

Melt-dispersion mechanism for fast reaction of aluminum particles: Extension for micron scale particles and fluorination

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The theoretically predicted relationship for the relative flame rate versus relative particle size based on the melt dispersion mechanism (MDM), which was previously confirmed for oxidation of 40–120 nm diameter aluminum particles, is found to be in agreement with experiments for 1–3 μm diameter Al particles and fluorination. The main physical parameters for MDM (pressure in molten particle, cavitation threshold, and nanoclusters' velocity) have been estimated for micron scale particles. The results suggest parameters that could be controlled during particle synthesis that would enable micron scale Al particles to react and achieve the performance of nanoscale Al particles. © 2008 American Institute of Physics. [DOI: 10.1063/1.2936855]

Understanding the oxidation and fluorination mechanisms for Al nano and micron size particles is of significant fundamental and applied importance and can impact the methods for improving the effectiveness of the particle's combustion and energy release. Recently,^{1–3} we theoretically predicted and experimentally measured justifications and confirmations for the melt-dispersion mechanism (MDM) for fast oxidation (i.e., heating rates 10^6 – 10^8 K/s) of Al nanoparticles. Using elasticity theory, we showed that at fast heating the alumina shell for nanoparticles does not break until Al melts. The main geometric parameter that determines stresses in a core-shell system according to elasticity theory is the ratio of Al core radius R to oxide thickness δ , $M = R/\delta$. It was found^{1–3} that for $M < 19$, the entire Al particle melts before oxide fracture. Fast melting of Al is accompanied by a 6% volume expansion which creates high dynamic pressures (1–3 GPa) in the liquid core. Such a pressure overloads the alumina shell with the hoop stresses σ_h that exceed the ultimate strength of alumina σ_u and causes the shell's dynamic fracture and spallation. After oxide spallation, pressure within the liquid core remains unchanged while at the bare Al surface the pressure is of the order of 10 MPa only due to surrounding gas pressure and surface tension. Due to the surface pressure unbalance, an unloading wave propagates to the center of the particle and creates a tensile pressure at the particle center of 3–8 GPa. A tensile pressure of such a magnitude exceeds the strength (cavitation limit) of molten Al, and disperses the liquid Al into small bare clusters that fly at a high velocity (100–250 m/s). Oxidation of these clusters is not limited by diffusion. Currently, measured flame rates are in good correspondence with the MDM predictions for particles with diameter $D \leq 120$ nm and $M \leq 35$.

For micron scale particles and nanoparticles at slow heating rates, oxidation is expected to occur by diffusion through a growing oxide shell, which is 10^5 times slower than MDM.^{2,4,5} Predictions based on elasticity theory suggest that the MDM may also be operative for micron size particles. Also, the question of whether or not the MDM operates for reactions other than oxidation has not been considered. The goal of this letter is to experimentally show that

predictions based on the MDM for 1–3 μm diameter Al particles can be applied to fluorination and theoretically predict how micron Al particles can achieve the performance of nanoparticles for both fluorination and oxidation. This is of significant practical importance, because nanoparticles are 30–50 times more expensive than the micron particles and have environmental and safety issues.

In Ref. 3, the following equation for the flame propagation rate V was derived:

$$V/V_{\max} = f; \quad f = (-B + \sqrt{B^2 - 4AC})/2A \quad \text{for } 0 < f \leq 1, \quad (1)$$

where V_{\max} is the maximum velocity that can be achieved for relatively small M (Fig. 1) in the same experimental setup, for the same mass density of the powder, and for the same oxidizer, f is the melt concentration in Al core necessary to fracture oxide shell, $A = 6\delta\epsilon^m\Delta K(2+m^3)MG_2K_2$, $m = 1 + 1/M$,

$$B = \Delta Km^2[\delta(1+M)p_g + 2\Gamma_2](2G_2 - 3K_2) + 6\delta(2 + m^3)M(\epsilon^m K_S + \Delta\alpha\Delta K\Delta T)G_2K_2 - \delta\Delta KM(4G_2 + 3m^3K_2)\sigma_u,$$

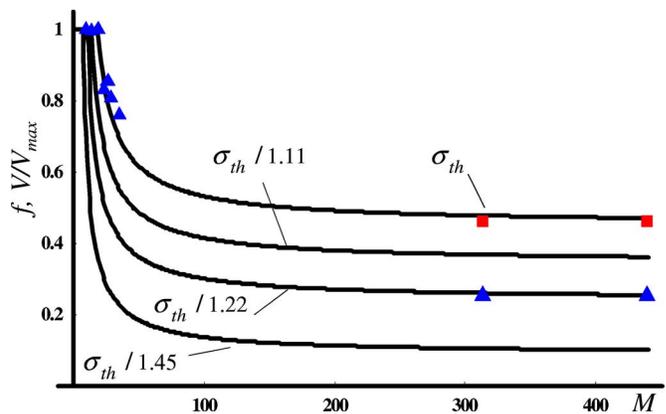


FIG. 1. (Color online) Relative flame velocity V/V_{\max} vs relative Al core radius $M = R/\delta$ for Al/MoO₃ mixtures (triangles) and Al/Teflon mixtures (squares). The lines are for the volume fraction of melt f necessary to fracture the oxide shell [Eq. (1)] for various oxide shell strengths (shown near the curves). Data for $M < 35$ are from Ref. 3.

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$$C = 6\delta(2 + m^3)M\Delta\alpha K_S\Delta T G_2 K_2 - 4(2 + m^3)\Gamma_1 G_2 K_2 \\ + m^2[\delta(1 + M)p_g + 2\Gamma_2][2K_S G_2 - 3(K_S + 2G_2)K_2] \\ - M\delta\sigma_u\{3K_S K_2 m^3 + 4G_2[K_S + (m^3 - 1)K_2]\}.$$

In this equation, $3\epsilon^m$ is the volumetric expansion during Al melting, ΔK is the difference in bulk moduli between liquid and solid Al, K_S is the bulk modulus of solid Al, G_2 and K_2 are the shear and bulk moduli of the oxide shell, p_g is the pressure of the gas, Γ_1 and Γ_2 are the surface tensions at the aluminum-alumina interface and alumina-gas interface, ΔT is the difference between the melting temperature and the passivation temperature T_0 at which the initial oxide shell was formed, and $\Delta\alpha$ is the difference in linear thermal expansion coefficients between solid Al and alumina. All parameters in Eq. (1) can be found in Ref. 2.

Proportionality of V/V_{\max} and f was empirically obtained (Fig. 1) for $M < 35$. Equation (1)₂ for f is obtained from the fracture criterion for oxide shell $\sigma_n = \sigma_u$. Physically, Eq. (1)₁ means that the entire molten Al which induced fracture of the oxide shell, participates in the MDM during time scales of $\sim 10 \mu\text{s}$ (i.e., while the flame front passes through). The remaining nondispersed Al reacts over longer time scales and does not contribute to V . Solid lines in Fig. 1 are predictions for f versus M for $T_0 = 300 \text{ K}$, $\delta = 4 \text{ nm}$ (f very weakly depends on δ) and several values of the ultimate strength of alumina σ_u expressed in terms of estimated value of theoretical strength $\sigma_{\text{th}} = E/30 = 11.33 \text{ GPa}$. They predict that even for large micron scale particles the MDM can provide a high flame rate. However, other processes which are not taken into account in Eq. (1) (e.g., cavitation and collision of nanoclusters with oxidizers) can limit the value M for which Eq. (1) will agree with experiment.

Sample powders of nanoscale Teflon® or MoO₃ were combined with either $D = 50 \text{ nm}$ Al powder (active Al content $C = 0.75$) or $1\text{--}3 \mu\text{m}$ Al particles ($C = 0.99$), producing mixtures with 10% of theoretical mass density. The micron Al particles had a very broad size distribution and contained a number of Al nanoparticles. The Al content $C = 0.75$ corresponds to $M = 14.2$ and $\delta = 1.6 \text{ nm}$. $C = 0.99$ corresponds to $M = 438$ and $\delta = 1.1 \text{ nm}$ for $1 \mu\text{m}$ particles and $\delta = 3.4 \text{ nm}$ for $3 \mu\text{m}$ particles. We consider also small deviation from the Al content given by manufacturer, e.g., $C = 0.986$, which leads to $M = 312$ and $\delta = 1.6 \text{ nm}$ for $1 \mu\text{m}$ particles and $\delta = 4.8 \text{ nm}$ for $3 \mu\text{m}$ particles. Change in δ in the range of $1.1\text{--}4.8 \text{ nm}$ for prescribed M does not visibly change f . For this reason, we choose $\delta = 4 \text{ nm}$ in Fig. 1 for all particles.

All experiments were performed in a confined burning chamber (see Ref. 6 for detail). Results of experiments for Al/Teflon and Al/MoO₃ with Al nano and micron particles for different mass fractions of pure Al in the mixture are presented in Table I. As we estimated in Ref. 7, if the flame rate exceeds 10 m/s , self-heating provides a sufficiently high heating rate for activation of the MDM. Based on this criterion, all experimental reactions occur via the MDM. Also, in select experiments (for 50% Al content in the micron-Al/Teflon mixture and for 40% nano Al content in both Al/MoO₃ and Al/Teflon mixtures), pressure evolution was measured, and pressure rise time can be used to estimate the reaction time. Dividing the estimated temperature increase of 2000 K by pressure rise time, we obtain estimates for the heating rate. Thus, for nano Al/MoO₃ and Al/Teflon mixtures the reaction time was 63 and $84 \mu\text{s}$, and the heating

TABLE I. Mixtures and flame velocities data.

Al (%)	V_n (m/s)	V_m (m/s)	V_m/V_n
Al/Teflon			
30	299.6	133.2	0.444
40	837.5	295.8	0.353
50	752.0	348.3	0.463
60	562.3	310.9	0.407
Al/MoO ₃			
20	557.2	82.8	0.149
30	901.6	120.1	0.133
40	960.2	244.0	0.254
50	756.4	80.9	0.107

rate was 0.32×10^8 and $0.24 \times 10^8 \text{ K/s}$, respectively. For micron Al/MoO₃ and Al/Teflon mixtures the reaction time was 245 and $784 \mu\text{s}$, and the heating rate was 0.82×10^7 and $0.26 \times 10^7 \text{ K/s}$, respectively. Diffusion theory requires a reaction time exceeding 1 s ,^{4,5} which is $10^4\text{--}10^5$ times more than these estimated reaction times. The obtained heating rates exceed our estimates 10^6 K/s (Refs. 2 and 7) required to activate the MDM. Thus, considering diffusion versus MDM, we conclude that both oxidation and fluorination for nano and micron Al can occur through the MDM.

Let us analyze the main parameters of the MDM in micron aluminum particles using Eq. (1). As it was shown in Ref. 3 that theoretical predictions (1) are in good correspondence with experiments for nano Al/MoO₃ mixtures with $M < 35$ for the ultimate strength of the oxide shell $\sigma_u = \sigma_{\text{th}} = 11.33 \text{ GPa}$ (Fig. 1). This value was obtained by fitting the curve for various σ_u (Fig. 1) to the experimental point $f = 1$ for $M = 19$. Thus, the experimentally measured flame rates for nano Al particles with $M < 19$ correspond to maximum flame rate V_{\max} . The ratio V_m/V_n is the flame rate for micron particles divided by the flame rate for nanoparticles in Table I. This ratio corresponds with V/V_{\max} . Equation (1) is valid for an optimal equivalence ratio only (i.e., for Al content corresponding to maximum V/V_{\max}). Thus, $V_m/V_n = 0.463$ for Al/Teflon mixtures and $V_m/V_n = 0.254$ for Al/MoO₃ mixtures (40%Al) can be compared with Eq. (1). The value V_m/V_n for Al/Teflon is in good correspondence with the relationship $f(M)$ for the same $\sigma_u = 11.33 \text{ GPa}$ in the range $M = 312\text{--}438$ (Fig. 1), which *strongly supports the MDM* for $1\text{--}3 \mu\text{m}$ particles. At the same time, V_m/V_n for Al/MoO₃ is 55% of the prediction of Eq. (1) only.

Since according to Fig. 1 the entire molten Al participates in reaction for an optimal Al/Teflon mixture, then the *cavitation of liquid Al (and collision and reaction rates of Al cluster with gaseous fluorine) is not a limiting process*. Based on this, we can estimate the upper bound for the cavitation threshold. Calculation of the pressure in the Al core at the instant of the oxide shell fracture is performed using Eq. (1) in Ref. 2 with the measured gas pressure $p_g = 4.2 \text{ MPa}$ (which contributes additively). For $1 \mu\text{m}$ particles with $M = 312$ and $\delta = 1.6 \text{ nm}$, the pressure is $p_0 = 85.3 \text{ MPa}$. With $M = 438$ and $\delta = 1.1 \text{ nm}$, the pressure is 64.7 MPa . For $3 \mu\text{m}$ particles with $M = 312$ and $\delta = 4.8 \text{ nm}$, the pressure is 79.6 MPa . With $M = 438$ and $\delta = 3.4 \text{ nm}$ the pressure is 58.8 MPa . For comparison, calculations for 50 nm particles ($M = 14.2$, $\delta = 1.64 \text{ nm}$) give pressure of 1.58 GPa .

To estimate the critical cavitation threshold $|p_c|$ (since cavitation pressure is tensile and negative, we use an absolute value), we will use Eq. (22) from Ref. 2 for pressure in Al core necessary to cause cavitation in Al sphere at the relative radius (normalized by R) equal or smaller than \bar{r} , $p_0 = (|p_c|\bar{r} + p_g)/(1 - \bar{r})$. Since the relative radius of the interface between solid Al sphere and external liquid part of Al is related to the volume fraction of the melt f by equation $f = 1 - \bar{r}^3$, then $\bar{r} = \sqrt[3]{1 - f}$. This interface is the best nucleation site for heterogeneous bubble nucleation or cavitation due to decohesion of melt from solid. For maximal f achieved for micron particles ($f = 0.463$), one obtains $\bar{r} = 0.81$. Taking $p_0 = 85.3$ MPa (or $p_0 = 58.8$ MPa) and $p_g = 4.2$ MPa, we can estimate critical cavitation threshold $|p_c| \leq 15$ MPa (or $|p_c| \leq 9$ MPa). These values are significantly lower than 1 GPa, which was estimated in Ref. 2 for homogeneous bubble nucleation. Knowledge of the nucleation threshold allows one to more precisely estimate possibility of extension of the MDM for larger particles using methods suggested in Ref. 2.

Let us discuss why the ratio V_m/V_n for an optimal Al/MoO₃ mixture is smaller than predicted by Eq. (1). Since heating and flame rate for all experiments in Tables I are high enough to activate the MDM, we assume that for all these experiments the same amount of melt in Al particles causes oxide fracture and disperses. Then the reduced flame rate in comparison with that for optimal Al/Teflon mixture is related to the efficiency of reaction between dispersed bare Al clusters and oxygen or fluorine. As discussed below, the velocity of the flying Al clusters for micron particles is much slower than for nanoparticles and their collisions with solid or gaseous oxidizer or gaseous fluorine may be a factor limiting reaction and flame rate. Decomposition of Teflon generates a lot of fluorine gas under high pressure (4.2 versus 0.8 MPa for Al/MoO₃) that has higher collision and reaction rates with slow Al nanoclusters and provides higher flame speeds than for Al/MoO₃ mixture. For Al+MoO₃ mixture, it is necessary to improve collision conditions between Al nanoclusters and oxygen for optimal equivalence ratio. It may be done by promoting sublimation of MoO₃, by reducing distance between Al and oxidizer particles and optimization of shape of oxidizer particles, as well as by increasing clusters' velocity. The reduced flame rate for nonoptimal equivalence ratio is related to incomplete reaction between dispersed bare Al clusters and oxygen or fluorine.

Let us evaluate particle velocity ν at the instant the unloading wave reached the center of the particle. Numerical solution for the velocity field is given in Ref. 2. We will evaluate the maximum value of velocity using an analytical expression in Eq. (14) from Refs. 2 [in which relative shell fracture time is substituted with \bar{r} , according to discussion after Eq. (21) in²] $\nu_m = (p_0 - p_g - 2\Gamma/R)/2\rho c\bar{r}$, where $c = 4166$ m/s is the sound velocity in melt, $\rho = 2380$ kg/m³ is the mass density of the melt, $\Gamma = 1.05$ GPa nm is the Al-gas interface energy, and \bar{r} corresponds to the point where pressure and velocity reached their maximum, i.e., $\bar{r} = 0.81$ in our case. Then for $p_0 = 85.3$ MPa, one obtains $\nu = 4.8$ m/s for 1 μ m particles and for $p_0 = 58.8$ MPa one obtains $\nu = 3.3$ m/s for 3 μ m particles. For comparison, for 50 nm particles ($p_0 = 1.58$ GPa) one obtains $\nu = 92.5$ m/s. This comparison supports our statement that the velocity of the flying Al clusters for micron particles is much slower than for nanoparticles and their collisions with solid or gaseous oxidizer may be a factor limiting reaction and flame rate.

Note that in Fig. 1, points V/V_{\max} for all Al contents (not shown) are located between theoretical curves for $\sigma_u = \sigma_{th}$ and $\sigma_u = \sigma_{th}/1.1$ for Al+Teflon mixtures and for $\sigma_u = \sigma_{th}/1.22$ and $\sigma_u = \sigma_{th}/1.45$ for Al/MoO₃ mixtures; however, we do not have any reasons to connect the reductions in V/V_{\max} with reduction in shell strength.

In summary, strong experimental support is received for the validity of the MDM for 1–3 μ m Al particles for fluorination. The validity of the equation $V/V_{\max} = f$ is extended from the $M < 35$ in Ref. 3 to $M < 312$ –438. Main physical parameters for MDM (pressure in molten particle, cavitation threshold, and nanoclusters' velocity) have been estimated for micron particles. The obtained results show the directions for improvement of the effectiveness of Al burning. For Al/MoO₃ mixtures, the effectiveness of nanoclusters collisions with solid or gaseous oxidizer is a factor limiting reaction and flame rate. Reaction rate may be increased by promoting sublimation of MoO₃, by reducing distance between Al and oxidizer particles and optimization of the shape of oxidizer particles, as well as by increasing clusters' velocity. However, this will increase V/V_{\max} up to 0.463 [predicted by Eq. (1)] only. For further increase in relative flame rate one can use methods suggested in Ref. 2, which are now much more justified by the result obtained in the current work. Indeed, we found that cavitation and low nanoclusters' velocity (as well as shell strength) are not limiting parameters for Al/Teflon mixture and obtained estimates for these parameters. However, nanoclusters' velocity is a limiting parameter for Al/MoO₃ mixture. Thus, increasing oxide thickness to 7.7 nm (the maximum size for which alumina is expected to possess possible maximum strength²) increases V/V_{\max} to 0.577 for 1 μ m particles and to 0.493, for 3 μ m particles, that is, not significantly. However, pressure and particle velocity grow to 367.2 MPa and 24.1 m/s for 1 μ m particles and 123.8 MPa and 7.5 m/s for 3 μ m particles, which can significantly increase collision and reaction rate for Al/MoO₃ mixture. If, in addition, we increase T_0 to 640 K for 1 μ m particles, we obtain $V/V_{\max} = 0.994$, $p_0 = 367$ MPa and $\nu = 99.8$ m/s. If we increase T_0 to 735 K for 3 μ m particles, we obtain $V/V_{\max} = 0.996$, $p_0 = 124$ MPa and $\nu = 36.8$ m/s. We intentionally keep a small residual solid Al to cause heterogeneous nucleation for which threshold is much lower. If this method will work, the micron scale particles can show the same performance as nanoscale particles while being significantly less expensive and do not possess environmental and safety issues.

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