



Finding new phases for precipitate-hardening in platinum and palladium alloys

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ABSTRACT

Precipitate hardening (via ordered phases rather than phase separation) of platinum and palladium can be effective even with a small volume-fraction of the ordered phase [M. Carelse, C.I. Lang, Scripta Materialia 54 (7) (2006) 1311]. The approach is particularly well suited to jewelry alloys which must be 95 wt.% pure and where ordered phases of 7:1 or 8:1 stoichiometries can be formed. We examined eight systems where this approach may lead to new applications: Pt–Al, Pd–Al, Pd–Cu, Pd–Mg, Pd–Nb, Pt–Mo, Pt–V, and Pd–V. In each system, using first-principles-based cluster expansion modeling, we have identified high stoichiometric-ratio phases that are stable. Furthermore, using Monte Carlo simulations, we have estimated the order–disorder transition temperatures to identify experimentally feasible phases. In three cases, the computational results are verified by experiment, suggesting that the remaining predictions are likely to be useful as well.

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1. Introduction

Catalysts are the primary application of platinum and palladium, but another economically important application is jewelry alloys. Over the last 10 years, 30% of the world's Pt and 10% of its Pd was used in jewelry [1,2]. In some market segments, jewelry is the primary use of these metals. Too soft for jewelry in their pure form, platinum and palladium are typically alloyed with other metals to increase their hardness. However, international hallmarking standards require that Pt/Pd alloys be 95 wt.% pure, so any alloying additions must be small. Solid solution hardening with <5 wt.% solute typically does not yield a sufficient improvement. On the other hand, precipitate hardening can increase the performance considerably, even if the precipitates occupy a small volume fraction [3].

This suggests an avenue for materials engineering—identifying phases that are effective for precipitate hardening. One would like to identify Pt-rich or Pd-rich ordered phases where the order–disorder transition temperatures are high enough that the precipitates form without undue difficulty. The first steps of the solution to the hardening problem are to quickly screen potential solutes and possible ordered phases and then identify from simulations those with a suitably high temperature order–disorder phase transition. This information drastically narrows the search on the experimental side. The task is well-suited to first principles calculations and lattice based simulations such as cluster expansion [4–11].

In A–B binary metallic systems where the majority A atom is one of the group 10 transition metals (Ni, Pd, Pt), there are several known A-rich phases (where $x_A \geq 7/8$). The phases occur primarily in two structures, namely the 7:1 structure, prototype CuPt₇ [12–16], and the 8:1 structure whose prototype is Pt₈Ti [17]. A recent first-principles survey of more than 400 binary A–B systems found many new predictions of systems where the 8:1 phase is stable [18].

Given the large number of predictions in Ref. [18] and the experimental difficulties of verifying predicted phases, we wish to screen the predictions for those where the order–disorder transition occurs at temperatures high enough that the practical difficulties of achieving thermodynamic equilibrium in the laboratory can be overcome. We begin with eight systems where first-principles calculations have shown a Pt-rich or Pd-rich phase to be stable (at $T = 0$ K) and where we suspect the transition temperature may be sufficiently high. In two cases, Pt–V and Pd–V, experiment has already found the 8:1 phase to be stable [19,20], but we include these both as a check on the accuracy of our approach and because there may be unknown phases at other compositions.

The systems we have modeled are Pt–Al, Pd–Al, Pd–Cu, Pd–Mg, Pd–Nb, Pt–Mo, Pt–V, and Pd–V. In each case, we have limited our reports to the Pt-rich and Pd-rich regions of the phase diagram, usually the concentration ranges $2/3 \leq x \leq 1$ or $3/4 \leq x \leq 1$.

2. Computational approach

The high-throughput-based [21–23] survey of Taylor [18] identified ground states in the eight systems we studied, but that

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approach is limited to the structures in the database (a nearly exhaustive list of experimentally-known structures and some enumerated derivative structures [24,25]).

One can search configurational space more systematically by using a faster Hamiltonian and testing essentially every configuration. A cluster expansion derived from first-principles data and a list of enumerated derivative structures [24,25] makes it possible to do a ground state search that explores millions of configurations in just a few minutes. Furthermore, the cluster expansion (CE) can also be used to estimate order–disorder transition temperatures via Monte Carlo (MC) simulations.

The formation enthalpy data for our cluster expansions were calculated using Vienna ab initio Simulation Package (VASP) software [26,27]. All structures were relaxed within 1 meV/cell. We used an equivalent k -point mesh [28] to reduce the systemic error in Brillouin-zone sampling (k -point density corresponding to at least $12 \times 12 \times 12$ in the fcc primitive unit cell) with projected-augmented wave (PAW) potentials [29] and the exchange–correlation functionals parameterized by Perdew, Burke, and Ernzerhof for the generalized gradient approximation [30]. In the PAWs we used, “semicore” p -electrons were included as valence electrons in V, Pd, Mg, and Mo. The energy cut-offs for the planewave basis were 125% of the default cutoffs in VASP’s standard PAWs. (That is, we used the “high precision” setting.) Typically the energy cutoff was ~ 375 eV or ~ 425 eV, depending on the system.

2.1. Pt–Al

The CE for Pd–Al was constructed from 65 first-principles enthalpies. The final CVS score is 8.4 meV with an average error of 2–3%. Each MC used an 8000 atom cell with 10^6 flips per temperature step.

2.2. Pd–Al

The CE for Pd–Al was constructed from 72 first-principles enthalpies. The final CVS score is 4.4 meV with an average error of about 3%. The MC used a 27,000 atom cell and 10^6 flips per temperature step.

2.3. Pd–Cu

The CE for Pd–Cu was constructed from 85 first-principles enthalpies. The final CVS score is 1.4 meV with an average error of about 8%. Each MC used an 8000 atom cell with 10^5 flips per temperature step.

2.4. Pd–Mg

The CE for Pd–Mg was constructed from 98 first-principles enthalpies. The final CVS score is 2.4 meV with an average error of 1–2%. The MC used an 8000 atom cell with 10^6 flips per temperature step.

2.5. Pd–Nb

The CE for Pd–Nb was constructed from 71 first-principles enthalpies. The final CVS score is 3.7 meV with an average error of 1–2%. The MC used an 8000 atom cell and 8×10^4 flips per step for the 2:1, 3:1, and 8:1 concentrations. 10^6 flips per step were used for the 4:1 and 5:1 concentrations.

2.6. Pt–Mo

The CE for Pt–Mo was constructed from 77 first-principles enthalpies. The final CVS score is 13.9 meV with 5% error. The

MC simulation used an 8000 atom cell and 2×10^7 flips per temperature step.

2.7. Pt–V

The CE for Pt–V was constructed from 36 first-principles enthalpies. The final CVS score is 2.21 meV with an average error of 1–2%. The MC used a 1000 atom cell with 10^6 flips per temperature step.

2.8. Pd–V

The CE for Pd–V was constructed from 46 first-principles enthalpies. The final CVS score is 3.12 meV with an average error of about 3%. The MC used a 1000 atom cell with 10^6 flips per step.

In Section 3.8 a typical plot of our results for the Monte Carlo simulations is shown. The order–disorder temperatures were estimated from the peaks of the specific heat, which was calculated using the fluctuation–dissipation approach. Many order–disorder transition temperatures are given in the tables, but only the results for these two cases are shown explicitly. In a few cases, extremely slow convergence in the MC simulations prevented an unambiguous identification of the order–disorder transition temperature, and so they are not indicated in the tables.

3. Results

3.1. Pt–Al

The experimental phase diagram reports nine ordered phase (see Table 1). The 3:1 composition marks the most Pt-rich phases reported in the phase diagram. At slightly off-stoichiometry (on the low side) or at higher temperatures, the common $L1_2$ structure is stable. At lower temperatures and closer to stoichiometry, the Pt_3Ga phase is stable. The second phase appears first at 1290 °C. It is unclear from the phase diagram which of the two 3:1 phases would be stable at $T = 0$ K. The phase diagram does not include any information below ~ 700 °C at any concentration.

Beyond 75% (the lowest atomic percent needed to meet the international hallmarking standard of 95 wt.%), no other phases are reported; a broad 2-phase region is indicated to the right of the Pt_3Ga phase. To the right of that (>90 at.% Pt), there is a solid solution region where Al is soluble in Pt.

Much like the Al-rich portion of the phase diagram, which shows many ordered phases, our first-principles and cluster expansion calculations find several new stable phases on the Pt-rich side of the phase diagram, beyond 75 at.% (see Fig. 1). At 3:1, we find the $L1_2$ phase to be stable, consistent with the reported phase diagram. We also find two new phases beyond at stoichiometries 7:2 and 8:1. The 8:1 phase is the Pt_8Ti phase, as might be expected. The 7:2 phase does not have a known prototype. The structural information for these new phases is given in Table 9 in the appendix.

Monte Carlo simulations for the 8:1 phase indicate an order–disorder transition temperature of about 700 °C. At this

Table 1
Experimental and ab initio comparison of ground states in the Pt–Al system.

Pt–Al system Comparison of low temperature phases		
% Pt	Experimental results [31–33]	Ab initio results
75.0	$L1_2$ and Pt_3Ga	$L1_2$
77.8	two-phase region	New structure ^a (650245)
88.9	two-phase region	Pt_8Ti ($T_c \approx 700$ °C)

^a See Structure Tables in the appendix for crystallographic description.

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