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Surface segregation in $Pt_{25}Rh_{75}$ alloys studied by Monte Carlo simulations and the modified embedded atom method

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Abstract

In this work, surface segregation in $Pt_{25}Rh_{75}$ alloys is studied by Monte Carlo (MC) simulations, combined with the modified embedded atom method (MEAM). First, for a more accurate description of the interatomic interactions, new MEAM parameters are derived, based on ab initio density functional theory (DFT) data. Subsequently, the temperature dependent surface segregation to the low index single crystal surfaces of a $Pt_{25}Rh_{75}$ alloy is calculated with this new parameter set. The simulation results are then confronted with available experimental and theoretical work. A peculiarity of the Pt–Rh system is the possible presence of a bulk demixing region at lower temperatures. This demixing behaviour is still contested up to now. Our results are in contradiction with such a phase separation behaviour.

Keywords: Monte Carlo simulations; Semi-empirical models and model calculations; Platinum; Rhodium; $Pt_{25}Rh_{75}$; Low index single crystal surfaces

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1. Introduction

Due to their technological applications, Pt–Rh alloys have already received considerable attention, both from a theoretical and from an experimental point of view. Pt–Rh alloys are indeed used for cleaning car exhaust gases [1,2]. Whereas a pure Pt oxidation catalyst cleans a diesel engines' exhaust, gasoline engines are equipped with 'three-way' Pt–Rh catalysts that also reduce the NO_x emissions to N_2. Moreover, Pt–Rh is the active catalyst in the Ostwald process for the production of nitric acid. Pt–Rh alloys also show a high resistance to corrosion and feature an outstanding thermal stability.

To understand the catalytic properties of binary alloys, a detailed knowledge of the composition and order at the surface is necessary. This knowledge can be obtained by various surface sensitive experimental techniques or by calculations on model systems. Both approaches are complementary and highly synergetic. In this work, Monte Carlo (MC) simulations are combined with the modified embedded atom method (MEAM) to unravel the segregation behaviour in the $Pt_{25}Rh_{75}$ alloy system. The MEAM has proven to be very successful for the calculation of surface properties of alloys [3]. In order to further improve the accuracy of the MEAM, new model parameters will be derived from ab initio DFT calculations of different surface and bulk quantities. By doing so, a more complete and highly 'coherent' set of input data is obtained, less prone to varying uncertainties or technique-specific deviations that are unavoidably associated with input data from diverse experimental measurements.

The result is a more reliable set of MEAM parameters which provide a sound basis for describing the energetics and physics of the material under study. By this approach, in principle, the accuracy of quantum-mechanical calculations is combined with the computational efficiency of semi-empirical models. The latter is a *conditio sine qua non* for studying surface segregation in slabs containing a few thousands of atoms in MC simulations.

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For surface segregation, three intrinsic driving forces can be distinguished: lowering of the surface energy, lowering of the mixing energy and (partial) release of elastic bulk strain energy. Apart from these effects, the gaseous environment of a catalyst material can also alter the surface segregation equilibrium. Preferential chemisorption can in some cases even cause a change in the segregating species. This phenomenon is indeed observed in the Pt–Rh system (see further). The material properties related to these driving forces are tabulated in Table 1 and the Pt–Rh phase diagram is shown in Fig. 1. Although Pt and Rh, which are both fcc metals, have almost identical heats of sublimation, the surface energies differ substantially, promoting Pt segregation. The reason for this unexpected effect lies in a different magnetic relaxation of the free atoms to their ground state [11]. As the atomic radii differ only slightly (3%), release of strain energy is not considered an important driving force for segregation. Finally, the heat of mixing is very small and negative (attractive interactions). This is confirmed by a slightly upward curvature of the solid–liquid two phase region in the phase diagram. However, at lower temperatures, a demixing region is suggested in the phase diagram, pointing at strong repulsive interactions between Pt and Rh atoms. This demixing behaviour was first proposed by Raub [12], who extrapolated the behaviour of Pd–Ir, Pt–Ir and Pd–Rh to the Pt–Rh system. In doing so, Raub predicted an upper critical temperature for Pt–Rh of 1033 K. Up to now, however, the existence of a miscibility gap is still a point of controversy. Lakis et al. [13–15] observed demixing in an indirect way in analytical electron microscopy experiments on alumina-supported Pt–Rh catalyst particles. On the basis of classical tight-binding d-band theory, Pt–Rh was predicted to separate into two phases [16,17]. Wouda et al. [18] observed a limited degree of clustering with scanneling tunneling microscopy (STM), however not sufficient to explain a demixing behaviour at low temperatures. Many other authors, on the contrary, found no evidence for a demixing behaviour [9,19–22]. In this work, the energy of formation for various ordered Pt–Rh compounds is calculated with DFT. These DFT calculations point at attractive interactions and are thus in contradiction with the demixing behaviour as proposed by Raub (Section 2).

Table 1
Relevant material properties of Pt and Rh for surface segregation

	Pt	Rh
Crystal structure	fcc	fcc
Lattice parameter	3.9158 [5]	3.7967 [5]
	3.9240 [6]	3.8036 [6]
Atomic radius	1.38 [6]	1.345 [6]
Heat of sublimation	565.3 [7]	556.9 [7]
Surface energy	2.203 [8]	2.350 [8]
	2.475 [9]	2.700 [9]

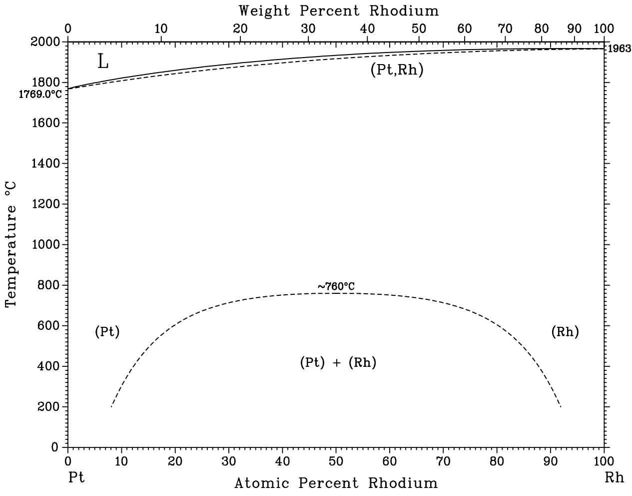

Fig. 1. Phase diagram for the Pt–Rh alloy system [10].

Surface segregation in the Pt–Rh alloy has been studied intensively, both from an experimental and from a theoretical point of view. The first surface composition experiments on $Pt_{10}Rh_{90}$, $Pt_{50}Rh_{50}$ and $Pt_{90}Rh_{10}$ alloys were performed by Williams and Nelson [23]. With ion scattering spectroscopy (ISS), they observed a Pt enrichment for all studied compositions. However, the surface composition showed an anomalous Pt increase at temperatures between 800 and 1100 K, which is an indication of non-equilibrium results. Other workers [24–27], on the contrary, found Rh segregation. This Rh segregation was later attributed to the presence of small amounts of impurities (carbon, sulfur, oxygen) in the samples [28,31]. The measurements of Tsong et al. [27–29] were repeated on samples without impurities [30], and revealed a Pt enrichment of the surface layer instead, accompanied by a Pt depleted second layer.

A lot of other experiments were performed on several Pt–Rh samples [18,31–37]. The general conclusions from this extended collection of experimental results can be summarized as: (i) Pt (strongly) segregates to the surface, (ii) the second layer is enriched in Rh even at high temperatures, (iii) in the case of vicinal surfaces, less coordinated sites are richer in Pt, (iv) it is hard to achieve thermodynamic equilibrium.

Even today, the explanation of the segregation behaviour in Pt–Rh from a theoretical point of view still is a challenge. Starting from the model of Williams and Nason [4] and deriving bond energies from the heat of sublimation of pure Pt and Rh leads to segregation of Rh. However, direct use of the surface energies for the calculation of the bond strengths, leads to Pt segregation. Earlier, the role of different surface vibrational properties of Pt and Rh was invoked as a possible mechanism to explain the experimental behaviour [37–39]. This role was later contested by Legrand et al. [40] in a tight-binding Ising model (TBIM). Within the TBIM, Pt enrichment of the surface and an oscillating depth profile was obtained for all compositions. Other studies using pair interactions [41–43], semi-empirical energy models [44,45], tight-binding linear muffin tin orbitals within the coherent potential approximation [46]