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Comment on “Mechanochemical Continuum Modeling of Nanovoid Nucleation and Growth in Reacting Nanoparticles”

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Oxidation of metal nanoparticles is of high interest from very different perspectives. One of the unusual specifics of this process is that it is sometimes accompanied by the formation of hollows (voids) as schematically shown in Figure 1 (reviewed by Fan et al.¹). The understanding of the

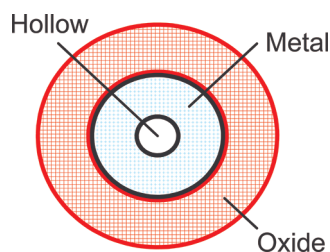


Figure 1. Schematic structure of a metal nanoparticle during oxidation.

mechanism(s) of this phenomenon is still limited. Specifically, the role of the lattice strain remains to be open for debate. The experiments indicate that the oxidation starts on the surface of a particle and results in the formation of an oxide shell. Due to material mismatch and expansion of the shell, the metal core is expected to be under tensile strain. Our analysis² (as well as refs 3 and 4) indicates that this strain may induce or facilitate the formation of a hollow. In a more recent analysis, Levitas and Attariani (LA)⁵ claim that this strain is negligible and focus their attention on the compressive strain related to surface tension. To discredit our work (and ref 3) and validate their model, LA refer to the experiments by Mei et al.⁶ (ref S2 in the quotation):

“... because in our problem the reaction occurs at the surface (rather than in the bulk) and the interface between the metal and oxide is incoherent, internal stresses due to chemical reaction are negligible. For example, an aluminum oxide shell is amorphous below some thickness (4 nm), and thus, the interface is incoherent and does not generate internal stresses. Even for a crystalline shell, for Al particles with $R_c = 20\text{--}40\text{ nm}$ and a shell growing during chemical reaction ..., lattice spacing in Al did not differ from that in the bulk sample;⁵² i.e., internal stresses are negligible.”

Our three comments on the LV work are as follows:

1. As noticed in our Letter,² the formation of hollows in metal nanoparticles is usually observed at mild conditions or, more specifically, at relatively low temperatures. In particular, we mentioned experimental data for six metals. The corresponding temperatures are: 295 K for

Al (Figure 3; ref 7); $\leq 520\text{ K}$ for Fe;⁸ $\leq 455\text{ K}$ ^{9,10} and $\leq 473\text{ K}$ (Figure 1; ref 11) for Co; 573–673 K for Ni (Figures 1 and 2; ref 12); 323–373 K for Cu;^{7,13} and 423 K for Zn (Figure 3; ref 14).

2. Mei et al.⁶ studied oxidation of three Al samples (see their Table 1). The corresponding temperatures and durations of experiments were: (A) 773 K/3 h + 873 K/1 h, (B) 773 K/3 h + 873 K/3 h, and (C) 773 K/3 h + 873 K/6 h. These temperatures are much higher than those in item 1 (especially for Al). Under such high temperatures, the stress could easily relax due to very rapid diffusion. For this reason, the fact that according to ref 6 the Al lattice expansion is negligible is, strictly speaking, irrelevant if one is interested in hollow formation.
3. In their model, LA postulate that the vacancies form a hollow in the center of a nanoparticle. If the oxide shell is amorphous so that the corresponding lattice strain is negligible as assumed by LA, one can wonder why the vacancies do not annihilate on the oxide/metal interface.

In summary, the LA criticism of our work is too categorical because the only reference they present is irrelevant. Their own model does not seem to be self-consistent.

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Notes

The authors declare no competing financial interest.

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