Crystal structure of dimagnesium monopalladium, Mg_2Pd

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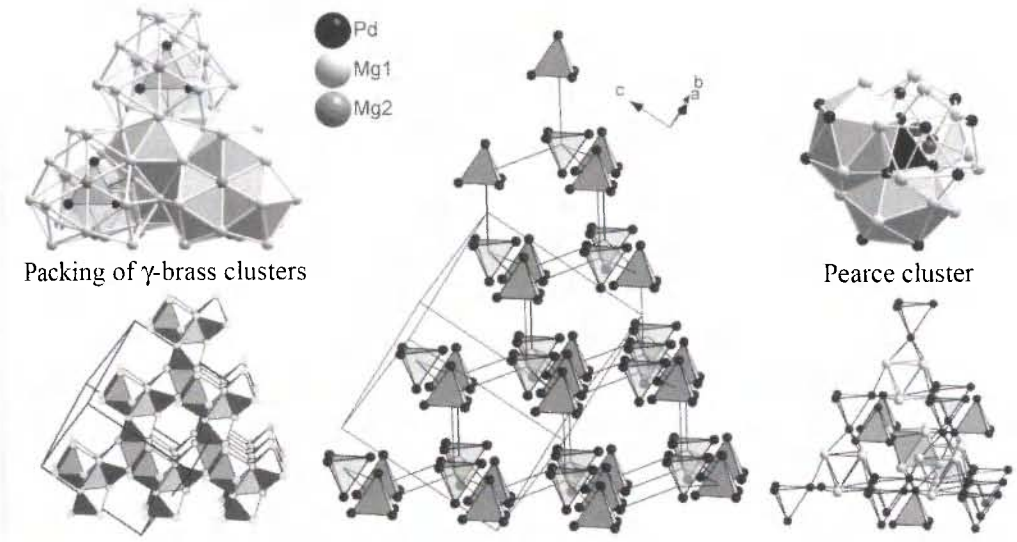

Abstract

Mg_2Pd, cubic, $Fd\bar{3}m$ (no. 227), a = 12.0535(4) Å, V = 1751.2 Å^3, Z = 32, $R_{gt}(F)$ = 0.015, $wR_{ref}(F^2)$ = 0.032, T = 293 K.

Source of material

A single crystal of the title compound with metallic lustre was obtained from a sample with Mg_2Pd as the majority phase (> 98 %) containing traces of Mg_5Pd_2 and MgPd. The alloy was prepared by induction melting a mixture of the elements (Mg, 99.99 %; Pd, 99.99 %) in stoichiometric amounts in argon filled and weld-sealed tantalum ampoules. For the following heat treatment at 923(5) K for 3 weeks the metal ampoule was encapsulated in a fused silica tube. Finally, the ampoule was quenched in water. Chemical analyses on impurities of O, N, C, H and Ta were carried out using the carrier gas hot extraction, the combustion technique and ICP-MS spectroscopy, respectively. All impurities were below the respective limit of detection (O < 750 ppm, N < 150 ppm, C < 1000 ppm, H < 60 ppm, Ta < 250 ppm). The number of phases has been obtained from a microscopic examination in combination with an EDXS analysis of the microstructure.

Experimental details

The unit cell parameters were determined from the least-squares refinements of the 2θ values of 30 reflections in the range $12° < 2\theta < 85°$ taken from a Guinier powder pattern (Huber G670, Ge monochromator, Cu $K\alpha_1$ radiation, λ = 1.540593 Å, Si powder SRM 640c as internal standard, a = 5.431195 Å). Alloys at the nominal composition 69 at-% Mg and 65 at-% Mg, which were subjected to the same heat treatment, contain Mg_5Pd_2 + Mg_2Pd (a = 12.0543(8) Å) and Mg_2Pd (a = 12.0529(5) A) + MgPd, respectively. According to DTA measurements, X-ray powder diffraction and metallographic examination Mg_2Pd undergoes a peritectoid reaction at 954(3) K into Mg_5Pd_2 and MgPd and shows no perceptible homogeneity range.

Discussion

The title compound is a complex metallic alloy phase with 96 atoms in the face-centred cubic unit cell. Its crystal structure is isotypic to $NiTi_2$ [1,2]. The Pd atoms (Pd1 at 32*e*) are surrounded icosahedrally with 3 Pd at 3.1228(6) Å and 9 Mg atoms with distances ranging from 2.6721(2) Å to 3.022(1) Å. The coordination polyhedron of Mg at 48*f* (Mg1) is a pentagonal prism of 10 Mg atoms, which is polarly and equatorially bi-capped by 4 Pd atoms. The interatomic distances Mg1—Mg and Mg1—Pd extend from 3.052(1) Å to 3.303(2) Å and from 2.7336(4) Å to 3.022(1) Å, respectively. The atomic environment type of Mg at 16*c* (Mg2) is a distorted icosahedron with 6 Pd at 2.6721(1) Å and 6 Mg at 3.052(1) Å. The crystal structure is conveniently described as a space-filling arrangement of γ-brass clusters and octahedra. The γ-brass cluster (26 atoms) is formed by 4 interpenetrating icosahedra centred by Pd atoms. The latter Pd atoms shape a Pd_4 tetrahedron capped above all faces by Mg2 atoms, i.e., Pd and Mg forming together a tetraederstern. The γ-brass clusters are centred at the positions of a diamond net building up an open framework with each cluster connected to four clusters of inverse orientation. Two neighboring clusters share six triangular faces. Additionally, each γ-brass cluster is vertex connected to twelve next-nearest clusters via common Mg1 atoms. The remaining space is filled by a framework of Mg1 octahedra, which is known as a

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pyrochlore packing [3]. Here, neighboring Mg_6 octahedra share common faces. The four icosahedra surrounding the Mg2 atoms of a tetraederstern are in face contact with the Pd_4 tetrahedron and with each other. This configuration is known as a Pearce cluster [4] or as augmented γ-brass cluster (38 atoms). A complementary description of the crystal structure is discussed in [5] in terms of the *I*3 cluster concept, which is based on a cluster of three vertex-connected icosahedra and a small set of connection rules. For a detailed description see [5]. In case of Mg_2Pd the icosahedra of the *I*3 clusters are centred by Pd with Mg1 as common vertices and Mg2 at the centre of bridge icosahedra, connecting different *I*3 clusters.

Table 1. Data collection and handling.

Crystal:	silver, irregular, size 0.025 x 0.060 x 0.070 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	85.70 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, ω/φ
$2\theta_{max}$:	64.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4577, 176
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 173
$N(param)_{refined}$:	11
Programs:	SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg(1)	48*f*	0.4313(1)	⅛	⅛	0.0149(7)	0.0115(4)	U_{22}	0	0	0.0015(5)
Pd(1)	32*e*	0.21660(2)	*x*	*x*	0.0119(1)	U_{11}	U_{11}	−0.00011(7)	U_{12}	U_{12}
Mg(2)	16*c*	0	0	0	0.0120(5)	U_{11}	U_{11}	0.0011(5)	U_{12}	U_{12}

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References

1. Duwez, P.; Taylor, J. L.: The Structure of Intermediate Phases in Alloys of Titanium with Iron, Cobalt, and Nickel. Trans. AIME **188** (1950) 1173-1176.
2. Nevitt, M. V.: Miscellaneous Structures of Fixed Stoichiometry. In: Intermetallic Compounds (Ed. J. H. Westbrook), p. 217-299. Wiley, New York 1967.
3. Hyde, B., Andersson, S.: Inorganic Crystal Structures, Wiley, New York 1989.
4. Pearce, P.: Structure in Nature is a Strategy for Design. MIT Press, Cambridge 1978.
5. Kreiner, G.; Franzen, H. F.: A new cluster concept and its application to quasi-crystals of the i-AlMnSi family and closely related crystalline structures. J. Alloys Compd. **221** (1995) 15-36.
6. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
7. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact GbR, Bonn, Germany 1998.