Melt dispersion mechanism for fast reaction of nanothermites

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An unexpected mechanism for fast oxidation of Al nanoparticles covered by a thin oxide shell (OS) is proposed. The volume change due to melting of Al induces pressures of $0.1-4$ GPa and causes spallation of the OS. A subsequent unloading wave creates high tensile pressures resulting in dispersion of liquid Al clusters, oxidation of which is not limited by diffusion (in contrast to traditional mechanisms). Physical parameters controlling this process are determined. Methods to promote this melt dispersion mechanism, and consequently, improve efficiency of energetic nanothermites are discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2335362]

Thermites are mixtures of metal fuel (e.g., Al, Mg, and B) and oxidizers (e.g., Fe_2O_3, MoO_3, and CuO) which react to produce high temperatures with slow oxidation reactions. Since fuel particles are covered by a thin OS, oxidation is controlled by diffusion of molecules through a growing OS. However, when the initial external radius $\tilde{R}$ of the fuel particle is reduced to $10-60$ nm (in contrast to traditional $1—100$ μm size), reaction rates drastically increase and flame propagation rates C reach $0.9-1$ km/s, [1–3] in contrast to cm/s for traditional thermites. Rise time for temperature and pressure at the reaction front is $t_f \simeq 10$ μs which characterizes the reaction time. For self-diffusion coefficients of oxygen and Al in α-alumina at $800-950$ °C, $D=10^{-19}$ and 10^{-18} cm^2/s,[4] the diffusion length $l_d=2\sqrt{Dt_f}=(2-6)\times 10^{-5}$ nm, which is 10^5 times smaller than the OS thickness. Also, C and ignition time delay t_{ig} are independent of particle size for $R<40-50$ nm, while for diffusion controlled oxidation $C \sim 1/R$ (Ref. 2) and $t_{ig} \sim R^n$.[5] Thus, the only known oxidation mechanism via diffusion does not apply for nanoparticle combustion; finding such a mechanism for nanosize thermites is one of the most important problems in combustion physics. In this letter, we suggest and justify theoretically and experimentally an unexpected oxidation mechanism during fast heating which explains numerous puzzles observed experimentally in flame propagation of $Al+MoO_3$ (Refs. 1, 2, and 6) and $Al+Fe_2O_3$ (Ref. 3) nanothermites. Fast heating creates huge thermal stresses due to a difference in thermal expansion coefficients α of Al and Al_2O_3 and volumetric strain $3\varepsilon^m$ during the Al melting. Due to the small size of the amorphous OS, $\delta=1-4$ nm, it is defect-free and its strength approaches the theoretical strength. For small particles (small $M=R/\delta$) the OS fractures after melting of an Al particle (in contrast to slow heating or micrometer size particles). Pressure in the melt is very high ($0.1-4$ GPa). Dynamic spallation of OS results in complete exposure of the liquid Al droplet which leads to an unloading wave within the liquid Al droplet and creates high tensile pressure. The tensile pressure disperses the Al droplet into small clusters that are ejected at a high velocity. The

oxidation of these clusters is not limited by diffusion. The suggested melt dispersion mechanism (MDM) is much faster than diffusion and is independent of the size of Al particle (below some critical size); fast reaction provides fast flame propagation and fast heating rates for the next particles. The necessary conditions for operation of this mechanism and controlling physical parameters are found. By altering controlling physical parameters we suggest ways to promote the MDM, and thereby improve the efficiency of energetic nanothermites. Increasing the temperature T_0 at which initial OS is formed, creating initial porosity in the Al, and alloying Al to decrease the cavitation pressure are ways to induce the MDM. Theoretical results are consistent with observations. A similar mechanism is expected for nitridation and fluorization of Al. The MDM may also be tailored for Ti and Mg fuels.

Let us consider internal stresses during the heating of spherical Al particle with radius R covered by a thin alumina OS with external radius $\tilde{R}$. The surface temperature of the particle varies from $T_r=300$ K to the final $T_f \simeq 1000$ K (just above melting temperature of Al, $T_m=933.67$ K) during a time t_f. It is easy to show that for $R<9$ μm the temperature in the Al sphere is homogeneous. Stresses for a large Al particle covered by OS were found in Ref. 7; we generalize these results for small particles and apply the proper strength criterion. Internal stresses arise during heating due to a difference in inelastic strains $\varepsilon_2^i - \varepsilon_1^i$ (subscript 1 is for Al and 2 is for Al_2O_3). Surface tensions at the $Al-Al_2O_3$ interface, Γ_1, and between alumina and gas, Γ_2, cause jumps in pressures of $2\Gamma_1/R$ (at $r=R$) and $2\Gamma_2/\tilde{R}$ (at $r=\tilde{R}$). Pressure in the Al sphere, p, and maximum hoop stresses in OS at $r=R$, σ_h, can be found from the elasticity theory:[8]

$$p = \frac{12(m^3-1)(\varepsilon_2^i - \varepsilon_1^i)G_2 K_1 K_2}{H} + \frac{2K_1(4G_2 + 3m^3 K_2)\Gamma_1}{RH}$$

$$+ \frac{2m^2 K_1(4G_2 + 3K_2)\Gamma_2}{RH}, \tag{1}$$

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TABLE I. Material parameters at $T=T_m$.

K_1^s (GPa)	K_1^m (GPa)	K_2 (GPa)	G_2 (GPa)	α_1^s $(10^5\ \mathrm{K}^{-1})$	α_1^m $(10^5\ \mathrm{K}^{-1})$	α_2 $(10^5\ \mathrm{K}^{-1})$	ε^m	Γ (GPa nm)	ρ_1^s (kg/m³)	ρ_1^m (kg/m³)
71.1[a]	41.3[b]	234.8[c]	149.5[c]	3.032[a]	4.268[d]	0.778[c]	0.02[e]	1.05[f]	2530[g]	2380[d]

[a]See Ref. 13.
[b]See Ref. 14.
[c]See Ref. 12.
[d]See Ref. 16.

[e]See Ref. 7.
[f]See Ref. 17.
[g]See Ref. 15.

$$\sigma_h = -\frac{6(m^3+2)(\varepsilon_2^i - \varepsilon_1^i)G_2K_1K_2}{H} + \frac{4(m^3+2)G_2K_2\Gamma_1}{RH}$$
$$+ \frac{2m^2(-2G_2K_1 + 3(2G_2+K_1)K_2)\Gamma_2}{RH}, \tag{2}$$

$$\varepsilon_1^i = -(\alpha_1^s(T_m - T_0) + (1-f)\alpha_1^s(T - T_m) + f\alpha_1^m(T - T_m) + f\varepsilon^m), \tag{3}$$

$$\varepsilon_2^i = -\alpha_2(T - T_0).$$

Here K and G are the bulk and shear moduli, $K_1 = fK_1^m + (1-f)K_1^s$, $m = \tilde{R}/R = 1 + \delta/R$, f is the volume fraction of the melt in Al particle, subscripts s and m are for the solid and melt phases, and $H = 3m^3K_1K_2 + 4G_2(K_1 + (m^3-1)K_2)$. The criterion for brittle fracture of OS (maximum tensile stress reaches the ultimate tensile strength σ_u) is $-\sigma_h = \sigma_u$.

All material parameters are given in Table I ($\Gamma_1 = \Gamma_2 = \Gamma$). For amorphous OS of $\delta = 1.5-8$ nm, defects are neglected, thus the ultimate strength is equal to theoretical strength, σ_{th}. For crystalline materials, $\sigma_{th} = E/20 - E/10$ but we conservatively take $\sigma_u = E_2/30 = 11.33$ GPa and consider much smaller σ_u as well. Also, because of lack of stress concentrators and fast loading, fracture and spallation occur throughout the entire OS.

Using Eq. (2) and applying the condition $-\sigma_h = \sigma_u$, the value of volume fraction of melt, $f_f(\sigma_u, M, \delta, T_0)$, necessary for the fracture of the OS is obtained. The functions $f_f(M)$ for $T_0 = 600$ K and several values of σ_u and $\delta = 3$ are shown in Fig. 1(a). They do not change significantly for $1.5 < \delta < 8$ nm. In small particles the fracture criterion is not fulfilled even at complete melting. Then OS spallation will occur at $T > T_m$, due to growth of thermal stresses and reduction in σ_u with the temperature increase. In such a case, an unloading wave in Al particle after OS spallation produces tensile pressure and disperses the liquid Al droplet (see below).

Relationships $p_0(M)$ for pressure in Al particle at the instant of OS fracture are shown in Fig. 1(b). For $\sigma_u = 9.0$ GPa and $M = 19.0$, pressure at the complete melting is 1.0 GPa; for smaller σ_u, complete melting occurs at smaller M and pressure is even larger. For comparison, for $T_0 = 300$ K we obtain complete melting at $M = 10.8$ and $p = 1.8$ GPa; for $T_0 = 900$ we have $M = 80$ and $p = 0.24$ GPa. Thus, T_0 is an important parameter controlling which MDM can be produced even for large particles.

Thus at fast heating, the major part of the Al nanoparticle melts before fracture of OS, producing high pressure. Then unloading wave after OS spallation disperses the liquid particle. For smaller particles, a larger portion of the Al melts and the pressure in the Al is higher (Fig. 1). The MDM

should not occur during slow heating[9] and for large particles. For $\sigma_u = 9.0$ GPa and $R/\delta = 2000$, we obtain $p_0 < 9.0$ MPa which may not produce sufficient tensile stress in the unloading wave to disperse solid Al particles. For $T = T_m$, $\sigma_u = 9.0$ GPa, and $T_0 = 300$ K, we have $f_f = 0.21$ only.

Let a sphere of radius R be initially in equilibrium under applied external pressure p_0. We found analytically pressure and velocity evolutions after reduction of the pressure at the boundary $r = R$ from p_0 to the final value p_f during the time of OS spallation, t_s, after which it remains constant. We define an acoustic time $t_p = R/c$ during which boundary regime propagates to the center of the sphere, where $c = \sqrt{K_1^m/\rho_1^m} = 4166$ m/s is the sound velocity in Al. Thus, for $R = 41.66$ nm we have $t_p = 10$ ps. We consider unloading and the first reflected wave only. For fast heating of an Al nanoparticle with a thin OS when the OS fractures at reaching its theoretical strength, $t_s \ll t_p$; we take $t_s = 0.2 t_p$. For $R = 40$ nm, we take $p_0 = 1$ GPa and $p_f = 2\Gamma/R \approx 0.05$ GPa.

The results shown in Fig. 2 are typical for the regime with $t_s \ll t_p$ and $p_f \ll p_0$. For $t_s < t < t_p$, a region with tensile pressure appears and propagates to the center of the sphere; the magnitude of tensile pressure grows drastically (Fig. 2). Maximum values of tensile pressure and velocity in the central part of the sphere reach $|p| = 3.75$ GPa and $v = 240$ m/s, respectively.

Fracture of liquid (cavitation) criterion is $p < p_c < 0$, where p_c is the critical tensile pressure; we can estimate p_c
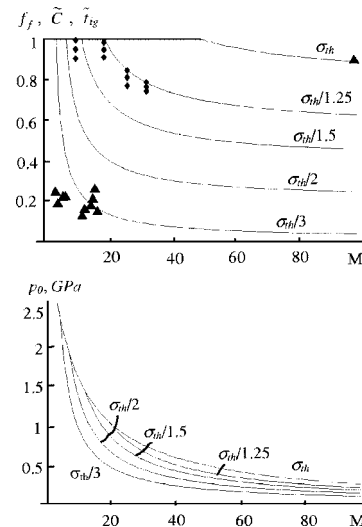

FIG. 1. Volume fraction of melt necessary for fracture of OS f_f (a) and pressure p_0 in Al particle at the fracture of OS (b) as a function of $M = R/\delta$ for various values of ultimate strength σ_u (shown near the curves); $\delta = 3$ nm, $T_0 = 600$ K. The upper line, common for all curves, corresponds to complete melting. Diamonds represent dimensionless flame velocity $\tilde{C} = C/(1\ \mathrm{km/s})$ vs M from experiments (Ref. 2). Triangles are the relative ignition time $\tilde{t}_{ig}/(100\ \mathrm{ms})$ from experiments (Ref. 5).
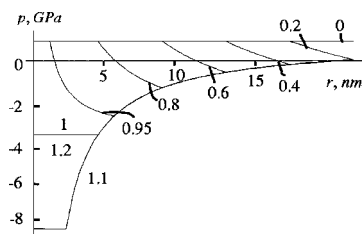
FIG. 2. Pressure (GPa) distribution in Al sphere after spallation of OS at different instances of propagation of the unloading wave (shown near the curves as a fraction of t_p). The upper line ($t=0$, $p=1$ GPa) and the lowest curve are common for all curves for $t \leq t_p$, i.e., at each time the pressure profile consists of straight horizontal line (1 GPa) in the central part, the line connecting to the lowest curve and part of the lowest curve.

$=-(0.01-1)$ GPa. For $p_c=-0.1$ GPa, the cavitation criterion is satisfied at radius $r_f=0.85R$ (Fig. 2). Cavitation results in separation of a thin liquid outer shell from the main droplet. The thickness of this shell during flight will get smaller down to atomic size then it will break into small sectors. Since tensile pressure without fracture exceeds significantly $|p_c|$ (Fig. 2), the thickness of each subsequent separated liquid shell is of order of several atomic sizes. Al clusters may react with oxygen and nitrogen in the air, gaseous MoO_3 which starts to sublimate at 973 K, with Teflon which decomposes at 825 K, or solid oxidizers.

For the same conditions but for $t_s=t_p$, there is no tensile pressure in Al for $t<t_p$. For $t>t_p$ cavitation is in principle possible but not very probable. For $t_s=2t_p$, tensile pressure does not appear in the unloading and first reflected waves, i.e., dispersion cannot occur.

If, e.g., $\sigma_u=9$ GPa, then for $M \leq 19$ the entire particle melts before OS fracture [Fig. 1(a)] (pressure $p_0=1.0$ GPa for $\delta=3$) and disperses providing maximum possible mixing, oxidation rate, energy release, and flame front velocity. According to the MDM, there should not be an essential difference in the mixing of components and oxidation rate of particles with $R/\delta \leq 19$. In our experiments,[2] flame velocity is approximately the same (950 m/s) for the Al particles with an averaged $R=20$ and 38 nm and reduces for particles with $R=53$ and 58.5 nm ($\delta \simeq 2$ nm) [Fig. 1(a)]. In our recent experiments,[5] laser induced ignition times are in the range of 12.4–25.5 ms for $R=6.7-99$ nm and grows to 6.039 s for $R=20$ μm [Fig. 1(a)]. These results support our theory.

Damage of the OS should suppress the MDM but promote traditional diffusion oxidation mechanism. Pressing thermite pellets in a die potentially damages the OS. That is why C is expected to decrease with sample density for nanothermites and grow for micro thermites. That is exactly what was observed in our experiments.[6] On the other hand, vibrational compaction without pressure should not damage OS and suppress the MDM. Indeed, vibrational change in density in the range of 5%–10% of TMD did not change C.[2]

Consider an ellipsoidal penny-shaped particle with semiaxes b and $R \gg b$ that mimics a nanoflake. The hoop stress in the circular section of radius R is $\sigma_h^{max} \simeq -pR/(2\delta)$, while the hoop stress in the elliptic section, $\sigma_h^{min} \simeq -p\pi b/(4\delta)$, is much smaller. Simultaneous spallation of the entire OS cannot occur. Fracture occurs along the circular section of radius R when $\sigma_h^{max}=-\sigma_u$, i.e., for $p=2\sigma_u\delta/R$ [like for large spherical particles]. For nanoflakes, $b=10-100$ nm, while $R=10-100$ μm.[10] Thus, fracture of a flake occurs at a similar pressure as a micro particle. Thus, according to the MDM,

nanoflakes would tend to react like micro particles, while traditional arguments (higher reactivity and large surface to volume ratio) suggest similar reactivity for nanoflake and nanospherical particles. In experiments,[10] nanoflakes did not produce higher flame rate than micro spherical particles.

The main conditions for the dispersion of the spherical Al particle are that it completely melts before OS spallation, that OS fracture time is smaller than wave propagation time ($t_s<t_p$), and that pressure in the particle before OS spallation is approximately equal to the cavitation pressure. These conditions can be fulfilled for a thin amorphous defect-free or nanocrystalline OS, and only during fast heating. We can predict several ways to increase particle radius for which the MDM is operative.

(1) Our analysis predicts that increasing T_0 may extend the MDM for large particles. If we increase T_0 up to 900 K, then for $\sigma_u=9.0$ GPa almost the whole particle melts for any particle radius. If we assume that $p_0=20$ MPa is sufficient for fracture and dispersion of Al particle, then for $\sigma_u=9.0$ GPa and $\delta=8$ nm, we obtain $R=7.2$ μm.

(2) To create the condition for fast heating of large particles, they have to be mixed with nanosized particles ($R<40-100$ nm) which have much higher probability to be dispersed in a liquid state. Indeed, a mixture of 70% of Al particles with $R=38$ nm ($R/\delta=8.3$) and with 30% particles with $R=2$ and 10 μm provided practically the same flame velocity as 100% of Al nanoparticles.[11]

(3) An alternative way to decrease internal stresses before melting and to ensure complete melting before OS fracture is to introduce initial porosity in the Al particles.

(4) Alloying the fuel particle may reduce its local surface energy and cavitation pressure.

[1] B. W. Asay, S. F. Son, J. R. Busse, and D. M. Oschwald, Propellants, Explos., Pyrotech. **29**, 216 (2004).
[2] B. S. Bockmon, M. L. Pantoya, S. F. Son, B. W. Asay, and J. T. Mang, J. Appl. Phys. **98**, 064903 (2005).
[3] K. B. Plantier, M. L. Pantoya, and A. E. Gash, Combust. Flame **140**, 299 (2005).
[4] E. Bergsmark, C. J. Simensen, and P. Kofstad, Mater. Sci. Eng., A **120**, 91 (1989).
[5] J. J. Granier and M. L. Pantoya, Combust. Flame **138**, 373 (2004).
[6] M. L. Pantoya and J. J. Granier, Propellants, Explos., Pyrotech. **30**, 53 (2005).
[7] V. Rosenband, Combust. Flame 137, 366 (2004).
[8] J. Lubliner, *Plasticity Theory* (Macmillan, New York, 1990).
[9] If melting of an Al nanoparticle covered by OS occurs during slow heating fracture occurs in the weakest place and then propagates. Pressure in liquid Al slowly reduces and liquid will slowly flow through the gap without dispersion, as observed experimentally by A. Rai, D. Lee, K. Park, and M. Zachariah, J. Phys. Chem. B **108**, 14793 (2004).
[10] B. Z. Eapen, V. K. Hoffmann, M. Schoenitzand, and E. L. Dreizin, Combust. Sci. Technol. **176**, 1055 (2004).
[11] K. Moore, M. L. Pantoya, and S. Son, Propulsion and Power (in press).
[12] O. L. Anderson, *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, Oxford, 1995), p. 362.
[13] S. Raju, K. Sivasubramanian, and E. Mohandas, Solid State Commun. **122**, 671 (2002).
[14] D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).
[15] V. E. Zinov'ev, *Handbook of Thermophysical Properties of Metals at High Temperatures* (Nova Science, New York, 1996), p. 140.
[16] P. M. Smith, J. W. Elmer, and G. F. Gallegos, Scr. Mater. **40**, 937 (1999).
[17] V. Sarou-Kanian, F. Millot, and J.-C. Rifflet, Int. J. Thermophys. **24**, 277 (2003).