X-Ray Determination of the Structure of the Cubic Gamma

Pd,Zn Phase

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The body-centered cubic gamma-brass like phase in the Pd—Zn system has a structure which is based on a Ni_4Zn_{22} type of ordering, with Pd in the outer tetrahedral position. The solid solubility of Pd in the phase appears to depend on substitution of Pd for Zn in the octahedral position in the structure.

Hansen[1] reports the somewhat discrepant results of two phase analysis investigations[2,3] of the palladium-zinc system. The reports agree upon the existence of two different gamma brass like phases in the system. One of these, γ, is cubic[4,5] and is homogeneous in the range $15—\sim19$ atomic % palladium. The other phase, γ', has a lower crystallographic symmetry, probably orthorhombic. Its range of homogeneity is $\sim20—24$ atomic % Pd.

According to Nowotny et al.,[3] the cubic γ phase decomposes peritectically at about 700°C into γ' and liquidus. Köster and Zwicker[2] maintain that γ is stable up to 880°C, where it melts congruently, and that it is homogeneous over the whole $15—24$ atomic % Pd range at about 780°C. Below this temperature, Pd rich γ is represented as transforming into γ'.

No investigation of the structures (i.e. the ordering of Pd and Zn atoms on different crystallographic sites) has been reported in the literature. The present article is concerned with the cubic structure of the γ phase.

EXPERIMENTAL

Weighed amounts of palladium (sponge, Matthey Spectrographically Standardized) and zinc (granular, Mallinkrodt Analytical Reagent) were heated together in sealed, evacuated capsules at $\sim950°C$ (above the melting point of γ) for two days. The capsules were quenched in water and the product examined. The reactions were considered to be satisfactorily completed when the resulting alloy pellets could be easily and completely crushed.

The pellets had lost weight to some extent with respect to the weighed-in starting materials. If the whole weight loss is attributed to zinc evaporation, the composition

of each sample changed approximately one atomic % during the reaction. The compositions reported in this article are based on that assumption.

The alloy samples were subsequently heat-treated at $650 \pm 10°C$ for two weeks. Each sample was enclosed in a sealed evacuated silica tube. No weight loss occurred in the process.

Density measurements were performed by weighing of the alloy specimens in air and in $CHCl_3$.

X-Ray powder diffraction photographs were taken with a Guinier-Hägg type focusing camera of 80 mm diameter, using monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å) and KCl ($a = 6.2919$ Å) as an internal standard.

Single crystal X-ray data were collected with a Weissenberg camera ($CuK\alpha$ radiation) employing the multiple film technique. The diffracted intensities were estimated visually by comparison with an intensity scale obtained from a similar alloy crystal (Γ-Ni,Zn; the different designations, γ and Γ, are used as they occur in the earliest publications concerning these phases. This is also the system adopted by Hansen [1]). The 254 diffracted intensities measured in this fashion were put on a common scale by intercomparison of equivalent reflexions from different layer line photographs after application of Lorentz and polarization corrections. No absorption correction was attempted, since the crystal was a tiny, fairly irregular fragment (diameter $\sim$0.02 mm). The scaling procedure [6] was carried out with the computer program KUSK written for the present problem, and produced a list of 48 independent structure factors.

Atomic scattering factor tables and dispersion corrections were taken from Cromer and Waber,[7] and Cromer,[8] respectively.

Seven-cycle, block-diagonal least squares refinements of the several structure models investigated were carried out with a modified version of the program SFLS (world list [9] No. 6023). In the final refinements, the weights (Cruickshank's weighting scheme) of the observed structure factors, F_o, were calculated as:

$$w = (40 + |F_o| + 0.04 \ |F_o|^2)^{-1}$$

which yielded a very level weight analysis.

All the computing was carried out on the IBM 1800 computer located at this Institute.

RESULTS AND INTERPRETATIONS

In the Pd,Zn alloy samples quenched from the reaction temperature $\sim$950°C, single phase cubic gamma was observed at the two compositions 18.0 and 20.0 atomic % Pd. Only one of the samples heat-treated at 650°C consisted exclusively of γ, namely the one containing 18.0 atomic % Pd. This finding appears to substantiate the description of the phase relationships advanced by Köster and Zwicker.[2]

The crystal used in the single-crystal X-ray investigation was picked from the 18.0 % Pd sample which had been heat-treated at 650°C. The measured lattice parameter of this sample was:

$$a = 9.1022 \pm 2 \ \text{Å}$$

The number of atoms per unit cell, derived from the observed density and composition of the sample was: $Z = 51.8$. Assuming $Z = 52$, one has:

$$d_{obs} = 8.30 \pm 2 \ \text{g cm}^{-3}; \quad d_{calc} = 8.33 \ \text{g cm}^{-3}$$

Both single crystal and powder X-ray data showed the structure to be body centered cubic. Thus, a description of the structure in space group $I\bar{4}3m$ (No. 217), in analogy with, e.g., Γ-Ni,Zn,[10] was attempted.
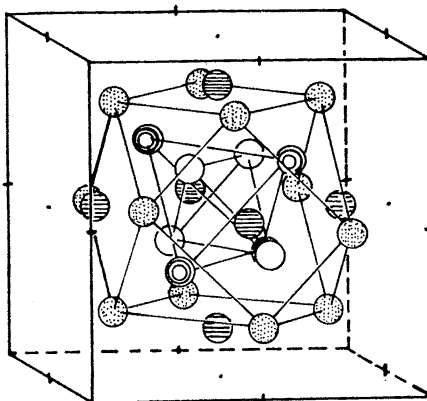
○	= IT	0.10	0.10	0.10
◎	= OT	-0.17	-0.17	-0.17
⊜	= OH	0.35	0	0
⊛	= CO	0.30	0.30	0.05

Fig. 1. Atomic sites in cluster A, around the origin. IT=inner tetrahedral, OT= outer tetrahedral, OH=octahedral, and CO=cubo-octahedral position.

Gamma-brass like structures, in general, may be described in terms of an Inner Tetrahedral (IT), an Outer Tetrahedral (OT), an OctaHedral (OH) and a Cubo-Octahedral (CO) position, centered around the origin of the unit cell and repeated at the body center (see Fig. 1):

IT	8(c)	xxx	etc.	$x \approx 0.10$
OT	8(c)	xxx	etc.	$x \approx -0.17$
OH	12(b)	x00	etc.	$x \approx 0.35$
CO	24(g)	xxz	etc.	$x \approx 0.30 \quad z \approx 0.05$

At first, a structure model containing Zn at all the crystallographic positions enumerated above, was refined. The refinement converged to:

$$R = 100 \cdot \sum ||F_o| - |F_c||/\sum |F_o| = 15 \%$$

A relatively very low temperature factor, $B=0.2$ Å^2, of the OT position indicated that this was the most probable location of the palladium atoms. The next refinement, of a structure model with Pd placed accordingly, converged to $R=7.6 \%$, and the marked discrepancies between $|F_o|$ and $|F_c|$, which occurred at low diffraction angles for the previous model, disappeared. Also, B_{OT} was raised to 2.4 Å^2, which was equal to the average value of the individual B's.

The structure thus arrived at is of the Ni_4Zn_{22} type.[10] A Pd_4Zn_{22} phase should, however, contain about 15 atomic % Pd and have the density $d_{calc}=8.25$ g cm^{-3}. These values correspond to the lower solubility limit for Pd in the phase. In this respect, too, γ-Pd,Zn appears to be analogous to

Ni_4Zn_{22}. The upper solubility limit reported is $\sim$19 atomic % Pd [2,3] (Pd_4Zn_{21}) at 650°C and $\sim$24 % Pd [2] (Pd_6Zn_{20}) at 800°C.

A variation in the composition of the phase might be due either to a subtraction of Zn or to a substitution of Pd for Zn (or, conceivably, both). It is very unlikely that a significant part of the solubility depends upon a subtraction mechanism, however, since the density determination clearly indicates that the number of atoms in the unit cell is $Z=52$. Nevertheless, several non-stoichiometric structure models with Zn vacancies were tested for correspondence between observed and calculated structure factors.

From the refinement of the Pd_4Zn_{22} (Ni_4Zn_{22} type) structure model ($R=7.6$ %), the following individual temperature factor values were obtained:

$$B_{Zn,IT} = 3.2 \text{ Å}^2 \qquad B_{Pd,OT} = 2.4 \text{ Å}^2$$
$$B_{Zn,OH} = 1.3 \text{ Å}^2 \qquad B_{Zn,CO} = 2.3 \text{ Å}^2$$

An improved model, then, is likely to contain less Zn in the IT position or to have Pd substituted for Zn in the OH position. A systematic exploration of these possibilities yielded the following results:

The refinement of a Pd_4Zn_{21} model (16 % Pd) produced a very slight lowering of the discrepancy index to $R=7.4$ % and a reduction of $B_{Zn,IT}$ to 1.8 Å², which appears to be an overcorrection. The theoretical density is

Table 1. Structure factors for refined Pd_6Zn_{20} model. $R=7.0$ %.

$h\,k\,l$	$|F_o|$	$|F_c|$	$h\,k\,l$	$|F_o|$	$|F_c|$
1 1 2	109	127	2 5 7	113	102
2 2 2	146	166	2 7 7	93	96
1 2 3	56	62	4 7 7	199	202
0 3 3	*a*	*a*	0 0 8	120	117
2 3 3	173	172	0 2 8	138	134
1 1 4	492	484	2 2 8	95	90
2 2 4	192	195	3 3 8	92	85
0 4 4	61	63	3 5 8	149	150
2 4 4	242	241	0 6 8	57	56
4 4 4	523	445	2 6 8	53	56
0 1 5	72	73	0 8 8	163	167
0 3 5	72	78	0 3 9	143	144
2 3 5	97	87	1 4 9	60	69
0 5 5	287	251	3 6 9	108	115
2 5 5	115	111	0 0.10	105	102
0 0 6	550	469	1 1.10	147	144
1 1 6	86	93	0 2.10	43	42
1 3 6	108	120	2 2.10	123	127
3 3 6	336	356	2 4.10	97	101
0 4 6	73	71	1 5.10	92	101
3 5 6	83	64	0 1.11	72	61
0 6 6	304	273	1 2.11	35	38
2 6 6	124	117	0 3.11	68	73
1 2 7	243	244			
2 3 7	81	70			
1 4 7	283	263			

[a] The 033 intensity was too strong to be measured reliably on any of the layer line films.

Table 2. Atomic distribution, positional and thermal parameters of the refined Pd_6Zn_{20} model.

	$a \pm \sigma$ Å	9.1022 ± 2
IT	Atom	Zn
	$x \pm \sigma$	0.1075 ± 16
	$B \pm \sigma$ Å^2	3.3 ± 3
OT	Atom	Pd
	$x \pm \sigma$	-0.1731 ± 8
	$B \pm \sigma$ Å^2	2.3 ± 1
OH	Atom	$\tfrac{2}{3}Zn + \tfrac{1}{3}Pd$
	$x \pm \sigma$	0.3572 ± 9
	$B \pm \sigma$ Å^2	2.1 ± 1
CO	Atom	Zn
	$x \pm \sigma$	0.3103 ± 8
	$z \pm \sigma$	0.0385 ± 9
	$B \pm \sigma$ Å^2	2.0 ± 1

$d_{\text{calc}} = 7.9$ g cm^{-3}. Further removal of Zn from the IT position resulted in a drastic increase of R.

Substitution of Pd for Zn at the OH position in the Pd_4Zn_{22} model resulted in a) a decrease of R, b) a moderate increase of B_{OH} as required, and c) an improvement of the relation between d_{obs} and d_{calc}. However, the three improvements did not reach optimum at the same time. Of the models refined, Pd_5Zn_{21} (19 % Pd) best matched the composition and density of the actual sample, Pd_6Zn_{20} (23 % Pd) exhibited the least spread of individual thermal parameter values, and Pd_7Zn_{19} had the lowest $R = 6.8$ %. The last model, however, clearly lies outside the range of homogeneity of the γ phase at any temperature. Attempts to improve the substituted models by removal of Zn from IT increased or, at best, did not affect the R value.

The atomic positional parameters obtained were independent of the model refined, within one standard deviation. Thus, it does not matter greatly which one of the refinements is reported as final. As a compromise, the result obtained with the Pd_6Zn_{20} model ($R = 7.0$ %) will be given. Table 1 lists observed and calculated structure factors, Table 2 the structural parameters and Table 3 interatomic distances.

The γ-Pd,Zn structure thus appears to tend towards the Cu_5Zn_8 type, which contains Cu in the OT and OH positions. It is reasonable to assume that, at the low-Pd phase limit, the structure is stoichiometric Pd_4Zn_{22}, with Pd in the OT position. The OH position, then, should be able to accommodate $\sim 1/6$ Pd at lower temperatures and $\sim 1/3$ Pd at higher temperatures, to correspond to the solid solubility of Pd.

Table 3. Coordinations, number and type of contacts, and interatomic distances (Å), with standard deviations, in the cubic gamma Pd,Zn phase.

3 IT(A)	—IT(A)	Zn—Zn 2.766±33 Å	2 OH(A)	—IT(A)	(Pd,Zn)—Zn 2.660± 7 Å
3	—OT(A)	Zn—Pd 2.690±12 Å	2	—OT(A)	(Pd,Zn)—Pd 2.788± 6 Å
3	—OH(A)	Zn—(Pd,Zn) 2.660± 7 Å	1	—OH(A)	(Pd,Zn)—(Pd,Zn) 2.599±16 Å
3	—CO(A)	Zn—Zn 2.684±19 Å	4	—CO(A)	(Pd,Zn)—Zn 2.877± 5 Å
(1	—OT(B)	Zn—Pd 3.459±28 Å)	2	—CO(B)	(Pd,Zn)—Zn 2.620± 9 Å
3 OT(A)	—IT(A)	Pd—Zn 2.690±12 Å	2	—CO(B)′	(Pd,Zn)—Zn 2.947±10 Å
3	—OH(A)	Pd—(Pd,Zn) 2.788± 6 Å	1 CO(A)	—IT(A)	Zn—Zn 2.684±19 Å
3	—CO(A)	Pd—Zn 2.612± 9 Å	1	—OT(A)	Zn—Pd 2.612± 9 Å
3	—CO(B)	Pd—Zn 2.633±11 Å	2	—OH(A)	Zn—(Pd,Zn) 2.877± 5 Å
(1	—IT(B)	Pd—Zn 3.459±28 Å)	1	—OT(B)	Zn—Pd 2.633±11 Å
			1	—OH(B)	Zn—(Pd,Zn) 2.620± 9 Å
			1	—OH(B)′	Zn—(Pd,Zn) 2.947±10 Å
			4	—CO(B)	Zn—Zn 2.722± 3 Å
			(2	—CO(B)′	Zn—Zn 3.498±15 Å)

REFERENCES

1. Hansen, M. *The Constitution of Binary Alloys*, 2nd Ed., New York 1958, p. 1130.
2. Köster, W. and Zwicker, U. *Festschrift aus Anlass des 100-jährigen Jubiläums der Firma W. C. Heräus G.m.b.H.*, Hanau 1951, pp. 76—90.
3. Nowotny, H., Bauer, E. and Stempfl, A. *Monatsh.* **82** (1951) 1086.
4. Ekman, W. *Z. physik. Chem.* **B 12** (1931) 57.
5. Westgren, A. *Z. Metallkunde* **22** (1930) 368.
6. Monahan, J. E., Schiffer, M. and Schiffer, J. P. *Acta Cryst.* **22** (1967) 322.
7. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
8. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
9. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., Cambridge, Mass. 1966.
10. Johansson, A., Ljung, H. and Westman, S. *Acta Chem. Scand.* **22** (1968) 2743.