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$Pd_2Cd_{11-\delta}$ ($0.21 \le \delta \le 0.51$)–a partly disordered γ-brass type phase and $Pd_{0.238}Cd_{0.762}$-a γ-brass related incommensurate phase in the palladium–cadmium system

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ABSTRACT

The Cd rich part of the Cd–Pd phase diagram was reassessed by means of synthesis and single crystal and powder X-ray diffraction. The region contains two phases that have been reported to have substantial compositional widths, $Cd_{11}Pd_2$ and Cd_4Pd. The phase $Cd_{11}Pd_2$ that has previously been reported to be a disordered γ-brass crystallizing is space group $P\bar{4}3m$ is here shown to crystallize in $I\bar{4}3m$ and the mechanism for compositional variation is explained. The phase Pd_4Cd has previously been shown to constitute a phase field or a phase bundle of modulated structures and here we determine the structure of a compound $Pd_{0.238}Cd_{0.762}$ which crystallizes in the orthorhombic superspace group $Fmmm(\alpha 00)0s0$ ($F=[(½, ½, 0, 0); (½, 0, ½, 0); (0, ½, ½, 0)]$ with the fundamental cell dimensions $a=4.687(2)$ Å, $b=10.000(1)$ Å, $c=14.140(2)$ Å, $q=0.6432(6)a^*$.

1. Introduction

Hume-Rothery deduced that for some compounds (now known as Hume-Rothery compounds), formation occurs at a specific valence electron concentration (vec) *i.e.* average number of valence electrons/atom [1,2,3]. In 1936, Mott and Jones give the first interpretation of this phenomenon in terms of the interaction between the Fermi surface of radius k_F and the Brillouin zone characterized by a reciprocal lattice vector based on the nearly free electron model [4,5]. A pseudogap occurs by the lowering of the kinetic energy of the valence electrons across the Fermi level and this plays a key role in stabilizing Hume-Rothery phases [4,6,7,8]. Among them, the γ-brass type phase had been implicitly assumed to be stabilized at $e/a=21/13$. Ekman studied the *TM*-Zn (*TM*=Ni, Pd, Pt)—phases and proposed that they obey the Hume-Rothery electron concentration rule with $e/a=1.60$, provided that the valency of the TM and zinc is zero and two, respectively [9]. Electron microscopy studies on Cu–Zn, Ni–Zn and Pd–Zn systems revealed that a slight variation of vec results in a structural modification of the γ-brass type or γ-brass related phases [10,11,12]. This finding suggests that γ-brass region of TM–Zn/TM–Cd may be much more complex than previously assumed [13] and this motivated us to reexamine the γ-brass region of the Pd–Cd system of which γ-brass type Pd_2Cd_{11} [14,15] and a set of γ-brass related orthorhombic phases were reported [16].

Pd_2Cd_{11} was initially reported to be a γ-brass type phase which crystallizes in the body center cubic space group $I\bar{4}3m$ with lattice parameter $a_\gamma=9.96$ Å [14]. A structural refinement was published by L. Arnberg who used a model in the space group $P\bar{4}3m$ (Table 1) [15]. In recent years Schmidt et al. [16] found that transition metal palladium–cadmium systems do not accommodate only the γ-brass type phase but also a closely related orthorhombic phase bundle or phase field. They reported structural models for two single crystal structures—$Pd_{0.213}Cd_{0.787}$ and $Pd_{0.235}Cd_{0.765}$ modeled as modulated composites in superspace group $Xmmm(00\gamma)s00$ with the cell dimensions $a=9.9013(28)$ Å, $b=14.0033(20)$ Å, $c1=2.8510(7)$ Å, $c2=4.6329(9)$ Å $q=(8/13)c^*$ and $a=9.9251(5)$ Å, $b=14.0212(7)$ Å, $c1=2.8635(2)$ Å, $c2=4.6293(3)$ Å, $q=(13/21)c^*$ corresponding to superstructures in the conventional three dimensional space groups *Ccme* and *F2mm*.

Against this background we reinvestigated the γ-brass region of the Pd–Cd binary system [17]. We present here structural models for γ-brass type $Pd_2Cd_{11-\delta}$ ($0.21 \le \delta \le 0.51$) an interval that includes that reported by Arnberg [15]. We also report an orthorhombic γ-brass related incommensurately modulated structure exists at slightly higher palladium content than that of the previously reported compounds $Pd_{0.213}Cd_{0.787}$ and $Pd_{0.235}Cd_{0.765}$.

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2. Material and methods

2.1. Synthesis and morphological features

The samples were synthesized starting from the pure elements: palladium (Alfa Aesar ≥ 99.995%) cadmium (ABCR, 99.999%) on a 300 mg scale. The metals were sealed in small, previously de-gassed fused silica ampoules (length: 3 cm, diameter: 0.8 cm) under a reduced argon pressure of about 0.5 Pa. The molar fraction x_{Pd} of the mixtures was systematically varied between 0.11 and 0.25. The ampoules were heated up to 973 K at a rate of 134.6 K h^{-1}, kept at this temperature for 12 h, then cooled down to 923 K during 400 h (0.125 K h^{-1}). Hereafter, the samples were cooled to room temperature during 12 h. Samples richer in cadmium contained excess cadmium in form of few tiny globules next to the binary phase.

2.2. XRD data collection and processing

Six distinct single crystals extracted from different loaded compositions were studied by means of single crystal X-ray diffraction. Suitable crystals of compounds were picked from the crushed sample, mounted on a glass fiber and diffraction intensities were measured with a four circle diffractometer (XCalibur) equipped with Mo$K\alpha$ radiation (λ=0.71073 Å) at room temperature 293 K. Data reduction was performed with an oxford diffraction Crysalis software. The structure solution and the refinement (Tables 2–4) were carried out using the JANA2006 program [18,19].

All the samples were examined by X-ray powder diffraction experiments to check the purity of single-phased samples, to determine the adjacent phases and to identify new phases. The powder diffraction data were collected by a STOE WinXPOW diffractometer (Cu$K\alpha$=1.5406 Å, 40 kV, 40 mA, Mythen 1 K detector). All the diffractograms were recorded between $5^\circ < 2\theta < 90^\circ$ at room temperature.

2.3. Energy dispersive X-ray analysis

The composition of selected specimens were examined in a scanning electron microscope (a JEOL 3000 with a secondary electron (SEI) detector) providing an energy dispersive X-ray spectrometer (EDS). EDS spectra were recorded from those samples which had been previously studied by single crystal X-ray diffraction experiments. No impurities of elements heavier than carbon were detected to be present in the selected specimens.

3. Results

3.1. Phase analysis

The homogeneity range and constitution of the cubic γ-brass type phase in the Pd–Cd system was examined by means of preparative methods, X-ray diffraction and EDS analyses.

Chemical composition determined by EDS and X-ray single crystal refinement shows a homogeneity range over $0.160 \le x_{Pd} \le 0.156$ i.e., from $Pd_2Cd_{10.49}$ to $Pd_2Cd_{10.79}$. The γ-brass type $Pd_2Cd_{11-\delta}$ coexists with a γ-brass related binary orthorhombic phase of approximate composition Pd Cd_4 at the palladium rich end. Experimental and calculated X-ray powder diffraction patterns of γ-brass type $Pd_2Cd_{10.79}$ over 2θ range 10°–90^o are shown in Fig. 1 together with those for $Pd_2Cd_{10.49}$, $Pd_2Cd_{10.72}$ and $Pd_2Cd_{10.79}$ over a 2θ range 10°–37^o. Progressive depletion of Cd is reflected in the modified intensities at the low angle diffraction intensities of the X-ray powder diffractograms of the γ-brass type $Pd_2Cd_{11-\delta}$ ($0.21 \le \delta \le 0.51$).

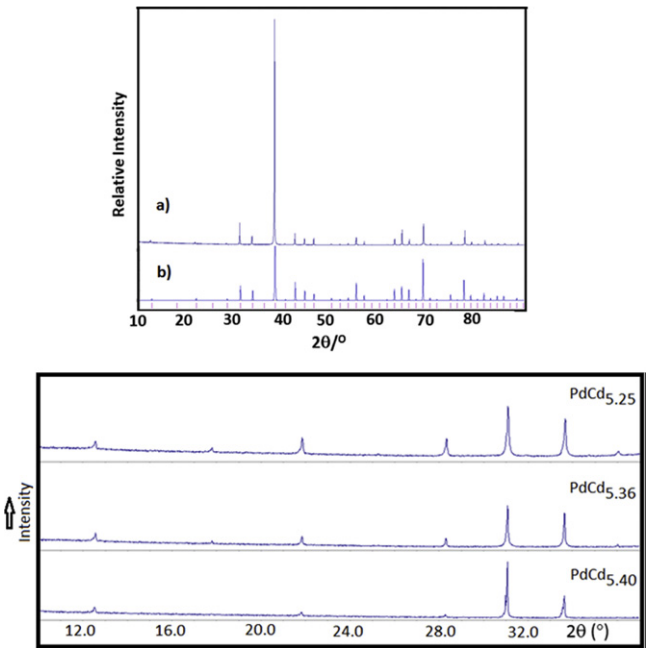

Fig. 1. (top) Experimental (a) and calculated (b) X-ray powder diffraction pattern of γ-brass type $Pd_2Cd_{10.79}$. Vertical bars indicate the corresponding Bragg positions. (bottom) X-ray powder diffraction patterns in the 2θ range 10°–37° observed for single phase samples $Pd_2Cd_{10.49}$, $Pd_2Cd_{10.72}$, $Pd_2Cd_{10.79}$.

Table 1
Refined structural data for $Pd_2Cd_{10.75}$ by Arnberg.

Cluster	Site			x	y	z	SOF	B [a] (Å^2)
1	Cd11	4e	IT	0.1048(9)	x	x	0.75	1.6(2)
	Pd12	4e	OT	−0.1734(6)	x	x	1	0.8(1)
	Cd13	6f	OH	0	0	0.3493(9)	0.184(18)	1.5(1)
	Cd14	12i	CO	0.3038(4)	x	0.0474(4)	1	1.1(5)
2	Cd21	4e	IT	0.6073(6)	x	x	1	1.3(1)
	Pd22	4e	OT	0.3292(5)	x	x	1	0.4(1)
	Cd23	6f	OH	½	½	0.8556(7)	1	0.7(1)
	Cd24	12i	CO	0.8076(4)	x	0.5448(5)	1	1.0(1)

[a] B=thermal parameters.

3.2. Refinement for $Pd_2Cd_{11-\delta}$

The intensity of the γ-brass type $Pd_2Cd_{11-\delta}$ could be indexed on the basis of a ~9.9 Å I-centered cubic unit cell. The structure was solved [18,19] in the space group $I\bar{4}3m$ (217).The structure solution yielded four atomic positions in the asymmetric unit. At this stage the structure refinement converged at $R(F) \approx 0.06$. Atomic sites displaying large thermal displacement parameters were checked for occupancy and positional disorder. The best fit to the data was achieved for a model where two of the original four positions where split. The occupation parameters of these occupationally disordered sites were refined independently. An isotopic extinction correction yielded $R(F)$ values between 0.018 and 0.038 at the final refinement.

3.3. Refinement for $Pd_{0.238}Cd_{0.762}$

Diffraction patterns of γ-brass related $Pd_{0.238}Cd_{0.762}$ display strong main reflections and additional satellite reflections typical for a modulated phase. The main reflections can be indexed in agreement with the orthorhombic space group *Fmmm* with the basic cell dimension: a=4.687(2) Å, b=10.000(1) Å, c=14.140(2) Å. The observed satellite reflections show a superstructure along the [100]