Thermodynamic remodeling of the Al-Pt system towards an assessment of the Al-Ni-Pt system

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Abstract

The thermodynamic CALPHAD description of the Al-Pt system is remodeled. The four sub-lattice (4SL) model for the ordered/disordered fcc and bcc phases is adopted resulting in improved agreement with experiment and first-principles information compared to previous descriptions. First-principles calculations are performed and the results are used in addition to available experimental data as input for the modeling. Modeling results agree well with most experimental phase equilibria and thermochemical data compiled. Special attention is also paid to the metastable phase diagrams to ensure that the parameters obtained in the modeling do not present unphysical results in the metastable regime. The obtained fcc and bcc descriptions are converted to two sublattice (2SL) models to enable combination with available multi-component Ni-base superalloy descriptions. The converted Al-Pt system is extended into the Al-Ni-Pt ternary system to study its extrapolation characteristics using available thermodynamic and thermochemical data. It is found that the 2SL model is not adequate in capturing the thermodynamic behavior of the fcc-based phases found in the ternary Al-Ni-Pt system. Possible approaches for future work is discussed.

Introduction

The calculated phase diagrams included in the most previous publication for thermodynamic modeling of the Al-Pt system [1] fail to show the global minimum of the Al-Pt system's total energy. If the suggested thermodynamic description is used to find the global minimum, disagreement with experiments is found as the B2 phase becomes too stable on the Al-rich side of the phase diagram, see Figure 1. These phase diagram thus only represents metastable phase equilibria at these conditions. Removal of vacancies from the substitutional sublattices in A2 and B2 in that description yields a phase diagram identical to the phase diagram included in the article but with L1₀ being stable at conditions for which B2 previously was stable. It is therefore realized that the energetics for all the phases need to be modified to accommodate a revision of the B2 phase. This work includes a remodeling of the Al-Pt system. Available experimental data and the first-principles results from the original article are accounted for. Some additional data sets are further included in the present modeling work to improve the overall thermodynamics of the system.

Thermodynamic models in this work have a direct applicability in designing oxidation/corrosion-resistant platinum-based alloys for process industries such as glass manufacturer to produce high quality glass products. In glass industry, platinum group metals are extensively employed in glass melting apparatus due to their high melting temperature and superior corrosion resistance, including refiners ($T > 1600^{\circ}\text{C}$), stirring chambers, and heating elements [2]. However, these platinum alloys suffer from high temperature degradation mechanisms where volatile oxides (e.g., PtO₂) are formed by oxidation, escape the substrate by gaseous transport, and decompose back to platinum condensates at temperatures below 650°C [Pt + O₂(g) $\leftrightarrow$ PtO₂(g)], leading to the premature failure of glass melting apparatus and/or Pt

inclusion defects in the glass products [3–5]. For rational design and selection of platinum alloys and coatings for enhanced high temperature oxidation resistance (e.g., Pt-Al), accurate thermodynamic models can provide essential information on the formation of alloy phases [6–8]. Hence, special attention is paid to the modeling of fcc- and bcc-based phases in this work due to their importance in high temperature diffusion coatings such as Pt-modified B2-(Ni,Pt)Al or Pt-based γ/γ' [9–11].

Platinum-modified B2-(Ni,Pt)Al or Pt-based γ/γ' coatings can be represented by the Al-Ni-Pt ternary system and prove crucial to Ni-base superalloys as protective coating systems. Unlike overlay coatings such as MCrAlYs, Al-Ni-Pt or so-called "platinum aluminide" coatings are often diffused into the surface of superalloy substrates [12]. For example, Jackson and Rairden [13] found that sputtering Pt on an investment cast IN-738 substrate followed by a pack aluminization produced an outer layer ($\sim 25\ \mu\text{m}$) that is essentially all Al, Ni, and Pt. Recent key phase stability results from Gleeson et al. [14], Zhu et al. [15] and Grushko et al. [16] have contributed to a better understanding of the Al-Ni-Pt ternary though some discrepancies still exist [17]. Experimental [18–20] and first-principles works [11,21–23] have also attempted to shed light on this complex system. In fact, the most recent studies by Grushko et al. [16] and Grushko and Kapush [17] reveals a gamut of new Al-Ni-Pt ternary phases. One such interesting phase is the superstructure ordering of the $L1_0$ -AlNiPt₂ into an orthorhombic phase, γ^* , with four-times larger volume of the unit cell as the Al content increases [16,17]. This new phase γ^* is believed to be the ternary extension of the Al₃Ni₅ phase and could potentially order from the $L1_0$. Modeling the ordering phenomena $\text{fcc} \gg L1_0 \gg \gamma^*$ would require at least a 8-sublattice model under the CALPHAD framework. To complicate things even further, B2 transforms to $L1_0$ martensite when cooling below approximately 973 K near the γ^* phase region. The uncertainty

of the phase stabilities in this region of the phase diagram provides a challenge in the current modeling efforts.

Since the thermodynamic description of the Al-Ni-Pt ternary is important for understanding the thermodynamic behavior of coating to Ni-base superalloy interactions during processing and use, a description of the Al-Ni-Pt system has also been modeled in this work and made compatible with the current Thermo-Calc Nickel Database (TCNI) [24] and the NIST Superalloy Database [25]. Previous modeling efforts on the Al-Ni-Pt [1,15,23,26] system focused on implementing 4SL order-disorder models to describe the fcc, $L1_2$ and $L1_0$ phases in one Gibbs energy framework. Lu et al. [11] and Kim [23] developed 4SL order-disorder model for the Al-Ni-Pt system based on the framework by Kusoffsky et al. [26] in the Ni-rich region of the phase diagram. Zhu et al. [15] also implemented a 4SL cluster/site approximation (CSA) model to assess the Al-Ni-Pt ternary in the Ni-rich region. For the implementation of these models into a Ni-base superalloy database such as the ones mentioned previously, conversion of those databases to 4SL models would be needed which would require an inordinate amount of work. Therefore, a new preliminary 2SL model is developed here to be compatible with the already established superalloy databases. It should be noted that the use of a 2SL model also compromises the correct phase diagram topologies seen with the 4SL model where configurational entropy and SRO dominate. After decoupling the 4SL model, the $L1_2$ phase is modeled as an ordered part of the fcc phase with the $L1_0$ phase modeled as a separate phase entirely.

The first part of the current work details the remodeling of the Al-Pt binary using the 4SL sublattice model for fcc and the 2SL sublattice model for bcc. In the second part, the 4SL model for the fcc phase is converted to a 2SL model to enable combination with available multi-

component Ni-base superalloy databases. Finally, the results are discussed along with suggestions for future work.

Remodeling of the Al-Pt system

Modeling of the fcc and bcc-based phases using the 4SL model

The model parameters for the fcc-Al/L1₂ phase are modified by introducing the formalism presented by Kusoffsky et al. [26] where the values for the disordered interaction parameters are derived from the ordered parameters. The original expressions for the fcc end-members and interactions used to describe the 4SL fcc ordering, imposed no relationships between the disordered and ordered phases. This, indirectly, produced unphysical, ordered phases that never disorder even at extremely high temperatures (> 6000 K). The fcc-Al, L1₀ and L1₂ phases can be better described using disordered interaction parameters derived from the ordered state with the introduction of order-*dependent* parameters only if needed. In binary systems, model parameters can be related closely to a bond energy between the two components, in this case Al and Pt. The bond energy, U_{AlPt} , can often be derived from first-principles calculations discussed in great detail by Kusoffsky et al. [26]. Following Kusoffsky et al. [26] reciprocal interaction parameters are added which are important as they approximate short range ordering (SRO) in the compound energy formalism (CEF) framework [27]. The disordered interaction parameters for the disordered fcc-Al state can be expressed as the following [26,28]:

Eq. 1:

$${}^0L_{Al,Pt}^{fcc} = G_{Al_3Pt}^{4SL} + 1.5G_{Al_2Pt_2}^{4SL} + G_{AlPt_3}^{4SL} + 1.5L_{Al,Pt:Al,Pt:***}^{4SL} + 4 {}^0L_{Al,Pt:***}^{4SL}$$

$${}^1L_{Al,Pt}^{fcc} = 2G_{Al_3Pt}^{4SL} - 2G_{AlPt_3}^{4SL} + 4 {}^1L_{Al,Pt:***}^{4SL}$$

$${}^2L_{Al,Pt}^{fcc} = G_{Al_3Pt}^{4SL} - 1.5G_{Al_2Pt_2}^{4SL} + G_{AlPt_3}^{4SL} - 1.5L_{Al,Pt:Al,Pt:**}^{4SL} + 4 {}^2L_{Al,Pt:***}^{4SL}$$

where the interaction parameters for the disordered fcc phase are related to the ordering parameters by the terms ${}^{0,1,2}L_{Al,Pt:***}^{4SL}$ as shown by Hallstedt and Kim [28]. The parameters $G_{Al_xPt_y}^{4SL}$ and $L_{Al,Pt:k:l:m}^{4SL}$ describe the ordered state end-members and interactions, respectively. In the notation, a comma separates interacting elements in the same sublattice, while a column separates sublattices (alternatively, the end-member $G_{Al_3Pt}^{4SL}$ can be written as $G_{Al:Al:Al:Pt}^{4SL}$ or its equivalent permutations). As such, $L_{Al,Pt:k:l:m}^{4SL}$ describes the interactions between Al and Pt while the other sublattices are occupied by species k , l , and m , respectively. Simultaneous reciprocal interactions are described with interactions $L_{Al,Pt:Al,Pt:k:l}^{4SL}$ where Al and Pt interact on the first and second sublattices while the remaining sublattices are occupied by species k and l . In Eq. 1, the reciprocal interaction parameters $L_{Al,Pt:Al,Pt:**}^{4SL}$ represent an estimate of SRO and can be set equal to the nearest neighbor bond energies U_{AlPt} as a first approximation [26,27]. These interactions are important in producing the correct phase diagram topologies. It can now be seen that the model parameters for the disordered state are expressed by the parameters of the ordered states. By evaluating the coupled model parameters, systems with only one of the phases fcc-Al, L1₂, or L1₀ stable, can be described effectively as well. In the current model, the fcc-Al and Pt-rich L1₂ phases are stable while the Al-rich L1₂, L1₀ and L6₀ (L6₀ is presented as F' by Kusoffsky et al. [26]) phases are metastable. Figure 2 details the possible order and disordered states present in the current system and the site ordering associated with each. The phase L6₀ is an intermediate ordered state between L1₂ and L1₀ where only two sites have the same site fractions.

The bcc-A2 and B2 phases are modified in two versions; one description where they are described by the sublattice formalism (SL) and one description when they are described by the modified sublattice (MSL) formalism. The two versions can be used interchangeably and details concerning the conversions between them are described by Dupin and Ansara [29]. Vacancies are retained in the substitutional sites to allow compatibility with other B2 containing systems such as Al-Ni [30]; e.g. to enable modeling of the Al-Ni-Pt ternary [11].

Franke [31] suggested that a non-zero value for the vacancy end-member, G_{Va}^{bcc-A2} , in the sublattice model $(A,Va)_1(Va)_3$ for the bcc-A2 phase has to be selected to make it possible to find the global minimum at high temperatures. In fact, in models where $G_{Va}^{bcc-A2} = 0$, equilibria are only found as a result of small starting vacancy concentrations. This was the case with the model in the original manuscript where global minimum was not found when calculating an equilibrium at 20 at. % Pt at 5500 K. In this work, G_{Va}^{bcc-A2} is set to a value of $0.2RT$ as recommended by Franke [31]. However, other values have been used; e.g. in recent work by Stein et al. [32] where $G_{Va}^{bcc-A2} = 30 T$ was adopted. Further, depending on which systems the Al-Pt description is intended to be combined with, a change of this value may also be required and the B2 modified accordingly. This would for example be needed if the system was to be combined with the Al-Fe system [33]. In the latter part of this manuscript, due to the use of $G_{Va}^{bcc-A2} = 0.2RT$, the Al-Ni binary modeled by Dupin et al. [30] (which used $G_{Va}^{bcc-A2} = 0$) shows a difference in the Al₃Ni melting temperature compared to the original description [30]. Remodeling of Al-Ni using new values of G_{Va}^{bcc-A2} has not been performed in the current work but should be investigated in the future for this very important system.

Inclusion of new data

Numerous authors have studied the phase stabilities of intermetallics near the Pt-rich portion of the phase diagram and come to various conclusions. These are summarized in Table 1. Since the review paper by McAlister and Kahan [34] in 1986, a number of new experiments and calculations have been performed on the Al-Pt system in the Pt-rich region of the phase diagram. [35–47].

The presence of a low-temperature (LT) AlPt₃ phase has marred the understanding of Pt-rich Al-Pt alloys, especially at low and high temperatures where there are indications of martensitic transformations. Experimental results by Oya et al. [35] suggested that there may be two LT variants of AlPt₃ that destabilize at 400 and 613 K. However, more recent experiments [41] [42] [43] as well as first-principles calculations [44] suggest that there is only one stable form of LT-AlPt₃ with the probable crystal structures tP16 or DO_c'. Long duration high temperature anneals at 1573 [41] , 1623 [42] and 1773 K [43] all indicated the presence of LT-AlPt₃ and hence, are in conflict with the findings by Oya et al. [35]. The transition electron microscope (TEM) studies by Douglas et al. [42] indicated that large HT-AlPt₃ L1₂ precipitates in their samples contained twin domains where LT-AlPt₃ existed as plates. Interestingly, first-principles calculations by Chauke et al. [44] showed that the ground state crystal structure for the composition AlPt₃ is tP16 rather than L1₂. This is in contrast to the Al-Ni system where L1₂ indeed represent the ground state. These phenomena are indicative of martensitic transformations and would require further analysis. Two crystallographic variants of AlPt₂ have also been reported with the low temperature form not being observed by all researchers [34,48]. The resolution of the debate about the stability of LT-AlPt₃ and LT-AlPt₂ is outside the scope of this work and consequently, the thermodynamics of these compounds are not modeled here.

Since the publication of the previous Al-Pt description [1], Grushko et al. [16,17,46,47,49] has performed a series of extensive experiments with regards to the Al-Pt and Al-Ni-Pt systems in order to rectify some of the disagreements present in the literature. These include the stability of B2 [46] and Al-rich intermetallics in the Al-Pt binary system [47]. McAlister and Kahan [34], based on the experiments by Bhan and Kudielka [50], rationalized that B2 is stable from approximately 1533 to 1783 K at ~52 at. % Pt while AlPt-B20 melts congruently at 50 at. % Pt. However, based on results of DTA and XRD investigations, Grushko [46] suggested that B2 becomes more stable than B20 at 50 at. % Pt at high temperatures and melts congruently based in binary and ternary systems. Grushko [46] also proposed a new B2 phase region (Figure 7 b) based on his experimental findings that attempts to resolve some of the conflicts present in the literature concerning this area of the phase diagram. This experimental investigation is judge to be the most complete analysis of the B2 phase in the Al-Pt system and is therefore accounted for in the modeling of the B2 phase in the current work. Grushko [47] also discovered a new phase ξ at ~25 at. % Pt with an orthorhombic structure that exists between 1074 and 1188 K. Structural determination for this phase is still ongoing [47] and the phase is not included in the current assessments.

In addition to the data sets accounted for in the previous assessment of the Al-Pt system [1], further data sets are included in this work to aid in the revision. In terms of thermochemical data, activity measurements [38,39,51] are accounted for as well as first-principles calculations by Feng et al. [45]. Due to a lack of thermodynamic information on the important $L1_2$ -AlPt₃ compound, the Debye-Grüneisen model is used to calculate the finite temperature properties of

the phase at the stoichiometric composition. The same settings as in the previous work [1] are used and an appropriate scaling factor is applied [52,53]. This method is also used to compute the thermodynamic properties of all other intermetallics except that of $\text{Al}_{21}\text{Pt}_5$, which is disregarded due to its massive unit cell size. Previously, only off-stoichiometry B2 anti-site defects were calculated where Al resides on Pt sites and vice versa. However, off-stoichiometry energies in B2 involving vacancies are highly important to the stability of this phase. For this reason, the special quasirandom structures (SQS) calculations with vacancies replacing either Al or Pt in B2 are performed following the method described by Jiang et al. [54]. The PARROT module [55] of Thermo-Calc [56,57] is used to evaluate the model parameters for the end-members and interactions based on the selected experimental and calculated information. The resulting values are shown in Table 2.

To the authors knowledge, only one complete set of liquidus and solidus measurements is available in the literature for the Al-Pt binary system [58]. The solid to liquid transformations at high temperatures were studied using DTA measurements for alloy compositions spanning the entirety of the phase diagram. However, it is difficult to determine the validity and accuracy of those measurements given some of the discrepancies shown in the phase diagram by Huch and Klemm [58]. At around ~56 at. % Pt, there is a sheer drop in the liquidus from 1397 to 1260 K, which is unphysical.

Extension into the Ni-rich part of Al-Ni-Pt

The Al-Pt binary developed here is extended into the Al-Ni-Pt ternary to determine its extrapolation "fitness" as well as the parameterization required to obtain a reasonable ternary phase diagram assessment. As is described in the introduction, the extrapolation is done using the 2SL "order-disorder" model where only the L_{12} is captured as the ordered phase to ensure compatibility with the TCNI [24] and NIST Superalloy Databases [25]. To convert the 4SL fcc model presented in this work into the 2SL fcc model, thermodynamic parameters determined for all phases except for the ordered part of the fcc-Al, i.e. 4SL-fcc, are retained. A set of constraints as implemented by Dupin et al. [30], are then used as the ordered part of the fcc describing only the L_{12} phase with 2SL $(Al,Ni,Pt)_{0.75}(Al,Ni,Pt)_{0.25}$ model. The implementation of these constraints for Al-Ni-Pt are essentially the same as Al-Cr-Ni presented by Dupin et al. [30] and the reader is referred to Ref. [30] for more on its background and derivation. Gibbs energy parameters for the 2SL- L_{12} ordered part are re-assessed to the same Al-Pt data used for the 4SL that is relevant to the L_{12} . The new 2SL- L_{12} parameters are shown in Table 3 for the converted Al-Pt system. As a result of this conversion, the L_{10} must be modeled as a separate phase.

To capture the ordering of Ni- and Pt-rich L_{10} in Al-Ni-Pt, a 3SL model is used with the following sublattices: $(Al,Ni,Pt)_{0.25}(Al,Ni,Pt)_{0.25}(Ni,Pt)_{0.5}$. Such a model allows both binary L_{10} -NiPt, and ternary L_{10} -AlNi₂Pt, L_{10} -AlNiPt₂ to be described as ordered compositions and mirrors the treatment of a similar L_{21} phase by Dupin [59]. For example, binary L_{10} -AlNi can be described as $(Al)_{0.25}(Al)_{0.25}(Ni)_{0.5}$ while ternary L_{10} -AlNiPt₂ can be described as $(Al)_{0.25}(Ni)_{0.25}(Pt)_{0.5}$. The end-member $(A)_{0.25}(B)_{0.25}(B)_{0.5}$ is evaluated to always be less stable

than the $L1_2$ phase with the same composition, $(A)_{0.25}(B)_{0.75}$. This treatment assumes that the tetragonal $L1_0$ is less stable than the cubic $L1_2$ phase at compositions such as $AlNi_3$. This new ordered part of the fcc and $L1_0$ are then re-evaluated using the same Al-Pt dataset to obtain the 2SL $L1_2$ ordered parameters and the 3SL $L1_0$ parameters.

Since no 2SL-fcc model of Ni-Pt exists in the open literature to the authors' knowledge, the conversion presented above is also performed on the 4SL Ni-Pt binary by Lu et al. [11] to convert it to 2SL-fcc/ $L1_2$ and 3SL $L1_0$ models for the purpose of modeling the ternary. Additionally, $L1_0$ -AlNi was added to the 2SL Al-Ni binary by Dupin et al. [30] to approximate the 4SL Al-Ni assessment [60] referenced by Lu et al. [11]. Due to the current poor understanding of the γ^* phase and the boundaries associated, it is precluded in the current modeling efforts. The preliminary conversion performed for Ni-Pt presented in this work requires more detailed assessments to finalize its 2SL- $L1_2$ and 3SL- $L1_0$ parameters.

Results and Discussion

Al-Pt system

The model parameters of the liquid phase and all intermetallics published by Kim et al. [1] are remodeled in the present work alongside those of the fcc- and bcc-based phases. Calculated enthalpies of mixing for fcc-A1, bcc-A2, $L1_0$, $L1_2$ and B2 agree well with the values from first-principles calculations (Figure 3 (a and b)). Figure 3 (b) also shows the importance of including substitutional vacancies in B2. When the A2-B2 phase is modeled with vacancies, it exists not only in two states (A2 and B2-Va), but in three states: A2, B2-(high Va) and B2-(low Va). This marks the distinction in the two different B2 curves seen in Figure 3 (b). Comparing

the calculated B2 formation energies with and without vacancies for off-stoichiometric compositions on the Al-rich side, the introduction of vacancies on Pt sites lowers the energies substantially. On the Pt-rich side, vacancies are shown to increase the formation energies slightly (Figure 3 (b)). Similar results are obtained in other B2 containing systems such as Al-Ni [54] and In-Pd [61]. Figure 4 (a) shows the calculated enthalpies of formation at 298 K for all the modeled phases. Agreement with experiments [36,37,62,63] as well as first-principles results from the previous Al-Pt work [1] can be concluded. The liquid energies seen in Figure 4 (b) are close to predicted energies using the surrounded atom model by Colinet et al. [64]. Presented in Figure 5 (a), the calculated Gibbs energies of formation in the fcc-Al and L1₂ regions (up to 32 at. % Al) at 973 K are shown to agree with the EMF measurements by Schaller [51] within expected experimental uncertainty. In Figure 5 (b), activities of Al at 1000 and 673 K are shown to be in line with EMF measurements by Nanko et al. [39] and Kobayashi et al. [38]. Figure 6 indicates that the Debye-Grüneisen predictions for pure Al and Pt (Figure 6 (a) to (f)) agree very well with the SGTE values [65–67]. Additionally, Figure 6 (g) and (h) show that the calculated molar entropy, heat capacity and enthalpy of L1₂-AlPt₃ are in accordance with predictions from the Debye-Grüneisen model. It is important to note that the hump seen in Figure 6 (h) results from the use of the Neumann-Kopp approximation for the heat capacity of the fcc phase from which the L1₂ orders from. The heat capacity of pure fcc Al is ill-defined above its melting point and discontinuous, producing this artifact. It is expected that future redefinition of the pure elements expressions could resolve this issue. By the use of first-principles calculations coupled with experiments the theoretical heat capacity could be defined at temperatures above the melting point until the phase becomes unstable.

Figure 7 (a) and (b) present the remodeled Al-Pt phase diagram compared to a series of experiments performed after 1964. The solubility in the fcc-Al+L₁₂ two-phase region is expected to decrease significantly at low temperatures and this is now captured by the revised description. Good agreement is seen for the majority of data sets [41–43,46,51,58,68–73] with some exceptions. The measurements of the Pt-rich fcc+L₁₂ phase boundary show a large scatter ranging from as high as 98 at. % [69] to as low as 89 at. % Pt [51,73] (Figure 7). The current assessment shows good agreement with the boundaries measured by Darling et al. [68], Volkl et al. [41], Douglas et al. [42], and Tshawe [43]. Also the AlPt₂ phase boundary with L₁₂ poses some challenges. The current model agrees with Al₃Pt₅-L₁₂ phase boundaries suggested by Tshawe [43] at high temperatures but disagrees with alloys from Chattopadhyay [70] at lower temperatures. Chatterji et al. [69] noted the difficulty of AlPt₂ to form in a series of diffusion studies using aluminized Pt samples and Guex and Feschotte [71] were unable to find the AlPt₂ phase in their anneals. These results question the stability of AlPt₂ altogether and its phase boundaries with the phases in proximity.

The calculated B2 phase region seen in Figure 7 (b) reproduced the phase region proposed by Grushko [46] where B2 becomes the stable phase instead of B20 before melting congruently. Figure 8 (a) and (b) demonstrate the calculated metastable phase diagram when only the fcc- and bcc-based phases are present. As can be deduced from the first-principles results, AlPt₃-L₁₂ and AlPt-L₁₀ are seen in the metastable phase diagram while the less stable Al₃Pt-L₁₂ is not. The presence of L₁₀ ordering in the center of the metastable phase diagram is not surprising given its highly exothermic formation energy of -90 kJ/mol-atom predicted by DFT, rivaling the formation energy of the stable AlPt-B20 phase and metastable B2. Additionally, L₁₀ ordering is seen near the Al-Pt side of the Al-Ni-Pt phase diagram at

temperatures as high as 1573 K [16] which further suggests its metastability. In Figure 8 (a) and (b), $\text{AlPt}_3\text{-L1}_2$, AlPt-L1_0 , and B2 all disorder at reasonable temperatures (less than 3000 K). This occurs through 1st order transformations for the fcc-based phases and a 2nd order transformation for the bcc-based B2. The associated site fraction changes are shown in Figure 9 (a) for B2 at its stoichiometric composition. In Figure 9 (b), the calculated defect concentrations in B2 at 1300 K are shown. Finally, the introduction of the 4SL model for the bcc-based phases can capture D03 and B32 ordering seen at lower temperatures such as in Al-Fe by Sundman et al. [74]. It is possible to then also model Al_2Pt as a Va-ordered structure using the 4SL bcc frame-work. Such a model could account for the ordering phenomena seen by Grushko et al. near the $\text{B2+Al}_2\text{Pt}$ region of the phase diagram [17].

Ni-rich part of the Al-Ni-Pt system

The resulting model parameters from the current assessment are shown in Table 3. First the bcc-based A2 and B2 phases are compared to thermochemical properties measured [19] and calculated [21,23] by various authors. Figure 10 (a)-(c) compares the calculated CALPHAD enthalpies of mixing for the bcc-A2 and B2 phases to first-principles values calculated by Kim [23] and Jiang et al. [21]. In all three isopleths, showing the composition ranges AlNi-AlPt , AlPt-NiPt , and NiPt-AlNi , good agreement is seen. Aluminum activities measured using Knudsen Effusion Mass Spectrometry (KEMS) [19] for four different alloys (Ni-47.2Al , Ni-47.5Al , Ni-39.5Al-15.0Pt , and Ni-46.9Al-14.9Pt) shown in Figure 10 (d) parallel the calculated CALPHAD values as well. Copland [20] made additional KEMS measurements for activities of species in a series of Ni-24Al-xPt and Ni-27Al-xPt alloys with the first set shown in Figure 11 (a). Calculated CALPHAD Al activities in L1_2 and liquid phases compared to those measured by

Copland [20] via KEMS show good agreement. One of the most important regions of the phase diagram is the AlNi_3 to AlPt_3 vertical section and modeling its phase stability first requires the correct thermochemical properties of the phases involved. Figure 11 (b) shows that the calculated CALPHAD enthalpies of mixing for the fcc, L1_0 and L1_2 phases are congruent with first-principles calculations by Kim [23], Jiang et al. [22] and Lu et al. [11].

Figure 12 (a) plots the AlNi_3 - AlPt_3 phase diagram with some melting information inferred from KEMS measurements by Copland in a series of alloys that are close in composition to this vertical section [20]. From this series of Ni-24Al-xPt and Ni-27Al-xPt alloys, the highest temperature solid and lowest temperature liquid observed are in accord with the calculated liquidus and solidus temperatures shown in Figure 12 (a). It can be seen from Figure 12 (b) that the calculated L1_0 disordering temperatures have the same trend as those predicted by Jiang et al. [22] using Monte-Carlo and SQS methods. Due to experimental observations of L1_0 - AlNiPt_2 at temperatures as high as 1573 K, however, the current assessment places its disordering temperatures much higher. Additionally, Figure 12 (b) shows that L1_0 - AlNi_2Pt and L1_0 - AlNiPt_2 both first disorder to L1_2 and then finally to fcc as suggested by predictions from first-principles [22].

Figure 13 (a) presents the Ni-rich partial isothermal section of the Al-Ni-Pt system at 1373 K. While most calculations are in consensus with the measured EPMA data by Gleeson et al. [14], Grushko et al. [16] and Kamm and Milligan [18], discrepancies exist near the B2-L1_0 phase boundary. Recent experiments by Grushko et al. [16,17] indicate that L1_0 - AlNiPt_2 orders into an orthorhombic superlattice phase, γ^* , with four-times larger volume of the unit cell as Al content increases near B2. It is suggested that this phase is the ternary extension of Al_3Ni_5 given their similar crystal structures [16,17]. Currently, there is no data to suggest if phase separation

occurs in the $L10-\gamma^*$ phase field. It is not expected that the calculated $L1_0$ -B2 phase boundaries could capture the EPMA data given that it really is the γ^* -B2 phase boundary. One sees the same story in Figure 13 (b) where the calculated isothermal section at 1428 K is in agreement with two-phase EPMA measurements by Gleeson et al. at 1423 K [14] and by Zhu et al. at 1433 K [15] except for the $L1_0$ -B2 phase region.

The 1523 K partial isothermal section shown in Figure 14 (a) indicates that the calculated phase boundaries are in reasonable agreement with EPMA measurements from Zhu et al. [15]. EPMA data from Zhu et al. [15] would suggest that the fcc+L12 phase region is actually growing wider as temperature increases despite the fact that it is shrinking rapidly in the Al-Ni binary. Such a contradictory result is non-intuitive and requires further experimental investigation. Figure 14 (b) shows that the calculated isothermal section is in accordance with the EDS measurements by Grushko et al. [16] with discrepancies again involving the $L10$ -B2 phase boundaries. It is expected that a model which captures the γ^* phase correctly, once enough experimental data is generated, should also improve the phase boundaries near the B2 phase.

Conclusions and suggestions for future work

This work presents a complete remodeling of the Al-Pt system. Calculated energies, especially in the Pt-rich section of the phase diagram are shown to agree well with experiments and DFT calculations. The B2 phase has been modified according to new results by Grushko [46]. Metastable phase diagrams are also presented to show the various ordered fcc phases that exist in the system. The 4SL binary Al-Pt model was converted to a 2SL model for ease of

integration into existing Ni-base superalloy databases. This 2SL Al-Pt model was then extrapolated into the Ni-rich portion of the Al-Ni-Pt system to determine its extrapolation characteristics as well as the parameterization required to obtain a reasonable assessment. Preliminary modeling of the fcc, $L1_0$, $L1_2$, and B2 phases indicate that the 2SL model presented here provides a reasonable assessment of the Ni-rich part of Al-Ni-Pt without the need of excessive ternary interaction parameters for the solution phases. Poor agreement was found for the phase boundaries involving $L1_0$ and B2 due to the presence of another superlattice phase, denoted γ^* , which orders from $L1_0$ near the B2 phase field.

The authors recommend the following to improve the assessment presented here:

- Additional experiments near the LT/HT-AlPt₃, B2 and LT/HT-AlPt₂, regions of the phase diagram to improve the understanding of their phase boundaries
- Phase stability studies to determine the LT phases for AlPt₂ and AlPt₃ and their possible martensitic characteristics
- Phase stability of γ^* and its relationship to Al₃Ni₅ near B2-(Ni,Pt)Al
- $L1_0$ - γ^* phase boundaries and if phase separation occurs at certain temperatures
- Introduction of the appropriate model (ordering from $L1_0$ or separate phase) for γ^*

The revised thermodynamic database is included in the supplemental document.

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Tables

Table 1: Compilation of experimental and theoretical studies involving the Al-Pt and Al-Ni-Pt systems from 1964 to the present.

References	Experimental or theoretical method	Comments
Al-Pt		
(1964) Huch & Klemm [58]	XRD	(Phase stability) Investigation of intermetallic phases, Al-Pt liquidus across entire composition
(1968) Ferro et al. [62]	Solution calorimetry	(Thermochemical) Heats of formation of intermetallics from 18-94 at. % Pt
(1970) Darling et al. [68]	XRD, EPMA	(Phase stability) Pt-AlPt ₃ phase equilibria, phase boundaries/compositions by EPMA
(1974) Tonejc et al. [75]	XRD	(Phase stability) Al-rich Al-Pt non-equilibrium alloys
(1975) Chattopadhyay & Schubert [70]	XRD	(Phase stability) Investigation of intermetallic phases for Pt-rich alloys; AlPt ₃ low and high temperature variants
(1975) Chatterji et al. [69]	XRD, EPMA	(Phase stability) Al-Pt alloys made from pack-aluminizing process; EPMA analysis of resulting layers
(1976) Chattopadhyay & Schubert [76]	XRD	(Phase stability) Low and high temperature variants of AlPt ₂
(1976) Guex & Feschotte [71]	XRD, EPMA	(Phase stability) Phase boundaries of Al-Pt intermetallics
(1977) Jackson & Rairden [13]	EPMA	(Phase stability) Pack aluminized Pt at 1060 °C for 3 hours indicates presence (detectable) of Pt, Al ₃ Pt ₂ , AlPt, AlPt ₂ and AlPt ₃
(1978) Bhan & Kudielka [72]	XRD	(Phase stability) High temperature XRD of arc-melted Al ₄₇ Pt ₅₃ sample from 1007 to 1340 °C
(1978) Schaller [51]	EMF	(Thermochemical) Al activity in Al-Pt alloys (0-35 at. % Al) were measured at 973-1073 K using CaF ₂ as a solid electrolyte
(1979) Schaller [73]	XRD, Magnetic analysis	(Phase stability) Determination of the range of Al in Pt solid solution at 1000 °C
(1980) Piatti & Pellegrini [77]	XRD	(Phase stability) Determination of the Al ₂₁ Pt ₅ phase and its related eutectic on the Al-Rich side of the phase diagram
(1981) Worrell & Ramanarayanan [63]	EMF	(Thermochemical) Gibbs energy of mixing of AlPt ₃
(1982) Ellner et al. [78]	XRD	(Phase stability, Thermochemical) Phase stabilities and lattice parameter changes as a function of composition; inclusion of

		enthalpies of formation for Al-Pt intermetallics
(1986) McAlister & Kahan [34]	Compilation	Compilation of all Al-Pt experimental data up to 1986
(1986) Colinet et al. [64]	Calorimetry	(Thermochemical) Partial enthalpy measurements in Al-Pt at very low Pt levels; prediction of full composition range based on surrounded atom model and compared to one set of Al-Pt liquid data
(1987) Oya et al. [35]	XRD, DTA, Dilatometry	(Phase stability) Detailed studies of the phase transformations of AlPt ₃ (LT) and AlPt ₃ (HT) at various temperatures
(1991) Jung et al. [36]	High temperature calorimetry	(Thermochemical) AlPt enthalpy of formation at 1473 K
(1993) Meschel & Kleppa [37]	XRD, Single unit differential microcalorimetry	(Thermochemical) AlPt ₃ and Al ₃ Pt ₂ enthalpy of formation at 1473 K
(1997) Kobayashi et al. [38]	XRD, EMF	(Thermochemical) Al activity in Al-Pt alloys with 35, 42, and 55 at. % Al using CaF ₂ as a solid electrolyte
(1998) Nanko et al. [39]	XRD, EPMA, EMF	(Phase stability, Thermochemical) Al activity in Al-Pt alloys with 4.6, 9.4, and 13.1 at. % Al using CaF ₂ as a solid electrolyte
(1999) de Waal & Pretorius [40]	NMP	(Phase stability) Phase stability in vacuum deposited Al-Pt diffusion couples; effective heat of formation model
(2005) Völkl et al. [41]	XRD, EPMA	(Phase stability) Phase stability of arc melted Al ₁₅ Pt ₈₅ samples heat treated at 1300 (96 hours) and 1500 °C (48 hours)
(2007) Douglas et al. [42]	EDS, HRTEM	(Phase stability) Phase stability of arc melted Al ₁₄ Pt ₈₆ samples heat treated 1350 °C (96 hours)
(2008) Tshawe [43] - Masters Thesis	EDS, XRD	(Phase stability) Phase stability studies of mostly Pt-rich compositions using arc melted samples heat treated for 1000 hours. Most samples heat treated between 1000 and 1400 °C. As-cast microstructures also characterized showing some weight loss in certain samples. Also included a detailed study of the LT and HT polymorphs of AlPt ₃
(2010) Chauke et al. [44]	F-P	(Phase stability, Thermochemical) Theoretical stability of AlPt ₃ polymorphs based on mechanical stability calculations; 0 K enthalpies of formation
(2011) Feng et al. [45]	F-P	(Thermochemical) Theoretical stabilities of Al-Pt intermetallics; 0 K enthalpies of formation
(2012) Grushko [46]	XRD, DTA	(Phase stability) Determination of stabilities of AlPt polymorphs using ternary alloys
(2013) Grushko et al. [47]	XRD, DTA	(Phase stability) Discovery of a new Al-rich intermetallic in Al-Pt around 25 at. % Al

Al-Ni-Pt		
(1994) Kamm & Milligan [18]	XRD, EPMA	(Phase stability) Arc melted alloys were heat treated at 1373 K for 7 days. Compositions spanned the AlNi ₃ to AlPt ₃ section to determine stabilities of L1 ₂ and L1 ₀ structures
(2004) Gleeson et al. [14]	XRD, EDS, EPMA, DTA	(Phase stability) Arc melted alloys were annealed at 1373 and 1423 K for at least one week to study phase stabilities across a range of Al-Ni-Pt compositions
(2005) Jiang et al. [21]	F-P	(Phase stability, Thermochemical) First-principles study of B2 in the Al-Ni-Pt system
(2005) Jiang et al. [22]	F-P	(Phase stability, Thermochemical) First-principles study of L1 ₀ and L1 ₂ phases in the Al-Ni-Pt system. Monte Carlo and SQS calculations were used to predict mixing behavior and transformation/disordering temperatures of L1 ₀ into L1 ₂
(2005) Copland [19]	KEMS	(Thermochemical) KEMS activity measurements of 2 Al-Ni and 2 Al-Ni-Pt B2 alloys in their solid states
(2007) Copland [20]	KEMS	(Thermochemical) KEMS activity measurements of 4 Ni-24Al-xPt and 4 Ni-27Al-xPt alloys in solid and liquid states
(2009) Lu et al. [11]	F-P	(Thermochemical) First-principles calculations of bcc- and fcc-based phases in the Al-Ni-Pt system including a CALPHAD assessment using the 4SL model for the fcc phase
(2010) Zhu et al. [15]	XRD, EPMA	(Phase stability) Arc melted Al-Ni-Pt alloys were annealed at 1433 K for 30 days and 1523 K for 30 days to study phase stabilities of fcc, L1 ₂ and B2. CALPHAD assessment was also performed using the 4SL CSA model for the fcc phase
(2011) Kim [23] Ph.D. Thesis	F-P	(Thermochemical) First-principles calculations of bcc- and fcc-based phases in the Al-Ni-Pt system including a CALPHAD assessment using the 4SL model for the fcc phase (chapter 5)
(2011) Grushko et al. [16]	XRD, EDS	(Phase stability) Induction melted Al-Ni-Pt alloys were annealed at 1373 K for 165 hours and at 1573 K for 90 hours to study phase stabilities across a range of ternary compositions. Ternary alloys were arc melted from previously melted Pt containing alloys with alloy mixtures due to the expense of Pt.
(2014) Grushko & Kapush [17]	XRD, EDS	(Phase stability) Induction melted Al-Ni-Pt alloys were annealed at 1063 K for 330 hours, 1173 K for 403 hours, 1273 K for 260 hours and 1373 K for 660 hours to study phase stabilities across a range of ternary compositions. Ternary alloys were arc melted from previously melted Pt containing alloys with alloy mixtures due to the expense of Pt.

DFT – Density Functional Theory

DTA – Differential Thermal Analysis

EDS – Energy-Dispersive X-ray Spectroscopy

EMF – Electro-Motive Force

EPMA – Electron Probe Micro-Analysis

F-P – First-principles

KEMS - Knudsen Effusion Mass Spectrometry

NMP – Nuclear microprobe

XRD – X-ray diffraction

Table 2 (Table 3 in the original publication [1]): Revised thermodynamic parameters of the Al-Pt system [J/mol atoms] with a 4SL fcc-based model.

Phase	Evaluated parameters	Reference
Liquid	${}^0L_{Al,Pt}^{liq} = -246324 - 0.506 \times T$	This work
	${}^1L_{Al,Pt}^{liq} = -61241 + 32.061 \times T$	This work
	${}^2L_{Al,Pt}^{liq} = +63347$	This work
fcc-A1 (disordered fcc)	${}^0L_{Al,Pt}^{fcc} = +ALPTG0 + 1.5 \times RECALPT + 4 \times UL0ALPT$	[26,28]
	${}^1L_{Al,Pt}^{fcc} = +ALPTG1 + 4 \times UL1ALPT$	[26,28]
	${}^2L_{Al,Pt}^{fcc} = +ALPTG2 - 1.5 \times RECALPT + 4 \times UL2ALPT$	[26,28]
L1 ₀ , L1 ₂ (ordered part of fcc)	$G_{Al:Al:Al:Pt}^{4SL} = \dots = G_{Pt:Al:Al:Al}^{4SL} = +AL3PT$	This work
	$G_{Al:Al:Pt:Pt}^{4SL} = \dots = G_{Pt:Pt:Al:Al}^{4SL} = +AL2PT2$	This work
	$G_{Pt:Pt:Pt:Al}^{4SL} = \dots = G_{Al:Pt:Pt:Pt}^{4SL} = +ALPT3$	This work
	${}^0L_{Al,Pt:*,*}^{4SL} = +UL0ALPT$	This work
	${}^1L_{Al,Pt:*,*}^{4SL} = +UL1ALPT$	This work
	$L_{Al,Pt:Al,Pt:*,*}^{4SL} = +RECALPT$	This work
	$ALPTG0 = +AL3PT + 1.5 \times AL2PT2 + ALPT3$	[26]
	$ALPTG1 = +2 \times AL3PT - 2 \times ALPT3$	[26]
	$ALPTG2 = +AL3PT - 1.5 \times AL2PT2 + ALPT3$	[26]
	$UALPT = -32900$	This work
	$RECALPT = UALPT$	This work
	$AL3PT = -43582 + 2.000 \times T$	This work
	$AL2PT2 = -93413 + 11.089 \times T$	This work
	$ALPT3 = -65861 + 7.013 \times T$	This work
	$UL0ALPT = +3820 + 2.032 \times T$	This work
	$UL1ALPT = +1069$	This work
bcc-A2 (disordered bcc)	$G_{Va:Va}^{A2} = 0.2 \times R \times T$	[31]
	${}^0L_{Al,Pt}^{bcc} = +B2ALPT + LB2ALPT$	This work
	${}^1L_{Al,Pt}^{bcc} = +L1A2ALPT$	This work
	${}^0L_{Al,Va}^{bcc} = B2ALVA + LB2ALVA$	[29]
	${}^0L_{Pt,Va}^{bcc} = B2APTA + LB2PTVA$	This work
B2 (ordered part of bcc)	$G_{Al:Pt}^{B2} = G_{Pt:Al}^{B2} = +0.5 \times B2ALPT - 0.5 \times LB2ALPT$	This work
	${}^0G_{Al:Va}^{B2} = {}^0G_{Va:Al}^{B2} = 0.5 \times B2ALVA - 0.5 \times LB2ALVA$	[29]
	${}^0G_{Pt:Va}^{B2} = {}^0G_{Va:Pt}^{B2} = 0.5 \times B2PTVA - 0.5 \times LB2PTVA$	This work
	$B2ALPT = -205828 + 23.000 \times T$	This work
	$LB2ALPT = -15000 - 25 \times T$	This work
	$L1A2ALPT = +25000$	This work
	$B2ALVA = +10000 - T$	[29]
	$LB2ALVA = +150000$	[29]
	$B2PTVA = B2ALVA - B2ALPT$ - same formulation as for Al-Ni	[29]
	$LB2PTVA = -51322 + 25 \times T$	This work
Intermetallic phases		

Al ₂₁ Pt ₅	$\frac{21}{26} {}^0G_{Al}^{fcc} + \frac{5}{26} {}^0G_{Pt}^{fcc} - 53729 + 7.894 \times T$	This work
Al ₂₁ Pt ₈	$\frac{21}{29} {}^0G_{Al}^{fcc} + \frac{8}{29} {}^0G_{Pt}^{fcc} - 81677 + 142.227 \times T - 24.4824018 * T * \ln(T) - .00180259094 * T ** 2 - 5.07905199E - 08 * T ** 3 + 73439.4837 * T ** (-1)$	This work
Al ₂ Pt	$\frac{2}{3} {}^0G_{Al}^{fcc} + \frac{1}{3} {}^0G_{Pt}^{fcc} - 94901 + 149.044 \times T - 25.3879657 * T * \ln(T) - 9.76971043E - 04 * T ** 2 - 1.24939625E - 07 * T ** 3 + 57838.2515 * T ** (-1)$	This work
Al ₃ Pt ₂	$\frac{3}{5} {}^0G_{Al}^{fcc} + \frac{2}{5} {}^0G_{Pt}^{fcc} - 104171 + 149.609 \times T - 25.5546046 * T * \ln(T) - 5.42160693E - 04 * T ** 2 - 1.70115474E - 07 * T ** 3 + 93033.608 * T ** (-1)$	This work
AlPt	$\frac{1}{2} {}^0G_{Al}^{fcc} + \frac{1}{2} {}^0G_{Pt}^{fcc} - 108753 + 150.500 \times T - 25.5681815 * T * \ln(T) - 6.07797546E - 04 * T ** 2 - 1.62526769E - 07 * T ** 3 + 80317.0116 * T ** (-1)$	This work
Al ₃ Pt ₅	$\frac{3}{8} {}^0G_{Al}^{fcc} + \frac{5}{8} {}^0G_{Pt}^{fcc} - 95922 + 144.916 \times T - 25.2063775 * T * \ln(T) - .00123884732 * T ** 2 - 1.57112248E - 07 * T ** 3 + 49147.617 * T ** (-1)$	This work
AlPt ₂	$\frac{1}{3} {}^0G_{Al}^{fcc} + \frac{2}{3} {}^0G_{Pt}^{fcc} - 91610 + 143.517 \times T - 25.1147341 * T * \ln(T) - .00118339103 * T ** 2 - 9.63850253E - 08 * T ** 3 + 47285.6272 * T ** (-1)$	This work

Table 3 (New table): Thermodynamic parameters of the Al-Ni-Pt system [J/mol atoms] with a 2SL fcc/L1₂ model. A set of constraints as implemented by Dupin et al. [30] are used to describe some of the following L1₂ parameters.

Phase	Evaluated parameters	Reference
Liquid	${}^0L_{Al,Ni,Pt}^{liq} = +25000$	This work
fcc-A1 (disordered fcc)	Al-Ni fcc binary interactions from Dupin et al. [30]	[30]
	Al-Pt fcc binary interactions taken from 4SL model shown in this work	This work
	Ni-Pt fcc binary interactions taken from Lu et al. [11]	[11]
	${}^0L_{Al,Ni,Pt}^{fcc} = +150219 - 102.276 \times T$	This work
L1 ₂ (ordered part of fcc) (Al,Ni) _{0.75} (Al,Ni) _{0.25}	$AL3PT = -40695 + 11.430 \times T$	This work
	$AL2PT2 = -92911 + 29.284 \times T$	This work
	$ALPT3 = -69052 + 11.430 \times T$	This work
	$L04ALPT = -7424$	This work
	$L14ALPT = +4617$	This work
	Al-Ni 2SL-L1 ₂ end-member and interaction parameter values from Dupin et al. [30]	[30]
	Ni-Pt 4SL order end-member values from Lu et al. [11] modified to 2SL model by using the following approximation after removal of SRO parameter $L_{Ni,Pt:Ni,Pt:*,*}^{4SL}$ $NI3PT = GNI3PT1 + 9 \times T$ $NI2PT2 = GNI2PT2 + 10 \times T$ $NIPT3 = GNI1PT3 + 9 \times T$	This work
	$U1ALNIPT = -10003 + 1.905 \times T$	This work
	$U2ALNIPT = +0$	This work
	$U3ALNIPT = +10754$	This work
bcc-A2 (disordered bcc)	Al-Ni bcc binary interactions from Dupin et al. [30]	[30]
	Al-Pt bcc binary interactions taken from current work	This work
	${}^0L_{Al,Ni,Pt}^{bcc} = -35.030 \times T$	This work
	${}^0L_{Ni,Pt}^{bcc} = +B2NIPT + LB2NIPT$	This work
B2 (ordered part of bcc)	$G_{Ni:Pt}^{B2} = G_{Pt:Ni}^{B2} = +0.5 \times B2NIPT - 0.5 \times LB2NIPT$	This work
	$B2NIPT = -22697 - 11.985 \times T$	This work
	$LB2NIPT = 0$	This work
L1 ₀ (separate phase) (Al,Ni,Pt) _{0.25} (Al,Ni,Pt) _{0.25} (Ni,Pt) _{0.5}	$G_{Ni:Ni:Ni}^{L10} = {}^0G_{Ni}^{fcc} + 0.5 \times T$	This work
	$G_{Pt:Pt:Pt}^{L10} = {}^0G_{Pt}^{fcc} + 0.5 \times T$	This work
	$G_{Al:Al:Ni}^{L10} = +0.5 {}^0G_{Al}^{fcc} + 0.5 {}^0G_{Ni}^{fcc} + GALNIL10$	This work
	$G_{Al:Ni:Ni}^{L10} = G_{Ni:Al:Ni}^{L10} = +0.25 {}^0G_{Al}^{fcc} + 0.75 {}^0G_{Ni}^{fcc} + ALNI3 + 2015 - 3 \times T$	This work
	$G_{Al:Al:Pt}^{L10} = +0.5 {}^0G_{Al}^{fcc} + 0.5 {}^0G_{Pt}^{fcc} + GALPTL10$	This work
	$G_{Al:Pt:Pt}^{L10} = G_{Pt:Al:Pt}^{L10} = +0.25 {}^0G_{Al}^{fcc} + 0.75 {}^0G_{Pt}^{fcc} + ALPT3 + 4118$	This work

	$G_{Ni:Ni:Pt}^{L10} = G_{Pt:Pt:Ni}^{L10} = +0.5^0G_{Ni}^{fcc} + 0.5^0G_{Pt}^{fcc} + \text{GNIPTL10}$	This work
	$G_{Pt:Ni:Ni}^{L10} = G_{Ni:Pt:Ni}^{L10} = +0.25^0G_{Pt}^{fcc} + 0.75^0G_{Ni}^{fcc} + \text{NI3PT} + 6014 - 6 \times T$	This work
	$G_{Ni:Pt:Pt}^{L10} = G_{Pt:Ni:Pt}^{L10} = +0.25^0G_{Ni}^{fcc} + 0.75^0G_{Pt}^{fcc} + \text{NIPT3} + 8834 - 6 \times T$	This work
	$G_{Al:Ni:Pt}^{L10} = G_{Ni:Al:Pt}^{L10} = +0.25^0G_{Al}^{fcc} + 0.25^0G_{Ni}^{fcc} + 0.5^0G_{Pt}^{fcc} + \text{GALNIPT2}$	This work
	$G_{Al:Pt:Ni}^{L10} = G_{Pt:Al:Ni}^{L10} = +0.25^0G_{Al}^{fcc} + 0.25^0G_{Pt}^{fcc} + 0.5^0G_{Ni}^{fcc} + \text{GALNI2PT}$	This work
	${}^0L_{Al:Ni:Al:Ni}^{L10} = {}^0L_{Al:Al:Ni:Ni}^{L10} = {}^0L_{Ni:Al:Ni:Ni}^{L10} = {}^0L_{Al:Ni:Ni:Ni}^{L10} = +1000$	This work
	${}^0L_{Pt:Ni:Pt:Ni}^{L10} = {}^0L_{Pt:Pt:Ni:Ni}^{L10} = {}^0L_{Ni:Pt:Ni:Ni}^{L10} = {}^0L_{Pt:Ni:Ni:Ni}^{L10} = +1000$	This work
	${}^0L_{Pt:Ni:Pt:Pt}^{L10} = {}^0L_{Pt:Pt:Pt:Ni}^{L10} = {}^0L_{Ni:Pt:Ni:Pt}^{L10} = {}^0L_{Pt:Ni:Ni:Pt}^{L10} = +1000$	This work
	${}^0L_{Ni:Ni:Ni:Pt}^{L10} = {}^0L_{Ni:Pt:Ni:Pt}^{L10} = {}^0L_{Pt:Ni:Ni:Pt}^{L10} = {}^0L_{Pt:Pt:Ni:Pt}^{L10} = +2000$	This work
	${}^0L_{Al:Al:Ni:Pt}^{L10} = {}^0L_{Al:Ni:Ni:Pt}^{L10} = {}^0L_{Ni:Al:Ni:Pt}^{L10} = {}^0L_{Al:Pt:Ni:Pt}^{L10} = {}^0L_{Pt:Al:Ni:Pt}^{L10} = +0$	This work
	$\text{GALNIL10} = -67000 + 11 \times T$	This work
	$\text{GALPTL10} = -92000 + 10 \times T$	This work
	$\text{GNIPTL10} = -14250$	This work
	$\text{GALNIPT2} = -66500 + 4.917 \times T$	This work
	$\text{GALNI2PT} = -56298 + 5.000 \times T$	This work
	Binary $L1_0$ end-member values ALNI3, ALPT3, NI3PT, and NIPT3 same as from 2SL-L1 ₂	This work
Intermetallic phases		
AlPt - (Al) _{0.5} (Ni,Pt) _{0.5}	$\frac{1}{2}^0G_{Al}^{fcc} + \frac{1}{2}^0G_{Ni}^{fcc} - 63481 + 9 \times T$	This work
	${}^0L_{Al:Ni:Pt}^{AlPt} = -4651$	This work

Figures

Figure 1 (Figure 6 in the previous publication [1]): Calculated erroneous phase (erroneous region marked in red dashed line) diagram of the Al–Pt system using the model parameters in the previous manuscript and experimental data (+) [58], ($\times$) [68], ($*$) [79], ($\triangle$, $\circ$, $\diamond$) [34].

Figure 2: The 4 fcc-based phases present in the current modeling of Al-Pt: disordered fcc-A1 (a), $L1_2$ (b), $L1_0$ (c), and $L6_0$ (d) with only two sites having the same fractions. Lattice sites with the same colors have the same compositions.

Figure 3: Enthalpies of mixing of (a) fcc-based and (b) bcc-based phases in the Al–Pt system with lines from the present CALPHAD modeling (4SL_AL_PT_2015.TDB) at 298 K and symbols from the first-principles calculations at 0 K [1]. The disordered and ordered phases have been plotted separately for both the fcc- and bcc-based phases. Symbols for SQS calculations: disordered state volume-only relaxed (■), disordered state fully relaxed (◆), ordered state volume-only relaxed (○), order-state fully relaxed (△). Fully ordered compounds ($L1_2$ -Al₃Pt, $L1_0$ -AlPt, $L1_2$ -AlPt₃, B2-AlPt) are shown with (▽). SQS calculations involving vacancies (Va) in B2 are shown with (◇). Note that pure Al in the B2-(high Va) structure is metastable with respect to the A2 state (itself metastable with respect to the stable phases of Al) and the enthalpy value resides above the 0-point, similar to the Al-Ni system [30].

Figure 4: (a) Calculated enthalpy of formation at 298 K as a function of Pt concentration in the Al-Pt system using the developed description (4SL_Al_PT_2015.TDB) along with measurements ($\boxtimes$) [62], (∇) [37], ($\circ$) [36], ($\diamond$) [80] from the literatures and first-principles results ($\bullet$) from the present work. (b) Enthalpy of mixing of the liquid phase at 1000 K from the present CALPHAD modeling (b, solid line) and the surrounded atom model by Colinet et al. [64] (dotted line)

Figure 5: (a) Gibbs energy of formation calculated at 973 K (solid line) using the developed description (4SL_AL_PT_2015.TDB) compared to EMF measurements by Schaller (○) [51]. (b) Activity of Al at 1000 K (left pane in b) and 673 K (right pane) compared to measurements by Nanko et al. (●) [39], and Kobayashi et al. (□) [38].

Figure 6: Calculated Al, Pt, and $L1_2$ -AlPt3 molar entropies (a, d, g), heat capacities (b, e, h), and enthalpies (c, f, i) from the current model (4SL_AL_PT_2015.TDB) compared to the predictions from the Debye-Grüneisen model ($\circ$, $\triangle$, $\diamond$).

Figure 7: (a) Calculated phase diagram of the Al–Pt system using the revised model (4SL_AL_PT_2015.TDB) with data from 1964-1975 [58,68–70]. (b) Calculated phase diagram of the Al–Pt system using the revised model (4SL_AL_PT_2015.TDB) with data from 1976-present [71] [72] [41–43,46,51,73]

Figure 8: Calculated metastable phase diagrams for the fcc-based (a) and bcc-based (b) phases showing the variety of ordered phases (Detailed in Figure 2) using the developed description (4SL_AL_PT_2015.TDB). Second order transitions are shown for both cases (dashed line). Note the presence of low Va and high Va B2 phases at low temperatures.

Figure 9: Calculated temperature-site fraction diagrams for AlPt-B2 (a), showing order and disorder of the phase using the developed description (4SL_AL_PT_2015.TDB). In (a), small vacancy fractions can be seen near the edge of the figure (zoomed inset). In (b), calculated defect concentrations in the B2 at 1300 K are shown: Vacancies on Pt sites (solid line), Pt on Al anti-site (dashed line), and Al on Pt anti-site (dotted line).

Figure 10: Enthalpies of mixing of A2 (dashed lines) and B2 (solid lines) phases in the Al-Ni-Pt system with lines from the present CALPHAD modeling (2SL_AL_NI_PT.TDB) at 298 K and symbols from the first-principles calculations at 0 K by Kim [23]. The AlNi-AlPt (a), AlPt-NiPt (b), and NiPt-AlNi (c) sections are shown here. The enthalpy of mixing for B2-NiPt ($\square$) comes from Jiang et al. [21]. For insets a, b, and c, reference states for Al, Ni, and Pt are bcc-A2 and symbols ($\triangle$) and ($\circ$) represent first-principles SQS calculations for the A2 and B2 phases, respectively. Calculated Al activities at four different compositions in B2 are shown in (d) and compared to KEMS measurements by Copland [19] from Al-Ni and Al-Ni-Pt alloys. In (d), symbols from experiments and lines from the current calculations are defined as Ni-47.2Al ($\circ$, dashed), Ni-47.5Al ($\square$, dotted), Ni-39.5Al-15.0Pt ($\triangle$, solid), and Ni-46.9Al-14.9Pt ($\diamond$, dot dashed).

Figure 11: Calculated Al activities at 4 different Al-Ni-Pt compositions using the developed description (2SL_AL_NI_PT_2015.TDB) compared to KEMS measurements of solid ($\triangle$) and liquid phases ($\circ$) by Copland [20] (a). In (a), lines from the current calculations are defined as Ni-24Al-2Pt (dotted), Ni-24Al-10Pt (dashed), Ni-24Al-18Pt (dot dashed), and Ni-24Al-25Pt (solid). For inset (b), calculated enthalpies of mixing in the AlNi_3 - AlPt_3 vertical section are plotted with first-principles calculations by Kim [23] shown in symbols. In (b), CALPHAD and first-principles results from Kim [23] are shown for fcc ($\triangle$, dashed), $L1_2$ ($\circ$, dot dashed) and $L1_0$ (solid) phases. Additional first-principles calculations by Jiang et al. [22] and Lu et al. [11] for the $L1_2$ ($\square$) and $L1_0$ ($\diamond, \nabla$) phases are also shown in (b).

Figure 12: Calculated stable (a) and metastable fcc-based (b) $\text{AlNi}_3\text{-AlPt}_3$ vertical sections using the developed description (2SL_AL_NI_PT_2015.TDB). Highest temperature solid ($\circ$) and lowest liquid ($\triangle$) points from Copland are shown for a series of Ni-24Al-xPt and Ni-27Al-xPt alloys [20]. L1_0 to L1_2 transition/disorder temperatures calculated from first-principles for the compositions $\text{L1}_0\text{-AlNi}_2\text{Pt}$ and $\text{L1}_0\text{-AlNiPt}_2$ by Jiang et al. [22] are shown with (*).

Figure 13 :Calculated partial isothermal section at 1373 K (a) using the developed description (2SL_AL_NI_PT_2015.TDB) together with two-phase EPMA measurements by Gleeson et al. [14] ($\triangle$) and EDS measurements by Grushko et al. [16] ($\circ$). Single- ($\square$) and two-phase alloys ($\diamond$) from Kamm & Milligan [18] are also included in (a). Calculated partial isothermal section (b) using the developed description (2SL_AL_NI_PT_2015.TDB) at 1428 K together with two-phase EPMA measurements by Gleeson et al. ($\circ$) at 1423 K [14] and by Zhu et al. at 1433 K ($\triangle$) [15].

Figure 14: Calculated partial isothermal section at 1523 K (a) using the developed description (2SL_AL_NI_PT_2015.TDB) with two-phase EPMA measurements by Zhu et al. [15] (○). Calculated partial isothermal section at 1573 K (b) using the developed description (2SL_AL_NI_PT_2015.TDB) together with two-phase EDS measurements by Grushko et al. [16] (○). Single- (□, ▽) and two-phase alloys (◇) from Copland [20] and Copland [19] are also included in (b).

Enthalpy of Mixing, kJ/mol

- Single phase
- △ Two phase
- + DTA
- × EPMA
- ⋈ EDS

1976 Guex & Feschotte

1978 Bhan & Kuidelka

1978/79 Schaller

2005 Volkl et al.

2007 Douglas et al.

2008 Tshawe

2012 Grushko (- -)

Figure(s)

(a) T=1373 K

(b) T=1428 K