

Reply to "Comment on 'Mechanochemical Continuum Modeling of Nanovoid Nucleation and Growth in Reacting Nanoparticles'"

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The problem of the mechanisms of void nucleation in nanoparticles and related problem of the stresses and their relaxation in nanoparticles are of significant importance and far from being resolved. It is not surprising that there are several approaches with different and, in the given case, opposite assumptions. Thus, in ref 1, surface tension is neglected, and volumetric strain due to oxidation is introduced in the oxide shell. It is stated that for linear lattice mismatch $\alpha \geq 0.3$ large tensile stresses in a metal core are sufficient for void nucleation.

1. Let us estimate radial stress in a metal core required for void nucleation according to eq 14 in ref 1

$$\sigma_{rr} = \frac{2\alpha E}{3(1-\sigma)} \left(1 - \frac{R^3}{R_m^3} \right) \quad (1)$$

where E , σ , R , R_m , and α are the Young modulus, Poisson's ratio, core radius, radius of bare particle, and linear mismatch parameter, respectively. Taking $E = 100$ GPa, $\sigma = 0.3$, and neglecting $(R/R_m)^3$ to get the higher stresses required for nucleation, the authors¹ found that void can nucleate at $\alpha = 0.3$. Substituting these parameters in eq 1, one obtains that the tensile radial stress necessary for void nucleation is $\sigma_{rr} = 28.6$ GPa, which is much above the theoretical strength. For Cu, the change in volume during oxidation is $J = V_{ox}/V_m = (1 + \alpha)^3 = 1.65$, where $\alpha = 0.18$. For one of the Cu particles that we consider in ref 2, the core radius was 9 nm, and the initial shell thickness was 2.5 nm. Since void nucleation occurs at the very initial stage of oxidation, we determine for these parameters that $R = 9$ and $R_m = 10.63$ nm (R_m is obtained based on eq A.5 in the Appendix). Substitution of these values in eq 1 along with $E = 128$ GPa and $\sigma = 0.34$ gives $\sigma_{rr} = 9.15$ GPa, which is 2.93 times smaller than that required for void nucleation. Since stress contributes as a factor of σ_{rr}^{-4} to the activation energy, reduction in σ_{rr} by a factor of 2.93 increases activation energy by a factor of 73.7, which makes nucleation completely unrealistic. For Cu particles with a core radius of 15.9 nm and shell thickness of 2.5 nm in ref 2 ($R = 15.9$ nm, $R_m = 17.48$ nm), the radial stress is 5.76 GPa which increases the activation energy by a factor of 468.65. For Al, $J = 1.25$ and $\alpha = 0.077$, which with $E = 70$ GPa and $\sigma = 0.35$ results in $\sigma_{rr} = 5.53$ GPa even for neglected $(R/R_m)^3$ and increases activation energy by a factor of 551.62.

In addition, the required stress of 28.6 GPa causes volumetric expansion of 0.2. Such an expansion and $\alpha = 0.3$ are significantly above the range of applicability of the linear elasticity theory and eq 1. When elastic nonlinearity is taken into account, one needs even larger α to obtain the same

stresses. And finally, the size of a critical void in ref 1 at $\alpha = 0.3$ is 0.16 nm, which is less than the radius of a vacancy in Cu of 0.199 nm.³ Why does one need all these troubles with unrealistically large tensile stresses, when we just can introduce a single vacancy?

Since one of us recently published a number of papers on nanovoid nucleation under tensile stresses due to fracture, sublimation, sublimation via virtual melting, and evaporation,^{4–6} based on a similar kinetic approach like in ref 1 but with allowing for plasticity, large strains, and surface tension, we also applied a similar approach to void nucleation in reacting nanoparticles, based on more advanced equations than in ref 1. However, due to the above reasons, we decided that this scenario is completely unrealistic. We did not want to discredit ref 1, which is why we did not include our numerical estimates in ref 2, but now we are forced to do this.

2. Does change in volume due to chemical reaction cause large tensile stresses in a core of a nanoparticle and compressive stresses in a shell or do they relax? Note that at the nanoscale diffusion coefficients are much higher; see some data in ref 2. Even at the low temperature mentioned in ref 7, diffusion was fast enough to transport the entire metallic core outside the initial shell. Such fast diffusion at the time scale of oxidation can cause stress relaxation during chemical reaction, similar to that observed in ref 8 at higher temperature.

Traditional technologies for passivation of Al particles consist of holding synthesized bare nanoparticles at room temperature in oxygen or air. Thus, if we include volumetric transformation strain and neglect stress relaxation, the core of all nanoparticles should be under high tensile pressure, estimated by eq 1. Thus, we obtain for Al nanoparticles ($\alpha = 0.077$, $E = 70$ GPa, $\sigma = 0.35$, and $R = 50$ nm) that $\sigma_{rr} = 0.61$ GPa for $R_m = 52$ nm and $\sigma_{rr} = 1.14$ GPa for $R_m = 54$ nm. Such stresses should be easily detected by X-ray; however, in ref 8 lattice parameters at room temperature were the same for bulk Al and nanoparticles with different R and R_m . In ref 9, linear compressive strain of 0.017 was detected, which corresponds to an internal compressive pressure of 3.84 GPa in a core.¹⁰ Also, as was mentioned in ref 10, thermal stresses during heating of particles with different R/R_m should be different (see eq 1 in which α should be substituted with difference in thermal strains of a metal and a core). However, lattice spacing for samples with different M in ref 8 does not show any appreciable difference between room

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temperature and 860 K, which means that internal stresses relax even at low temperature.

Also, one of the methods to increase the reactivity of nanoparticle suggested in refs 11 and 12 was based on the increase in temperature T_0 at which the particle is stress free. It was assumed that for purchased particles $T_0 = 298$ K, because this was their passivation temperature and based on data from ref 8, that lattice spacing for nanoparticles is the same as that of bulk Al. Prestressing was produced by heating particles to several elevated temperatures, holding them at a temperature for 10 min to relax thermal stresses, and cooling them at several rates to room temperature. For the optimal thermal treatment conditions (heating to 378 K and cooling at 0.13 K/s), the flame propagation speed increased by 31% for nanoparticles and 41% for micrometer particles, which was quantitatively consistent with theoretical predictions. Cooling at 0.06 K/s did not change the flame rate, which was explained by the slower cooling rate which allowed thermal stresses to relax during cooling. Change in stress-free temperature T_0 from 298 to 378 K induced at room temperature the thermal tensile radial stress in a core of 0.04 GPa and compressive hoop stress in a shell of 0.74 GPa, which suppressed fracture of the oxide shell, as desired. These results indirectly demonstrate that internal stresses may relax at temperatures as low as in the case for nanovoid nucleation and during a similar time range.

3. The main reason why internal stresses are strongly overestimated when eq 1 is applied is not related to stress relaxation due to diffusion only. The main reason is that the volumetric expansion due to reaction is applied in eq 1 isotropically, i.e., equally in all three directions, considering this transformation strain tensor as a spherical one. In reality, the expansion may occur anisotropically, driven by reduction in internal stresses. Indeed, if the entire expansion in the shell will occur in radial direction, no internal stresses will appear at all. At the macroscale, the anisotropic transformation strain tensor was measured for NiAl and Zr,^{13,14} and the ratio of a strain normal to an interface, ϵ_n , to a strain along the interface, ϵ_v , was $\epsilon_n/\epsilon_t = 87$ and 108. Thus, actual mismatch along the interface is approximately 2 orders of magnitude smaller than α . Similar anisotropic transformation strain was discussed in ref 15 for crystallization of amorphous alumina and in ref 16 for a phase field approach to melting. Later, in ref 17, the kinetic equation was derived that determines the deviatoric part of the transformation strain tensor for melting. We are working on a similar approach for oxidation now. Thus, we do not claim that change in volume due to chemical reaction does not produce internal stresses. However, they are 2 orders of magnitude lower than predicted by eq 1 (or more advanced eqs 40 and 41 in ref 2). That is why it was more accurate to ignore them, when we formulated and solved the problem on nanovoid nucleation and growth, than to introduce them as an isotropic mismatch strain.

4. Concerning our assumption that vacancies form a hollow at the center of a particle, why do vacancies not annihilate at the metal–amorphous oxide interface? An amorphous interface is observed for Al for interface width below 4 nm.¹⁸ For Cu, we did not find references that the interface is amorphous. We stated in ref 2 that while often multiple voids nucleate near the core/shell interface^{19,20} we placed the void at the center to obtain a simple, one-dimensional model, similar to all previous works. Very little is known about the structure of the metal–amorphous oxide interface for a nanoparticle during oxidation to claim that it serves as a sink for vacancies. In molecular

dynamic simulations²¹ for Ni–Zr core–shell structure, vacancies nucleated at the incoherent Ni–Zr interface then diffused into the core and formed a void. Due to mixing, the Ni–Zr shell undergoes amorphization, which does not prevent void growth due to generation of new vacancies. Thus, we do not see why the assumption that in some cases the shell is amorphous and interface is incoherent would make our model not self-consistent.

■ APPENDIX

To make an estimate of the stress according to eq 1, we need to determine the initial radius R_m of a bare particle that transforms to the core–shell structure with the prescribed oxide shell thickness t and corresponding volume $V_{ox} = 4\pi/3 ((R + t)^3 - R^3)$. This can be done by utilizing the mass balance. For the oxide shell with a volume V_{ox} and mass density ρ_{ox} , the oxide mass, m_{ox} , is

$$m_{ox} = n_m M_m + \frac{y}{x} n_m M_O = \rho_{ox} V_{ox} \quad (\text{A.1})$$

where n_m is the number of moles of a metal; M_m and M_O are the molar masses of a metal and oxygen; and y and x are the stoichiometric coefficients of an oxide M_xO_y . From eq A.1, the number of moles of metal in the oxide shell can be calculated as

$$n_m = \rho_{ox} V_{ox} / \left(M_m + \frac{y}{x} M_O \right) \quad (\text{A.2})$$

Therefore, the volume of the reacted metal, V_r , that produced volume of an oxide V_{ox} is

$$V_r = \frac{n_m M_m}{\rho_m} = \frac{\rho_{ox} M_m V_{ox}}{\rho_m \left(M_m + \frac{y}{x} M_O \right)} \quad (\text{A.3})$$

where ρ_m is the mass density of a metal. For a spherical particle, V_r can be written as

$$V_r = \frac{4\pi}{3} (R_m^3 - R^3) \quad (\text{A.4})$$

By equating eqs A.3 and A.4, the radius of the bare nanoparticle is

$$R_m = \left(\frac{3\rho_{ox} M_m V_{ox}}{4\pi\rho_m \left(M_m + \frac{y}{x} M_O \right)} + R^3 \right)^{1/3} \quad (\text{A.5})$$

In calculations, we used $M_m = 63.55$ g/mol, $M_O = 16$ g/mol, $\rho_m = 8.94$ g/cm³, $\rho_{ox} = 6$ g/cm³, $x = 2$, and $y = 1$.

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Notes

The authors declare no competing financial interest.

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