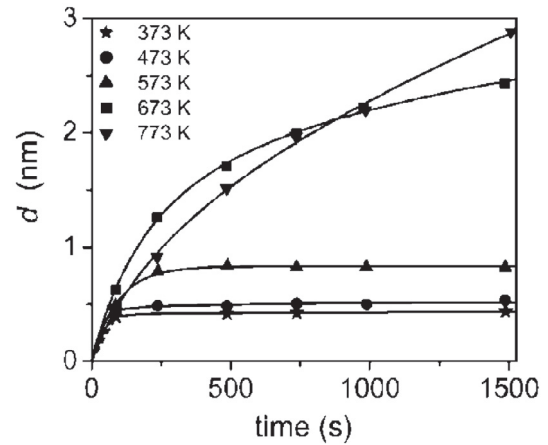


Fig. 34. Experimentally obtained temporal evolution of the oxide layer thickness for pure aluminum substrates for different temperatures (reprinted from [246] with permission of American Institute of Physics).

the constraint of coupled currents of electrons and cations, oxide-film growth stops at low temperatures, because the chemical diffusion of ions across the oxide layer and the contribution of electron transport by thermionic emission are negligibly small. During the slow oxidation stage, the initially Al-enriched, amorphous oxide film attained the stoichiometric composition and became crystalline $\gamma\text{-Al}_2\text{O}_3$. As soon as $\gamma\text{-Al}_2\text{O}_3$ crystallites formed, the inward chemical diffusion of oxygen along grain boundaries established the growth of the oxide layer. The Mott potential and energy barrier were calculated for the limiting oxide layer thickness condition ($d\delta/dt = 10^{-15} \text{ m/s}$) [246]. Parameters can also be calculated by integrating the Cabrera–Mott equation and plotting the inverse of the oxide layer thickness as a function of $\log(t/\delta^2)$ [247,248]. The resulting slope and intercept can be used to obtain the values of the Mott potential, energy barrier, and number of cations per unit area jumping across the interface.

For thicker oxide layers and higher temperatures, experimental evidence suggests that oxidation may no longer follow the logarithmic law [243]. The oxidation of single aluminum crystals has been studied for temperatures as high as 800 K using ellipsometry [243]. The pressure was varied between 10^{-9} and 10^{-2} torr. The initial fast oxidation stage involved chemisorption of oxygen molecules on the particle surface and formation of a thin oxide layer. This was followed by a slow oxidation stage, corresponding to the growth of the oxide layer. The oxidation kinetics followed the logarithmic law over a temperature range of 500–600 K, but a parabolic law was observed at higher temperatures (650–800 K). As mentioned earlier, in the parabolic regime, the oxidation rate is governed by mass diffusion through the oxide layer and the driving force is the presence of concentration gradients (Fickian diffusion). The resulting oxide growth rate can be expressed as:

$$\frac{d\delta}{dt} = V_0 J, \quad (36)$$

where V_0 is the volume of the oxide formed per mole of species diffusion and J is the Fickian diffusion flux, which is given by:

$$J = -D \frac{dC}{dx} = D \frac{\Delta C}{\delta}, \quad (37)$$

where D is the diffusion coefficient, ΔC is the difference between species concentrations at two locations, typically the metal-oxide and oxide-gas interfaces. Substituting Eq. (37) into Eq. (36), the oxide growth rate can be written as:

$$\frac{d\delta^2}{dt} = 2V_0 D \Delta C, \quad (38)$$

which describes the parabolic growth of the oxide layer.

5.2. Metal nanoparticles

The Mott–Cabrera equation, as discussed in the previous section, is applicable only for planar substrates. For spherical particles, appropriate corrections must be incorporated. For example, the electric field across the oxide layers of a nanoparticle is greater than its counterpart in a planar substrate [249], so the model must incorporate the electric field correction and volume changes associated with particle oxidation [250]. The following equations have been developed to characterize the oxidation rate of metal nano-particles [250]:

$$\frac{d\delta}{dt} = \left[(\Omega_1 + \Omega_2) \left(\frac{R_c}{R_p} \right)^2 - \Omega_1 \right] n v \exp \left(-\frac{W}{k_B T} \right) \exp \left(-\frac{q a V R_p}{k_B T R_c \delta} \right), \quad (39)$$

$$\frac{dR_c}{dt} = \Omega_1 n v \exp \left(-\frac{W}{k_B T} \right) \exp \left(-\frac{q a V R_p}{k_B T R_c \delta} \right),$$

where R_c is the core radius. Table 4 lists the model constants for aluminum [250]. Such models can be used to simulate oxidation of passivated metal nanoparticles [251,252]. Caution must, however, be exercised when using these models, as particle oxidation may not always be governed by Mott–Cabrera kinetics over the entire range of conditions.

Molecular dynamics simulations also indicate a two-stage oxide layer growth process for aluminum nanoparticles [32,253]. A 20 nm aluminum particle was placed at the center of an 80 nm long cubic box. A total of 530,720 oxygen atoms were distributed randomly in the box. The temperature of the system was 300 K. Inter-atomic interactions were captured using the Streitz–Mintmire potential. Fig. 35 shows a snapshot of the dissected particle and the temporal evolution of the oxide layer thickness [32]. The oxide layer thickness attains a limiting value of about 3.5 nm, which is in good agreement with the experimental data [254]. Diffusion coefficients of aluminum and oxygen atoms were estimated to be on the order of $10^{-4} \text{ cm}^2/\text{s}$. A similar study was conducted to understand the oxidation of nanoscale aluminum crystals at room temperature [244]. After a time period of about 100 ps, the growth kinetics followed the logarithmic law and the thickness of the oxide layer reached a limiting value of 3 nm.

A two-stage oxidation process has also been observed for bare silicon nanoparticles in oxygen [255]. Particles were initially passed through a differential mobility analyzer that was set to transmit only those particles having mobility diameters of about 10 nm. The mono-dispersed particle streams were mixed with oxygen/nitrogen mixtures of different oxygen volume fractions and allowed to react over a broad temperature range (600–1100 °C) for approximately one second. Particles were size-classified after reaction with a second differential mobility analyzer. Changes in particle size were used to determine the growth rate of the oxide layer and infer mechanism of oxidation of silicon nanoparticles. The observed oxidation behavior was similar to that of bare aluminum, with an initial fast oxidation process followed

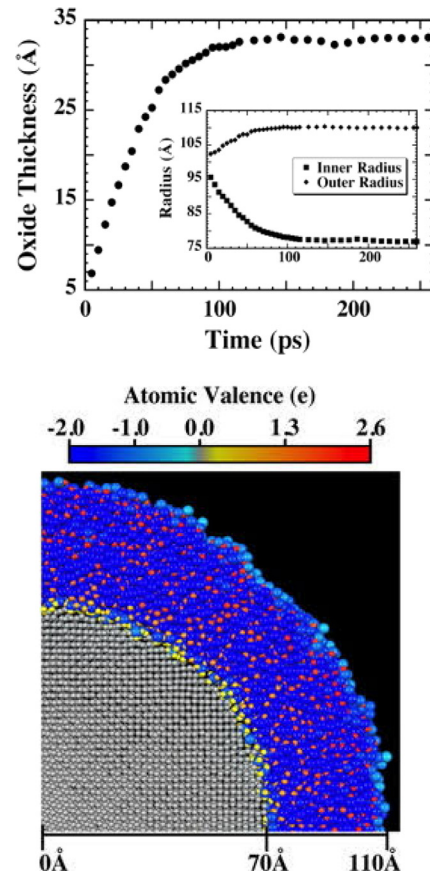


Fig. 35. (a) Temporal evolution of the oxide layer thickness of an aluminum particle; (b) snapshot of the dissected aluminum particle with a stable 4 nm thick oxide layer; MD simulations with Streitz–Mintmire potential (reprinted from [32] with permission of American Physical Society).

by an abrupt transition to a slow oxidation regime at $\Delta D_p \sim 0.3 \text{ nm}$. This roughly corresponds to the growth of the monomolecular oxide layer. The oxygen molecules reacted directly with the silicon particle. Once the oxide monolayer was formed, oxidation proceeded by mass diffusion through the oxide layer. A theoretical model was developed to describe this process. Reasonably good agreement between model predictions and experimental data was achieved.

Oxidation of passivated aluminum nanoparticles has been extensively studied using a single particle mass spectrometer (SPMS) for temperatures in the range of 25–1100 °C and at low heating rates ($< 10^3 \text{ K/s}$) [103]. The particle size range was 50–150 nm. The particles did not react completely. For example, at a temperature of 1373 K, only about 40% of the particle had oxidized after 15 s. Diffusion through the oxide layer and chemical kinetics were considered to ascertain the rate-controlling step. Analysis of the temporal variations of the measured extent of conversion suggested that the oxidation of nanoaluminum particles was controlled by mass diffusion across the oxide layers of the particles. The particle burning time, t_b , was thus expressed as [103]

$$t_b = \frac{\rho_p D_p^2}{32 D C_{O,a}}, \quad (40)$$

where $C_{O,a}$ is the molar concentration of the oxidizer in the ambient gas. The diffusion coefficient, D , has a temperature dependence of the form

$$D = D_0 \exp \left(\frac{-E_A}{RT} \right), \quad (41)$$

Table 4
Constants for the Mott–Cabrera equation of spherical nano-aluminum particles [250].

Constant	Value
n	10 nm^{-2}
v	10^{12} s^{-1}
a	0.12 nm
φ_m	-1.6 V
W	2.6 eV
q	$3e$
Ω_1	-0.0166 nm^3
Ω_2	0.023 nm^3

where E_a is the activation energy and D_0 the pre-exponential factor. For DC arc generated particles of size ~ 50 nm and temperature range of 600–900 °C, the activation energy and preexponential constant were 69.5 kJ/mol and $1.72 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively [103]. The resulting diffusion coefficients are on the order of 10^{-9} – $10^{-8} \text{ cm}^2/\text{s}$ over the temperature range of concern [103] and these are orders of magnitude lower than the values obtained by Campbell et al. [32]. A theoretical model of oxidation of aluminum nanoparticles was also developed [205]. In another study [256], a two-stage oxidation process was proposed for aluminum nanoparticles. The first step was the formation of a 6–10 nm thick oxide layer, which was dictated by chemical kinetics. The second step involved mass diffusion across the oxide layer and chemical reactions.

It is apparent that the diffusion coefficient is an important parameter at low temperatures. Diffusion coefficients were calculated using molecular dynamics simulations for nano aluminum particles of diameters 5.6 and 8.0 nm [257]. Two different oxide layer thicknesses of 1 and 2 nm were considered. Both crystalline and amorphous oxide layers were considered. The particle was heated from 300 to 3000 K at a heating rate of 10^{12} K/s and particle oxidation was characterized by mass diffusion across the oxide layer. The electric field accounted for approximately 90% of the mass flux of aluminum ions through the oxide shell. At a temperature of 600 K, the diffusion coefficient was on the order of $10^{-6} \text{ cm}^2/\text{s}$, which is substantially greater than the values obtained by Park et al. [103]. It is important to note that the particle sizes in MD simulations are of the order of 10 nm, while Park et al.'s study used 50 nm particles. The diffusion coefficient could thus be a size-dependent property; unfortunately, the size dependence of the diffusion coefficient of aluminum particles is still poorly understood.

An alternative equation has also been proposed to model oxidation of passivated metal particles before ignition [258]:

$$\frac{dh}{dt} = \frac{KC_{ox}^m}{h^n} \exp\left(-\frac{E}{RT}\right), \quad (42)$$

where h is the oxide layer thickness, E the activation energy, R the gas constant, T the temperature, K the pre-exponential factor, and C_{ox} the oxidizer concentration near the particle surface. As can be seen, there is no diffusion coefficient in the equation, but only a pre-exponential factor and activation energy. The exponent n determines the dependence of the oxidation rate on oxide layer thickness. The exponent $n=0$ corresponds to the linear oxidation law and is typically employed for magnesium, which is covered by a permeable oxide layer [258]. This can be attributed to the presence of cracks and pores in the oxide layer. For aluminum, the exponent $n=1$ is typically used, corresponding to the parabolic oxidation law [258]. The oxidation rate is controlled by mass diffusion through the oxide layer. Two sets of data are available for the pre-exponential factor and activation energy. For $n=1$, the pre-exponential factor and activation energy are $1.9 \times 10^{-9} \text{ m}^2/\text{s}$ and 17 kcal/mole, respectively [258]. For $n=0$, they are $18 \times 10^3 \text{ m/s}$ and 20 kcal/mole, respectively [258]. A detailed and more accurate evaluation of pre-exponential constant can be found in [258].

It is evident that oxidation of bare metal nanoparticles, in general, consists of rapid formation of the oxide monolayer followed by relatively slow growth of the oxide layer. The kinetics of the formation of the monomolecular oxide layer is not well understood. For particles with intact oxide layers, the second stage of oxidation may follow either the logarithmic growth rate law or the parabolic law, depending on temperature and oxide layer thickness. While the general features and mechanisms of low temperature oxidation of metal nanoparticles appear to be fairly well established, quantitative prediction of important properties such as ignition delay still remains a challenge, due to uncertainties in parameters such as the rate constants associated with the diffusion process and chemical reactions. Moreover, such parameters are not strictly constants, but depend on many factors such as

sample size, temperature, and so forth. Furthermore, different mechanisms come in to play under different conditions and transition between underlying mechanisms is not completely understood. Future studies can thus attempt to address these challenges and problems.

6. Pyrophoricity of metal nanoparticles

An important consequence of the extreme reactivity of nanoparticles is pyrophoricity. Pyrophoricity is the tendency of a substance to burn spontaneously at room temperature. When a nascent particle is exposed to an oxidizing gas at room temperature, chemical reactions result in the formation of an oxide layer on the particle surface. For micron-sized and larger particles, the heat release due to chemical reactions is not sufficient to heat the particle to the ignition temperature and particle ignition is thus not achieved. If the particle size is decreased below a critical value, however, self-ignition can occur [22]. Pyrophoricity is a major safety issue during synthesis, handling, and storage, although it can be useful in applications like decoy flares for defending against heat-seeking missiles [259]. Therefore, it is important to know the particle size at which metal particles become pyrophoric. Theoretical analyses have been performed to determine the critical particle size, but sufficient experimental evidence supporting these predictions is lacking.

Analysis of ignition was pioneered by Semenov and Frank-Kamenetskii [260]. One of the earliest models on metal pyrophoricity was based on the assumption of homogeneous gas-phase reactions [33], neglecting the transient energy balance, heat losses to the ambient gas, and size dependence of physicochemical properties. Under these assumptions, the critical particle size was obtained by equating the chemical energy release to the sum of the energies needed to heat the particle to its boiling point and vaporize the metal [33]:

$$\frac{(1 - (\delta/R_p)_{cr})^3}{1 - (1 - (\delta/R_p)_{cr})^3} = \frac{\rho_{Al_2O_3} \{ (-H_{ox}^0) - (H_{T_b}^0 - H_{298}^0) \}_{Al_2O_3}}{\rho_{Al} (H_{T_b}^0 - H_{298}^0 + H_{vap})_{Al}}, \quad (43)$$

where T_b is the boiling point of metal, and H_{vap} the enthalpy of vaporization of metal. The subscripts ox and cr refer to oxidation and critical condition, respectively. Eq. (43) was used to obtain the critical particle size for various metals. The oxide layer thickness was taken as 2.5 nm and the critical particle size was below 100 nm. It was shown that pyrophoricity is of concern only for nanoparticles.

When a nascent particle is exposed to an oxidizing gas, the oxide layer thickness, core diameter, and temperature vary continuously with time. Particle ignition is thus a transient process dictated by the competing effects of heat release due to chemical reaction and heat loss to the ambient gas, so the steady-state assumption is strictly not valid. A transient energy balance is thus required to obtain a more accurate estimate of the critical particle size [22,34]. The energy conservation equation was expressed as follows [22]:

$$m_p C_p \frac{dT}{dt} = \dot{Q}_{chem} - \dot{Q}_{cond} - \dot{Q}_{rad}, \quad (44)$$

where m_p is the particle mass, C_p the specific heat, and $\dot{Q}$ the rate of energy loss/release. The subscripts $chem$, $cond$, and rad refer to chemical, conduction, and radiation, respectively. In the continuum regime, the conduction heat transfer rate is given by [261]

$$\dot{Q}_{cond} = 4\pi R_p \lambda_a (T - T_a). \quad (45)$$

where λ is the thermal conductivity. In the free-molecular regime, the conduction heat transfer rate is expressed as follows [261]:

$$\dot{Q}_{cond} = \alpha \pi R_p^2 \frac{p_a \sqrt{8k_B T_a / \pi m_a}}{2} \left(\frac{\gamma^* + 1}{\gamma^* - 1} \right) \left(\frac{T}{T_a} - 1 \right), \quad (46)$$

where m is the mass of the oxygen molecule, γ^* the adiabatic constant calculated at a temperature $T^* = (T + T_a)/2$, and α the accommodation coefficient. The accommodation coefficient is the ratio of the

actual average energy transferred during collision to the theoretical value under complete energy accommodation. The radiation heat transfer rate was calculated using the Stefan-Boltzmann law

$$\dot{Q}_{rad} = \varepsilon A \sigma (T^4 - T_a^4), \quad (47)$$

where ε is the emissivity of the oxidized aluminum surface [262]. The chemical energy release rate can be expressed as [22]

$$\dot{Q}_{chem} = 4\pi R_c^2 \rho_{Al} H_R \frac{dR_c}{dt}, \quad (48)$$

where H_R is the heat of reaction. Particle oxidation was modeled using the Cabrera-Mott oxidation kinetics.

Chemical equilibrium analysis was first performed to calculate the particle temperature after the formation of the monomolecular oxide layer. The thickness of the monomolecular oxide layer was taken to be 0.3 nm. Transient energy balance analysis was then conducted to determine the minimum ignition temperature for particles covered by the oxide monolayer of thickness 0.3 nm. Ignition was assumed to be achieved when the particle temperature increased monotonically beyond the melting point of the oxide film. As a result, the minimum ignition temperature was the minimum initial temperature of the particle (in the transient energy balance analysis) that resulted in ignition. If the minimum ignition temperature was lower than the particle temperature obtained using chemical equilibrium analysis, the particle was considered to be pyrophoric. Fig. 36 shows a comparison of the results of chemical equilibrium and transient energy balance analyses [22]. The two curves intersect at the critical particle size of about 32 nm. Nascent aluminum particles smaller than 32 nm were thus predicted to be pyrophoric.

Sensitivity analysis was also conducted to determine how sensitive the predictions are to changes in the physicochemical properties and polymorphic state of the oxide layer. The temperature dependence of the energy accommodation coefficient was included by considering Altman's equation [263]

$$\alpha < \frac{\theta^2}{(2\frac{C_v}{R} + 1)T_a T_p}, \quad (49)$$

where C_v is the molar specific heat of the gas and $\theta = 428$ K, the Debye temperature of aluminum. The resulting critical particle size was 40 nm. This is a marginal change, considering the fact that the accommodation coefficient is a strong function of gas and particle temperatures. Parameters of the Mott–Cabrera oxidation model influenced the results as well. For example, increasing the Mott

potential from 1.6 to 1.75 V resulted in an increase in the critical particle size by 18%. Predictions were quite sensitive to changes in material properties and heat transfer model. The critical particle size increased by 40%, when bulk material properties calculated at ambient temperature were used and the oxide layer was assumed to be in a crystalline form. It decreased by 43% when free-molecular effects were neglected in the analysis. For an oxide layer thickness of 0.3 nm, the critical particle size was predicted to be 3.8 nm. Commercially available aluminum nanoparticles with oxide layer thickness in the range of 2–4 nm were thus predicted to be non-pyrophoric. A similar analysis can be conducted to predict the critical particle size for pyrophoricity for other metals.

7. Ignition of metal nanoparticles

Ignition refers to the onset of vigorous self-sustaining exothermic chemical reactions. In metal particles, ignition is typically caused by phase transformations of the metal core or oxide layer, which occurs at high temperatures, so high ignition temperatures are a matter of concern. In order to maximize energy release rates, it is desirable to have low ignition temperatures and ignition delays, without compromising the metal content, safety characteristics, and shelf life. This is one of the major challenges in the field of energetics, since approaches to lower ignition temperatures have thus far resulted in undesirable side effects [24,40]. For example, decreasing the particle size from micron to nano results in loss of energy content [40] and poses processing issues [24]. A few approaches, such as replacing the oxide layer with nickel coating, have contributed to substantial reduction in ignition temperatures without significant undesirable side effects [264].

Ignition temperature depends not only on the nature of the metal and the oxide layer, but also on other factors such as heating rate, particle size, pressure, and gas composition. Table 5 shows the observed ignition temperatures of metal particles. For aluminum, ignition temperatures are in the range of 933–2350 K [45,265,266]. Ignition of aluminum particles is attributed to melting and/or cracking of the oxide layer. Cracking may be due to tensile stresses exerted by the aluminum core [267] or polymorphic phase transformations in the oxide layer [236]. For boron, ignition is attributed to polymorphic phase transformations of boron [268] and vaporization of the oxide layer [269]. The measured ignition temperatures of boron particles lie in the range of 1400–2000 K [270–272]. Ignition of beryllium particles was thought to be caused by the fracture of the oxide layer due to vaporization of beryllium [273], since the boiling point of beryllium (2744 K) is lower than the melting point of beryllium oxide (2820 K). Measured ignition temperatures of beryllium particles are, however, as high as 2820 K [274,275], which suggests that melting of the beryllium oxide layer could also play an important role. For magnesium, permeability of the magnesium oxide layer facilitates ignition [276–279]. As a result, ignition of magnesium particles occurs at temperatures of 710–1200 K [276–279], substantially lower than the melting and boiling temperatures of magnesium oxide (3125 and 3430 K). Ignition of titanium

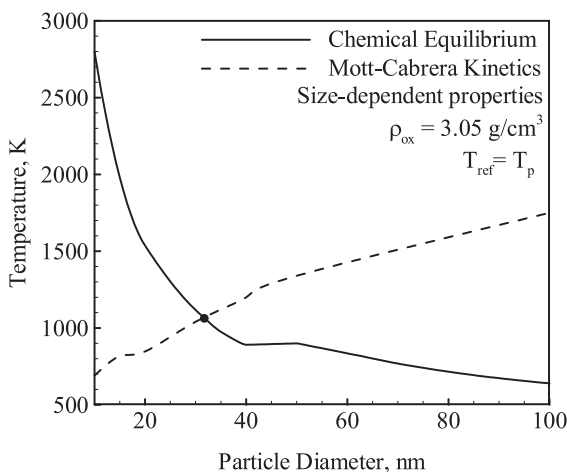


Fig. 36. Results of energy balance analysis showing comparison of the particle temperature after the growth of 0.3 nm thick oxide layer and the minimum temperature necessary for ignition, suggesting a critical particle size of 32 nm for pyrophoricity (reprinted from [22] with permission of Elsevier).

Table 5

Ignition temperatures of micron-sized and larger metal particles.

Metal	Ignition Temperature, K	Important factors
Al	933–2350	Melting of Al core and oxide shell, polymorphic phase transformations in oxide layer
B	1400–2000	Polymorphic phase transformations of boron, vaporization of oxide layer
Be	1500–2820	Vaporization of Be and melting of BeO
Mg	710–1200	Melting of Mg, Permeability of oxide layer
Ti	1100–1700	α - β Ti phase transformation, gas dissolution

particles occurs in the range of 1100–1700 K [280–283] and is attributed to α - β Ti phase transformations and changes in absorptivity due to formation of titanium oxide [280].

Among all metals, aluminum and boron have received the most attention. While the ignition behavior of micron-sized metal particles has been more extensively studied, ignition of metal nanoparticles has been the subject of recent research and is not yet fully understood. In the following sections, the effect of particle size on the ignition properties of metal nanoparticles is discussed. Emphasis is placed on aluminum particles, since the size dependence of ignition of aluminum nanoparticles has been relatively well studied. Studies on ignition of nanoparticles of other metals are limited.

7.1. Ignition of aluminum nanoparticles

7.1.1. Size dependence of ignition temperature

The ignition temperature of aluminum particles is a strong function of the particle size. Fig. 37 shows the effect of particle size on the ignition temperature of aluminum particles [40]. Experimental data are taken from Refs. [265,266,274,284–296]. There is considerable scatter in the experimental data, owing to differences in experimental conditions, including apparatus, sample type, heating rate, oxide layer thickness, and oxidizer composition. Care must therefore be taken when analyzing and interpreting data. For example, ignition temperatures of aluminum particles with diameters of the order of 10 μm lie in the range of 1000–2350 K. Nonetheless, there appears to be a general trend of decreasing ignition temperatures with decreasing particle size. Aluminum nanoparticles ignite at temperatures as low as ~ 1000 K, substantially lower than the bulk melting point of the oxide shell (2350 K).

7.1.2. Theories

7.1.2.1. Aluminum core melting. Ignition of aluminum nanoparticles may be attributed to cracking of the oxide layer upon melting of the aluminum core [267]. Rai et al. [267] studied the thermomechanical and oxidation behaviors of nanoaluminum particles using hot-stage transmission electron microscopy (TEM) and single-particle mass spectrometry over a temperature range of 293–1173 K. Particles with an oxide layer thickness of about 3 nm and diameters in the range of 20–30 nm were considered. Images of particles heated in a hot-stage TEM appeared to suggest that the oxide layer cracked upon melting of the aluminum core. Upon melting, the density of the aluminum core decreases from 2700 to 2400 kg/m^3 , an 11.1% change. This leads to the buildup of compressive and tensile stresses in the core and oxide shell, respectively.

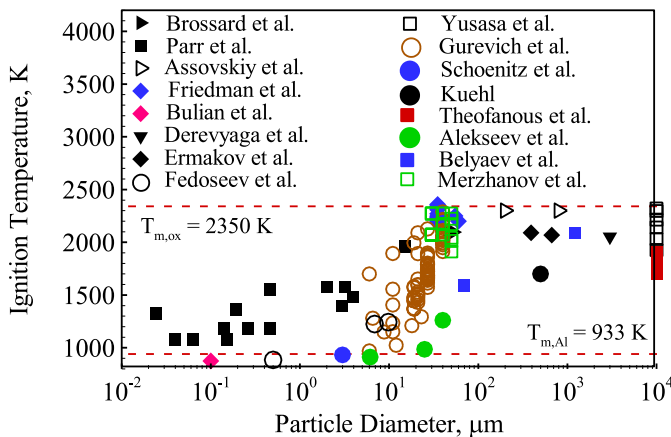


Fig. 37. Effect of particle size on ignition temperature of aluminum particles (adapted from [40] with permission of Springer).

Under the assumption of rigid oxide layers, the core pressure can be estimated as follows [297]:

$$\Delta p_c = -\Delta \rho_c \frac{K}{\rho_c}, \quad (50)$$

where K is the bulk modulus of bulk aluminum, taken to be 50 GPa at 933 K. The resulting core pressure is 3.35 GPa. The interfacial stresses in the oxide shell can be calculated using the following equations [298]:

$$\sigma_r = -p, \quad (51)$$

$$\sigma_\theta = \sigma_\phi = p \frac{(D_p - 2\delta)^3 + D_p^3/2}{D_p^3 - (D_p - 2\delta)^3}, \quad (52)$$

where σ is the stress. The subscripts r , θ , and ϕ refer to the radial, azimuthal, and polar directions, respectively. The radial stress is calculated to be 3.35 GPa, regardless of the particle size. The polar and azimuthal stresses are substantially greater than the radial counterpart, especially for larger particles. Note that the measured tensile strength of bulk alumina is on the order of 0.1 GPa [299], an order of magnitude lower than the calculated tensile stresses in the oxide layer. If the oxide layer is rigid and brittle, the analysis suggests that it could fracture upon melting of the molten aluminum core. The cracks provide pathways for the oxidizing gas to react with the aluminum core, and the ensuing energy release results in ignition of the nanoaluminum particles. Note that the mechanical properties of the oxide layer are not completely understood. It is not clear if the oxide layer is rigid or flexible. Depending on the properties, the oxide layer may crack upon melting of the aluminum core or expand to accommodate the developed stresses.

7.1.2.2. Polymorphic phase transformations in oxide layer. Trunov et al. [236] attribute ignition of aluminum particles to polymorphic phase transformations in the oxide layer. In their study [236], oxidation of 3–14 μm aluminum powders was studied using thermogravimetric analysis. The powders were heated in oxygen up to 1500 $^\circ\text{C}$ at heating rates on the order of 10 K/min. Aluminum oxide exists in different forms; the three major polymorphs of concern are amorphous, gamma, and alpha alumina [236]. Fig. 38 shows the stages of oxidation of 10–14 μm aluminum particles in oxygenated environments [236]. At about 550 $^\circ\text{C}$, or when the critical oxide layer thickness of 5 nm is achieved, the amorphous oxide layer transforms into gamma alumina. The density of gamma alumina is 3660 kg/m^3 , greater than that of amorphous polymorph (3050 kg/m^3) [236]. A similar phenomenon occurs during the gamma-alpha phase transformation. As a result, the newly formed oxide layer does not completely cover the particle surface, and the resulting openings facilitate ignition of the aluminum particle over a broad range of temperatures.

For each polymorph, the rate of mass growth of the oxide polymorph, dictated by mass diffusion across the oxide layer, was expressed as [236]

$$\dot{m}_{i,ox} = \frac{C_i \exp(-E_i/RT_p)}{1/R_{i-1} - 1/R_i}, \quad (53)$$

where R_g is the gas constant and R the radius. The subscript $i-1$ refers to the parent material. Eq. (53) is strictly valid for polycrystalline oxide layers ($\delta > \delta_e$). For thinner oxide layers, the pre-exponential constant was modified as follows [236]:

$$C'_i = C_i \left[X_i - (X_i - 1) \frac{\delta_i - \delta_{m,i}}{\delta_{e,i} - \delta_{m,i}} \right], \quad (54)$$

$$\delta_{e,i} = 2\delta_{m,i} + G_i \exp(-L_i\beta), \quad (55)$$

where δ_m is the transition thickness and β the heating rate. The oxide layer was proposed to offer negligible diffusion resistance

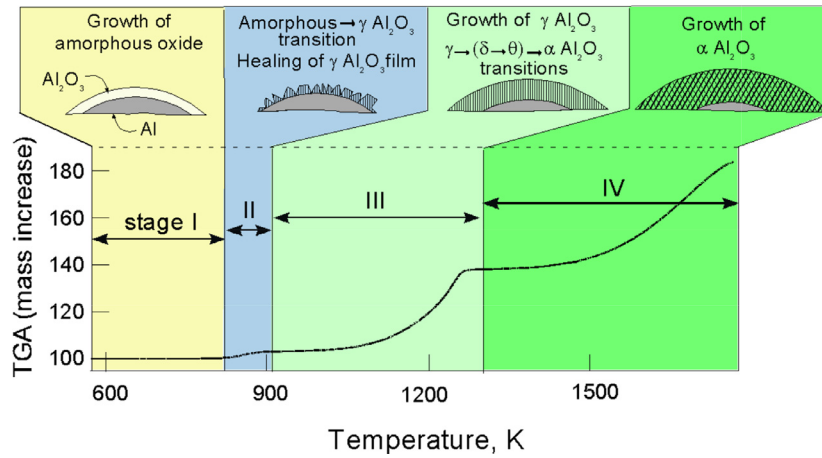


Fig. 38. Stages of oxidation of 10–14 μm aluminum particles in oxygenated environments obtained using thermogravimetric analysis (reprinted from [236] with permission of Taylor and Francis).

when the thickness is lower than the transition value, and the oxidation rate was assumed to be controlled by mass diffusion to the particle surface [236]. The rate of mass change of an oxide polymorph due to polymorphic phase transformation is expressed as [236]

$$\dot{m}_{tr,(i-1) \rightarrow i} = 4\pi R_{i-1}^2 \rho_{i-1} F_{(i-1) \rightarrow i} T_p \exp\left(-\frac{E_{(i-1) \rightarrow i}}{RT_p}\right) \left\{1 - \exp\left(-\frac{K_{(i-1) \rightarrow i} \delta_{i-1}}{RT_p}\right)\right\}, \quad (56)$$

where δ is the thickness of the oxide polymorph layer. The model parameters were obtained by fitting the model to the experimental TGA data.

Table 6 lists the parameters of the model [236]. An energy balance analysis was also conducted to determine the ignition temperature of aluminum nanoparticles. In the analysis, the particle was assumed to ignite when its temperature reaches the melting point of the oxide layer (2320 K). Although the analysis predicted a size-dependent ignition temperature, it over-estimated ignition temperatures of aluminum nanoparticles. For a particle size of 100 nm, the predicted ignition temperature was 1350 K, substantially greater than the experimentally measured value of ~ 1000 K. The disparity was attributed to

the fact that the analysis considered an isolated aluminum particle, whereas the experiments dealt with a collection of particles that could undergo sintering and agglomeration. Note that the model employed the continuum heat transfer model. Free-molecular effects can be considered to obtain better agreement with experimental data.

Note that the parameters listed in Table 6 were developed using experiments involving low heating rates (~ 1 K/min) and micron-sized particles. Experiments with heating rates as high as 500 K/min have also been conducted to elucidate the heating rate effect [300]. Activation energies obtained using high heating-rate experiments are consistent with the values listed in Table 6, although some refinements to other parameters were made. In a more recent study [301], the oxidation kinetics of aluminum nanoparticles was studied using thermogravimetric analysis in order to identify the distinguishing features at nanoscales. Fig. 39 shows the mass gain for an oxidizing aluminum nanopowder at different heating rates [301]. It is clear that the oxidation of aluminum nanoparticles is qualitatively similar to that of micron-sized particles. As with micron-sized particles, the first oxidation step can be attributed to amorphous-gamma phase transformation of the oxide layer, whereas the second step can be attributed to the gamma-alpha phase transformation. The TG results were processed to account for particle size distribution, and the oxidation of particles of different sizes was characterized. Activation energy and pre-exponential factors were

Table 6

Parameters of the polymorphic phase transformation model (adapted from [236] with permission of Taylor and Francis).

Parameter	Value
E_{am}	120 kJ/mol
E_{γ}	227 kJ/mol
E_{α}	306 kJ/mol
C_{am}	5.098×10^{-8} kg/m/s
C_{γ}	4.0784×10^{-3} kg/m/s
C_{α}	2.3791×10^{-2} kg/m/s
$E_{am \rightarrow \gamma}$	458 kJ/mol
$E_{\gamma \rightarrow \alpha}$	394 kJ/mol
$K_{am \rightarrow \gamma}$	1×10^{12} J/mol/m
$K_{\gamma \rightarrow \alpha}$	1×10^8 J/mol/m
$F_{am \rightarrow \gamma}$	2×10^{15} m/s/K
$F_{\gamma \rightarrow \alpha}$	5×10^6 m/s/K
δ_{am}^m	5 nm
δ_{α}^m	30 nm
G_{γ}	7.71 nm
G_{α}	116 nm
L_{γ}	1.066 s/K
L_{α}	0.439 s/K
X_{γ}	200
X_{α}	150

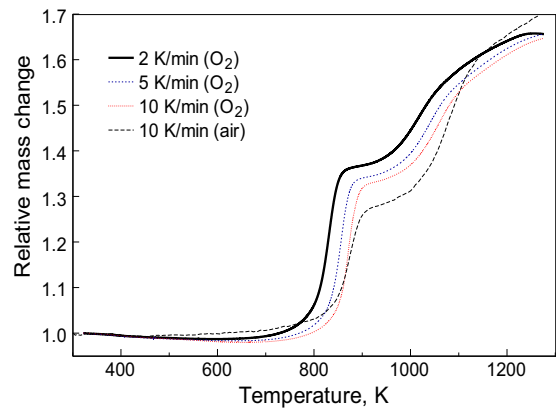


Fig. 39. TGA results showing mass gain for an oxidizing aluminum nanopowder heated at different heating rates in oxygen-containing environments. A qualitative similarity between micron- and nano-powder oxidation is seen (reprinted from [301] with permission of Elsevier).

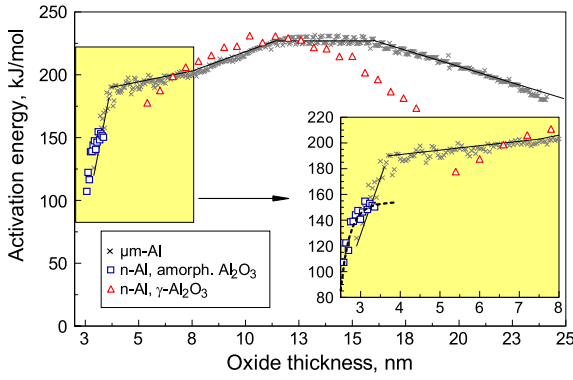


Fig. 40. Activation energy of growth of oxide layers as a function of thickness of the oxide layer showing overall good agreement with the values obtained for micron-sized particles for oxide layer thickness up to 13 nm; thermogravimetric analysis (reprinted from [301] with permission of Elsevier).

determined as well. Fig. 40 shows the effect of oxide layer thickness on the activation energy [301]. For diffusion-controlled oxidation, assuming that the product $\rho D = C \exp(-E/RT)$, the changes in the activation energy and pre-exponential constant were described by the following equations [301]:

$$E_{am} = 154.2 - \frac{1.8 \cdot 10^6}{h^{11.1}}, \quad (57)$$

$$\ln(C_{amorph}) = -5.01 - \frac{1.69 \cdot 10^7}{h^{15.4}}, \quad (58)$$

where E_{am} is the activation energy for the growth of the amorphous oxide layer in kJ/mol, C_{amorph} is the preexponential factor with units of g/m-s, and h the oxide layer thickness in nm. The activation energy increased with increasing oxide layer thickness due to increased homogeneity of the amorphous oxide layer, which initially contained defects and imperfections [301]. Fairly good agreement is achieved with the data obtained for micron-sized particles for oxide layer thicknesses up to about 13 nm. The disparity for greater oxide layer thicknesses was attributed to changes in powder morphologies due to sintering of particles [301]. Eqs. (57) and (58) can be used to better describe the growth of the oxide layer thickness for nanoparticles and predict when phase transformation and ignition are likely to occur.

7.1.3. Characteristic time scale considerations

Characteristic time scales of core melting and polymorphic phase transformations can be compared to further understand their role in oxidation of aluminum particle [297]. The melting time can be obtained by considering the following energy balance [297]:

$$h_m \frac{dm_p}{dt} = \dot{Q}_{loss}. \quad (59)$$

where h_m is the enthalpy of melting, m_p the particle mass, and $\dot{Q}_{loss}$ the total heat loss due to conduction and radiation. For nanoparticles, the rate of heat loss due to conduction and radiation are given by [297]

$$\dot{Q}_{cond} = \alpha \pi D_p^2 \frac{p_a \sqrt{8k_B T_a / \pi m_a}}{8} \left(\frac{\gamma + 1}{\gamma - 1} \right) \left(1 - \frac{T}{T_a} \right), \quad (60)$$

$$\dot{Q}_{rad} = \varepsilon \sigma A (T_a^4 - T^4), \quad (61)$$

where α is the accommodation coefficient, D_p the particle diameter, p_a the ambient pressure, k_B the Boltzmann constant, T_a the ambient temperature, m_a the mass of ambient gas molecule, γ the adiabatic constant, ε the emissivity, σ the Stefan-Boltzmann constant, and A the particle surface area. For micron-sized and larger particles, a continuum heat transfer model was employed. The characteristic time scale for polymorphic phase transformations, τ_{poly} , was

calculated as follows [297]:

$$\tau_{poly} \approx \frac{\rho_{ox} V_{ox}}{\dot{m}_{tr}}, \quad (62)$$

where V_{ox} is the volume of the oxide layer, and $\dot{m}_{tr}$ is the mass loss of the polymorph due to polymorphic transformation to another polymorph.

Fig. 41 shows a comparison of times scales of completion of core melting and polymorphic phase transformations in the oxide layer [297]. The oxide layer thickness was taken as 2 nm. At temperatures near the core melting point, the characteristic time scales of polymorphic phase transformations are substantially greater than those of core melting. This is due to the fact that there is significant activation energy, and polymorphic phase transformations are important only at higher temperatures. As a result, the oxide shell is probably not completely converted to a crystalline state during/upon melting of the aluminum core, although this does not imply that the crystallization process is completely absent. It is also important to note that the conditions considered in Ref. [297] correspond to high heating rates. At lower heating rates ($<10^5$ K/s), polymorphic phase transformations may be significant. Further studies are necessary to quantify the extent of crystallization of the oxide layer and understand the importance of core melting and polymorphic phase transformations to ignition of aluminum particles.

7.1.4. Oxide layer integrity and reaction front location

It was mentioned previously that the mechanical properties of the oxide shell are not completely understood. Recent studies have provided some new insight into the microstructural behavior of aluminum nanoparticles. Rufino et al. [302] studied the properties of the oxide layer and structural changes upon oxidation for aluminum nanopowders. The particle size was about 200 nm and the oxide layer thickness was about 3 nm. Particles were synthesized using the electric explosion process and passivated in air (nano-G) and in a solution of stearic acid (nano-L). In addition, an oxidized powder (nano-L-Ox) with an oxide layer thickness of 23 nm was considered. The heating rate was on the order of $1^\circ\text{C}/\text{min}$. Using calorimetric measurements and in situ neutron diffraction experiments, crystallization of the amorphous oxide layer was observed. In addition, thermal expansion was quantified by monitoring the variations of the cell parameter. Results are shown in Fig. 42 [302]. For all the samples, the thermal expansion of the aluminum core was nearly the same as that of bulk aluminum and was not affected by the crystallization of the oxide layer. This implies that the aluminum core is free to expand and was not constrained by the oxide layer. This

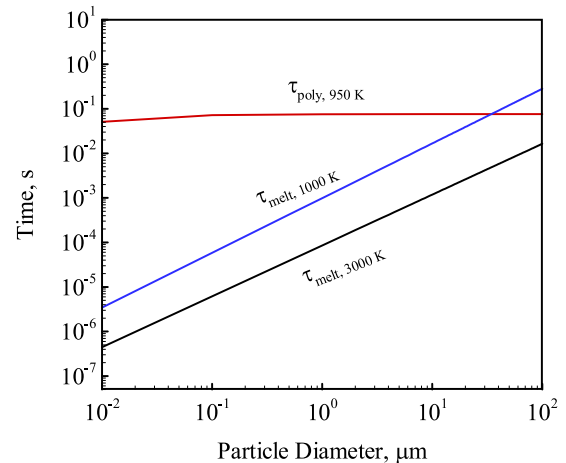


Fig. 41. Comparison of time scales of core melting and polymorphic phase transformations of the oxide layer (reprinted from [297] with permission of Elsevier).

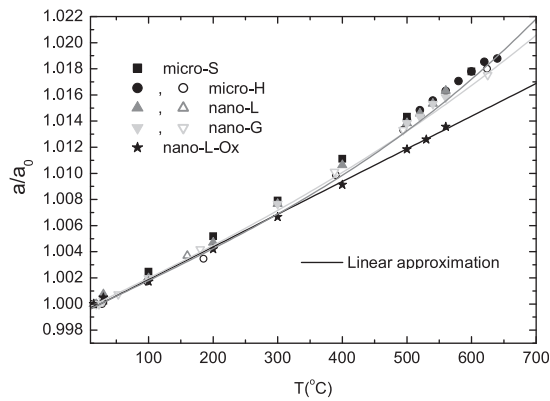


Fig. 42. Thermal expansion of the cell parameter for micro- and nano-aluminum powders obtained from diffraction measurements. (nano-L: nanoparticles passivated in a liquid; nano-G: air passivated nanoparticles; nano-L-Ox: Oxidized nanoparticles). Heating rates were on the order of 10 °C/min (reprinted from [302] with permission of Elsevier).

apparently contradicts the theory of cracking of the oxide layer upon melting of the aluminum core. For particles with thicker oxide layers (~20 nm), the thermal expansion of the aluminum core was strongly reduced, suggesting the possible development of internal stresses in the aluminum core.

In a subsequent study, the microstructural behavior of nano-aluminum particles before and after melting of the aluminum core was studied experimentally [303]. The particle diameter was 100 nm and the oxide layer thickness was 2 nm. High-temperature X-ray diffraction analysis, hot-stage transmission electron microscopy, and high-resolution transmission electron microscopy were employed. Lattice spacings were monitored to probe the expansion of the aluminum core and oxide shell. Fig. 43 shows the resulting variations of lattice expansion and core pressure with temperature [303]. When the particle was heated beyond the core melting point, the aluminum core expanded under almost no constraint. This is in agreement with the findings of Rufino et al. [302]. It is evident there is no significant compression or pressure buildup in the core upon melting. This suggests that the oxide layer is flexible in nature. It is important to note that the amorphous oxide layer transforms to γ -alumina when the particle is heated. As the crystalline phase is denser than the amorphous phase, it was proposed that crystallization should facilitate pressure buildup in the core. Given that no pressure buildup was observed, it was speculated that the crystallization process was inhomogeneous and incomplete and existing amorphous regions facilitated relaxation of pressure. Experimental evidence appears to support this argument, as shown in Fig. 44 [303]. In addition, in situ observation using hot-stage TEM was used to trace the overall morphology change of the powder. Fig. 45 shows TEM images for 300 and 750 °C [303]. When the temperature reaches 750 °C, the major portion of the particle melts and liquid Al is seen to flow out. This study reveals a rather interesting mechanism of core melting and crystallization operating in tandem to fracture the oxide layer.

An important aspect of particle oxidation is the structure of oxidized aluminum particles. The question is whether reactions occur on the outer surface of aluminum particles or at the interface between the aluminum core and oxide layer. Rai et al. [304] conducted an experimental study to investigate morphology of aluminum nanoparticles oxidized at different temperatures. Fig. 46 shows TEM micrographs of aluminum particles oxidized at different temperatures [304]. For temperatures lower than the melting point of the aluminum core, oxidized particles were solid spheres, while at higher temperatures, hollow particles were formed. This is further substantiated by the results of recent experimental investigations [305]. Oxidation is proposed to be governed by inward diffusion of oxidizer or outward diffusion of aluminum through the oxide layer before aluminum melting, while at higher temperatures outward

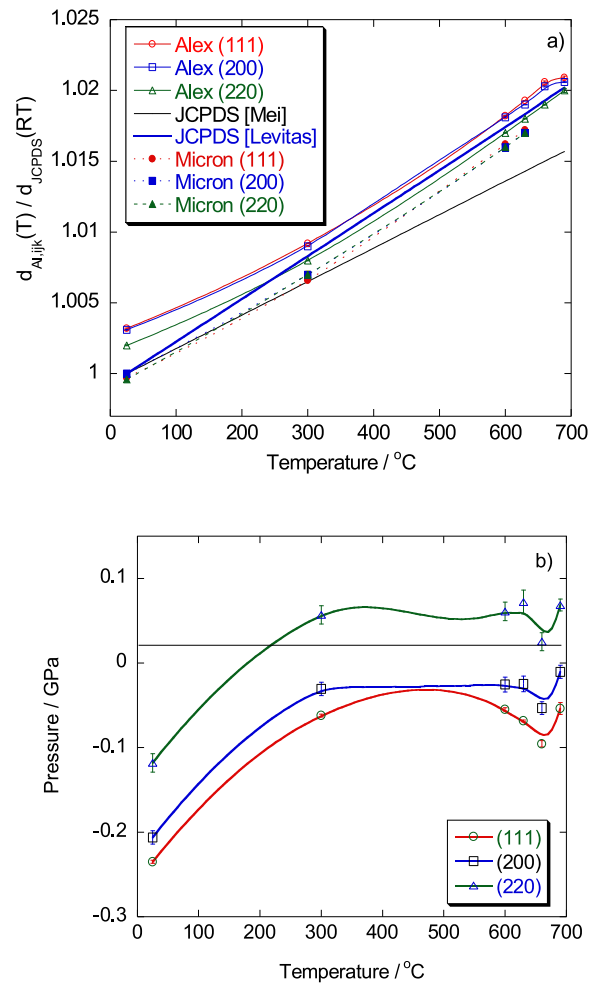


Fig. 43. (a) Lattice expansions and (b) resultant pressure in the aluminum core as a function of temperature showing pressure relaxation cause by unrestrained expansion of the molten aluminum core. Heating rates were on the order of 10 °C/min (reprinted from [303] with permission of American Chemical Society).

diffusion of aluminum is the rate-controlling process. The outward diffusion process results in the formation of hollow particles.

Another important issue is the location of the reaction front, which has some influence on the structure of oxidized particles. This has been the focus of recent experimental studies [306,307]. Thermogravimetric analysis was performed for two sets of powders with nominal size ranges of 3.0–4.5 and 10–14 μm , respectively. For each powder, the measured weight gain was distributed among particles under the assumption that the oxidation rate is proportional to the reaction surface area. The resulting temporal variations of the particle mass gain obtained from the two different powders were compared for a specific particle size. Three different oxidation models were employed, corresponding to ductile and rigid shells and reactions occurring at the core-shell interface and the outer particle surface. Results suggested that reactions occurred at the outer surface of the rigid oxide shell and are thus controlled by outward diffusion of aluminum cations for a broad range of temperatures (400–1500 °C) [306]. This is also consistent with the observation of hollow particles [205,305]. On the contrary, in wet environments, results indicate that the rigid oxide layer fractured multiple times and reactions occurred at the interface or outer surface of the particles [307]. This underlines the important role of nature of the oxidizer on the integrity of the oxide layer. Note that these studies were conducted for micron-sized particles.

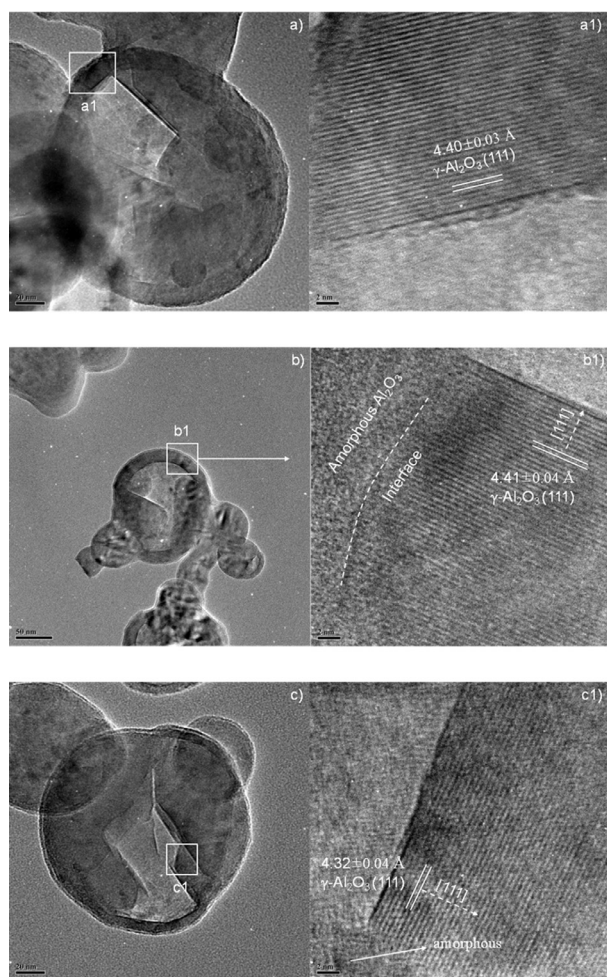


Fig. 44. High resolution TEM images of aluminum nanoparticles obtained at 660 °C showing inhomogeneous crystallization of oxide layer. Insets of low-magnification (a)–(c) as indicated with boxes are shown on the right (reprinted from [303] with permission of American Chemical Society).

The heating rate employed in these experimental studies was of the order of 1 K/min, orders of magnitude lower than the heating rates of concern to most practical applications ($\sim 10^6$ K/s). The mechanical properties of the oxide shell may depend on the heating rate, shell thickness, and temperature. Further studies are warranted to understand the properties of the oxide shell at high heating rates. Puri and Yang [207] conducted molecular simulations of the thermo-mechanical behavior of passivated nano-aluminum particles during melting. The heating rate was on the order 10^{13} K/s, orders of magnitude greater than those in DSC studies. The particle size range was 5–10 nm and the oxide layer thickness varied in the range of 1.0–2.5 nm. Fig. 47 shows a snapshot of 5 nm aluminum particles with crystalline and amorphous oxide layers [207]. An important observation is the prevalence of mass diffusion across the oxide layers of the particles. No cracking of the oxide layer was observed. Similar observations were made by Li et al. [308] and Henz et al. [257] in their MD simulations. Note that these MD simulations do not treat the presence of defects and the ability of interatomic potential functions to treat complex thermo-mechanical behaviors is not well established.

7.1.5. Modes and mechanisms of ignition

Based on the results described above, it is possible to identify different modes and mechanisms of ignition [297]. This is shown in Fig. 48 [297]. On one extreme, if the oxide layer is rigid and brittle and stresses are not relaxed, the oxide layer will fracture

due to the tensile stress exerted by the molten aluminum core. The molten aluminum reaches the particle surface by flowing through the cracks and openings in the oxide layer. The ensuing reactions and heat release can result in the ignition of nano-aluminum particles due to their low volumetric heat capacity. On the other extreme, if the oxide layer is flexible and the pressure is relaxed (e.g., by diffusion or expansion), cracking will not be observed and particle oxidation will be characterized by mass diffusion across the oxide layer. Depending on the diffusion coefficients of the aluminum and oxidizer molecules, reactions occur at the core-shell interface or outer surface of the particle. Note that the interfacial oxidation results in tensile stresses on the oxide layer. The particle mass nearly doubles upon oxidation, while the product density increases by only about 50%. This results in the development of additional stresses within the particle and the oxide layer may crack continuously due to geometrical constraints. No such behavior is expected if reactions occur at the outer surface of the particles. Note that the diffusion process speeds up upon melting of the aluminum core and oxide shell. For example, the diffusion coefficient increases by two orders of magnitude as the temperature increases from 600 to 2000 K [257]. This corresponds to a tremendous increase in the oxidation rate of aluminum particles.

Another possibility is that the oxidation mechanism can lie between the two extremes and involve both these processes and mechanisms. While some regions of the shell might permit expansion and relaxation of stresses, other regions could crack. The relative importance of the cracking and diffusion mode can depend on factors such as core size, oxide layer thickness, oxidizer composition, heating rate, and so forth. This is a very important question that needs to be addressed in future studies. It is also important to note that many of the processes described in this section can also occur in micron-sized particles, but they may not provide sufficient energy to ignite the particles, due to the relatively high volumetric heat capacity of micron-sized particles. For example, the oxide layer may crack, but these cracks are expected to heal quickly through oxidation. More importantly, the energy release from the oxidation process may not heat the particle to the critical ignition point (such as the melting of the oxide layer) and hence particle ignition may not be achieved. A unified and generic ignition model is desired that is applicable to particles over a broad range of sizes from 10 nm to 100 μ m. This theory must account for the changes in particle volumetric heat capacity and oxide layer characteristics, stress generation and relaxation mechanisms, and cracking and healing of the oxide layer.

7.1.6. Ignition delay

Ignition delay can be determined by means of energy balance analysis [297]. Fig. 49 shows the effect of particle size on the ignition delay of aluminum particles [297]. The gas temperature was taken to be 2500 K. For simplicity, particle oxidation was modeled using Mott–Cabrera kinetics. Model predictions were compared with experimental data. For micron-sized and larger particles, ignition delay is quadratically proportional to the particle size [265,309]. Predictions of the continuum model are in good agreement with experimental data. At nano-scales, particle size exerts a weak effect on the ignition delay. Note that the continuum model significantly underpredicts the ignition delay and overestimates the size dependence of the ignition delay of aluminum nanoparticles. Better agreement with experimental data was achieved using a free-molecular model and treating the effect of incomplete energy accommodation. Note that the analysis did not address the complexities associated with cracking of the oxide layer [310] and sintering and agglomeration of particles [35]. These phenomena can be considered in a more advanced model of ignition of aluminum particles. The analysis provided reasonable estimates of the time scales associated with

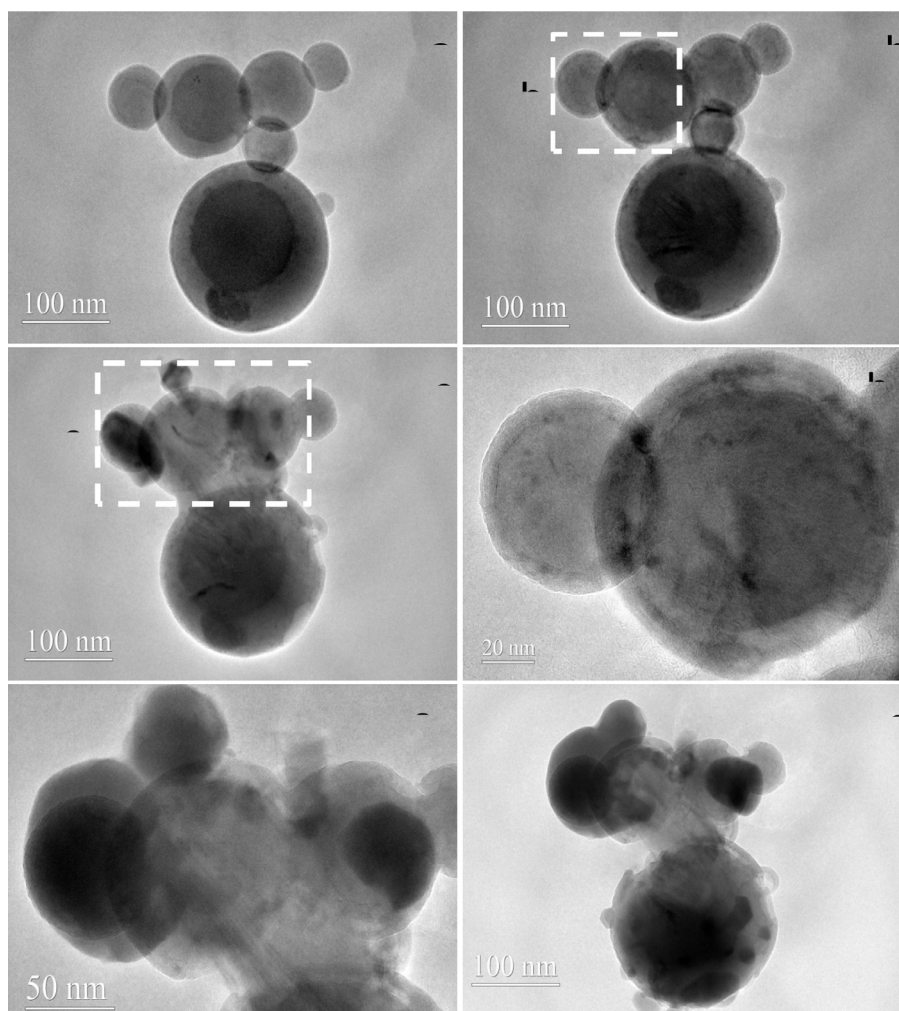


Fig. 45. TEM images of aluminum nanoparticles obtained at different temperatures in the range of 300–750 °C showing flow of molten aluminum out of the oxide layer (reprinted from [303] with permission of American Chemical Society).

ignition of an isolated aluminum particle, and it also offered an explanation for the change in the size dependence of the ignition delay of aluminum particles. Note that the ignition delay is a strong function of gas temperatures, as shown in Fig. 50 [285].

7.2. Ignition of boron nanoparticles

Ignition of boron particles has been extensively studied in the past. A comprehensive review of important findings pertaining to boron particle ignition and combustion is beyond the scope of the present work, but such a review is presented by Yeh and Kuo [7]. Only a brief summary of the most important aspects of boron particle ignition is presented here, so that distinguishing features of nano-scale behavior can be identified.

Boron particles are covered by a protective boron trioxide (B_2O_3) layer. The boiling temperature of the oxide layer is 2316 K, lower than that of the melting and boiling temperatures of boron, which are 2450 and 3931 K, respectively. As a result, vaporization of boron oxide plays an important role in ignition of boron. A two-stage burning mechanism has been proposed for boron particles [7]. The first stage concerns particle oxidation when the oxide layer is intact. The particle is heated due to heat transfer from the hot ambient gas. The oxide layer then melts and species diffusion through the oxide layer facilitates oxidation. As the particle is heated

to the boiling temperature of the oxide, the oxide layer is removed by vaporization. This marks the onset of the second stage, which involves combustion of the bare boron particle. As an alternative theory, Dreizin and Calcotte [311] proposed the formation of boron-oxygen liquid solution and attributed transition from the first stage to attainment of oxygen solubility limit. Ignition temperatures of boron particles vary in the range of 1400–2000 K [270–272]; this is attributed to vaporization of oxide layer and polymorphic phase transformations of boron [268].

Ignition of boron nanoparticles was first studied by Li and Williams [312]. A flat-flame methane-oxygen-nitrogen burner was employed. Boron particles were transported by the nitrogen stream into the high-temperature, oxygen-containing product gas of the flat-flame burner. The particle radius was 50 nm. In these boron-particle flames, a bright yellow region was clearly visible and its thickness was greater than 5 mm. On the other hand, the white-glow zone was hardly seen, since its thickness was less than 0.5 mm. The bright yellow region corresponds to particle ignition, while the white-glow zone corresponds to combustion. It was therefore proposed that the particle combustion time is much lower than the ignition time for boron nanoparticles. Ignition times were inferred from the heights of the yellow region of the flame. Ignition time decreased from about 6 to 1.5 ms when the flat-flame temperature increased from about

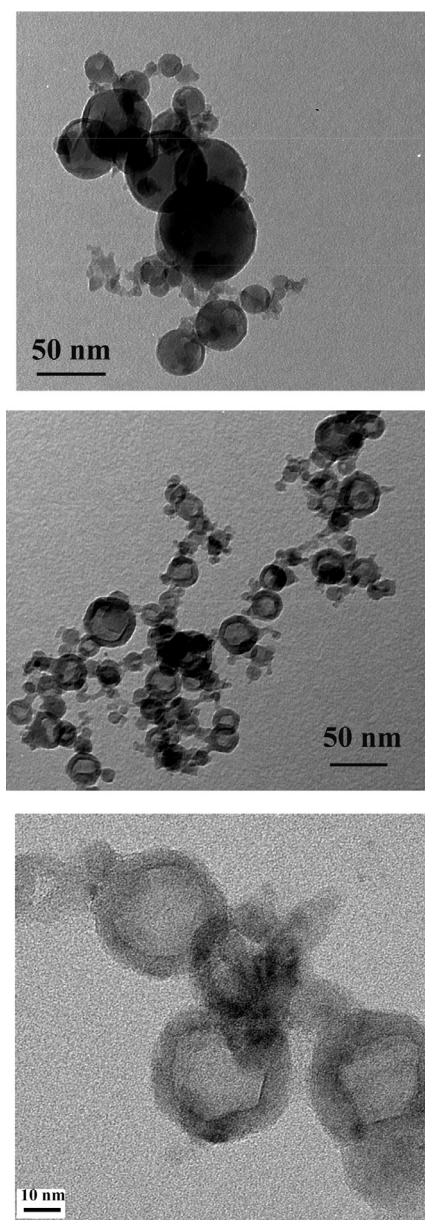


Fig. 46. TEM micrographs of aluminum nanoparticles oxidized at different temperatures (a) 800 °C, (b) 1000 °C, (c) HRTEM of hollow particles upon oxidation (reprinted from [304] with permission of Taylor and Francis).

1900 to 2500 K. No ignition was observed for temperatures lower than 1900 K.

The overall rate of the ignition process was characterized by the following equation [312]:

$$\frac{dc}{dt} = A \exp(-E/RT), \quad (63)$$

$$c = 1 - h/h_0,$$

where h is the oxide layer thickness, t the time, E the activation energy, R the gas constant, and T the temperature. The variable c measures progress towards ignition, with $c=0$ initially and $c=1$ corresponding to complete removal of the oxide layer at the end of bright yellow zone. Integrating the equation and curve-fitting gives the activation energy as 209 kJ/mol and the pre-exponential factor as $6.1 \times 10^8 \text{ s}^{-1}$ over an ignition temperature range of 1690–1800 K [312]. For high ignition temperatures, activation energy is 42 kJ/mol and the pre-exponential factor is $1.1 \times 10^4 \text{ s}^{-1}$ [312]. At high particle

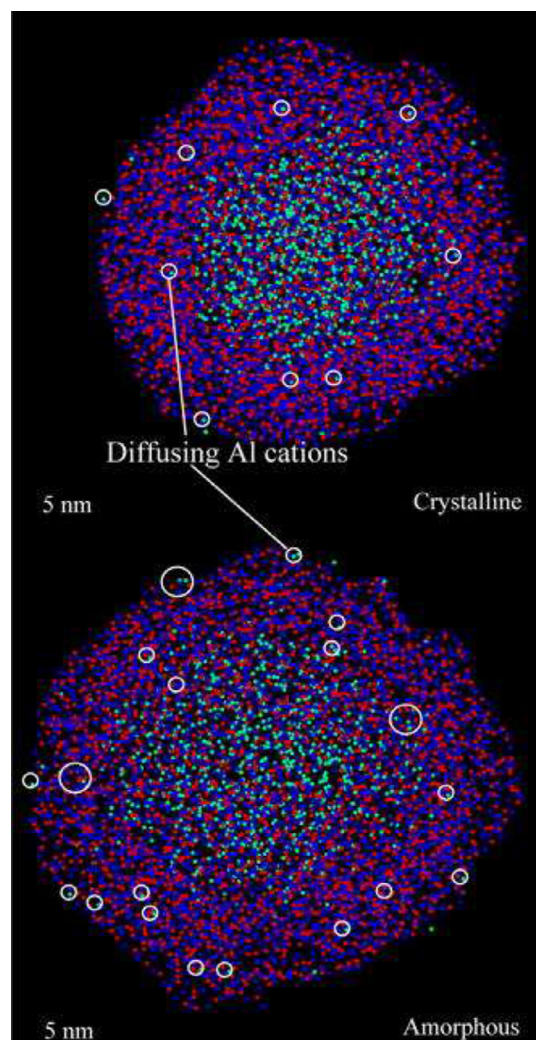


Fig. 47. Diffusion of Al cations during heating of 5 nm aluminum particles with crystalline and amorphous oxide layers of thickness 1 nm; MD simulations with Streitz–Mintmire potential (reprinted from [207] with permission of Springer).

temperatures, ignition of passivated boron particles was attributed to vaporization of boron oxide and exothermic reactions at the particle surface. Specifically, exothermic rate-controlled consumption of B or BO at the oxide-gas interface dominates the ignition process [312]. At particle temperatures lower than the cut-off value, ignition is controlled by diffusion of oxidizer gas molecules through the oxide layer [312].

In another study on ignition of boron nanoparticles [8], particles were ignited in the post-flame region of a methane-oxygen-air flat flame burner. Particle image velocimetry measurements coupled with intensified charge coupled device (ICCD) camera images were used for the determination of the ignition times of boron particles. Injected particles were agglomerates of small primary particles, with mean mass diameters of 679 nm. Average burner temperatures varied in the range of 1500–2000 K, and four different oxygen mole fractions of 0.10, 0.15, 0.20, and 0.30 were considered. A two-stage burning behavior was observed for boron nanoparticles, similar to the observations of Li and Williams [312]. A yellow/orange glow followed by a bright white glow zone was observed, representing ignition and combustion, respectively. For oxygen concentrations exceeding 0.1, ignition was observed over a temperature range of 1578–1872 K. Ignition did not occur for temperatures lower than 1800 K for an oxygen concentration of 0.1. An analytical expression for the ignition

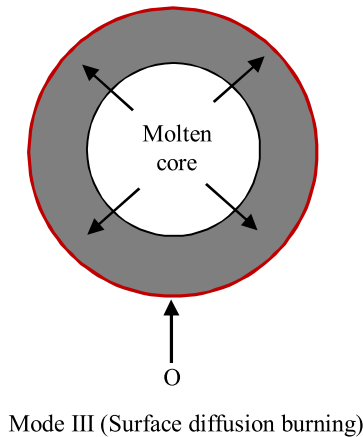
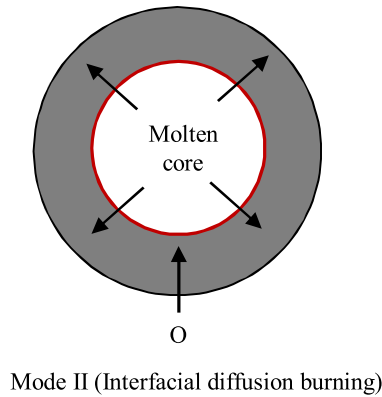
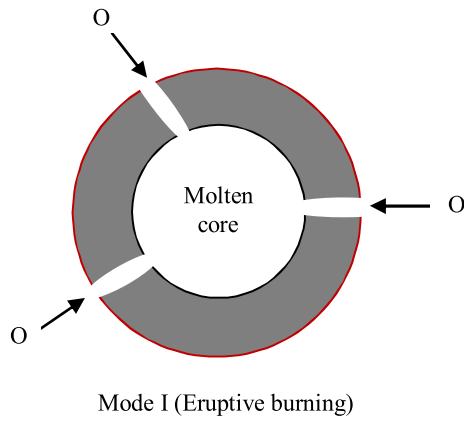


Fig. 48. Different modes of oxidation of aluminum particles: (a) eruptive burning; (b) interfacial diffusion burning; (c) surface diffusion burning (reprinted from [297] with permission of Elsevier).

delay, t_{ign} , was obtained using an energy balance analysis [8]:

$$t_{ign} = \frac{\rho_p C_p D_p}{6h} \ln \left(\frac{T_{init} - T_a}{T_{cr} - T_a} \right), \quad (64)$$

where h is the heat transfer coefficient. Subscripts *init* and *cr* refer to initial and critical states, respectively. The measured ignition delay was substituted into Eq. (64) to obtain the critical ignition temperature of boron nanoparticles. For oxygen concentrations of 0.2 and 0.3, the calculated ignition temperatures were 1610 and 1550 K, respectively [8]. This falls within the ignition temperature range reported in the literature for micron-sized particles. This suggests that, unlike aluminum nanoparticles,

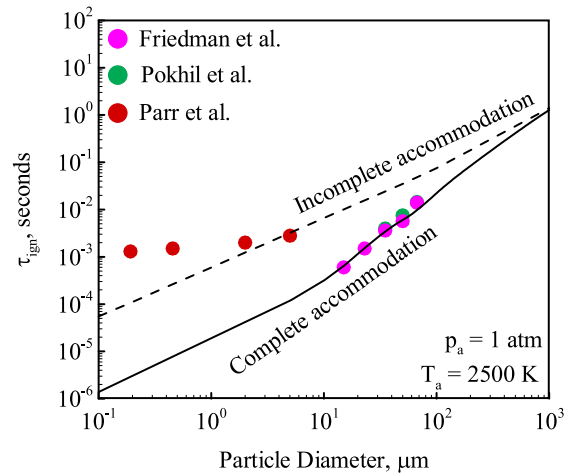


Fig. 49. Effect of particle size on ignition delay of aluminum particles (reprinted from [297] with permission of Elsevier).

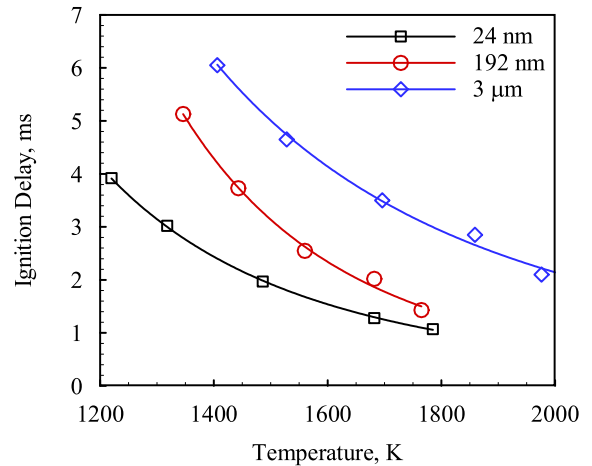


Fig. 50. Effect of gas temperature on ignition delay of aluminum particles (data points taken from [285]).

ignition temperatures of boron particles is not a strong function of the particle size.

The ignition time of boron nanoparticles is weakly dependent on oxygen concentration, and strongly dependent on the gas temperature, as shown in Fig. 51 [8]. The ignition delay decreases by a factor of roughly three when the temperature increases from 1600 to 1800 K. Furthermore, ignition delays of boron nanoparticles are comparable to those of micron-sized counterparts. This may be attributed to particle agglomeration, since the powder consisted of particle agglomerates of diameter 679 nm, which is substantially greater than the size of the primary particles (62 nm). Furthermore, the oxide content of the powder is quite high. The 679 nm agglomerates consisted of only 72% by weight of boron.

While ignition of micron-sized boron particles is relatively well understood, ignition of boron nanoparticles remains poorly understood. Some features, such as the two-stage burning process with associated flame color changes, are common to both micron and nano-particles. Preliminary investigations suggest that ignition temperatures and delays are not strongly dependent on particle size. It may be speculated that these could be a result of sintering and agglomeration of particles. Further studies are necessary to clearly elucidate the ignition mechanisms and the size dependence of the ignition properties of boron nanoparticles.

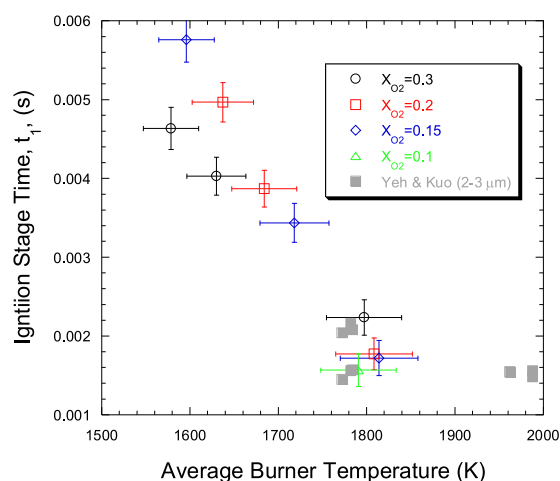


Fig. 51. Effect of gas temperature on ignition delay of boron particles reprinted from [8] with permission of Elsevier).

8. Combustion of metal particles

8.1. Combustion mode

The mode of combustion of metal particles can be classified based on the thermophysical properties of the metal and its oxide [276,313]. Fig. 52 shows three possible modes of combustion of metal particles [40]. Vapor-phase combustion involves reactions between metal vapor and oxidizing gas. Reactions occur away from the particle surface and a detached flame is thus established. Alternatively, reactions can occur at the particle surface between oxidizer gas and metal fuel in the condensed state. In certain cases, vapor phase and surface reactions occur simultaneously and this is referred to as dual mode combustion.

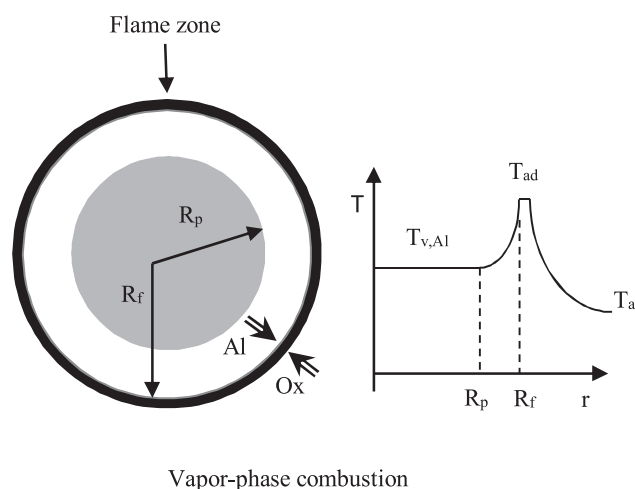
8.1.1. Adiabatic flame temperature considerations

For metals, the flame temperature typically does not exceed the boiling temperature of the oxide, because the heat of reaction is lower than the energy required to raise the temperature of the oxide above its boiling point [313]

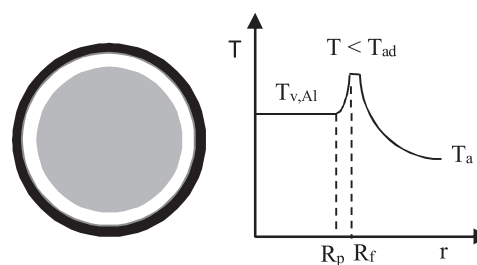
$$H_R < H_{T_{vol}} - H_{298} + \Delta H_{vol}, \quad (65)$$

where H_R is the heat of reaction of the metal at 298 K, and ΔH_{vol} the enthalpy of volatilization of the oxide. This constrains the flame temperature to be lower than or equal to the boiling point of the oxide. As the flame temperature cannot exceed the oxide's boiling point, it is logical to expect that vapor phase combustion cannot be dominant if the boiling point of the metal is greater than that of the oxide. This does not imply that vapor-phase reactions do not occur at all, since there is significant vapor pressure even at temperatures lower than the boiling point for many metals. Table 7 shows the adiabatic flame temperatures of various metals in oxygen at 1 atm pressure. The thermophysical properties of metals and their oxides are shown in Table 8. For all metals except boron, the heat of reaction is lower than the energy required to raise the temperature of the oxide above its boiling point. Metals such as Al, Be, Li, Mg, and Ti can thus undergo vapor-phase reactions in pure oxygen. Surface combustion is expected to be important for zirconium, since the boiling point of zirconium is greater than that of its oxide. For boron, although there is sufficient energy to vaporize the oxide, there is insufficient energy to heat the metal to its boiling temperature and vaporize the metal. Surface reactions must therefore play an important role during combustion of boron and zirconium particles.

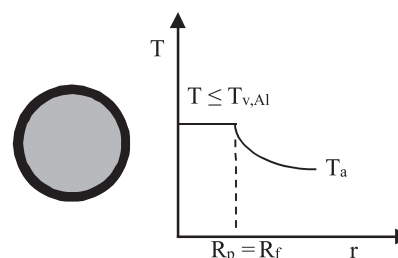
The adiabatic flame temperature depends not only on particulate material, but also on the type and concentration of the oxidizing gas [40]. Table 9 shows the adiabatic flame temperatures of micron-



Vapor-phase combustion



Dual mode combustion



Heterogeneous surface combustion

Fig. 52. Combustion modes for metal particles (a) vapor-phase combustion; (b) dual mode combustion; (c) surface combustion (adapted from [40] with permission of Springer).

sized aluminum particles for different oxidizers at a pressure of 1 atm [40]. Calculations were performed using the NASA Chemical Equilibrium with Applications (CEA) program [314]. The adiabatic flame temperature strongly depends on the oxidizing gas; it takes a

Table 7
Adiabatic flame temperatures of various metals in oxygen at 1 atm pressure.

Metal	T_{ad} (K)
Al	3968
B	3812
Be	4200
Mg	3391
Ti	4000

Table 8
Properties of metals and their oxides.

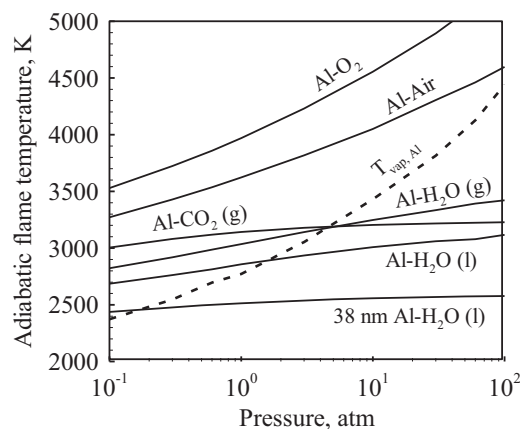
Metal	T _{bp} (K)	Oxide	T _{vol} (K)	$\Delta H_{f, 298}$ (kJ/mol)	ΔH_{vol}	$H_{T, vol} - H_{298} + \Delta H_{vol}$
Al	2791	Al ₂ O ₃	4000	−1676	1860	2550
B	4139	B ₂ O ₃	2340	−1272	360	640
Be	2741	BeO	4300	−608	740	1060
Li	1620	Li ₂ O	2600	−599	400	680
Mg	1366	MgO	3350	−601	670	920
Ti	3560	Ti ₃ O ₅	4000	−2459	1890	2970
Zr	4703	ZrO ₂	4280	−1097	920	1320

Table 9
Adiabatic flame temperatures of micron-sized aluminum particles for different oxidizers at 1 atm pressure.

Reactants	Adiabatic flame temperature(K)
2Al(s)+1.5O ₂	3977.0
2Al(s)+1.5(O ₂ +3.76Ar)	3624.8
2Al(s)+1.5(O ₂ +3.76N ₂)	3546.5
2Al(s)+3N ₂ O	3746.9
2Al(s)+3H ₂ O	3052.8
2Al(s)+3CO ₂	3144.4
2Al(s)+3CO	2277.2
2Al(s)+1.5F ₂	4414.5
2Al(s)+1.5(F ₂ +3.76Ar)	3873.5

value of 3052 K for water vapor, substantially lower than for oxygen (3977 K). It is also a function of the oxidizer concentration, decreasing from 3977 K at 100% to 3546 K at 21% oxygen. For most cases, the adiabatic flame temperature is lower than the boiling temperature of oxide (4000 K). An exception is the Al-F₂ system, which is characterized by a flame temperature of ~4400 K. Note that the adiabatic flame temperature is typically greater than the boiling temperature of aluminum at 1 atm. Vapor-phase reactions are thus expected for most oxidizers at a pressure of 1 atm.

Gas pressure affects the adiabatic flame temperature and combustion mode [40]. Fig. 53 shows the effect of pressure on the adiabatic flame temperature of aluminum particles for different oxidizers and particle sizes under stoichiometric conditions [40]. The boiling temperature of aluminum is a strong function of pressure, increasing from 2373 K at 0.1 atm to 4441 K at 100 atm. The

**Fig. 53.** Effect of pressure on adiabatic flame temperature of aluminum particles for different oxidizers and particle sizes; chemical equilibrium calculations (reprinted from [40] with permission of Springer).

flame temperature is lower than the boiling temperature of aluminum for pressures over a threshold value. The threshold pressure is around 2, 5, and 100 atm for liquid water, carbon dioxide, and air, respectively. Surface reactions are thus more important for water and carbon dioxide, especially at higher pressures. Note that the cut-off pressure in water decreases from ~2.0 to 0.2 atm when the particle size decreases from 1 μ m to 38 nm. This can be attributed to the fact that the inert oxide layer constitutes a greater portion of the particle mass at nano scales; a 38 nm aluminum particle, for example, contains 47 wt.% oxide.

8.1.2. Experimental evidence

As discussed in the previous section, metal particles can burn homogeneously in the gas-phase and/or heterogeneously at the particle surface. For micron-sized and larger particles, experimental evidence is strongly in favor of the argument that vapor-phase reactions are dominant for micron-sized and larger aluminum [43,44,315,316], magnesium [317, 318], and beryllium [275,319] particles in oxygen-containing gases. An important indicator of presence of vapor-phase reactions is the flame stand-off ratio (D_f/D_p). For aluminum, the observed flame stand-off ratios in oxygenated environments are in the range of 2.0–5.0, depending on various parameters such as oxidizer composition and pressure [315,316,320,321]. Flame stand-off ratios in the range of 1.15–1.35 and as high as 10 are observed for micron-sized beryllium particles [275,319] and magnesium particles [317], respectively. This demonstrates the presence of vapor-phase reactions and detached flame surrounding the particle.

Surface reactions are more prominent for aluminum particles in water and carbon dioxide, as evidenced by lower flame standoff ratios [315,321–323]. For example, the flame standoff ratio of micron-sized aluminum particles in water vapor is about 1.3–1.5 [309,324] and the radiation intensity of aluminum particles in carbon dioxide decreases with increasing distance away from the particle surface [322]. No such behavior was observed for magnesium particles [322]. Surface reactions are also more important for other solid fuels such as boron [7] and titanium [325,326]. For titanium particles, a two-stage combustion phenomenon was observed [326]. In the initial stage of combustion, a luminous halo formed around the droplet. The size of the halo was about 3–5 times the particle diameter. The halo was however present only for about 25% of the total burning time, so surface reactions were dominant for the majority of the burning period. It is important to note that flame temperatures of micron-sized and larger particles, in general, are approximately equal to those of their adiabatic counterparts [43,320,324,327,318]. Some deviations have been observed for titanium particles [325] due to heat losses to the ambient gas.

A number of studies have probed the combustion modes and flame structures of metal nanoparticles, especially aluminum. The flame structures of aluminum nanoparticles are substantially different from those of their micron-sized counterparts. Based on heat transfer arguments, it is logical to expect that combustion temperatures of aluminum nanoparticles could be substantially lower than the adiabatic counterparts [297]. The flame temperature is dictated by the competing effects of heat generation due to chemical reactions and heat losses to the ambient gas. If the rate of heat generation is significantly greater than that of heat loss to the ambient gas, the particle could be heated to the boiling point of aluminum (2700 K at 1 atm), thereby facilitating vapor-phase reactions. This is typically the case for micron-sized and larger particles. For nano-sized particles, on the other hand, the rate of heat loss to the ambient gas is comparable to that of heat generation. This can be attributed to the high surface-to-volume ratio at nano-scales. The particle temperature is thus likely to be lower than the adiabatic flame temperature. Note that diameters of nanoparticles are lower than the mean-free-path of the oxidizing gas. As a result, heat and mass transfer occur in the free-molecular regime. In the free-molecular regime,

conduction heat transfer rate is proportional to pressure, while the radiation heat transfer rate is independent of pressure. Also, radiation heat transfer could be more important than conduction heat transfer due to lower energy accommodation coefficients. The heat generation rate is also directly proportional to pressure. Deviations from thermal equilibrium conditions thus become significant at higher pressures (> 1 atm). Furthermore, as the heat generation rate is a function of the oxidizer composition, thermal equilibrium conditions are more prevalent for carbon dioxide and water vapor and in dilute oxygenated environments.

Experimental studies and theoretical studies suggest heat transfer peculiarities in aluminum nanoparticles at high temperatures. Allen et al. [328] conducted shock tube experiments to measure burning times and combustion temperatures of aluminum nanoparticles in oxygenated environments. The particle size was in the range of 18–110 nm and ambient gas temperature was 1500 K. The concentration of oxygen in the gas was 20%. An energy balance analysis was also performed to calculate burning times and flame temperatures. The burning rate was assumed to be controlled by the collision of gas molecules on the particle surface. Heat losses to the ambient gas by conduction and radiation were considered [328].

$$\Delta T(t) = \frac{E_{in} - E_{sur} - E_{rad}}{m_p C_p}, \quad (66)$$

$$E_{in} = A_{eff} \frac{N_{O_2} c}{4} q \phi, \quad (67)$$

$$E_{sur} = \frac{\alpha p}{8 T_a} c \frac{\gamma + 1}{\gamma - 1} (T_p - T_a) A, \quad (68)$$

$$E_{rad} = \epsilon \sigma (T_p^4 - T_w^4) A, \quad (69)$$

where E is the energy, T the temperature, p the pressure, t the time, m_p the particle mass, C_p the specific heat, N_{O_2} the number density of oxygen molecules, c the speed of gas molecules, q the heat of reaction, α the energy accommodation coefficient, ϕ the sticking probability, γ the adiabatic constant, σ the Stefan-Boltzmann constant, ϵ the emissivity, and A the particle surface area. The energy accommodation coefficient is the ratio of the actual energy transfer during gas-particle collision to the theoretical maximum value corresponding to thermal equilibration. The sticking probability gives the fraction of gas molecule collisions that result in chemical reactions. Fig. 54 shows variations of burning time and flame temperature with sticking probability for different heat transfer models [328]. Satisfactory agreement between predicted and measured flame temperatures and burning times could be achieved only by using the free-molecular heat transfer model with accommodation coefficients and sticking probabilities on the order of 0.001 [328]. These are orders of magnitude lower than the value commonly reported in the literature for an oxidized aluminum surface [329]. Experiments and high-fidelity theoretical studies such as molecular dynamics simulations, with reliable gas-surface interaction potential functions, need to be conducted to explore the temperature and size dependencies of accommodation coefficients of aluminum nanoparticles. Sticking probabilities also need to be determined.

Fig. 55 shows the effect of particle size on the measured flame temperatures of aluminum particles in oxygenated and carbon dioxide environments [40]. Measurements at 1 atm pressure correspond to laser ignited particles [315,320,330] and those at higher pressures correspond to particles ignited in a shock tube [331,332]. The flame temperature was determined by monitoring the intensity of the light emitted by the particles. For micron-sized aluminum particles, the measured flame temperatures are approximately equal to their adiabatic counterparts. At nano-scales, flame temperatures are substantially lower than the adiabatic counterparts over a pressure range of 4–8

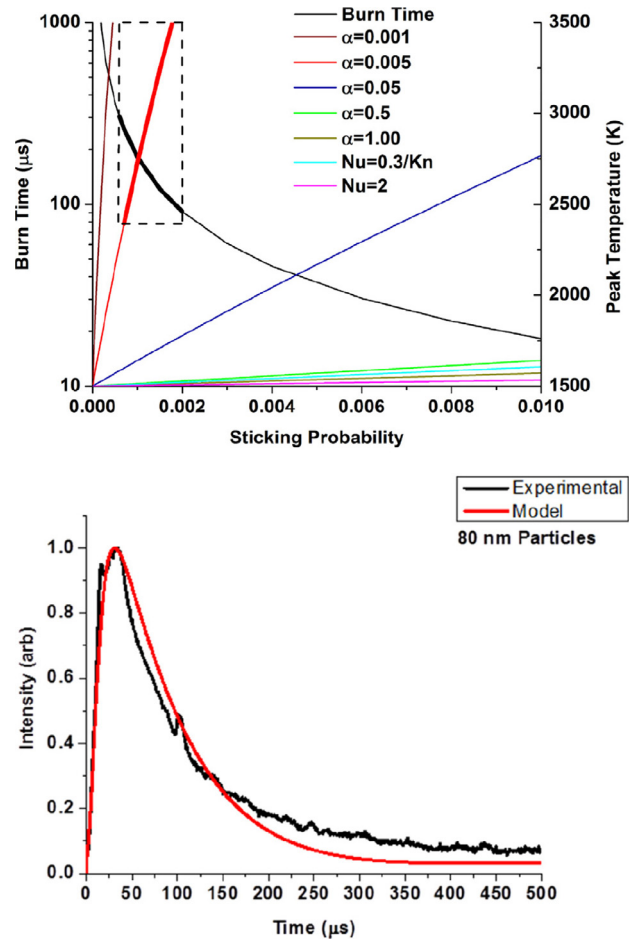


Fig. 54. (a) Variations of burning time and flame temperature with sticking probability; (b) temporal evolution of intensity; particle size is 80 nm, pressure is 20 atm, and temperature is 1500 K (reprinted from [328] with permission of Elsevier).

atm. Note that a similar phenomenon is observed for boron particles; the combustion temperatures were approximately equal to ambient gas temperatures [8]. This trend is in agreement with the results of the heat transfer analysis. The scatter in the experimental data of Bazyn

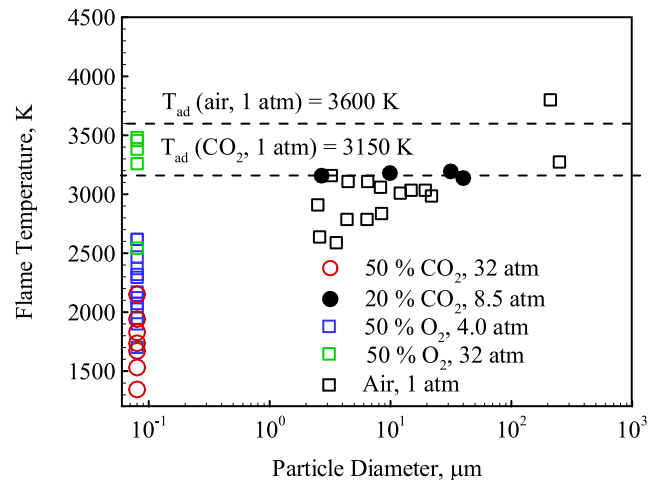


Fig. 55. Effect of particle size on flame temperature of aluminum particles in oxygenated and carbon dioxide environments (adapted from [40] with permission of Springer).

et al. stems from the fact that the ambient gas temperature was varied in the range of 1200–2100 K. The flame temperature is, however, as high as ~ 3400 K at 32 atm, suggesting that deviations from thermal equilibrium conditions are substantial at a pressure of 32 atm. Note that the boiling temperature of bulk aluminum is also a pressure-dependent parameter and it takes a value of 3800 K at 32 atm. As a result, surface reactions are expected to be important over the pressure range of concern. This is more so, if size dependence of boiling temperature is considered. Another important observation to note is that the flame temperature is nearly independent of ambient gas temperature at a pressure of 32 atm. This suggests that some limiting temperature is achieved, possibly the boiling temperature at that pressure.

Transition from continuum to the free-molecular heat transfer regime is yet another factor that drives the flame closer to the particle surface [333]. To sustain a vapor-phase flame, it was postulated that the energy released in the stationary flame zone must balance heat losses to the particle and ambient gas. Energy balance analysis was conducted to determine the critical particle size at which vapor-phase flame ceases to exist [333]. For a given particle size, a large flame is harder to sustain, due to greater heat losses to the ambient gas and reduced heat transfer to the particle. This can be attributed to the fact that the vaporization rate (and chemical energy release rate) decreases with decreasing rate of heat transfer to the particle. Fig. 56 shows the effect of particle size on the maximum value of the flame-to-particle diameter ratio ($D = D_f/D_p$) for different oxidizers. The continuum model indicates that the flame is detached from the particle surface, irrespective of the particle size. The calculated flame-to-particle diameter ratio D is in the range of 1.5–2.5 [333], which agrees with experimental data. The free-molecular model, on the other hand, suggests that the flame is located closer to the particle surface for smaller particles. The calculated critical particle diameters are 6.1, 7.2, and 15.1 μm for air, carbon dioxide, and water vapor, respectively [333]. Results suggest that surface reactions are important for combustion of nano aluminum particles. This is consistent with the predictions of heat transfer analysis and results of experimental studies.

Another important indicator of the presence of vapor-phase reactions is gas-phase Al and AlO emission. [331]. If gaseous aluminum were present, atomic aluminum lines would probably be seen at 394.4 and 396.1 nm, and banded aluminum monoxide (AlO) emission from the B–X transition would probably be seen in the range from 460–530 nm. Fig. 57 shows the emission spectra for 38–45 μm and 80 nm Al particles [331,332]. For micron-sized Al particles, spectra indicate significant gas-phase AlO emission [332]. No such emission was detected for nano-aluminum particles in

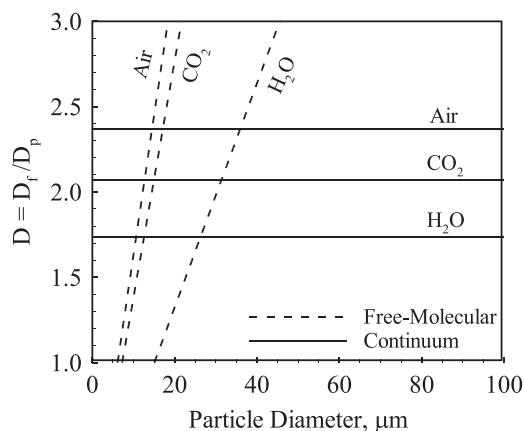


Fig. 56. Results of energy balance analysis showing the effect of particle size on maximum value of flame-to-particle radius ratio for different oxidizers (adapted from [333] with permission of Elsevier).

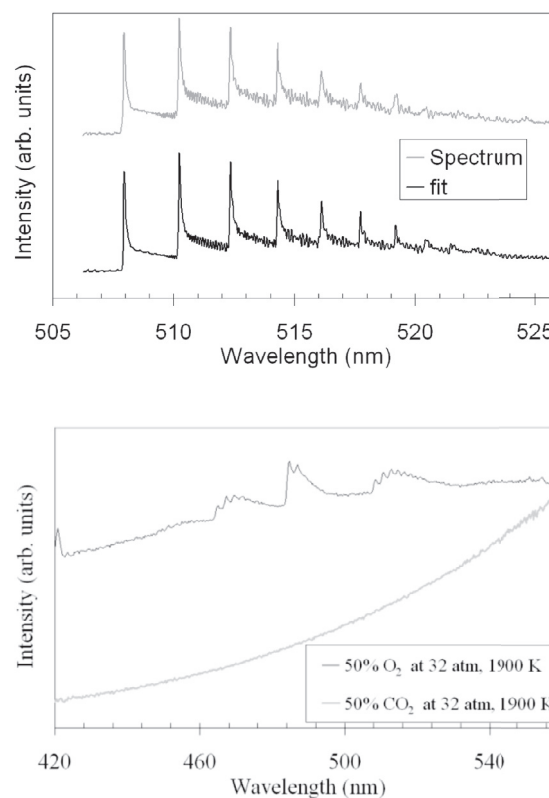


Fig. 57. (a) AIO B–X $\Delta v = -1$ emission spectra with the fitted spectral simulation for 38–45 μm particles; (b) emission spectra of 80 nm Al particles in oxygenated and carbon dioxide environments at 32 atm (reprinted from [331,332] with permission of Elsevier).

carbon dioxide environments for pressures as high as 32 atm and in oxygenated environments for pressures as high as 8 atm [331]. At 32 atm, AlO emission is detected, suggesting the presence of vapor-phase reactions [331]. This is in agreement with the hypothesis that the limiting combustion temperature ~ 3400 K is perhaps associated with boiling of aluminum particles. The general lack or insignificance of gas phase emission suggests the importance of surface reactions during combustion of nanoaluminum particles.

While all the evidence suggests that surface reactions are more prominent for aluminum nanoparticles, it is unclear at what critical particle size, transition from vapor-phase to surface combustion regime occurs for a given set of conditions. Note that the transition process could be a function of pressure, nature and concentration of the oxidizing gas, and so forth. This needs to be investigated and experimental evidence is required. Furthermore, studies are necessary to ascertain the relative importance of surface and vapor-phase reactions over a broad range of pressures (1–100 atm). In this regard, the size and pressure dependencies of combustion temperatures also need to be studied, especially for pressures exceeding 32 atm. This would be helpful in determining the mode of combustion of aluminum nanoparticles over the pressure range of concern.

8.2. Rate controlling processes

In order to understand the mechanism of combustion of metal nanoparticles, it is essential to know and understand the underlying physicochemical processes. The particle consists of a metal core and an oxide layer, which is enveloped by the oxidizing gas. The three important processes that typically control the burning rate of the particle are (1) mass diffusion through the gas-phase mixture; (2) mass diffusion across the oxide layer of the particle; and (3) chemical reactions [334]. In this analysis, it is assumed that the oxide layer

offers negligible diffusion resistance. The phenomenon of mass diffusion across the oxide layer will thus not be considered. It is useful to first understand particle burning behaviors in the limit of diffusion and kinetically-controlled conditions.

Certain metals are volatile and can undergo vapor-phase reactions, while others do not vaporize and reactions occur at the particle surface. For vaporizing particles, the droplet mass burning rate per unit area under diffusion-controlled conditions can be obtained from classical droplet combustion theory [260]:

$$\dot{m}_f'' = \frac{\rho D}{r_s} \ln(1+B), \quad (70)$$

$$B = \frac{iY_{O,a}\Delta h_c + c_p(T_a - T_s)}{h_{fg}}, \quad (71)$$

where ρ is the density, D the diffusivity, B the transfer number, ν the stoichiometric fuel-oxidant ratio, C_p the specific heat, r_s the particle radius, Y_O the oxidizer mass fraction, Δh_c the enthalpy of combustion, and h_{fg} the latent heat of vaporization. The subscripts a and s refer to ambient gas and particle surface, respectively. Here, the driving force for metal droplet consumption is primarily the energy released during combustion and supplied to the droplet. The transfer number can also be expressed in terms of the fuel mass fraction [260]:

$$B = \frac{Y_{F,s} + iY_{O,a}}{1 - Y_{F,s}}, \quad (72)$$

In this case, the driving force is the presence of concentration gradients. If the metal fuel is non-volatile, then the fuel vapor mass fraction at the surface is zero and the transfer number can be simplified as

$$B = iY_{O,a}. \quad (73)$$

For kinetically-controlled conditions, the particle mass consumption is driven by inelastic collisions of oxidizing gas molecules on the particle surface. The resulting mass consumption rate per unit area can be written as [37]

$$\dot{m}_f'' = MW_p k_s p X_{O,a}, \quad (74)$$

where X_O is the oxidizer mole fraction and k the surface reaction rate with the oxidizer. Here, a first order reaction is considered, in which reaction rate is proportional to the concentration of the oxidizing gas molecules.

8.3. Particle burning time

8.3.1. Characteristic time scales

Burning time is an important measure of the reactivity of the particles. It is typically a function of many parameters such as particle size, oxide layer thickness, pressure and temperature of the gas, and gas composition. For diffusion-controlled conditions, Eq. (70) can be integrated to obtain an expression for the particle burning time:

$$t_{b,diff} = \frac{\rho_p D_p^2}{8\rho_a D_O \ln(1+B)}, \quad (75)$$

Under diffusion-controlled conditions, the burning time is quadratically proportional to particle size and is independent of gas pressure, since the pressure effects of density and diffusivity counteract each other. On the other hand, if particle combustion is limited by chemical kinetics, an expression for the burning time can be obtained by integrating Eq. (74):

$$t_{b,chem} = \frac{\rho_p D_p}{2M_p k p_a X_{O,a}}, \quad (76)$$

where k is the rate constant and X the mole fraction. For kinetically-controlled conditions, the burning time is strongly dependent on

temperature, since the chemical rate constant is an exponential function of temperature. Furthermore, the burning time is inversely proportional to pressure, since we assumed a first order reaction.

Transition from diffusion to kinetically controlled conditions occurs at a threshold particle size, which is a function of the temperature and pressure of the ambient gas. The threshold particle size can be determined by calculating the Damkohler number, which is the ratio of diffusion and chemistry time scales [37]:

$$Da = \frac{M_p k p_a D_p X_{O,a}}{4\rho_a D_O \ln(1+B)}. \quad (77)$$

Eq. (77) suggests that diffusion controlled conditions are prevalent at high pressures and for large particles, while kinetically-controlled conditions are applicable at low pressures and for small particles. Increasing the temperature also appears to favor diffusion-controlled conditions.

To determine the threshold particle size, the diffusion coefficient and chemical rate constant must be known. The diffusion coefficient of oxygen in air is a well-known parameter [335]. The chemical rate constant, on the other hand, is not well known. In Yeh and Kuo's study [7], the chemical rate constant for boron combustion was obtained as 0.0625 mol/cm²-s-atm [312]. Substituting the values of various parameters, the critical particle size is obtained as 75 μ m at 1 atm pressure. A similar estimate can be obtained for aluminum particles [40]. The chemical rate constant can be estimated from the experimental data of Bazyn et al. [331]. In Bazyn et al.'s study, the particle size was 80 nm and the gas consisted of 50% oxygen and 50% nitrogen by mole. The activation energy was obtained using a curve-fit to burning time vs. temperature. At a pressure of 8 atm, the activation energy was 71.6 kJ/mol and the burning time was 0.29 ms at 1400 K. The resulting preexponential constant is 1618.5 mol/m²-s-atm. The resulting threshold particle size is $\sim$ 100 μ m at 1 atm pressure. As a result, to a good approximation, it may be generally said that deviations from diffusion-controlled conditions become important at a particle size of 100 μ m. Kinetically-controlled conditions are prevalent for nanoparticles at 1 atm pressure. For intermediate particle sizes ($1 < D_p < 100 \mu$ m), both the diffusion process and chemical reactions control the burning rate. Note that the threshold particle size is also a function of the pressure and temperature of the ambient gas. For example, the threshold particle size decreases from 100 to 10 μ m, as the pressure increases from 1 to 10 atm. As a result, mass diffusion could also be rate-limiting for nanoparticles at very high pressures and temperatures. Note that the calculated threshold particle sizes should be regarded as estimates rather than exact values.

8.3.2. Burning time of micron-sized particles

For micron-sized and larger particles, the burning time has a size dependence of the form $\tau_b = a D_p^n$, where the exponent n is in the range of 1.5–2.0, as observed for aluminum [45,295,316,336], magnesium [317,318,337], titanium [338,326], beryllium [275,319] and boron particles [269]. In this regime, the burning time is weakly dependent on the temperature and pressure of the ambient gas [339,340]. For aluminum particles, Beckstead [340] assimilated numerous experimental data from various sources and proposed the following correlation for the burning time of aluminum particles

$$t_b = \frac{c D_p^{1.8}}{X_{eff} p^{0.1} T_o^{0.2}}, \quad (78)$$

where X_{eff} is the effective oxidizer concentration, $X_{eff} = C_{O_2} + 0.6 C_{H_2O} + 0.22 C_{CO_2}$, p the pressure in atm, T_o the initial temperature in Kelvin, D_p the particle diameter in μ m, and c a constant ($= 7.35 \times 10^{-6}$). The burning time is measured in seconds. Suitable

corrections should be made to describe particle combustion in turbulent conditions [341]. Note that Eq. (78) is valid only for particle diameters greater than 20 μm [15].

Deviations from diffusion-controlled conditions have been observed as the particle size approaches 10 μm at high pressures [332]. This is in agreement with the Damkohler number analysis. For a 10 μm aluminum powder, the burning time is roughly inversely proportional to gas pressure [332]. This is contrary to the weak pressure dependence of burning time of larger particles. The following correlation has been proposed for the burning time of micron-sized aluminum particles in the transition regime [342]:

$$t_b = a_0 X_O^{a_1} \left(\frac{p}{p_0} \right)^{a_2} D_p^n, \quad (79)$$

$$n = 2 \exp(-4.3 X_O) \left(\frac{p}{p_0} \right)^{-0.3}, \quad (80)$$

The constants are given in Table 10 [342]. In Eq. (79), the particle diameter is in microns. The diameter exponent, n , decreases with increasing oxidizer concentration, from 2.0 at 0% to 0.0 at 100%. For oxygen and carbon dioxide, the burning time is roughly inversely proportional to the square root of the oxidizer concentration. A stronger concentration effect is observed for water vapor. The pressure exponents are -0.50 , 0.30 , and 0.75 for oxygen, carbon dioxide, and water vapor, respectively. Models for combustion of particles in transition regime have also been recently developed [343].

Deviations from the classical behavior have been observed for particulates of other metals. Fig. 58 shows the effect of particle size on the burning time of titanium and zirconium particles [344]. Experimental data for titanium are taken from Refs.

Table 10

Constants in Lynch et al.'s burning time correlation for fine micron-sized aluminum particles (reprinted from [342] with permission of Elsevier).

Oxidizer	a_0 (μs)	a_1	a_2
O ₂	200	0.5	-0.5
CO ₂	500	0.6	0.3
H ₂ O	86	-1.7	0.75

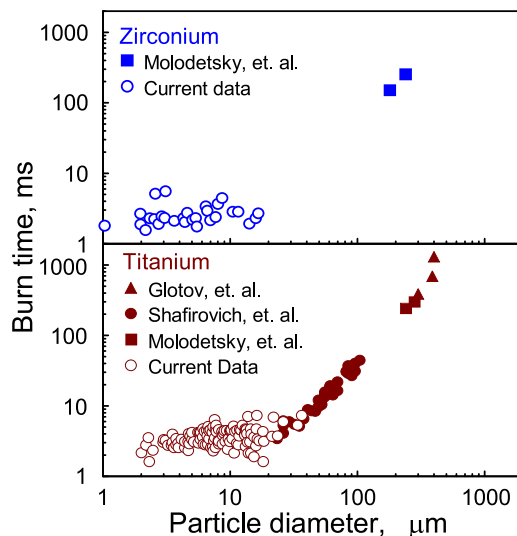


Fig. 58. Effect of particle size on burning time of micron-sized titanium and zirconium particles, showing deviations from the classical d^2 -law (reprinted from [344] with permission of Elsevier).

[325,326,344,345], while those for zirconium are taken from Refs [344,346]. For particles larger than about 20 μm , the burning time is nearly quadratically proportional to the particle size. For smaller particles, the burning time is weakly dependent on the particle size; the burning-time diameter exponent is 0.22 for titanium particles. A similar trend is observed for boron particles [7].

Many aspects of the combustion of metal particles in the transition regime are not completely understood. It is not completely clear at what particle size the effects of finite-rate kinetics become important for different conditions. While theoretical predictions give us rough estimates, sufficient empirical evidence is lacking and there is considerable uncertainty in burning time data of fine micron-sized metal particles that burn in the transition regime. Effects of different parameters such as the particle size, pressure, and gas composition also needs to be clearly understood.

8.3.3. Burning time of nanoparticles

Substantially different burning behaviors have been observed for metal nanoparticles. Ambient gas temperature has a pronounced effect on the burning properties of nanoparticles [40]. Fig. 59 shows the effect of gas temperature on the burning time of nanoaluminum particles [40]. In the study of Parr et al. [285], the oxidizer was water vapor and the gas pressure was 1 atm, while the work of Bazyn et al. [331], particles burned in an oxygen-nitrogen gas over a pressure range of 4–32 atm. The burning time has a temperature dependence of the form [40]

$$t_b = A \exp(-E_A/RT), \quad (81)$$

where the activation energy, E_A , falls in the range of 50–144 kJ/mol. The strong temperature dependence of burning time supports the theory that the combustion of aluminum nanoparticles is controlled by chemical kinetics. Such a temperature dependence of burning time was also observed for boron nanoparticles [8] and in a more recent study on aluminum nanoparticles [347]. Fig. 60 shows the effect of gas temperature on the burning time of boron nanoparticles [8]. The activation energy is about 33 kJ/mol. These results are contrary to those obtained for micron sized and larger particles; the burning time of micron-sized particles is weakly dependent on the gas temperature.

Particle size exerts a weak effect on the burning time of metal nanoparticles [40]. Fig. 61 shows the effect of particle size on the burning time of aluminum particles in different oxidizing environments [40]. Experimental data are taken from Refs. [45,285,330,336,348–350]. The burning time has a size dependence

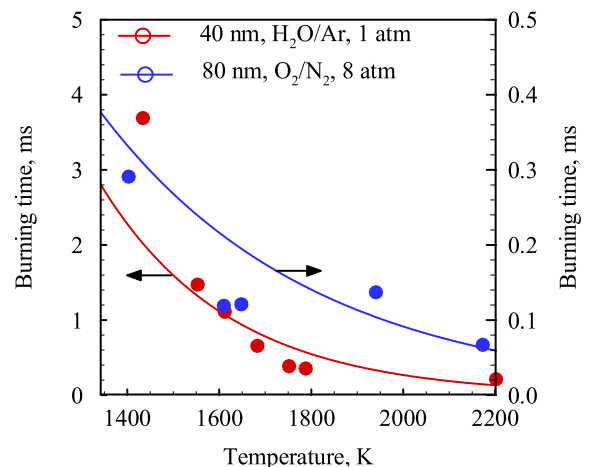


Fig. 59. Effect of gas temperature on burning time of nanoaluminum particles; an Arrhenius trend is observed (adapted from [40] with permission of Springer).

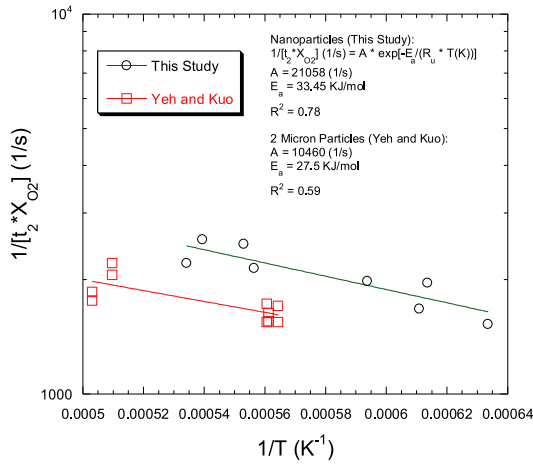


Fig. 60. Effect of gas temperature on the burning time of boron nanoparticles, showing an Arrhenius trend (reprinted from [8] with permission of Elsevier).

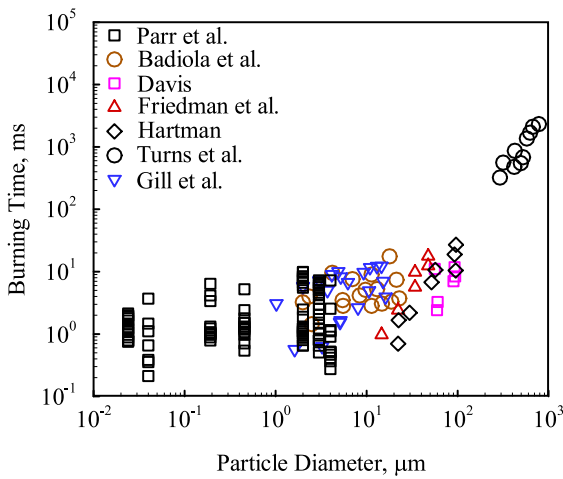


Fig. 61. Effect of particle size on burning time of aluminum particles, showing a weak size effect at nano-scales (adapted from [40] with permission of Springer).

of the form [40]

$$t_b = a D_p^n, \quad (82)$$

where the exponent n is 0.3, substantially lower than unity. A similar size dependence of the burning time was observed for boron nanoparticles, as shown in Fig. 62 [8]. Experimental data are obtained from Refs. [8,269,312]. While a weak size dependence of burning time is expected from a chemical kinetics standpoint, the fact that the diameter exponent is lower than unity is puzzling.

The weak particle size effect on the burning time has been attributed to sintering and aggregation of particles [35,351,352] and/or the fractal nature of the particle surface [310]. The presence of cracks in the oxide layer necessitates a fractal analysis. For fractal surfaces, the surface area is related to particle diameter as follows [40]:

$$A = A_{ref} \left(\frac{D}{D_{ref}} \right)^{D_f}, \quad (83)$$

where A is the area, D the particle diameter, and D_f the fractal dimension. The subscript ref refers to the reference size. For particles burning in the kinetic regime, the particle mass consumption equation can be written as follows:

$$\frac{dM_p}{dt} = A_p \dot{\omega}, \quad (84)$$

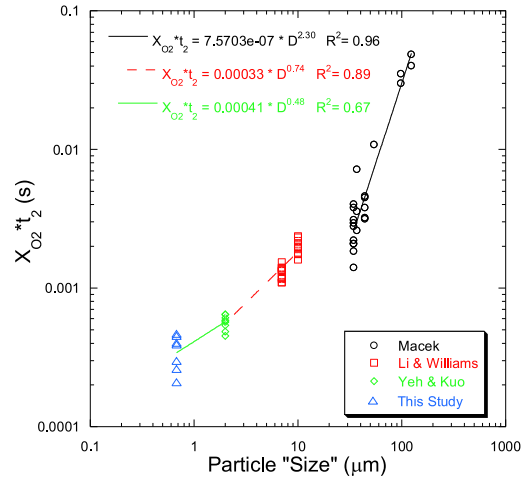


Fig. 62. Effect of particle size on burning time of boron particles; a weak size effect is also observed for boron nanoparticles (reprinted from [8] with permission of Elsevier).

where M_p is the particle mass, A_p the particle surface area, and $\dot{\omega}$ the chemical reaction rate per unit area (kg/m²s). Eq. (84) can be rewritten, noting that the fractal aspect alters the surface area significantly with negligible changes in the particle volume [310]:

$$\frac{dD_p^3}{dt} = c D_p^{D_f} \dot{\omega}, \quad (85)$$

where c is a constant. Integration of the above equation results in the following burning-time law

$$t_b = A D_p^{3-D_f}, \quad (86)$$

where A is the burning time constant. Note that $D_f = 2$ corresponds to a non-fractal surface and a linear relationship between burning time and particle size is recovered. For fractal surfaces ($D_f > 2$), the diameter exponent is lower than unity and the exponent depends on the fractal dimension. The fractal theory is not without its limitations. For example, the oxide layer is likely to melt during combustion, since combustion temperatures are as high as ~ 3400 K and melting temperatures of nano-scale oxide layers could be substantially lower than the bulk value. Once the oxide layer melts, the surface is no longer expected to be fractal and the applicability of this theory becomes questionable. Another theory that has been put forward to explain the anomalous behavior is that sintering and aggregation of nanoparticles results in loss of surface area and the measured burning times may not correspond to initial particle size [35,351]. Recent studies [353–355] have attempted to understand the combustion of nanoparticle aggregates, but further research is necessary. The phenomenon of weak size dependence of burning time still remains poorly understood and further studies are required.

Oxidizer concentration and pressure are two other parameters that dictate the burning behaviors of nanoparticles [40]. Fig. 63 shows the effects of oxidizer concentration and pressure on the burning time of 80 nm aluminum particles in oxygenated environments [331]. The burning time decreases with increasing oxidizing concentration. The effect of pressure on the burning time of nano-aluminum particles is not completely understood. At temperatures lower than 1600 K, the burning time decreases by a factor of three when the gas pressure increases from 8 to 32 atm. The burning time is, however, a relatively weak function of the gas pressure at temperatures greater than 1600 K. The following correlation can be used to calculate the burning time of nanoaluminum particles at 1 atm pressure [40]:

$$t_b = \frac{D_p^{0.29} \exp(-E_a/RT)}{A C_O^{0.4}}, \quad (87)$$

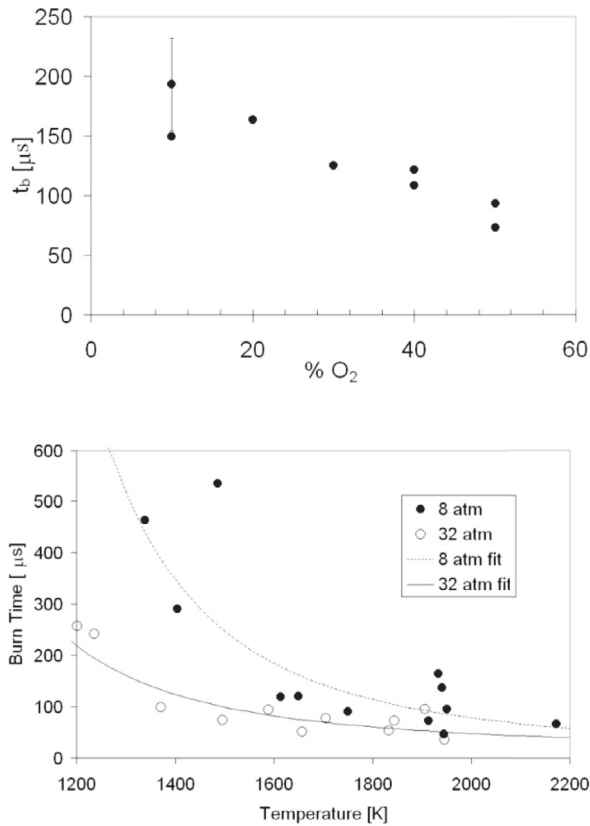


Fig. 63. (a) Effect of oxygen concentration on burning time of 80 nm aluminum particles at pressure of 32 atm and temperature of 1500 K; (b) effect of pressure on burning time of 80 nm aluminum particles in an oxygenated environment (reprinted from [331] with permission of Elsevier).

where $E_a = 80$ kJ/mol is the activation energy, R the gas constant, T the temperature, C_o the oxidizer mole fraction, and A the constant ($= 162,127$). Note that the correlation does not consider effects of oxidizer and pressure on the burning time, since they are poorly understood. In general, experimental data on burning times of nanoparticles are scarce, and more studies are needed.

8.4. Other processes and mechanisms

Comparison of diffusion and chemical time scales suggest that nanoparticles typically burn under kinetically-controlled conditions. Note that Eq. (70) is strictly valid in the continuum regime. In the free-molecular regime, the mass burning rate under diffusion-controlled conditions can be expressed as [30]

$$\dot{m} = -r_p^2 p Y_{O,a} M_a \sqrt{\frac{8\pi}{RT_a M_o}}, \quad (88)$$

Integration of the mass burning rate gives the following expression for the burning time in the free-molecular regime [40]:

$$t_{b,diff} = \frac{\rho_p D_p}{i p_a Y_{O,a} M_a} \sqrt{\frac{\pi R_g T_a M_o}{2}}. \quad (89)$$

Here, the burning time is a linear function of the particle size and inversely proportional to gas pressure. This may suggest that the burning time of nanoparticles can be diffusion-controlled, but the diffusion theory cannot account for the strong temperature dependence of the burning time. Furthermore, the resulting burning time of 80 nm Al particles under diffusion-controlled conditions are several orders of magnitude lower than the measured burning times

[40]. This suggests that mass diffusion through the gas-phase mixture does not control the burning rate of metal nanoparticles, even when free-molecular effects are considered.

Note that mass diffusion across the oxide layer of the particle was not treated, perhaps the oxide layer fractures due to tensile stresses exerted by the molten aluminum core [267] or polymorphic phase transformations [236]. The role of the oxide layer during combustion of nanoaluminum particles remains poorly understood; it is possible, but unlikely, that the oxide layer imposes significant diffusion resistance during combustion. To account for diffusion resistance, the diffusion coefficient must be specified. Unfortunately, there is substantial uncertainty in the diffusion coefficient. In the study of Park et al. [103], the diffusion coefficient was estimated to be on the order of 10^{-13} – 10^{-12} m²/s over a temperature range of 873–1173 K. Diffusion coefficients obtained from MD simulations were of the order of 10^{-9} – 10^{-7} m²/s over the temperature range of 1000–2000 K [257]. These values are orders of magnitude greater than the experimental data, but it is important to recognize that MD predictions correspond to particles smaller than 10 nm and high heating rates ($> 10^{10}$ K/s), while experimental studies correspond to larger particles and much lower heating rates (~ 1 K/s). Further studies are required to establish a database for diffusion coefficients in the oxide layer for various conditions. More importantly, efforts must be made to elucidate the role of the oxide layer during combustion of aluminum nanoparticles.

Alternative theories have been proposed to explain the combustion mechanisms of nano-aluminum particles. Levitas et al. [224] proposed a melt-dispersion mechanism for high heating rate situations ($> 10^6$ K/s). Melting of the aluminum core creates pressures of 1–4 GPa, which causes spallation of the oxide shell. The ensuing pressure imbalance between the core and the exposed surface results in an unloading wave and disperses small liquid aluminum clusters and these clusters react with the oxidizing gas. Sufficient empirical evidence of the proposed melt-dispersion mechanism is, however, still lacking. Lynch et al. [356] employed absorption spectroscopy to detect the presence of aluminum vapor for 80 nm aluminum particles in argon at 7 atm with the help of a shock tube. The gas temperature was decreased from 3000 K in increments of about 100 K until no aluminum vapor was seen in the absorption spectrum. Aluminum vapor was not present at temperatures lower than 2275 K. If aluminum clusters were present, measurements should have detected the aluminum vapor corresponding to the equilibrium partial pressure. This suggests that spallation of the oxide layer and dispersion of aluminum clusters do not occur upon melting of the aluminum core. Experimental evidence of the proposed melting dispersion mechanism is quite scarce [357]. The applicability of melt-dispersion theory is thus still debated.

8.5. Stages of oxidation of aluminum particles

Observations from various studies can be used to develop a phenomenological theory of oxidation of aluminum particles [297]. Oxidation behaviors of nanoparticles can be distinguished from those of micron-sized particles. In general, the oxidation of aluminum particles can be divided into different stages based on phase transformations and chemical reactions [297]. Figs. 64 and 65 show the stages of oxidation of nano- and large micron-sized aluminum particles, respectively [297]. In the first stage, the particle is heated to the melting temperature of the aluminum core. The key processes are heat and mass transfer between the gas and particle surface and diffusion of mass and energy inside the particle. The second stage begins upon melting of the aluminum core. Melting results in pressure buildup and facilitates outward motion of the molten aluminum by diffusion and/or flow through the cracks in the oxide layer. Melting may also be accompanied or followed by polymorphic phase transformations, which also result in the formation of openings in

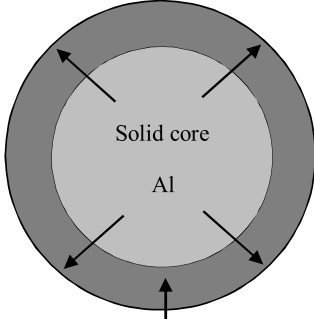
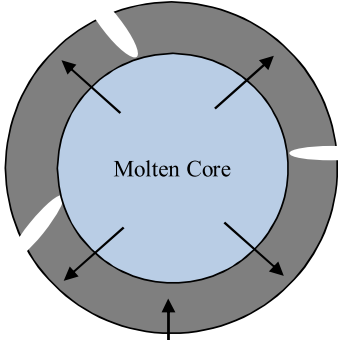
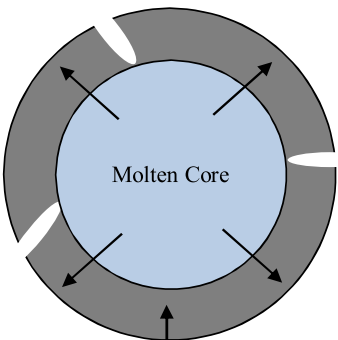
Evolution	Key processes and mechanisms	Time scales
 Particle heating to core melting point (Stage I)	1. Heat and mass transfer from gas to particle 2. Heat and mass diffusion inside particle	$\tau_{heat} \approx \frac{\rho_p C_p D_p T_a}{\alpha p_a c} \frac{\gamma - 1}{\gamma + 1}$ $\tau_{diff} \approx \frac{\delta^2}{6D}$
 Phase transformations and ignition (Stage II)	1. Melting of aluminum core 2. Phase transformations in the oxide layer 3. Fracture of oxide layer and outward flow of aluminum 4. Mass diffusion across the oxide layer 5. Heterogeneous chemical reactions	$\tau_{melt} \approx \frac{4\rho_p h_m D_p T_a}{3\alpha c p_a \Delta T} \frac{\gamma - 1}{\gamma + 1}$ $\tau_{frac} \approx \frac{\delta}{V_{crack}}$ $\tau_{poly} = \frac{\rho_{ox} V_{ox}}{\dot{m}_{ox}^{tr}}$
 Surface combustion (Stage III)	1. Diffusion of oxidizing gas to the particle surface 2. Mass diffusion across the oxide layer 3. Chemical reactions between aluminum and oxidizing gas 4. Heat and mass exchanges between particle and ambient gas	$t_{b,diff} = \frac{\rho_p D_p}{ip_a Y_{O,a} M_a} \sqrt{\frac{\pi R T_a M_o}{2}}$ $t_{b,chem} = \frac{\rho_p D_p}{2M_p k p_a X_{O,a}}$ $t_{b,diff} \approx \frac{R_p^2}{6D}$ $\tau_{poly} = \frac{\rho_{ox} V_{ox}}{\dot{m}_{ox}^{tr}}$

Fig. 64. Three stages of oxidation of aluminum nanoparticles (reprinted from [297] with permission of Elsevier).

the oxide layer. The cracks and openings provide pathways for the molten aluminum to react with the oxidizing gas. The ensuing energy release results in ignition of aluminum nanoparticles. For large micron-sized particles, ignition is not achieved, due to their greater volumetric heat capacity. In the third stage, nanoparticles undergo vigorous self-sustaining reactions with the oxidizing gas.

Reactions typically occur heterogeneously in the particle, and the burning rate is limited by chemical kinetics. For large micron-sized particles, polymorphic phase transformations result in the formation of a crystalline oxide layer. The oxide layer melts and particle ignition is achieved. In the fourth stage, the large micron-sized particle burns through gas-phase or surface reactions, depending on the

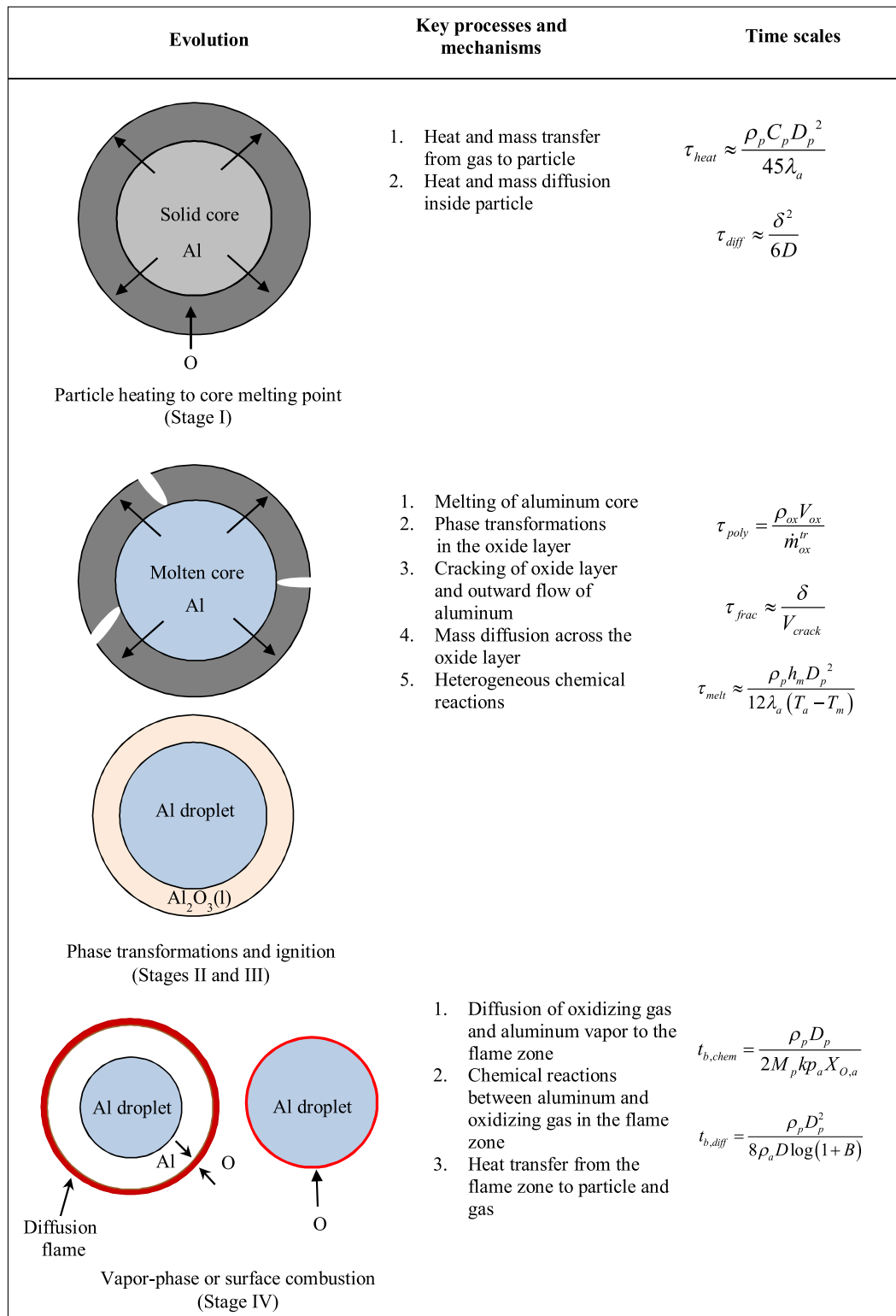


Fig. 65. Four stages of oxidation of large micron-sized aluminum particles (reprinted from [297] with permission of Elsevier).

oxidizer and pressure. The burning rate is controlled by mass diffusion through the gas-phase product layer.

Although new insights have been obtained and a crude picture of nano-aluminum combustion has been established, there are many uncertainties and several physicochemical phenomena remain incompletely understood. Experimental studies are needed to quantify burning time and combustion temperatures of aluminum nanoparticles over a broader range of pressures, particle sizes, and for

different oxidizing gases. Attempts must be made to elucidate the mode and mechanism of combustion. Recently, efforts have been made to conduct meso/macro-scale [328,358–363] and atomistic-scale simulations [207,257,308,364] of aluminum nanoparticle combustion. A comprehensive multi-scale model of combustion of metal nanoparticles can be developed. Results from atomistic-scale simulations can be used as inputs to develop a predictive model and minimize the number of empirical and adjustable parameters.

Results of such models can also be compared with experimental data to ensure validity.

9. Nanoparticle-laden dust clouds

A dust cloud consists of particles suspended in an oxidizing gas (such as air) at very low particle concentrations. Dust clouds pose explosion hazards due to the extreme reactivity of fine particles. From a safety perspective, it is thus important to understand conditions that favor explosions, so that appropriate precautions can be taken. Explosion characteristics are typically studied in a spherical vessel under constant volume conditions, while combustion behaviors are investigated under constant pressure conditions.

9.1. Explosion characteristics of dust clouds

Various parameters can be used to characterize the explosion of dust clouds. These include ignition temperature, ignition energy, minimum explosion concentration, and peak values of the pressure and pressurization rate. Explosion characteristics are commonly investigated using a 20 L apparatus, as shown in Fig. 66 [365], in accordance with the principles of the standard ISO 6184-1 [365]. The test chamber is a hollow spherical vessel made of stainless steel. A cooling water jacket dissipates heat generated due to explosion. The dust is dispersed into the sphere from a pressurized storage chamber via the outlet valve and a disperser. Ignition is achieved using two 5 kJ pyrotechnic ignitors. The ignition delay is set at 60 ms as per standards. The goal of the experiment is to determine whether an explosion occurs for a given set of adjustable conditions. The adjustable conditions include type, size, and concentration of the particles. The energy supplied by the ignitors promotes reactions and creates conditions favorable for explosion, while heat losses to the ambient environment attempt to prevent an explosion. Note that prevalence of reactions does not necessarily imply explosion, as the rate of the reactions may not always be sufficient to cause an explosion.

Explosions occur when the dust concentration exceeds the Minimum Explosion Limit (MEL) [366]. Fig. 67 shows the effect of particle size on the minimum explosion limit of aluminum

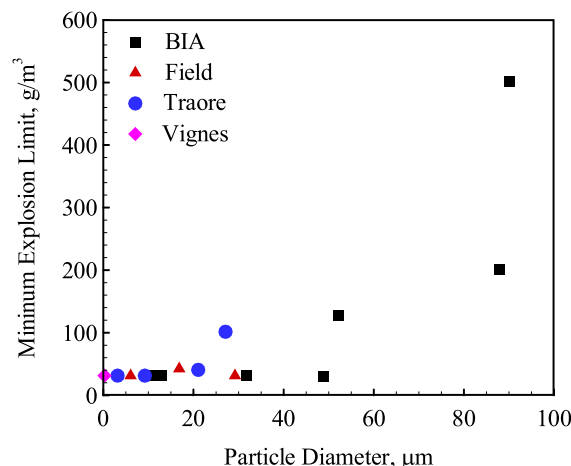


Fig. 67. Effect of particle size on the minimum explosion limit of aluminum particle dust clouds (adapted from [366] with permission of Elsevier).

particle dust clouds [366]. Results from different sources [367–370] are shown. For particles with diameters greater than $\sim 50 \mu\text{m}$, the minimum explosion limit increases with increasing particle size, from about 30 g/m^3 at $50 \mu\text{m}$ to 500 g/m^3 at $90 \mu\text{m}$. The minimum explosion limit is a weaker function of particle size for finer particles and attains a limiting value of $\sim 30 \text{ g/m}^3$. The minimum explosion limit can be determined based on the Van't Hoff and Taffanel Le Floch conditions [366]:

$$MECX\Delta H_c > (c_{pg}\rho_g + c_{ps}MEC)(T_{ign} - T_u) + Q_{loss}, \quad (90)$$

where ρ_g is the gas density, c_p the specific heat, T_u the unburned gas temperature, X the reaction conversion factor, and Q_{loss} the heat loss to the ambient environment due to radiation and convection. Physically, explosion occurs if the amount of heat released during combustion is greater than the sum of heat loss to the ambience and the energy required to heat the mixture to the ignition temperature. If heat losses are neglected, the minimum explosion limit can be expressed as [366]:

$$MEC = \frac{(c_{pg}\rho_g)(T_{ign} - T_u)}{X\Delta H_c - c_{ps}(T_{ign} - T_u)}, \quad (91)$$

As can be seen, the primary effect of particle size stems from the size dependence of ignition temperature. It must be cautioned that aggregation and agglomeration could occur in dust clouds and the resulting ignition temperatures could be different from those of isolated particles. This may partly explain the plateauing of the minimum explosion limit for smaller particles. A more rigorous energy balance analysis considering the effect of heat losses can be performed to achieve better understanding.

The minimum ignition energy is also a size-dependent parameter [366]. Fig. 68 shows the effect of particle size on the minimum ignition energy of aluminum particle dust clouds [366], using the experimental data from Refs. [367–369,371,372]. The minimum ignition energy decreases with decreasing particle size. A similar trend was observed for titanium and iron particles [373]. The size dependence of minimum ignition energy can be obtained from classical ignition theory. Essentially, the ignition energy is the energy required to heat up a region of the dust cloud to the adiabatic flame temperature [260]

$$E_{min} = \rho V C_p (T_{ad} - T_u), \quad (92)$$

where ρ is the dust cloud density, V the volume of ignition kernel, C_p the specific heat, and T_{ad} the adiabatic flame temperature. The critical volume of the ignition kernel can be obtained by equating the

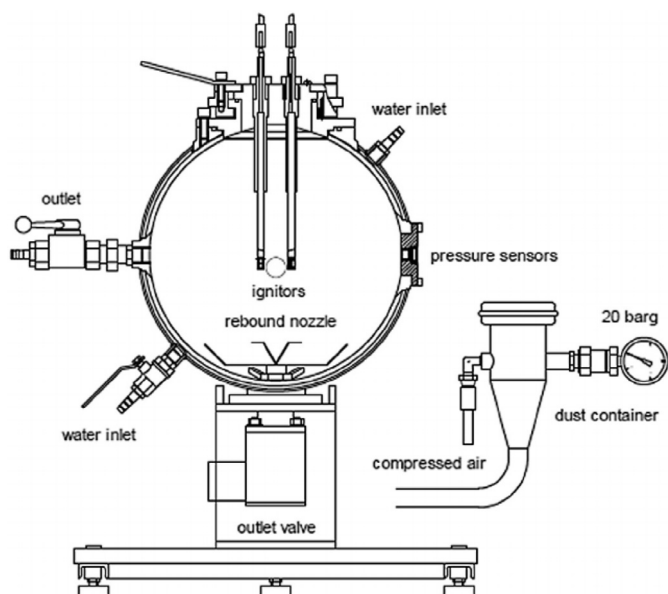


Fig. 66. Schematic of the apparatus used to study explosion characteristics of dust clouds (reprinted from [365] with permission of Elsevier).

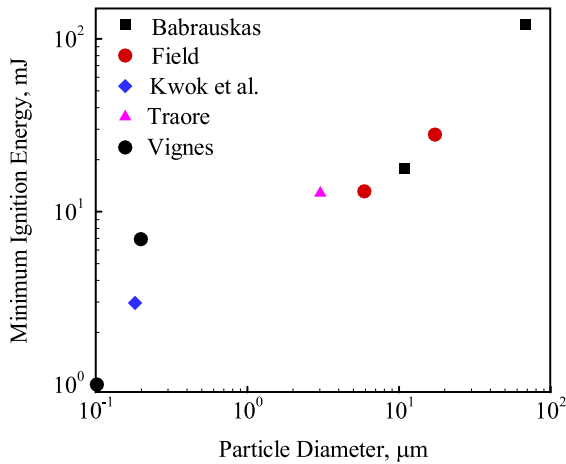


Fig. 68. Variation of the minimum ignition energy with particle size for aluminum particle dust clouds (adapted from [366] with permission of Elsevier).

rates of energy release and heat loss to the ambience. The resulting minimum ignition energy can be expressed as [260]

$$E_{\min} \propto \rho \frac{\alpha}{S_L} C_p (T_{ad} - T_u), \quad (93)$$

where α is the thermal diffusivity and S_L the laminar flame speed. From Mallard and Le Chatelier's theory, the flame speed can be expressed as [260]

$$S_L \propto \sqrt{\alpha \dot{\omega}}, \quad (94)$$

where $\dot{\omega}$ is the reaction rate, which is inversely proportional to particle burning time. The size dependence of ignition energy can thus be attributed to variations of burning time with particle size. Physically, lowering the burning time increases the heat-generation rate within the ignition kernel compared to the rate of heat loss from the ignition kernel to the ambience. This would facilitate heat up of the ignition kernel to the adiabatic flame temperature.

The explosion pressure and pressurization rate are two other parameters of concern [366]. Fig. 69a shows the effect of particle concentration on the maximum explosion pressure of an aluminum particle dust cloud [366]. The maximum explosion pressure is a strong function of the dust concentration and typically peaks for fuel-rich conditions. Note that the stoichiometric fuel concentration of the Al-air dust cloud is 305 g/m³. As the explosion pressure is dependent on the adiabatic flame temperature, it is logical to expect it to peak near stoichiometric conditions. The unexpected behavior can be explained by considering the effect of incomplete combustion of particles [365]. Similar trends have been reported for other metal particle dust clouds [374,375]. Note that the maximum explosion pressure is expected not to be a strong function of the particle size, as the explosion studies of Li et al. for nano-aluminum dust clouds suggest [376]. This is because pressure is merely a thermodynamic property and does not depend on the reaction rate of particles. Micron-sized particle dust clouds however reveal a significant size-dependence of explosion pressure [375,376]. The discrepancy could be due to the effects of heat losses and energy consumption during the ignition process [375]. Unused energy supplied during ignition can increase the explosion pressure. Also, heat losses to the ambience, which lower the explosion pressure, could be more important for micron-sized particles that burn relatively slowly.

Fig. 69b shows the effect of specific surface area on the maximum pressurization rate [366]. Experimental data are taken from Refs. [377–379]. For micron-sized particles, the maximum pressurization rate increases with increasing specific surface area. This is not surprising, since the pressurization rate depends on the reaction

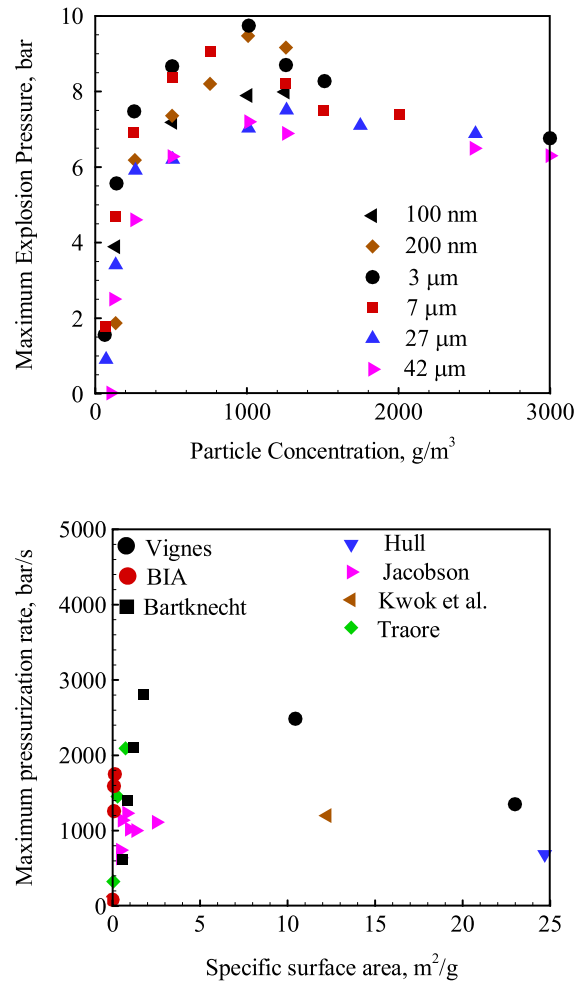


Fig. 69. (a) Effect of particle concentration on the maximum explosion pressure for different particle sizes; (b) variation of maximum pressurization rate with specific surface of aluminum particles (adapted from [366] with permission of Elsevier).

kinetics, which is a strong function of the particle size [365]. At nano-scales, the maximum pressurization rate decreases with decreasing particle size. In a more recent study, the maximum pressurization rate was found to be a weak function of the particle size over a size range of 30–110 nm [376]. For magnesium particles, the peak pressurization rate decreases with decreasing size in the range of 30–200 nm [380]. These surprising results can be attributed to particle agglomeration and enhanced oxide layer content in the particle at nanoscales [381–383].

While many of the experimental observations can be qualitatively explained by classical theories, there are several unexpected results and trends that warrant further investigations. In particular, the size and concentration effects on many explosion parameters appear to be strongly influenced by the effects of incomplete combustion, heat losses, and particle agglomeration. The effect of the oxide layer also needs to be explored. Future studies should focus on these problems, with the objective of quantifying the explosion severity of nanoparticle-laden dust clouds for a wide range of particle sizes and dust concentrations. A more rigorous energy balance analysis that considers the aforementioned phenomena would be a good starting point in this direction.

9.2. Flame propagation characteristics of dust clouds

One of the most important parameters pertaining to the combustion of a homogeneous fuel-oxidizer system is the laminar flame speed. The flame speed of metal particle-laden dust clouds can be

measured in a number of different ways, including Bunsen burner [384,385], latex balloons [386], and open field flame propagation [386]. Fig. 70 shows a schematic of one of the more common experimental setups used to measure flame speeds of aluminum particle dust clouds [387]. A cylindrical quartz tube is packed with aluminum powder and cartridge-loaded at the base. The powder is fed into the break-up region by a linear actuator located at the bottom of the aerosol assembly. A high velocity oxidizer shear flow emerging from a 75 μm thick annular flow removes a layer of the powder to form a homogeneous aerosol. The dust cloud is ignited using a hydrogen-air pilot flame atop the tube exit. Early studies on micron-sized particle dust clouds made some interesting observations. The flame speed was found to be weakly dependent on the dust concentration for fuel-rich mixtures [15,384,385]. This was attributed to the fact that the flame temperature is not strongly dependent on equivalence ratio for these equivalence ratios and the particle burning time is a weak function of temperature in the diffusion regime [384,388]. For particle concentrations exceeding 750 g/m^3 , however, the flame speed decreased with increasing dust concentration [389]. This was attributed to the increase in the heat capacity of the mixture with increasing loading density of particles [389].

The flame speed of particle-laden dust clouds can be enhanced by substituting nanoparticles for their micron-sized counterparts [385,390]. Fig. 71 shows photographs of burner stabilized flames for nanoaluminum particle concentrations of 0 and 20% [387]. Two sets of powders with particle diameters of 5–8 μm and 100 nm were employed. The dust concentration in this study was varied in the range of 263–448 g/m^3 . Addition of nanoaluminum particles results in a thicker flame due to the presence of two distinct reaction zones corresponding to micron and nanoparticles. This is not surprising, considering that micron and nanoparticles have different ignition temperatures. Fig. 72 shows the effect of loading density of nanoaluminum particles on the flame speed of aluminum particle dust cloud [385]. The flame speed increases with increasing loading density, from $\sim 10\text{ cm/s}$ at 0 wt.% to 30 cm/s at 30 wt.%. It is apparent that

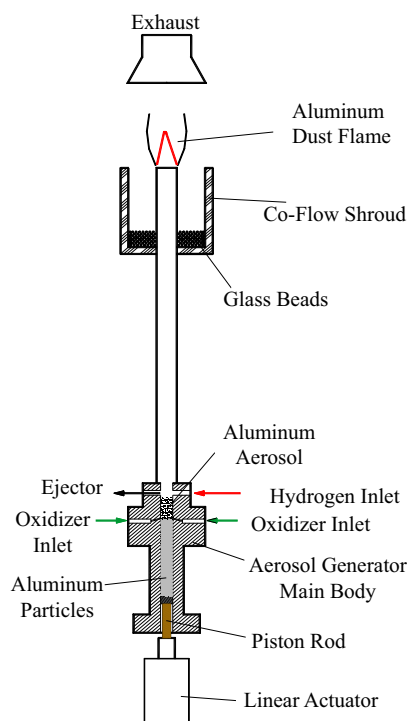


Fig. 70. Schematic of the burner-based experimental setup used to measure flame speeds of particle-laden dust clouds (reprinted from [387] with permission of Elsevier).

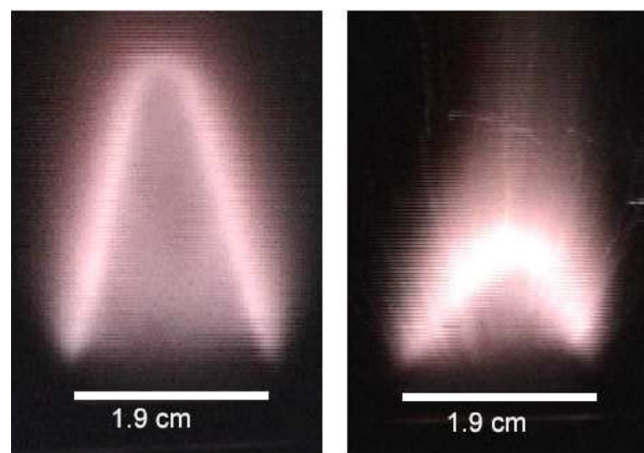


Fig. 71. Photographs of the burner stabilized aluminum particle dust flame for (a) 100% micron-sized particles; (b) 20% nanoparticles (reprinted from [387] with permission of Elsevier).

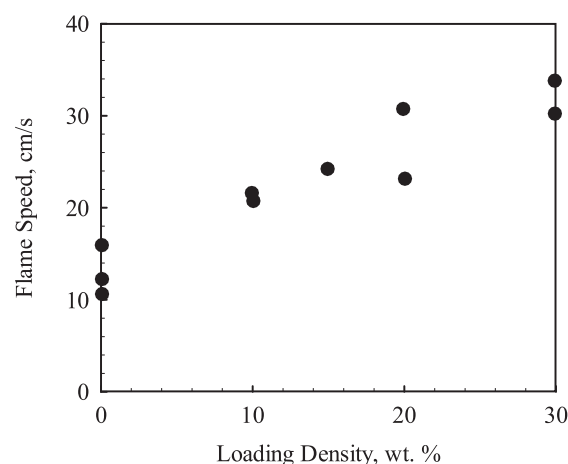


Fig. 72. Effect of loading density of nanoaluminum particles on the flame speed of the aluminum particle dust cloud; $p = 1\text{ atm}$, $\phi = 1.201$ (adapted from [385]).

nanoparticles have a positive effect on the flame speed of aluminum particle dust clouds. This can be attributed to the fact that the ignition temperatures and burning times of aluminum nanoparticles are lower than those of micron-sized particles.

Theoretical analysis has been conducted to gain insight into the underlying processes and mechanisms [15,388,391]. The work considered mass and energy balances and enforced continuities of temperature and heat flux at the interfacial boundaries. Ignition temperatures and burning times of particles were inputs to the analysis. Fig. 73 shows the effect of particle size on the flame speed of the aluminum dust cloud in air [15]. The flame speed increases with decreasing particle size and the obtained trend is consistent with the experimental data. For premixed systems, the flame speed expression takes the following form:

$$S_L \propto \sqrt{\alpha \bar{\omega}}, \quad (95)$$

where α is the thermal diffusivity and $\bar{\omega}$ the reaction rate. As the reaction rate is inversely proportional to burning time, the flame speed is greater for smaller particles. Furthermore, as the particle diameter decreases from the micron to the nano-scale range, the flame speed increases and the combustion transitions from a diffusion-controlled to a kinetically controlled mode. For micron-sized and larger particles, the flame speed can be correlated with the particle size according to a d^{-m} relationship, with m being 0.92. A similar trend has been observed for iron dust clouds [392]. At

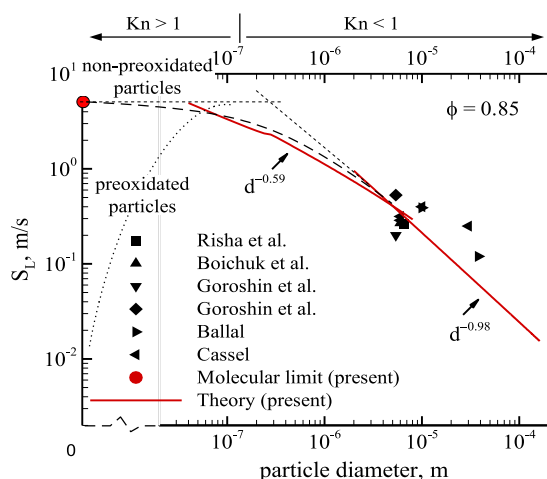


Fig. 73. Effect of particle size on flame speed of aluminum particle dust cloud in air (solid lines: calculated; black solid symbols: experimental data; red filled circle: flame speed at molecular limit; dashed lines: projected or conjectured flame speed (reprinted from [15] with permission of Elsevier). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

nanoscales, $d^{-0.52}$ or $d^{-0.13}$ law was obtained, depending on whether $d^{1.0}$ or $d^{0.3}$ – law of the particle burning time was employed. No universal law of flame speed exists for the entire range of particle sizes. Recently, an attempt has been made to conduct a more advanced analysis, in which the single particle combustion model is integrated into computational fluid dynamics analysis [393]. Future work should attempt to eliminate empiricism and external input parameters such as ignition temperature and burning time from the analysis. A full detailed chemical mechanism with treatment of radiation heat transfer, multi-phase flow physics, and particle agglomeration is likely to yield better predictions.

10. Additives to liquid propellants and fuels

Metal nanoparticles may be added to liquid fuels and propellants for any of a number of reasons. First, metals have higher volumetric energy densities compared with many liquid fuels and propellants, and can thus help to lower the volume and weight of the propulsion system and increase the payload. Second, nanoparticles can improve the ignition and combustion characteristics of the base fuel/propellant and result in better ignition and burning properties [394]. Third, nanoparticle-laden liquid propellants are less prone to leakage and generally less susceptible to cracking, and are less sensitive to impact, friction, and electrostatic discharge [37]. Prior studies have considered a wide range of nanoparticle concentrations, with consistencies ranging from nanofluids to gels and pastes.

10.1. Additives to liquid fuels

Nanoparticles can be added to enhance the ignition characteristics of conventional fuels. Tyagi et al. [394] conducted one of the first studies demonstrating the beneficial effects of adding metal nanoparticles to liquid fuels. Effects of aluminum and aluminum oxide nanoparticles on ignition characteristics of diesel fuel were studied over a temperature range of 688–768 °C. Two different particle sizes of 15 and 50 nm were considered. The particle volume fraction varied in the range of 0.0–0.5%. Particle-laden droplets were dropped on a hot plate and the ignition probability was calculated based on the number of droplets that ignited. The ignition probability of diesel increased due to the addition of the nanoparticles. For example, at a temperature of 708 °C, the ignition probability increased from 15 to 50%, when the concentration of nanoaluminum particles increased from 0 to 0.5 vol.%. This was attributed to the enhancement of the

heat and mass transfer properties of the fuel. Addition of metal nanoparticles also reduces the ignition delay of other fuels. For ethanol and JP-8, ignition delay reductions of 32 and 50% have been achieved by adding 2% aluminum nanoparticles [395].

Slurry fuels, which are mixtures of liquid and solid fuels, are attractive high-energy fuels for volume-limited air-breathing propulsion applications. The burning characteristics of slurry droplets consisting of micron-sized boron [396–399] and aluminum [349,400,401] particles at relatively high loading densities (40–80 wt.%) have been studied experimentally. A detailed review on slurry fuels was published in Ref. [402]. The oxidation of slurry droplets begins by vaporization of the liquid fuel and aggregation of left-over particles [402]. The formation of agglomerates due to vaporization of liquid fuel presents a critical problem, however, since the burning time of the resulting agglomerate is substantially greater than that of individual particles [402]. The disruption/microexplosion of the slurry droplet, an important event during slurry droplet combustion, alleviates the problem to some extent [402]. This phenomenon was first observed for slurries of boron/JP-10 droplets [397]. Two boron samples, amorphous (0.20–0.32 μm) and crystalline (3.57 μm), were employed. The micro-explosion phenomenon can be explained by Law's diffusion limit model [403]. The droplet surface becomes more concentrated with the less volatile, high-boiling-point component, and the droplet interior has a higher concentration of the more volatile, low-boiling-point component. The latter can be heated beyond its local boiling point, leading to the onset of homogenous nucleation and intense internal pressure buildup, and resulting in fragmentation of the droplet. The fragmentation is accompanied by ejection of particles or aggregates, which provides a means for dispersal and ignition of the metal particles. This behavior was also observed for aluminum slurries [401].

While combustion of microparticle-laden fuel droplets appears to be relatively well studied, nanoparticle-laden fuel droplets have received limited attention. In a recent study, combustion of ethanol and n-decane droplets with aluminum particles of diameters 80 nm, 5 μm , and 25 μm were qualitatively described [404]. Experiments were performed in a closed cylindrical stainless-steel chamber. A silicon carbide fiber with a diameter of 78 μm was used to suspend the droplet. Droplets were ignited in air at 1 atm pressure. Ignition was achieved by heating a nickel-chromium wire located beneath the droplet. The burning process was recorded by two high-speed digital cameras and the droplet temperature was measured using thermocouples. Particle concentration was 10 wt.%. A surfactant was used to minimize particle agglomeration.

Fig. 74 shows the burning sequence of a stabilized n-decane/nano-aluminum droplet [404]. The corresponding droplet size and temperature histories are shown in Fig. 75 [404]. Five distinct stages were observed: (1) preheating and ignition; (2) classical droplet combustion; (3) micro-explosion; (4) surfactant flame; (5) aluminum droplet flame. In the first stage, vaporization occurred on the droplet surface and a vapor cloud was formed around the droplet. The second stage is characterized by steady vaporization and burning of the droplet. This is similar to the classical burning behavior of a single-component droplet. A distinct flame envelope was observed and the droplet diameter decreased steadily with time, approximately following the classical d^2 law. Near the end of the second stage, strong oscillations were observed, which were caused by the formation and growth of bubbles in the droplet. The bubbles are the result of homogeneous nucleation of vapor phase, resulting in pressure buildup and droplet micro-explosion [404]. The ejected particles and aggregates ignite and burn, thereby disturbing the envelope flame. This is followed by combustion of surfactant or its pyrolysis products. The final stage is marked by combustion of a

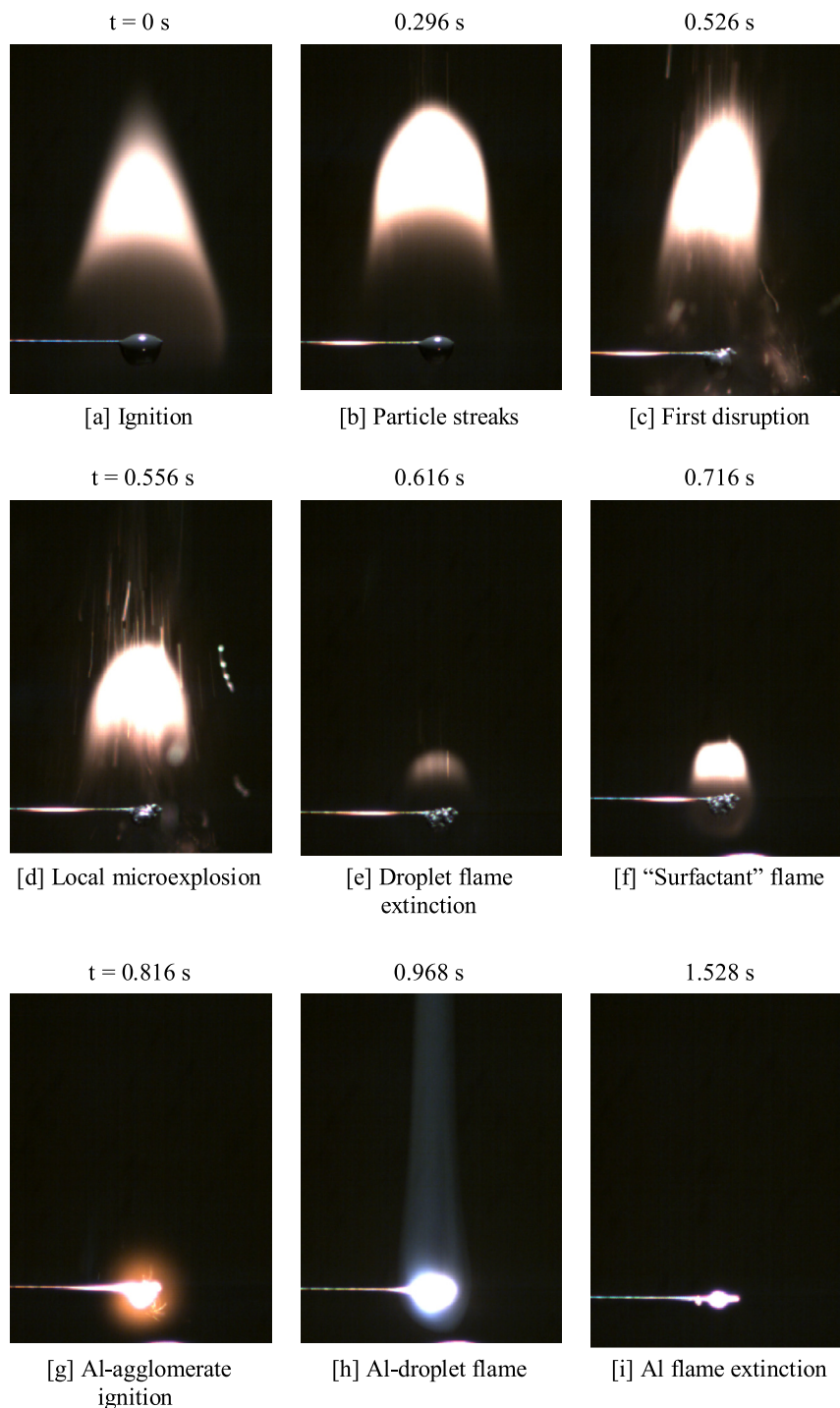


Fig. 74. Burning sequence of a n-decane droplet containing aluminum nanoparticles; particle size is 80 nm and particle concentration is 10 wt.% (reprinted from [404] with permission of Elsevier).

large aluminum aggregate (see Fig. 76 [404]), which is a main issue in nanofluid fuels.

In a more recent study [405], the burning behaviors of dilute and dense suspensions were compared. Both boron and iron nanoparticles were considered. For dilute suspensions ($< 1\%$), the burning characteristics were characterized by the simultaneous burning of the droplet and particles. In dense nanosuspensions, most particles burned as large agglomerate at a later stage when all the liquid fuel had been consumed. In cases when the energy provided by the droplet flame was insufficient, the agglomerate did not burn. Incomplete and slow combustion of large particle agglomerates thus remains a

major problem for slurry fuels with metal nanoparticles, especially under dense loading conditions.

Studies [406,407] have attempted to gain in-depth understanding of evaporation of nanoparticle-laden fuels. Heptane fuel droplets and aluminum nanoparticles were considered. The ambient temperature was varied in the range of $100\text{--}600\text{ }^{\circ}\text{C}$. Particle concentrations up to 5 wt.% were considered. As in the studies discussed above, the classical d^2 -law was observed for the nano-particle laden fuels for conditions considered in this study. At low temperatures ($< 300\text{ }^{\circ}\text{C}$), aluminum nanoparticles were bonded by surfactant to form large agglomerates, resulting in a compact shell that suppressed the

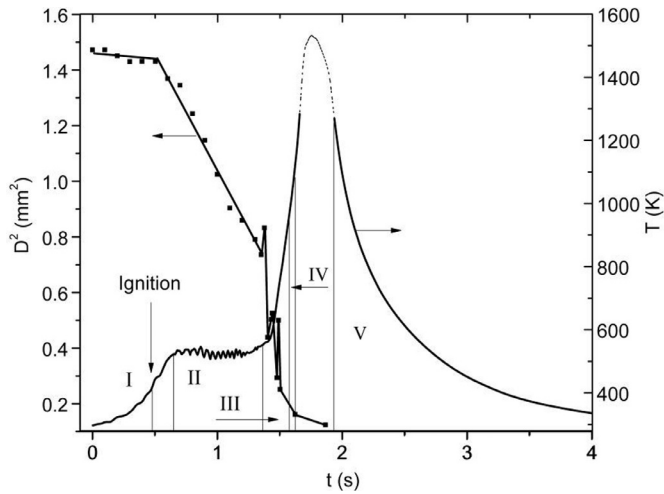


Fig. 75. The droplet size and temperature histories for an n-decane droplet with aluminum nanoparticles, showing deviations from the classical d^2 -law at later stages; single droplet combustion experiments (reprinted from [404] with permission of Elsevier).

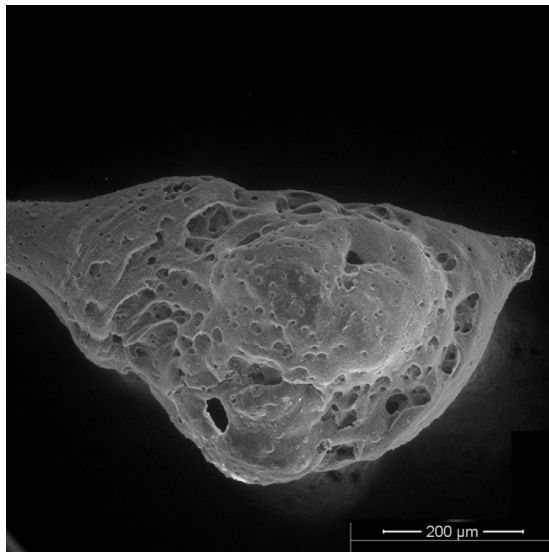


Fig. 76. SEM image of combustion residue of stabilized n-decane/nano-Al droplet; micron-sized agglomerate is observed (reprinted from [404] with permission of Elsevier).

evaporation rate. At higher temperatures ($> 400^\circ\text{C}$), the surfactant decomposed and smaller agglomerates and a porous shell was formed. The evaporation rate was thus enhanced.

Recently, considerable efforts have been made to quantify the effect of the added nanoparticles on liquid fuel ignition and combustion. Substantial enhancements in burning rates of ethanol have been reported due to the addition of 80 nm aluminum particles [408]. The burning rate increases as much as 140%, when the concentration of 80 nm particles increases from 0 to 5 wt.%. This was attributed to strong radiation absorption of nanoparticles suspended within the droplet.

In another recent study [409], ignition and combustion of heptane droplets with aluminum nanoparticles was studied. Three different concentrations of 0.5, 2.5, and 5% were considered. Particles were coated with oleic acid. Fig. 77a shows the ignition delay of

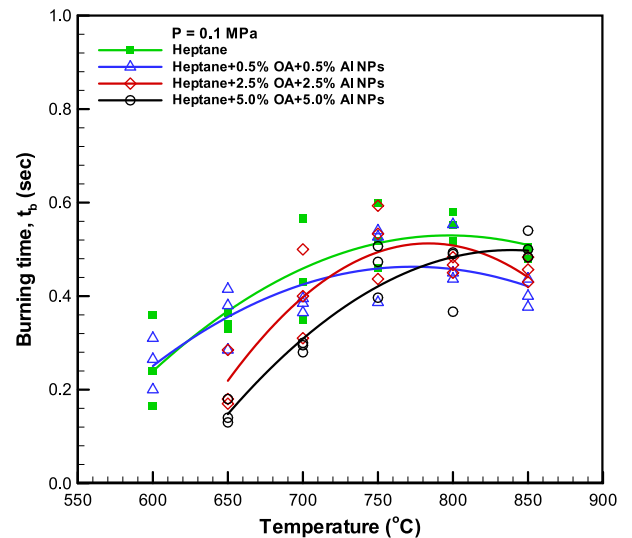
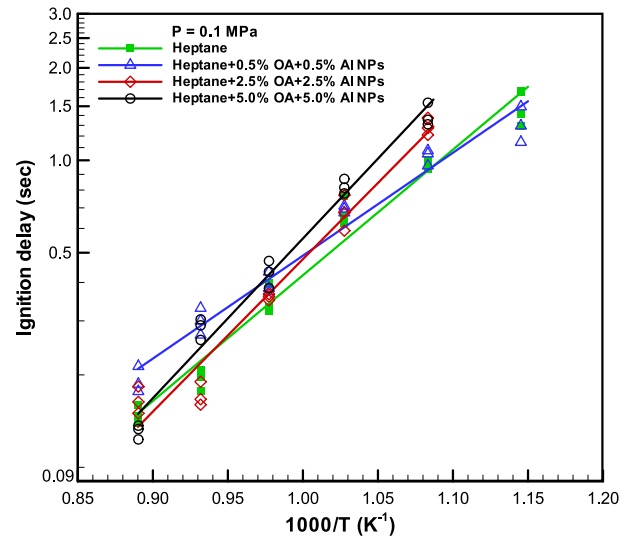


Fig. 77. Ignition delay and burning time of pure heptane and heptane-based nanofluid droplets containing 0.5%, 2.5% and 5.0% Al nanoparticles as a function of ambient temperature; droplet combustion experiments (reprinted from [409] with permission of Elsevier).

heptane droplets as a function of temperature for different nanoparticle concentrations [409]. The ignition delay is an exponential function of temperature, similar to pure heptane droplets. At relatively low temperatures (600–700 °C), the ignition delay decreased as the concentration increased from 0 to 0.5%. The ignition delays of heptane droplets with 2.5% and 5.0% nanoparticles were however greater than those of pure heptane droplets. At higher temperatures (750–850 °C), the ignition delay of the n-Al/heptane droplets was comparable to that of the pure heptane droplets. It is evident that addition of metal nanoparticles does not always result in a reduction in ignition delay.

Fig. 77b shows the burning times of heptane droplets for different nanoparticle concentrations [409]. At higher temperatures, burning times of heptane droplets with 0.5% and 2.5% nanoparticle loading are generally lower than those of pure heptane, with the effect more noticeable at low temperatures (the latter trend is an artifact arising from delayed ignition of droplet near the end of the droplet life time). In order to understand the reason for faster burning of nanofluid droplets, gasification rates were also studied. Results suggested that at low temperatures (650–700 °C), gasification rates of 2.5% and 5% n-Al/heptane droplets was equal to or slightly lower than those of pure heptane droplet. At higher

temperatures, nanofluid droplets exhibited much higher gasification rates. The presence of microexplosions and disruptive burning was observed, and the droplet burning did not follow the classical d^2 -law. Furthermore, there was almost no residue or agglomerated nanoparticles.

These observations are contrary to the findings of Gan and Qiao and appear to offer a solution to the agglomeration issue that has plagued the slurry fuels. The lack of classical combustion stage was attributed to bubble formation inside the droplet, due to easier droplet heat up in the presence of nanoparticles [409]. Also, the heterogeneous nature of the n-Al/heptane droplet provided nucleation sites for vapor formation [409]. These facilitated micro-explosions at an earlier stage and the classical combustion stage was thus not observed [409]. This was also responsible for higher gasification rates [409]. Furthermore, it was suggested that the presence of oleic acid was the reason for the absence of agglomerates. These factors contributed to the overall reduction in burning time for nanofluid droplets. Such novel strategies which accelerate and intensify micro-explosions and minimize aggregation can render nanofluids viable fuel candidates for next generation energy-conversion applications.

10.2. Additives to liquid propellants

One of the main reasons for the addition of metal particles to liquid propellants is to increase the specific impulse. Fig. 78 shows the effect of aluminum particles on the specific and density impulses of LH₂/LOX propellant. The chamber pressure is 100 bar and the nozzle exit-to-throat area ratio is 45. Calculations were performed using the NASA Chemical Equilibrium with Applications (CEA) program [314]. Note that the stoichiometric O/F ratio is 8. For O/F ratios near the stoichiometric condition, the specific impulse at a given O/F ratio decreases with increasing particle loading density. An opposite trend is observed for much lower O/F ratios. At the very best, the specific impulse increases only marginally with the addition of metal particles. The density impulse, however, always increases with increasing particle loading density at a given O/F ratio.

The specific impulse can be expressed as [5]:

$$I_{sp} \propto \sqrt{\frac{T_c}{MW_p}}, \quad (96)$$

where T_c is the chamber temperature and MW_p the molecular weight of combustion products. Addition of aluminum particles may result in an increase in the combustion temperature. The molecular weight of the product, however, increases due to the formation of alumina particles. This is the primary reason for the observed reduction in specific impulse at higher O/F ratios. Note that the stoichiometric O/F ratio also decreases with increasing particle loading density. For a very low O/F ratio, the propellant composition thus moves towards the stoichiometric state when particle loading density is increased, thereby resulting in an increase in the specific impulse. For most conditions, the net result is only a marginal increase or even a reduction in the specific impulse. The density impulse, a product of the propellant density and specific impulse, however, always increases, since the density of aluminum particles is much greater than that of the conventional propellant (Note that the density impulse decreases with decreasing O/F ratio due to lower fuel density compared with oxidizer density). This results in a lower tank mass and higher payload. Metal particles are thus attractive additives to liquid propellants, especially for volume-limited propulsion applications.

Gelling agents can be added to liquid propellants to tune their rheological properties. Gelling can be accomplished using inorganic agents such as silicon dioxide [410] or cellulose-based derivatives

[411]. Alternatively, metal nanoparticles can act as a gellant due to their high specific surface area [412]. Gelling reduces the risk of leakage, while maintaining the possibility of pumping and throttling [37]. Gelled propellants are not susceptible to cracking and are less sensitive to impact, friction, and electrostatic discharge [37]. The specific and density impulses of gelled propellants are comparable to those of liquid propellants, but gelled propellants are more difficult to break up into droplets [37].

Prior studies have quantified the theoretical gain in propulsive performance of gelled propellants by the addition of metal particles. Palaszewski et al. [413] explored the possibility of replacing the solid rocket boosters and main propulsion system in the Space Transportation System (STS) with metalized gelled propulsion systems. The specific impulse did not monotonically increase with increasing metal loading density in the fuel. Loading densities corresponding to the maximum specific impulse are 65%, 5–10%, and 40% for H₂/O₂, RP-1/O₂, and NTO/MMH propellants, respectively [413]. Note that these mixtures correspond to lower O/F ratios compared with those of non-metalized propellants. This is consistent with the trend shown in Fig. 78 that the O/F ratio corresponding to peak specific impulse decreases with increasing metal loading density. For a given booster size, a payload increase of ~14–35% was achieved using O₂/RP-1/Al and NTO/MMH/Al propellants. This was attributed to the increase in density impulse of the propellant. No such benefit was obtained for O₂/H₂/Al propellant, since the maximum specific impulse was attained for a very low O/F ratio. As shown in Fig. 78b,

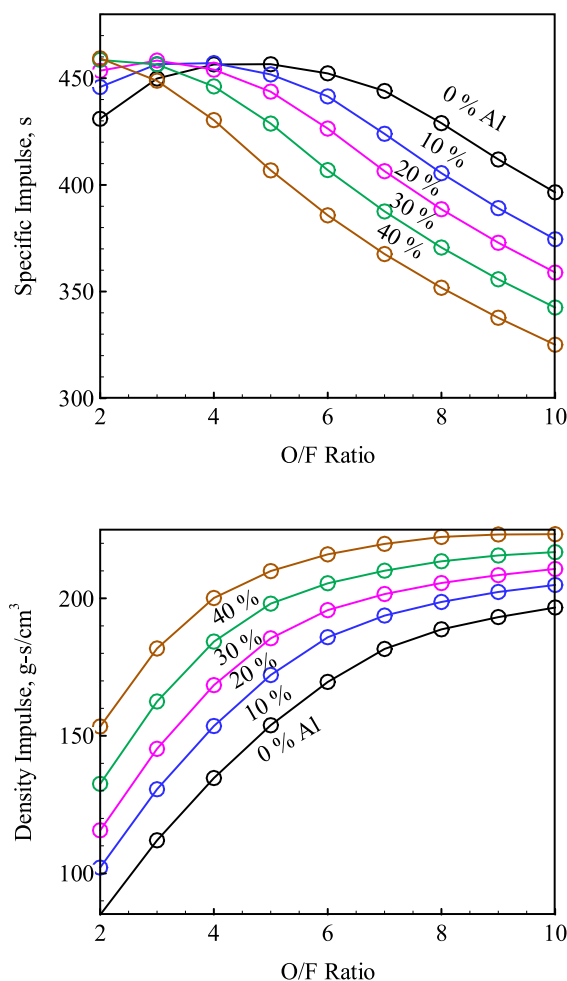


Fig. 78. Effect of aluminum particles on theoretical specific and density impulses of LH₂/LOX propellant; $p = 100$ bar, $A_e/A_t = 45$; NASA CEA calculations.

density impulse decreases with decreasing O/F ratio. Lowering the O/F ratio thus offsets the payload gain obtained by the addition of metal particles.

Note that the actual gain is expected to be lower than the theoretically achievable, due to two-phase flow losses and other inefficiencies during combustion and expansion. It is therefore important to quantify these losses and inefficiencies. The combustion of gelled RP-1/O₂ propellant with ultra-fine aluminum has been studied experimentally in a rocket motor [414]. The gellant was fumed silica powder of diameter less than 44 μm . The diameter of aluminum nanoparticles was ~ 100 nm. Three different metal loading densities of 0, 5, and 55% were considered. The chamber pressure varied in the range of 1.0–2.8 MPa. The characteristic velocity (c^*) was measured and c^* efficiency was obtained. Of the three metal loading densities, the propellant with 5% metal loading exhibited the highest c^* efficiency. Note that the study of Palaszewski et al. [413] suggests that the propellant with 5–10% metal loading offers the best specific impulse. The propellant with 55% metal loading had a slightly lower c^* efficiency. This was attributed to the accumulation of condensed phase material within the chamber and on nozzle exit wall, as well as incomplete combustion of particles. A judicious choice of metal loading density must be made based on the requirements. In addition to ideal performance metrics such as theoretical specific and density impulses, effects of combustion inefficiencies and two-phase flow losses must be considered.

As mentioned before, nanoparticles are attractive gelling agents because of their high specific surface area; a separate gelling agent is not required. Prior studies [412,415] have explored the effect of metal nanoparticle additions on the combustion behavior of conventional propellants. Fig. 79 shows the burning rate as a function of pressure for nitromethane with fumed silica and nanoaluminum particles [412]. The baseline particle size was 38 nm and particle loading densities up to ~ 15 wt.% were considered. The mixture was packed in a quartz tube and the propellant strands were burned in an optical pressure vessel. The burning rate of nitromethane is positively affected by the addition of nanoaluminum particles. For example, at a pressure of 5 MPa, the burning rate increases by a factor of four when the particle loading density increases from 0 to 12.5%. This trend was attributed to the enhancement in the energy content and thermal diffusivity of the mixture. Note that the burning rate increases sharply at a loading density of $\sim 13\%$ and the resulting value is about an order of magnitude greater than the burning rate of pure nitromethane. The sharp increase in the burning rate corresponds to a transition in the consistency of the mixture from gel to

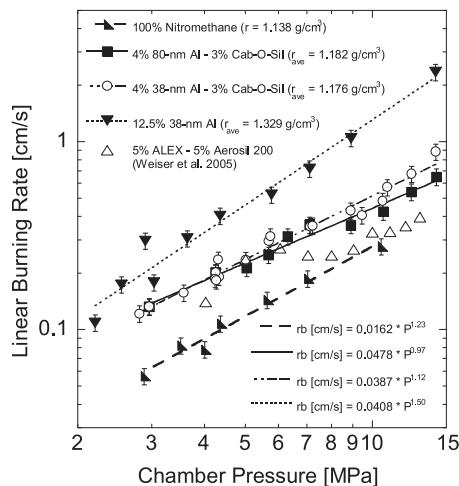


Fig. 79. Burning rate as a function of pressure for nitromethane with nanoaluminum particles and fumed silica (reprinted from [412] with permission of Wiley).

clay-like. Theoretical calculations suggest that the specific impulse is also positively affected by the addition of metal nanoparticles.

In addition to metals, oxide nanoparticles and functionalized graphene sheet (FGS) have been considered. Fig. 80 shows the burning rate of nitromethane as a function of additive concentration for a pressure of 5.24 MPa [415]. The additive concentration varied in the range of 0–0.6% and the enhancement of the burning rate is roughly linearly proportional to the additive concentration. Silica and alumina nanoparticles result in similar enhancement of the burning rate. Functionalized graphene sheets, however, result in enhancements as high as 175%. The obtained enhancements were attributed to the thermal [416] and catalytic [417] effects. It should be noted that addition of nanoparticles may cause an anomalous enhancement in thermal conductivity [416] through mechanisms such as nanolayering, Brownian motion, and ballistic heat transfer; the issue of anomalous thermal conductivity of nanofluids is a much debated topic and is beyond the scope of this paper. It is also logical to expect that the surfaces of nanoparticles can act as a site for chemical reactions to occur and thus enhance the reaction rate. The significance of thermal and chemical effects should be investigated. Modeling and simulations can be performed to determine dominant parameters that control the burning rate and clearly elucidate the effect of metal nanoparticles on combustion of propellants.

11. Metals with liquid oxidizers

11.1. Aluminum and water

Novel energetic materials can be created by mixing metal nanoparticles and liquid oxidizers such as water. The reaction of metal, such as aluminum, with water is given by



The reaction is quite exothermic and the enthalpy of reaction is 813 kJ/mol of aluminum. The metal-water mixture is of particular interest for underwater propulsion, since the oxidizer (water) need not be carried on board [418]. The mixture is also attractive for space propulsion and energy-conversion applications [419] and hydrogen generation [14]. Fig. 81 shows the vacuum specific impulse of Al-H₂O propellants for different water concentrations. The chamber pressure is 100 bar and the gas is assumed to be expanded to near vacuum conditions. The calculated theoretical maximum vacuum specific impulse is 360 s. Note that the actual impulse would be lower due to inefficiencies associated with combustion and expansion processes.

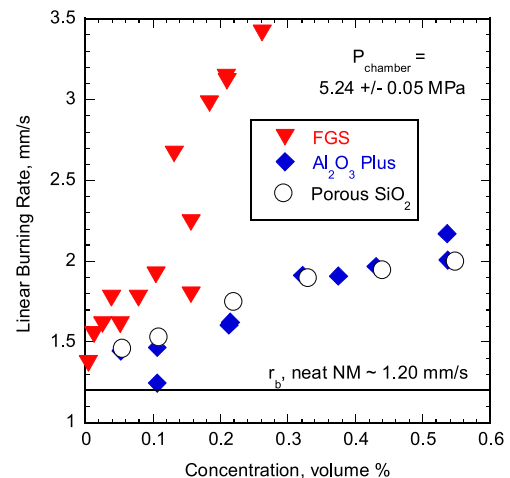


Fig. 80. Burning rate of nitromethane as a function of additive concentration for a pressure of 5.24 MPa (reprinted from [415] with permission of American Chemical Society).

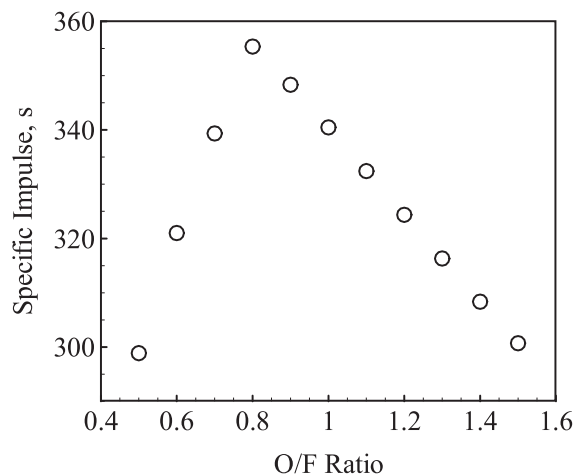


Fig. 81. Vacuum specific impulse of nAl-H₂O propellant as a function of O/F ratio; theoretical calculations for a chamber pressure of 100 bar, particle oxide content of 20 wt.%, product expanded to near vacuum pressure.

One of the first studies on nanoaluminum-water combustion was conducted by Ivanov et al. [420,421]. An experimental study was performed to investigate the combustion of nanoaluminum-water mixtures. The particle size was 120 nm. Gelling agent was reported to be necessary to achieve self-sustained flame propagation. The burning rate increased from 0.1 to 1.1 cm/s, when the pressure increased from 0.1 to 7 MPa. The combustion efficiency was in the range of 52.5–62.5%. Incomplete combustion was attributed to partial boiling-out of water from the reaction zone.

Self-sustained flame propagation of nanoaluminum and water mixtures was later achieved without any gelling agent [27]. Fig. 82 shows the effect of pressure on the burning rate of nanoaluminum and water mixtures for a particle size of 38 nm [27]. Particle diameters were in the range of 38–130 nm and the pressure range was 0.1–10 MPa. The burning rate has a pressure dependence of the form $r_b = ap^m$, with an exponent of 0.47. Furthermore, the burning rate is substantially greater than those of conventional monomolecular energetic materials such as ADN and CL-20, demonstrating the superior reactivity of the mixture. For the particle size range of concern (38–130 nm), the burning rate was inversely proportional to particle size. It was speculated that both transport and chemistry affect the burning behavior, but key mechanisms and parameters were not understood at that time.

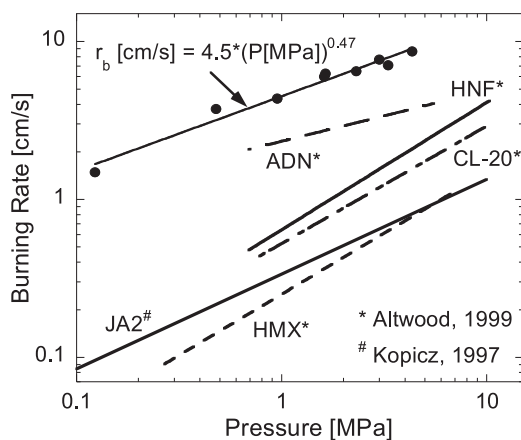


Fig. 82. Effect of pressure on the burning rate of nanoaluminum and water mixture for a particle size of 38 nm; strand burner experiments (reprinted from [27] with permission of Elsevier).

Theoretical analysis of combustion processes was later conducted to gain insight into the underlying processes and determine the rate-controlling mechanism [422]. A multi-zone theoretical framework was established to predict the burning properties and flame structure by solving the conservation equations in each zone and enforcing the mass and energy continuities at the interfacial boundaries. The ignition temperature and burning time of nano-aluminum particles were input parameters to the model. Particle aggregation and entrainment were neglected in the first version of the model. The parameters that dictate the burning rate were found to be thermal diffusivity, enthalpy of combustion, ignition temperature, and burning time. The predicted pressure exponent ~ 0.3 falls within the experimental data (0.27–0.47). However, the inverse relationship between the burning rate and particle size could be reproduced only by using a d^2 -law for the particle burning time. It was thus speculated that mass diffusion across the oxide layers of the particles controls the burning rate of nanoaluminum and water mixtures and this is inconsistent with general observations on the combustion of aluminum nanoparticles in oxidizing gas environments.

The model was therefore later refined to treat the effects of particle entrainment and agglomeration [423]. The particle size was chosen to be 80 nm and the pressure range of concern was 1–10 MPa. The particle entrainment effect was characterized by the particle velocity, u_p , expressed as [423]

$$\frac{u_p}{r_b} = \left(\frac{\rho_{lw}}{\rho_{wv}} \right)^n, \quad (98)$$

where r_b is the burning rate. The entrainment index, n , varies between zero (no entrainment) and unity (complete entrainment). Subscripts lw and wv refer to liquid water and water vapor, respectively. Note that the sudden increase in fluid velocity is required to satisfy mass conservation at the vaporization front. The following closed-form expression for the burning rate was obtained [423]:

$$r_b = \sqrt{\frac{\lambda}{\rho_m C_p} \frac{2C_p(T_f - T_{ign})}{2C_p(T_{ign} - T_u) + h_{fg}} \frac{1}{t_b} \left(\frac{\rho_{wv}}{\rho_{lw}} \right)^n}. \quad (99)$$

where λ is the thermal conductivity, ρ_m the mixture density, C_p the specific heat, T the temperature, t_b the burning time, h_{fg} the enthalpy of water vaporization, and ρ the density. The subscripts f , ign , u , lw , and wv refer to flame, ignition, unburned mixture, liquid water, and water vapor, respectively. The particle-size effect on the burning rate of the mixture originates primarily from the size dependence of the burning time, whereas the pressure effect stems from the pressure dependence of the burning time and velocity of particles.

Fig. 83 shows the pressure exponent for different entrainment indices, n [423]. For diffusion-controlled conditions, entrainment causes the pressure exponent to increase from 0 to 0.5. A similar trend is observed in the kinetic regime, although the corresponding values exceed the diffusion counterparts by 0.5. The reaction zone thickness increases and interfacial temperature gradient decreases with increasing particle velocity (entrainment). This lowers the rate of heat feedback to the preheat zone, thereby resulting in a lower burning rate. As the water vapor velocity (which is the particle velocity when fully entrained) depends on pressure (due to mass conservation), the pressure exponent increases when entrainment is considered. Note that the pressure exponent may depend on mixture consistency, which can be altered by changing the particle size [424] or the pH of the water [425]. For example, the pressure exponent increases from 0.34 at pH = 6.16 to 0.68 at pH = 3.23, since the consistency changes from a paste to a fluid. It is logical to expect loosely packed particles to be more easily entrained by the gas flow, so differences in measured pressure exponents may be attributed to the particle entrainment phenomenon.

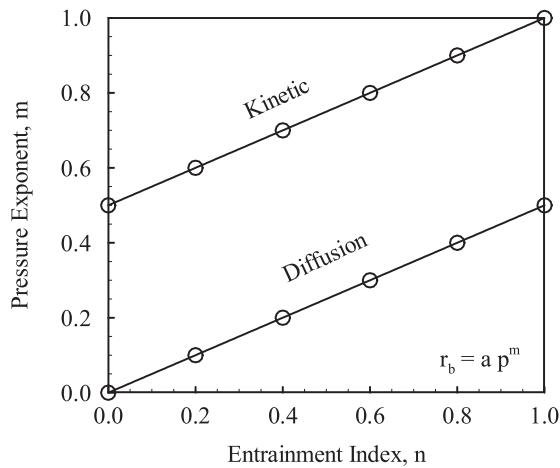


Fig. 83. Pressure exponent in the burning-rate law as a function of entrainment index for diffusion and kinetic controlled combustion mechanisms; multi-zone combustion model and analysis (reprinted from [423] with permission of Elsevier).

The attractive forces may also cause nanoparticles to cluster and agglomerate, especially at higher particle loading densities, so the effect of agglomeration must be considered. Fig. 84 shows the effect of pressure on the burning rate of stoichiometric aluminum-water mixture containing 80 nm particles [423]. Different combustion models are considered. For the kinetics model, predictions are greater than the experimental data by a factor of as much as ten if particle entrainment is not considered. More accurate results are obtained when the entrainment index, n , is increased from 0.0 to 0.4. The diffusion model offers predictions that are in reasonably good agreement with experimental data when both entrainment and agglomeration of particles are considered. It is likely that the inverse dependence of the burning rate on particle size is a result of the combustion of particle agglomerates as opposed to original particles. A model of the agglomeration of nano-aluminum particles in water vapor is therefore desired. Future works must explore the effects of agglomeration and entrainment in more detail in an effort to develop a predictive model of combustion. Efforts must be made to remove empirical input parameters from the analysis.

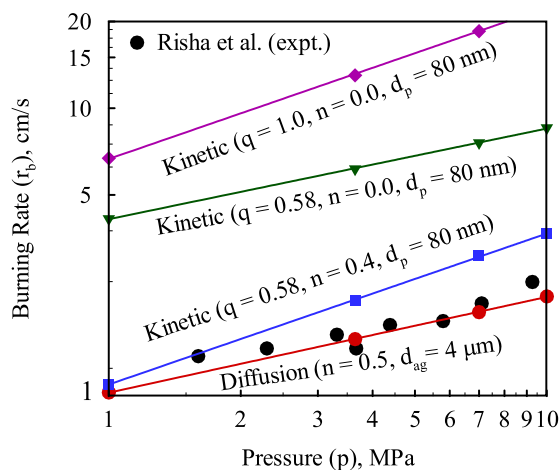


Fig. 84. Effect of pressure on the burning rate of stoichiometric aluminum-water mixture containing 80 nm particles; multi-zone combustion model and analysis (reprinted from [423] with permission of Elsevier).

11.2. Aluminum and ice (ALICE)

One of the main drawbacks of nano-aluminum and water mixture is aging, which is caused by low-temperature reactions and evaporation of water. This issue can be overcome by freezing the water in the mixture [419]. The resulting aluminum-ice (ALICE) mixture is a solid propellant characterized by relatively environmentally benign exhaust products. Fig. 85 shows a comparison of the burning rates of 80 nm aluminum-ice (ALICE) and aluminum-water mixtures [426]. It is apparent that the burning behavior of ALICE mixture is similar to that of aluminum-water mixture. The burning rate has a pressure dependence of the form, $r_b = a p^n$. The pressure exponent, n , of the ALICE mixture is 0.41, greater than that of the aluminum-water counterpart (0.27). This is partly attributable to differences in the combustion efficiencies of the two mixtures.

In order to determine the propulsive performance of the ALICE propellant, laboratory-scale static fire motor experiments were conducted for motors with three different combustion chamber diameters of 1.91, 3.81, and 7.62 cm [426]. Both end burning and center-perforated grain configurations were considered. For each configuration and motor size, a post combustion chamber with a length of 7.62 cm was used. For center-perforated motors, the grain length was 7.62 cm. Three different grain lengths of 3.81, 7.62, and 15.2 cm were considered for end-burning motors. Two pressure transducers were employed to monitor the pressure near the post combustion chamber region. The graphite nozzle consisted of conical converging and diverging sections. The latter had a contraction ratio of 10 and divergence half-angle of 15 degrees. Ignition was achieved using a commercially available model rocket. An OMEGA load cell was used to measure the instantaneous thrust of the motor.

Table 11 summarizes the propulsive performance of the ALICE propellant [426]. The specific impulse increases with increasing motor size, from 56 s for a 1.91 cm motor to 133 s for a 7.62 cm motor. These values are substantially lower than theoretical values obtained using the NASA Chemical Equilibrium with Applications (CEA) program. The combustion efficiency increased with increasing motor size, from 43% at 1.91 cm to 69% at 7.62 cm. This suggests that incomplete combustion was primarily responsible for the poor specific impulses seen in the experiment. Incomplete combustion was attributed to low combustion temperatures, insufficient residence time, and particle agglomeration. The study revealed some serious issues concerning ALICE propellants; in order to make ALICE propellants viable for practical applications, efforts must be made to completely understand the

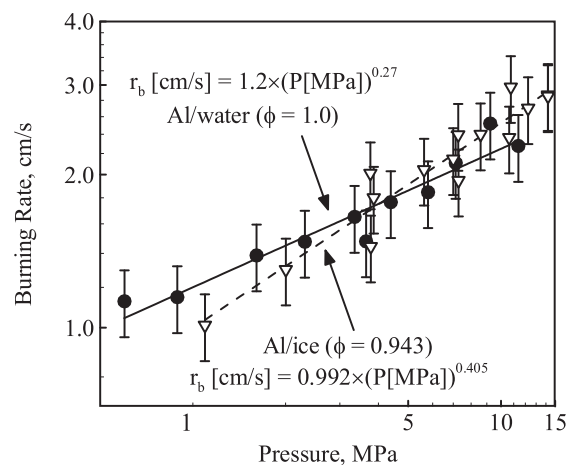


Fig. 85. Comparison of burning rates of 80 nm aluminum-ice ($\phi = 0.943$) and aluminum-water ($\phi = 1.0$) mixtures; strand burner experiments (reprinted from [426] with permission of American Institute of Aeronautics and Astronautics).

Table 11

Performance parameters for ALICE propellants at an equivalence ratio of 0.71 (reprinted from [426] with permission of American Institute of Aeronautics and Astronautics).

Parameter	Motor Size [cm]		
	1.91	3.81	7.62
Peak Thrust (N)	166	318	908
$\bar{C}^*$ (m/s)	528	784	848
η_c (%)	43	64	69
I_{sp} (s)	56	83	133
η_{isp} (%)	27	40	64
I_{sp} @ Peak Pressure (s)	97	124	203
$\bar{I}_{sp}$ with Al_2O_3 retained (s)	63	117	233

combustion of ALICE propellant and to devise methods to improve combustion and specific impulse efficiencies.

11.3. Alternative formulations

Another important drawback of the nanoaluminum-water mixture is the low active aluminum content, since the high oxide content of nanoparticles lowers the energy and hydrogen contents of the mixture. One way to improve the active aluminum content and energy density is by replacing a portion of the nanoaluminum particles with micron-sized particles [427], since the active aluminum content of micron-sized particles is nearly 100%. The burning rate, however, decreases by a factor of four when the loading density of micron-sized particles reaches 80% [427]. This is not surprising since the burning time of micron-sized particles is much greater than that of nano-sized particles.

The addition of hydrogen peroxide increases the energy content and burning rate of the mixture [428]. This is because the heat of $Al-H_2O_2$ reaction is 1388 kJ/mol, which is nearly twice that of $Al-H_2O$ counterpart (813 kJ/mol). Consequently, the specific impulse increases by about 15 s when water is replaced by hydrogen peroxide [428]. Substantial enhancement of the burning rate is also observed [428–430]. For a particle size of 38 nm and pressure of 3.65 MPa, the burning rate increases by a factor of five, as the H_2O_2 concentration increases from 0 to 32% [429]. Concentrations greater than 35% were not considered in the experiments due to an anomalous burning behavior characterized by over pressurization and rupture of the quartz tube. Aluminum hydride is yet another additive that can be used to enhance the hydrogen content and specific impulse of nanoaluminum-water mixtures [419].

Another method by which the theoretical hydrogen yield of metal-water mixtures can be increased is by using borohydride compounds [14]. The reaction of aluminum and sodium borohydride with water can be written as [14]



The enthalpy of the aluminum-water reaction is 409.1 kJ/mol, greater than that of the sodium borohydride-water reaction, 212.2 kJ/mol [14]. The burning rate is thus expected to decrease with increasing sodium borohydride content in the mixture. The hydrogen yield of sodium borohydride-water reaction is 10.8 wt.%, nearly twice that of the aluminum-water counterpart [14].

Alternatively, magnesium particles can be used instead of aluminum particles [431]. The magnesium-water reaction is given by [431]



The enthalpy of reaction and hydrogen yield are 315.4 kJ/mol and 4.76 wt.%, respectively, lower than those of aluminum-water mixtures [431]. The magnesium-water mixture, however, burned more

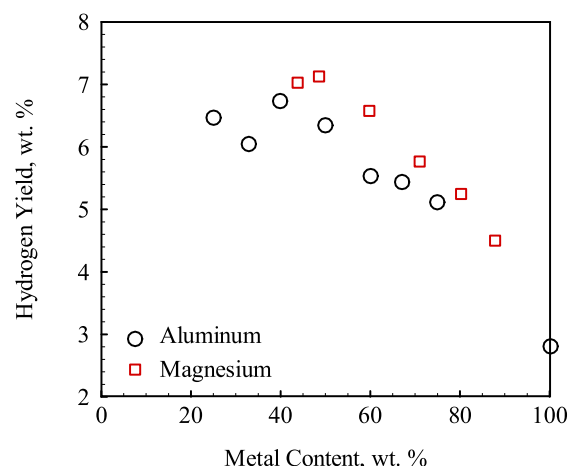


Fig. 86. Effect of metal content on the hydrogen yield of sodium borohydride-water reaction (adapted from [432] with permission of Elsevier).

completely, resulting in better conversion efficiency [431]. Fig. 86 shows the effect of metal content on the hydrogen yield of the sodium borohydride-water mixture [432]. The hydrogen yield decreases with increasing metal content in the mixture. Furthermore, the hydrogen yields of micron-sized magnesium particles are comparable to those of nanoaluminum particles. The combustion of magnesium-water mixtures has been studied theoretically and experimentally [433]. The flame speed is inversely proportional to particle size and the burning rate is controlled by mass diffusion through the gas-phase product layer surrounding the particles [433].

12. Additives to solid propellants

Metal particles can be used to enhance the specific impulse of composite solid propellants [4]. The composite solid propellant primarily consists of a polymeric binder such as HTPB, oxidizer crystals such as ammonium perchlorate (AP), and a metal fuel. Fig. 87 shows the effect of HTPB content on the specific impulse of AP/HTPB/Al composite solid propellants for different Al loading densities. It is apparent that the maximum specific impulse is achieved for a propellant with HTPB content of about 10%, Al content of about 18%, and AP content of about 72%. The decomposition of AP and reaction with HTPB produces gases consisting of carbon dioxide, water vapor, and hydrogen chloride [434]. Al particles react with these product gases to increase the combustion temperature

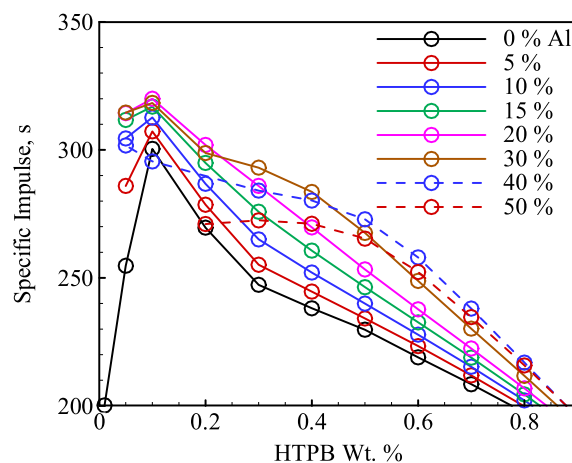


Fig. 87. Specific impulse of AP/HTPB/Al composite propellants for various binder and Al loading densities; NASA CEA calculations.

and lower the gas molecular weight, thereby resulting in a higher specific impulse [434].

It is important to understand the burning behavior of metalized composite solid propellants. Particle size exerts a strong effect on combustion of metalized composite solid propellants and the burning rate can be enhanced by substituting nanoaluminum particles for micron-sized counterparts [435,436–440]. Fig. 88 shows the effect of Al particle size on the burning rate of AP/HTPB composite propellant for different pressures [440]. The propellant consisted of 17% HTPB binder, 68% ammonium perchlorate, and 15% aluminum by weight. The burning rate is nearly doubled when nanoaluminum particles are substituted for micron-sized counterparts. This is not surprising, since aluminum nanoparticles have lower ignition temperatures and burning times than micron-sized counterparts. Similar burning rate enhancements using nanoparticles have been reported for other solid propellants including RDX [441], GAP/AN, and HTPB/AP mixtures [439,442]. Numerous studies suggest that the pressure exponent in the burning rate law is not significantly affected by the addition of nanoaluminum particles [17,443,444], while some studies suggest lower pressure exponents at elevated pressures [445,446]. A lower pressure exponent typically helps to mitigate combustion instabilities in a rocket motor.

In order to further understand the reason for burning rate enhancement through the addition of metal nanoparticles, studies have been conducted to explore the particle burning mechanisms. Fig. 89 shows photographs of combustion of aluminized AP/HTPB solid propellant at a pressure of 10 bar [447]. For the propellant with micron-sized particles, the aluminum particles are held in the propellant surface by the effects of surface tension imposed by the binder, where they combine to form large agglomerates [448]. These agglomerates have high ignition temperatures and burn far away from the propellant surface. Particle agglomeration is substantially lower for nanoparticles and particles burn relatively near the propellant surface. This may be attributed to the low ignition temperatures of aluminum nanoparticles. Nanoparticles thus provide better heat feedback to the propellant surface and improve the burning rate [448]. Fig. 90 shows scanning electron microscopy images of the combustion products of a solid propellant for two different aluminum particle sizes, 30 μm and 150 nm [449]. For the nanocomposite propellant, the maximum diameter of the oxide particles is around 6 μm . Although the final agglomerate size is reduced, agglomeration remains an issue since the diameter of the condensed phase product particle is micron-sized. As a result, the issue of two-phase flow losses is not resolved. Note that while smaller agglomerates tend to

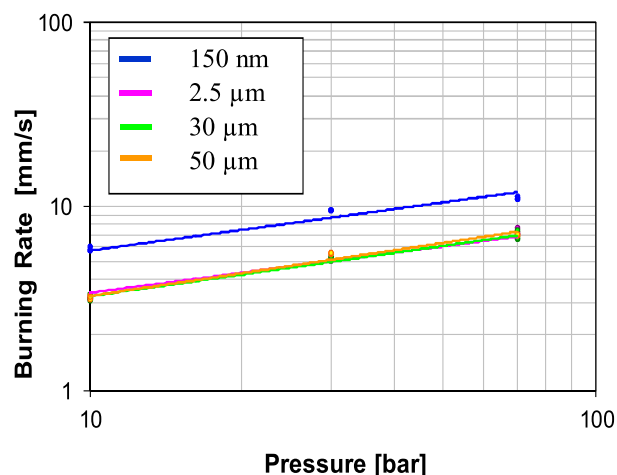


Fig. 88. Burning rate of AP/HTPB composite solid propellants as a function of pressure for different aluminum particle sizes (adapted from [440] with permission of Elsevier).

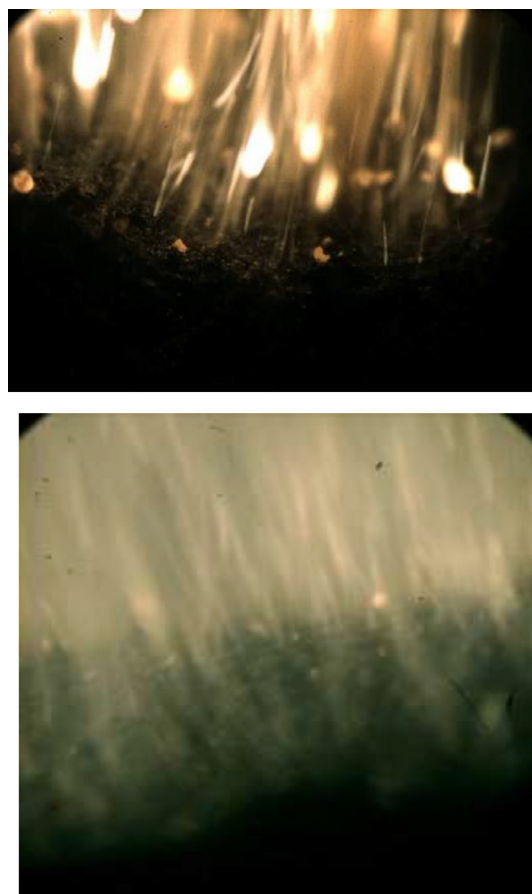


Fig. 89. Combustion of AP/HTPB propellant with (a) 30 μm ; (b) 150 nm aluminum particles at a pressure of 10 bar [447].

have lower two-phase flow losses, particle damping of instabilities is also reduced, especially at low pressures [18].

A more detailed examination of the particle behavior near the propellant surface is shown in Fig. 91 [18]. It is clear that particle aggregation becomes a serious issue for propellants with aluminum nanoparticles. Another serious issue is the increased viscosity of the propellant [24]. The high specific surface area of nanoparticles ($\sim 10\text{--}50\text{ m}^2/\text{g}$), can result in high propellant viscosity and poor mechanical strength [25]. These can decrease propellant density, produce erratic combustion, or even cause motor failure [26]. Furthermore, the high oxide content at nanoscales lowers the specific impulse significantly. For all these reasons, nanoaluminum particles are not currently used in practical solid propellant formulations, but there is growing interest in the use of micron-sized particles with appropriate modifications to mitigate the agglomeration phenomenon. Micron-sized particles offer important benefits over nanoparticles, including better processability and high active metal content. It is however essential to find ways to improve the reactivity of micron-sized particles.

The reactivity of micron-sized particles can be increased by activation [18]. Activation, which can be done mechanically or chemically, can be used to increase the specific surface area of micron-sized powders. Enhancement of specific surface area has been achieved using a pitting corrosion procedure, involving a solution of water and magnesium chloride [450]. The resulting specific surface area was comparable to that of nanoparticles ($10\text{--}18\text{ m}^2/\text{g}$) and enabled a good increase in reactivity [450]. The higher reactivity further contributed to reduction in agglomerate size [451]. Another approach is to replace the oxide layer with

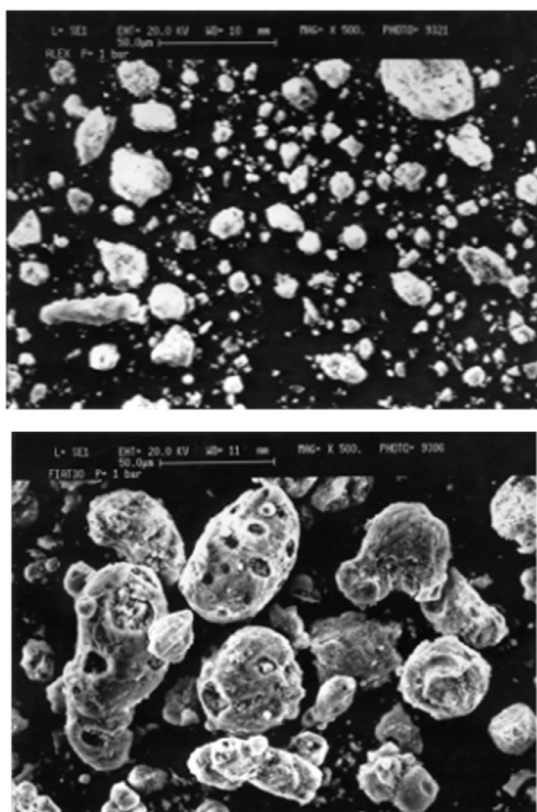


Fig. 90. Scanning electron microscopy (SEM) images of combustion products for a solid propellant for aluminum particle diameters (a) 150 nm and (b) 30 μm (reprinted from [449] with permission of Elsevier).

nickel coating for micron-sized particles [200,264,452]. Ni-coated Al particles have lower ignition temperatures due to exothermic intermetallic reactions. As a result, particle agglomeration can be reduced [199].

Other novel approaches, in addition to coatings, are being explored to mitigate the agglomeration phenomenon. One such approach is the inclusion of other materials, such as fluorocarbons, in the aluminum particles [26,453]. The inclusion material must be able to react exothermically with aluminum and lower the ignition

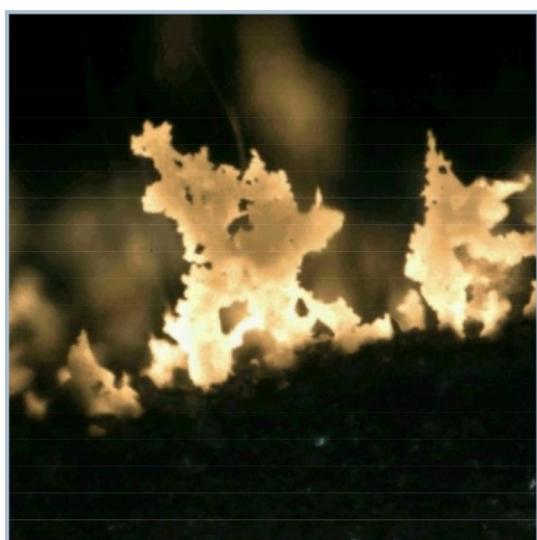


Fig. 91. Aggregation of nanoparticles on/near the propellant bed during composite solid propellant combustion (reprinted from [18] with permission of Springer).

temperature, while generating more gas-phase products (to shatter the particle) and fewer and smaller condensed phase product particles [26]. This would lower the two-phase flow losses. Another option is multicomponent fuel particles with disparate boiling points, such as aluminum-lithium alloys [454]. The lower boiling point metal will boil first, causing particle expansion and eventual shattering of the particle [454]. A yet another approach is to build micron-sized particles that contain several nanoparticles and a suitable gas generator [455]. The gases generated during decomposition of the gas generator facilitate disintegration of the micron-sized particles and minimize sintering of nanoparticles. As a result, composite solid propellants based on these composite particles exhibit higher burning rates compared to those with micron-sized particles and reduced agglomerate size [455]. Future studies must attempt to tap the benefits inherent at both nano and micron scales in an effort to create propellants that are not only reactive and have low two-phase flow losses, but are also easier to process and have high energy content.

13. Nanothermites

Thermite is an energetic material consisting of metal and metal-based oxide particles. Aluminum is the most commonly used metal, while oxidizers such as MoO_3 , CuO , WO_3 , Fe_2O_3 , and Bi_2O_3 have been considered. Fundamental research on combustion of nanothermites can be traced back to the study of Aumann et al. [456]. Flame propagation velocities of Al/ MoO_3 nanothermites with average particle sizes of 20–50 nm were found to be orders of magnitude greater than conventional thermite with micron-sized particles, and this was attributed to reduced diffusion length scales as a result of intimate contact at nano-scales. The study demonstrated the superior reactivity of nanothermites and marked the beginning of extensive research on these materials. Nanothermites not only feature high energy densities, but the burning rates can be easily tuned by adjusting fuel and oxidizer particle sizes, packing density, and composition [457]. Nanothermites can be used as nontoxic primers for conventional munitions [457], additives to solid propellants and explosives [457], microthrusters [458], MEMS-based smart ignition systems [459], and so forth. In the following sections, studies on synthesis, ignition, and combustion characteristics of nanothermites are reviewed.

13.1. Synthesis

There are three methods commonly used to prepare nanothermites consisting of metal and metal-oxide nanoparticles: (1) physical mixing; (2) arrested reactive milling (ARM); (3) sol-gel methodology. Physical mixing is the simplest method of preparing nanothermites. In this method, metal and metal oxide nanopowders are mixed in an inert volatile liquid and sonicated to ensure good mixing and breakup of agglomerates [460,461]. The liquid is then evaporated. This process can be used to synthesize nanocomposites of various thermite systems [462,463]; some of its major disadvantages are particle aggregation and the necessity of starting with nanoscale powders.

In arrested reactive milling, metal and oxide particles are milled in a ball or shaker mill [464]. A liquid such as hexane is added to the mill for lubrication and cooling. The product typically consists of particles in the size range of 1–50 μm . These particles are composed of 10–100 nm thick layers of metal and metal oxide. Note that ignition may occur during prolonged milling, but milling is stopped before ignition, thereby arresting reactions and yielding a useable thermite mixture. One of the main advantages of arrested reactive milling is that the process yields fully dense materials [464]. Furthermore, the metal is not directly exposed to the ambient gas, so it has low oxide content [465].

Sol-gel methodology, which is described in detail in Section 2.4, takes advantage of the unique structural and mixing properties available from sol-gel chemistry [1]. Metal particles reside in the pores of an oxide matrix, facilitating enhanced reactivity [1,164]. An important issue is the oxidation of the metal particles in water [466]. This can be overcome by using sol-gel chemistry to prepare oxide precursors and then physically mixing in metal particles [466]. This approach, however, results in reduced interfacial contact [466].

13.2. Ignition characteristics

Ignition delay, an important property of concern, is a function of the size of metal particles. Fig. 92 shows the effect of fuel particle size on ignition delay of Al-MoO₃ thermites [3]. The packing density was 38% of the theoretical maximum density (TMD). Ignition was achieved using a 50-W CO₂ laser, and high-speed digital images were used to determine the ignition time. Ignition delays of nanothermites are orders of magnitude lower than those of their micron counterparts, demonstrating the enhanced reactivity at nano-scales. Note that the ignition delay is weakly dependent on particle size at nano-scales, perhaps due to high oxide content and aggregation of nanoparticles.

Numerous studies have been conducted to understand the ignition mechanism of nano thermites. Fig. 93 shows a comparison of differential scanning calorimetry (DSC) traces of Al-MoO₃ nanothermites prepared by physical mixing and arrested reactive milling methods [467]. Heating rates varied in the range of 5–40 K/min. For ARM composites, a broad exothermic hump beginning at ~500 K is observed, whereas a narrower hump at a higher temperature is observed for mixed nanopowders. It was proposed that oxygen gas resulting from oxidizer decomposition escaped for mixed nanopowders, but not for those prepared by arrested reactive milling due to the fully dense nature of the composites. Reactions between oxygen gas and aluminum particles were thus promoted, thereby resulting in a lower onset temperature of exothermic reactions. A similar analysis was performed for Al-CuO nanothermites [223]. The proposed reaction mechanism consists of decomposition of oxidizer particles and release of oxygen gas, followed by mass diffusion across the oxide layers of the aluminum particles. Ignition temperatures were also measured by igniting powders in air on the surface of an electrically heated metal filament. The resulting heating rates were in the range of 10³–10⁴ K/s, higher than those in DSC experiments. The measured ignition temperatures were in the range of 650–750 K, over the heating rate range of concern.

The ignition mechanism of nanothermites has been explored through simultaneous measurements of pressure and optical signals

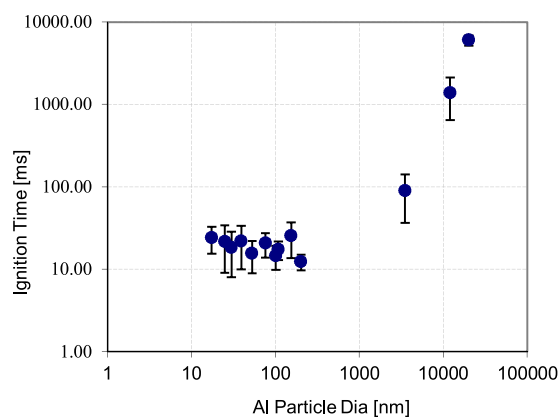


Fig. 92. Effect of particle size on ignition delay of Al-MoO₃ thermites (reprinted from [3] with permission of Elsevier).

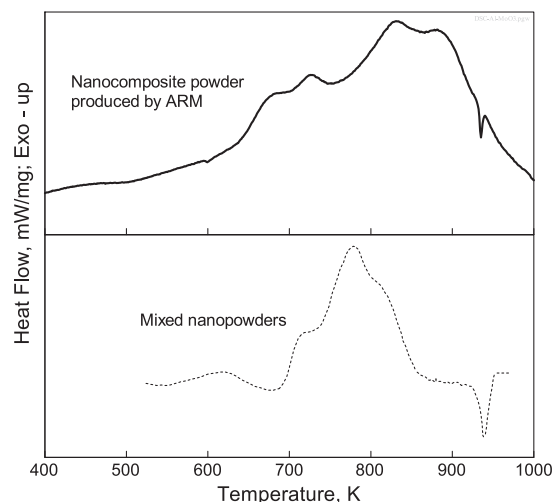


Fig. 93. Differential scanning calorimetry (DSC) traces of Al-MoO₃ nanothermites prepared using physical mixing and arrested reactive milling (reprinted from [467], [38] with permissions of American Institute of Aeronautics and Astronautics and Elsevier).

for CuO, SnO₂, and Fe₂O₃ oxidizers [468]. The intention was to see if there is any correlation between pressure (due to gas generation) and optical signals. The diameters of the aluminum and oxide particles were 50 nm and 100 nm, respectively. The powder was placed in a combustion cell and a nichrome coil was placed in contact with the top layer of the powder for ignition. Instrumentation consisted of photo detectors and a piezoelectric pressure sensor. For CuO and SnO₂ oxidizers, the pressure signal attained its peak value before the optical signal. This appears to suggest that CuO and SnO₂ decompose easily to form gas-phase products. The reaction between the produced oxidizing gases and aluminum particles appeared to control the burning rate. No such behavior was observed for the Al/Fe₂O₃ system, suggesting that oxidizer decomposition could be the rate-limiting step.

The role of oxygen release in reactivity was further explored for Al/CuO, Al/Fe₂O₃, and Al/ZnO nanothermites using a T-Jump/time-of-flight mass (TOFMS) spectrometer [469]. Flash-heating experiments with time-resolved mass spectrometry were performed with heating rates on the order of 10⁵ K/s. Among all the oxidizers considered, CuO released oxygen gas most readily and the Al/CuO mixture also exhibited the highest pressurization rate. It appears that there might be a correlation between the reactivity of the thermite and its ability to release oxygen from oxidizer particles. Chemical equilibrium calculations suggest that CuO is stable up to a temperature of 750 K, whereas Fe₂O₃ decomposition occurs only at temperatures exceeding 1100 K. The measured ignition temperatures of Al/CuO and Al/Fe₂O₃ thermites are 850 and 1100 K, respectively. A connection between oxidizer decomposition and ignition was thus proposed. The proposed reaction mechanism is also in agreement with the findings of Dreizin's group.

It is apparent that gas production and subsequent reaction with Al particles are of concern in the ignition of nanothermites. As nanoparticles are prone to sintering and aggregation, it is worth asking whether condensed-phase reactions also contribute to ignition. The importance of condensed phase reactions was investigated for several nanoaluminum based thermites at high heating rates [208]. The diameter of the aluminum particles was 50 nm and the size range of oxidizer particles was ~50–210 nm. Samples were heated rapidly in situ within electron microscopes. Sintering of aggregated and/or agglomerated particles was observed. High resolution image sequences of thermites ignited on the Pt wire suggested that reactive sintering contributed to rapid melting and coalescence of aggregated particles. A new reactive sintering mechanism was thus proposed. According to this mechanism, fuel and oxidizer aggregates come into contact and condensed phase reactions begin at the interface.

The ensuing energy release is conducted away from the interface and to adjacent particles in aggregate chains. As particles melt, capillary and surface tension result in coalescences of aggregated particles.

One of the open questions concerning the ignition mechanism of nanothermites is the relative role of gas-solid and condensed phase reactions. Recent studies [470,471] do indicate that reactive sintering is an important component of combustion of nanocomposite thermites. Extensive efforts have been made to compare ignition temperatures and oxygen/gas release temperatures of different thermites by conducting T-jump rapid heating and oxygen/gas release experiments. A good correlation between oxygen release from oxidizer and ignition was observed for Al–CuO, Al–Fe₂O₃, and Al–AgIO₃, and Al–KClO₄. Among all the systems considered, Al–Bi₂O₃ and Al–SnO₂ ignited at temperatures lower than the corresponding oxygen release temperatures, while Al–Co₃O₄ ignited above its oxygen release temperature. Al–MoO₃, Al–Sb₂O₃ and Al–WO₃, for which oxidizers did not release any oxygen/gas, ignited as well, showing that oxygen/gas release is not the sole deciding factor in initiation of reactions, at least for some of the nanothermite systems. It was concluded that ignition before oxygen release or without oxygen release is probably a result of direct interfacial contact between fuel and oxidizer, leading to condensed state mobility of reactive species. Future studies can attempt to gain an in-depth understanding of both gas-release and condensed phase reaction pathways, and develop models for ignition of nanothermites.

13.3. Combustion characteristics

Early studies suggested that the burning rate of thermites is negatively affected by the substitution of nanoaluminum particles for micron-sized particles [461]. This was attributed to the fact that micron-thermites were exposed to the laser beam for a longer period of time, resulting in significant preheating and higher burning rates. Subsequent studies, however, have clearly shown that the burning rate is enhanced by the addition of nanoparticles. The burning rate is typically measured by loosely packing the thermite in a burn tube and then igniting it [472]. Photodetectors and pressure sensors are commonly used to obtain optical and pressure signals and a high speed camera is employed to record images of the burning process. Fig. 94 shows the effect of fuel particle size on the burning rate of Al–MoO₃ thermites [472]. The powder density was ~5–10% of the theoretical maximum density. The burning rate increases with decreasing particle size and is independent of the particle size below a threshold value in the range of 80–110 nm.

In addition to fuel particle size, oxidizer particle size can have a strong effect on the burning rate [473]. Fig. 95 shows the effect of fuel and oxidizer particle sizes on the burning rate of Al/CuO and Al/MoO₃ thermites [473]. Two different aluminum particle sizes of 38 nm and 2 μ m were considered. The diameters of the nano and micron CuO particles were 33 nm and 2.92 μ m, respectively. The molybdenum trioxide particles had a sheet-like morphology. The burning rate is greatest for the mixture with nano-sized fuel and oxidizer particles. Furthermore, composites with micron-sized aluminum and nano-sized oxidizer particles have much higher burning rates than those with nano-sized aluminum and micron-sized oxidizer particles. This was attributed to the fact that the oxide layer constitutes a greater portion of the mass of nanoaluminum particles, resulting in lower reaction temperatures. Furthermore, thermites with nano-sized oxidizer particles have the ability to release oxygen more quickly and can thus result in higher pressurization and burning rates. This is consistent with the theory that ignition of CuO and MoO₃ based thermites is primarily caused by oxidizer decomposition and gas generation.

Experimental studies have provided some insight into the combustion mechanisms of nanothermites by monitoring pressure and optical signals. In Bockman et al.'s study [472], measured peak values of pressure and pressurization rates of Al–MoO₃ thermites suggested that convection controls the propagation rate. A similar

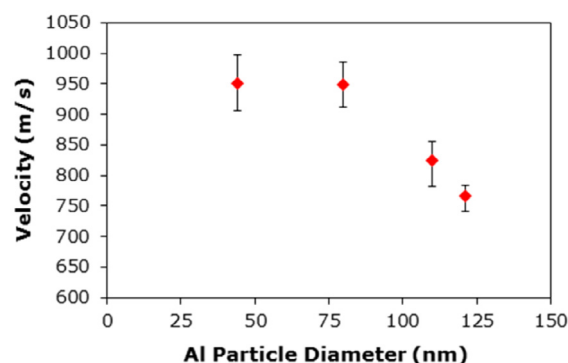


Fig. 94. Effect of fuel particle size on the burning rate of Al–MoO₃ composites (reprinted from [472] with permission of American Institute of Physics).

result was obtained by Sanders et al. [474] for thermites with different oxidizers, including CuO, MoO₃, WO₃, and Bi₂O₃. For all cases, pressure and burning rate attained their respective peak value at the same equivalence ratio. A similar correlation was however not observed between reaction temperature and burning rate. This suggests that flame propagation is likely not controlled by conduction due to the presence of temperature gradient, but by convection due to pressure variations within the thermite. The burning rate of nanothermites was found to be highest for fuel-rich conditions, with the exception of Al/CuO mixture. This is in agreement with results of other studies [461,472]. Chemical equilibrium calculations were performed to understand the anomalous behavior of Al/CuO mixtures. For Al/ MoO₃ and Al/Bi₂O₃ mixtures, peak values of temperature and

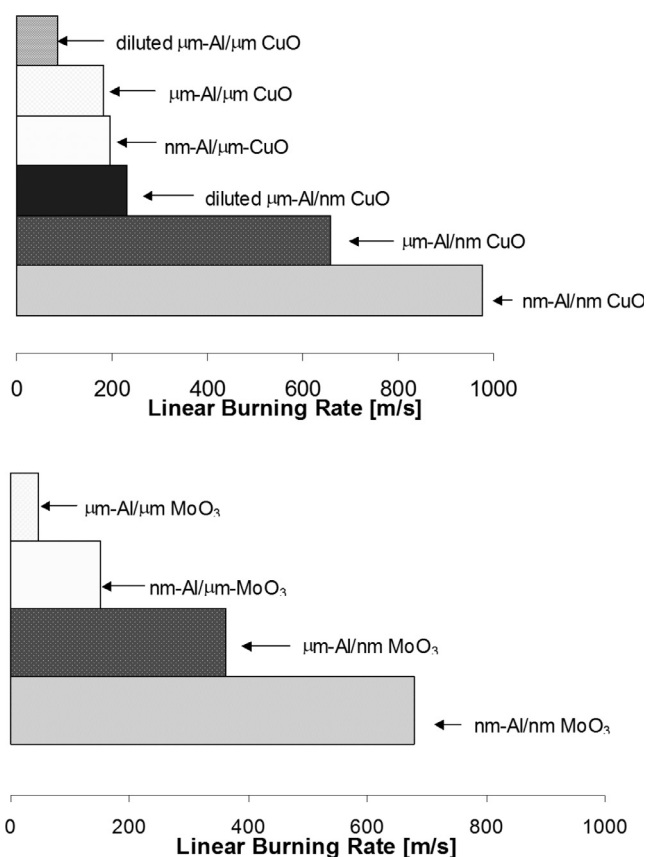


Fig. 95. Effect of fuel and oxidizer particle sizes on the flame speed of nanoaluminum thermites (reprinted from [473] with permission of Elsevier).

gas production were observed at equivalence ratios of 1.0 and 1.3–1.4, respectively. As flame propagation is dictated by convection, it is not surprising that the burning rate attains its maximum value at $\phi = 1.3–1.4$. For Al/CuO mixture, both temperature and gas production peaked near stoichiometric conditions.

Further insights into combustion mechanisms were obtained by adding diluents such as aluminum oxide particles [475] or changing the ambient pressure [462]. The oxide particles act as a diluent, decreasing the flame temperature and inhibiting gas production. Three different burning regimes were observed, depending on the loading density of oxide particles: (1) steady regime up to 5%; (2) accelerating regime at 10 and 15%; (3) unstable regime at 20% alumina. The transition from steady to accelerating and unstable regimes was attributed to the reduction in gas concentration, thereby hindering the convective burning mode.

Ambient pressure can also affect the propagation mode as well. Fig. 96 shows the effect of pressure on the burning rate of Al/CuO thermite in argon and helium gases [462]. The flame temperature and gas concentration decreased with increasing pressure, altering the flame propagation mechanism. Three modes of flame propagation were observed. At low pressures (0–2 MPa), the flame propagated at a constant velocity of ~ 1000 m/s and the propagation rate was dictated by convection. For argon, an accelerating regime was observed over a pressure range of 2–5 MPa. The corresponding flame speed varied in the range of 100–800 m/s. No such behavior was observed for helium. An oscillating regime was observed at

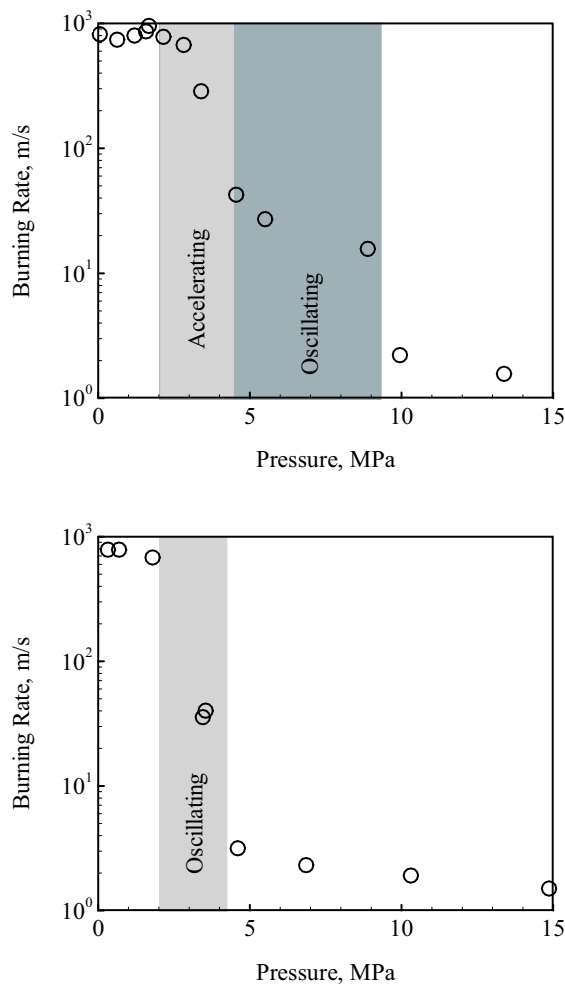


Fig. 96. Effect of pressure on the burning rate of Al/CuO thermite in (a) argon; and (b) helium environments (adapted from [462] with permission of Elsevier).

higher pressures. At much higher pressures, the flame propagated at a constant speed of ~ 1 m/s, about three orders of magnitude lower than the counterparts at low pressures. This was attributed to the transition from convective to conductive flame propagation mode.

The packing density is yet another parameter that affects the burning rate and propagation mechanism of thermites. Fig. 97 shows the effect of packing density on the burning rate of Al/MoO₃ thermites with nano- and micron-sized aluminum particles [476]. For micron thermites, the burning rate increases with increasing packing density. Combustion of micron thermites is governed by heat and mass diffusion phenomena [476]. The thermal diffusivity increases with increasing packing density. Furthermore, the oxide layer can be damaged in densely packed mixtures, thereby promoting mass diffusion [476]. These promote the burning rate for denser mixtures. For nanothermites, an opposite trend is observed, since flame propagation is dictated by convection [476]. The resistance to gas flow increases with increasing packing density, suppressing convective flame propagation [476]. Similar trends have been reported in Refs. [461] and [472]. Other factors that affect the burning rate include preheating [477] and the presence of impurities [156]. Self-sustained propagation in micro-channels, not achievable for conventional thermites, has been observed for nanothermites owing to their high reactivity [478].

In most experiments, the reactivity of nanothermites is characterized by loosely packing the thermite in a tube, igniting it at one end, and measuring the resulting burning rate. Caution must therefore be exercised when using the measured burning rates to obtain burning time scales of nanothermites [479]. The burning rate is not only a function of thermite reactivity, but also of other parameters that aid the propagation of the flame front. As mentioned earlier, under most conditions, flame propagation of nanothermites is driven by gas generation, pressure buildup, and convection. In combustion cells, the pressure is observed to rise on the order of a few microseconds, but the light emission extends from hundreds of microseconds to milliseconds [468]. As a result, it is difficult to determine whether the mixture behind the flame front has burned completely [468].

The traditional flame propagation experiments has therefore been redesigned into an extended burn tube test in order to clarify this point and directly infer burning time scales of nanothermites [479]. The thermite was loosely and partially packed in the tube and one end of the tube was closed. A steadily-propagating luminous

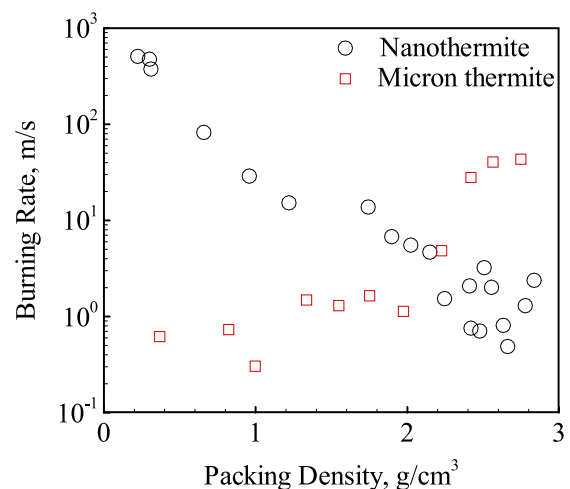


Fig. 97. Effect of packing density on the burning rate of Al/MoO₃ thermites with nano and micron-sized aluminum particles (adapted from [476] with permission of American Institute of Aeronautics and Astronautics).

front was observed, which extended part, or all, of the way down the length of the tube. For certain cases, the flame initially propagated steadily, as evidenced by the linear trend in plot describing the temporal evolution of the flame front location. At later times, the flame speed began to decay and non-linearities were observed, suggesting completion of reactions and quenching of the flame. The completion/quenching point was identified and the resulting quenching distance was calculated. The burning time was defined as the ratio between the quenching distance and the steady-state burning rate. The calculated burning time was independent of thermite mass and tube dimensions and approached a constant value of 3.29 ms. This is also comparable to the measured burning times of metal nanoparticles in various oxidizing environments, and this suggests that the obtained value is a good estimate of intrinsic reaction time scales of nanothermites. Recent studies have shed light on heat transport mechanisms during combustion of nanothermites. Specifically, entrainment and convection of condensed phase species is thought to play a critical role in heat transfer and flame propagation of nanothermites [480].

Experimental studies have provided valuable insight on the combustion of nanothermites. Theories on the combustion mechanisms under different conditions have been proposed and the effects of different parameters on the burning rate have been determined. In spite of these extensive efforts, however, only a global understanding of nanothermite combustion has been achieved, and the underlying processes and mechanisms are not completely understood. It is essential that the experiments be supported by high fidelity modeling and simulations to explain the experimental observations. Firstly, the kinetics of nanothermite combustion needs to be determined, including oxidizer decomposition, condensed phase reactions and metal particle combustion kinetics. This needs to be combined with multi-phase flow models to accurately describe flame propagation. Special efforts must be made to identify combustion mechanisms and parameters that control the burning rate. The role of different mechanisms such as heat conduction, radiation, and convection of gases and condensed phase species can also be explored in detail. This would enable us to control and improve the reactivity of nanothermites.

13.4. Novel formulations

One of the major drawbacks of conventional synthesis methods is the formation of highly non-uniform and disorganized aggregates, as shown in Fig. 5 [36]. Novel approaches to minimize aggregation and non-uniformity are desired. In this regard, a bottom-up approach to synthesize nanocomposite reactive microspheres using electrostatic self-assembly of Al and CuO nanoparticles has been considered [36]. The diameter of the resulting microspheres was 1–5 μm . The surface of nanoaluminum particles was coated with ω -functionalized alkanolic acid, $[\text{COOH}(\text{CH}_2)_{10}\text{NMe}^3+\text{Cl}^-]$, while that of CuO particles was coated with ω -functionalized alkanethiol $[\text{SH}(\text{CH}_2)_{10}\text{COO}^-\text{NMe}^4+]$. The coated particles were then added to dimethyl sulfoxide solvent separately. When the two solutions were mixed together, charge neutralization resulted in self-assembly and precipitation of thermite microspheres. Fig. 98 shows scanning electron microscopy (SEM) images of thermite microspheres composed of nano-scale Al and CuO particles [36]. Experimental results suggest that these mixtures ignite and permit self-sustained combustion in rectangular micro-channels. This was not the case for thermites with conventional particles. Other formulations considered include self-assembled CuO nanorods and Al nanoparticles [458,481,482], porous Fe_2O_3 and Al nanoparticles [483], silicon nanostructures or nanoporous silicon with sodium perchlorate oxidizer [459,484], self-assembled Al and Bi_2O_3 nanoparticles [485], core-shell structured nanothermites [486], composite oxide particles [487], nanothermite fibres [488].

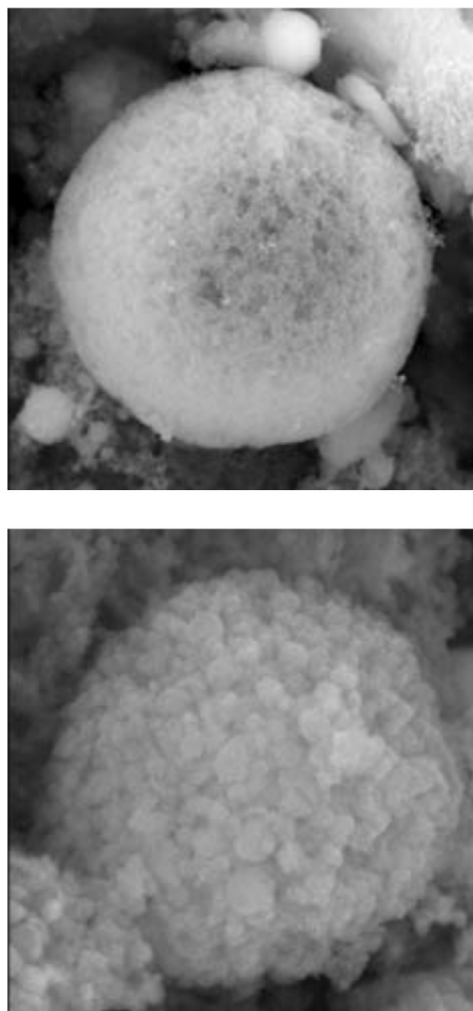


Fig. 98. Scanning electron microscopy (SEM) images of self-assembled nano-composite reactive microspheres composed of nano-scale aluminum and CuO particles (reprinted from [36] with permission of American Chemical Society).

14. Intermetallic systems

Exothermic reactions between metals are of concern in various applications including joining materials [489], igniting other reactions [490], neutralizing biological materials [491], and material synthesis [492,493]. Table 12 shows the heats of formation and adiabatic reaction temperature of various intermetallic systems [490,492,494]. The adiabatic reaction temperature is as high as $\sim 3000\text{ K}$, which demonstrates the high energy content of intermetallic systems. Of all the systems, the nickel-aluminum system has received the vast majority of attention from the scientific community, although there are studies on other systems as well [495–498].

14.1. Multilayer foils

The materials of concern include multi-layered foils [499,500], core-shell structured particles [501,502], and consolidated blends of nickel and aluminum particles [501,502]. Multilayer foils have been the subject of extensive investigation in the recent past and will be the main focus here. Multilayer foils are typically fabricated either by physical vapor deposition (PVD) methods, such as sputtering [489] or electron beam evaporation [499], or by mechanical processing techniques, such as rolling [503] or compacting of reactants into a fully dense laminate [504]. The characteristic dimension is typically the total thickness of the two layers, referred to as the bilayer

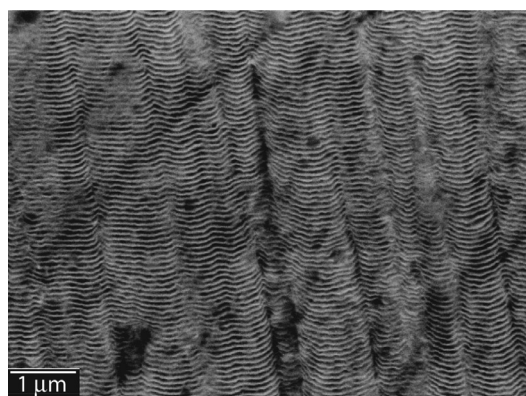
Table 12

Heats of formation and adiabatic reaction temperatures of various inter-metallic systems.

Compound	Heat of formation, kJ/mol	Reaction temperature, K ($T_{\text{initial}} = 298 \text{ K}$)
Ni_3Al	−153.1	1586
NiAl	−118.4	1911
Ni_2Al_3	−282.4	1406
NiAl_3	−150.7	1127
PtAl	−200.4	3073
PdAl	−183.8	2653
TiAl_3	−146.4	1591
FeAl	−47.0	1423

thickness. Fig. 99 shows the SEM images of vapor-deposited and mechanically processed Al/Ni multilayer foils [505]. As can be seen in the figure, vapor deposition provides excellent control of the reactant bilayer. The process is however quite time consuming and expensive. Mechanically processed materials, on the other hand, typically contain a range of bilayer thickness, but are preferred for their quick turnaround and lower costs.

One of the first studies on combustion of multilayer foils was conducted by Dyer and Munir [499], who considered multi-layer Ni–Al foils (atomic ratios of 1:1). Foils were prepared using electron beam vaporization under ultra-high vacuum conditions. The layer thickness was 150–510 nm for aluminum and 100–400 nm for nickel. Samples contained 8–30 layers and had an overall thickness of 5 μm . Ignition was achieved using a tungsten coil in vacuum. The propagation



(a)



(b)

Fig. 99. SEM images of (a) vapor-deposited and (b) mechanically processed Al/Ni multilayer composites (reprinted from [505] with permission of American Institute of Physics).

velocity, measured using a camera, decreased with increasing layer thickness, from $\sim 2 \text{ m/s}$ at 200 nm to 0.75 m/s at 500 nm.

An important parameter that affects the propagation velocity is the bilayer thickness. Fig. 100 shows the effect of bilayer thickness on the propagation velocity of Ni–Al foils [505]. The propagation velocity increases with decreasing bilayer thickness, from $\sim 2 \text{ m/s}$ at 200 nm to $\sim 13 \text{ m/s}$ at $\sim 19 \text{ nm}$. This was attributed to shorter diffusion distances for thinner bilayers, enabling reactions to be completed quickly [505]. The propagation velocity decreased, however, with further reduction in the bilayer thickness due to the loss of chemical energy due to the interfacial premixing process [505]. For foils with a range of bilayer thicknesses, as in mechanically processed materials, volume-averaged bilayer spacing is a good indicator of foil reactivity [505].

A number of studies have been conducted to explore the solid-state reaction mechanisms of multilayer nanofuels for different heating rates. Fig. 101 shows DSC traces of Ni/Al multilayer foils for different bilayer thicknesses [506]. The heating rate is $40^\circ\text{C}/\text{min}$. The foil featured unequal Ni and Al layers, such that the expected final product is Ni_2Al_3 . Multiple peaks are observed for thicker bilayers and the number of peaks decreases with decreasing bilayer thickness. A similar trend has been reported elsewhere [505]. The study

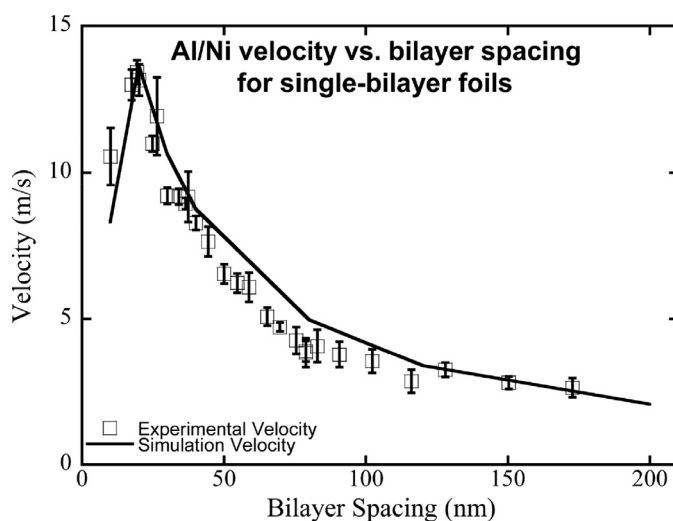


Fig. 100. Effect of bilayer thickness on the propagation rate of Ni–Al multilayered foils (reprinted from [505] with permission of American Institute of Physics).

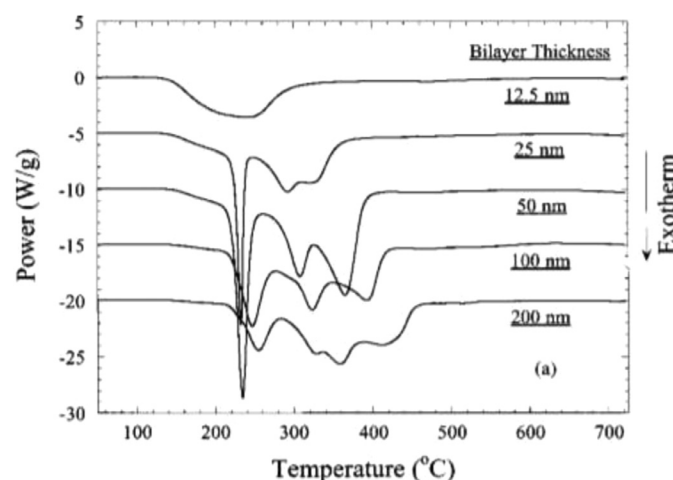
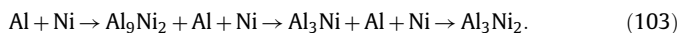


Fig. 101. DSC traces of Al/Ni multilayer foils at low heating rates (reprinted from [506] with permission of American Institute of Physics).

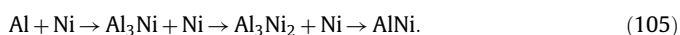
suggested that the intermixed region near the interface consisted of meta-stable Al_9Ni_2 phase, while the final phase of the foil was Ni_2Al_3 . In a subsequent study [507], the effect of heating rate on phase transformations was explored. At low heating rates, (~ 1 K/s), the phase transformation sequence was expressed as:



The proposed sequence is in agreement with study of Gavens et al. [506]. At high heating rates ($\sim 10^6$ K/s), the following sequence was proposed:



A notable difference is the absence of some intermetallic phases and more direct precipitation of the final product. A similar conclusion was obtained in a more recent study on equiatomic Ni-Al system [508]. The proposed phase transformation sequence was



The meta-stable Al_9Ni_2 phase was not observed. Increasing the heating rate generally delays reactions, causes the exothermic peak to shift to higher temperatures, and suppresses nucleation of intermediate phases [508].

Studies have attempted to explore the reaction mechanisms during combustion of Ni/Al multilayer foils. Here, the heating rates are quite high (10^5 – 10^6 K/s) and temperatures as high as 1911 K could be achieved. In theoretical studies [509], it is commonly assumed that the Al and Ni layers are initially separated by a thin product layer and reaction occurs by diffusion through the product layer. As a result, the diffusion coefficient is an input parameter to the model. Although there is quite an extensive database on diffusion coefficients for Ni/Al system [211,212,510–513], there are considerable uncertainties. Diffusion coefficients obtained using atomistic simulations overestimate the propagation rate of Ni/Al multilayer foils [509]. Also, formation of intermediate phases could alter the diffusion coefficients [513]. Theoretical studies have not explored or considered reaction pathways in detail. The product layer is typically assumed to be NiAl, although it is well known that other intermetallic phases, liquid or solution mechanisms may be formed.

Experimental studies have provided some unique insight into the reaction mechanisms of Ni/Al multilayer foils by measuring temperature profiles and studying the microstructure of quenched samples. Fig. 102 shows the temperature-time profiles for equiatomic Ni/Al multilayer samples for bilayer thickness of 50 nm [514]. The maximum combustion temperature is 1700 K, which is greater than the melting point of Al (933 K) and near the melting point of Ni (1728 K). A two-stage process is observed: the leading stage with an extremely rapid ($\sim 10^6$ K/s)

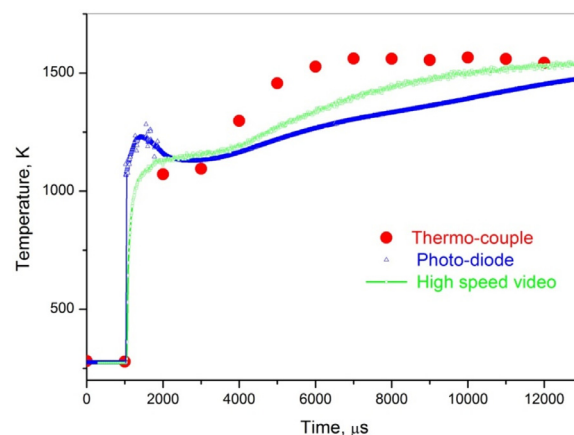


Fig. 102. Temperature-time profiles of the reaction wave for equiatomic Ni/Al multilayer foil with bilayer thickness of 50 nm indicating a two-stage reaction mechanism (reprinted from [514] with permission of American Institute of Physics).

temperature rise, followed by a slower second stage. The study proposed that the direct exothermic dissolution of nickel in the molten aluminum layer controls the propagation rate. This is different from the reaction diffusion model used in theoretical studies, in which diffusion through the solid product layer controls the propagation rate.

Recent studies [515,516] have investigated the relative importance of the reaction-diffusion and dissolution mechanisms. Fig. 103 shows the three proposed mechanisms of combustion of Ni/Al multilayer foils [515]. The first two represent the reaction-diffusion and dissolution mechanisms. The third is the new mechanism, referred to as mosaic dissolution-precipitation mechanism. Here, the first step is the dissolution of Ni atoms in the molten aluminum layer. After saturation of the Al melt by Ni atoms, crystallites of the intermetallic product (NiAl) nucleate at the solid-liquid interface and grow along the surface forming a mosaic layer, which consists of solid NiAl grains separated by liquid solution. Further growth of the NiAl crystals occurs via diffusion of Ni through the liquid channels and precipitation at the intermetallic-melt interface. This mechanism needs to be explored in more detail.

14.2. Particulate systems

In addition to multi-layer foils, particulate based systems have also been explored [517]. The diameter of aluminum particles varied in the range of 25 nm–20 μm and the diameter of nickel particles was 1 μm . Emphasis was placed on measuring the ignition delay.

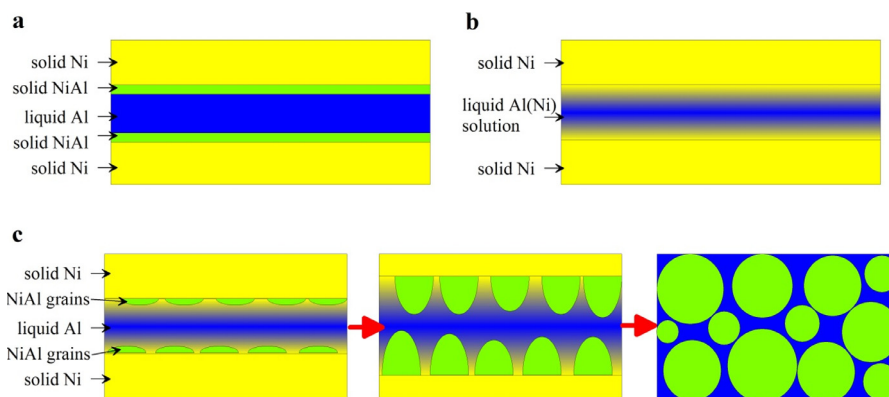


Fig. 103. Three reaction mechanisms in Ni/Al multilayer foils: (a) diffusion through the solid product layer; (2) dissolution of solid in the melt; (3) mosaic dissolution-precipitation mechanism (reprinted from [515] with permission of Elsevier).

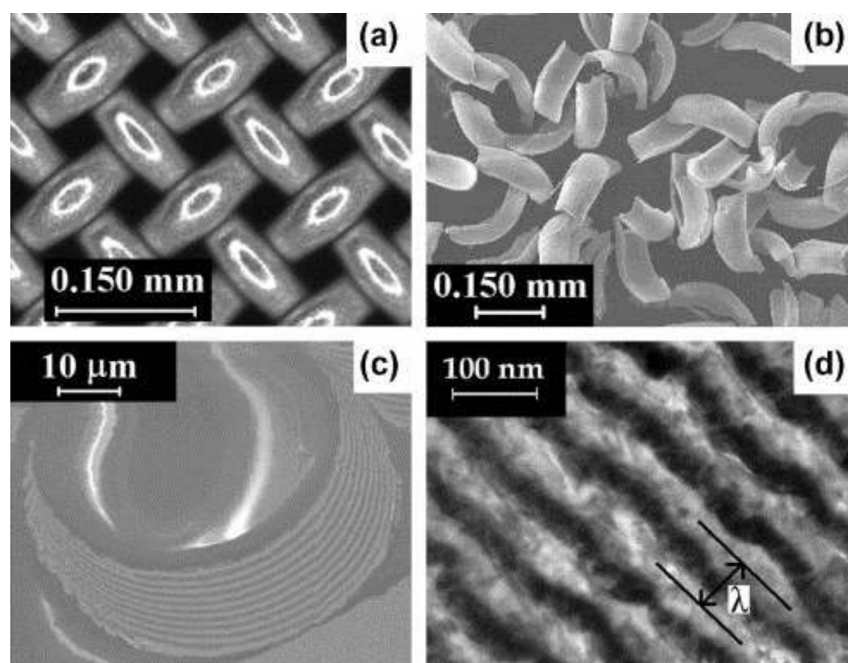


Fig. 104. a) Nanolayered particles are fabricated by sputtering onto a rotating nylon mesh with a square weave where the wire diameter is equal to the mesh opening. (b) The particles break at the weave intersections during removal so that the particle length is three times the particle width for all particles. (c) The layers within a particle vary due to the curvature of the woven fibers. The maximum bilayer for the particle seen here is $1.5\ \mu\text{m}$ and the volume-averaged bilayer spacing is $1.2\ \mu\text{m}$. (d) A cross-sectional TEM micrograph of the bilayers (λ) of a particle with a maximum bilayer spacing of $105\ \text{nm}$ and a volume-averaged bilayer spacing of $87\ \text{nm}$. The bilayers seen here are approximately $68\ \text{nm}$ (reprinted from [519] with permission of Elsevier).

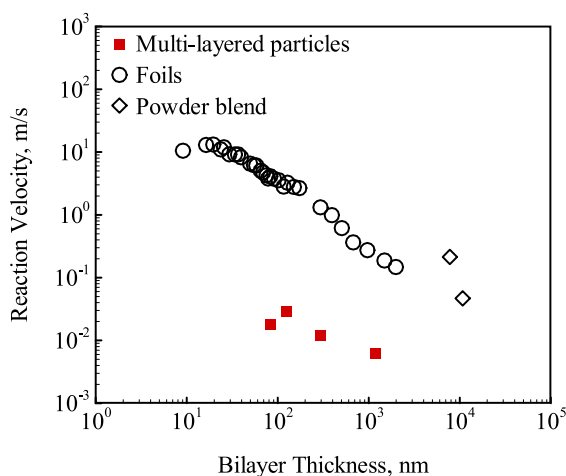


Fig. 105. Comparison of propagation velocities of Ni/Al multilayered particles and multilayered foils (adapted from [519] with permission of Elsevier).

The ignition delay of Ni–Al powder blend decreased by a factor of 10 when the particle size decreased from $20\ \mu\text{m}$ to $25\ \text{nm}$. For mixtures with nanoaluminum particles, flame speeds were in the range of $8\text{--}6\ \text{mm/s}$, substantially lower than those of mixtures with micron-sized particles ($\sim 62\ \text{mm/s}$). One possible reason for this is the high oxide content in nanoparticles; the oxide layer acts as a heat sink and retards flame propagation. Sintering and aggregation of particles could be yet another factor. These problems may be overcome by using core-shell structured particles [502,518] or particles with Ni/Al multilayers within them [519]. Multilayer particles can be synthesized by DC magnetron sputtering on a rotating nylon mesh with a square weave, as shown in Fig. 104 [519]. The length of particles was three times their width. Fig. 105 shows the effect of bilayer thickness on the propagation velocity of loosely packed Ni–Al multilayered

particles [519]. Propagation velocities of multi-layered particles are orders of magnitude lower than those of continuous foils. Such low propagation velocities might be of concern for certain applications such as chemical time delays and neutralization of biological or chemical weapons [519].

15. Concluding remarks and future research

Metals, in the form of micron-sized particles, have been employed in many propulsion and energy-conversion applications. Micron-sized particles suffer from several drawbacks such as high ignition temperatures and burning times, as well as particle agglomeration in solid rocket motor. As a result, energy release rates are substantially diminished. Nanotechnology has created renewed interest in metals due to the unique and favorable properties of nanoparticles, which are attributed to their higher specific surface area and excess energy of surface atoms. Tremendous progress has been made in the synthesis of nanoparticles, but controlling the particle size, and minimizing cost and agglomeration during synthesis remains a major challenge. Nanoparticles also suffer from several drawbacks such as sintering and aggregation of particles, high oxide content, processing and safety issues. Alternative passivation materials are being explored in an attempt to enhance the energy content, lower the ignition temperature, and mitigate processing issues.

The physicochemical properties of metal nanoparticles have been studied extensively. At nano-scales, particle properties are generally size-dependent, and deviate substantially from those of the bulk. In past studies, studies have attempted to elucidate the size dependence of various properties including melting and boiling points, enthalpy of combustion, and emissivity. Deviations from bulk values are generally important at nano-scales, but more so for particle sizes lower than $10\ \text{nm}$. Theoretical analyses also reveal some interesting trends such as elevation of boiling points and reduction in enthalpy of combustion, which have important implications on combustion of metal nanoparticles. These trends however need to be verified

experimentally. Furthermore, it is important to consider the effect of passivation layer on particle properties, as they not only alter the surface properties, but could also influence the state of the entire particle. Heating rate must also be given due attention when describing dynamics of various phenomena including phase transformations.

In spite of the work done in this field over the past two decades, the ignition and behaviors of metal nanoparticles are not yet completely understood. Most of the studies have focused on aluminum, and nanoparticles of other metals have received very limited attention and further studies are required. Ignition temperatures of aluminum nanoparticles are typically substantially lower than the bulk melting point of the oxide layer (2350 K). There is, however, considerable scatter in measured ignition temperatures, especially for particle sizes on the order of (and lower than) $\sim 1\text{--}10\text{ }\mu\text{m}$. This is partly due to the fact that that ignition temperature depends on various parameters, including the nature of the oxidizing gas, oxidizer concentration, particle size, oxide layer properties, and so forth. A systematic study on the dependence of ignition temperature on these parameters is much needed. The ignition mechanism of nanoparticles also remains an unsettled problem. Different ignition theories have been proposed including core melting and fracture of oxide layer, polymorphic phase transformations of the oxide layer, mass diffusion, and melting of the oxide layer. The thermomechanical properties of the oxide layer are poorly understood; it is unclear if the oxide layer is flexible/ductile or hard/rigid. Recent experiments provide evidence of interesting phenomena such as relaxation of pressure (generated due to heating and core melting), inhomogeneous polymorphic phase transformations, and cracking of oxide layer at weak spots (corresponding to amorphous regions). These experiments however correspond to restricted set of conditions such as low heating rates and specific oxidizer compositions and particle sizes. A complete picture of particle ignition is however not yet attained. In this regard, the role played by different phenomena such as core melting, polymorphic phase transformations, mass diffusion, and oxide layer melting needs to be understood for a wide range of conditions.

A limited number of studies have attempted to characterize combustion of metal nanoparticles. As with ignition, most of the studies considered aluminum nanoparticles. Results of experimental and theoretical studies reveal several unique burning properties of aluminum nanoparticles. The flame appears to be located at (or near) the particle surface and the flame temperatures could be substantially lower than the adiabatic counterparts (This appears to be the case for other metals such as boron). At low pressures (near standard atmospheric pressure), the combustion temperature is as low as the ambient gas temperature. At higher pressures, combustion temperatures as high as $\sim 3500\text{ K}$ are observed. Furthermore, AIO gas phase emission is observed only for pressures greater than 20 atm. This suggests that surface reactions are important for nanoparticles and vapor-phase reactions may not always be negligible. The situation is quite different for other oxidizers. For example, peaks temperatures in carbon dioxide are approximately equal to the ambient gas temperatures, regardless of the pressure. The relative importance of vapor-phase and surface reactions is thus not fully understood and needs to be investigated. The observed variations in combustion temperature are explained based on free-molecular heat transfer theory and considering low energy accommodation coefficients. There is however no (or limited) reliable experimental data on accommodation coefficients at high temperatures and pressures. Experiments and high fidelity modeling and simulations can be used to accurately determine accommodation coefficients for these conditions. There is also considerable uncertainty in determining reaction rates. If a collision-based reaction model is to be adopted, it is not fully clear if reactions are occurring on the outer surface of the particle or at the core-shell interface. Furthermore, sticking probabilities

needs to be determined to account for the fraction of collisions that actually result in chemical reactions.

Whereas the burning time of micron-sized particles depends primarily on particle size and gas composition, the burning time of nanoparticles is a strong function of the pressure and temperature of the gas. Particle size, however, exerts a weak effect on the burning time; the diameter exponent is significantly lower than unity. It is generally believed that combustion of metal nanoparticles is controlled by chemical kinetics and not by mass diffusion through the gas-phase mixture. Comparison of gas-phase diffusion time scales and measured burning times do support this argument. The integrity of the oxide layer (and the resultant diffusion resistance) is not fully understood; kinetics of mass diffusion and chemical reactions are also poorly known. A direct comparison cannot be made to ascertain the relative importance of chemical kinetics and mass diffusion across the oxide layer. Measured burning times are as yet available only for limited sets of conditions. Effects of pressure and oxidizer on burning time need further investigation. The weak effect of particle size on the burning time, presently attributed to cracking of the oxide layer and sintering and aggregation of particles, is poorly understood. This issue needs to be resolved as well. Further measurements, especially for pressures exceeding 32 atm, are necessary to develop a correlation for the burning time of aluminum nanoparticles. High-fidelity modeling and simulation of combustion of metal particles should complement experiments to achieve a complete understanding of the essential physics of the problem.

Studies have shown that the reactivity of liquid fuels and propellants can be enhanced by substituting nanoparticles for their micron-sized counterparts. For liquids fuels, one of the major challenges is the agglomeration of nanoparticles; the agglomerate burn slowly and incompletely after combustion of the liquid droplet, especially for nanofluids with dense particle loading densities. Recent experiment studies appear to offer some solutions to this problem. One of the ways the agglomeration issue can perhaps be mitigated is by taking advantage of the micro-explosion phenomena. Appropriate surface coatings can also be considered. Future studies must attempt to tackle the agglomeration issue to make nanofluid fuels more viable fuel candidates.

Metal nanoparticles can also be added to conventional liquid propellants to increase the specific impulse. It must be noted that addition of metal nanoparticles does not always increase the specific impulse due to higher molecular weight of product particles. The density impulse can be increased to enable more payloads. Note, however, inefficiencies associated with combustion and expansion typically tend to lower the impulse. Substantial gains in burning rates have also been obtained due to the addition of metal nanoparticles. This has been attributed to both thermal and catalytic effects, but a full understanding is not achieved.

In addition, novel energetic materials consisting of metal nanoparticles and liquid oxidizers (such as water) are being considered for propulsion, energy-conversion, and hydrogen-generation applications. Experimental studies offered some insight on the combustion and propulsive performances, while theoretical studies helped understand the underlying processes and mechanisms. A frozen mixture of nano-aluminum and water (ALICE) was also considered as a “green” refrigerated solid propellant. Although the propellant features high burning rates in a strand burner setup, the actual specific impulse in a lab-scale motor is quite low due to inefficiencies associated with combustion and expansion processes. Fundamental understanding of combustion and multi-phase flow dynamics in the nozzle are necessary to improve the performance.

One of the major applications of metal nanoparticles is in a solid propellant to increase the specific impulse. Addition of nanoparticles results in an increase in the burning rate due to particle burning near the propellant surface, thereby resulting in a better heat

feedback. Although the problem of agglomeration is less severe, sintering and aggregation is prevalent at nano-scales. As a result, two-phase flow losses persist and potential benefits are not fully realized. Furthermore, propellants with nanoparticles suffer from processing and mechanical strength issues. As a result, there is a growing interest in reconsidering micron-sized particles, but appropriate modifications to increase the reactivity and minimize agglomeration. The approaches considered so far include nickel coating, inclusion of fluorocarbons, metal alloys, and gas generating polymers. Future works must leverage the benefits of micron-sized particles and nanotechnology to engineer a solid propellant formulation that not only offers high burning rates and impulses, but are also easier to process and have no safety and strength issues. Modeling and simulations can also be conducted to better understand the underlying processes, especially the agglomeration phenomenon, to assist the development of advanced propellant formulations.

Metal nanoparticles are also used as an ingredient in thermites. The ignition of nanothermites has been extensively studied. Early studies suggested that ignition of nanothermites is primarily initiated by decomposition of oxidizer particles and subsequent reaction between oxidizing gas and metal particles. Recent studies however indicate that gas-condensed-phase reactions are also important. One of the open questions is the relative role of gas-phase and condensed phase reactions. The combustion of nanothermites has been widely studied. These probed the effects of fuel and oxidizer particle sizes, pressure, packing density, and diluents. Convection typically appears to be the rate-controlling mechanism for flame propagation, whereas conduction becomes important when gas generation and transport are suppressed. While a crude picture of nanothermite combustion has been achieved, full details of underlying processes have not been obtained. Kinetics of condensed-phase reactions and oxidizer decomposition needs to be established. This needs to be coupled with multi-phase flow models to accurately describe flame propagation. Special efforts must be made to identify combustion mechanisms and parameters that control the burning rate. The role of different mechanisms such as heat conduction, radiation, and convection of gases and condensed phase species can also be explored.

Of all intermetallic systems, multilayer foils have been extensively studied. The variations of propagation velocity and enthalpy of combustion with bilayer spacing is quite well described. Both low and high heating experiments have been conducted to shed light on the solid-state reaction pathways. Increasing the heating rate generally delays reactions, causes the exothermic peak to shift to higher temperatures, and suppresses nucleation of intermediate phases. Actual reaction mechanism during combustion of multilayer foils is still being investigated. The proposed mechanisms include dissolution of Ni atoms in the molten aluminum layer, diffusion through the solid product layer, and the mosaic dissolution-precipitation mechanism. The latter consists of dissolution of Ni atoms followed by precipitation of NiAl. Further diffusion occurs through the liquid channels between NiAl grains. Modeling and simulations of combustion of multilayer foils is also a challenge due to uncertainties in reaction mechanism and parameters such as diffusion coefficients. Future studies should attempt to address these issues in an effort to fully understand the combustion mechanism and predict the propagation rates for different conditions.

Acknowledgments

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