J|A|C|S
COMMUNICATIONS

Published on Web 10/09/2004

High Velocity Interparticle Collisions Driven by Ultrasound

Tanya Prozorov,[†] Ruslan Prozorov,[‡] and Kenneth S. Suslick*,[†]

School of Chemical Science, University of Illinois at Urbana−Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801, and Department of Physics & Astronomy, University of South Carolina, 712 Main Street, Columbia, South Carolina 29208

Received January 28, 2004; E-mail: ksuslick@uiuc.edu

Ultrasonic irradiation of liquids produces transient cavitation: the formation, growth, and implosive collapse of bubbles.[1] During bubble collapse, intense shock waves are generated and propagate through the liquid at velocities above the speed of sound.[1−4] Unusual sonochemical effects are induced by these shock waves, most importantly, high velocity collisions among solid particles suspended in such liquids.[4] These collisions result in extreme heating at the point of impact, which can lead to effective local melting and dramatic increases in the rates of many solid−liquid reactions.[5−8] In this work, we describe a quantitative model of the melting induced by high-speed interparticle collisions and test this kinematic model against the effects of varying initial particle size and slurry concentration on the morphology of zinc particle agglomerates.

Sonication[9] of a decane slurry containing 2% w/w fine Zn powder (5 μm diameter) rapidly produces Zn agglomerates (cf. scanning electron micrographs in Figure 1 and Supporting Information). As sonication proceeds, agglomeration reaches its maximum effect after ~90 min. The resulting 50−70 μm agglomerates have nearly round shapes (Figure 1B). Sonication of 5 μm Zn powder as a slurry in alkanes, for example, produces dense agglomerates consisting of ~1000 fused particles.

Because of turbulent flow and shock waves generated by cavitation in liquids irradiated with ultrasound, metal particles are driven together at extremely high speeds, which induces effective melting at the point of impact.[4] The estimated velocity of colliding particles approaches half the speed of sound in the liquid.[4] The low melting point of Zn (419.6 °C)[10] obviously contributes to the facile agglomeration process. One would expect to alter the velocity of interparticle collisions by varying the concentration of impinging particles. This should influence the temperature at the site of impact, resulting in agglomeration with diminished efficacy at sufficient slurry density. To verify this effect, the slurry loading was systematically increased. Loadings up to 50% w/w showed no significant effect, but further increases to 70% w/w resulted in considerably less pronounced agglomeration (Figure 1C and Supporting Information).

The particle size has a very strong effect on the outcome of the ultrasonic irradiation. From previous observations,[8] we know qualitatively that agglomeration does not occur for particles either too large (~100 μm) or too small (~100 nm). For example, no aggregation was observed for coarse Zn powder (Figure 2), although particle deformation does occur (Supporting Information). Interestingly, by mixing the fine and coarse Zn powders and sonicating them together as a slurry at high loading, a porous aggregated product is formed (Figure 2B). The large particles are literally welded together by collision with the smaller particles.

To model the interparticle collisions, some simplifying approximations will be made: (1) the collisions are perfectly inelastic (i.e., all kinetic energy ends as thermal energy within the particle colliding) and (2) complete melting of a particle occurs in order to form the observed dense agglomerates. To estimate the critical speed required to melt a particle upon a direct impact, then, the kinetic energy is equal to the thermal energy required to heat the particle to its melting temperature plus the heat of fusion. From this, we obtain the critical (i.e., minimum) velocity required to melt the particle:

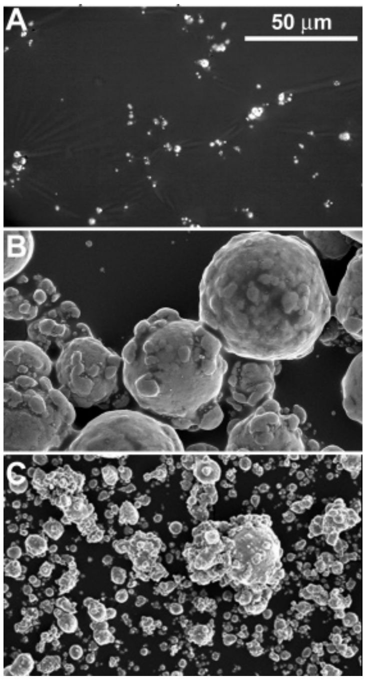

Figure 1. Effects of ultrasonic irradiation on slurries of fine Zn powder (5 μm diameter, roughly spherical; obtained from Goodfellow, Inc.). (A) SEM before ultrasonic irradiation. (B) Dense agglomeration after 90 min sonication of 2% w/w decane slurry at 20 kHz, 50 W/cm², 283 K, where agglomerates are made from ~1000 of the initial particles and loadings up to 50% w/w show similar results. (C) Poor agglomeration after 90 min sonication of a 70% w/w decane slurry. Size bar applies to the whole figure.

$$v_c = \sqrt{2}\sqrt{C(T_m - T_b) + L} \approx 728.5 \text{ m/s} \qquad (1)$$

where m is mass (kg), C specific heat (388 J/(kg K) for Zn), L heat of fusion (1.13×10^5 J/kg for Zn), T_m melting temperature (692.7 K for Zn), and T_b bath temperature (300 K). Note that the critical velocity *does not depend* on the particle mass.

The actual speed a particle reaches during sonication, however, depends strongly on the particle size. Let us consider a spherical particle of a radius R. Suppose that the propagating shock wave exerts an average pressure P as it passes over particles in near proximity to the collapsed bubble. This pressure exerts a force

---

[†] University of Illinois at Urbana−Champaign.
[‡] University of South Carolina.

10.1021/ja049493o CCC: $27.50

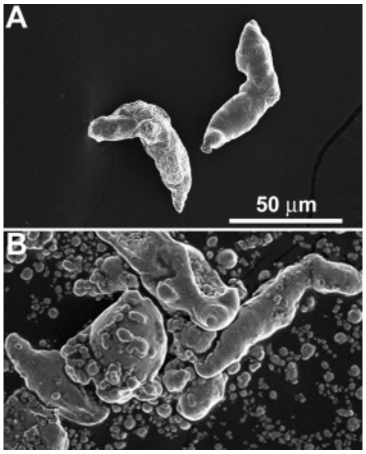

Figure 2. Effects of ultrasonic irradiation on slurries of coarse Zn powder (elongated 50 × 10 μm Zn powder was obtained from Union Minere, U.K.). (A) Coarse Zn powder before ultrasonic irradiation. Ultrasonic irradiation of slurries of the coarse Zn powder alone does not lead to agglomeration (cf. Supporting Information). (B) Dense agglomeration after 90 min of sonication of 95% w/w decane slurry of mixed fine and coarse Zn powders (10−1 fine to coarse) at 20 kHz, 50 W/cm^2, 283 K.

proportional to the particle's cross-section area, $F = \pi PR^2$. A particle's mass is simply $m = 4\pi R^3\rho/3$, where ρ is the density of the particle (for Zn, 7.14×10^3 kg/m^3). Taking into account viscous drag, $F_d = 6\pi\eta Rv$ in a laminar flow regime and $F_d = 12R^2\rho_L v^2/Re$ in the turbulent flow regime (where η is the viscosity coefficient, ρ_L the liquid density, and Re = Reynolds number = 3000 is the critical value for onset of turbulence).[11] We can solve the simple Newtonian equation, $ma = \pi R^2 P - F_d$ to obtain eq 2 for the laminar regime.

$$v \approx \frac{PR}{6\eta}\left[1 - \exp\left(-\frac{9\eta\Delta t}{2\rho R^2}\right)\right] \qquad (2)$$

Here Δt is the duration of the shock wave acceleration or collision time. The equation with F_d for turbulent flow gives numerically similar results in the velocity regime of interest.

To roughly estimate Δt, we take the mean free path λ of the interparticle collisions divided by the speed of sound in the liquid (v_l). The mean free path in our experiment is the average interparticle distance and it decreases with increasing R. From the electron micrographs we estimate $\lambda \approx 10/R$ [μm]. Therefore, $\Delta t \approx \lambda/v_l = 10 \times 10^{-6}/1100/R = 1 \times 10^{-8}/R$ [m] s. Taking the shock wave pressure to be 1 MPa (as measured for laser-induced cavitation[3]) and average viscosity $\eta = 5 \times 10^{-4}$ Pa s, we obtain for zinc particles colliding in decane the following equation:

$$v\,[\mathrm{km/s}] \approx 0.33R\,[\mu\mathrm{m}]\left(1 - \exp\left(-\frac{3151.26}{(R\,[\mu m\,])^3}\right)\right) \qquad (3)$$

Equation 3 is plotted in Figure 3. Solving for the critical velocity (728.5 m/s), we calculate that particle melting upon interparticle collisions is expected over the radius range of $2.2 \le R \le 38$ μm. Equation 3 describes our current and prior observations surprisingly well: agglomeration of metal particles occurs only over a fairly narrow range of radius in the regime of a few microns. Neither particles too large nor too small will be accelerated to a sufficient velocity to induce local melting and consequent agglomeration. Consistent with this, as we have demonstrated here, particles too large to agglomerate by themselves can still be welded together by the addition of proper sized particles, leading to large mixed agglomerates.

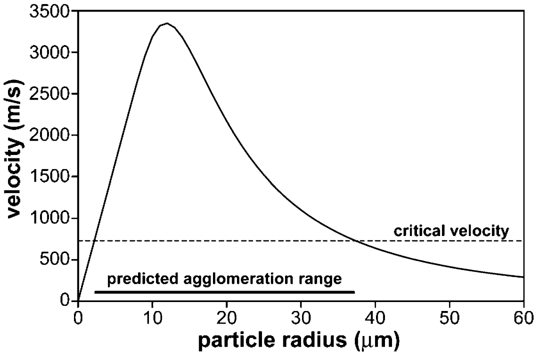

Figure 3. Calculated velocity as a function of Zn powder radius from eq 3. The critical velocity necessary for collisional agglomeration determines the particle size range over which agglomeration will occur.

In conclusion, the effects of cavitation in this phenomenon of interparticle collisions come from the shock waves released into the liquid and *not* from the temperature of the localized hot-spot formed within the collapsing bubble. While heating within a collapsing bubble is strongly affected by the vapor pressure of the solvent within the bubble,[12,13] the departing shock wave is not. We also note that volatility of the liquid in the slurry has at best a modest effect on the nature of the interparticle collisions: for example, decane and heptane give very similar results. In addition, over a fairly wide range (~2 to ~50% w/w), slurry concentration has only limited effects on the interparticle collisions. Importantly, the initial size of the solid particles is critical in affecting interparticle collisions: with Zn as an example, particles smaller than a few micrometers or larger than a few tens of micrometers will not collide with sufficient energy to agglomerate.

Acknowledgment. We appreciate the support of the NSF (CHE0315494) and the UIUC Center for Microanalysis of Materials (partially supported by the U.S. DOE, Grant DEFG02-91-ER45439). R.P. acknowledges support from the NSF (EPS-0296165), the University of South Carolina Research and Productive Scholarship Fund, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supporting Information Available: Figures showing additional micrographs. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Suslick, K. S.; Crum, L. A. In *Encyclopedia of Acoustics*; Crocker, M. J., Ed.; John Wiley & Sons: 1997; pp 271−282.
(2) Vogel, A.; Lauterborn, W. *J. Acoust. Soc. Am.* **1988**, *84*, 719.
(3) Gompf, B.; Gunther, R.; Nick, G.; Pecha, R.; Eisenmenger, R. *Phys. Rev. Lett.* **1997**, *79*, 1405.
(4) Suslick, K. S.; Doctycz, S. J. *Science* **1990**, *247*, 1067.
(5) Suslick, K. S.; Price, G. J. *J. Annu. Rev. Mater. Sci.* **1999**, *29*, 295.
(6) Luche, J. L. *Organic Sonochemistry;* Plenum: New York, 1998.
(7) (a) Suslick, K. S.; Doctycz, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 2342. (b) Suslick, K. S.; Casadonte, D. J.; Doktycz, S. J. *Chem. Mater.* **1989**, *1*, 6.
(8) Suslick, K. S.; Docktycz, S. J. *Adv. Sonochem.* **1990**, *1*, 197−230.
(9) Materials were transferred into an inert atmosphere box and stored under Ar (<0.5 ppm O$_2$). Decane and heptane (Aldrich) were distilled under Ar and stored in the glovebox. Sonications of Zn slurries in decane and heptane were carried out at 0 °C under Ar. SEM: Hitachi 4700.
(10) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 82 ed.; CRC Press: Boca Raton, FL, 2002.
(11) E M Lifshitz and L D Landau, *Fluid Mechanics (Course of Theoretical Physics*), 2nd ed.; Butterworth-Heinemann: London, 1987; Vol. 6.
(12) Suslick, K. S.; Hammerton, D. A.; Cline, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5641.
(13) Suslick, K. S.; Gawienowski, J. W.; Shubert, P. F.; Wang, H. H. *J. Phys. Chem.* **1983**, *87*, 2299.

JA049493O