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To cite this article: Libor Ďuriška *et al* 2017 *J. Phys.: Conf. Ser.* **809** 012008

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Contribution to thermodynamic description of Al-Pd system

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Abstract. The homogeneity range around the Al₃Pd stoichiometry, representing the family of quasicrystalline approximants denoted as ε_n and/or (Al₃Pd), was involved in the calculated Al-Pd phase diagram. The calculations were performed by means of the CALPHAD method using the Thermo-Calc software. A novel thermodynamic description of the ε_n /(Al₃Pd) phase was proposed based on the (Al%,Pd)₃(Al,Pd%)₁ two-sublattice model. Existing thermodynamic parameters of stoichiometric phases Al₄Pd and Al₂₁Pd₈ were slightly adjusted. The transition between phases ε_n /(Al₃Pd) and γ -Al₂₁Pd₈ was predicted thermodynamically at 619°C.

1. Introduction

The Al-Pd system has been studied several times so far. McAlister [1] published a provisional Al-Pd phase diagram with nine equilibrium intermediate phases in 1986. The diagram was later adopted by Massalski et al. [2]. In 2001, Yurechko et al. [3] published a revised phase diagram in the compositional range between 0 and 40 at.% Pd. The revised diagram comprises two high-temperature phases around the Al₃Pd stoichiometry. In 2003, Okamoto [4] published the phase diagram based on previous findings. The latest Al-Pd phase diagram has been published by Grushko [5], bringing new information about constitutions around both Al₃Pd and AlPd stoichiometries.

Considering previously published results, following phases have been referenced in the Al-Pd system [4,5]: (Al), λ -Al₄Pd, γ -Al₂₁Pd₈, ε_6 (\sim Al₃Pd), ε_{28} (\sim Al₃Pd), δ /(Al₃Pd₂), β /(AlPd), μ /(AlPd), ν /(Al₃Pd₅), ρ /(AlPd₂), τ /(Al₂Pd₅), and (Pd). In the thermodynamic notation, all the non-stoichiometric phases are placed between round brackets in this work, e.g. β /(AlPd). Quasicrystalline approximants ε_6 and ε_{28} belong to so-called ε -family subsuming five orthorhombic phases (ε_6 , ε_{16} , ε_{22} , ε_{28} , and ε_{34}) differing from each other in a lattice parameter. For the common denotation of at least two phases of the ε -family, the symbol ε_n [6] is used in this work. Although ε_6 and ε_{28} were found in Al-Pd alloys, an exact boundary between ε_6 - and ε_{28} -areas has not been determined in the corresponding phase diagram [3-5].

The Al-Pd system has been thermodynamically assessed by Li et al. [7]. All the experimental phase equilibria and thermodynamic data from the available literature have been evaluated using the CALPHAD method. Despite of a good coincidence between both calculated [7] and experimental phase diagrams [5], several differences are evident around stoichiometries Al₃Pd and AlPd-Al₃Pd₅. The ε_n area, occurring in the experimental phase diagram proposed by Grushko [5], is described by stoichiometric phases Al₃Pd and Al₂₁Pd₈ in the calculated phase diagram [7].



The main aim of this work is to use the CALPHAD method for the calculation of the high-temperature Al_3Pd as a non-stoichiometric $\varepsilon_n/(\text{Al}_3\text{Pd})$. Since the experimental results related to the distribution of ε_6 and ε_{28} in the ε_n area are not unambiguous yet, $\varepsilon_n/(\text{Al}_3\text{Pd})$ was considered in thermodynamic calculations as a non-stoichiometric “single phase”. At this stage, the optimization of the parameters using PARROT has not been done. Taking into account the differences between both calculated and experimental phase diagrams, the effort was paid to approach the shape of the ε_n area to that recently published by Grushko [5] by evaluation of the parameters of $\varepsilon_n/(\text{Al}_3\text{Pd})$ in the new thermodynamic model.

2. Thermodynamic model

Li et al. [7] described Al_3Pd as a stoichiometric phase. Since the experimental results published recently [3-5] confirmed the occurrence of ε_n with homogeneity range around the Al_3Pd stoichiometry, it is thermodynamically described by the two-sublattice $(\text{Al}\%,\text{Pd})_3(\text{Al},\text{Pd}\%)_1$ model in this paper (the symbol % denotes the major component in the corresponding sublattice). The Gibbs energy per mole of the formula unit (Al_3Pd) is given by the following expression:

$$G_m^{(\text{Al}_3\text{Pd})} - H_{(\text{Al}_3\text{Pd})}^{\text{SER}} = y_{\text{Al}}^{(1)} y_{\text{Al}}^{(2)} {}^0G_m^{\text{Al}_3\text{Al}} + y_{\text{Al}}^{(1)} y_{\text{Pd}}^{(2)} {}^0G_m^{\text{Al}_3\text{Pd}} + y_{\text{Pd}}^{(1)} y_{\text{Al}}^{(2)} {}^0G_m^{\text{Pd}_3\text{Al}} + y_{\text{Pd}}^{(1)} y_{\text{Pd}}^{(2)} {}^0G_m^{\text{Pd}_3\text{Pd}} + 3RT(y_{\text{Al}}^{(1)} \ln y_{\text{Al}}^{(1)} + y_{\text{Pd}}^{(1)} \ln y_{\text{Pd}}^{(1)}) + RT(y_{\text{Al}}^{(2)} \ln y_{\text{Al}}^{(2)} + y_{\text{Pd}}^{(2)} \ln y_{\text{Pd}}^{(2)}) + {}^{\text{ex}}G_m^{(\text{Al}_3\text{Pd})}, \quad (1)$$

where $H_{(\text{Al}_3\text{Pd})}^{\text{SER}}$ is equal to $(3y_{\text{Al}}^{(1)} + 1y_{\text{Al}}^{(2)})H_{\text{Al}}^{\text{SER}} + (3y_{\text{Pd}}^{(1)} + 1y_{\text{Pd}}^{(2)})H_{\text{Pd}}^{\text{SER}}$. Terms $y_i^{(1)}$ and $y_i^{(2)}$ represent site fractions of the component i ($i = \text{Al}, \text{Pd}$) in the first and the second sublattices, respectively. Terms ${}^0G_m^{\text{Al}_3\text{Al}}$, ${}^0G_m^{\text{Al}_3\text{Pd}}$, ${}^0G_m^{\text{Pd}_3\text{Al}}$, and ${}^0G_m^{\text{Pd}_3\text{Pd}}$ correspond to Gibbs energies of hypothetical stoichiometric compounds Al_3Al , Al_3Pd , Pd_3Al , and Pd_3Pd which are formed when each sublattice is occupied by one component only ($y_{\text{Al}}=1$ or $y_{\text{Pd}}=1$). They are modeled using formulas of Gibbs energy for stoichiometric compounds. The term ${}^{\text{ex}}G_m^{(\text{Al}_3\text{Pd})}$ is the excess Gibbs energy that can be expressed by formula:

$${}^{\text{ex}}G_m^{(\text{Al}_3\text{Pd})} = y_{\text{Al}}^{(1)} y_{\text{Pd}}^{(1)} (y_{\text{Al}}^{(2)} L_{\text{Al,Pd:Al}}^{(\text{Al}_3\text{Pd})} + y_{\text{Pd}}^{(2)} L_{\text{Al,Pd:Pd}}^{(\text{Al}_3\text{Pd})}) + y_{\text{Al}}^{(2)} y_{\text{Pd}}^{(2)} (y_{\text{Al}}^{(1)} L_{\text{Al:Al,Pd}}^{(\text{Al}_3\text{Pd})} + y_{\text{Pd}}^{(1)} L_{\text{Pd:Al,Pd}}^{(\text{Al}_3\text{Pd})}). \quad (2)$$

The symbol L in Equation (2) stands for interaction parameters, writable as:

$$L_{\text{Al,Pd:k}}^{(\text{Al}_3\text{Pd})} = \sum_{j=0} (a_j + b_j T) (y_{\text{Al}}^{(1)} - y_{\text{Pd}}^{(1)})^j, \quad (3)$$

$$L_{\text{k:Al,Pd}}^{(\text{Al}_3\text{Pd})} = \sum_{j=0} (a_j + b_j T) (y_{\text{Al}}^{(2)} - y_{\text{Pd}}^{(2)})^j, \quad (4)$$

where $L_{\text{Al,Pd:k}}$ and $L_{\text{k:Al,Pd}}$ correspond to the interaction parameters between Al and Pd in one sublattice, whereas the other sublattice is occupied by the element k only ($k = \text{Al}, \text{Pd}$). To reduce the number of optimizing variables, it can be assumed:

$$L_{\text{Al,Pd:Al}}^{(\text{Al}_3\text{Pd})} = L_{\text{Al,Pd:Pd}}^{(\text{Al}_3\text{Pd})}, \quad (5)$$

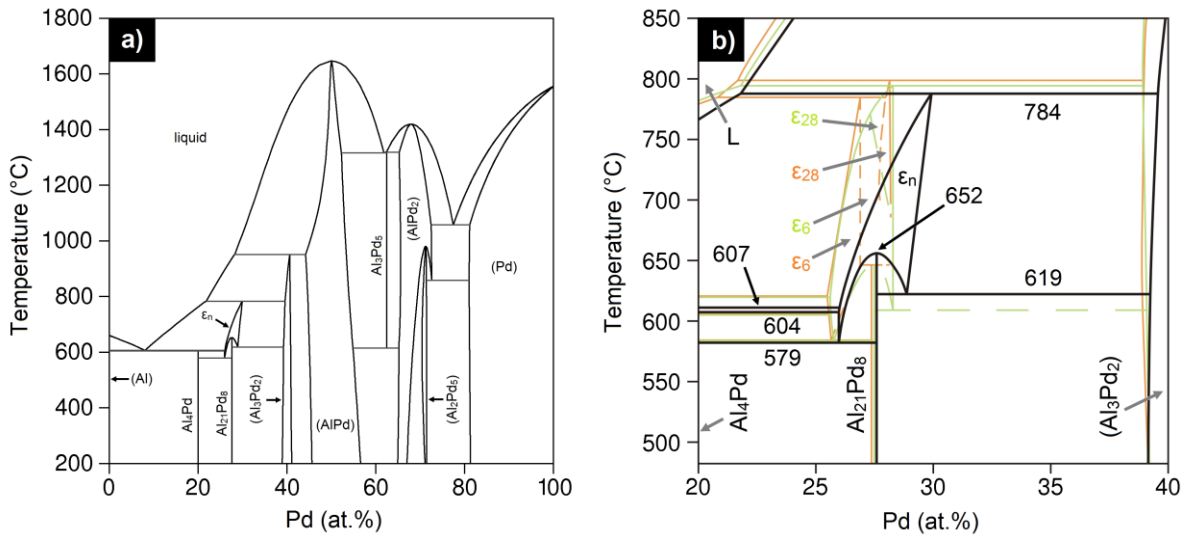
$$L_{\text{Al:Al,Pd}}^{(\text{Al}_3\text{Pd})} = L_{\text{Pd:Al,Pd}}^{(\text{Al}_3\text{Pd})}. \quad (6)$$

3. Results

Thermodynamic descriptions of phases $\varepsilon_n/(\text{Al}_3\text{Pd})$, $\lambda\text{-Al}_4\text{Pd}$, and $\gamma\text{-Al}_{21}\text{Pd}_8$ reflecting newly evaluated parameters are given in Table 1. In the calculations, thermodynamic parameters of remaining phases were taken from [7]. The phase diagram calculated subsequently by means of Thermo-Calc using modified parameters (Table 1) is shown in Figure 1a.

Table 1. Thermodynamic parameters of phases $\epsilon_n/(Al_3Pd)$, $\lambda-Al_4Pd$, and $\gamma-Al_{21}Pd_8$ evaluated in this work; energy terms are given in J/(mole of formula unit).

Phase	Thermodynamic model	Parameters
$\lambda-Al_4Pd$	$(Al)_4:(Pd)_1$	${}^0G_m^{Al_4Pd} = 4 {}^0G_{Al}^{fcc} + {}^0G_{Pd}^{fcc} - 170737.44 + 51.21T$
$\gamma-Al_{21}Pd_8$	$(Al)_{21}:(Pd)_8$	${}^0G_m^{Al_{21}Pd_8} = 21 {}^0G_{Al}^{fcc} + 8 {}^0G_{Pd}^{fcc} - 1246650.94 + 275.07T$
$\epsilon_n/(Al_3Pd)$	$(Al\%,Pd)_3(Al,Pd\%)_1$	${}^0G_m^{Al_3Al} = {}^0G_{Al:Al}^{(Al_3Pd)} = 4 {}^0G_{Al}^{fcc} + 100000$ ${}^0G_m^{Pd_3Pd} = {}^0G_{Pd:Pd}^{(Al_3Pd)} = 4 {}^0G_{Pd}^{fcc} + 41000$ ${}^0G_m^{Al_3Pd} = {}^0G_{Al:Pd}^{(Al_3Pd)} = 3 {}^0G_{Al}^{fcc} + {}^0G_{Pd}^{fcc} - 156506.48 + 35.41T$ ${}^0G_m^{Pd_3Al} = {}^0G_{Pd:Al}^{(Al_3Pd)} = {}^0G_{Al}^{fcc} + 3 {}^0G_{Pd}^{fcc} - 55000 + 20.0T$ $L_{Al,Pd:Al}^{(Al_3Pd)} = -486700 + 28.7T$ $L_{Al,Pd:Pd}^{(Al_3Pd)} = -486700 + 28.7T$ $L_{Al:Al,Pd}^{(Al_3Pd)} = -25000 + 140.0T$ $L_{Pd:Al,Pd}^{(Al_3Pd)} = -25000 + 140.0T$

**Figure 1.** Calculated Al-Pd phase diagram proposed in this work (a), detail view in vicinity of $\epsilon_n/(Al_3Pd)$ area (b). In view (b), dark wider lines represent diagram proposed in this work, finer lines distinguished in colour represent experimental diagrams published in [3] (light-orange) and [5] (light-green). Characteristic concentrations to invariant reactions are given in text. For interpretation of figure in colour, reader is referred to web-version of article.

4. Discussion

The currently available versions of the Al-Pd phase diagram in vicinity of the $\epsilon_n/(Al_3Pd)$ area (i.e. published in [3], [5], and proposed in this work) are graphically compared in Figure 1b. In compliance with the latest published experiments related to the $\epsilon_6+\epsilon_{28}$ area in the Al-Pd system [5], the single phase $\epsilon_n/(Al_3Pd)$ was thermodynamically described using the $(Al\%,Pd)_3(Al,Pd\%)_1$ two-sublattice thermodynamic model. In the calculated phase diagram shown in Figure 1, this phase occurs between 579°C and 784°C. The lower temperature limits of the $\epsilon_n/(Al_3Pd)$ occurrence are defined by eutectoid

points at 26.0 at.% Pd (579°C) and 28.9 at.% Pd (619°C), whereas the upper temperature limit is defined by the peritectic point at 29.9 at.% Pd (784°C). According to the earlier published results [3], the ε_{28} phase is formed by peritectic reaction, $L + \delta/(Al_3Pd_2) \leftrightarrow \varepsilon_{28}$, at 792°C and about 28.1 at.% Pd. In the present thermodynamic description, the peritectic point of the $\varepsilon_n/(Al_3Pd)$ formation is at about 29.9 at.% Pd (Figure 1). The lowest temperature limit of the $\varepsilon_n/(Al_3Pd)$ occurrence, 579°C, coincides with those previously experimentally determined [3] and calculated [7]. Between the calculated (784°C) and the earlier published (789°C [5]) upper temperature limits, there is the difference of 5°C only. The $\gamma-Al_{21}Pd_8$ phase was estimated to be stable up to 652°C. In the present work, the eutectoid reaction, $\varepsilon_n/(Al_3Pd) \leftrightarrow \gamma-Al_{21}Pd_8 + \delta/(Al_3Pd_2)$, was calculated at 619°C (Figure 1), whereas it was not predicted in the phase diagram calculated previously [7]. The $\lambda-Al_4Pd$ phase was calculated to be stable up to 604°C. However, thermodynamic parameters of it had to be slightly adjusted to reach the same formation temperature after involving the new thermodynamic model of $\varepsilon_n/(Al_3Pd)$ in the calculations. As a consequence, the temperature of eutectic reaction, $L \leftrightarrow (Al) + \varepsilon_n/(Al_3Pd)$, dropped to 607°C, Figure 1.

In the proposed calculated phase diagram, the peritectic point at 784°C, the eutectoid point at 619°C, and the eutectic point at 579°C are all shifted to higher Pd-concentrations in comparison to the experimental diagrams published in [3] and [5] (see Figure 1b). As a consequence the whole $\varepsilon_n/(Al_3Pd)$ -area is shifted to a bit higher Pd-concentrations as expected. Nevertheless, reasonable agreement was reached between the results of thermodynamic calculations and published experimental results.

5. Conclusions

The results obtained in a limited re-investigation of the Al-Pd system using CALPHAD method can be summarised as follows:

- $\varepsilon_n/(Al_3Pd)$ was firstly described as a non-stoichiometric phase reflecting the two-sublattice thermodynamic model $(Al\%,Pd)_3(Al,Pd\%)_1$,
- thermodynamic parameters of the (Al_3Pd) phase were evaluated,
- thermodynamic parameters of phases $\lambda-Al_4Pd$ and $\gamma-Al_{21}Pd_8$ were slightly adjusted,
- using the Thermo-Calc software, the Al-Pd phase diagram was re-calculated with respect to the newly involved (Al_3Pd) .

Acknowledgements

The authors wish to thank the European Regional Development Fund (ERDF) for financial support of the project ITMS:26220120014 “Center for Development and Application of Advanced Diagnostic Methods in Processing of Metallic and Non-metallic Materials” funded within the Research & Development Operational Programme, the Grant Agency VEGA for the financial support under contracts 1/0018/15 and 1/0811/14, the Slovak Research and Development Agency for the financial support under the contracts APVV-0076-11 and APVV-15-0049, and the Slovak University of Technology for the financial contribution from the grant scheme number 1352 for supporting young researchers.

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