

Melt dispersion versus diffusive oxidation mechanism for aluminum nanoparticles: Critical experiments and controlling parameters

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(Received 13 September 2007; accepted 21 November 2007; published online 8 January 2008)

Critical experiments were performed on Al and MoO₃ thermites. The diameter and alumina shell thickness of the Al nanoparticles were varied, and flame propagation velocities were measured. The results strongly support the melt-dispersion mechanism and contradict the diffusion oxidation mechanism. The parameters that control the oxidation rate and flame velocity are justified and directions for the synthesis of Al nanoparticles (which are opposite to the current directions based on diffusion oxidation) are suggested. An equation for the flame velocity versus Al nanoparticle geometrical parameters, thermomechanical properties, and synthesis parameters is formulated.

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When the diameter of the Al particle reduces to 20–120 nm (in contrast to the traditional 1–100 μm size), its reactivity drastically increases: flame propagation velocities V reach 1 km/s for reactive nanocomposite thermites as opposed to 1 m/s for microcomposite thermites,^{1,2} and ignition delay times are reduced by three orders of magnitude.³ Knowledge of the oxidation mechanism for Al nanoparticles is of great importance since it impacts the direction of development in nanoparticle synthesis. There are currently two candidates. The first one is the oxidation mechanism by diffusion of Al and oxygen atoms toward each other through the growing oxide shell.^{4–7} For relatively slow heating rates (10³ K/s), this diffusion oxidation mechanism (DOM) is consistent with transmission electron microscopy studies and corresponds well with theoretical modeling.⁵ The oxidation time in the experiments in Ref. 4 exceeds 1 s. However, the oxidation time for experiments reported in Refs. 1 and 2 (in which the heating rate is estimated at 10⁸ K/s) is five orders of magnitude shorter and, consequently, oxidation cannot occur by DOM.^{8,9} To resolve this and some other contradictions between experiments and the DOM, a mechanochemical mechanism for fast oxidation for high heating rates called the melt-dispersion mechanism (MDM) has recently been suggested.^{8,9} It is shown, theoretically, that at fast heating rates the alumina shell for nanoparticles does not break due to the difference in thermal expansion coefficients of Al and alumina until the Al melts. The fast melting of Al is accompanied by a 6% volume expansion which creates high dynamic pressure (1–3 GPa) in the molten Al. This high pressure overloads the alumina shell with hoop stresses that exceed the ideal (theoretical) strength of alumina σ_{th} and cause its dynamic spallation. Immediately after shell spallation, pressure within the molten particle remains unchanged while at the bare Al surface it is ~ 10 MPa due to gas pressure and surface tension.⁹ Subsequently, an unloading wave propagates to the center of the particle and creates a tensile pressure of the same order of magnitude. This tensile pressure exceeds the cavitation limit (strength) of liquid Al, and disperses the molten Al into small bare clusters that fly at high velocity (100–250 m/s). The oxidation of these clusters is not limited by diffusion.

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The goal of this letter is to perform critical experiments that confirm predictions based on the MDM theory. These experimental confirmations of the MDM enable the justification of parameters that control the rate of oxidation and V , and suggest unexpected directions of synthesis for Al nanoparticles.

Traditional wisdom based on the diffusive mechanism of oxidation suggests that the flame rate will grow if (a) the radius of the Al particle (R) is reduced, since the ratio of surface area to volume increases and the particles burn time is proportional to $R^{1.16}$ (Ref. 5); (b) the thickness of the oxide shell is reduced, since this reduces the length of the diffusion path, the primary barrier for diffusive reaction; and (c) the Al content in a particle increases. The alumina shell does not participate in the reaction and is considered deadweight.

The MDM predicts the opposite effects. (i) The radius of the Al particle and the oxide shell thickness are not, separately, controlling parameters. (ii) The key controlling parameter is the ratio of Al core radius (R) to shell thickness (δ), $M=R/\delta$. Note that Al content is an increasing function of M . Below the critical value $M=19$, V reaches its maximum possible value and is independent of M . For $M>19$, the flame velocity grows with reduction in M (and consequently Al content). (iii) To increase (or decrease) V for $M>19$ and fixed Al core radius, the oxide shell thickness must be increased (or decreased).

Experiments to elucidate the operative mechanism (i.e., MDM or DOM) have been performed for Al particles with various R , δ , and M (see Table I, where V and S are the averaged flame rate and standard deviation). Experiments not

TABLE I. Particle and velocity data.

D (nm)	δ (nm)	M	V (m/s)	S (m/s)
44	2	10.00	950	46
50*	1	24.00	789	72
80	2	19.00	948	37
110*	1.5	35.67	721	30
110	2	26.50	810	37
121	2	29.25	765	23
120*	4	14.00	947	64

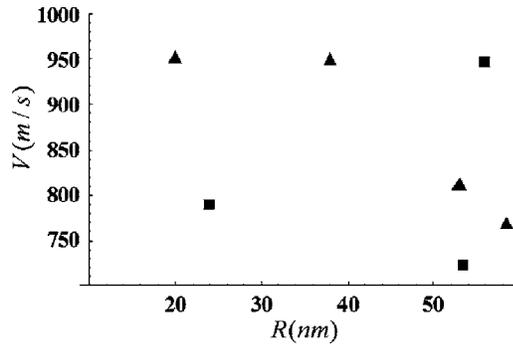


FIG. 1. Flame speed vs Al particle core radius for several oxide thicknesses. It is evident that there is no relationship between flame speed and particle size. The triangles correspond to current data, while the squares represent data taken from Ref. 1.

marked with * were reported earlier in Ref. 1. The main conclusions in Ref. 1 were that below a certain particle diameter $D=2(R+\delta)=80$ nm, V reaches a maximum value and does not change. These results cannot be explained by the DOM, for which the burn time is a function of $R^{1.16}$ (Ref. 5) and the reason for the flame velocity independence of the particle size was not clear. However, in Ref. 1 the oxide shell thickness was constant. Three additional experiments in Table I have been chosen with R , δ , and M values selected such that unambiguous conclusions regarding the main controlling parameters could be made.

All experiments were performed with loose powders (low density mixtures of Al and MoO_3 , at 7%–8% theoretical maximum density) in a confined burning chamber. Visible emission data were collected at 51 000 frames/s using a high speed camera; pressure measurements were also recorded using picosecond response time pressure transducers at 40 kHz (see Ref. 1 for details). The results are reported for an optimal equivalence ratio that provides the maximum V for each particle reported in Table I. The experimental data are plotted as a function of R and M in Figs. 1 and 2, respectively. The following conclusions are made:

- In agreement with item (i), V is not a function of particle radius alone (Fig. 1); it is different for the same R and different shell thicknesses.
- The main parameter controlling V is $M=R/\delta$ (Fig. 2). For $M < 19$, the flame velocity reaches its maximum possible value and is independent of M , R , δ , and Al

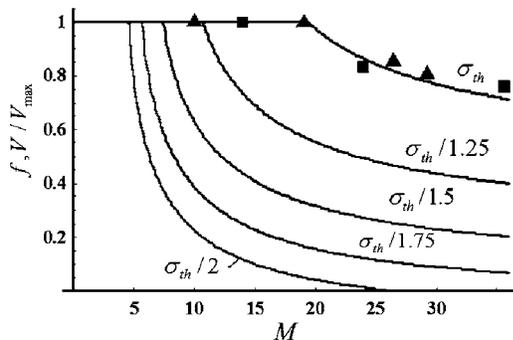


FIG. 2. Flame speed divided by $V_{\max}=950$ m/s vs relative Al core radius $M=R/\delta$. For various oxide shell strengths (shown near the curves) the lines correspond to the volume fraction of melt f necessary to fracture of the oxide shell; they are based on Eqs. (1) and (2).

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content. For $M > 19$, V grows with reduction in M . This is in agreement with item (ii).

- For the Al particles with $D=120$ nm and two different δ (2 and 4 nm), V for particles with smaller δ (and consequently larger Al content) was 765 m/s while for particles with the thicker δ the maximum V was 947 m/s. This is consistent with prediction (iii) based on the MDM (since $M=33$ for $\delta=2$ nm and $M=15 < 19$ for $\delta=4$ nm) but contradicts items (b) and (c) typical of the diffusive mechanism.
- For Al particles with $D=50$ nm and $\delta=1$ nm, V is expected to be higher than for all other particles with larger D and δ [according to diffusive mechanisms (a)–(c)]. However, the maximum V was only 785 m/s, since $M=24 > 19$. Similarly, particles with $D=110$ nm and $\delta=1.5$ nm should produce higher V than particles $D=120$ nm and $\delta=2$ nm and $\delta=4$ nm [according to diffusive mechanism (a)–(c)]. However, according to the MDM, V is lower because of the larger M .
- Based on previous experiments, it was concluded that V reaches its maximum value for particles with $D < 80$ nm. Current experiments show that the maximum V was measured for Al particles with $D=120$ nm and thick (4 nm) oxide shells. Thus, V reaches a maximum value for $M \leq 19$, independent of R and δ .
- The experimental data in Fig. 2 are in close agreement with the theoretical prediction of the volume fraction of melt f necessary to fracture of the oxide shell, versus M . This strongly supports the MDM and suggests that f is an integral physical controlling parameter. Namely, V is proportional to the volume fraction of molten Al that induces fracture of the oxide shell and participates in the MDM during time scales of ~ 10 μs (i.e., while the flame front passes through). The remaining nondispersed Al may react over longer time scales but does not contribute to V . This correlation also suggests that, in the given range of parameters, cavitation of the molten Al core is not the limiting process since the entire molten Al core contributes to the reaction and flame velocity. Another conclusion is that the ultimate tensile strength of the alumina σ_u reaches the estimated theoretical strength $\sigma_{th}=11.33$ GPa.⁹

The value f can be found from the fracture criterion that hoop stresses in the shell reach the ultimate tensile strength of the alumina σ_u .⁹ Taking an expression for the hoop stress from Ref. 9, the fracture criterion can be transformed to

$$Af^2 + Bf + C = 0, \quad (1)$$

where $m=1+1/M$,

$$A = 6\delta\epsilon^m \Delta K (2 + m^3) M G_2 K_2,$$

$$B = \Delta K m^2 [\delta(1 + M) p_g + 2\Gamma_2] (2G_2 - 3K_2) + 6\delta(2 + m^3) M (\epsilon^m K_5 + \Delta\alpha\Delta K \Delta T) G_2 K_2 - \delta\Delta K M (4G_2 + 3m^3 K_2) \sigma_u,$$

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

. In this equation, $3\epsilon^m$ is the volumetric expansion during the melting of Al, 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 that appears during the reaction, respectively, 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. The flame velocity can be expressed in the form

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

$$V = V_{\max}, \quad \text{for } f = 1, \quad (2)$$

where V_{\max} is the maximum velocity that can be achieved in the experimental setup under study. All parameters in Eq. (1) can be found in Ref. 9; $T_0 = 300$ K. While currently Eq. (1) is confirmed for a relatively narrow set of parameters (Fig. 2) and for specific experimental conditions (confined with loose powder), this equation may be predictive for a much wider range of parameters for which the MDM is operative. The dependence of f on M , T_0 , δ , and σ_u was analyzed numerically in Ref. 9 for given material properties. The current study presents an explicit analytical expression and empirically connects f with V . Note that the dependences of f and V on δ are very weak for the considered experiments. Plots of f versus M for several values of σ_u are presented in Fig. 2 and the significance of the shell's high strength is evident.

The current trends in Al nanoparticle synthesis that are based on DOM are directed to decrease the particle size and the oxide shell thickness to keep the Al content high. The current results suggest the opposite direction should be taken in order to increase the reaction and flame velocities. The oxide shell thickness should be increased up to a maximum value for which the shell still possess the maximum strength due to a lack of defects, and to increase the particle size up to the value $R_{\max} = M_{\max} \delta_{\max} = 19\delta_{\max}$. It was argued in Ref. 9, based on experiments in Ref. 3, that the alumina shell possesses maximum strength at least up to $\delta = 7.7$ nm, i.e., $R_{\max} = 146.3$ nm. The increase in the strength of the oxide shell (due to optimal passivation condition, creating a homogeneous shell thickness, and reducing inclusions of other elements) should also lead to an increase in V for $M > 19$. The substitution of the oxide shell with a stronger metal than alumina (such as tungsten) will promote the MDM and increase the reaction and flame velocity, in contrast to current trends.¹⁰ Tungsten also increases the density of the nanocomposite which is important for applications of reactive materials.

To summarize, the experimental data on flame velocity versus Al nanoparticle size and oxide shell thickness strongly support the MDM and contradict the classical diffusive oxidation mechanism. Namely, the main parameter controlling V is the ratio of the Al core radius to shell thickness M rather than R , δ , and Al content separately. Below the critical value $M = 19$, V reaches a maximum value and is independent of M , R , δ , and Al content. For $M > 19$, V grows with reduction in M . In this case, an increase in oxide thickness under fixed R leads to an increase in V . These results will significantly change the directions in which Al nanoparticle synthesis progress. The current trends are directed at decreasing the particle size and oxide thickness while trying to keep the Al content high. The results suggest that the preferred course is to increase the oxide shell thickness up to a maximum value at which it is still possess the maximum strength due to a lack of defects, and to increase the particle size up to the value $R_{\max} = M_{\max} \delta_{\max} = 19\delta_{\max}$. The increases in the oxidation temperature and strength of the shell (an alumina shell or a specially designed shell made of a strong metal such as tungsten) will increase V as well. It was found that V is proportional to the volume fraction of the molten Al that causes the fracture of the shell and participates in the MDM. This correlation suggests that in the given range of parameters cavitation of the molten Al does not limit the reaction. An analytical equation for V versus Al nanoparticle geometric parameters, thermomechanical properties, and synthesis parameters was derived. The maximum particle diameter corresponding to the fastest V was increased from 80 nm in Ref. 1 to 120 nm by increasing the oxide shell thickness to 4 nm.

The authors gratefully acknowledge the ONR (N00014-07-1-0318). M. Pantoya acknowledges the ARO (W911NF-04-1-0217).

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¹⁰Current trends are to substitute the oxide shell with metals such as gold, nickel, and silver [T. J. Foley, C. E. Johnson, and K. T. Higa, *Chem. Mater.* **16**, 4086 (2005)] or $C_{13}F_{27}COOH$ [R. J. Jouet, J. R. Carney, R. H. Granholm, H. W. Sandusky, and A. D. Warren, *Mater. Sci. Technol.* **22**, 422 (2006)] to reduce the dead weight and initial barrier for diffusion. This is useful for some applications but not for those where the goal is to increase the reaction and flame velocity, because the strength of such shells is significantly lower compared to alumina and MDM cannot operate. Indeed, even bare Al nanoparticles with $D = 20$ nm require more than 1 s for complete oxidation at $T = 900$ °C (Ref. 4).