

Phase field modeling of oxidation

In the previous phase-field model, molar fraction was considered as the conserved parameter to track the composition of materials in the Iron/Oxygen system. Although results based on this model was in good agreement with the molar fraction of the FeO oxide, they were not suitable to explain the real physical problem. In reality, even though the composition (molar fraction) of oxygen in the fluid phase remains the same, the amount of Oxygen and thus the molar concentration of Oxygen in the fluid phase is reduced as Oxygen is consumed to form the oxide. To address this problem, phase-field model equations were modified such that molar concentration is the conserved parameter. One problem utilizing this model is the huge difference between molar volumes of Iron and Oxygen, such that for oxidation of one volume unit of Iron approximately 1,000 volume unit of Oxygen is required which needs huge simulation domain size. Thus, without the loss of generality, we defined an artificial molar volumes for Fe and O such that they have one order of magnitude difference and the mobilities and other simulation parameters were updated accordingly. Simulation results for this modified model has been depicted in the Figure 1. As the Oxygen is consumed by the Iron to form oxide, the Oxygen concentration drops in the air phase while the concentrations remains constant in other phases which is very close to the real case. Furthermore, the oxide layer growth is more internally than externally which is also in more agreement with cases observed in experiments. Additionally, the oxide layer growth rates were compared considering two cases of with and without elastic energy and the growth rate trend showed good agreement with other trends reported in experimental and simulated results. We are working on making this model multi-phase and multi-component to include various oxide phases of alloying elements such as Fe_2O_3 , SiO_2 , MnO.

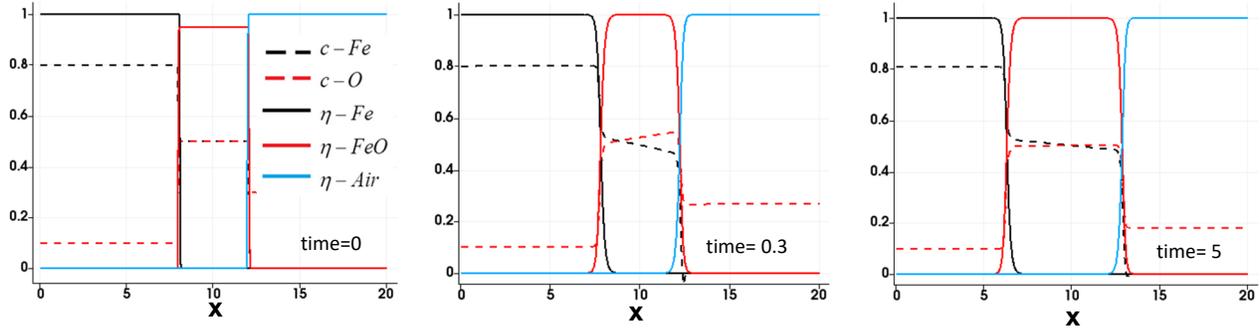


Figure 1. Formation and evolution of the oxide phase (FeO) considering molar concentration as the conserved variable.

Atomistic simulations of oxidation of nanowires under tension

The ReaxFF potential was implemented in our molecular dynamics (MD) simulation as initial stage of studying effect of oxidation on plastic deformation of single crystal iron nanowires (NW) under tensile load. The potential was changed from MEAM to ReaxFF because it can accurately predict creation and breakage of bonds and complex chemical reactions in addition to predict the nucleation and propagation of crystalline defects such as dislocations and twins in metallic materials. Initially, the pure Fe NWs were placed in the middle of the simulation box and oxygen molecules were randomly distributed above the Fe NWs. Then, a Berendsen thermostat with separate velocity rescaling factors for oxygen and iron atoms was applied to keep the temperature of the system at 300 K. Velocity rescaling constraints were performed to prevent the translational and the angular movement of the substrate, conserving the total kinetic energy of the iron atoms. After completing the oxidation simulations and obtaining the desired oxide layer thicknesses, the conjugate gradient method is used to minimize the potential energy of the models. In tensile deformation step, 16% strain was obtained by applying uniaxial strain rate of $0.01\% \text{ ps}^{-1}$ in the Z-direction and the virial definition of stress by averaging over all components of atomic stresses is used to obtain the engineering stress-strain curve. MD oxidation simulation showed that oxygen and iron atoms diffuse inward and outward of the oxide shell, respectively, leading to the formation of Fe_2O_3 in the outer region and FeO and Fe_3O_4 in the inner region of the oxide shell layer. This results in the formation of voids and crystal irregularities on the surface of NW, leading to stress concentration on the surface and promoting dislocation nucleation. In addition, Radial Distribution Function (RDF) analysis was performed to examine the crystal structure of oxide shell (Figure 2). For a range of atomic distance between 1 Å and 2 Å, the Fe-O bond length has a peak located at ~ 1.6 Å and a relatively smaller peak located at ~ 1.7 Å. Previous studies reported peak locations at ~ 1.65 Å, ~ 1.7 Å, and ~ 2.0 Å, corresponding to FeO, Fe_2O_3 , and Fe_3O_4 , respectively. This means the crystal structure of oxide shell in our work is a combination of FeO and Fe_2O_3 , which is in a great agreement with the previous studies.

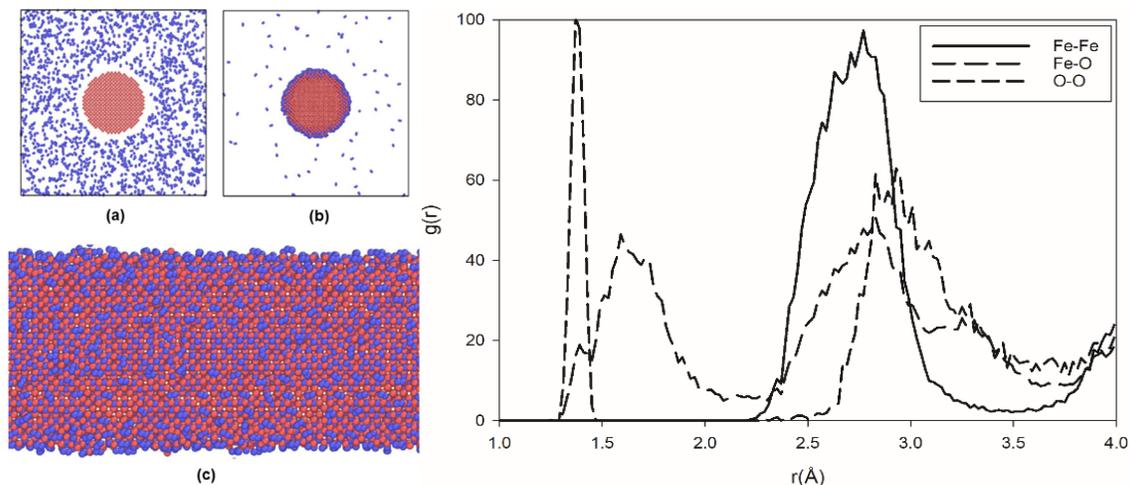


Figure 2. Atomic configuration of the oxide-coated Fe NW for a model with cylinder axis oriented along $\langle 100 \rangle$: (a) top view at $t=0$ (b) top view at $t=3$ ns (c) side view at $t=3$ ns. RDF analysis of oxide shell for model with cylinder axis oriented along $\langle 100 \rangle$ is on the right side.

Electronic scale calculations of oxidation on three different surfaces

As the first step of oxidation, adsorption behavior of oxygen on the surface of $\text{Al}_{0.3}\text{CoCrCuFeNi}$ was studied. First principle calculations were executed based on the density functional theory (DFT), and performed using Vienna Ab initio Simulation Package (VASP). The core electrons were treated using projected augmented wave (PAW) pseudopotentials. Surfaces from three different direction [001], [110], [111] of $\text{Al}_{0.3}\text{CoCrCuFeNi}$ were considered to determine the orientation effect of oxidation. With the DFT calculation, it was found that for [001] and [110] surface, oxygen atom was adsorbed at 4 site hollow, which has 4 neighbor atoms around. While for [111] surface, oxygen was adsorbed at 3 site hollow. From our analysis, the adsorption energy was determined by the neighboring atoms. All possible combinations were simulated in this study. Adsorption energy of oxygen on these surfaces has consistent pattern as shown in Figure 3. Oxygen atom is more attempt to adsorb on the position with more Cr and Al atoms around, which may be able to explain the promising oxidation resistance of this alloy. Because as we know, Cr and Al oxides are easily to form passive layer, which can resist the further oxidation.

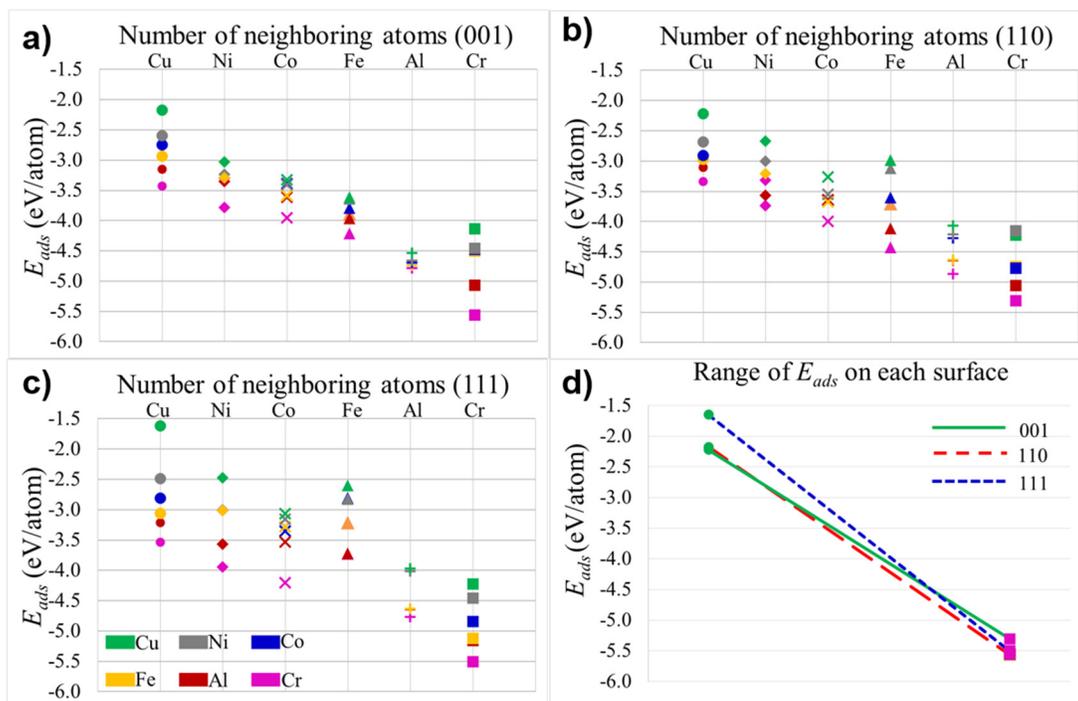


Figure 3. Adsorption energy of oxygen on three surfaces. Same mark shape means the neighboring atoms combined with one kind of main atom, which means 3 and more atoms showed on x axis, and one other atom, distinguished by color. a) Surface [001]. b) Surface [110]. c). Surface [111]. d) Total range of adsorption energy on each surface.