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Pt surface segregation in bimetallic Pt_3M alloys: A density functional theory study

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Abstract

A simplified 5-layer slab model is used to study Pt segregation at Pt_3M(1 1 1) surfaces (M = Ag, Au, Co, Cr, Cu, Fe, Ir, Mn, Mo, Ni, Pd, Re, Rh, Ru, Ti, V). The calculated segregation energies are generally in good agreement with the experimental results. However, for Pt_3Ti(1 1 1) and Pt_3Mn(1 1 1), the model is unable to give the correct prediction because the experimental subsurface compositions are very different from those of the model. Pt segregation is found to be correlated with the subsurface atomic structure, the size of metal atoms and the surface energy. Interestingly, the calculations show that the displacement of M atoms at the topmost Pt_3M layer can be used to predict the surface segregation trend. The local geometries for the segregation and non-segregation structures are carefully compared and the surface geometric effect on the oxygen reduction reaction (ORR) activity is discussed. In particular, it is determined that the enhanced ORR activity for the Pt-skin surfaces of Pt_3Ni(1 1 1) and Pt_3Co(1 1 1) alloys are not caused by geometric effects.

Keywords: Density functional calculations; Surface energy; Surface segregation; Surface structure, morphology, roughness, and topography

1. Introduction

For many alloys, the chemical composition at the surface is significantly different from that in the bulk. In general, one metal species enriches the surface or the first subsurface layers over other components. The phenomenon called surface segregation has drawn much experimental and theoretical attention due to its importance to materials science and surface chemistry [1,2]. It influences many important physical and chemical properties such as permeation, surface adsorption, crystal growth, metal corrosion, etc. Particularly, it has been found that the catalytic activities of alloys can be altered dramatically through surface segregation.

As an efficient catalyst, Pt is used in many important chemical reactions such as methanol oxidation and hydrocarbon reforming. In particular, Pt has become the most widely used electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells. However, as a noble metal, Pt is extremely expensive. Moreover, the relatively sluggish ORR kinetics on Pt surface considerably limits its catalytic efficiency. Therefore, it is indispensable to develop new catalysts with lower cost and higher activities. For many years, numerous efforts to search alternative catalysts to Pt have mainly focused on Pt-based bimetallic alloys, in which some of the platinum is replaced by less expensive metals [3–11]. Since the catalytic properties are chiefly determined by the surface geometry and the electronic structure which can be modified by the chemical composition of the bimetallic alloys, the catalytic effect can be considerably improved when appropriate structures are achieved. Enhanced ORR activities have been reported in the case of Pt alloyed with 3d metals [4,7,12–14]. Notably, surface segregation plays a key role in the ORR [10,14]. For instance, Stamenkovic et al. compared the kinetics of the ORR on bulk Pt_3Co alloy and on the Pt-skin structure produced by Pt segregating on the outmost layer of the annealed alloy surface. They noted that the ORR is uniquely

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active on the Pt-skin surface and the reaction rate is 4 times that for the pure Pt catalyst [14].

Numerous experimental studies have been carried out to investigate surface segregation of Pt alloys [5,8,10,14–31]. For some of them, the surface and subsurface structures have been unambiguously identified. However, the details of segregation are not completely understood. Theoretical approaches can help to elucidate the driving force and the tendency of this phenomenon. So far, surface segregation has been investigated by various theories such as thermodynamic [32], tight-binding [33,34], embedding atom (EAM) [35,36] and first-principles methods [37,38]. The thermodynamic method estimates the surface segregation energy by phenomenological factors such as the mixing heat of alloys and the metal surface energy. In the tight-binding method, pairwise energies are introduced to evaluate the segregation behavior. In the EAM and its modified version (MEAM), the total energy is computed based on the local electron density. The first-principles approaches are usually performed within the frame of density functional theory (DFT), using various approximations. Quantum–mechanical surface segregation studies of an impurity in a matrix of a host metal have been reported [37]. However, for Pt-based alloys where the second element is present in larger proportions, surface segregation has only been studied by MEAM [39–42], by atomistic modeling [43], and by linear-muffin-tin-orbitals calculations with the coherent potential approximation (CPA) [37,44].

In this paper, we chose the well-investigated $Pt_3M(1\,1\,1)$ (M = Ag, Au, Co, Cr, Cu, Fe, Ir, Mn, Mo, Ni, Pd, Re, Rh, Ru, Ti, V) alloy systems [5,7,9,10,13,14,27,45]. It has been reported that Pt segregates to the surface and the metal M enriches the second layer in many Pt-based bimetallic alloys. For example, a recent study with crystal truncation rod (CTR) analysis showed that a highly structured compositional oscillation takes place at the first top layers for the $Pt_3Ni(1\,1\,1)$ structure: The first layer is composed entirely of Pt, whereas the second layer only contains 48% of Pt, the third layer is again Pt-enriched (87%) [7]. Our segregation model was thus built by exchanging the positions of the topmost layer M atoms and the second layer Pt atoms. Surface structures and segregation energies on the (1 1 1) surface were calculated for 15 different transition metals. It should be noted that surface segregation is also governed by temperature and by the presence of adsorbates. In some cases, these factors could be important [46] and they will be discussed in a future report.

2. Computational details

The DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) [47–51], in which the Kohn–Sham equations are solved by self-consistent algorithms. For improving the calculation efficiency, core electrons were replaced by the projector augmented wave (PAW) pseudo–potentials [52,53] and the valence electrons were described by plane wave basis set. In this work, the plane wave was expanded up to a cutoff energy of 340 eV. Brillouin zone integration was made on a $11 \times 11 \times 11$ Monkhorst–Pack k-point mesh for the bulk calculations and a $11 \times 11 \times 1$ mesh for the slab calculations. The choice of the grid was based on calculations done with various grids, from $4 \times 4 \times 1$ to $15 \times 15 \times 1$; energy fluctuations were found when the grid is small than $10 \times 10 \times 1$. The exchange-correlation functional was described within the generalized gradient approximation (GGA) proposed by Perdew, Burke and Ernzerhof (PBE) [54]. Spin polarization was taken into account in the calculations and the Methfessel–Paxon method was employed to determine electron occupancies with a smearing parameter σ of 0.2 eV. The convergence criteria for the electronic self-consistent iteration and the ionic relaxation loop were set to 10^{-5} eV and 10^{-4} eV, respectively.

Ordered fcc-like structures have been widely used to model various Pt_3M crystalline alloys [55–59]. Therefore, we assumed that the Pt_3M alloys possess close-packed fcc structures, in which the Pt atoms occupy the face-centered positions and the M atoms are located at the corners in the unit cell, as shown in Fig. 1. For each Pt_3M structure, the lattice constant was obtained after a bulk optimization. In this work, a 2×2 (1 1 1) unit cell was used for all the slab models. The supercell consists of a 5-layer slab and a 5-layer vacuum (>10 Å). In the super cell, each slab layer contains 3 Pt atoms and 1 M atom. As illustrated in Fig. 2, the segregation structures were reached by exchanging M atoms at the first layer and Pt atoms at the second layer. Thus the topmost layer is fully covered by Pt atoms and the second layer contains 50% Pt atoms for each Pt segregation structure. The atoms in the top three layers were allowed to relax to the lowest energy configuration, while the atoms of the bottom two layers were fixed to their bulk positions in keeping with the optimized lattice constants. In general, the surface segregation energy, E_{segr}, is

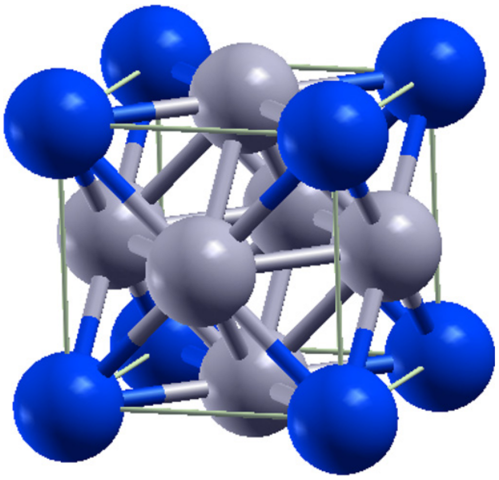

Fig. 1. Unit cell of close-packed fcc Pt_3M crystal. Grey and blue spheres represent the Pt and M atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)