UNEXPECTED OCCURRENCES OF THE PT$_8$TI STRUCTURE

by

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ABSTRACT

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The hardness of platinum and palladium alloys can be signicantly improved by precipitate hardening. One application of this is in Pt/Pd jewelery alloys where only small amounts of the alloying agent may be added (less than 5 wt.-%). For these alloys, one needs to identify platinum- and palladium-rich ordered phases that will form precipitates in nearly pure alloys. Using rst principles calculations, we identified 22 systems where a platinum- or palladium-rich phase (prototype Pt$_8$Ti) is stable but has not yet been observed. In the case of Pt-Mo, we constructed a cluster expansion and predicted the order-disorder transition temperature. Using our results as a guide, further experimental work may well turn up additional elements that will be useful for precipitate hardening in Pt-rich and Pd-rich alloys.

ACKNOWLEDGMENTS

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Chapter 1

Background and Motivation

Nearly one half of the world's yearly production of platinum and palladium is used in jewelry. Pure platinum and pure palladium are too soft for jewelry, requiring that they be alloyed with another metal. International marketing standards on platinum and palladium jewelry require that all platinum and palladium jewelry be 95% pure by weight. The addition of only 5 wt-% or less of the other metal is usually not enough to achieve the desired hardness of the platinum or palladium alloy. In order to get the desired hardness, namely enough to be made into jewelry, some ordering of the atoms, i.e., a crystal structure needs to occur in the alloy.

An example of how a crystal structure can significantly increase the hardness of an alloy is illustrated by a recent advance in the processing of Pt-Cu alloys. The addition of about 5 wt-% of copper to platinum causes the hardness to double compared to before. [1] Researchers Carelse and Lang induced ordered domains of the structure $CuPt_7$ in this type of sample. They found that the presence of these ordered domains causes this alloy to be harder than some grades of stainless steel. With this example in mind, we need to find a potential crystal structure that would have a high ratio, like that of $CuPt_7$, so that the weight percentage requirement for platinum and palladium
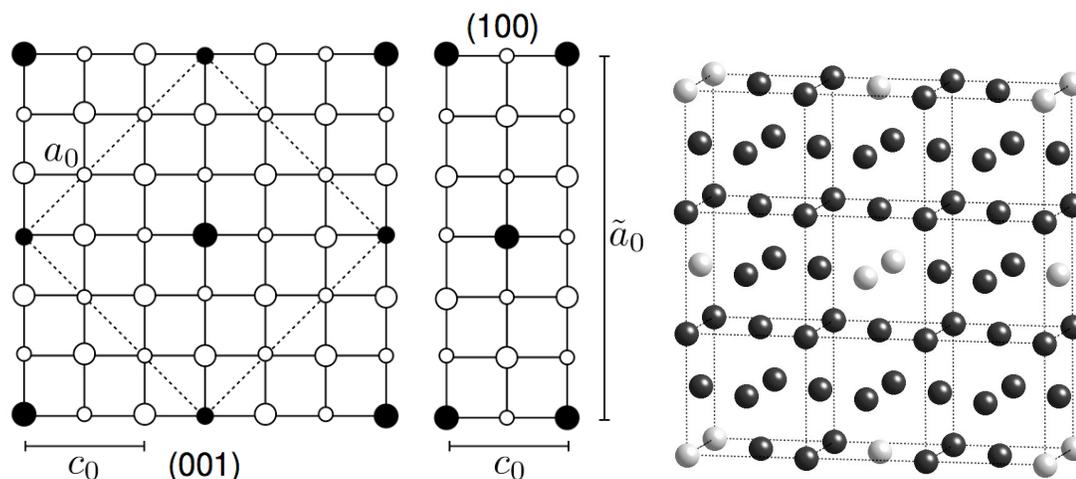
Figure 1.1 Three different views of the Pt_8Ti structure. The first is the front, second the side, and third the entire conventional unit cell. The dark grey and light grey balls represent platinum and titanium respectively.

jewelry can be met.

A good crystal structure is the structure of Pt_8Ti [2] that has stoichiometry 8:1. This structure was discovered [2] in 1965. Its structure can characterized as a face-centered tetragonal cell (see Fig. 1.1). A face-centered tetragonal cell is a cell where the sides of the cell are orthogonal to each other and there's an atom in the center of each face of the cell. Many alloys are assigned a *Strukturbericht* symbol yet this structure does not have one. Calling this structure by its prototype (Pt_8Ti) would be confusing, especially when other platinum and palladium rich systems are being discussed. Therefore, for clarity we will refer to this structure as $L1_4$ [1].

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[1]Here is an explanation of how we came up with this *Strukturbericht* symbol. *Strukturbericht* designations for pure elements start with A; the face centered cubic (fcc) structure is A1. For crystal structures with one-to-one stoichiometries, their designations start with B; the NaCl structure is designated B1, the 1 coming from A1, indicating fcc. Alloy structures are indicated by a beginning L. Fcc-based alloys are indicated by L1, again the 1 indicating fcc. A second number in the *Strukturbericht* symbol, $L1_x$, indicates the order of discovery or assignment. For example, the designation for CuAu is $L1_0$, indicating that CuAu was the first fcc-based alloy to be given a symbol. We use $L1_4$

Since its discovery, the $L1_4$ structure has been studied in several platinum and palladium systems. The literature on $L1_4$ [3–5] shows that platinum and palladium have typically been alloyed with the nine elements of groups IVB, VB, VIB of the periodic table. Of these 18 systems (Pt-X and Pd-X, where X is an element of those groups), $L1_4$ has been observed in seven of them: Pt-Cr [6], Pt-Ti [2], Pt-V [7], Pt-Zr [8], Pd-Mo [9], Pd-V [10], and Pd-W [11]. For reasons not discussed in the literature, other Pt-X and Pd-X systems have not been examined for the $L1_4$ structure. Implicit in this omission is the assumption that the structure would only occur in these 18 Pt/Pd-X systems.

However, we know that many metals are quite soluble in platinum and palladium. Therefore, our goal is to find other Pt/Pd-X systems that are good candidates to form $L1_4$. We computationally calculated the energy of 71 total systems (35 platinum and 36 palladium) and found that 22 of these systems are good candidates for the $L1_4$ structure. Furthermore, we computed a cluster expansion for the system Pt-Mo, one of the good candidates, and found that $L1_4$ has the lowest energy for that concentration. This means that the Pt-Mo system will form $L1_4$ at that concentration.

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because the structure occurs in alloys, is fcc based, and the $L1_4$ symbol has not been used before.

Chapter 2

Methods

2.1 First Principles Calculations

The following is a basic procedure of how we determined which of the 71 systems we chose were good candidates: calculate the formation enthalpy[1] [Eq. (A.1)] of $L1_4$ in each system, calculate the formation enthalpy of the nearest experimental ground state in concentration to $L1_4$ for each system, and use the ground state's formation enthalpy to make a tie-line to compare $L1_4$'s formation enthalpy to that line.

To help illustrate the above procedure, consider the Pt-Mo system. The most Pt-rich ground state reported in the Pt-Mo phase diagrams is Pt_2Mo. For any structure with a higher stoichiometry than 2:1 to be thermodynamically stable, its formation enthalpy must be *less than* the weighted average formation enthalpy of pure platinum and Pt_2Mo (see Fig. 2.1). This weighted average is represented by a line called a tie line. In the case of Pt-Mo, the formation enthalpy of Pt_8Mo is -227 meV/atom, putting it 148 meV/atom *below* the tie line.

This rather simple procedure was applied to all 71 systems (35 platinum and 36

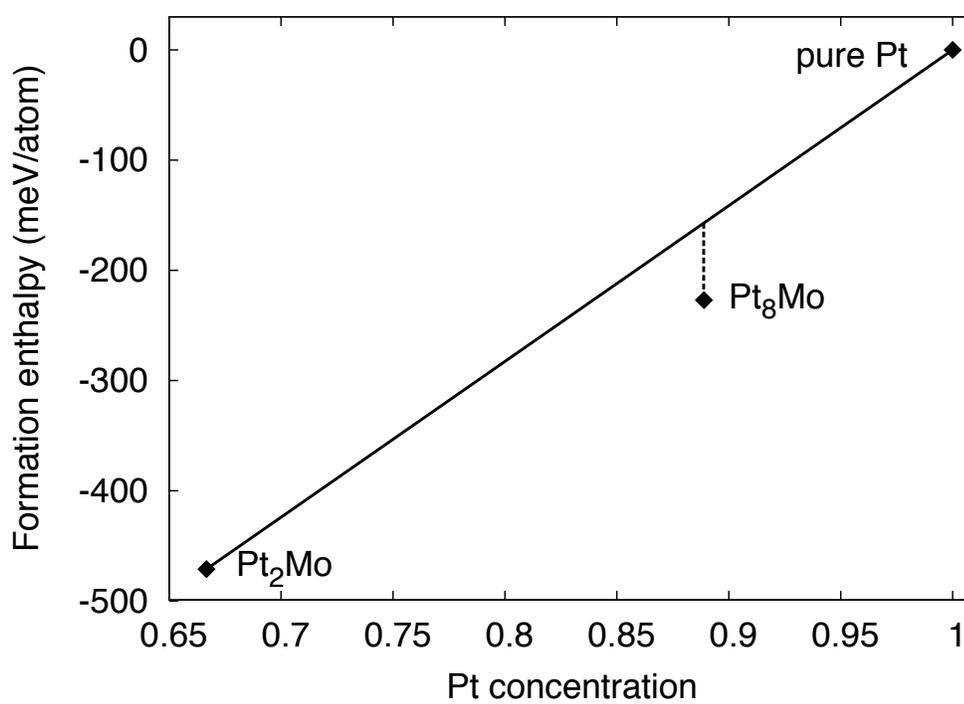[1]In general, a negative formation enthalpy means that the structure can potentially form.

Figure 2.1 Depiction of the tie line for the Pt-Mo system. Pt_8Mo lies below the tie line making this system a good candidate for forming the $L1_4$ structure.

palladium). The Vienna ab-initio Simulation Package [12–14] (VASP) was used for the energy calculations (see Appendix A.1 for parameters used). The experimental ground states were taken from the phase diagrams [15–29] included in the Pauling File [30].

2.2 Cluster Expansion: Pt-Mo

As mentioned in the beginning, the motivation for studying $L1_4$ for jewelry applications is that it may form ordered domains that can significantly increase the hardness and because it is a likely candidate for precipitate hardening because it occurs relatively frequently. However, it is possible that $L1_4$ is not the most thermodynamically stable structure; there may be other structures with even lower formation enthalpies. From an application standpoint, it does not matter which structure is the most stable as long as it results in significant hardening and meets the hallmarking purity standards, 95 wt-% platinum or palladium. The fact that $L1_4$ is below the tieline (Fig. 2.1) in 22 systems shows that *some* ordered phase must exist—thermodynamically, there must be a stable phase more platinum- or palladium-rich than the reported (experimental) phases.

To ascertain what structure is stable, one must explore all possible competing structures. Doing this by first principles, i.e., with VASP is not practical because we can only calculate one structure at a time. However, a cluster expansion (CE) [31–33] can quickly explore all possible structures (see Appendix A.2). [2] Given a set of structures and their energies, the CE attempts to fit the given energies to Eq. (A.2). Once a good fit [36–38] is achieved in the CE, we then use that fit to run a ground

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[2]More precisely, the CE can only explore derivative superstructures [34, 35] but experimental evidence in these systems indicates that such structures are the likely ground states, especially in the platinum- and palladium-rich regions of the phase diagrams.

state search (GSS) that generates formation enthalpies for all the possible structures up to a certain number of atoms per unit cell. Many runs of the CE and GSS are usually required to achieve the best predictions for a given system. From the predicted formation enthalpies, we can verify if $L1_4$ or another structure is most stable. Due to the large number of good candidates, we decided to start doing the CE and GSS for at least one of those systems. We chose the Pt-Mo system.

Chapter 3

Results and Outlook

We tested the stability of $L1_4$ in 71 systems. In 36 cases, the formation enthalpy is negative. Furthermore, in 22 of those 36 cases the formation enthalpy lies *below* the tie line between pure platinum or palladium and the nearest experimentally-observed ground state. These 22 cases are the new good candidates for $L1_4$. In these systems, $L1_4$ had not yet been reported experimentally. Fig. 3.1 shows three periodic tables. In Fig. 3.1(a) the highlighted elements represent the initial 71 systems. In Fig .3.1(b), the highlighted elements represent the platinum systems that lie *below* the tie line and Fig. 3.1(c) is the same thing but for palladium. Furthermore, from the CE and GSS, we found that $L1_4$ is the *most* thermodynamically stable structure for Pt-Mo at a stoichiometry of 8:1.

When our new candidates are depicted in this way (Fig. 3.1), we noticed that the 22 new candidates are clustered together in two areas of the periodic table, where the first cluster is in the early transition metals and the second in the transition metals with full or almost full d-shells. The same kind of clusters occur when the elements are arranged by Mendeleev number as assigned by Pettifor [39] (Table 3.1). This clustering is very interesting and will need further investigation.

Finding that there are 22 new candidates beyond those seven already experimentally observed and in Pt-Mo $L1_4$ is the most thermodynamically stable are very exciting results. This means that experimentalists have more to look for in these 22 new candidates and hopefully our computational results can be confirmed by experiment.

Figure 3.1 Pictorial representation of our results. The highlighted elements in (a) represent the initial 71 Pt-X and Pd-X systems, (b) shows the good candidates for the platinum systems, and (c) shows the good candidates for the palladium systems

Mendeleev #	Element	Pt	Pd	Mendeleev #	Element	Pt	Pd
8	Cs	+	+	58	Re	—	+
9	Rb	+	+	59	Tc	—	+
10	K	+	+	62	Ru	+	+
11	Na	—	—	63	Os	+	+
12	Li	—	—	65	Rh	—	+
14	Ba	+	—	66	Ir	+	+
15	Sr	—	—	70	Au	+	+
16	Ca	—	—	71	Ag	+	+
19	Sc	●	●	72	Cu	—	●
25	Y	—	—	73	Mg	—	●
49	Zr	⊙	●	75	Cd	●	●
50	Hf	●	●	76	Zn	●	—
51	Ti	⊙	●	77	Be	—	—
52	Ta	●	●	79	In	●	—
53	Nb	●	●	80	Al	—	●
54	V	⊙	⊙	81	Ga	●	—
55	W	●	⊙	83	Sn	—	●
56	Mo	●	⊙	84	Ge	—	—
57	Cr	⊙	—	85	Si	—	—

Table 3.1 The elements arranged by Mendeleev number as assigned by Pettifor [39]. A + indicates systems where the formation enthalpy is positive, a — indicates systems where the formation enthalpy is negative but *above* the tie line, and a ●indicates systems that lie *below* the tie line. ⊙ indicates those systems that have already been experimentally observed.

Appendix A

Appendix

A.1 VASP

The Vienna ab-initio Simulation Package [12–14] (VASP) is a program that calculates the energy of a given lattice structure. Essentially, VASP solves the Schrodinger equation, $H\psi = E\psi$, for the lattice where H in this equation represents the Hamiltonian and E represents the energy. After VASP solves this equation and provides a value for E, then we use that value to determine the formation enthalpy of the lattice. The formation enthalpy for an alloy A_xB_{1-x} is given by the following equation:

$$\Delta H = 100 \times [(\frac{E_L}{N_L}) - (\frac{N_A}{N_L}E_A + \frac{N_B}{N_L}E_B)], \qquad (A.1)$$

where E_L, E_A, and E_B are the energies of the whole lattice, pure element A, and pure element B respectively; N_L, N_A, and N_B represent the total number of atoms in the lattice, the number of A atoms, and the number of B atoms respectively. All energies are in units of eV where ΔH is in meV/atom.

VASP requires four files that describe the lattice vectors, the properties of the elements in the lattice, how to break up the lattice in reciprocal space, and precision

of the calculations. Below are the specific parameters used in the first principles calculations for this project.

An equivalent k-mesh [40] was used to eliminate systematic errors when calculating the formation enthalpy. The default cutoff energies for the "high accuracy" setting was used in all cases: 350 eV was used for all the palladium systems and 230 eV for platinum except where the other element had a higher default cutoff. For Pt-Ag, Pt-Al, Pt-Be, Pt-Cd, Pt-Cu, Pt-Pd, Pt-Si, and Pt-Zn the energy cutoffs for the plane wave basis were 250 eV, 240 eV, 300 eV, 274 eV, 273 eV, 350 eV, 245 eV, and 277 eV respectively. Standard projector augmented wave (PAW) potentials were used for the majority of metals except where semicore states are important. For Ba, Cs, Sr, Ti, and Y, the highest occupied s states were included in the valence. For K, Nb, Pd, and Rb, the p states were included in the valence. Our extensive testing in another context [41] indicates that formation enthalpies in all of these systems are relatively insensitive to spin-orbit effects so spin-orbit coupling was not included here.

A.2 Cluster Expansion

The cluster expansion (CE) is a way to describe the energy of a lattice [31–33]. The following equation is a mapping of the energy to an Ising Hamiltonian.

$$E_{CE}(\sigma) = J_0 + \sum_i J_i \hat{S}_i(\sigma) + \sum_{j<i} J_{ij} \hat{S}_i(\sigma) \hat{S}_j(\sigma) + \sum_{k<j<i} J_{ijk} \hat{S}_i(\sigma) \hat{S}_j(\sigma) \hat{S}_k(\sigma) + ... \quad \text{(A.2)}$$

where the first sum is over all lattice sites, the second all site pairs, the third all site triplets, etc. $\hat{S}_i$ represents a set of "spin" variables that are associated with the site "i", σ represents a configuration in the lattice, and J represents "interaction energies". E_{CE} is usually calculated by VASP and then the CE uses this equation to determine the J's. In essence, we are trying to fit a "function" to a set of "data

points". These "data points" are energies of structures that we calculate in VASP and then give them to the CE code as input structures.

When a good fit is found [36–38], we can then use that fit to predict the energies of other structures. This idea is used in the ground state search (GSS) where the fit is used to predict formation enthalpies of hundreds of lattice structures of varying stoichiometries.

For our CE and GSS, we used the Universal Cluster Expansion code (UNCLE) [38] using 78 input structures. A leave-many-out cross validation (CV) method was used to make accurate fits. The CV score for the final fit was 15 meV/atom which is about a 3% error on average.

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