



Modelling Segregation of Transition Metals in the (111) Surface of Platinum Using DFT

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Surface segregation of an alloy is the enrichment of the surface with one of the components in comparison to the bulk concentration. Surface segregation phenomenon in materials significantly influences material properties. In this project the segregation of Gold, Nickel, Rhodium, Ruthenium, and Palladium in (111) surface fcc Platinum were modeled using DFT by comparing only the total free energies of the surfaces with the solute atom B on host atom A at different λ th layer. The results show that Gold segregates in Platinum. Nickel, Rhodium, and Ruthenium antisegregate in Platinum. Palladium neither segregates nor antisegregates in Platinum. The current results match the results of the predicted segregate behavior from previous calculations by Ruban, et. al. (2009). The segregation behavior of a solute atom seems to be correlated to the size of its Wigner–Seitz radius relative to the host atom. Verifying this correlation is beyond the scope of this project but can be investigated in future works.

1. Introduction

Surface segregation of an alloy is the enrichment of the surface with one of the components in comparison to the bulk concentration [1]. The surface segregation process in alloy materials normally causes their chemical composition in the surface region to differ from their bulk composition. Thus, the surface segregation phenomenon in materials significantly influences material properties such as adsorption, wetting, oxidation, corrosion, electrical contact, friction and wear, crystal growth, and catalysis [2].

The paper of Ruban, et. al. in 2009, provided a way to characterize the trends of the surface segregation phenomena in transition metal alloys [3]. In that paper, the segregation energy is calculated using the formula:

$$E_{segr-\lambda}^B = \left. \frac{dE_{surf}(A_{1-c_\lambda}B_{c_\lambda})}{dc_\lambda} \right|_{c_\lambda=0} \quad (1.1)$$

where $E_{surf}(A_{1-c_\lambda}B_{c_\lambda})$ is the surface energy of a system which consists of an alloy of host atom A and solute atom B embedded in the λ th layer of an otherwise pure host atom A and given by the formula:

$$E_{surf}(A_{1-c_\lambda}B_{c_\lambda}) = \sum_{\lambda} (E_{\lambda} - E_{bulk}) - \mu c_\lambda \quad (1.2)$$

E_{λ} is the total energy per atom of the λ 'th layer, E_{bulk} is the total energy per atom of the host, and μ is the effective chemical potential of the solute atom B atom in the host atom A, which is defined as:

$$\mu = \left. \frac{dE_{bulk}(A_{1-c}B_c)}{dc} \right|_{c=0} \quad (1.3)$$

In this convention, having a segregation energy of less than -0.05 eV denotes a segregation of solute atom B (solute atom B goes to the surface of host atom A), a segregation energy of -0.05 to 0.05 eV denotes no segregation, and a segregation energy greater than 0.05 eV denotes an antisegregation of solute atom B (solute atom B goes to the subsurface of host atom A).

Using equations 1.1 to 1.3 would require the calculation of the surfaces energies with the solute atom B on host atom A at different λ th layer as well as the bulk energies of solute atom B on host atom A at different λ 'th layer, which would take some computation time.

A faster method might be to just calculate the surfaces energies with the solute atom B on host atom A at different λ th layer and see which has the most negative total free energy. A more negative total free energy denotes a more stable configuration and solute atom B should naturally segregate to layer with the most stable configuration.

For this project the segregation of Gold, Nickel, Rhodium, Ruthenium, and Palladium in (111) surface fcc Platinum were modeled using Density Functional Theory (DFT).

A (111) surface of fcc Platinum was created (Figure 1 a) and the total free energy of the surface was calculated to provide a baseline. A single atom on a given layer the (111) fcc Platinum was replaced with a given solute atom and the total free energy of the new alloy was calculated. This was done with the solute atom at the 1st (Figure 1 b), 2nd (Figure 1 c), and 3rd layer (Figure 1 d).

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The calculations were done in a periodic structure so the 4th and 5th layer is just equal to the 1st and 2nd layer respectively.

The calculated total free energy of the 1st layer is used as a baseline and subtracted from the calculated total free energy of each layer.

$$E_{\lambda,diff} = E_{\lambda} - E_{1st} \quad (1.4)$$

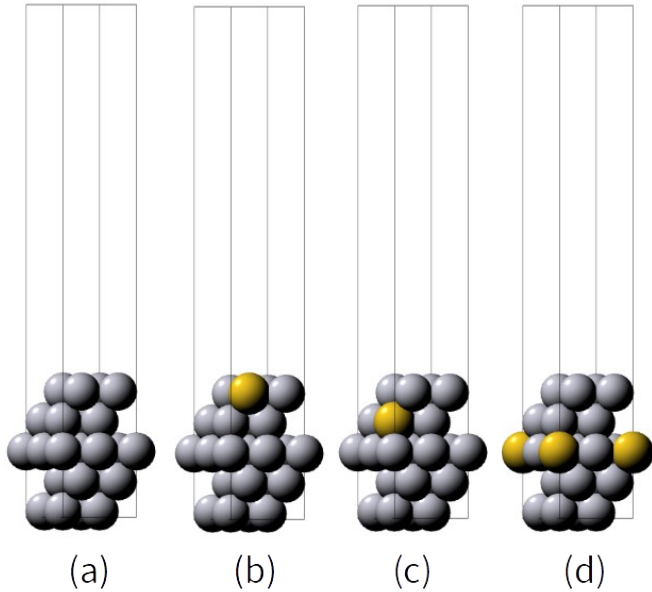


Figure 1: (a) Pure (111) surface fcc Platinum and (111) surface fcc Platinum with solute atom at the (b) 1st, (c) 2nd, and 3rd layer

In this convention, $E_{\lambda,diff}$ will always be 0 for pure Platinum at all layers and 0 for all solute atoms at the 1st layer. The $E_{\lambda,diff}$ for the 2nd and 3rd layer give different values. A positive value of $E_{\lambda,diff}$ for the 2nd and 3rd layer means the 1st layer has the most negative total free energy and is the most stable configuration so the solute should segregate to the 1st layer or the surface. A negative value of $E_{\lambda,diff}$ for the 2nd and 3rd layer means the lower layers have a more negative total free energy and is the more stable configuration so the solute should antisegregate to the 2nd and 3rd layer or the subsurface. A value of $E_{\lambda,diff}$ for the 2nd and 3rd layer close to 0 means total free energy of all the surfaces are close to each other and the solute is stable at all layers so the solute will neither segregate nor antisegregate.

The DFT calculations were implemented using Quantum Espresso.

2. Results and Discussion

Table 1 shows the calculated total free energy for the surface of a given solute at a given layer.

Table 1: Total free energy of the surface mixed with a given solute at a given layer

Solute	Total Free Energy (Rydberg)		
	1st Layer	2nd Layer	3rd Layer
No Solute (Pure Pt)	-14945.55	-14945.55	-14945.55
Au	-14973.40	-14973.37	-14973.37
Ru	-14629.87	-14629.91	-14629.91
Rh	-14668.40	-14668.42	-14668.42
Ni	-14383.94	-14383.98	-14383.97
Pd	-14529.33	-14529.34	-14529.33

From these values the $E_{\lambda,diff}$ for each solute at a given layer was calculated. Table 2 shows the $E_{\lambda,diff}$ calculated for each solute at a given layer and Figure 2 shows the comparison graph for the $E_{\lambda,diff}$ values.

Table 2: $E_{\lambda,diff}$ for a given solute at a given layer

Solute	$E_{\lambda,diff}$ (Rydberg)		
	1st Layer	2nd Layer	3rd Layer
No Solute (Pure Pt)	0.000	0.000	0.000
Au	0.000	0.021	0.028
Ru	0.000	-0.041	-0.043
Rh	0.000	-0.023	-0.023
Ni	0.000	-0.035	-0.029
Pd	0.000	-0.006	-0.001

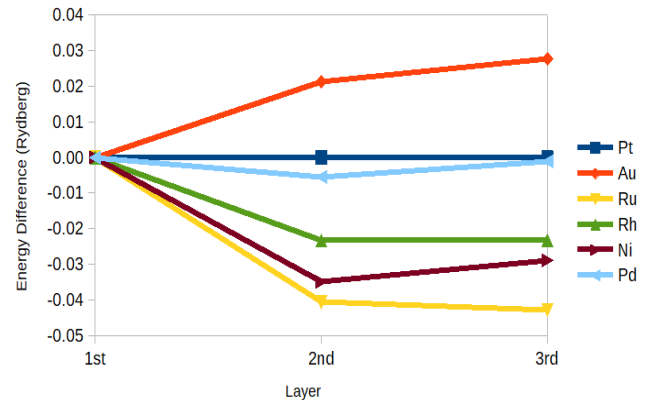


Figure 2: Comparison graph for the $E_{\lambda,diff}$ values for different solute atoms at different layers

The results show that Gold is more stable at the 1st layer and should segregate in Platinum. Nickel, Rhodium, and Ruthenium are more stable at either the 2nd or 3rd layer and it should antisegregate in Platinum. Palladium is just as stable at the 1st, 2nd, and 3rd layer and it should neither segregate nor antisegregate in Platinum

Table 3 shows the previous DFT calculations by Ruban, et. al. (2009) [3].

Table 3: Calculated segregation energy and interpretation by Ruban, et. al. (2009)

Solute	Segregation Energy in Pt (eV)	Interpretation
No Solute (Pure Pt)	0.00	No Segregation
Ni	0.43	Strong Antisegregation
Ru	0.60	Strong Antisegregation
Rh	0.26	Moderate Antisegregation
Au	-0.36	Strong Segregation
Pd	0.00	No Segregation

Table 4: Segregation behaviour in Pt and Wigner–Seitz radius of certain elements [4]

Element	Segregation Behavior in Pt	Wigner–Seitz Radius (Bohr)
Ni	Strong Antisegregation	2.60
Ru	Strong Antisegregation	2.80
Rh	Moderate Antisegregation	2.81
Pd	No Segregation	2.84
Pt	No Segregation	2.90
Au	Strong Segregation	3.01

The current results match the results of the predicted segregate behavior from the previous calculations. Gold segregates in Platinum. Nickel, Rhodium, and Ruthenium antisegregate in Platinum. Palladium neither segregates nor antisegregates in Platinum.

Intuitively the behavior of segregation would be affected by the size of the atoms and the number of valence electrons. A structure that is compressed requires more energy to maintain and results in a less stable configuration. The size of the atoms and the number of valence electrons would affect how much compression a structure experiences.

A solute atom with a larger lattice constant will be compressed if placed in a host that is composed of atoms with a smaller lattice constant. A larger solute atom will experience more compression in the subsurface compared to being in the surface so it will naturally segregate to the surface. A solute atom with a smaller lattice constant will reduce the compression around it if placed in a host that is composed of atoms with a larger lattice constant. A smaller solute atom will reduce more compression in the subsurface compared to being in the surface so it will naturally antisegregate to the subsurface.

A solute atom with a more filled up valence electron will exert more repelling force on other atoms so it would naturally segregate to the surfaces where there is less number of atoms to repel.

From this it would seem that the Wigner–Seitz radius would give an idea if the a given solute atom would segregate or antisegregate in a given host atom. Wigner–Seitz radius is the radius of a sphere whose volume is equal to the volume per a free electron. Table 4 shows the segregation behavior in Platinum of the elements used in this project along with their Wigner–Seitz radii.

It would seem that the solute atom would experience lesser segregation the closer its Wigner–Seitz radius is to the host atom. It also suggests that if the solute atom has a larger Wigner–Seitz radius than the host atom, then it will segregate. If the solute atom has a smaller Wigner–Seitz radius than the host atom, then it will antisegregate. Verifying this pattern is beyond the scope of this project but can be investigated in future works.

3. Conclusion

In this project the segregation behavior of Gold, Nickel, Rhodium, Ruthenium, and Palladium in (111) surface fcc Platinum were modeled using DFT by comparing only the total free energies of the surfaces with the solute atom on Platinum at different λ th layer.

The results show that Gold segregates in Platinum. Nickel, Rhodium, and Ruthenium antisegregate in Platinum. Palladium neither segregates nor antisegregates in Platinum. The current results match the results of the predicted segregation behavior from the previous calculations by Ruban, et. al. (2009).

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Computational Model

DFT calculations were implemented using Quantum Espresso with exchange correlation term described using the generalized gradient approximation (GGA) based on Perdew–Burke–Ernzerhof (PBE) functional. The interaction between ions and electrons were described using the projector augmented wave (PAW) method. Plane wave basis sets will be employed with an energy cut-off of 52.9163 Rydberg. The surface Brillouin zone integrations will be performed on a grid of $4 \times 4 \times 1$ Monkhorst-Pack k-points using Methfessel–Paxton smearing of $\sigma = 0.01$ Rydberg.

Notes and references

- [1] Boom, R., & de Boer, F. R. (2006). Energy Effects in Bulk Metals.
- [2] Duan, Z., Zhong, J., & Wang, G. (2010). Modeling surface segregation phenomena in the (111) surface of ordered Pt 3 Ti crystal. The Journal of chemical physics, 133(11), 114701.

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- [3] Ruban, A. V., Skriver, H. L., & Nørskov, J. K. (1999). Surface segregation energies in transition-metal alloys. *Physical review B*, 59(24), 15990.
- [4] Nilekar, A. U., Ruban, A. V., & Mavrikakis, M. (2009). Surface segregation energies in low-index open surfaces of bimetallic transition metal alloys. *Surface Science*, 603(1), 91-96.