First principles calculations of beryllium stability in zirconium surfaces

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Abstract

High-temperature oxidation of zircalloys poses a serious safety risk for nuclear fuel cladding applications, thus driving the search for oxidation resistant alloys. Ellingham diagrams suggest preferential oxidation of beryllium over zirconium, but the atomic-scale behavior of Be near Zr surfaces is unknown. We perform first principle calculations using density functional theory to investigate the stability of Be at possible sites in the Zr surfaces and bulk. Our calculations predict that Be favors substitutional sites and prefers to segregate to the surface layers. Charge density analysis shows charge redistribution around the solute atom in substitutional sites which leads to increased bonding and explains the high stability of these sites. The calculated surface segregation energy suggests that Be migrates towards the surface at high temperatures, which could enhance oxidation resistance.

Keywords: zirconium; zirconium alloys; surface segregation; electronic structure; first-principles calculation

1. Introduction

High temperature oxidation of metals and alloys has been a challenge due its detrimental effects on material properties[1]. Oxidation mechanisms have been thoroughly investigated for several metallic systems such as steels, and two main approaches have
5 been developed to improve the oxidation resistance.[2] The first involves deposition

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of oxidation resistant coatings on the alloy surface, such as thermal barrier coatings used in Ni-based superalloy systems. However this approach suffers from inherent difficulties such as loss of protective oxide-forming elements due to interfacial diffusion, which limit the temperature range of the application and the component lifetime. The second approach involves selective oxidation[3] of additional solutes in the matrix to form a protective oxide layer on the surface. These additional solutes must have a higher oxidation potential compared to the matrix atoms and prefer to segregate to the surface. The most common example of this approach is the addition of chromium to martensitic steels where Cr forms an inert oxide layer on the alloy surface which prevents further oxidation.[2] These approaches are in general applicable to any material and help guide the development of new oxidation resistant alloys. Nuclear fuel cladding materials in light water power reactors—such as zirconium and its alloys (Zircalloys)—are susceptible to high temperature oxidation[4, 5]. Zirconium reacts with steam at elevated temperatures to form ZrO_2 and H_2 gas. The primary cause of the hydrogen explosion at Fukushima Daichi was the uncontrolled oxidation of Zr due to a cooling system failure that lead to accumulation and subsequent ignition of H_2 gas[6]. This incident highlights a critical need to improve the high temperature oxidation resistance of Zircalloys for both accident safety and longevity.

A number of studies have investigated the oxidation behavior of HCP Zr and its alloys, and suggest improvements.[4, 7, 8, 9, 10, 11] Experimental as well as theoretical studies have shown that the Zr basal (0001) surface has lower energy and higher oxidation resistance than the prismatic (10 $\bar{1}$ 0) surface[12, 13, 14, 15], suggesting that a textured Zr surface should improve resistance to oxidation. Nie and Xiao used first principle calculations to study the adsorption of water molecule on a metal-doped Zr surface[16] and found that certain elements in the 4th and 5th period of the periodic table could enhance the oxidation resistance of zircalloys by repelling the water molecules. The Ellingham diagram shows that beryllium oxidizes in preference to Zr[17], which suggests that doping Zircalloys with Be could potentially enhance the oxidation resistance if Be segregates to the Zr surface and forms a protective oxide layer. Beryllium improves the oxidation resistance of Cu[18] and Mg[19]. Tendler et al. experimentally studied the temperature dependence of Be diffusion in HCP and

BCC phases of Zr and suggested an interstitialcy diffusion mechanism due to the low activation barrier[20]. Feng et al. investigated the influence of Be addition to Zr and reported an improvement in tensile properties[21], which could be an additional benefit. However, there is no experimental or theoretical literature available on the segregation behavior of Be, or any other element, in the Zr surface.

In this work, we examine the stability of Be at the interstitial, substitutional and adatom sites in HCP bulk Zr, the Zr(0001) surface and the Zr(10 $\bar{1}$ 0) surface using first principle calculations. Density functional theory (DFT) predicts that beryllium favors substitutional sites over interstitial sites in bulk Zr and prefers to segregate to the Zr surfaces. The combined analysis of projected density of states, charge transfer, and isosurfaces of charge density, shows that the increased metallic bonding near Be is responsible for the high stability of surface substitutional sites. Our results indicate that Be is a suitable alloying candidate to improve the oxidation resistance of zircaloys.

2. Computational Method

We perform first principles calculations using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[22] and the projector augmented wave (PAW) method[23] implemented in the Vienna Ab initio Simulation Package (VASP)[24, 25]. We use a plane wave energy cut-off of 500 eV to converge the total energy of Zr below 1 meV per atom. For bulk calculations we use a supercell of size $4 \times 4 \times 3$ (96 atoms) which requires a Monkhorst-Pack k-point mesh of $6 \times 6 \times 4$ to sample the Brillouin Zone. We use a smearing[25] width of 0.2 eV to integrate the density of states. We relax the geometries until the forces on all atoms are less than 0.5 meV/Å. The lattice constants for bulk Zr obtained from structural relaxation are $a = 3.234\text{Å}$ and $c = 5.171\text{Å}$, which agree well with the experimental data[26] and previous DFT studies[27]. We perform Bader analysis with the all-electron charge density obtained from DFT calculations using the algorithm proposed by Yu and Trinkle[28].

We use the $p(3 \times 3)$ 54 atom basal surface supercell, the $p(3 \times 2)$ 120 atom prism surface and the $4 \times 4 \times 3$ bulk supercell shown in Figures 1 and 2 to study the stability of Be at various adatom, interstitial, and substitutional sites in Zr. We model the Zr(0001)

Figure 1: Supercell geometries showing solute configurations and the Zr (0001) basal surface. (a) The top view of the basal surface supercell shows four adatom sites in orange: On Top, FCC, Bridging and HCP. (b) The side view of the basal surface supercell shows adatom sites (orange) and three substitutional sites in red: Sub1, Sub2 and Sub3. We fix the atoms in the bottom two layers of the supercell at their bulk positions. (c) The side view of the bulk supercell shows the substitutional site Sub in red and the octahedral interstitial site Oct in orange. Beryllium is unstable in the bridging site and relaxes to the HCP site.

surface using a slab geometry of $3c$ thickness (6 atomic planes) and $2c$ vacuum thickness, and fix the atoms in the bottom two layers at their bulk positions. Similarly, we model the $\text{Zr}(10\bar{1}0)$ prismatic surface using a slab geometry of 20 atomic planes and vacuum thickness equivalent to 4 atomic planes while keeping the bottom 4 layers fixed at their bulk positions. We calculate the surface energy as $\gamma = (E_{\text{DFT}}^{\text{slab}} - E_{\text{DFT}}^{\text{bulk}})/2A_0$, where A_0 is the area of one surface, $E_{\text{DFT}}^{\text{slab}}$ is the DFT energy of the slab configuration and $E_{\text{DFT}}^{\text{bulk}}$ is the DFT energy of a bulk configuration with the same number of atoms as the slab geometry. The calculated surface energies are $0.0993 \text{ eV}/\text{\AA}^2$ for the $\text{Zr}(0001)$ basal surface, $0.1033 \text{ eV}/\text{\AA}^2$ for the low energy $\text{Zr}(10\bar{1}0)$ prismatic surface and $0.1184 \text{ eV}/\text{\AA}^2$ for the high energy $\text{Zr}(10\bar{1}0)$ prismatic surface. These energies agree well with

Figure 2: Supercell geometries showing solute configurations in the high and low energy $\text{Zr}(10\bar{1}0)$ prismatic surfaces. We only show the top twelve layers of the supercells in the side view. The full supercell contains 20 atomic planes. The geometries show four adatom configurations (orange), and the eight substitutional configurations (red). The adatom sites On Top 1 and On Top2 are directly above the atoms in layer 1 and 2 of the surface respectively, with On Top1 being closer to the surface. The Bridge1 and Bridge2 sites are located between two atoms in layer 1 and 2, and at the same distance from the surface as the corresponding On Top sites.

previous theoretical[27, 29, 30] and experimental studies[31]. We define the interlayer relaxation as $\Delta_{ij} = (d_{ij} - d_0)/d_0$, where d_{ij} is the average interlayer spacing between layers i and j and d_0 is the interlayer spacing in bulk. The supercell sizes we choose are large enough to avoid interactions between periodic images of the solute atom. We identify four high symmetry adatom sites that Be solute can occupy in both surfaces. Beryllium is unstable at the bridging site in the basal surface and relaxes to the HCP site. We also look at the substitutional Be in layers 1 to 3 of the basal surface and layers 1 to 8 of the prismatic surface. The segregation energy when a single solute atom

moves from bulk to a surface site is

$$E^{\text{segregation}} = E^{\text{solute}}(\text{surface}) - E^{\text{solute}}(\text{bulk}), \quad (1)$$

where $E^{\text{solute}}(\text{surface})$ is the energy of the solute in the surface and $E^{\text{solute}}(\text{bulk})$ is the energy of solute in bulk. We calculate the energy of the solute at a surface site from DFT using the $p(3 \times 3)$ 54 atom surface slab

$$E^{\text{solute}}(\text{surface}) = E_{\text{DFT}}^{\text{slab}}(\text{solute}+N) - E_{\text{DFT}}^{\text{slab}}(54) + E_{\text{DFT}}^{\text{bulk}}(54 - N) - E_{\text{DFT}}^{\text{solute}}(\text{solute}), \quad (2)$$

where $E_{\text{DFT}}^{\text{slab}}(\text{solute}+N)$ is the DFT energy of the slab supercell containing a solute and N matrix atoms, $E_{\text{DFT}}^{\text{slab}}(54)$ is the DFT energy of pristine Zr $p(3 \times 3)$ slab containing 54 atoms, $E_{\text{DFT}}^{\text{bulk}}(54 - N)$ is the DFT energy of $(54 - N)$ matrix atoms in bulk and $E_{\text{DFT}}^{\text{solute}}(\text{solute})$ is the DFT energy of an isolated solute atom. For the $p(3 \times 3)$ slab, N is 54 if the solute occupies an adatom site and 53 if it occupies a substitutional site. Similar expressions are applicable to the 120 atom prismatic surface cell, where N is 120 if the solute occupies an adatom site and 119 if it occupies a substitutional site. We use the 96 atom supercell to calculate the energy of solute at a bulk site as

$$E^{\text{solute}}(\text{bulk}) = E_{\text{DFT}}^{\text{bulk}}(\text{solute}+M) - E_{\text{DFT}}^{\text{bulk}}(M) - E_{\text{DFT}}^{\text{solute}}(\text{solute}), \quad (3)$$

where $E_{\text{DFT}}^{\text{bulk}}(\text{solute}+M)$ is the DFT energy of the bulk supercell containing a solute and M matrix atoms. For the $4 \times 4 \times 3$ bulk supercell, M is 96 if the solute occupies an interstitial site and 95 if it occupies a substitutional site. Finally, when we calculate the segregation energy, the $E_{\text{DFT}}^{\text{solute}}(\text{solute})$ term cancels out.

3. Results

Figure 3 and 4 show that Be favors substitutional sites over interstitial and adatom sites in the bulk, and prefers to segregate to the surface. We plot the segregation energies relative to the most stable site in bulk which is the substitutional site (Sub). The low energy substitutional sites suggest a possible network through which the solute can migrate from bulk to the surface. Among the adatom sites in basal surface, the HCP site is more stable than FCC and On Top, but its energy is higher than the substitutional

Figure 3: Segregation energy of Be at various sites in the Zr(0001) basal surface. For comparison, we also show the energy of the bulk Oct site. The symbols for adatom and Oct sites are orange, and the symbols for the substitutional sites are red. All energies are relative to the energy of Sub site, the substitutional site in bulk. The most stable site in the basal surface is the Sub1 site. The most stable adatom site in the basal surface is the HCP site but it is higher in energy compared to the substitutional sites in the surface. In the bulk, the Sub site is more stable than the Oct site. We connect the substitutional sites in the basal surface to indicate a possible migration path from bulk to surface.

sites. The most stable site for Be in the basal surface and the low energy prismatic surface is Sub1, which is the substitutional site in the top surface layer. The segregation energy to Sub1 in the basal surface is -0.291 eV and in the low energy prismatic surface it is -0.5 eV. A negative segregation energy indicates a driving force for Be to segregate to the surfaces. In the high energy prismatic surface, the Bridge2 adatom site has the lowest energy of all. The substitutional site in the third layer of the high energy prismatic surface (Sub3) shows a positive segregation energy of 0.22 eV, which is a potential barrier to segregation should this surface form. The prismatic geometries from Sub5 to Sub8 reproduce bulk behavior and any energy differences from the Sub site can be attributed to the finite size effect. We next analyze the geometric relaxations and electronic changes induced by Be to understand the relative stability of the sites.

85 Figure 5 shows that Be contracts the adjacent atomic layer(s) of the surface configurations relative to the pristine basal surface. We analyze these distortions by computing the interlayer relaxations Δ_{ij} of the relaxed geometries. The interlayer spacing between any two layers in the relaxed geometries is the difference between the average atom coordinates of the two layers along the direction perpendicular to the surface. The Δ_{ij} for
 90 the layers adjacent to Be in the substitutional configurations is larger than the pristine surface and shows a contraction towards the solute. In the adatom configurations, both Δ_{12} and Δ_{23} are lower in magnitude compared to the pristine surface but Δ_{34} is nearly the same. These values indicate that the top layer moves away from the second layer while the second and third layers contract towards each other. The solute atom pulls
 95 more strongly on the top surface layer causing it to move towards the solute. The distortions in the surface geometries decay away from the solute and become comparable to the distortion in Sub configuration, evident from the low values of Δ_{34} for adatom, Sub1 and Sub2 configurations, and Δ_{12} for the Sub3 configuration. The distortion in the Oct configuration is the only outlier, which is due to the nearest neighbors in the adjacent layers moving away from Be atom. The contraction of layers towards the solute
 100 atom suggests that a localized interaction is present between Be and its nearest neighbor Zr atoms in the surface configurations. The interlayer relaxations in the prismatic surface from figure 6 are more complex and do not show a clear pattern of contraction followed by expansion between the adjacent layers. This lack of pattern can be
 105 attributed to the distortions in the relaxed surface geometry. The nearest neighbors in the prismatic surfaces are present in two layers above and below the solute atom and not limited to the adjacent layers. However, the relaxations decay two to three layers from the solute in both surfaces and reproduce the pristine surface behavior, suggesting localized interactions between Be and Zr.

110 Our analysis of the site projected density of states (PDOS) shows that Be does not significantly alter the occupation of states near the Fermi energy, when compared to the pure Zr cell or the clean slab geometry, suggesting an absence of covalent bonding. Figure 7 shows that the nearest neighbors of Be in substitutional configurations have slightly higher occupation of states at lower energies compared to the corresponding
 115 bulk or pristine surface references, indicating localized bonding between Be and its

neighbors. The occupation of states is nearly the same at the Fermi energy in both bulk and surface substitutional sites, but a higher occupation in the range of 0.5 to 0.75 eV below the Fermi level results in an overall reduction in the total energy of these sites. The PDOS for adatom configurations do not show same trends of higher
120 occupation at lower energies as in the substitutional sites, but the nearest neighbors of Be show shifts in the occupation of states towards lower energies when compared to the pristine surface reference. These shifts can be explained due to the changes in the Fermi energy and the additional bonding induced in the top surface layer by the presence of an adatom. The Oct configuration is the only one to show a marked increase
125 in the occupation near the Fermi energy for both Be and the nearest neighbor Zr atoms, consistent with its relatively high site energy. Based on the PDOS plots we conclude that even though some localized changes are present near the solute, the absence of new bonding states suggests that charge transfer maybe responsible for the energy changes instead of covalent bonding between Be and its neighbors. The prismatic surface PDOS
130 plots (not shown here) are similar to the basal surface, showing negligible changes relative to the pristine surface and absence of new bonding states.

Bader analysis of charge transfer in the basal surface shows that the nearest neighbors of Be gain excess charge in the Sub1 configuration relative to the pristine surface indicating a net charge transfer towards the top surface layers, while they lose charge
135 in all other surface configurations. We analyze the charge transfer between Be and its neighbors to verify our assertion that charge transfer is causing the localized bonding in the various solute configurations. Bader charge analysis[32] identifies basins of attraction of charge density, by following the charge density gradient to local (atom-centered) maxima; each atom is then assigned the total charge density within that basin
140 of attraction. Unlike other charge partitioning methods, such as Mulliken or Löwdin, Bader relies entirely on the charge density without reference to the atomic orbitals. It provides complimentary data to the site projected density of states, which rely on atom-centered spheres to define the projections, and has a particularly efficient and accurate implementation from `vasp` data[28]. We plot these results as average charge differences
145 for Be and its nearest neighbors in figure 8. In the substitutional configurations Sub, Sub3 and Sub2, the charge differences on the basal neighbors remain close to zero

and the charge transfer between Be and the six pyramidal neighbors is responsible for bonding. However, in the Sub1 configuration all nine neighbors of Be participate in the bonding, evident from the positive charge differences of both Be and its nearest
150 neighbors. Therefore, there is a net charge transfer in Sub1 configuration towards Be and its nearest neighbors which leads to increased bonding. In the adatom configurations, the total charge lost by the nearest neighbor Zr atoms accounts for the excess charge on Be and explains the bonding. However, the bonding is limited by the number of nearest neighbors—three in HCP and FCC configurations, and one in the On top
155 configuration. Beryllium gains nearly four electrons in the Oct configuration but the charge difference on the nearest neighbors is close to zero, as the excess charge comes from the next nearest neighbor. This excess charge on an otherwise electropositive Be atom is responsible for the high energy of the Oct configuration. Therefore, our analysis confirms that charge transfer is correlated with the increased local bonding present
160 between Be and its nearest neighbors in the substitutional configuration. However, the charge transfer analysis provides no information on the spatial distribution of charges which can further help us understand the local bonding characteristics in substitutional configurations.

The charge transfer in the prism surfaces from figure 9 also shows increased charge
165 concentration on the nearest neighbors of Be in the substitutional geometries which indicates a net charge flow towards the top surface layers, similar to the basal surface but not limited to the Sub1 configuration. In the low energy surface, all substitutional configurations show excess charge on the nearest neighbors which increases towards the top two surface layers and leads to increased bonding. In Sub4, charge transfers
170 away from the neighbors closer to the vacuum and towards the bulk. In Sub3, Sub2 and Sub1, the charge transfers away from the layers closer to the bulk towards the top surface layers. In the adatom configurations of low energy surface, the nearest neighbors balance the excess charge on Be, similar to the basal surface but bonding is limited by the fewer nearest neighbors, except Bridge2 where Zr atoms in the second layer
175 also contribute towards bonding. In the high energy surface, Sub4 and Sub1 show a high concentration of charge in the surface layers leading to increased bonding. But Sub3 and Sub2 show a very different behavior where the charge difference of the near-

est neighbors is either zero or negative. Further, the charge gained by Be atom does not account for the charge lost by nearest neighbors, which indicates charge transfer
 180 between Zr atoms but not between Be and its neighbors. Consequently, there is less bonding in this configuration even though there is ionic charge transfer, similar to the Oct configuration. The Sub2 on the other hand shows a large concentration of charge on Be which is balanced by the negative charge difference on nearest neighbors closer to bulk and surface. In addition, there is a small charge on the nearest neighbors in
 185 the plane of Be. This combined effect of the excess charge transfer to Be and the charge concentration on in plane neighbors leads to increased bonding and is the likely cause of the relatively low energy of this configuration. The adatom geometries in the high energy surface also show increased charge concentration on the nearest neighbors in the top surface layer, but the bonding in On Top1 and Bridge1 is limited by
 190 the fewer neighbors. However, the On Top2 and Bridge2 sites behave similarly to the substitutional sites with increased charge concentration in top surface layer that leads to increased bonding, balanced by the charge transfer away from the second layer.

Figure 10 shows increased metallic bonding for substitutional Be atoms and ionic charge transfer to the interstitial and adatom Be atoms. The charge difference plots
 195 show the spatial distribution of charge difference relative to atomic charges indicated by blue negative isosurfaces and red positive isosurfaces. Substitutional configurations show charge redistribution in the interstitial region surrounding Be with the charge transferring away from the neighboring Zr atoms. In the Sub and Sub3 configurations, the charge redistributes mostly outside the nearest neighbor cage of Be. Some charge
 200 localization occurs inside the neighbor cage with majority of the contribution from pyramidal neighbors. The contribution from the six basal neighbors becomes significant in the Sub2 configuration where charge concentrates in the basal plane. Finally, the Sub1 configuration shows maximum charge concentration in the basal plane of Be. The concentration of charge between Be and its neighbors results in increased metallic
 205 bonding in the substitutional configurations and explains their stability. The Oct configuration shows charge localization on Be atom and charge concentration between Zr atoms, but not between Be and the nearest neighbors. The positive isosurface around Be is consistent with the results of Bader analysis which shows an excess of charge

on Be atom, and also with the PDOS plots which shows a higher occupation of states
 210 near the Fermi energy for Be and its neighbors. The behavior of adatoms is between
 the two extremes of the substitutional and the Oct configurations, consistent with their
 relative energies. Charge around the Be adatom moves towards the Zr surface and
 away from the vacuum; in addition, charge in the interstitial region in the Zr surface
 moves up towards the Be atom. The charge localization on Be atom in the adatom
 215 configurations is less than the Oct configuration. The isosurfaces of the low energy
 prismatic geometries from figure 11 and 12 show similar behavior to the basal surface,
 with increased charge concentration between the Be atom and its nearest neighbors for
 the low energy configurations and charge localization for the high energy configura-
 tions. Of particular interest are the Bridge2 geometries in both surfaces, Sub3 in the
 220 high energy surface and Sub2 in the high energy surface. The Be atom in the Bridge
 site relaxes towards the second layer in both prismatic surfaces resulting in increased
 charge transfer between Be and the nearest neighbor Zr atoms in the top two surface
 layers, which leads to bonding. On the other hand, the Sub3 configuration in the high
 energy prismatic surface shows little charge concentration within the neighbor cage of
 225 Be. Most of the charge transfer in Sub3 occurs among the Zr atoms to compensate for
 the localized charge on Be atom, similar to the Oct configuration which is also high in
 energy. The Sub2 configuration in the high energy surface shows a dense charge con-
 centration within the neighbor cage of Be, which results in increased metallic bonding
 and explains the relatively low energy of this site. Thus, our analysis of the differences
 230 in charge density shows increased metallic bonding for the most stable substitutional
 sites and more ionic charge transfer for the less stable interstitial and adatom sites.

4. Discussion

We use DFT to investigate relative stability of Be at various sites in Zr(0001) and
 Zr(10 $\bar{1}$ 0) surfaces, and the bulk. Our results show that Be is more stable at a substitu-
 235 tional site than an interstitial site in bulk Zr and prefers to segregate to both surfaces.
 Analysis of the interlayer relaxations in the surface geometries and the site projected
 density of states suggest that localized changes in the bonding induced by Be explain

the differences in site energies. The charge transfer near substitutional Be atoms reveals increased metallic bonding between Be and its nearest neighbors which is responsible for the stability of the substitutional site in the top surface layer. Although our analysis is limited to the basal and prismatic surfaces only, literature shows that the Zr surface energy changes little with orientation.[13, 29, 30] Our results show similar quantitative values of segregation energies for both surfaces and identical physical mechanisms responsible for surface segregation: increased charge transfer in top surface layers leading to metallic bonding. Based on these observations, we expect Be to have similar behavior in any surface oriented between the basal and prismatic planes.

The presence of Be in the grain boundaries of polycrystalline Zr should prompt similar responses in the charge density, leading to a lower site energy and faster transport along grain boundaries. Our results suggest that surface segregation should be stronger than grain boundary or dislocation segregation due to the larger changes in electronic environment at free surfaces that attracts Be. In fact, both grain boundaries and dislocation cores could act as short-circuit diffusion pathways to aid in the migration of Be solutes to the surface and out of solid solution, even in a polycrystal. The gradient in segregation energy approaching the surface can act an additional driving force to aid surface segregation kinetics. Combining our surface segregation predictions and experimental data of oxide formation thermodynamics, we conclude that Be could be a promising alloying candidate for improving the oxidation resistance of zircaloys and merits further investigation.

Our study presents a fundamental understanding of how Be interacts with Zr, both in bulk and surface, and can be applied to segregation in other dilute binary systems. We expect isoelectronic metals to behave similarly in the Zr matrix because the changes in the site energies are largely due to the localized charge transfer around the Be atom. The group IIA elements all oxidize in preference to Zr according to the Ellingham diagram.[17] However, only Be and Mg satisfy all the Hume-Rothery rules and we expect changes in relative stability of sites starting from Ca which has a FCC crystal structure.[33, 34] As we move further down the group, the changes in electronegativity and atomic size also become significant.

Acknowledgements

This research was supported by the US Department of Energy Energy University
270 Programs Integrated Research Project under contract number IRP-12-4728.

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Figure 4: Segregation energy of Be at various sites in the $\text{Zr}(10\bar{1}0)$ prismatic surfaces. The symbols for adatom sites are orange, and the symbols for the substitutional sites are red. All energies are relative to the substitutional site in bulk. In the low energy prismatic surface, Sub1 is the most stable site and Bridge2 is the most stable adatom site. In the high energy prismatic surface, Bridge2 is the most stable site followed by Sub1 and Sub2. Sub3 has a positive segregation energy which could act as a barrier to segregation in the high energy prismatic surface. We connect the substitutional sites in the basal surface to indicate a possible migration path from bulk to surface.

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Figure 5:

Figure 5: Relaxed geometries for Be in HCP, FCC, On Top and Sub1 sites, followed by the changes in interlayer relaxations for all basal surface configurations, and the bulk Oct and Sub configurations. The presence of the solute distorts the slab geometry, most notable in the layers adjacent to the solute. The Zr atoms below Be in the adatom geometries show the largest distortions. We use the interlayer relaxations Δ_{ij} to quantify these distortions, which is the change in the average interlayer spacing of the adjacent layers i and j in the relaxed geometry, relative to the interlayer spacing in the bulk lattice. The dashed lines are the corresponding interlayer relaxations in the pristine surface. In all three adatom configurations, Δ_{12} and Δ_{23} are lower in magnitude than the pristine surface, showing that the top surface layer is displaced towards Be more than the next two surface layers. In the substitutional configurations, there are large contractions between the layers adjacent to the one containing Be.

Figure 6: Changes in interlayer relaxations for prismatic surface configurations. The change in average interlayer spacing Δ_{ij} of the adjacent layers i and j in the relaxed geometry is relative to the interlayer spacing in the bulk lattice, and dashed lines correspond to interlayer relaxations in the pristine surface. The relaxations in the prismatic surfaces also show the largest changes are near the Be atom, where the adjacent layers either contract or expand.

Figure 7: Projected density of states (PDOS) at the sites occupied by Be and its nearest neighbor Zr atoms in the bulk and the basal surface. The reference is set to the Fermi energy for all the plots. In the surface configurations, we show the PDOS for the nearest neighbors located in different layers. For comparison, we also show the PDOS of pure Zr for bulk configurations and the PDOS of a Zr atom located in the pristine surface layers for the surface configurations.

Figure 8: Changes in electronic charge Δn_e of Be and its nearest neighbor Zr atoms from Bader analysis for the bulk and basal surface geometries. The symbols for the adatom and Oct sites are orange, and the substitutional sites are red. The charge differences for Be are relative to the charge of bulk Be. We choose the pristine surface as the reference for surface geometries, and bulk Zr for the bulk geometries. The charges on Zr atoms are averaged over the nearest neighbors lying in the same basal plane. We show the charges on the nearest neighbors located in different planes separately. Be gains charge in all configurations with a maximum of nearly four electrons in Oct. The charge transfer between nearest neighbor Zr atoms accounts for this excess charge on Be, except in the Oct configuration where the charge difference on the Zr neighbors is almost zero.

Figure 9: Changes in electronic charge Δn_e of Be and its nearest neighbor Zr atoms from Bader analysis for the prismatic surfaces. The symbols for the adatom and Oct sites are orange, and the substitutional sites are red. The charge differences for Be are relative to the charge of bulk Be. We choose the corresponding pristine surface as the reference for surface geometries. We show the charges on the nearest neighbor Zr atoms located in different planes separately. The charges on Zr atoms are averaged over the nearest neighbors. Be gains charge in all surface configurations which is balanced by the charge transfer between Zr atoms.

Figure 10: Isosurfaces of charge density differences for solute and its nearest neighbors in the bulk and basal surface configurations. We set the isosurface level to $0.0075\text{\AA}^{-3}$ for each configuration. In the Oct configuration, the Be atom is surrounded by a positive isosurface indicating charge transfer from nearest neighbor Zr atoms towards Be. In the adatom configurations, the isosurface of charge on Be moves away from the vacuum region and concentrates between Be and the top surface layer. Among the substitutional configurations, the charge concentration in the nearest neighbor cage of Be is minimal in Sub and Sub3, and increases near the surface with a maximum in Sub1 configuration.

Figure 11: Isosurfaces of charge density differences for solute and its nearest neighbors in the low energy prismatic surface configurations. We set the isosurface level to $0.0075 \text{ \AA}^{-3}$ for each configuration. Similar to the basal surface, the isosurface of charge on Be in the adatom configurations moves away from the vacuum region and concentrates between Be and the top surface layer. The Bridge2 site is particularly interesting as Be moves closer to the second layer and shows charge transfer from both first and second surface layers.

Figure 12: Isosurfaces of charge density differences for solute and its nearest neighbors in the high energy prismatic surface. We set the isosurface level to $0.0075 \text{ \AA}^{-3}$ for each configuration. Similar to the low energy prismatic surface, Bridge2 site moves closer to the second layer and shows increased charge transfer. In addition, the Sub3 site shows very little charge concentration within the neighbor cage of Be and most of the charge transfer is between the Zr atoms close to the surface.