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Comment on "*In situ* imaging of ultra-fast loss of nanostructure in nanoparticle aggregates" [J. Appl. Phys. 115, 084903 (2014)]

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One of the conclusions of a recent article by Egan *et al*. [J. Appl. Phys. **115**, 084903 (2014)] was that since the melt-dispersion mechanism (MDM) of the reaction of aluminum nanoparticles was not observed in their experiments, this mechanism is very unlikely. Our main point here is to demonstrate that, in fact, these experiments do not disprove the MDM. © *2016 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4941263]

Unique *in situ* experiments were performed in Ref. 1 for the agglomeration and sintering of Al nanoparticles and in the following paper[2] for reactions within the nanoscale Al and CuO mixture for heating rate 10^{11} K/s. The main conclusion is that both Al and CuO nanoscale particles first agglomerate and sinter in a larger scale Al and CuO contacting aggregate, which then react through a condensed state reaction. It was stated that because the melt-dispersion mechanism (MDM)[4–6] of an Al reaction was not observed in Refs. 1 and 2, this mechanism is very unlikely. According to MDM, high pressure in a molten Al core leads to fracture and spallation of alumina followed by propagation of the pressure-release wave toward the center of the Al core and creation of huge tensile mean stress of 3–8 GPa in the melt, which may cause cavitation and disperse the Al core into smaller bare clusters. The reaction of such clusters is not limited by diffusion through an oxide shell.

We do not doubt excellent experiments in Refs. 1 and 2, which study sintering and reaction in real time. Our main point of discussion here is that, in fact, the experiments[1,2] do not disprove the MDM. Below, we consider several alternative scenarios.

1. One of the problems in the interpretation of the data in Refs. 1 and 2 is a significant indeterminacy in the temperature. The agglomeration and sintering after 50 ns of laser heating are more or equally pronounced than after 1 ms of hot stage heating, which may indicate different mechanisms. The example in the authors' Response[3] also confirms that similar microstructures are obtained during these times, which differ by more than four orders of magnitude. A typical Al particle is considered to have an Al core radius $R = 40$ nm and oxide shell thickness $\delta = 3$ nm. However, finite element method (FEM) simulations in the supplementary material in Ref. 1 (in particular, Fig. 3S) show that, to heat an aggregate of seven contacting particles to 1200 K (which is still below the threshold of 1300 K for sintering), a gap between Al cores should be less than 1 nm, which means local shell thickness $\delta = 0.5$ nm (Fig. 1). For this case, our FEM simulations for uniform temperature with properties from Ref. 4 exhibit that the maximum principle stress σ in the thin part of a shell and near the fillet of the sintered particles is more than twice the stress in the 3-nm-thick parts before melting (Fig. 1(a)). Then heterogeneous heating was modeled by prescribing a heating rate of 0.9×10^{11} K/s to the part of the Al surface at O′C. Melting was modeled using the phase-field approach coupled to mechanics.[7,8] Melting drastically increases heterogeneity of stresses (Fig. 1(b)), which will lead to fracture of the shell near the sintered part well before the rest of the shell. After fracture, melt flows out of the shell through this hole. The main condition for the MDM, that the shell is loaded homogeneously[4–6] and fractures in multiple places necessary for fast disappearance of the oxide shell and formation of spherical pressure release wave, is not met. Thus, the MDM is not expected for the heterogeneous shell thickness described in Refs. 1 and 2, and the results obtained in Refs. 1 and 2 do not compromise it.

Note that Al nanoparticles from the same supplier, Novacentrix, have been used in experiments[4,6] in which the MDM was claimed. Thus, if locally thin shells and necks prevent the MDM in Refs. 1 and 2, why do not they prevent the MDM in Refs. 4 and 6? We believe that one of the reasons for this is the difference in statistics used in Refs. 1, 2, 4, and 6. Only specially selected particle aggregates were sintered in Refs. 1 and 2, while others did not show sintering. Thus, "larger aggregates were far more likely to coalesce than small (<10 particles) aggregates"[1] and "superficially similar aggregates behaving differently when exposed to identical laser pulses."[1] In the flame tube, there is no significant scatter in the flame rate, i.e., there were no cases that flame rates for the same Al particles and conditions correspond to the MDM predictions in some experiments and do not correspond in others. Thus, while there are particles with various defects (e.g., pre-sintered, with non-homogeneous shell width, or with defective shell), the major portion of particles satisfy MDM conditions. Also, electromagnetic heating through local hot spots and unstudied effects of oscillatory electric field on diffusion, electromigration, and reaction in Refs. 1 and 2 is much different from

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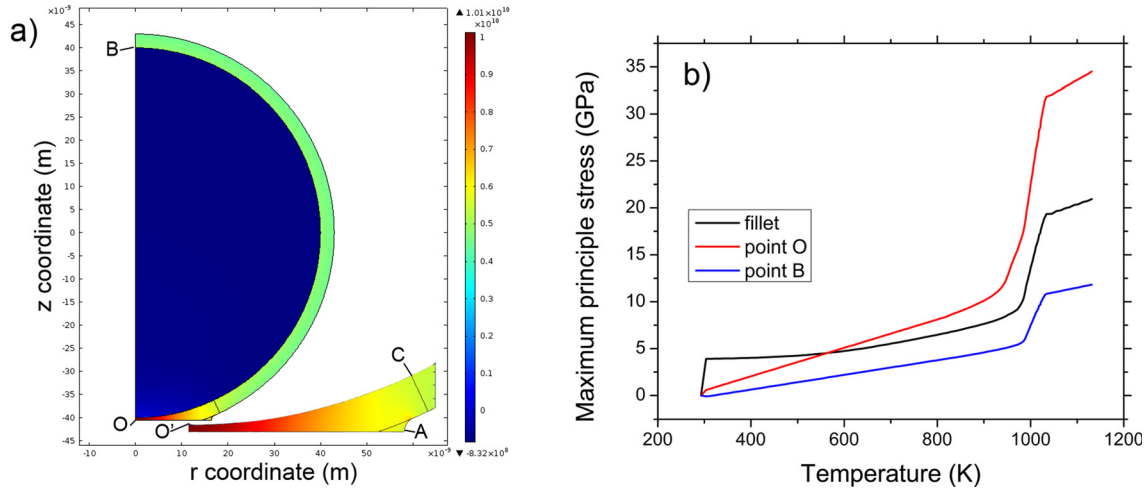

FIG. 1. (a) Distribution of the maximum principle stress σ in the oxide shell for the Al particle radius $R = 40$ nm and oxide shell nominal thickness $\delta = 3$ nm at 933 K. OA is the symmetry plane. (b) σ at three points versus temperature at the center of Al core for the heating rate of 0.9×10^{11} K/s. Change in slope corresponds to initiation of melting.

homogeneous heating by moving gases in the flame tube. Other differences are described in item #5.

2. The authors of Refs. 1 and 2 (and any other researchers) never claimed that they observed such a thin shell; they stated that in their FEM simulation they cannot obtain the desired high temperature for a larger shell gap. Also, small geometric changes can alter the temperature by 1000 K.[1,2] Here, we assume a scenario opposite to that in item 1: that high temperature is somehow possible for a homogeneous shell, all conditions for MDM are fulfilled for some particles, and dispersion happens. The propagation time of the unloading wave for $R = 40$ nm is $\sim$10 ps, the same is true for the reflected wave and for shell fracture,[4] i.e., the time for dispersion is $<$50 ps. The time to the first observations in Refs. 1 and 2 is at least 100 times longer. Due to the stochastic direction of velocity, the closeness of particles that can be heated above melting temperature to each other, and the short time frame, the majority of dispersed particles could not fly away from the coalescing material zone.[18] They land on other non-dispersed particles or substrate, mostly within the same zone as initial particles, and continue to be heated by laser, like initial particles. Thus, dispersion just reduces the size and increases the number of particles within the same group during time negligible with the heating and observation times. Consequently, dispersed particles have enough time to coalesce back and produce larger particles, similar to or easier than initially large non-dispersed particles. That is why the dispersed particles could not be observed in experiments in Refs. 1 and 2 on the time scale of the study. To detect them, one must either quench particles after a time sufficient for MDM but smaller than that required for coalescence (in particular, to stop further heating them), or prevent coalescence. While the authors mention in Ref. 3 that the silicon nitride substrate is cold and should quench dispersed particles, it is also cold for initial particles, and heating of all particles continues, so there is no difference between initial and dispersed particles at the time scale of observation.[19] The example with Ta-Bi_2O_3 in Ref. 3 is irrelevant because it is related to vaporization and condensation over a large area, and conditions for initial and condensed particles may be different. At the same time, in the experiments on flash ignition of Al nanoparticles (obtained from a different supplier than in Refs. 1 and 2) and CuO mixture,[9] the quenched sample contained Al and alumina particles of a much smaller size along with fragments of ruptured shells. This is consistent with MDM and contrasts with the reactive sintering mechanism,[1] which means that different conditions for heating and cooling in Refs. 1, 2, and 9 have been realized. Also, according to Ref. 2, the "shell is not left behind as an empty container" but probably "fractured into small enough pieces." This is also in line with the fracture in MDM. Still, we do not claim here that MDM took place in experiments[1,2] because there are several reasons why it should not; we just consider it to be one of the possible scenarios.

3. Heating with a rate 10^6 K/s in Refs. 1 and 2 is at the borderline of the assumed heating rate required for MDM, so it is not surprising that MDM was not observed (see detail in Ref. 10).

4. Estimating the threshold temperature for sintering in Ref. 1 as 1300 ± 50 K, the authors wrote that "This result provides direct experimental evidence that the volumetric expansion upon melting is not sufficient to cause spallation of the aluminum oxide shell, which is the main premise behind the MDM." This incorrect statement is probably based on misunderstanding of the authors in Ref. 11 that fracture of the shell occurs at melting temperature. In reality, temperature T_f of an Al nanoparticle required for brittle fracture of the oxide shell after complete melting of Al vs. $m = \delta/R$ for two δ, obtained with the help of the MDM theory (see detail in Ref. 10), is shown in Fig. 2. The effect of δ is small. Nominally, in Refs. 1 and 2, $m = 3/37 = 0.08$, for which $T_f = 1107$ K. However, for all particles in Fig. 3 in Ref. 1, for which shell thickness is visible, the value m is greater than 0.21, for which $T_f = 1805$ K. Since temperature is not well defined in experiments[1,2] and also based on simulations in Ref. 1, it is very probable that it did not reach T_f, or sintering started and homogeneity of the shell was violated below T_f. Both would prevent MDM.

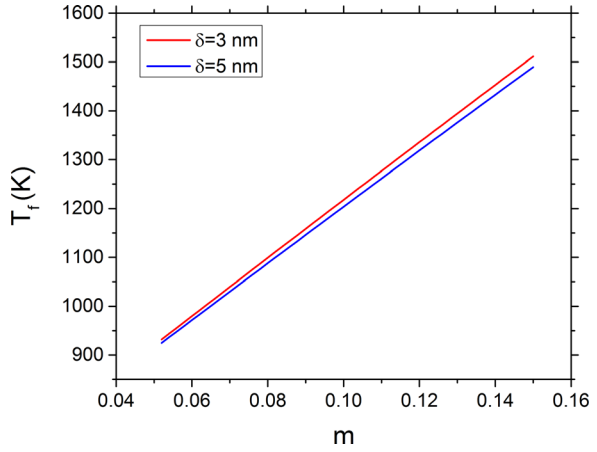

FIG. 2. Temperature T_f of an Al nanoparticle required for fracture of the oxide shell after complete melting of Al vs. $m = \delta/R$ for shell thickness $\delta = 3$ nm and 5 nm.

5. The main quantitative support for MDM comes from the flame tube experiments.[4–6,10,12–14] Namely, there is a quantitative agreement between the theoretical relationship for the normalized flame rate versus $M = 1/m$ and temperature T_0 (at which the core-shell structure is stress-free) and experiments for particles with diameters 31–4500 nm, amorphous and crystalline alumina shells with $\delta = 1$–4 nm, and $296 \le T_0 \le 473$ K. Various oxidizers (Mo_2O_3, CuO, Fe_2O_3, and Teflon) were used. These predictions are exactly opposite to those based on diffusion mechanisms. They are already utilized for improvement of the reactivity of Al particles.[6,12] Conditions in experiments in Refs. 1 and 2 and in the flame tube are very different. In particular, in the flame tube, the final temperature is much higher and there is convective gas flow with the speed 100 to 1000 m/s, which may prevent long-term contact between the same particles below 1300 K and, consequently, reactive sintering. To heat particles to 1300 K with the heating rate 10^8 K/s in the flame tube requires 10 μs; thus, convective flow has enough time to eliminate agglomeration of most of particles, while the short sintering time advocated in Ref. 3 is relevant above 1300 K only.

As a possible option, convective flow may promote dispersion of bare Al particles. As it was mentioned in Ref. 4 and obtained in phase field simulations,[15] after spallation of the shell the unloading wave may not disperse the Al core but produce a spherical ring. Further dispersion can be caused by a collision with other liquid rings or Al or oxidizer particles, the interaction with gas flow, or a large temperature rise during initiation of the oxidation reaction at the bare surface. In experiments,[1,2] the expanding spherical ring may only move the nearby particle and may not cause dispersion. These are all possible but not mandatory conditions for MDM because, in Ref. 9, results on flash heating are consistent with MDM, but there was not intense convective flow. Thus, in response to statements in Ref. 3, fast moving gases may promote, but are not necessary for, MDM. That is why the implication in Ref. 3 that MDM cannot operate on early stages of combustion is not supported.

6. It is stated in Ref. 3 that "our results clearly show that molten Al can escape its shell and coalesce in <50 ns (Ref. 1)." It is suggested that instead of diffusion through the oxide shell, one has to consider a reaction of bare molten Al with an oxidizer, which may explain the high flame rate. First, in Ref. 1, escape of Al was not proven but was considered as one of the possible mechanisms. In any case, such a short time scale for sintering, independent of the possible mechanism, was not expected and this is indeed a breakthrough result. Coalescence of bare molten Al increases particle size, which is opposite to what MDM does. We believe that, due to oxidation, a new oxide shell of thickness 3–4 nm re-appears shortly. For small dispersed particles, this will require reaction of the major portion of a particle; for a large sintered Al particle, this will produce a core-shell system larger than the initial one, and the problem of diffusion through the oxide shell remains. Thus, the next Al escape is required.

However, our main point against diffusion mechanism versus MDM in the flame tube is not just too long of a time required for diffusion; diffusion coefficients in literature vary by ten orders of magnitude and can be fitted to produce any reaction rate. There is some qualitative data that is inconsistent with the diffusion mechanism, such as the increase (decrease) of the flame rate with increase (decrease) of the shell thickness,[16] reduction in flame rate with increasing mass density of the reactive mixture for nanoparticles and opposite trends for micron scale particles (which cannot react by MDM),[17] suppressing effect of the damage of the shell on flame propagation,[4,16] much smaller particle size after reaction,[9,10] and some other results presented in Refs. 4–6, 10, and 12.

To summarize, we can conclude that the very interesting experimental results in Refs. 1 and 2 do not allow one to eliminate the validity of the MDM. We are glad that, in their Response,[3] the authors of Refs. 1 and 2 agreed that their experiments "cannot and did not disprove melt dispersion." There are still many poorly understood steps and conditions for each of the known mechanisms: diffusion, reactive sintering, and MDM.

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The authors declare no competing financial interest.

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[18]While velocities of 200 m/s are mentioned in Refs. 3–5, these are the maximum velocities of material particles in the melt before dispersion; velocities of the dispersed particles were not estimated in the MDM.
[19]It is written in the supplementary material to Ref. 1 that it is practically impossible to heat Al particles on the silicon nitride substrate to high temperature, i.e., this substrate probably was not used in experiments. At the same time, formvar substrate absorbs light and heats up to 500 K.