Phase equilibria and ordering in solid Pt–Rh calculated by means of a refined bond-order simulation mixing model

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Abstract

The equilibrium phase diagram of solid Pt–Rh is calculated by means of semi-grand canonical lattice Monte Carlo simulations using thermodynamic integration. Configurational energies are described by a refined BOS model (bond-order simulation mixing), which is fitted to reference data obtained from first-principles calculations. The calculated equilibrium phase diagram shows the ordered face-centered cubic structure 40 and $D0_{22}$ structure as stable phases at low temperatures (<250 K) and has no miscibility gap at higher temperatures, which is in contrast to existing assumptions. The calculated short-range order parameters of the solid solution are in full agreement with experimental values and thus confirm that the BOS model provides a sound description of configurational energies.
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1. Introduction

Pt–Rh is a technologically important metallic alloy because of its catalytic activity in various reactions. The widely accepted phase diagram [1–5] of Pt–Rh shows a pronounced miscibility gap with a critical temperature of 1033 K. This phase diagram is based on a prediction by Raub [6] dating back to 1959. He inferred from the experimentally confirmed phase separation in Ir–Pt, Ir–Pd and Pd–Rh that Pt–Rh would also show demixing at low temperatures. The critical temperature was estimated from the difference in the melting points of the two constituents. Although the phase diagram has since been reprinted many times, a miscibility gap has never been observed experimentally. In contrast to Raub's prediction, the theoretical calculations by Lu et al. [7,8] based on density functional theory (DFT) indicate that Pt–Rh has a negative enthalpy of mixing. Lu et al. predicted that Pt–Rh is miscible even at low temperature and identified various stable ordered structures, including the phases $D1_a, D0_{22}, X2,$ "40" and

$D1_a$ for concentrations $x_{Pt} = \frac{1}{5}, \frac{1}{4}, \frac{2}{7}, \frac{1}{2}$ and $\frac{4}{5}$, respectively. Recently, another DFT study by Curtarolo et al. [9] confirmed that the structures $D1_a, D0_{22},$ "40" and $D1_a$ are energetically the most stable configurations at zero temperature. Curtarolo et al. did not identify the X2 structure, but predicted the $D0_{22}$ phase to be stable for $x_{Pt} = \frac{3}{4}$. This is in agreement with another theoretical study treating the Pt–Rh system on the basis of a Green's function formalism [10]. Again, the "40" and $D0_{22}$ structures were found to be stable ground state modifications, and in addition Kolb et al. [11] identified the structure "40" (which they named "CH") as a stable phase.

Finally, the cluster expansion (CE) method has been used to examine not only the ground state structures but also the short-range order (SRO) at high temperatures and surface segregation tendencies of Pt–Rh [12]. Once again the 40 structure at 50% Pt and the $D0_{22}$ structure at 25% Pt are found to be stable, along with three other structures that are denominated only by their symmetry group ($Pmmn, Pmn2_1, Pmna$). The ordering temperature of the "40" structure was found to be only about 100–110 K. The first experimental evidence for the ordering of Pt–Rh was provided by Steiner et al. [13], who probed

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the local order of a sample consisting of Pt–47 at.% Rh with X-ray and neutron scattering. The Warren–Cowley short-range order (WC-SRO) parameters were deduced from the diffuse X-ray scattering experiments and clearly give evidence for the existence of the structure "40". By applying the inverse Monte Carlo technique the order–disorder transition temperature of the "40" structure was estimated to be 185 K. All of these studies provide evidence for ordering tendencies in Pt–Rh. While many different structures with face-centered cubic (fcc) lattices are found in ab initio studies, only the "40" and the $D0_{22}$ structure are univocally identified as minimum energy structures by all the theoretical papers. Most importantly, there is no evidence for phase separation in solid Pt–Rh. However, there is still no complete assessment of the equilibrium phase diagram of the solid phases and it remains an open question as to in what temperature range the ordered phases can be expected.

This paper aims to fill this gap by calculating the equilibrium phase diagram from configurational free energies obtained by thermodynamic integration of lattice Monte Carlo simulations. In doing so a refined "bond-order simulation mixing" (BOS) model is parameterized that extends the model previously introduced by Zhu and DePristo [14]. This lattice-based Hamiltonian very accurately reproduces first-principles data and is fully appropriate for modelling Pt–Rh. The model is validated by comparison to results obtained from the cluster expansion formalism and to experimental SRO data. Starting from the high-temperature expansion of the semi-grand canonical thermodynamic potential, the complete free energy surface is calculated by thermodynamic integration. Finally, the phase diagram that incorporates the ordered structures "40" and $D0_{22}$ is derived from the free energy hypersurface.

2. Method

2.1. Modified BOS mixing model

All relevant solid phases in Pt–Rh can be mapped on a fcc sublattice. Therefore lattice-based Monte Carlo simulations are an appropriate means for investigating phase stability of this alloy system at finite temperatures. While cluster-expansion methods of total energies calculated from first principles have become popular over recent years, physically motivated model Hamiltonians such as the BOS model provide an interesting alternative, since in contrast to the CE method they can be straightforwardly extended for modelling surfaces of various orientations. The BOS model was originally developed by De Pristo et al. [14] as an advanced version of the "site energy formalism" model [15]. Our modifications of the model will be described in this section. We implemented the model for the case of a fcc lattice with coordination number $Z = 12$.

The total energy of a system in the BOS mixing model is given by the sum over the site energies of all atoms

$$E = \sum_{i \in sites} \epsilon_{Z_i}^{T_i}(M_i). \tag{1}$$

The energy $\epsilon_{Z_i}^{T_i}(M_i)$ of site i depends on the type T_i of atom i, which may be A_i or B_i, the total coordination Z_i and the number of odd neighbors M_i of type other than T_i. In the following we implicitly assume that all parameters depend on the specific site i.

The site energies as given in the work of DePristo et al. [14] have the following form:

$$\epsilon_Z^T(M) = \epsilon_Z^T + M\Delta E_Z^T + \frac{1}{2}M(M-1)\lambda_Z^T. \tag{2}$$

In the original BOS model the energy correction terms for sites with coordination Z are written in the following form for a binary A–B system:

$$\Delta E_Z^A = \frac{\Delta E_{Z=12}^A + \Delta E_{Z=12}^B}{2} - \frac{\epsilon_Z^A - \epsilon_Z^B}{Z}, \tag{3}$$

$$\Delta E_Z^B = \frac{\Delta E_{Z=12}^A + \Delta E_{Z=12}^B}{2} + \frac{\epsilon_Z^A - \epsilon_Z^B}{Z}. \tag{4}$$

However, this specific choice, which introduces an asymmetry in binding energies, leads to undesired artefacts. When simulating surfaces, we found that the term $\pm\frac{\epsilon_Z^A - \epsilon_Z^B}{Z}$ leads to surface segregation even in the case of a vanishing mixing energy and in the absence of a difference in surface energies of the two alloy constituents.

We therefore modified the linear energy correction term by replacing the type- and coordination-dependent correction energy through a summation over the n-neighbor shells around site i:

$$M\Delta E_Z^T \rightarrow \frac{1}{2}\sum_{n=1}^{4} M_n \Delta E_n^{AB}. \tag{5}$$

Moreover, the coordination dependence of parameter λ is abandoned in our modification and the nonlinear term is evaluated over nearest neighbor positions only as in the original model. In our modified form the site energies then read as:

$$\epsilon_Z^A(M_n) = \epsilon_Z^A + \frac{1}{2}\sum_{n=1}^{4} M_n \Delta E_n^{AB} + \frac{1}{2}M_1(M_1-1)\lambda_1^A, \tag{6}$$

$$\epsilon_Z^B(M_n) = \epsilon_Z^B + \frac{1}{2}\sum_{n=1}^{4} M_n \Delta E_n^{AB} + \frac{1}{2}M_1(M_1-1)\lambda_1^B. \tag{7}$$

Here, M_n is the number of odd neighbors in the nth shell. Note that asymmetry in the site energies, i.e. nonlinearity in M, is only assumed for nearest neighbors and is expressed in the λ-parameters.

The site energies of the pure phases in ϵ_Z^A and ϵ_Z^B (see Eqs. (6) and (7)) represent another 24 parameters ($Z = 1, \ldots, 12$ for nearest neighbors in a fcc lattice). These parameters allow an accurate modelling of the dependence of the binding energy on the total coordination Z. This would not be possible in a simple Ising model in which the dependence of binding energy on the coordination is always linear. A straightforward approach for determining