No miscibility gap in Pt–Rh binary alloys: A first-principles study

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Abstract

Recently, diffraction experiments and bond-order calculations gave given cause for distrust in the widely accepted phase diagram of binary Pt–Rh, suggesting it forms a solid solution below 1100 K. This is in contrast to the phase diagram published by Raub in 1959. In order to clarify this situation, we use a first-principles approach to conduct an exhaustive ground-state search and set up a cluster-expansion Hamiltonian. This allows for grand-canonical Monte-Carlo simulations in order to investigate the phase behavior. We show that the miscibility gap does not in fact exist. We also present simulated diffraction patterns extracted from the cluster-expansion Hamiltonian, which are in good agreement with experimental data.

1. Introduction

Binary Pt–Rh has been heralded as an alloy of great technological interest over the last 10 years due to its excellent corrosion resistance and catalytic properties [1]. Not surprisingly, it has been investigated in a number of publications over the last few years from both experimental [2,3] and theoretical [4–6,25,31] groups. Most publications on Pt–Rh are concerned with its surface [5,6,31,32] properties (due to the catalytic applications); findings regarding the ordering properties within the bulk are rather sparse and quite often in strong disagreement with each other [4,7,9,31]. However, a thorough understanding of the bulk ordering phenomena is crucial for designing models for the various Pt–Rh surfaces.

The corresponding phase diagram [7] has been widely used as the bulk reference in Pt–Rh. This diagram dates back to Raub [8], who assembled it along with the Pt–Pd and Rh–Ir phase diagrams through extrapolation of sparse data sets [9] taken for supposedly similar alloys: Pt–Ir, Pd–

Ir and Pd–Rh. According to his extrapolation, all of the three proposed phase diagrams (Pt–Rh, Pt–Pd, Rh–Ir) were supposed to exhibit large miscibility gaps below critical temperatures of about $T \approx 1000$ K. One decade later, experiments by Kidron et al. [10] showed that the extrapolation technique did not work for the Pt–Pd alloy and falsely spoke for the existence of a miscibility gap in Pt–Pd. This has prompted intense research on the Pt–Rh and Rh–Ir phase diagrams. A survey of the contemporary literature reveals that the phase diagram published in 1959 [8] is in complete disagreement with recent scattering experiments performed by Steiner et al. [3] and even the earliest theoretical works [11] dating back to 1995.

The need for a reliable ground-state description of Pt–Rh is discussed in a work by Pohl et al. [4], where the authors point out how the suspected ground states of the Pt–Rh system have changed in publications over the years from 1995 [11] to 2008 [5], quite frequently in works that would have required their ground-state assumptions to be reliable. In another publication [31] and references therein, the failure of d-band tight-binding methods to predict any low-temperature ordering whatsoever in late-transition metal binaries is pointed out. In the following we will discuss how to calculate the bulk ground states, short-

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range ordering and how to access the binary phase diagram from first-principles density functional theory (DFT) calculations. We compare our results with calculations using semi-empirical potentials [4] and experimental work [3].

A recent publication [5] has investigated the vibrational properties within bulk Pt–Rh and their effects on the surface by means of a DFT-fed cluster expansion. Their work employs a cluster-expansion Hamiltonian based on only 15 input structures. The Hamiltonian was specifically designed to be suited for calculating the vibrational properties. While this is undoubtedly a suitable approach to investigate the vibrational properties, it does not produce a complete ground-state line or the phase diagram. We provide a fully converged cluster expansion with over 100 input structures and up to 15 basis atoms which will reveal all ground states and provide a correct phase diagram. This would greatly simplify works such as that by Yuge et al. [5], simply by providing a reliable bulk reference.

2. Methodology

In order to understand the ground-state behavior, a cluster expansion was performed. This method goes back to works such as Refs. [12–15] and uses an analytical decomposition of the many-body interactions inherent in any crystal. An arbitrary quantity that is strictly a function of the atomic arrangement on a lattice (like the energy E) can be expanded into a sum over correlation functions, which was rigorously proven by Sanchez et al. [13]. The different possible atomic arrangements on the lattice will in the following be called structures and will be denoted by σ. In the present work, we restrict ourselves to the special case of binary structures formed by Pt and Rh atoms on a face-centered cubic (fcc)-based lattice. The lattice is chosen because binary Pt–Rh alloys crystalize on fcc-based lattices throughout the concentration range. We then expand the system's total energy. The formalism by Sanchez et al. [13] suggests the following expansion for the formation enthalpy $\Delta H_f(\sigma)$ of a given structure σ with Pt and Rh content x_{Pt} and x_{Rh} respectively:

$$\Delta H_f(\sigma) = -x_{Pt}E_{Pt} - x_{Rh}E_{Rh} + E(\sigma)$$
$$= -x_{Pt}E_{Pt} - x_{Rh}E_{Rh} + \sum_F J_F \Pi_F(\sigma). \quad (1)$$

Here, the energy $E(\sigma)$ was expanded into a sum over correlation functions $\Pi_F(\sigma)$ which correspond to different n-particle interactions F, with J_F being their respective effective interaction coefficients. The simplest (but insufficient) case would be a restriction to two-body interactions, and the expansion would reduce to an Ising-type Hamiltonian. The general expression Eq. (1) can be evaluated for any given structure σ. To that end, we assign the artificial spin $+1$ to Pt and spin -1 to Rh and map each structure σ to an abstract spin distribution on an fcc-based lattice. The correlation function $\Pi_F(\sigma)$ can then be evaluated via the

appropriate spin product for F, in direct analogy to the Ising model. Although Eq. (1) is analytically exact, for all practical purposes it has to be truncated. Sophisticated methods to truncate Eq. (1) have been discussed in the literature. This work utilizes an evolutionary approach outlined in Ref. [16] and realized in the UNCLE package [17] to truncate the expansion and calculate the expansion coefficients. The coefficients are determined in such a way that the Hamiltonian Eq. (1) reproduces first-principles energies calculated using the VASP package [18,19]. Computational details of the first-principles calculations can be found in Appendix A.

Using the cluster-expansion Hamiltonian Eq. (1) as a guideline, one can filter out the most important structures (i.e. structures close to the ground-state line), verify their total energies by means of DFT and add these structures to the database to which the expansion coefficients J_F are fitted, therefore increasing the resolution of the fit close to the ground-state line. This procedure can be iterated until a fit of desired quality has been obtained. In our case, 13 iterations of this prediction–verification scheme have been applied, increasing the number of input structures to 110 after the final iteration.

To quantify the agreement, the leave-many-out cross-validation score [17] has been employed, with an additional constraint of fixing the absolute deviation of the energies close to the ground-state line (see Refs. [15,17]). In our case, this cross-validation score is 1.35 meV. A cross-validation score of roughly 1 meV translates into completely recapturing the behavior of the DFT data, which in turn is converged to an accuracy of roughly 1 meV per atom. To obtain this accuracy, 11 expansion terms in Eq. (1) had to be retained.

After generating a Hamiltonian that is bound to reproduce the first-principles behavior of the system at $T = 0$ K, we turn to the behavior at finite temperatures. As discussed in Ref. [5], phononic contributions to the free energy are negligible in binary Pt–Rh alloys up to very high temperatures. Therefore, a purely thermodynamic approach that takes only the configurational entropy into account is adequate to realize the temperature. The results presented in the following sections rely on Monte-Carlo simulations that minimize the free energy $F = E - TS$ with

$$E(\sigma) = \mu_{Rh}x_{Rh} + \mu_{Pt}x_{Pt} + \sum_F J_F \Pi_F(\sigma) \quad (2)$$

in an indirect way. The direct calculation of the entropic contribution TS would require full information about the partition function, but using the Metropolis algorithm [20] with $E(\sigma)$ from Eq. (2) enables us to find the thermodynamic equilibrium state, which also minimizes F. A parallel version of this algorithm was published recently [21] and is used throughout this work. This allows for tracking down phase transitions (see Section 4) and synthesizing crystals to simulate diffraction patterns (see Section 5).