Graphical Abstract

The interaction of hydrogen with substitutional surface alloys of Au and Ni was investigated using periodic, self-consistent DFT-GGA (PW91) calculations. Surface adsorption of H at the best binding sites was weaker than on Ni(111), but subsurface absorption was stronger, suggesting that a different distribution of surface and subsurface hydrogen is expected in the Ni-Au alloys as compared to pure Ni.

Stability of Surface and Subsurface Hydrogen on and in Au/Ni Near-Surface Alloys

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Abstract

Periodic, self-consistent DFT-GGA (PW91) calculations were used to study the interaction of hydrogen atoms with the (111) surfaces of substitutional near-surface alloys (NSAs) of Au and Ni with different surface layer compositions and different arrangements of Au atoms in the surface layer. The effect of hydrogen adsorption on the surface and in the first and second subsurface layers of the NSAs was studied. Increasing the Au content in the surface layer weakens hydrogen binding on the surface, but strengthens subsurface binding, suggesting that the distribution of surface and subsurface hydrogen will be different than that on pure Ni(111). While the metal composition of the surface layer has an effect on the binding energy of hydrogen on NSA surfaces, the local composition of the binding site has a stronger effect. For example, fcc hollow sites consisting of three Ni atoms bind H nearly as strongly as on Ni(111), and fcc sites consisting of three Au atoms bind H nearly as weakly as on Au(111). Sites with one or two Au atoms show intermediate binding energies. The preference of hydrogen for three-fold Ni hollow sites alters the relative stabilities of different surface metal atom arrangements, and may provide a driving force for adsorbate-induced surface rearrangement.

Keywords

DFT, near-surface alloys, hydrogen, gold, nickel, adsorption, surface, subsurface

1. Introduction

Nickel catalysts are at the heart of many industrial hydrogenation reactions [1]. In order to understand the function of the Ni catalyst in these reactions, it is important to understand the hydrogen species present and identify those species that are responsible for the hydrogenation activity of the catalyst. In addition to hydrogen atoms present on the surface of Ni, there is a growing body of evidence that suggests that hydrogen absorbed in interstitial sites of the metal play an active role in many hydrogenation reactions, and, for that, the role of subsurface hydrogen is the subject of ongoing investigation [2– 10].

Near-surface alloys (NSAs) are a class of bimetallic alloys that restricts alloying to the top few layers of a metal surface such that the composition near the surface differs from that in the bulk. NSAs have already been shown to possess unique properties [11], especially concerning hydrogen binding, hydrogen diffusion, and H_2 dissociation [12– 14]. NSAs with weak affinities for hydrogen binding that also possess low activation energy barriers for H_2 dissociation have been predicted in previous calculations [12]. Amongst NSA compositions, the Au/Ni system consisting of Au atoms occupying lattice positions in the (111) and (110) facets of Ni [15–16] and in Ni catalyst particles [17] has attracted attention for its enhanced stability in steam reforming reactions [17–20] and enhanced activity in low temperature CO oxidation [21–22].

While the effect of alloy composition has been investigated in the context of these reactions, no studies have been carried out to understand the effect of the amount of Au on the distribution of hydrogen on the surface and in the subsurface of the Au/Ni NSA system. Developing a fundamental understanding of the interaction of atomic H with

Au/Ni NSAs can lead to insight into the role of subsurface hydrogen in hydrogenation reactions as well as the development of new applications for Au/Ni NSAs. In the present work, a systematic study of the stability of surface hydrogen adsorption and subsurface hydrogen absorption with varying Au surface coverages and Au-atom arrangements is reported.

Recent work has shown that the diffusion barrier for hydrogen atoms to move from the surface layer to the subsurface of a transition metal is dominated by the thermochemical energy difference between these two states [13,23]. For several NSA compositions, this energy difference between surface and subsurface states is predicted to be smaller than the respective difference on the pure metals [14] and a correspondingly lower diffusion barrier for surface to subsurface sites has been calculated [13]. In this context, the binding energies calculated in the present paper provide a first-order approximation of the expected effect of alloying Au in the (111) surface of Ni on the activation barriers for surface to subsurface hydrogen diffusion.

2. Methods

Periodic, self-consistent DFT calculations were performed using the VASP code [24–25] within the generalized gradient approximation (GGA-PW91) [26] (with spin polarization for all calculations involving Ni) and the projector-augmented wave (PAW) [27–28] potentials. The single-electron wave functions were expanded using plane waves with an energy cutoff of 400 eV. All Ni-containing slabs were based on the (111) surface of pure fcc Ni, and modeled by a (3 x 3) unit cell and 6 atomic layers for a total of 54 metal atoms (Ni or Au). To generate Au/Ni near-surface alloys, surface Ni atoms were

substituted by Au atoms and the surface was reoptimized by relaxation. Calculations on the (111) surface of fcc Au were similarly performed on a (3 x 3) slab with 6 atomic layers. The lattice constants of Ni and Au were calculated as 3.52 Å and 4.17 Å respectively, in good agreement with the experimental values of 3.52 Å and 4.08 Å respectively [29]. A vacuum layer of 12 Å was used to separate any two successive slabs in the z direction, and a dipole correction was applied and the electrostatic potential was adjusted to ensure the interactions between the surface of one slab and its periodic images are negligible [30]. The Brillouin zone was sampled using a (4x4x1) Gamma-centered Monkhorst-Pack k -point mesh [31]. The bottom two layers of each metal slab were fixed while the top four layers were allowed to relax in all calculations. Binding energy is defined as $BE = E_{\text{ads}} - E_{\text{slab}} - E_{\text{gas}}$, where E_{ads} , E_{slab} , and E_{gas} are the total energies calculated for the slab with the adsorbate on it, the clean slab, and the adsorbate in the gas phase, respectively. All results are given for $1/9$ monolayer (ML) coverage of hydrogen, which corresponds to one hydrogen atom added to each 54-atom metal slab.

3. Results and Discussion

3.1 Au/Ni near-surface alloy structures with no adsorbates

Experimentally, when synthesizing Au/Ni NSAs, no more than 30% of the surface Ni atom lattice positions may undergo 1:1 atom substitutions by Au without forming epitaxial Au overlayers or Au islands [16,21], corresponding to a maximum 0.3 monolayer (ML) coverage by Au in the surface layer of Ni(111). To model the Au/Ni NSA surface, between one and four of the surface layer metal atoms of a 3x3 Ni surface cell were substituted by Au, corresponding to 0.11 ML (i.e. $1/9$ ML), 0.22 ML, 0.33 ML,

and 0.44 ML Au coverage. The 0.44 ML coverage case was included to explore arrangements of Au and Ni atoms in Au-rich areas of a 0.3 ML Au coverage NSA, where the local coverage may exceed the threshold value. Since scanning tunneling microscopy (STM) images of Au/Ni NSA (111) surfaces show no long-range order [16,20–22,32–33], the local density of Au in the surface layer shows spatial variance for a given surface. As STM experiments have demonstrated complex phase transition beyond 0.3 ML of Au coverage, the models used in the present study with 1:1 substitution of Ni with Au in the Ni lattice without any reconstruction with 0.33 ML and 0.44 ML Au coverage may not capture all the features exhibited by Au/Ni NSAs as such high Au coverages.

While only one arrangement of Au atoms is possible for 0.11 ML Au coverage modeled by a 3x3 surface unit cell, there are two possible configurations for 0.22 ML Au coverage, five arrangements for 0.33 ML, and five arrangements for 0.44 ML. These are shown in Table 1. STM images of Au/Ni NSA surfaces show regions with different ensembles of Au and Ni atoms, which resemble different model surfaces from Table 1 [22, 32–33]. For instance, an approximately 0.2 ML Au coverage surface from Ref. [33] shows regions that resemble isolated Au atoms, as in the arrangement (sp2) from Table 1, as well as regions of higher Au atom density that more closely resemble arrangement (sp3) and areas with three gold atoms arranged together at an obtuse angle as in arrangement (cn3).

The total energy of each surface ensemble is reported in Table 1 referenced to the most stable arrangement of Au atoms for a given surface coverage. The structures (tf3) and (th3) at 0.33 ML Au coverage and (af4) and (ah4) at 0.44 ML Au coverage differ only in that three Au atoms surround a three-fold fcc hollow site in (tf3) and (af4) as

compared to a three-fold hcp hollow site in (th3) and (ah4). As the binding sites in each of these pairs of surfaces are nearly identical, and as H atom binding energies are similar on hcp and fcc sites (e.g. Table 2), hydrogen adsorption was modeled on only (tf3) and (af4) of these pairs, and not on (th3) and (ah3). Additionally, hydrogen adsorption was not modeled on the (ln3) structure, as it is 0.63 eV less stable than the most stable 0.33 ML Au coverage surface and 0.42 eV less stable than the next-least stable configuration at the same Au coverage.

Table 1. Model Au/Ni NSA (111) surfaces used in this study.

Au coverage: 0.11 ML		Au coverage: 0.22 ML
ΔE (eV)	0			0	0.13
μ (μ_b)	0.62			0.61	0.61
$\Delta z_{\max}$ (Å)	0.43			0.47	0.51
code	(sp1)			(sp2)	(ad2)
Au coverage: 0.33 ML
ΔE	0	0.18	0.20	0.21	0.63
μ (μ_b)	0.60	0.61	0.61	0.61	0.61
$\Delta z_{\max}$ (Å)	0.50	0.68	0.64	0.63	0.45
code	(sp3)	(cn3)	(tf3)	(th3)*	(ln3)*
Au coverage: 0.44 ML
ΔE	0	0.15	0.24	0.30	0.31
μ (μ_b)	0.61	0.60	0.60	0.62	0.62
$\Delta z_{\max}$ (Å)	1.13	0.67	0.66	1.20	1.23
code	(rm4)	(cy4)	(sn4)	(af4)	(ah4)*

ΔE is the energy difference of a structure relative to the most stable arrangement of Au atoms for the same Au coverage. μ is the mean magnetization per Ni atom in the slab. $\Delta z_{\max}$ is degree of corrugation, defined as the maximum absolute difference in z position of surface atoms. A three-letter **code** for each structure is given, which is referred to throughout the text. The dashed lines indicate the unit cell used in the calculations.

* Hydrogen adsorption calculations not carried out on these surfaces.

Neither the extent of Au substitution nor the arrangement of the surface layer atoms has a strong effect on the magnetization of the NSA surfaces per Ni atom, as reported in Table 1. The magnetization per Ni atom for the pure Ni slab was calculated as $0.62 \mu_b$, and the values for the NSA slabs vary between $0.60 \mu_b$ and $0.62 \mu_b$.

The degree of corrugation of the surfaces ($\Delta z_{\max}$) is given in Table 1 and calculated as the largest difference in the z coordinates of the atoms in the top metal layer. The deepest metal atom is a Ni atom (lowest z coordinate) and the highest metal atom is a Au atom (largest z coordinate) for all the slabs in Table 1. A value of $\Delta z_{\max} = 0.43 \text{ \AA}$ is obtained for the (sp1) surface (0.11 ML Au coverage), in which a single Au atom protrudes slightly from the plane containing all the remaining Ni atoms. This value was the smallest degree of corrugation calculated for any of the Au/Ni NSA surfaces with both Au and Ni atoms in the surface layer. Increasing the Au coverage generally increases the degree of corrugation of the different surfaces. Both the (sp2) and (ad2) surfaces at 0.22 ML Au coverage are slightly more corrugated ($\Delta z_{\max} = 0.47 \text{ \AA}$ and $0.51 \text{ \AA}$), and the degree of corrugation varies between $0.45 \text{ \AA}$ and $0.68 \text{ \AA}$ for 0.33 ML Au coverage. At 0.44 ML Au coverage, the degree of corrugation varies by nearly a factor of two, with (cy4) and (sn4) surfaces exhibiting lower $\Delta z_{\max}$ values of $0.67 \text{ \AA}$ and $0.66 \text{ \AA}$, while values for the (rm4), (af4), and (ah4) surfaces are much larger at $1.13 \text{ \AA}$, $1.20 \text{ \AA}$ and $1.23 \text{ \AA}$ respectively. For a given Au coverage, the surface geometries with the most

Au-Au nearest neighbor interactions (eg. (ad2) for 0.22 ML Au coverage, (tf3) and (th3) for 0.33 ML, and (rm4), (af4), and (ah4) for 0.44 ML) have the highest degrees of corrugation as compared to surfaces with fewer such interactions, but beyond that, no clear trend exists. The effect of corrugation on the stability of the surfaces follows no discernible trend, and the most stable arrangement for a given Au coverage was neither the most nor the least corrugated. However, having no Au-Au interactions, the (sp2) and (sp3) arrangements were the most stable for their respective Au coverages.

3.2 Hydrogen surface adsorption and subsurface absorption on Ni(111) and Au(111)

The binding energies calculated for the monometallic (111) facets of Ni and Au are given in Table 2. The nomenclature for binding sites is given in Figure 1. In agreement with previous calculations [7,9,13,23,34], hydrogen prefers fcc three-fold hollow sites on the (111) facets of both Ni and Au, with binding energies of -2.83 eV and -2.13 eV respectively. hcp sites were only 0.01 eV less favorable on Ni (111) and 0.02 eV less favorable on Au(111) as compared to fcc sites. The calculated binding energy on Ni(111) compares favorably with the experimentally measured desorption energy of hydrogen atoms from Ni(111) surfaces of 1.00 eV [35]. Using the formula $\Delta E_{\text{desorption H}_2} = -2 \cdot \text{BE}_{\text{H}} - 4.55 \text{ eV}$, where 4.55 eV is the bond energy of the H₂ molecule calculated here, and taking BE_H calculated for H on Ni(111) given in Table 2, a desorption energy of 1.11 eV is obtained from our calculations. The difference between the experimental and calculated values can likely be attributed to the PW-91 exchange-correlation functional, which is known to overestimate hydrogen binding energies [13], and the lack of zero-

point energy corrections in the present study, which similarly overestimates binding energies.

The most favorable binding sites in the first and second subsurface layers also agree with previous results [7,13,23], with octahedrally coordinated interstitial sites preferred in Ni, whereas the preferred site in Au is the tetrahedrally coordinated interstitial site immediately below a Au atom in the layer above. Ref. [23] reports that the preferred subsurface sites for eight fcc metals did not change between the first and second subsurface layers. The octahedrally coordinated sites in Ni, with binding energies of -2.19 eV in the first subsurface layer and -2.17 eV in the second subsurface layer, are at least 0.2 eV more stable than any tetrahedrally coordinated sites in the same surface layer. By contrast, octahedral sites are unstable in the Au subsurface and the hydrogen atoms spontaneously move between the Au atoms to settle at other coordination sites. This likely arises due to the small size of hydrogen atoms and the large interatomic distances in Au. The tetrahedral under top site of Au is the only stable absorption site in the first subsurface layer ($BE_H = -1.49$ eV), and both tetrahedrally coordinated absorption sites in the second subsurface layer have binding energies within 0.02 eV of each other (-1.48 eV for tetrahedral above a Au atom, -1.50 eV under a Au atom). The tetrahedral under hcp sites in the first subsurface layer of both Ni and Au are also unstable, and the hydrogen atoms moves though the surface layer to settle at a surface hcp site.

Table 2. Properties of $1/9$ ML hydrogen surface and subsurface sorption on Ni(111) and Au(111) surfaces

Metal	Sorption layer	Site preference ^a	BE (eV)	Ni CN	Au CN	μ (μ_b)	$\Delta z_{\max}$ (Å)	d_{H-Ni} (Å)	d_{H-Au} (Å)
Ni	surface	Top	-2.25	1	0	0.62	0.03	1.47	
Ni	surface	bridge	-2.69	2	0	0.62	0.04	1.63	
Ni	surface	Hcp	-2.82	3	0	0.62	0.04	1.70	
Ni	surface	Fcc	-2.83	3	0	0.62	0.04	1.71	
Ni	1 st subsurface	T _d under hcp ^b		4	0				
Ni	1 st subsurface	T _d under top	-1.94	4	0	0.61	0.22	1.57	

Ni	1 st subsurface	O _h	-2.19	6	0	0.61	0.04	1.73
Ni	2 nd subsurface	T _d above Ni	-1.92	4	0	0.61	0.03	1.60
Ni	2 nd subsurface	T _d under Ni	-1.94	4	0	0.61	0.04	1.61
Ni	2 nd subsurface	O _h	-2.17	6	0	0.61	0.03	1.79
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Au	surface	Top	-1.92	0	1		0.09	1.61
Au	surface	bridge	-2.08	0	2		0.15	1.79
Au	surface	Hcp	-2.11	0	3		0.09	1.91
Au	surface	Fcc	-2.13	0	3		0.11	1.90
Au	1 st subsurface	T _d under hcp ^b		0	4			
Au	1 st subsurface	T _d under top	-1.49	0	4		0.31	1.89
Au	1 st subsurface	O _h ^c		0	6			
Au	2 nd subsurface	T _d above Au	-1.48	0	4		0.05	1.91
Au	2 nd subsurface	T _d under Au	-1.50	0	4		0.05	1.89
Au	2 nd subsurface	O _h ^d		0	6			

BE is the binding energy of atomic hydrogen. **Ni CN** and **Au CN** are the coordination numbers of hydrogen to Ni and Au respectively at the binding site. **μ** is the mean magnetization per Ni atom in the slab. **$\Delta z_{\max}$** is degree of corrugation, defined as the maximum absolute difference in z position of surface atoms.

$d_{\text{H-Ni}}$ and **$d_{\text{H-Au}}$** are the minimum hydrogen-metal distances to Ni and Au respectively.

^a T_d = tetrahedrally coordinated subsurface site, O_h = octahedrally coordinated site.

^b Hydrogen atom placed in T_d hole under hcp site in calculations moves to surface hcp site.

^c Hydrogen atom placed in O_h hole in first subsurface layer in calculations moves to surface fcc site.

^d Hydrogen atom placed in O_h hole in second subsurface layer in calculations moves to the third subsurface layer.

Figure 1. Surface (left), first subsurface (middle), and second subsurface (right) binding sites for hydrogen atoms on and in (111) surfaces of fcc metals.

The addition of a small adsorbate such as hydrogen does not significantly cause corrugation in the metal surfaces of Ni and Au in most cases. From Table 2, it can be seen that on Ni, only placing a hydrogen atom directly underneath a Ni atom in the surface layer (at the tetrahedral under top position) is able to deform the surface by more than 0.04 Å. All deformations in the surface layer of Au upon hydrogen addition are larger than on Ni, but remain below 0.1 Å in almost all cases. The only exceptions are

when hydrogen is placed in the tetrahedral under top site which pushes the Au atom above it by 0.31 Å, and when hydrogen adsorbs at a bridge site, where the Au atoms adjacent to hydrogen are elevated and the next-nearest Au neighbors are depressed, such that $\Delta z_{\text{max}} = 0.15$ Å. Addition of hydrogen to Ni has no significant effect on the magnetization of the Ni atoms.

3.3 Surface hydrogen adsorption on Au/Ni NSAs

Table 3 reports the best binding sites on the surface and in the first and second subsurface layers of ten Au/Ni NSA (111) model surfaces studied here. In all cases, the best surface binding sites remain fcc three-fold hollow sites, similar to the site preference on both Ni and Au, and the best hcp three-fold hollow site is between 0 and 0.05 eV less stable than the best fcc site. For the NSA surfaces that still possess three-fold hollow sites consisting of three Ni atoms, the binding energy of surface adsorbed hydrogen atoms at these three-fold Ni hollows is within 0.22 eV of the binding energy on pure Ni, and is within 0.12 eV in all but two cases, (rm4) and (af4). By contrast, the (sp3) and (cy4) structures possess no three-fold hollow sites consisting only of Ni atoms, and the best binding sites on these surfaces involve coordination of the adsorbed hydrogen atom to two Ni atoms and one Au atom, resulting in a weaker binding of -2.48 eV in both cases, which is 0.35 eV weaker than on pure Ni.

Hydrogen adsorption on NSA surfaces has a weak ($\leq 0.02 \mu_B$) effect on the magnetization per Ni atom relative to the clean slabs, reducing the magnetic moment of the surface only slightly. The effect of hydrogen adsorption on surface corrugation is also typically weak (≤ 0.10 Å) relative to the clean slabs, with exceptions at 0.44 ML Au

coverage. While the (rm4) and (af4) surfaces show no change in their corrugation upon hydrogen adsorption on the surface, hydrogen adsorption increases the surface corrugation on the (cy4) surface by 0.27 Å and on the (sn4) surface by 0.42 Å relative to their clean slabs. The clean (cy4) and (sn4) slabs show much less corrugation as compared to the other 0.44 ML Au coverage surfaces, as discussed in Section 3.2, and these differences are smaller upon hydrogen adsorption.

Table 3. Properties of $1/9$ ML hydrogen surface and subsurface sorption on Au/Ni NSA (111) surfaces

Alloy Au coverage	code ^a	Adsorption layer	Site Preference ^b	BE (eV)	Ni CN	Au CN	μ (μ_B)	$\Delta z_{\max}$ (Å)	d_{H-Ni} (Å)	d_{H-Au} (Å)
0.11 ML	sp1	Surface	Fcc	-2.81	3	0	0.61	0.42	1.70	3.85
0.11 ML	sp1	1 st subsurface	O _h	-2.21	6	0	0.60	0.44	1.74	3.13
0.11 ML	sp1	2 nd subsurface	O _h	-2.23	6	0	0.60	0.45	1.78	3.41
0.22 ML	sp2	Surface	Fcc	-2.75	3	0	0.60	0.43	1.69	3.00
0.22 ML	sp2	1 st subsurface	O _h	-2.17	6	0	0.60	0.44	1.73	3.19
0.22 ML	sp2	2 nd subsurface	O _h	-2.22	6	0	0.60	0.45	1.78	3.43
0.22 ML	ad2	Surface	Fcc	-2.76	3	0	0.60	0.50	1.69	3.78
0.22 ML	ad2	1 st subsurface	O _h	-2.21	6	0	0.60	0.51	1.74	3.14
0.22 ML	ad2	2 nd subsurface	O _h	-2.23	6	0	0.60	0.51	1.78	3.46
0.33 ML	sp3	Surface	fcc/hcp	-2.48	2	1	0.60	0.60	1.69	1.96
0.33 ML	sp3	1 st subsurface	O _h	-2.16	5	1	0.59	0.85	1.70	2.49
0.33 ML	sp3	2 nd subsurface	O _h	-2.22	6	0	0.59	0.53	1.78	3.47
0.33 ML	cn3	Surface	Fcc	-2.71	3	0	0.59	0.62	1.68	2.97
0.33 ML	cn3	1 st subsurface	T _d under top	-2.24	3	1	0.60	1.22	1.64	2.77
0.33 ML	cn3	2 nd subsurface	O _h	-2.23	6	0	0.60	0.71	1.76	3.63
0.33 ML	tf3	Surface	Fcc	-2.72	3	0	0.59	0.61	1.69	3.81
0.33 ML	tf3	1 st subsurface	O _h	-2.22	5	1	0.60	1.12	1.75	2.56
0.33 ML	tf3	2 nd subsurface	O _h	-2.24	6	0	0.60	0.67	1.76	3.54
0.44 ML	rm4	Surface	Fcc	-2.61	3	0	0.60	1.13	1.69	2.70
0.44 ML	rm4	1 st subsurface	O _h	-2.33	3	3	0.60	1.19	1.64	2.52
0.44 ML	rm4	2 nd subsurface	O _h	-2.23	6	0	0.60	1.13	1.75	4.02
0.44 ML	cy4	Surface	Fcc	-2.48	2	1	0.60	0.94	1.71	1.95
0.44 ML	cy4	1 st subsurface	O _h	-2.42	4	2	0.60	1.29	1.69	2.71
0.44 ML	cy4	2 nd subsurface	O _h	-2.29	6	0	0.59	1.23	1.75	4.11
0.44 ML	sn4	Surface	Fcc	-2.74	3	0	0.59	1.08	1.67	2.78
0.44 ML	sn4	1 st subsurface	O _h	-2.41	5	1	0.60	1.28	1.74	2.63
0.44 ML	sn4	2 nd subsurface	O _h	-2.35	6	0	0.60	1.15	1.75	3.97
0.44 ML	af4	Surface	Fcc	-2.68	3	0	0.60	1.21	1.69	3.05
0.44 ML	af4	1 st subsurface	T _d under top	-2.41	3	1	0.60	1.53	1.64	2.74
0.44 ML	af4	2 nd subsurface	O _h	-2.25	6	0	0.60	1.43	1.74	4.04

BE is the binding energy of hydrogen. **Ni CN** and **Au CN** are the coordination numbers of hydrogen to Ni and Au respectively at the binding site. **μ** is the magnetization per Ni atom. **$\Delta z_{\max}$** is degree of corrugation,

defined as the maximum absolute difference in z position of surface atoms. $d_{\text{H-Ni}}$ and $d_{\text{H-Au}}$ are the minimum hydrogen-metal distances to Ni and Au respectively. Note that the nearest Ni atom is always at the binding site, but $d_{\text{H-Au}} > 3.0 \text{ \AA}$ represents the Au atoms near but not at the binding site.

^a See Table 1 for Au arrangement corresponding to each code.

^b T_d = tetrahedrally coordinated subsurface site, O_h = octahedrally coordinated site.

Figure 2. Binding energies of hydrogen at all surface adsorption sites on Au/Ni NSAs (111), compared to binding energies of hydrogen on similar sites on Ni(111) and Au(111); a) 0.11 ML, 0.22 ML, and 0.33 ML Au coverage, b) 0.44 ML Au coverage. ◆ (sp1), ● (sp2), ○ (ad2), ▲ (sp3), ▲ (cn3), ▲ (tf3), ◆ (rm4), ◆ (cy4), ◆ (sn4), ◆ (af4), ■ Ni(111), ■ Au (111). More negative Binding Energy means stronger interaction.

Figure 2 compares the binding energies of hydrogen at all stable binding sites on the 10 NSA surfaces from Table 1, as well as the binding energies on the Ni(111) and Au(111) surfaces for similar binding geometries. The best binding sites across all surfaces

are always fcc sites with three Ni neighbors, followed closely by hcp sites with three Ni neighbors. It can be seen that amongst binding sites with the same binding geometry (i.e. top, bridge, hcp, fcc sites), hydrogen binding energies are weaker with more Au neighbors at the coordination site. For example, hydrogen binding at fcc sites consisting of only Ni atoms (and zero Au atoms) is strongest, followed by fcc sites with one Au atom and two Ni atoms, which bind hydrogen stronger still than fcc sites with two Au atoms and one Ni atom. At the extreme, fcc and hcp sites consisting of three Au atoms result in binding energies nearly identical to those on pure Au surfaces. For all binding geometries, the binding energies are always intermediate between the binding energies for similar sites on pure Au and pure Ni. In many cases, bridging sites between Au and Ni atoms (coordination to Au/total coordination = $\frac{1}{2}$) are unstable, and hydrogen atoms placed at those sites at the beginning of calculations drift to other adsorption sites. For this reason, there are fewer data points for this coordination environment than expected.

Figure 3a shows how the increase in Au substitution in the NSA surface layer decreases the binding energy of hydrogen atoms on the surface. However, when comparing adsorption at sites with similar metal compositions, the effect is small. From Figure 2, the three-fold hollow sites consisting of three nickel atoms on the NSA surfaces are at most only 0.24 eV weaker than on pure Ni, bridge sites with two Ni atom neighbors are at most 0.24 eV weaker than the bridge site on Ni(111), and top sites above Ni atoms are at most 0.06 eV less stable than on Ni. Compare these small differences to the effect of varying the metal composition at the binding site on surfaces at the same Au coverage. For example, the strongest binding sites with fcc geometry consisting of only Ni atoms bind hydrogen 0.6 eV more strongly than fcc sites consisting of only Au atoms,

even at the same Au atom coverage (Figure 2). In Figure 3b, the binding energies of fcc sites on all Au/Ni NSA surfaces as well as on pure Ni and Au (111) surfaces are grouped according to the Au coordination of the hydrogen atom, and these similar binding sites are plotted against the Au content of the surface layer of the alloy (or pure metal). The slopes of the trend lines for each coordination environment are small or zero, indicating the weak dependence of binding energy on Au coverage. The trend lines themselves are roughly 0.2 eV apart, such that three substitutions of a Ni atoms at the binding site by Au accounts for the $0.6 \text{ eV} = 3 * 0.2 \text{ eV}$ range in binding energy seen in the 0.33 ML and 0.44 ML Au coverage surfaces. The local arrangement of Au atoms at the adsorption site plays a more important role in determining the binding energy for hydrogen than does the local or average Au coverage across the NSA surface.

However, as the results from the (sp3) and (cy4) surfaces show in Figure 3a, the local arrangement of surface Au atoms at higher Au coverages (0.33 ML and 0.44 ML respectively) can eliminate the availability of favorable hollow sites with three Ni atoms, requiring hydrogen to bind to sites with one or more Au neighbors.

Figure 3. a) Hydrogen Binding energies of best surface (◆), first subsurface (▲), and second subsurface (▼) binding sites on Ni(111) and Au/Ni NSAs against the Au coverage; b) Hydrogen binding energies of all fcc sites on Au/Ni NSAs and Ni(111) and Au(111) plotted against Au coverage and grouped according to Au fraction of metal atoms at binding site.

3.4 Subsurface hydrogen absorption on Au/Ni NSAs

Figure 4. Binding energies of hydrogen at all subsurface absorption sites on Au/Ni NSAs (111), compared to binding energies of hydrogen on similar sites on Ni(111); a) 0.11 ML, 0.22 ML, and 0.33 ML Au coverage, b) 0.44 ML Au coverage. ◆ (sp1), ● (sp2), ○ (ad2), ▲ (sp3), ▲ (cn3), ▲ (tf3), ◆ (rm4), ◆ (cy4), ◆ (sn4), ◆ (af4), ■ Ni(111), ■ Au (111)..

Whereas binding for a given adsorption site geometry on the surface layer is typically weaker on the NSAs than on pure Ni (Figure 2), binding in the first and second subsurface layers can be either stronger or weaker than in pure Ni (Figure 4, Table 3). Figure 4 compares the binding energies of hydrogen atoms at all possible binding sites in the first subsurface layer in the NSA surfaces from Table 1 to the binding energies for octahedral and tetrahedral under top absorption sites in the Ni(111) surface. The trends in the binding energies with both increasing Au content in the NSA and increasing Au coordination at the binding are different from those found for surface adsorption sites. Figure 3 a) shows that binding energies for the best binding sites in the first and second subsurface layers of the Au/Ni NSAs are more or less independent of the fractional coverage of Au in the NSA surface up to 0.33 ML Au substitution. Binding energies for the best binding sites are within ± 0.05 eV of the binding energy on Ni(111) for the first subsurface layer interstitial sites and between 0.05 eV and 0.07 eV stronger binding for second subsurface layer interstitial sites. As with Ni, the best interstitial absorption sites are octahedrally coordinated in both the first and second subsurface layers, except in the (cn3) structure, where a tetrahedral under top site under a Au atom is the best octahedral site.

When the Au coverage is increased to 0.44 ML, the best subsurface absorption sites become even more stable as compared to similar sites on pure Ni, with the first subsurface sites being 0.14 eV–0.23 eV more stable than on Ni, and the second subsurface sites being 0.06 eV–0.18 eV more stable. This is readily observed in Figure 3 a), where the binding energies at subsurface sites for 0.44 ML Au coverage are stronger than would be expected from the trend at lower Au coverages. The best absorption sites

are octahedrally coordinated, just as with Ni(111), except for the (af4) structure, where the optimal absorption site in the first subsurface layer is a tetrahedrally coordinated site under a Au atom.

On the surface, for a given adsorption site geometry, the best adsorption sites are those with the fewest Au atom neighbors. In the first subsurface layer, this trend also holds for the tetrahedral under hcp sites. For octahedral binding sites, there is no clear trend, especially for Au coverages of 0.33 ML and below, and the binding energy is nearly independent of the number of Au atom neighbors. For octahedral sites at Au coverages of 0.44 ML and for tetrahedral under top sites at all Au coverages, sites with more Au neighbors bind hydrogen atoms more strongly as compared to sites with fewer Au neighbors. This stabilization of subsurface sites near Au atoms arises partly from the mobility of Au atoms within the surface layer. When hydrogen atoms are placed at subsurface binding sites adjacent to Au atoms, the Au atoms move perpendicularly to the surface to more positive z positions, enlarging the interstitial holes below them and increasing the total surface corrugation (Table 3). This is most readily apparent at tetrahedral under top sites. When the hydrogen atom is placed under a Au atom, the Au atom is able to move upwards and away from the hydrogen atom, creating a more stable “pocket” for absorption, with hydrogen effectively bonding to Ni under-coordinated sites. Ni atoms are not able to move to such an extent, and Ni-hydrogen atom distances at tetrahedral under top sites under Ni atoms are consequently smaller, and these sites bind hydrogen more weakly.

In the second subsurface layer, the best binding sites in each NSA bind hydrogen in octahedral sites between 0.03 eV and 0.16 eV more strongly than does the octahedral

second subsurface site in Ni. The binding energies in the second subsurface are similar to those in the first subsurface layer. Larger differences between first and second subsurface layer binding energies exist when the first subsurface layer binding site includes coordination to Au. At 0.44 ML Au coverage, placement of hydrogen atoms at octahedral sites in the second subsurface layer is sufficient to induce and increase the surface corrugation by up to 0.56 Å (on the (cy4) structure, see Table 3). As with adsorption on the 0.44 ML Au coverage surfaces, the largest increase in surface corrugation occurs for the Au arrangements with the smallest corrugation in the clean slabs. As even second subsurface layer absorption of hydrogen atoms is able to nearly double the degree of surface corrugation, the change is likely attributable to breaking the symmetry of the surface Au arrangements in the clean slab rather than reflecting a significant increase in strain among surface Au atoms. For the clean (cy4) and (sn4) surfaces, the high surface symmetry balances the Au atoms in a low corrugation arrangement that is disrupted by the symmetry-breaking addition of a hydrogen atom. The low degree of corrugation in the (ln3) structure may also be attributable to its symmetry, but this possibility was not explored as hydrogen adsorption calculations were not performed on this surface.

3.5 Distribution of surface/subsurface hydrogen

On Ni(111), hydrogen binding is 0.64 eV stronger on surface fcc sites as compared to subsurface octahedral sites. At room temperature, a 0.06 eV energy difference would correspond to an order of magnitude difference in relative state populations. This large thermodynamic preference for surface adsorption indicates that the ratio of surface to subsurface hydrogen on Ni(111) surfaces would be expected to be

large in general, except perhaps at high temperatures and/or high H_2 pressures. This energy difference is smaller for the Au/Ni NSAs, and decreases with increasing Au coverage. This is consistent with recent results that show a smaller difference in binding energy between surface and subsurface binding sites in NSAs than in pure metals [14]. At 0.11 ML Au coverage, the subsurface octahedral binding site is still 0.60 eV less stable than the surface fcc site, but at 0.33 ML Au coverage, the differences are 0.31 eV, 0.47 eV, and 0.50 eV on the (sp3), (cn3), and (tf3) surfaces. At 0.44 ML, the difference is as small as 0.06 eV on the (cy4) surface, where surface fcc sites are disfavored due to hydrogen coordination to Au at the best binding site. Although in the model systems studied here, subsurface hydrogen is never more stable than surface hydrogen, the smaller difference in binding energies indicates that more subsurface hydrogen is expected to coexist with surface hydrogen at higher Au coverages under all conditions of temperature and H_2 partial pressure. Additionally, if the activation barrier for surface to subsurface diffusion arises primarily from the thermodynamic energy difference between these states [13,23], then the barriers for diffusion may similarly be expected to be smaller for high Au coverages in Au/Ni NSAs than for low Au coverages and for Ni(111).

3.6 Relative stabilities of Au/Ni arrangements in the presence of hydrogen

In Table 1, the most stable surface arrangement for a given Au coverage was identified as the one with the lowest total energy, assigned $\Delta E = 0$, and used as the basis for comparing the stability of other surface arrangements with the same Au coverage. The most stable clean slab does not always have the strongest binding energy for hydrogen, so that the difference in total energy between two surfaces with hydrogen may be different

than the difference for the clean slabs. This effect is summarized in Table 4, where the difference in total energy of the clean NSA surfaces is compared to the difference in total energy of the NSA surfaces with hydrogen sorbed onto the best surface or subsurface binding sites. For 0.22 ML Au coverage, the difference in stability between the (sp2) and (ad2) surfaces does not change much in the presence of hydrogen (1/9 ML), and the (sp2) arrangement is still more stable in all cases. However, the difference in stabilities is slightly smaller (0.02 – 0.04 eV) in the presence of hydrogen. At 0.33 ML Au coverage, both the (cn3) and (tf3) surfaces are more stable in the presence of hydrogen than the (sp3) surface. This is due to the weak binding of hydrogen on the (sp3) surface, which possesses no hollow sites consisting of only Ni atoms. Although the effect is small (0.05 eV), it suggests that a real Au/Ni NSA surface consisting of ensemble of Au atoms arranged such that favorable hollow binding sites do not exist between them may experience a thermodynamic driving force to *rearrange* themselves into ensembles that do create these favorable sites between them. It is also possible that this driving force for rearrangement may depend on the adsorbate, and that species that bind to Ni more strongly than hydrogen may exaggerate this effect.

Table 4. Total energy differences between slabs at the same Au coverage with and without hydrogen adsorbed on the surface and absorbed in the subsurface.

Au coverage Surface (ML)	0.22 (sp2)	0.22 (ad2)	0.33 (sp3)	0.33 (cn3)	0.33 (tf3)	0.44 (rm4)	0.44 (cy4)	0.44 (sn4)	0.44 (af4)
Δ TE clean slab (eV)	0	+0.13	0	+0.18	+0.20	0	+0.15	+0.24	+0.30
Δ TE H on surface (eV)	0	+0.11	0	-0.05	-0.05	0	+0.27	+0.10	+0.23
Δ TE H in 1 st subsurface (eV)	0	+0.09	0	+0.10	+0.14	0	+0.07	+0.16	+0.22
Δ TE H in 2 nd subsurface (eV)	0	+0.11	0	+0.17	+0.18	0	+0.09	+0.12	+0.28

At 0.44 ML Au coverage, some surfaces are more stable upon hydrogen adsorption as compared to the lowest energy clean surface, and the (cy4) structure was more unstable. Addition of hydrogen to the first subsurface layer always increased the

stability of alternative Au arrangements relative to the most stable clean surface. These data indicate that the distribution of hydrogen atoms across the surface and subsurface will influence the local arrangement of Au atoms by changing the relative stabilities of different Au surface ensembles.

Given the stronger binding of H atoms to Ni atoms, the addition of H adsorbates may also influence the surface composition by favoring segregation of Ni atoms to the surface, pushing the less reactive Au atoms into subsurface metal layers. To test this hypothesis, and in the presence of $1/9$ ML of H coverage, a 0.11 ML Au/Ni NSA surface was constructed with the Au atom in the first subsurface layer of metal atoms, leaving a surface consisting only of Ni atoms (structure code ss1). This arrangement was 1.18 eV less favorable as compared to (sp1). With no Au atoms on the surface, the binding energy of H on (ss1), -2.89 eV, is 0.08 eV stronger than on (sp1). However, this small difference in binding energy is not enough to overcome the energetic penalty from forcing the much larger Au atom into the much smaller subsurface Ni lattice position, and the net difference is that the total energy with H adsorbed on (ss1) is 1.09 eV less favorable than H adsorbed on (sp1). For this reason, H adsorption is not expected to lead to Ni atoms segregating to the surface of these NSAs, at the $1/9$ ML H coverage modeled in this study.

4. Conclusions

Au/Ni near-surface alloys consisting of Ni(111) surfaces with several surface Ni atoms substituted by Au were modeled at different Au coverages and with different arrangements of Au atoms in the surface layer. Calculations of the binding energy of hydrogen on surface and in subsurface sorption sites revealed that the hydrogen prefers to

bind at hollow sites surrounded by three Ni atoms. Any Au arrangement that does not possess such sites necessarily binds hydrogen significantly weaker. The binding energy is influenced by both the total amount of Au in the surface layer as well as the coordination environment of the hydrogen atom, the latter of which has the stronger effect. For an fcc hollow site, the binding energy for any hydrogen coordination environment and for any Au coverage may be obtained to first approximation from the plot in Figure 3b.

As with pure Ni(111), hydrogen typically prefers fcc hollow sites on the surface and octahedrally coordinated interstitial sites in the subsurface of Au/Ni NSAs. As the coverage of the surface by Au increases, the stability of hydrogen in the surface decreases and the stability of hydrogen in the subsurface increases, such that at 0.44 ML of Au coverage, some Au arrangements place these two states only 0.06 eV apart in stability. This indicates that the Au coverage in the surface layer will influence the distribution of hydrogen between the surface and subsurface layers of the NSA. If the activation barrier for hydrogen atom diffusion from the surface to the subsurface is dominated by the energy difference between sorption in these two locations, then diffusion of hydrogen atoms from the surface to the subsurface is expected to become more facile as the Au content increases in the NSA.

While comparing the total energies of different Au arrangements for a single Au coverage predicts one particular ordering of their relative stabilities, the presence of hydrogen on the surface or in the subsurface of the NSA will change the relative stabilities. While the most stable arrangement for a clean surface is typically the most stable upon hydrogen sorption as well, this is not always the case. This opens the possibility that hydrogen sorption will drive the rearrangement of the surface Au

ensembles to the best surface structure under specific conditions of temperature and dihydrogen partial pressure.

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Figure and Table Captions

Table 1. Model Au/Ni NSA surfaces used in this study.

Table 2. Properties of $\frac{1}{9}$ ML hydrogen surface and subsurface sorption on Ni(111) and Au(111) surfaces.

Table 3. Properties of $\frac{1}{9}$ ML hydrogen surface and subsurface sorption on Au/Ni NSA surfaces

Table 4. Total energy differences between slabs at the same Au coverage with and without hydrogen adsorbed on the surface and absorbed in the subsurface.

Figure 1. Surface (left), first subsurface (middle), and second subsurface (right) binding sites for hydrogen atoms on and in (111) surfaces of fcc metals.

Figure 2. Binding energies of hydrogen at all surface adsorption sites on Au/Ni NSAs (111), compared to binding energies of hydrogen on similar sites on Ni(111) and Au(111); a) 0.11 ML, 0.22 ML, and 0.33 ML Au coverage, b) 0.44 ML Au coverage. ◆ (sp1), ● (sp2), ○ (ad2), ▲ (sp3), ▲ (cn3), ▲ (tf3), ◆ (rm4), ◆ (cy4), ◆ (sn4), ◆ (af4), ■ Ni(111), ■ Au (111). More negative Binding Energy means stronger interaction.

Figure 3. a) Hydrogen Binding energies of best surface (◆), first subsurface (◆), and second subsurface (◆) binding sites on Ni(111) and Au/Ni NSAs against the Au coverage; b) Hydrogen binding energies of all fcc sites on Au/Ni NSAs and Ni(111) and Au(111) plotted against Au coverage and grouped according to Au fraction of metal atoms at binding site.

Figure 4. Binding energies of hydrogen at all subsurface absorption sites on Au/Ni NSAs, compared to binding energies of hydrogen on similar sites on Ni(111); a) 0.11 ML, 0.22 ML, and 0.33 ML Au coverage, b) 0.44 ML Au coverage. ◆ (sp1), ● (sp2), ○ (ad2), ▲ (sp3), ▲ (cn3), ▲ (tf3), ◆ (rm4), ◆ (cy4), ◆ (sn4), ◆ (af4), ■ Ni(111), ■ Au (111).