

Response letter:

Dear Prof. Misra, Prof. Kioupakis, Prof. Gao, and Prof. Qi,

Thank you for all your comments and suggestions. They are really helpful. I have made changes to my thesis. Beside typographical and stylistic corrections, the following changes have been made to respond to your kind comments and suggestions:

1. For Prof. Misra's comment about "how does anchor sites on ZnO substrates change the interfacial separation energies between Ag/ZnO?" (rephrased):

Thank you for your comment! We don't expect a great change of Ag/ZnO interfacial energies globally because the number of anchor sites is limited. But the anchor sites might increase the interfacial energies locally. The mechanisms of anchor sites to increase Ag wettability are from two aspects: 1) the increase of adsorption energies of individual Ag atoms on ZnO saturated surfaces; 2) the increase of Ag surface diffusion barriers. The corresponding changes in the thesis are highlighted on Page 58 highlighted in red color.

2. For Prof. Misra's comment about estimating the effects of different concentration of alloying elements on impeding Mg corrosion rate.

Thank you for your suggestion! The concentration effects of alloying elements can be addressed in three steps. First, the stability of alloying elements when their surface coverage is increased needs to be investigated based on DFT calculations. Second, the H adsorption energies on surfaces with different surface concentrations of alloy elements will be calculated. Third, the exchange current for hydrogen evolution reactions on surfaces with different concentrations of alloy elements can be estimated based on the H adsorption energies and the kinetics model of HER (References: [1] [J. Nørskov et al 2005 J. Electrochem. Soc. 152 J23](#) and [2] [J. Greeley et al Nature materials. 2006 Nov;5\(11\):909-13](#)). The corresponding changes in the thesis are highlighted on Page 97 highlighted in red color.

3. For Prof. Kioupakis's comment about "using pretrained neural network model to study vacancy migration barriers in a more statistic way." (rephrased):

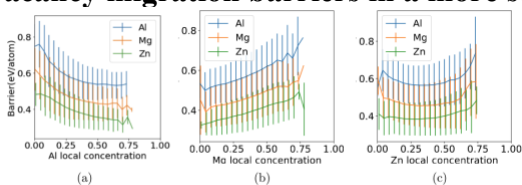


Figure 6.15: Vacancy migration barrier changes vs. different local environment concentrations. Vacancy migration barriers of a vacancy jumping to its adjacent lattice site that is occupied by Al, Mg, or Zn for different local environments are plotted. (a), (b), and (c) are local environments with concentration change of Al, Mg, and Zn, respectively. 500,000 different local environments are used to calculate this vacancy migration barrier distribution by a pre-trained neural network model. Blue, orange, and green lines are the migration barriers for a vacancy jumping to adjacent Al, Mg, and Zn, respectively. The X-axis is the local concentration of Al, Mg, and Zn defined by the lattice occupations on the first and second-nearest neighbors of the vacancy sites. The vertical line is the corresponding error bars. Concentration values of Mg and Zn are shifted by 0.001 to avoid error bars overlapping.

Thank you for your comment! Using this method, vacancy migration barriers can be studied under different amounts of local concentration change more systematically. As shown in Figure 6.15, we plotted vacancy migration barriers of a vacancy jumping to its adjacent lattice site that is occupied by Al, Mg, or Zn for different local environments. We take advantage of our pre-trained neural network model to randomly sample 500,000 different local environments. We found when Al local concentration is very low in Figure 6.15 (a), Zn and Mg mobility is much higher than Al since the migration barriers of the vacancy jumping to the adjacent Zn and Mg atoms are always lower than their counterpart for Al atoms. A local environment with very low Al concentration usually means Mg/Zn atoms are enriched. Highly mobile Zn and Mg atoms might provide the opportunity for Zn and Mg atoms to reorganize and form stable clusters under low Al concentration. In addition, lower barriers of the vacancy jumping to Zn compared with their counterparts of Mg could result in the slightly Zn-rich clusters during the early stage of clustering. As shown in Fig. 6.15 (b) and (c), the migration barriers of the vacancy jumping to the adjacent Zn, Mg, and Al atoms always rank in the order of $Zn < Mg < Al$ regardless of the local concentration, further suggesting the tendencies of high mobility of Zn atoms and the formation of Zn-rich clusters. Corresponding changes have been made on Page 133 and 134 highlighted in red color.

4. For Prof. Gao's comment "In multiscale simulations of Ag film quality during sputtering by changing substrate structures and chemistry, a simple L-J potential is used to describe different bonding strength of Ag-substrate atoms and substrate-substrate atoms. The comments on how accurate this potential is may be helpful."

Thank you for pointing it out! I should not neglect this benchmark calculation in my previous thesis. We tune our L-J potential so that the adsorption strength of Ag on the substrate is equivalent to the Ag adsorption energy on ZnO surfaces that is fully saturated by $\frac{1}{2}$ ML H based on DFT calculations. A plot of the most stable Ag adsorption site was added in Figure 4.2 on Page 41. The corresponding discussions have been also added on Page 42.

5. For Prof. Gao's second comment: "In the summary, it seems that Chapter VI summarizes the methods to study simulate the solute clustering kinetics in Al 7000 series alloys. It could be nice to summarize what we have really learnt from these simulations."

Thank you for your suggestion! We can learn the following from our neural network model and kinetic Monte Carlo simulation: 1) during the early stage of clustering, Zn-rich clusters appear first, and these clusters become stable very soon, only after 3 seconds; 2) for early-stage clusters, Zn/Mg ratio is converged to 1.2, which is consistent with experimental observations; 3) one possible reason for slightly Zn-rich early-stage clusters is the migration barriers for the vacancy to jump to the adjacent Zn atom is lower than their counterparts for Mg or Al. The corresponding conclusion has been added on Page 147 and 151.

Thank all my committee members again for your insightful suggestions and comments to make my thesis more sound and solid.

Yours Sincerely,
Mingfei Zhang