

Supplementary information

A. Description of the force field used in the oxidation simulations

The details of the potential function utilized in this work as well as the MD simulation details of the oxidation process are discussed here. The MD simulation technique utilized in the present work is based on the modified charge transfer potential model developed by Zhou et al.^{1, 2} The interaction potential is divided into an electrostatic contribution (E_{es}) for ionic interactions and a non-electrostatic energy (E_m) based on the alloy embedded atom method to model metal interactions.

$$E_t = E_{es} + E_m \quad (1)$$

The modified charge transfer potential model imposes charge bounds on the metal and gas atoms and prevents the atoms from exceeding their valence charges, thereby overcoming the limitations of the original Streitz-Mintmire potential³. The electrostatic energy used in the modified CTIP model is given below²:

$$E_{es} = E_0 + \sum_{i=1}^N q_i X_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N q_i q_j V_{ij} + \sum_{i=1}^N \omega \left(1 - \frac{q_i - q_{min,i}}{|q_i - q_{min,i}|} \right) (q_i - q_{min,i})^2 + \sum_{i=1}^N \omega \left(1 - \frac{q_{max,i} - q_i}{|q_i - q_{max,i}|} \right) (q_i - q_{max,i})^2 \quad (2)$$

where $q_{min,i}$ and $q_{max,i}$ are the charge bounds of atom i , $q_{min,i} < q_i < q_{max,i}$. The coefficient ω corresponds to the energy penalty for the metal atoms to gain electrons or lose inner shell electrons or for the oxygen atoms to lose electrons or receive more than two electrons. X_i and V_{ij} are terms representing the self energy and Coulomb interaction, respectively³.

$$X_i = \chi_i + \sum_{j=i_1}^{i_N} k_c Z_j \left([j|f_i] - [f_i|f_j] \right) \quad (3)$$

$$V_{ij} = J_i \delta_{ij} + \sum_{k=j(i_i)}^{j(i_N)} k_c Z_j (|f_i|f_k) \quad (4)$$

In the above equations, χ_i and J_i refer to the electro-negativity and atomic hardness (or self Coulomb repulsion), respectively. The expressions for Coulomb integrals such as $[a|f_b]$ and $[f_a|f_b]$ calculated based on the assumption of atomic charge density distribution for spherical Slater-type orbitals are given below³:

$$[a|f_b] = \frac{1}{r_{ab}} - \xi_b \exp(-2\xi_b r_{ab}) - \frac{1}{r_{ab}} \exp(-2\xi_b r_{ab}) \quad (5)$$

$$\text{For } \xi = \xi_a = \xi_b, [f_a|f_b] = \frac{1}{r_{ab}} \left[1 - \left(1 + \frac{11}{8} \xi r_{ab} + \frac{3}{4} \xi^2 r_{ab}^2 + \frac{1}{6} \xi^3 r_{ab}^3 \right) \right] \exp(-2\xi r_{ab}) \quad (6)$$

$$\begin{aligned} \text{For } \xi_a \neq \xi_b, [f_a|f_b] = & \frac{1}{r_{ab}} - \frac{\xi_a \xi_b^4 \exp(-2\xi_a r_{ab})}{(\xi_a + \xi_b)^2 (\xi_a - \xi_b)^2} - \frac{\xi_b \xi_a^4 \exp(-2\xi_b r_{ab})}{(\xi_a + \xi_b)^2 (\xi_a - \xi_b)^2} \\ & - \frac{(3\xi_a^2 \xi_b^4 - \xi_b^6) \exp(-2\xi_a r_{ab})}{r_{ab} (\xi_a + \xi_b)^3 (\xi_a - \xi_b)^3} - \frac{(3\xi_b^2 \xi_a^4 - \xi_a^6) \exp(-2\xi_b r_{ab})}{r_{ab} (\xi_a + \xi_b)^3 (\xi_b - \xi_a)^3} \end{aligned} \quad (7)$$

Here $a=i,j$, $b=i,j$ and $a \neq b$. The charge parameters χ_i , J_i , ξ and Z_i as well as the charge bounds for the various elements are listed in Table 1.

Table 1. CTIP parameters for the simulated elements (based on Zhou et al. Ref (4))

Element	q_{\min}	q_{\max}	χ (eV)	J (eV)	$\xi(\text{\AA}^{-1})$	$Z(e)$
O	-2	0	2.00000	14.99523	0.00000	0 2.144
Al	0	3	1.47914	9.07222	0.968	1.07514
Ni	0	2	-1.70804	9.10954	1.087	1.44450

The non-electrostatic interactions which occur between the metal atoms can be modeled using the embedded atom method (EAM). The non-electrostatic energy is expressed as⁵:

$$E_m = \frac{1}{2} \sum_{i=1}^N \sum_{j=i_1}^{i_N} \phi_{ij}(r_{ij}) + \sum_{i=1}^N F_i(\rho_i) \quad (8)$$

Where $\phi_{ij}(r_{ij})$ represents the pair-wise interaction energy between atoms i and j separated by distance r_{ij} . The generalized elemental pair potentials for the alloy systems are written as^{1,2}:

$$\phi(r) = \frac{A \exp\left[-\alpha\left(\frac{r}{r_e} - 1\right)\right]}{1 + \left(\frac{r}{r_e} - \kappa\right)^{20}} - \frac{B \exp\left[-\beta\left(\frac{r}{r_e} - 1\right)\right]}{1 + \left(\frac{r}{r_e} - \lambda\right)^{20}} \quad (9)$$

F_i represents the embedding energy to embed an atom i into a local site with electron density ρ_i which can be calculated using⁵:

$$\rho_i = \sum_{i=1}^N f_i(r_{ij}) \quad (10)$$

In the above expression, $f_j(r_{ij})$ represents the electron density at the site of atom i arising from atom j at a distance r_{ij} away. The functional form of the electron density is taken similar to the attractive term in the pair potential expression with same values of β and λ ²:

$$f(r) = \frac{f_e \exp\left(-\beta\left(\frac{r}{r_e} - 1\right)\right)}{1 + \left(\frac{r}{r_e} - \lambda\right)^{20}} \quad (11)$$

The embedding energy functions F are chosen to work well over a wide range of electron density. For a smooth variation of the embedding energy, they are fitted to spline functions across different density ranges. The various fitted parameters used in the embedded atom model are listed in Tables 2-4.

Table 2. EAM parameters for metal-metal interaction(based on Zhou et al. Ref⁽¹⁾)

Metal	$r_e(\text{\AA})$	f_e	ρ_e	ρ_s	A	B	A (eV)
Al	2.86392	1.20378	17.51747	19.90041	6.61317	3.52702	0.31487
Ni	2.48875	2.21149	30.37003	30.37137	8.38345	4.47117	0.42905

Metal	$F_0(\text{eV})$	$F_1(\text{eV})$	$F_2(\text{eV})$	$F_{3+}(\text{eV})$	$F_{3-}(\text{eV})$	$\eta(\text{eV})$	$F_0(\text{eV})$
Al	-2.83	0.0	0.62225	-2.48824	-2.48824	0.78591	-2.82453
Ni	-2.70	0.0	0.26539	-0.15286	4.58568	1.01318	-2.70839

Metal	$B(\text{eV})$	κ	Λ	$F_{n0}(\text{eV})$	$F_{n1}(\text{eV})$	$F_{n2}(\text{eV})$	$F_{n3}(\text{eV})$
Al	0.36555	0.37985	0.75969	-2.80760	-0.30144	1.25856	-1.24760
Ni	0.63353	0.44360	0.82066	-2.69351	-0.07644	0.24144	-2.37563

Table 3. EAM parameters for some pair potentials (based on Zhou et al. Ref⁽¹⁾)

Pair	$r_e(\text{\AA})$	α	β	A (eV)	B (eV)	K	λ
O-Al	2.98520	8.49741	4.52114	0.09738	0.38121	0.18967	0.95234
O-O	3.64857	5.44072	3.59746	0.34900	0.57438	0.08007	0.39310
O-Ni	2.95732	7.96528	4.42411	0.13521	0.25332	0.47077	0.65524
Ni-Al	2.71579	8.00443	4.75970	0.44254	0.68349	0.63279	0.81777

Table 4. EAM parameters for oxygen embedding energy spline function (based on Zhou et al. Ref (1))

i	$F_{0,i}(eV)$	$F_{1,i}(eV)$	$F_{2,i}(eV)$	$F_{3,i}(eV)$	$\rho_{e,i}$	$\rho_{\min,i}$	$\rho_{\max,i}$
0	-1.56489	-1.39123	1.77199	1.59833	54.62910	0	54.62910
1	-1.58967	1.30636	9.81033	0.00000	54.62910	54.62910	∞

B. Set-up of the oxidation simulations

The minimum energy configurations obtained using the Monte-Carlo simulations are first equilibrated at room temperature. The equilibration run for each alloy configuration comprised of 100000 equilibration steps ignoring the dynamic charge transfer between the metal atoms. The temperature was maintained constant at 300 K using a Nose-Hoover thermostat⁶. The particles are allowed to freely relax during these equilibration runs. The equilibrated samples are then simulated in a NVT ensemble for 1 ps with dynamic charge transfer using the modified CTIP potential model to generate the final 300 K relaxed configuration. The atomic charges in the alloy metal samples were found to fluctuate around zero with a magnitude of $\pm 0.06e$ at the outermost layers and $\pm 0.02e$ in the bulk alloy. Similar charge fluctuation was observed in the simulations of Hasnaoui *et al*⁷.

The oxidation of the alloy nanoparticles is initiated by introducing O₂ molecules in the vacuum with their radial positions chosen randomly (Fig. S1). The velocities of the O₂ are chosen from a Maxwell-Boltzmann distribution corresponding to the required temperature. Additionally, spherical reflecting boundary conditions are imposed to the molecules that might reach the simulation box limit. The gas pressure is maintained constant during the simulation by introducing a new O₂

molecule only when the previous molecule dissociates and forms bonds with the metal atoms. The equations of motion are integrated using a leapfrog scheme with time steps of 1fs.⁸ The charge relaxation procedure used to minimize the electrostatic energy subject to the electro-neutrality principle is very time consuming. Hence, the atomic charges were updated every 10th MD step. The influence of a more frequent charge update was found to have no influence on the observed simulation results.

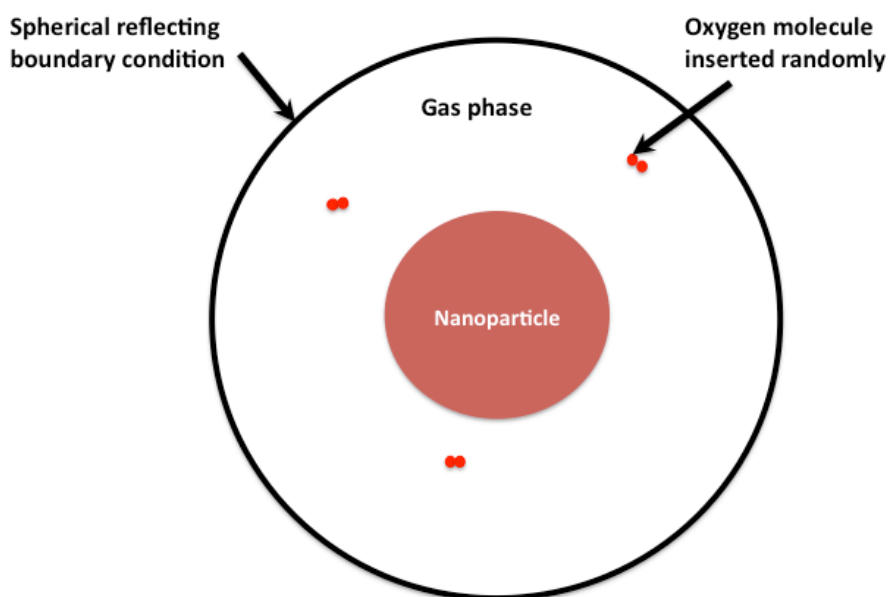


Figure S1: Schematic showing the simulation cell of alloy nanoparticle and the vacuum surrounding it. The nanoparticle of radius R is at the center of the simulation cell. A spherical reflecting wall located at $2.5 \cdot R$ holds the gas phase oxygen atoms.

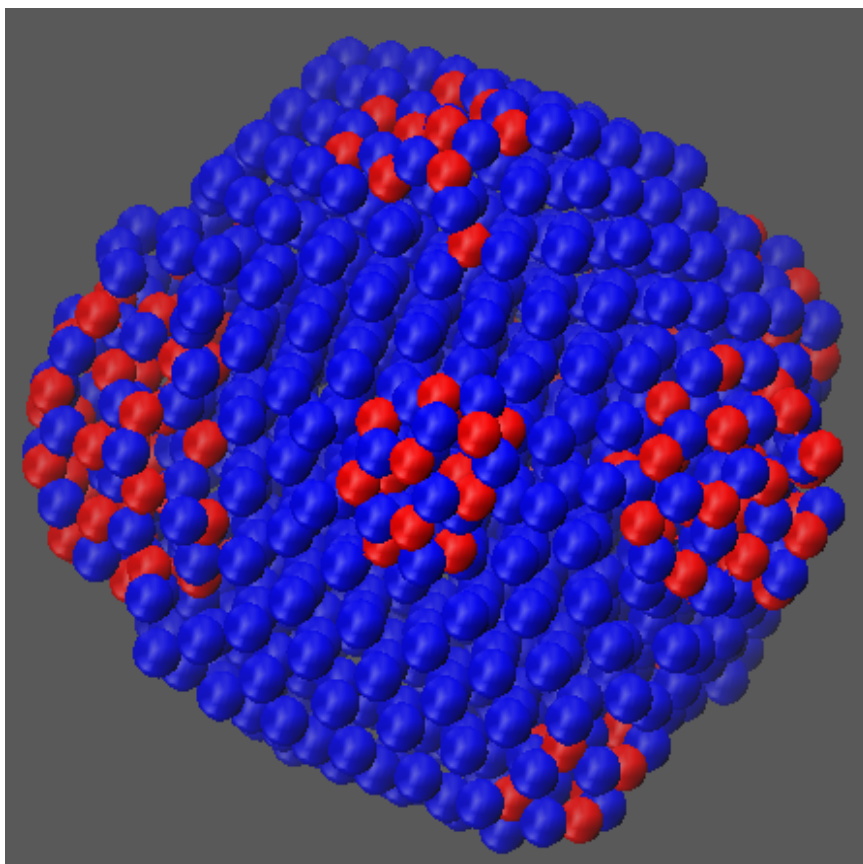


Figure S2: Snapshots showing oxidation of Ni nanocluster at room temperature and 2 O₂ molecules gas pressure.

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