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A case study of complex metallic alloy phases: Structure and disorder phenomena of Mg-Pd compounds

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In order to achieve a deeper insight into the relation between the homogeneity range, crystal structure and disorder phenomena of complex metallic alloy phases (CMAs) we have re-determined the Mg-Pd phase diagram in the range 60 to 100 at-% Mg. The existence of the intermediate phases Mg_6Pd (β), $\text{Mg}_{57}\text{Pd}_{13}$ (γ), $\text{Mg}_{56.4}\text{Pd}_{13.5}$ (δ), $\text{Mg}_{306}\text{Pd}_{77}$ (ϵ), $\text{Mg}_{78.5}\text{Pd}_{21.5}$ (ζ), Mg_3Pd (η), Mg_5Pd_2 (θ) and Mg_2Pd (ι) has been reconfirmed. The first five of them are CMA's. The β -phase melts congruently whereas the CMAs γ , δ , ϵ and ζ form in a cascade of peritectoid and peritectic reactions in a narrow window of approx. 30 °C and 3 at-%. It is assumed that the stability of the Mackay icosahedron plays an important role in the phase formation of these CMA's. However, the β -phase reveals an intricate pattern of disorder at the atomic positions of the Mackay icosahedron (MI). Therefore, the concept of the stability of the Mackay cluster should be used only as a rule of thumb.

1. Introduction

Complexity in the sense of giant unit cells and inherent structural disorder is one of the most pronounced features of complex metallic alloy phases (CMAs). Prominent examples of CMAs are approximant phases of icosahedral quasicrystals with the Mackay cluster as fundamental structural unit. Recently, we reported on the synthesis and crystal structure of Mg-rich complex alloys in the binary Mg-Pd system [1]: Mg_6Pd (β), $\text{Mg}_{57}\text{Pd}_{13}$ (γ), $\text{Mg}_{56.4}\text{Pd}_{13.5}$ (δ), $\text{Mg}_{306}\text{Pd}_{77}$ (ϵ), $\text{Mg}_{78.5}\text{Pd}_{21.5}$ (ζ), Mg_3Pd (η), Mg_5Pd_2 (θ) and Mg_2Pd (ι). The first five intermetallic compounds are CMAs of the Mackay cluster type with giant unit cells containing several hundred atoms. In order to achieve a deeper insight into the relation between the homogeneity range, crystal structure and disorder phenomena in the CMAs we have determined the extent of the single-phase fields for the above listed phases by chemical, metallographic, thermal and X-ray powder and single crystal analyses. The current results of a re-determination of the Mg-rich part of the phase diagram are presented. For Mg_6Pd the origin of the homogeneity range is discussed in more detail.

2. Experimental

Samples of the nominal composition $\text{Mg}_x\text{Pd}_{1-x}$ with $0.6 \leq x < 1$ in steps of approx. 0.01 were prepared by induction melting mixtures of the elements (Pd, 99.99%; Mg, 99.99%) in argon filled and weld-sealed tantalum ampoules. Subsequently, the ampoules were encapsulated in

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fused silica tubes and annealed several weeks at appropriate temperatures. Finally, the ampoules were quenched in water.

Chemical analyses on impurities of O, N, C, H and Ta were carried out using carrier gas hot extraction, the combustion technique and ICP-MS spectroscopy, respectively. All impurities were below their respective limit of detection. The microstructures of the samples were analyzed via microscopic examination in combination with EDXS to determine the number of phases and their compositions. For single phase materials, the Mg and Pd content was analyzed by atomic emission spectrometry with plasma excitation (ICP-OES). The deviations between the nominal and the experimental determined compositions were smaller than 0.1 at-%.

The unit cell parameters of the phases were obtained from least-squares fits of Guinier powder data with $\text{CuK}\alpha_1$ radiation and internal calibration. X-ray powder diffraction patterns for Rietveld refinements were collected on a diffractometer in Bragg-Brentano geometry and single crystal data on a CCD diffractometer with $\text{MoK}\alpha$ radiation. DTA and DSC measurements were carried out to determine the liquidus and the solidus curves as well as the temperatures of the invariant reactions with the samples weld-sealed in Nb crucibles under dry argon.

Figure 1. The Mg-rich part (44 – 100 at-% Mg) of the Mg-Pd phase diagram according to data of this study; only data points obtained from thermal analysis measurements are shown in the graph; question marks and dashed lines indicate unresolved problems; phase labels are located in the Pd-rich two-phase fields.

Figure 2. Mg_6Pd : a) Concentric shell structure of the MI. b) Packing of the MIs with interpenetrating and pentagonal face-sharing MIs. c) Arrangement of the remaining space-filling polyhedra at the nodes of a diamond net.

3. Results

The revised Mg-rich part of the phase diagram is shown in figure 1. Mg_6Pd (β) has the highest Mg content of all intermediate phases in the Mg-Pd system with a range of homogeneity extending from 87.4(1) to 85.0(1) at-% Mg at 530(5) °C. Mg_6Pd melts congruently at 571(3) °C and forms eutectic alloys with Mg (α) at 91.5(5) at-% Mg and $\text{Mg}_{56.4}\text{Pd}_{13.5}$ (δ) at 83(1) at-% Mg. The eutectic temperatures are 539(3) °C and 559(3) °C, respectively.

Close to 80 at-% Mg the CMAs γ , δ , ϵ and ζ were observed. $\text{Mg}_{57}\text{Pd}_{13}$ (γ) crystallizes with no perceptible homogeneity range at 81.4(1) at-% Mg. The γ -phase undergoes a peritectoid ($\beta + \delta = \gamma$) and a eutectoid ($\gamma = \beta + \epsilon$) reaction at 554(3) °C and 534(5) °C, respectively. $\text{Mg}_{56.4}\text{Pd}_{13.5}$ (δ) forms peritectically ($L + \epsilon = \delta$) at 562(3) °C and 80.7(3) at-% Mg with a small homogeneity range of about 0.3 at-%. Presently, sufficient data to define the δ phase boundaries at lower temperatures are not available. $\text{Mg}_{306}\text{Pd}_{77}$ (ϵ), forms peritectically at 565(3) °C ($L + \zeta = \epsilon$) with no perceptible homogeneity range at 79.9(1) at-% Mg. Finally, the ζ -phase extends from 78.8(2) to 78.3(2) at-% Mg at 500(5) °C and undergoes a peritectic reaction at 580(3) °C ($L + \eta = \zeta$). Due to its unknown crystal structure a crystallographic formula can not be assigned. However, a preliminary study supports that the crystal structure of the ζ -phase is built up from Mackay clusters.

η , θ and ι are no CMA's. Mg_3Pd (η) crystallizes with no perceptible homogeneity range at 75.0(1) at-% Mg and forms in a peritectic reaction ($L + \theta = \eta$) at 625(3) °C. Mg_5Pd_2 (θ) exhibits a small homogeneity range extending from 72.7(1) to 71.4(1) at-% Mg at 500(5) °C. Mg_5Pd_2 melts congruently at 697(3) °C and forms an eutectic alloy with MgPd (κ) at approx. 68(2) at-% Mg and at 690(3) °C. Finally, Mg_2Pd (ι) crystallizes with no perceptible homogeneity range at 66.7(1) at-% Mg and undergoes a peritectoid reaction ($\theta + \kappa = \iota$) at 681(3) °C.

To study the origin of the homogeneity range of Mg_6Pd including disorder phenomena, its crystal structure has been investigated in more detail. Mg_6Pd crystallizes [2] with a large face-centred cubic unit cell in the space group $F-43m$. The unit cell parameter a decreases linearly from 20.1985(6) Å at the Mg-rich limit to 20.045(5) Å at the Pd-rich limit.

Figure 3. Point defects in the crystal structure of Mg_6Pd : a) Four inner icosahedra of pentagonal face-sharing MIs form a truncated tetrahedron with Mg1 at the vertices, Mg10 at the centre and M1 capping the four hexagons; for clarity two icosahedra are omitted. b) Isosurfaces of the electron density ($4 \text{ e}/\text{\AA}^3$) at M1 and Mg10 for Mg_6Pd at 87.4 at-%, 86.7 at-% and 85.0 at-% Mg obtained from X-ray single crystal structure refinements. c-e) Selected polyhedra in the crystal structure of Mg_6Pd at the Pd-rich limit (top row) and Mg-rich limit (bottom row). c) Z16 Frank-Kasper polyhedron and Mg_4 stuffed truncated tetrahedron. d) Coordination type polyhedra of M1a and M1b. e) modified and nearly perfect MI.

The crystal structure is conveniently described as an arrangement of interpenetrating and pentagonal face-sharing distorted Mackay icosahedra (MI) as shown in figure 2b. The concentric shells of the MI are shown in figure 2a neglecting any kind of disorder: 12 Mg at the vertices of the inner icosahedron with Pd at the centre, 30 Mg at the vertices of the icosidodecahedron and 6 Mg plus 6 Pd at vertices of the outer icosahedron. The large voids of the MI packing are filled by polyhedra bounded by 24 Mg atoms. The polyhedra are arranged at the positions of a diamond net as shown in figure 2c. Half of the polyhedra contain tetrahedral units of face-sharing PdMg_{12} icosahedra. This building block is commonly known as a Pearce cluster. The remaining space-filling polyhedra contain tetrahedral units of four PdMg_9 tri-capped trigonal prisms.

Four of the 14 crystallographic sites of Mg_6Pd are influenced by disorder. The positions of the defect sites M1, Mg1, Mg5, and Mg10 are shown in figure 3a. Here, the inner icosahedra of four MIs form a truncated tetrahedron with Mg1 at the vertices. For clarity two of the icosahedra as well as all surrounding icosidodecahedral shells are omitted. The

truncated tetrahedron is occupied at the centre by Mg10 and its hexagon faces are capped by M1. Mg5 is located at the vertices of the inner icosahedra adjacent to Mg1.

Isosurfaces obtained from X-ray single crystal structure refinements of the electron density at M1 and Mg10 for Mg₆Pd at 87.4 at-%, 86.7 at-% and 85.0 at-% Mg are shown in figure 3b. At the Mg-rich limit the M1 site reveals an electron density distribution corresponding to an atomic split position. M1a is occupied by Pd or Mg and M1b by Mg. The following restraints for the site occupancy factors (s.o.f.) of M1a, M1b and Mg10 have been introduced in the refinement to avoid non-physical short interatomic distances: $\text{s.o.f.}(\text{Pd@M1a}) + \text{s.o.f.}(\text{Mg@M1a}) + \text{s.o.f.}(\text{Mg@M1b}) = 1$ and $\text{s.o.f.}(\text{Mg@M1b}) + \text{s.o.f.}(\text{Mg10}) = 1$. A higher Pd content in Mg₆Pd increases and reduces the observed electron densities at M1a and M1b, respectively. At the Pd-rich phase limit the density at M1b disappears. However, the density at Mg10 increases until the position is fully occupied by Mg. Constitutional vacancies appear simultaneously at the Mg1 site in combination with a large anisotropic displacement of Mg5.

An interpretation of the observed electron density at the defect sites of Mg₆Pd is as follows. At the Pd-rich phase boundary the atomic environment of Mg10 is a Frank-Kasper Z16 coordination type polyhedron with maximal two vacancies at the Mg1 positions as shown in figure 3c. The centre of the Z16 is fully occupied by Mg whereas the hexagon caps are randomly mixed occupied by Pd and Mg. The M1 site is maximal surrounded by 13 Mg atoms (figure 3d). In case of Pd at M1 a vacancy in the neighbourhood yields the coordination number 12. The displacement of Mg5 shortens the interatomic distances between Pd and three Mg5 atoms. A vacancy at Mg1 creates a truncated inner icosahedron whereas the icosidodecahedral shell is modified by inserting a Mg10 atom slightly above a triangular face as shown in figure 3e.

Part of the excess Mg in the crystal structure of Mg₆Pd occupies the M1a site. The higher percentage of Mg at M1a minimizes the number of vacancies at Mg1 and the number of displaced Mg5 atoms. However, some of the excess Mg occupies the additional M1b site. In that case an occupation of the neighbouring M1a and Mg10 is **due to short non-physical** interatomic distances forbidden. Here, the most likely scenario is a simultaneous occupation of the four M1b positions by Mg per truncated tetrahedron. The truncated tetrahedron forms with the Mg₄ tetrahedron together a structural unit which is e.g. part of the crystal structure of *hcp*-Mg. Moreover, the icosidodecahedral shells of the surrounding MIs are then nearly perfect. The coordination type polyhedron of Mg at M1b is an anti-cuboctahedron formed by 12 Mg atoms. From a geometrical point of view the occupation of Mg at M1b seems to be the “natural decoration” for Mg₆Pd resulting in the formula Mg₄₃Pd₆ ($Z = 8$, 87.8 at-% Mg). However, in the crystal structure of Mg-rich Mg₆Pd about 1/3 of the truncated tetrahedra are decorated with Mg₄ tetrahedra and the remaining 2/3 with (Pd_xMg_{1-x})₄Mg units similar as found in the crystal structure at the Pd-rich limit.

4. Conclusion

The re-determination of the Mg-rich part of the Mg-Pd phase diagram reconfirmed the existence of the intermediate phases β , γ , δ , ϵ , ζ , η , θ , and ι . Close to 80 at-% Mg the CMAs γ , δ , ϵ and ζ form in a cascade of peritectoid and peritectic reactions in a small range of temperature (~ 30 °C) and composition (~ 3 at-%). It is to assume that the stability of the fundamental structural unit, i.e. the Mackay cluster, plays an important role in the phase formation. From the crystal structures and the narrow regions of homogeneity of Mg₅₇Pd₁₃ (γ), Mg_{56.4}Pd_{13.5} (δ), and Mg₃₀₆Pd₇₇ (ϵ) it can be shown that a small variation of about 1 at-% in the Mg concentration yields a much higher percentage of variation in the “glue atoms” region inducing a rearrangement of the cluster packing. From this point of view an

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3 accumulation of CMA's of nearly equal composition is understandable. However, the results
4 of the origin of the homogeneity range of Mg_6Pd advice caution. Here, the Mackay cluster
5 shows an extremely high degree of disorder. Therefore, the stability of the Mackay cluster
6 should be used only as a rule of thumb. Due to the many degrees of freedom for CMA's,
7 extrapolations even for such a tiny homogeneity range of 2.4 at-% as found in Mg_6Pd are not
8 allowed.
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