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Crystal structure of a solid solution in the Mg–Pd–Al system

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A search for new ternary palladium aluminides was carried out in the system Mg–Pd–Al. A new phase was observed in two alloys of nominal compositions $Mg_{7.1}Pd_{28.6}Al_{64.3}$ and $Mg_{11.1}Pd_{33.3}Al_{55.6}$; phase and structural analyses were performed based on X-ray powder diffraction data. A crystal structure corresponding to partial substitution of Mg in the binary compound Pd_8Al_{21} (Pt_8Al_{21}-type, Pearson symbol *tI*116, space group *I*4$_1$/*a*) was established. The approximate composition $Mg_5Pd_8Al_{16}$ was determined by energy-dispersive X-ray spectroscopy for the phase in the Mg-poor sample (a = 13.0429(2), c = 10.6880(1) Å) and it was assumed, based on geometrical arguments, that Mg atoms replace Al atoms in Wyckoff position 4*a* and one of the seven positions 16*f*. The phase in the Mg-rich sample (a = 13.1928(4), c = 10.6488(5) Å) was found to contain more Mg, indicating the existence of a solid solution. Compared to the binary compound Pd_8Al_{21}, the *a*-parameter is also larger but the *c*-parameter shorter, leading to an overall increase of the cell volume with increasing Mg content.

Ternary palladium aluminide / X-ray powder diffraction / Energy-dispersive X-ray spectroscopy / Crystal structure

Introduction

Seven ternary compounds have been reported in the {Mg,Ca,Sr,Ba}–Pd–Al systems [1,2]. The crystal structures of these aluminides belong to seven different structure types, among which five are defined on ternary compounds with alkaline-earth metals and three of them are own types (Table 1). Four structure types, Ca_2Ir_2Si, CaPdAl, Ca_2Pd_2Ge, and $Sr_2Pd_4Al_5$, are characterized by well-defined compositions and complete ordering of the atoms in the structures, whereas the compounds crystallizing with the other three structure types, $Li_{13}(Cu_{0.53}Si_{0.47})_{27}$, $Ca_2Pd_6Al_{10}$, and $LaFe_9Al_4$, exhibit partial Pd/Al atom disorder. The aim of the present work was to search for new ternary palladium aluminides with alkaline-earth metals, in particular with magnesium.

Experimental

Samples of nominal compositions $Mg_{7.1}Pd_{28.6}Al_{64.3}$ and $Mg_{11.1}Pd_{33.3}Al_{55.6}$ were synthesized from the elements (purity for Mg ≥ 99.4, Pd ≥ 99.99, Al ≥ 99.998 mass %) by arc melting in a water-cooled copper crucible with a tungsten electrode under a purified argon atmosphere (using Ti as a getter). The ingots were annealed at 400°C under vacuum in quartz ampoules for 1000 h and subsequently quenched in cold water.

The crystal structures of the phases were established by X-ray powder diffraction. The data were collected at room temperature on an automatic diffractometer STOE Stadi P (Cu $K\alpha_1$ radiation, λ = 1.5406 Å, in the angular range $5 \leq 2\theta \leq 110.615°$ with step 0.015° and scan time 320 s). The structural parameters were refined by the Rietveld method [10], using the program DBWS [11]. The elemental compositions of the phases in the sample with lower Mg content were determined by energy-dispersive X-ray spectroscopy on a scanning electron microscope REMMA-102-02. The structure drawings were made with the program ATOMS [12].

Results and discussion

The phase analysis of the alloys showed that the samples contained a phase with a structure related to the tetragonal Pt_8Al_{21}-type and the known binary compound Pd_2Al_3. The compositions of both phases were determined by EDX analysis (Fig. 1). Based on the X-ray diffraction data, the structural parameters of the new phase were refined.

Table 1 Crystallographic parameters of compounds reported in the {Mg,Ca,Sr,Ba}–Pd–Al systems.

Compound	Structure type	Pearson symbol	Space group	*a*, Å	*b*, Å	*c*, Å	Ref.
$Mg_{16}Pd_{4.4}Al_{19.6}$	$Li_{13}(Cu_{0.53}Si_{0.47})_{27}$	*cI*160	*Im*-3	14.245	–	–	[3]
Ca_2Pd_2Al	Ca_2Ir_2Si	*mS*20	*C*2/*c*	10.017	5.7669 β = 102.54°	7.7421	[4]
CaPdAl	CaPdAl	*oP*12	*Pbcm*	5.75	7.79	5.62	[5]
$Ca_2Pd_6Al_{10}$	$Ca_2Pd_6Al_{10}$	*hP*18	*P*6/*mmm*	9.373	–	4.248	[6]
Sr_2Pd_2Al	Ca_2Pd_2Ge	*oF*40	*Fdd*2	10.4145	15.5824	6.0437	[7]
$Sr_2Pd_4Al_5$	$Sr_2Pd_4Al_5$	*oP*44	*Pnma*	18.1449	4.3164	11.0247	[8]
$BaPd_{4.5}Al_{8.5}$	$LaFe_9Si_4$	*tI*56	*I*4/*mcm*	8.7259	–	12.4571	[9]

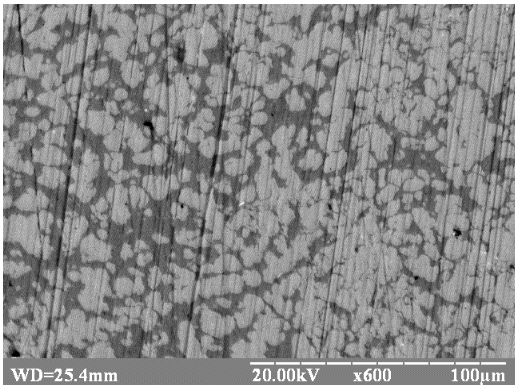


Fig. 1 Electron microscope photograph of the alloy $Mg_{7.1}Pd_{28.6}Al_{64.3}$: $Mg_{16.7}Pd_{27.3}Al_{56.0}$ ($Mg_5Pd_8Al_{16}$) – dark gray, $Pd_{39.7}Al_{60.3}$ (Pd_2Al_3) – light gray).

In the case of the alloy $Mg_{7.1}Pd_{28.6}Al_{64.3}$, the composition of the new phase, for which an ordered arrangement of atoms in the structure is proposed, can be described by the approximate formula $Mg_5Pd_8Al_{16}$, and in the case of the alloy $Mg_{11.1}Pd_{33.3}Al_{55.6}$, by the formula $Mg_{5+x}Pd_8Al_{16-x}$. The crystal structure of the ternary phase is a derivative of the Pt_8Al_{21}-type structure [13], with the same space group $I4_1/a$ and 116 atoms per unit cell. Comparing the unit-cell parameters of the binary compound Pd_8Al_{21} (a = 12.998, c = 10.729 Å, V = 1812.6 Å^3 [14]) with those of the ternary phase synthesized here (a = 13.0429(2), c = 10.6880(1) Å, V = 1818.19(4) Å^3 for the composition $Mg_5Pd_8Al_{16}$ and a = 13.1928(4), c = 10.6488(5) Å, V = 1853.42(12) Å^3 for the composition $Mg_{5+x}Pd_8Al_{16-x}$), we observe an increase of the *a*-parameter and a decrease of the *c*-parameter for the Mg-containing phase.

Experimental details and crystallographic data for the Rietveld refinement of the sample $Mg_{7.1}Pd_{28.6}Al_{64.3}$ are presented in Table 2. Atomic coordinates and isotropic displacement parameters for $Mg_5Pd_8Al_{16}$ are given in Table 3. A comparison of the experimental and calculated diffraction diagrams for the sample $Mg_{7.1}Pd_{28.6}Al_{64.3}$ is shown in Fig. 2.

Due to the similar atomic form factors of Mg and Al (12 and 13 electrons, respectively) the distribution of Mg and Al atoms on the different atom sites was made based on crystal chemical considerations. Hence, the larger, Mg atoms (atomic radii r_{Mg} = 1.60, r_{Al} = 1.43 Å [15]), were assumed to occupy the site in Wyckoff position 4*a*, for which the longest contact interatomic distances (2.674-2.863 Å) were observed, and one of the seven sites in Wyckoff position 16*f*, for which the highest coordination number was observed (15). For the Al atoms, the values of the shortest distances within the coordination polyhedra are: Al1 – 2.578, Al2 – 2.573, Al3 – 2.576, Al4 – 2.562 Å.

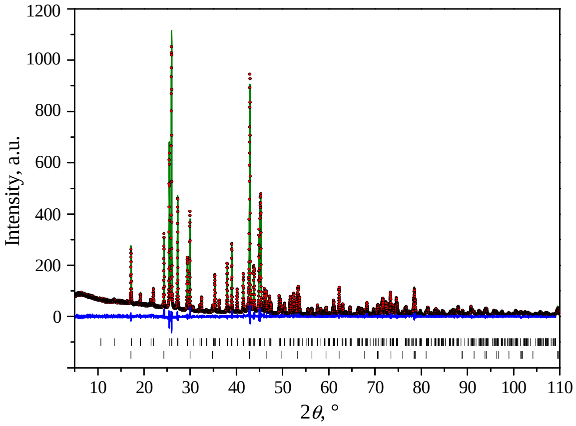


Fig. 2 Experimental, calculated and difference between experimental and calculated X-ray powder diffraction patterns (Cu $K\alpha_1$ radiation) for the sample $Mg_{7.1}Pd_{28.6}Al_{64.3}$. Vertical bars indicate the positions of the reflections of $Mg_5Pd_8Al_{16}$ and Pd_2Al_3.

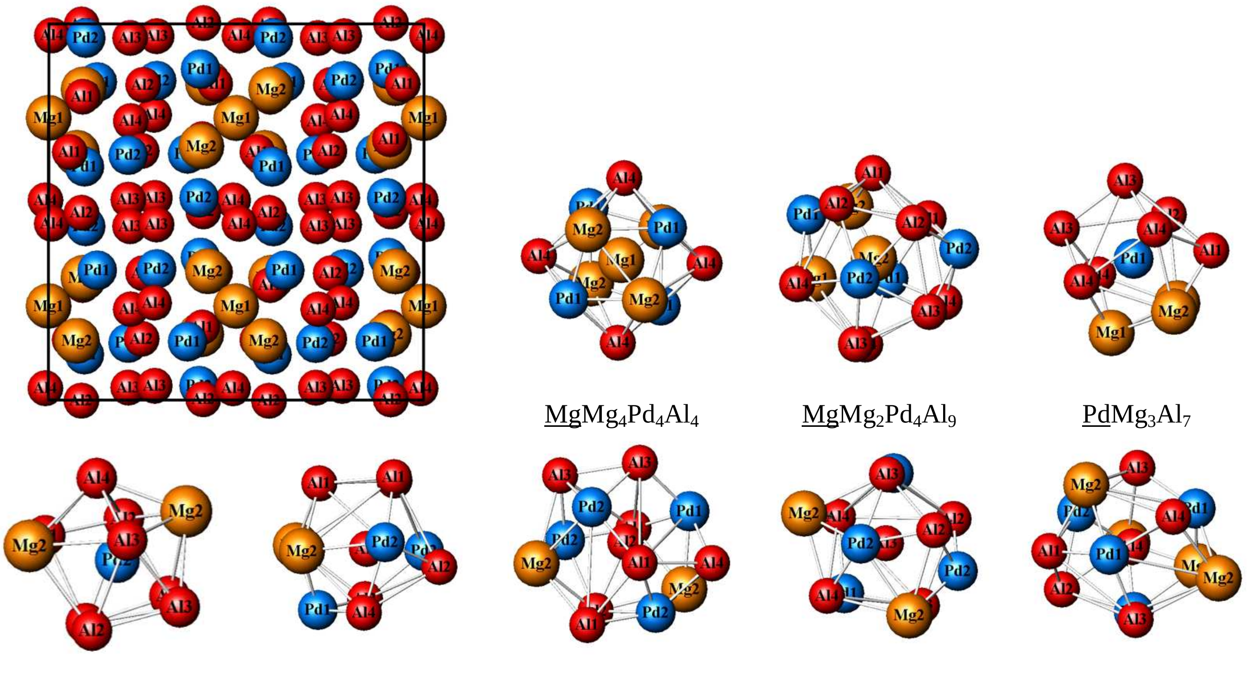
A projection of the unit cell of the structure of the new compound along the crystallographic direction [001], and the different coordination polyhedra, are presented in Fig. 3. The coordination polyhedra of the Mg atoms are icosahedra of composition $Mg_4Pd_4Al_4$ (site Mg1, Wyckoff position 4*a*) and 15-vertex Frank-Kasper polyhedra of composition $Mg_2Pd_4Al_9$ (Mg2, 16*f*). The Pd atoms are situated inside defective icosahedra of compositions Mg_3Al_7 (site Pd1) and Mg_2Al_8 (Pd2).

Table 2 Details of the Rietveld refinement of the sample $Mg_{7.1}Pd_{28.6}Al_{64.3}$.

Compound	$Mg_5Pd_8Al_{16}$ ($Mg_{17.2}Pd_{27.6}Al_{55.2}$)	Pd_2Al_3
Content, mass %	82.1(3)	17.9(4)
Structure type	$Mg_5Pd_8Al_{16}$	Ni_2Al_3
Space group	$I4_1/a$	$P\text{-}3m1$
Cell parameters a, c, Å	13.0429(2), 10.6880(1)	4.2196(1), 5.1517(1)
Cell volume V, Å^3	1818.19(4)	79.437(2)
Formula units per cell Z	4	1
Density D_X, g cm^{-3}	5.132	6.143
Texture parameter G [direction]	0.904(2) [001]	1.020(1) [001]
Number of reflections	699	69
Reliability factor R_B	0.0459	0.0557
FWHM parameters U, V, W	0.0339(6), 0.0094(3), 0.0089(1)	
Mixing parameter η	0.591(5)	
Asymmetry parameter C_M	-0.078(5)	
Number of refined parameters	38	
Reliability factors R_p, R_{wp}	0.0587, 0.0807	
Goodness of fit S	0.97(1)	

Table 3 Atom coordinates and isotropic displacement parameters for $Mg_5Pd_8Al_{16}$: *tI*116, $I4_1/a$, a = 13.0429(2), c = 10.6880(1) Å.

Site	Wyckoff position	x	y	z	B_{iso}, Å^2
Mg1	4*a*	0	¼	⅛	0.87(9)
Mg2	16*f*	0.4246(5)	0.1570(6)	0.1531(6)	
Pd1	16*f*	0.1296(1)	0.1546(2)	0.2800(1)	0.42(2)
Pd2	16*f*	0.0989(2)	0.5380(1)	0.3287(1)	
Al1	16*f*	0.0906(6)	0.1937(5)	0.5231(5)	1.02(6)
Al2	16*f*	0.0877(6)	0.0020(5)	0.4266(5)	
Al3	16*f*	0.2171(7)	0.0376(6)	0.0986(6)	
Al4	16*f*	0.0085(5)	0.0311(6)	0.1418(6)	



$\underline{Mg}Mg_4Pd_4Al_4$ $\underline{Mg}Mg_2Pd_4Al_9$ $\underline{Pd}Mg_3Al_7$

$\underline{Pd}Mg_2Al_8$ $\underline{Al}Mg_2Pd_3Al_6$ $\underline{Al}Mg_2Pd_4Al_7$ $\underline{Al}Mg_2Pd_4Al_6$ $\underline{Al}Mg_4Pd_4Al_5$

Fig. 3 Projection of the structure of $Mg_5Pd_8Al_{16}$ along [001] and coordination polyhedra.

The Al atoms from the site Al3 are located inside icosahedra of composition $Mg_2Pd_4Al_6$, whereas the Al atoms from the site Al1 center defective icosahedra of the composition $Mg_2Pd_3Al_6$. The polyhedra surrounding the Al atoms from the two other sites, Al2 and Al4, have 13 vertices and can be considered as pseudo Frank-Kasper coordination polyhedra of compositions $Mg_2Pd_4Al_7$ and $Mg_4Pd_4Al_5$, respectively.

The structure of the compound $Mg_5Pd_8Al_{16}$ is an ordered ternary derivative of the binary structure type Pt_8Al_{21}. Another ordered ternary derivative of the Pt_8Al_{21}-type is the $Pd_8Al_{17}Si_4$ structure [16], where the Si atoms occupy the position of Al1, which is characterized by the smallest coordination number.

As mentioned above, the only compound reported previously in the Mg–Pd–Al system, $Mg_{16}Pd_{4.4}Al_{19.6}$, crystallizes with a structure for which partial disorder Pd/Al was found, whereas the other sites were occupied exclusively by Mg atoms [3]. In the solid solution studied here, the Pd atoms were found to occupy two of the atom sites at all compositions, whereas preferential substitution of Mg for Al on certain atom sites is proposed for $Mg_5Pd_8Al_{16}$. Partial Mg/Al disorder is expected to occur within the homogeneity range of the solid solution. Both statistical mixtures Pd/Al and Mg/Al are well known in the literature [1].

Conclusions

A ternary phase of approximate composition $Mg_{5+x}Pd_8Al_{16-x}$, crystallizing with the structure type Pt_8Al_{21}, was identified in the ternary system Mg–Pd–Al at 400°C. The substitution of Al atoms by slightly larger Mg atoms is accompanied by an increase of the volume of the unit cell, however, the cell parameters change anisotropically (a increases, c decreases). For the composition $Mg_5Pd_8Al_{16}$, an ordered structure model is propose, in which the Mg atoms occupy the sites with the longest contact distances and the largest coordination number. Further investigation of the phase diagram of the Mg–Pd–Al system is needed to establish the extension of the solid solution and the existence, or absence, of a two-phase region between Pd_8Al_{21} and $Mg_5Pd_8Al_{16}$.

Acknowledgements

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