

The New Face of Rhodium Alloys: Revealing Ordered Structures from First Principles

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Abstract: The experimental and computational data on rhodium binary alloys is sparse despite its importance in numerous applications, especially as an alloying agent in catalytic materials. Half of the Rh-transition metal systems (14 out of 28) are reported to be phase separating or are lacking experimental data. Comprehensive high-throughput first-principles calculations predict stable ordered structures in 9 of those 14 binary systems. They also predict a few unreported compounds in the known compound-forming systems. These results indicate the need for an extensive revision of our current understanding of Rh alloys through a combination of theoretical predictions and experimental validations.

1. Introduction

Like other elements in the platinum group metals (PGMs) (ruthenium, osmium, iridium, palladium, and platinum), rhodium has a high catalytic potential for a variety of chemical reactions.^{1,2} It is used as an alloying agent with platinum and palladium to improve catalytic activity and selectivity, or for coating to improve hardness and corrosion resistance in applications requiring high chemical and mechanical durability. Despite the wealth of existing and potential applications, the experimental data on Rh alloys is very limited. Of the 28 Rh-transition metal binary systems,³ 12 are reported as not being compound forming and two (Cd and Zn) are listed with insufficient experimental data to determine the existence of suspected compounds.^{4,5} These systems are concentrated in columns IB, IIB, VIIB, and VIIIB of the periodic table. The 11 binary systems of Rh with the transition metals of columns IIIB–VIB are all reported to be compound forming.

Rhodium's importance as a catalytic agent has led to numerous density functional theory (DFT) studies of its surface and nanoparticle properties.^{6–19} Recent increased interest in

intermetallic catalysts led to preliminary studies of a few PGM alloys and surface alloys^{20–24} that clarified the need to evaluate the stability of new potential alloy catalysts. However, investigations of rhodium binary systems are less common. Theoretical studies of the Co–Rh, Mn–Rh, and Fe–Rh systems,^{25–29} motivated by their peculiar magnetic properties, did not address phase stability of possible compounds. A study of Rh bimetallic

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alloys with Ag, Au, Cu, and Pd³⁰ confirmed the experimentally observed phase separation in those systems. An early indication that the existing experimental data may be incomplete appeared in ref 31, where first-principles local-density approximation (LDA) and cluster expansion (CE) calculations found unobserved compounds in the Rh–Pt system. Later studies, using similar methods, confirmed this finding^{32–35} and showed that Cd–Rh, Rh–Ru, Rh–Tc,³² and Ir–Rh^{33,34} are also compound forming at low temperatures. The importance of re-examining the Rh binary systems is underscored by the recent finding that certain surface alloys of ReRh and CuRh might be better electrocatalysts than pure PGMs for hydrogen-evolution reactions;^{21,22} these two binary systems were believed to be phase separating but are predicted in this work to be compound forming.

2. Predictions via a High-Throughput Approach

High-throughput (HT) calculations of material properties based on DFT have acquired an increasing role in recent years as an important tool for rational material development.^{32,36–40} They can be used to explore the phase stability landscape of binary alloys by calculating the formation enthalpies of a large number of structures, identifying the minima at various component concentrations. A minimum-free-energy convex hull is constructed from these minimum-energy structures. These calculations give insight into general trends of material properties, indicating the possible existence of hitherto unobserved compounds and their characteristics. The results reported in this contribution demonstrate the effectiveness of this approach in studying binary metallic systems where experimental data are scarce and difficult to obtain.

The HT approach finds new stable structures both in systems known to order and those thought to be phase separating. Of the 14 rhodium binary intermetallic systems that are either reported as phase separating or essentially unreported in the experimental literature,^{4,5} we show that nine actually exhibit ordering tendencies, forming stable compounds at low temperatures (Figure 1). Specifically, we find new structures in four binary systems not previously studied: Re–Rh, Os–Rh, Cu–Rh, and Zn–Rh, and a few previously unreported stable structures in the five systems already predicted to be ordering, as discussed above (Rh–Pt, Ir–Rh, Cd–Rh, Rh–Ru, and Rh–Tc). In addition to these nine systems, we also predict new stable structures in two of the three binary systems known to be compound forming, Mn–Rh and Fe–Rh. In the third system,

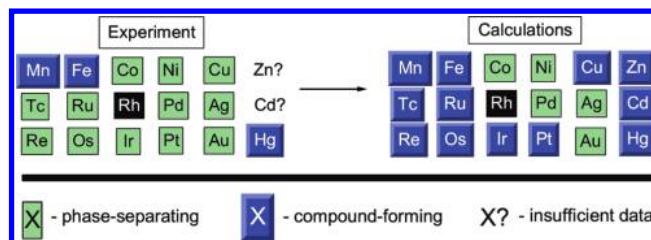


Figure 1. The phase-separating or compound-forming characteristics of 17 Rh–alloy systems as found in experiments (left) and in *ab initio* calculations (right).

Hg–Rh, the HT method confirms a single stable compound Hg₂Rh, of prototype Hg₂Pt.

3. Methods

The calculations were performed using the high-throughput framework AFLOW^{32,42} based on *ab initio* calculations of the energies by the VASP software.⁴³ We used projector augmented waves (PAW) pseudopotentials⁴⁴ and the exchange–correlation functionals parametrized by Perdew, Burke, and Ernzerhof⁴⁵ (PBE) for the generalized gradient approximation (GGA). The energies were calculated at zero temperature and pressure, with spin polarization and without zero-point motion or lattice vibrations (zero-point motion is negligible because we do not consider light elements). All crystal structures were fully relaxed (cell volume and shape and the basis atom coordinates inside the cell). Numerical convergence to about 1 meV/atom was ensured by a high energy cutoff (30% higher than the highest-energy cutoff for the pseudopotentials of the components) and dense 6000 k-point Monkhorst–Pack meshes. Since the calculations are performed at zero temperature and pressure and the volume is fully relaxed, the calculated energies coincide with the enthalpies, and their accuracy is the same. For each system, the energies of 200 crystal structures were calculated. In addition to the 176 configurations described in ref 32 these included all the symmetrically distinct hcp-, bcc-, fcc-based superstructures^{46,47} with up to four atoms per cell, and the prototypes A5, A6, A7, A8, A9, A11, B20, C36, D5₁₉, Al₂Zr₄, Al₃Zr₂, CdTi, CuPt₇, Cu₃Ti₂, Ga₂Hf, Ga₄Ni, Ga₃Pt₅, Ga₄Ti₅, Hg₂Pt, ITl, InTh, LiB-MS1/2,⁴⁸ NbNi₈, NiTi₂, SeTl, and V₄Zn₅. The prototypes were considered because they are common or related to Rh alloys.^{4,5} This protocol gives reasonable results. In ref 32 it was shown that the probability of reproducing the correct ground state, if well-defined and not ambiguous, is $\eta_c^* \sim 96.7\%$ (“reliability of the method”, eq 3). There is no guarantee that the true ground states of a system will be found among the common experimentally observed structures or among small unit-cell derivative structures. However, even if it is impossible to rule out the existence of an unexpected ground state, this protocol (searching many enumerated derivative structures and exhaustively exploring experimentally reported structures) is expected to give a reasonable balance between high-throughput speed and scientific accuracy to determine miscibility (or lack thereof) in Rh alloys.

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Table 1. Compounds Observed in Experiments or Predicted by *ab Initio* Calculations in Rh Binary Alloys (Structure Prototype or Space Group Number in Parentheses)^a

	compounds			ΔH meV/at.	M_z μ_B /at.
	experiments ^{4,5}	calculations (previous)	calculations (present)		
Tc	—	Rh ₂ Tc (ZrSi ₂) ³² RhTc (B19) ³² RhTc ₃ (D0 ₁₉) ³²	Rh ₂ Tc (ZrSi ₂) RhTc (B19) RhTc ₃ (D0 ₁₉)	−157 −175 −158	0 0 0
Re	—	N/A	Re ₃ Rh (D0 ₁₉) ReRh (B19) ReRh ₂ (ZrSi ₂)	−163 −181 −173	0 0 0
Mn	Mn ₃ Rh (Cu ₃ Au) MnRh (B2)	N/A	MnRh (B2) MnRh ₃ (D0 ₁₁) MnRh ₇ (CuPt ₇)	−188 −124 −66	2.0 0.6 0.4
Fe	FeRh (B2)	N/A	Fe ₃ Rh (#123) Fe ₂ Rh (C11 _b) FeRh (B2) FeRh ₃ (D0 ₂₄)	−49 −56 −56 −56	2.3 2.2 2.1 0.9
Os	—	N/A	OsRh (#164)	−8	0
Ru	—	RhRu (#164) ³² RhRu ₂ (#63) ³²	RhRu (#164) RhRu ₂ (#63)	−8 −6	0 0
Co	—	—	—	—	—
Ir	—	not described ³⁴	Ir ₃ Rh (#12) Ir ₂ Rh (#74) IrRh (W2) IrRh ₂ (MoPt ₂) IrRh ₃ (#12)	−15 −19 −21 −15 −12	0 0 0 0 0
Ni	—	N/A	—	—	—
Pt	—	Pt ₄ Rh (D1 _a) ^{31,32} Pt ₃ Rh (D0 ₂₂) ^{31,32} PtRh (FCC ^{[201]_{A2B2})(CH40))^{31,32} PtRh₂ (C49)³² PtRh₃ (D0₂₂)³² PtRh₄ (D1_a)^{31,32}}	Pt ₃ Rh (D0 ₂₂) PtRh (FCC ^{[201]_{A2B2})(CH40))}	−12 −23	0.2 0
Pd	—	—	—	—	—
Au	—	—	—	—	—
Ag	—	—	—	—	—
Cu	—	—	Cu ₇ Rh (CuPt ₇)	−4	0
Hg	Hg ₂ Rh “Hg ₅ Rh” “Hg _{4.63} Rh” “Cd ₂₁ Rh ₅ ” (γ -brass ^{5,41})	N/A Cd ₃ Rh (D0 ₂₄) ³² Cd ₂ Rh (C37) ³²	Hg ₂ Rh (Hg ₂ Pt) Cd ₂ Rh (Hg ₂ Pt)	−5 −166	0 0
Zn	“Rh ₅ Zn ₂₁ ” (γ -brass ^{5,41})	N/A	RhZn (B2) RhZn ₂ (ZrSi ₂) RhZn ₃ (D0 ₂₃)	−391 −389 −351	0 0 0

^a “—” denotes no compounds, and “N/A” no available data. Suspected, but unconfirmed, compounds are shown in quotes. ΔH and M_z are, respectively, the formation enthalpies and magnetic moments found in the present study.

4. Results and Discussion

The results are summarized in Table 1. In the first column, the 17 alloying metals are ordered according to their Mendeleev number (or Pettifor’s chemical scale).^{49,50} The next three columns indicate whether the corresponding binary system is phase separating or compound forming, according to the experimental data and to *ab initio* calculations reported here and in previous studies. Ordered in this way, the experimentally reported compound-forming systems are scattered: Two, Mn–Rh and Fe–Rh, near the top of the table and one, Hg–Rh, near the bottom. (Ordering in Rh–Zn and Rh–Cd is suspected but unconfirmed experimentally.) Our calculations find stable structures in all the systems nearby these three in the list. The remaining phase-separating systems form a small cluster of three, Pd–Rh, Au–Rh, and Ag–Rh, and two more systems, Co–Rh and Ni–Rh, slightly above it. This grouping of the predicted phase-separating systems essentially complements the trend indicated by the Pettifor chemical scale. The ratio of phase-

separating to compound-forming systems is completely reversed from that in the experimental picture.

The convex hulls for the systems predicted to be compound forming are shown in Figure 2. In the Cu–Rh system we find one ordered structure Cu₇Rh, with the same CuPt₇ prototype that appears in the Cu–Pt system.⁴ In the Os–Rh system one ordered structure is found for OsRh. It is the same hcp superstructure with four atoms per unit cell (space group $P\bar{3}m1$, #164) found previously for RhRu.³² Three ordered structures are found in the RhZn system. They are RhZn (prototype B2), RhZn₂ (prototype ZrSi₂), and RhZn₃ (prototype D0₂₃). Three ordered structures with prototypes ZrSi₂, B19, and D0₁₉, are also found in the Re–Rh system. These same structures were found in the Rh–Tc system³² and are reproduced in this study. The Rh–Ru results follow the same ground states of ref 32.

In the Pt–Rh system, previous studies using the CE method and LDA first-principles calculations^{31,34} found a convex hull defined by four stable structures, FCC^{[201]_{A2B2}} (prototype NbP, also called CH40 in refs 31 and 32) for PtRh, D0₂₂ for PtRh₃, and Pt₃Rh, and D1_a for PtRh₄. Two additional structures, D1_a for Pt₄Rh and C49 for PtRh₂, were found in later LDA calculations. Our PAW–PBE calculations³² confirm the appearance of the

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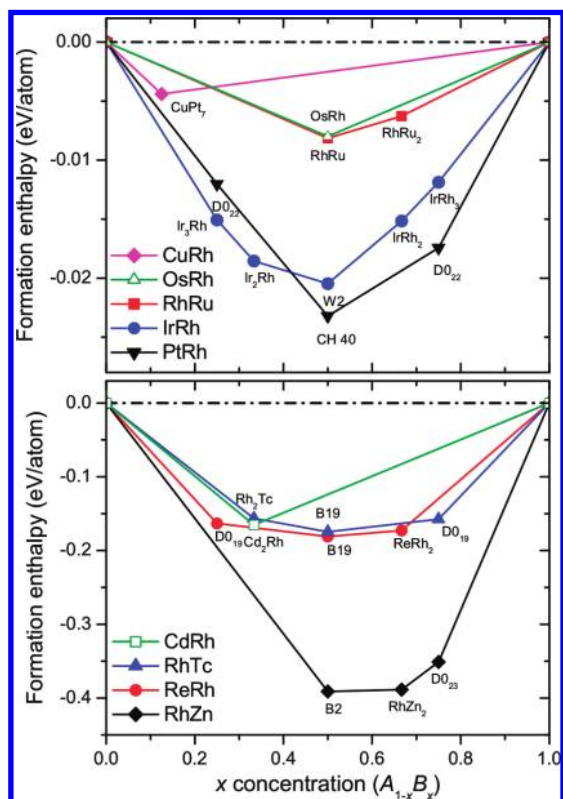


Figure 2. Ground-state convex hulls of the nine Rh–M binary systems predicted to be compound forming by HT *ab initio* calculations in contrast to phase diagrams reported in the literature. CH40 is the short name for FCC_{A2B2}^[201] as in refs 31 and 32.

FCC_{A2B2}^[201] and two D0₂₂ structures but predict that C49 and D1_a are metastable, lying just above the convex hull.

An extensive CE search of $\sim 3 \times 10^6$ configurations in the Ir–Rh system, based on 73 LDA structure calculations, found a few ground-state structures with large unit cells, of about 20 atoms per cell.³⁴ Our current search of 200 PAW–PBE calculations found a very similar convex hull defined by a few fcc superstructures with much smaller cells. The lowest structure, at -21 meV/atom, has four atoms per cell. It is an A2B2 stacking in the [311] direction (space group $C2/m$, #12). It is designated W2 in ref 51 and FCC_{A2B2}^[311] in ref 32. The additional structures are the MoPt₂ prototype, with three atoms per unit cell, for IrRh₂ and Ir₂Rh, and four atoms per unit cell FCC_{AB3}^[113] (space group $C2/m$, #12),³² for IrRh₃ and Ir₃Rh.

In the Cd–Rh system, a previous LDA study found the ordered structures D0₂₄ for Cd₃Rh and C37 for Cd₂Rh.³² Our more extensive PAW–PBE search finds a convex hull defined by a single structure Cd₂Rh with prototype Hg₂Pt. The two previous structures lie a few meV above the convex hull. This is the same single structure reported in the Hg–Rh system.⁴ It is interesting to note that the experimentally observed Hg₂Rh structure defines a much shallower convex hull than the unobserved Cd₂Rh structure (see Figures 2,3).

In agreement with the experimental data, we find stable compounds in the Hg–Rh, Fe–Rh, and Mn–Rh systems. The convex hulls of these systems are shown in Figure 3. As mentioned above, the existence of a single compound in the Hg–Rh is reproduced with the reported prototype Hg₂Pt. The reported B2 compound in the Mn–Rh and Fe–Rh systems⁴ is

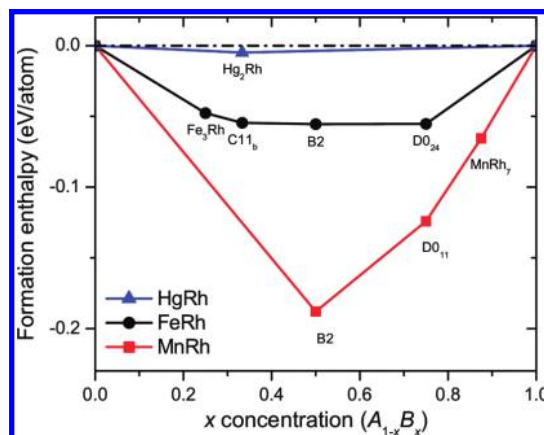


Figure 3. Calculated ground-state convex hulls of three Rh–M binary systems experimentally reported as compound forming. New structures are predicted in the Mn–Rh and Fe–Rh systems, in addition to the known one, B2.

also reproduced. However, additional stable structures are found in these two systems (Fe₃Rh–BCC_{AB3}^[001], Fe₂Rh–C11_b, FeRh₃–D0₂₄, MnRh₃–D0₁₁, and MnRh₇–CuPt₇). Similar to the B2 compounds, the appearance of these ordered structures is accompanied by large magnetic moments which contribute to their stability (Table 1). Without magnetic degrees of freedom, the calculated energies of these ordered structures would have been higher. The reported Mn₃Rh compound is found to lie above the convex hull in our calculations and is therefore unstable at low temperatures (the experimental data are available at temperatures above 400 °C⁵). At this composition, the lowest-energy structure with fcc superlattice is 27 meV/atom above the Mn–MnRh(B2) tie line. At high temperatures, it is perhaps stabilized by vibrational entropy, which is of the order of 0.1 to 0.2 k_B /atom, comparable to the typical values of configurational entropy differences in binary alloys ($\leq 0.693 k_B$ /atom).⁵² Configurational entropy is not expected to play a major role in the phase stability at the fixed stoichiometry of Mn₃Rh, because of the high energy cost of substitutional and interstitial defects. Vibrational stabilization is common, e.g. in ref 53 the vibrational entropy difference is shown to stabilize the θ –Al₂Cu (C16) phase over the competing Al₂Cu– θ' phase (distortion of θ_c –C1), which has the lowest energy and is, therefore, stable at low temperatures.

The crystal structure of rhodium is fcc. In 7 of its 14 binary systems reported as phase separating, the alloying element shares the fcc structure. In the other seven, the alloying element's structure is hcp. As discussed above, it was previously predicted that two of these fcc elements (Pt and Ir) and three of the hcp elements (Cd, Ru, and Tc) form stable ordered structures when mixed with Rh. The study reported in this contribution complements this picture and shows that Rh forms ordered structures with three of these fcc elements and six of the hcp elements. Its phase-separating bimetallic systems are only those with the fcc elements Ag and Au and its immediate neighbors in the periodic table Co (hcp) and Ni and Pd (both fcc).

5. Conclusion

The bulk phase behavior of alloys determines to a large extent the surface and small particle properties that dominate catalytic processes. A detailed understanding of Rh alloys is crucial for

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a better realization of its potential as a catalytic agent in currently known processes and in developing new ones. This is demonstrated by the recent finding that certain surface alloys of ReRh and CuRh might be better electrocatalysts than pure PGMs for hydrogen evolution reactions.^{21,22} These two binary systems were believed to be phase separating but are predicted here to be compound forming.

A recent study of the Cu–Pt–Rh ternary system was also motivated by the search for better catalysts.⁵⁴ It presents a calculation of the ternary formation energy diagram based on the assumption that the binary Cu–Rh system is phase separating. This ternary diagram would be considerably modified by our prediction of compound formation in the Cu–Rh system. Similar modification of other relevant ternary systems would ensue from all the predicted compound-forming systems in this study. As remarked in ref 54, the theoretical prediction of phase ordering and stability in these systems should be the starting point for designing desirable alloy catalysts.

The picture of Rh alloys that emerges from this study is very different from that depicted by current experimental data. Instead

of many phase-separating systems, we predict that all but just five form ordered structures. It should be emphasized that we consider the alloys in thermodynamical equilibrium which can be difficult to reach at low temperatures due to slow kinetics. At higher temperatures, configurational disorder and vibrational entropic promotion might destabilize the predicted compounds. Experimental validation is the ultimate proof of compound existence. The theoretical predictions presented here complement the woefully incomplete experimental picture and serve as a guide for future experimental and theoretical studies of these important catalytic materials.

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