



Design of highly efficient Ni-based water-electrolysis catalysts by a third transition metal addition into Ni₃Mo

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ABSTRACT

The surface composition segregation can have important effects on the catalytic and electrochemical properties of an alloy catalyst. We have performed density-functional theory (DFT) calculations to investigate the effects of a third transition metal (M) addition into the Ni₃Mo alloy on the surface segregation and the stability of bulk-terminated and Ni-segregated Ni₃Mo/M(111) surfaces. The third transition metals (M=Ti, V, Cr, Mn, Fe, Co, Cu, Ni, Nb, Rh, Hf, Ta, or Ir) are found to enhance the Ni surface segregation, while M=Ti, V, Cr, Mn, Fe, Co, Cu, Ni, Nb, Rh, Hf, Ta, or Ir retain the Ni-segregated surface but weaken the Ni surface segregation tendency. The remaining transition metals (M=Sc, Zn, Y, Zr, Pd, Ag, Cd, Pt, or Au) show a complete suppression of the Ni surface segregation. We find the transition metals (Ti, V, Cr, Mn, Fe, Co, Cu, Hf, and W) can stabilize a special atomic configuration that is predicted to have an outstanding catalytic performance for water electrolysis. Furthermore, we analyze the factors that control the Ni surface segregation behavior in the Ni₃Mo/M(111) surface. The present study provides useful theoretical guide for developing highly active Ni-Mo-M hydrogen evolution electrodes.

1. Introduction

The enrichment/depletion of the surface composition in an alloy catalyst can dramatically affect its catalytic properties [1,2]. For example, low surface Pd concentrations in Pd-Au alloy nanoparticles and bulk Pd-Au catalysts have been found to enhance reactivity in synthesis of vinyl acetate by acetoxylation of ethylene [3]. Pb segregation on the annealed aluminum foil surfaces can improve the capacitance of the capacitors [4,5]. The Pt-Ni and Pt-Co alloys have a better catalytic performance for oxygen reduction reaction (ORR) than pure Pt [6,7]. Ag and Cu segregations on palladium based membrane surfaces lead to reduce long-term mechanical stability of the membranes [8]. Therefore it is important to understand the surface segregation behavior of various components in an alloy system, and such knowledge can be very useful for designing better alloy catalysts for specific applications.

Among various metal catalysts, nickel-based catalysts with low cost and high electro-catalytic activity have been widely used in a number of catalytic reactions, including aqueous-phase reforming of oxygenated hydrocarbons [9], the synthesis gas reactions such as partial oxidation of methane, dry reforming with CO₂, and mixed reforming with O₂ [10], CO₂ reforming of CH₄ to syngas [11]. In the context of hydrogen

evolution reaction (HER), bimetallic Ni-Mo electrodes have been proved to possess an outstanding electro-catalytic activity by experiments [12–19]. Many experimental studies have also shown that adding a third component into Ni-Mo based electrodes would improve the catalytic performance of the electrodes [20–27]. By adding tungsten into Ni-Mo binary alloy coating, Fan et al. had found that the formed Ni-Mo-W coatings could increase the HER activity effectively [23]. Also, Panek et al. had shown the ternary alloy Ni₅₀Mo₄₀Ti₁₀ annealed at 1173 K exhibits the higher electro-catalytic activity for the HER compared with the Ni₅₀Mo₅₀ [20]. The increase in the intrinsic activity could be attributed to the presence of Ni-Mo intermetallic phase and Ni (Ti) solid solution. For Ni-Mo-Co and Ni-Mo-Fe alloy electrodes, their better catalytic activities had been experimentally testified [24,25]. Recently, Zhang et al. [30] had pioneered a density-functional theory (DFT) study to investigate the effect of the third component addition on the Pt surface segregation behavior in the Pt₃Ni(111) surfaces. Although such theoretical studies are obviously very important for developing highly active trimetallic catalysts for water electrolysis they have been scarcely carried out so far due to the complication of surface segregation behavior in a trimetallic system [28,29].

Inspired by Zhang's work, we perform first-principles calculations to

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investigate the effects of a third transition metal (M) addition in the Ni₃Mo alloy on the Ni surface segregation and the stability of various bulk-terminated and Ni-segregated Ni₃Mo/M(111) surfaces. Our main goal is to design highly active Ni-based electrodes for water electrolysis. We consider three bulk-terminated and four Ni-segregated Ni₃Mo/M(111) surfaces and see that the different surface atomic configurations are stabilized by doping with different transition metals. The Ni segregation energies in the Ni₃Mo/M(111) surfaces are calculated and we find some transition metals (M=Tc, Ru, W, Re, Os, Ti, V, Cr, Mn, Fe, Co, Cu, Nb, Rh, Hf, Ta, or Ir) stabilize the Ni-segregated surface, while other transition metals (M=Sc, Zn, Y, Zr, Pd, Ag, Cd, Pt, or Au) destabilize the Ni-segregated alloy surface. The special atomic configuration of the Ni₃Mo/M(111) surface that has been predicted to have an outstanding catalytic performance for water electrolysis can be stabilized by certain third component additions. Furthermore, we discuss the factors that determine the Ni surface segregation behavior in the Ni₃Mo/M(111) surface.

The remainder of the paper is organized as follows. In Section 2, the theoretical methods and computational details are described. Section 3 presents the calculated results and discussion. Finally, a brief summary is given in Section 4.

2. Computational methods

The calculations are performed within the framework of DFT as implemented in Vienna Ab-initio Simulation Package (VASP) code [31–33]. The DFT method has proven to be one of the most accurate methods for the calculations of the energetic and electronic structures of solids. The electron-ion interaction is described using the projector augmented wave method [34,35] and the exchange-correlation potential using the Perdew-Burke-Ernzerhof (PBE) functional of the generalized-gradient approximation (GGA) [36]. The energy cutoff for the plane wave basis set is 450 eV for all the calculated systems. As the previous experiments have shown that for the Mo_xNi_{1-x} (0 ≤ x ≤ 0.25) alloys, the phase structure is mainly approximate to the intermetallic compounds Ni₃Mo [13]. Therefore, we employ the Ni₃Mo(111) surface to study the effects of a third transition metal on the surface segregation in Ni-Mo alloys. The lattice constant of the Ni₃Mo (L1₂) crystal is calculated to be 3.644 Å. Here, we model the Ni₃Mo (111) surface by a periodic surface slab composed of five-layer atoms separated by a vacuum of 1.3 nm in the [111] direction normal to the surface. The unit cell is extended by forming a (2 × 2) surface structure with four atoms in each layer. The top three layers are relaxed and atoms in other layers are fixed to mimic the bulk-like environment. Spin polarization has been taken into accounts in the calculations and the Brillouin zone integration of the supercell is performed using a 6 × 6 × 1 Monkhorst-Pack grid [37]. The geometry optimization for each system is continued until the forces on all the atoms are less than 0.02 eV/Å.

Following the previous work by Zhang et al. [30], the Ni surface segregation energy $E_{segr}^{Ni_3Mo/M}$ is defined as the energy difference between the lowest-energy configurations of the Ni-segregated and bulk-terminated Ni₃Mo/M(111) surfaces. The possible configurations of the bulk-terminated and Ni-segregated Ni₃Mo/M(111) surfaces are shown in Figs. 1 and 2, respectively. The Ni surface segregation energy can be calculated as follows

$$E_{segr}^{Ni_3Mo/M} = [E_{Ni_3Mo/M}^{Ni-segr}]_{lowest} - [E_{Ni_3Mo/M}^{bulk-term}]_{lowest}, \quad (1)$$

where $E_{Ni_3Mo/M}^{Ni-segr}$ and $E_{Ni_3Mo/M}^{bulk-term}$ are the total energies of the lowest energy configurations for the Ni-segregated and bulk-terminated Ni₃Mo/M(111) surfaces doped with a transition metal M. According to this definition, a negative $E_{segr}^{Ni_3Mo/M}$ indicates the doped transition metal M promotes the Ni segregation, while a positive $E_{segr}^{Ni_3Mo/M}$ means the doped M hinders the Ni surface segregation.

Similarly, the Ni surface segregation energy, $E_{segr}^{Ni_3M}$, in the binary Ni₃M surface can be defined as the energy difference between the Ni-segregated Ni₃M(111) surface and the bulk-terminated Ni₃M(111)

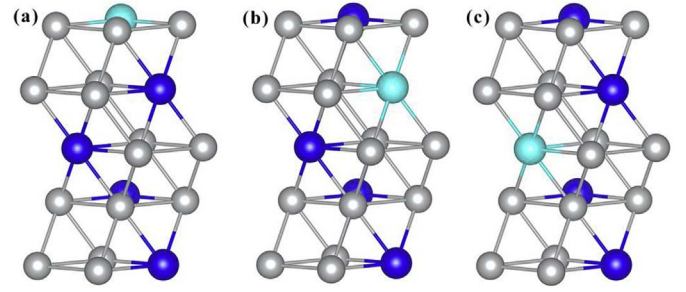


Fig. 1. Atomistic structures of bulk-terminated Ni₃Mo/M(111) surfaces. Distinct from the bulk-terminated Ni₃Mo(111) surface, the Mo atom, located in the (a) first, (b) second, or (c) third surface layer, is replaced by the transition metal M atom in the bulk-terminated Ni₃Mo/M(111) surface. The gray balls represent Ni atoms, dark blue balls represent Mo atoms, and light blue balls represent M atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

surface. It can be calculated by

$$E_{segr}^{Ni_3M} = E_{Ni_3M}^{Ni-segr} - E_{Ni_3M}^{bulk-term}, \quad (2)$$

where $E_{Ni_3M}^{Ni-segr}$ and $E_{Ni_3M}^{bulk-term}$ are the total energies of the Ni-segregated and bulk-terminated Ni₃M(111) surface supercells. The Ni-segregated surface structure is constructed by exchanging the positions of the M and Ni atoms in the top two layers of Ni₃M(111) surface model, leading to the pure-Ni (namely, 100 at.% Ni) topmost layer and the second layer containing 50 at.% Ni atoms and the rest layers containing 75 at.% Ni as in the bulk environment, while the bulk-terminated Ni₃M(111) surface consists of 75 at.% Ni and 25 at.% M for all atomic layers. For the Ni₃Mo(111) surface, $E_{segr}^{Ni_3Mo}$ is calculated to be -0.92eV, which suggests that Ni favors to segregate up to the outermost layer of the Ni₃Mo(111) surface and the Ni-segregated Ni₃Mo(111) surface is more stable than the bulk-terminated Ni₃Mo(111) surface. These results are in good agreement with the experimental observations that Mo atoms do not segregate to the surfaces of NiMo alloys under ultrahigh vacuum (UHV) conditions [38].

For the convenience to discuss the segregation behavior, we also calculate the relative Ni surface segregation energy $E_{segr}^{relative}$ and the lattice mismatch Δa . They are defined as

$$E_{segr}^{relative} = E_{segr}^{Ni_3M} - E_{segr}^{Ni_3Mo}, \quad (3)$$

$$\Delta a = \frac{a(Ni_3M) - a(Ni_3Mo)}{a(Ni_3Mo)} \times 100\%, \quad (4)$$

where $E_{segr}^{relative}$ is the difference of the Ni surface segregation energy between the Ni₃M(111) surface and the Ni₃Mo(111) surface, and Δa is the lattice-parameter difference between the Ni₃M and Ni₃Mo crystals.

In this work, the heat of solution of the alloying element M in Ni is also invoked to explain the surface segregation behavior. For an M atom in the Ni bulk, the heat of solution is defined as

$$E_h = E_{Ni_3M} - 3E_{Ni} - E_M, \quad (5)$$

where E_{Ni_3M} is the total energy of the Ni₃M unit cell, which contains 3 Ni atoms and one M atom, E_{Ni} denotes the total energy of one Ni atom in fcc Ni and E_M denotes the total energy of an M atom in its ground state phase. We employ a (2 × 2 × 2) supercell and a Monkhorst-Pack grid [37] of 6 × 6 × 6 k-points in our calculations.

3. Results and discussion

3.1. Bulk-terminated Ni₃Mo/M(111) surfaces

As shown in Fig. 1, there are three possible structural configurations of the bulk-terminated Ni₃Mo/M(111) surface, which are formed by replacing the Mo atom in the first (Fig. 1(a)), second (Fig. 1(b)) or third (Fig. 1(c)) layer with a doped atom of the transition metal M,

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