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Vaporization thermodynamics of Pd-rich intermediate phases in the Pd–Yb system

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ABSTRACT

The vaporization thermodynamics of several intermediate phases in the Pd–Yb system was investigated by means of vaporization experiments performed under Knudsen conditions (KEML, Knudsen Effusion Mass Loss). The following thermal decomposition processes were studied in the overall temperature range 819–1240 K and their enthalpy changes determined: 4 PdYb(s) = Pd_4Yb_3(s) + Yb(g); 5/3 Pd_4Yb_3(s) = 4/3 Pd_5Yb_3(s) + Yb(g); 21/13 Pd_5Yb_3(s) = 5/13 $Pd_{21}Yb_{10}$(s) + Yb(g); 1/3 $Pd_{21}Yb_{10}$(s) = 21/9 Pd_3Yb(s) + Yb(g). Additional measurements were performed by KEMS (Knudsen Effusion Mass Spectrometry) on a Pd-rich two-phase sample, which allowed to detect both Yb(g) and Pd(g) in the vapor phase and to determine the atomization enthalpy of the Pd_3Yb phase (Pd-rich composition boundary, $Pd_{3.08}Yb_{0.92}$): $Pd_{3.08}Yb_{0.92}$(s) = 0.92 Yb(g) + 3.08 Pd(g). The enthalpy of formation of this compound was thereafter determined as -68 ± 2 kJ/mol at. and, by combining this value with the decomposition enthalpies derived by KEML, the enthalpies of formation of the studied Pd–Yb intermediate phases were evaluated (kJ/mol at.): -75 ± 4 ($Pd_{21}Yb_{10}$), -75 ± 3 (Pd_5Yb_3), -73 ± 3 (Pd_4Yb_3), and -66 ± 3 (PdYb). A modified version of the Pd–Yb phase diagram is also reported, re-drawn on the basis of literature data and of new experimental information recently become available.

1. Introduction

Ytterbium compounds display a number of interesting physical properties, in large part due to strong correlation between electrons and possible hybridization between *f*-type electrons with conduction band electrons [1,2]. While Yb atoms are divalent in the isolated atom state and in the pure bulk metal, with a filled, localized f^{14} shell, in solid state compounds *f* electrons can hybridize into conduction states, giving rise to intermediate or trivalent valence states [3]. For example, a temperature-independent valence of 2.8 was determined for the PdYb compound [4]. In this situation, physical phenomena such as heavy fermion, surface valence change, and unconventional magnetic and superconducting properties can be observed [1–5]. In particular, the first example of an Yb-based heavy fermion superconductor was reported in 2009 [6]. This finding further stimulated research on electronic and energetic properties of Yb intermetallics [7].

The phase relations and thermodynamic properties of Yb-based systems are far from being well assessed. In particular, energetic properties such as formation and atomization energies, which are directly related to valence behavior, are in large part unknown. In this paper, we give a contribution to the thermodynamic characterization of several intermediate phases in the Pd–Yb system by using two tensimetric techniques based on vaporization under Knudsen effusion conditions, namely the classic Knudsen Effusion Mass Loss (KEML) method and the Knudsen Effusion Mass Spectrometry (KEMS) one, which were used in the past by our group to investigate several Yb-containing binary phases [8–10].

The phase diagram of the Pd–Yb system assessed by Okamoto [11] contains 11 intermediate phases (Pd_7Yb, $Pd_{2.13}Yb$, Pd_2Yb, α- and β-$Pd_{1.63}Yb$, Pd_4Yb_3, α- and β-PdYb, α- and β-Pd_2Yb_5, $PdYb_3$). Most of these phases were characterized many years ago by Iandelli and Palenzona [12]. Very recently, two of the present authors characterized the phases indicated as $Pd_{1.63}Yb$ and $Pd_{2.13}Yb$ in Refs. [11,12], and ascertained their exact stoichiometry, which should now be more correctly indicated as Pd_5Yb_3 and $Pd_{21}Yb_{10}$, respectively [13,14]. The phase diagram updated according to the findings of Refs. [13,14] was re-drawn in Fig. 1 on the basis of the original

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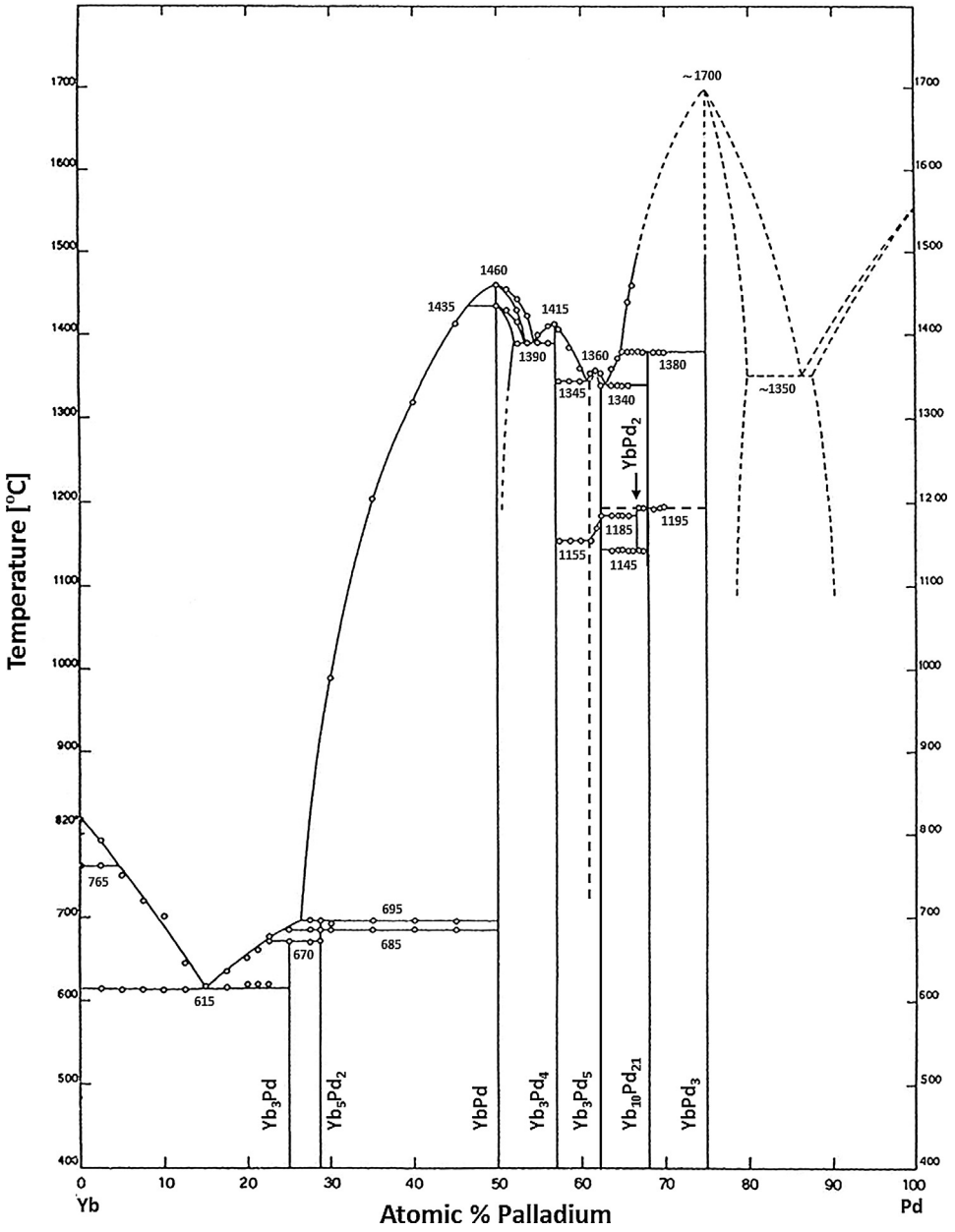

Fig. 1. Phase diagram of the Pd–Yb system, re-drawn on the basis of the experimental data of Ref. [12] (circles) taking into account the new stoichiometries of the $Pd_{1.63}Yb$ and $Pd_{2.13}Yb$ phases, recently reported as Pd_5Yb_3 and $Pd_{21}Yb_{10}$, respectively [13,14].

diagram of Ref. [12], whose experimental points are also reported in the figure.

With regard to thermodynamic data, to the best of our knowledge the only information available on this system is a semi-empirical estimate of the enthalpy of formation of the phase PdYb, −54 kJ/mol at. [15,16], derived by interpolating calorimetric values obtained for other PdRE (RE = rare earth) compounds and by taking into account the 4*f* promotion energy to the trivalent state of Yb. More generally, thermodynamic data for Yb compounds are much scarcer compared to other RE systems, in part owing to the high volatility of Yb. While representing a serious drawback for calorimetric measurements [17,18], high volatility makes Yb-based systems more suitable for tensimetric investigations.

In this work, we have studied the vaporization behavior and thermodynamics of the Pd–Yb intermediate phases in the Pd-rich part of the phase diagram. The decomposition enthalpies of the phases PdYb, Pd_4Yb_3, Pd_5Yb_3, and $Pd_{21}Yb_{10}$, and the atomization enthalpy of Pd_3Yb are presented. From the latter, the formation enthalpy of Pd_3Yb is derived, and, on this basis, an estimate of the formation enthalpies of the PdYb, Pd_4Yb_3, Pd_5Yb_3, and $Pd_{21}Yb_{10}$ phases is also proposed.

2. Experimental

The samples (total mass of 2.0–3.0 g) were prepared following a procedure reported elsewhere [19,20] from commercial high-purity elements [99.99 wt.% purity for Yb (distilled pieces) and 99.95 wt.% purity for Pd (powders or foil) from Smart Elements GmbH, Vienna, Austria] weighed in stoichiometric proportion. Alloys with Pd contents lower than 65 at.% Pd were prepared into outgassed Ta crucibles (sealed by arc welding) by reacting the metals compacted in form of a pellet (prepared by cold pressing Yb turnings and Pd powders) by high-frequency induction heating and melting. For alloys with Pd contents of 70 at.% Pd or higher,