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Kinetic Monte Carlo modeling of reaction-induced phase separation in Au/Ni(111) surface alloy

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ABSTRACT

Kinetic Monte Carlo (KMC) simulations of Au–Ni phase separation in Au/Ni(111) surface alloy during nickel carbonyl formation reaction were performed at room temperature by taking into account realistic rates of Au and Ni adatom diffusion and CO adsorption and desorption, while keeping the rate of nickel carbonyl formation reaction as a free parameter. We also obtained pair and three-body interaction constants between Au and Ni adatoms using the ab initio calculations and demonstrated that their proper choice is crucial for understanding the Au–Ni separation process. Three regimes with qualitatively different Ni–CO reaction propagation kinetics in Au/Ni(111) surface alloy were found by varying the constants of trio-triangle interactions within the limits of their accuracy. The sensitivity of the proposed model to interaction parameters leads to the regimes that differ by step flow rate, Au islands formation mechanism (channel-type or homogenous flow), Au island contamination level by Ni impurities and reaction damping tendency at the reaction front. Nucleation of nickel-free Au islands was observed for a homogeneous step flow pattern, and the corresponding step flow rate is in a good quantitative agreement with existing experimental data.

1. Introduction

Electronic, magnetic and catalytic properties of bimetallic systems on metal surfaces attract nowadays a considerable attention. Advances in surface growth technologies allow one to produce the so-called surface alloys which are formed only in the surface layer by two thermodynamically bulk-immiscible metals. Surface alloying by adatom exchange with surface atoms occurs [1–4] at submonolayer coverage of adatom component.

In pursuit of a novel catalyst with improved properties in activity and selectivity working at industrial conditions, the Au–Ni surface alloy stability on Ni(111) was recently studied at high CO pressures [1]. However, a phase separation of Au and Ni components was observed, caused by gold-catalyzed Ni + CO reaction producing nickel carbonyl gas, $Ni(CO)_4$, and facilitating nucleation of remaining Au into islands at the reaction front.

The Kinetic Monte Carlo (KMC) approach [5–8] is a standard method used to model the microscopic details of such reaction-induced behavior. The KMC provides an advantage of studying activated, non-equilibrium processes in real time, while maintaining computational efficiency. However, a particular attention has to be paid to a reliable selection of diffusion, reaction and interaction parameters characterizing the dynamics of phase separation experiment [1]. For example, the range of diffusion rates might comprise many orders of magnitude: from very fast hopping ($10^6 \div 10^7\ s^{-1}$) in the absence of nearest neighbor (NN) adatoms [9] to a complete immobility at kink sites, where a surface atom is attracted by, e.g., three NN adatoms [10]. Similarly, a large difference in magnitude of nickel carbonyl reaction (formation) rate for pure Ni foil [11] and Au/Ni(111) surface alloy [1] is observed being much higher for the alloy. In addition, the reaction rate could be modified by Au–CO and Ni–CO repulsion, which leads to reduction of CO in NN sites that are neighbors of both Ni and Au adatoms.

It should be noted that in the first computer simulations [8] reproducing the experiment [1] the role of CO was neglected, assuming that at high pressures all Au and Ni atoms are completely covered by CO molecules. By neglecting the CO-induced effects, it is impossible to simulate the experimentally observed step flow rate dependence on CO pressure (CO surface coverage, c). It also contradicts the X-ray diffraction study [12] indicating the existence of $c = 0.57$ phase and strong CO–CO repulsion on Ni(111) even at high CO pressures.

In this paper, we estimate parameters of pair- and three-body (trio) interactions between Au and Ni adatoms using ab initio calculations. Further, these interactions are used in the KMC simulation to model the reaction-induced phase separation in Au/Ni(111) surface alloy. We study the effect of trio interactions on qualitative (Au islands formation and purity, homogenous/inhomogeneous reaction flow) and quantitative (reaction delay, step flow rate) features of the reaction front

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propagation process. The rate and mechanism of front propagation are shown to be very sensitive to the values of interaction parameters, and at least three different reaction mechanisms can be predicted.

2. Calculation of interaction parameters

Calculations of formation energies of various ordered surface configurations were performed using ab initio Vienna simulation package (VASP) based on the density functional theory (DFT) [13]. The adsorbate structure was created on top and bottom of symmetrically terminated 5 Ni layer slab where the lower plane was a mirror plane of the upper plane. The positions of adatoms and all atoms in 5-layer slab were allowed to relax. The unit cell size periodicity varied from 1 × 1 to 4 × 4. A surface is modeled by a large (ca.10 Å) vacuum gap. A plane wave cutoff energy of 320 eV and a Monkhorst Pack k-point mesh of 8 × 8 × 1 were used in our calculations [14].

Plane waves were constructed using the ultrasoft Vanderbilt pseudopotentials (10 and 11 electrons in Ni and Au pseudopotentials, respectively) [15] and modified by projector-augmented-wave (PAW) method as described in Ref. [16]. All calculations were performed using the generalized gradient approximation and Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [17]. We have used the first order Methfessel-Paxton smearing scheme [18] for the partial occupancies (with smearing parameter 0.2 eV). These parameters predict the bulk lattice constant (3.526 Å) and magnetic moment for Ni in good agreement with experimental values and offer a good compromise between computational speed and accuracy.

In order to obtain pair- and trio- interaction energies that can be directly used in KMC simulations, we adapt the methodology [19]. On one hand, using first-principle (FP) calculations, we obtain the total interaction energy, E^{FP}, for configuration of N_{Ni} Ni and N_{Au} Au adatoms

$$E^{FP} = E_N - E_0 - N_{Ni}\left(E_1^{Ni} - E_0\right) - N_{Au}\left(E_1^{Au} - E_0\right) \tag{1}$$

where E_N is the total energy of a slab with $N = N_{Ni} + N_{Au}$ adatoms, E_1^{Ni} and E_1^{Au} are the total energies of slabs containing a single Ni and Au adatom, respectively, and E_0 is the corresponding total energy of a bare slab. Since we use symmetric adatom configurations on both top and bottom planes of the slab, a single adatom configuration corresponds to one atom on the top and one — on the bottom plane, respectively. On the other hand, using many-body interaction terms of the lattice-gas (LG) Hamiltonian [19–21], the total adatom interaction energy, E^{LG}, can be expressed as

$$E^{LG} = \frac{1}{2!}\sum_{ij}{}' V_{ij}^{pair} n_i n_j + \frac{1}{3!}\sum_{ijk}{}' V_{ijk}^{trio} n_i n_j n_k + \ldots \tag{2}$$

where $n_\alpha = 1$ if the site $\alpha = i, j, k$ is occupied and zero — otherwise. The summation indices j and k run over all sites of the lattice, while i is limited to the original supercell. The self-interaction in both sums of Eq. (2) is excluded (indicated by prime symbol). The V_{ij}^{pair} and V_{ijk}^{trio} denote pair and trio interactions, respectively. We limit the pair interaction potentials V_{ij}^{pair} by the third NN adatoms and denote NN, next-NN and third NN interactions as V_1^γ, V_2^γ and V_3^γ respectively ($\gamma =$ Au–Au, Ni–Ni or Au–Ni). Trio interactions are calculated for three typical configurations on triangular lattice: trio in a line, trio-triangle and trio-bent.

Finally, assuming that interactions in FP calculations are additive, we relate the total interaction energies obtained from ab initio calculations Eq. (1) to lattice-gas energies Eq. (2), $E^{FP} \equiv 2E^{LG}$, (a co-factor 2 arises for a slab with top and bottom adatom symmetric configurations) and obtain a set of linear equations. The number of unknown interaction energies determines the minimal set of required different adatom configurations that contain either just Au or just Ni (see Ref. [22]) adatoms, or mixed both Au and Ni adatom combinations (see Fig. 1). Additionally to cases in Fig. 1, we use two trivial configurations for Ni (or Au) adatoms: (i) a single adatom on 3 × 3 supercell for determination of E_1^{Ni} (or E_1^{Au}) energy and (ii) a single adatom on 2 × 2 supercell for determination of V_3^γ. We use the nontrivial configurations of Fig. 1 for calculation of: (a) V_1^γ, (b) V_2^γ, (c) V_{TT}^{trio}–trio in triangle, (d) V_{TB}^{trio}–trio bent, and (e) V_{TL}^{trio}–trio in a line interactions, respectively. For mixed configurations with both Ni and Au adatoms we use the following Fig. 1 configurations: (a) V_1^{Au-Ni} with $[i\ j] =$ [Ni Au], (b) V_2^{Au-Ni} with $[i\ j\ k] =$ [Ni Au Ni], (c) V_{TT}^{trio} with $[i\ j\ k] =$ [Au Ni Ni] and $[i\ j\ k] =$ [Au Au Ni], (d) V_{TB}^{trio} with $[i\ j\ k] =$ [Au Ni Ni], $[i\ j\ k] =$ [Ni Au Ni], $[i\ j\ k] =$ [Au Au Ni], $[i\ j\ k] =$ [Au Ni Au], and (e) V_{TL}^{trio} with adatom $[i\ j\ k]$ sequences identic to case (d). Finally, we used Fig. 1 (f) configuration with $[i\ j] =$ [Au Ni] for V_3^{Au-Ni} interaction calculation.

We assume that energy of each configuration (E_N, E_0, E_1^{Ni}, E_1^{Au}) is determined by FP calculations with the accuracy up to 10 meV, see Ref. [22]. The calculated interactions are less accurate if their determination requires a larger number of both FP configurations and single

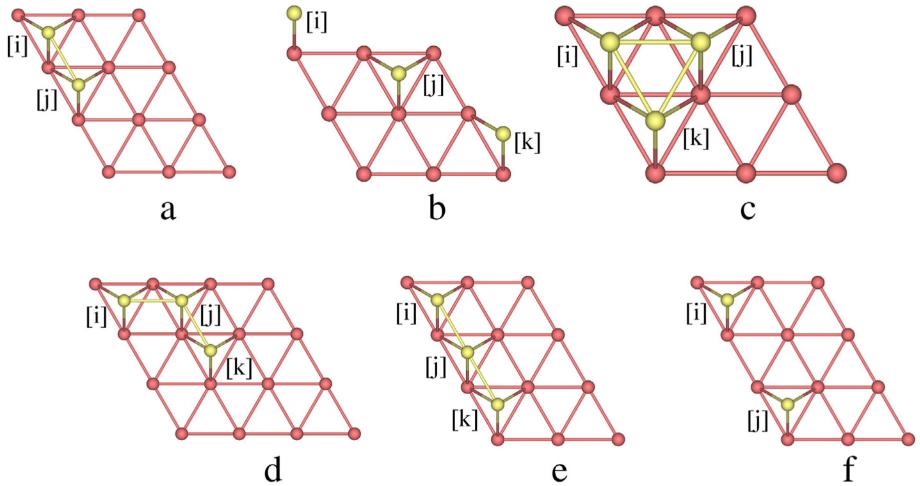

Fig. 1. Adatom (yellow and marked by letters in square brackets) configurations on the corresponding supercells used in FP calculations to determine pair and trio interactions on Ni(111) surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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