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Note on the Structure of the Gamma Brass Like Phase Ir_4Zn_{22}

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The body-centered cubic gamma-brass like phase Ir_4Zn_{22} has a structure based on the Ni_4Zn_{22} type of ordering, with Ir in the outer tetrahedral position. The solid solubility of Ir in the phase ranges from 15.3 to 15.7 atomic per cent.

The gamma brass like structures of binary alloys of zinc with iron,[1] nickel,[1] palladium,[2] and platinum [3] have been investigated earlier in the present research program, and the results reported in previous articles in this series. Ruthenium and osmium do not form gamma alloys with zinc, whereas the Rh – Zn and Ir – Zn systems do contain phases of this kind.[4]

The present investigation of the gamma phase in the Ir – Zn system was undertaken in order to fill the gap in the sequence of studies, *i.e.* to investigate a *T* – Zn alloy of a transition metal from group 9 (Co, Rh, Ir) in the periodic table.

EXPERIMENTAL

The methods of preparation, investigation, and calculation have been described in detail in earlier publications. The experimental details are closely analogous to those used in the Pd – Zn study.[2]

The starting materials in the present case were iridium (sponge, Matthey spectrographically standardized) and zinc (granular, Analar Analytical Reagent) which were reacted at 1050°C for one day and homogenized at 900°C for one week. The single crystal X-ray film data were collected with an integrating Weissenberg camera and evaluated by means of the automatic SAAB film scanner-IBM 1800 computer system available at this institute. A description of the program system [5] and an account of the accuracy obtainable with this technique [6] have been published by Werner.

In the refinement of the structure, 80 independent structure factors were used and Cruickshank's weighting scheme with

$$w = (80 + |F_o| + 0.001|F_o|^2)^{-1}$$

was employed.

RESULTS

A preparation with a final iridium content of 15.3 at. % was found to be single phase. Both powder and single crystal data showed it to be body centered cubic; the space group was assumed to be the same as for Pd_4Zn_{22}, *viz.* $I\bar{4}3m$. Some data concerning the preparation are collected in Table 1.

Table 1. Structural parameters of the Ir_4Zn_{22} phase.

Composition = $Ir_{0.153}Zn_{0.847} = Ir_4Zn_{22.1}$
Assumed model = Ir_4Zn_{22}

$a = 9.1075 \pm 6$ Å
$z = 52$ atoms/cell
$d_{obs} = 9.57 \pm 6$ g cm^{-3}
$d_{calc} = 9.70$ g cm^{-3}

IT	8(*c*)	*xxx*	Atom	Zn
			$x \pm \sigma$	0.1043 ± 14
			$B \pm \sigma$ Å^2	0.1 ± 0.2
OT	8(*c*)	*xxx*	Atom	Ir
			$x \pm \sigma$	-0.1732 ± 4
			$B \pm \sigma$ Å^2	-0.2 ± 0.1
OH	12(*e*)	*x*00	Atom	Zn
			$x \pm \sigma$	0.3574 ± 13
			$B \pm \sigma$ Å^2	0.0 ± 0.2
CO	24(*g*)	*xxz*	Atom	Zn
			$x \pm \sigma$	0.3072 ± 6
			$z \pm \sigma$	0.0431 ± 9
			$B \pm \sigma$ Å^2	0.3 ± 0.1

The lattice parameter a of the cubic phase has been determined in two two-phase samples with the compositions 14.9 and 16.7 at.% Ir and three single phase samples with the compositions 15.3, 15.4, and 15.5 at.% Ir. The results are summarized in Fig. 1. The gamma Ir,Zn phase seems to be homogeneous between the compositions 15.3 and 15.7 at.% Ir. The lower phase limit (15.3)

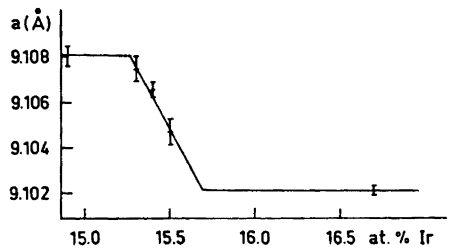

Fig. 1. Lattice parameter a (Å) *versus* at. % Ir.

corresponds almost exactly to the stoichiometric composition Ir_4Zn_{22}; at the upper limit (15.7), 0.2 atoms of Ir per unit cell have been substituted for Zn.

A starting model structure, with the same atomic position parameters as those used in the Pd_4Zn_{22} investigation [2] and with all atoms assumed to be identical (Zn) was refined, and the following results obtained:

The atomic coordinates shifted very little, but the resulting thermal parameters showed very clearly that the iridium atoms ought to be placed in the OT position (8 (*c*) *x x x etc.* with $x \approx -0.17$); the B_{OT} temperature factor became negative (≈ -3 Å^2) whereas the three others remained positive – although with somewhat scattered values. The discrepancy index was

$$R = 100 \times \sum||F_o| - |F_c||/\sum|F_c| = 23\ \%$$

Table 2. Structure factors for refined Ir_4Zn_{22} model. $R = 5.8$ %.

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
1	1	2	262	249	3	4	7	118	113
0	2	2	119	94	0	5	7	70	68
2	2	2	120	119	2	5	7	240	242
0	1	3	109	112	4	5	7	253	229
1	2	3	51	38	5	6	7	60	56
0	3	3	923	1067	2	7	7	237	234
2	3	3	272	273	4	7	7	491	508
0	0	4	97	95	0	0	8	337	342
1	1	4	648	674	1	1	8	127	130
0	2	4	51	12	0	2	8	285	290
2	2	4	318	349	2	2	8	229	232
1	3	4	66	58	1	3	8	133	126
0	4	4	139	125	3	3	8	314	291
2	4	4	389	392	2	4	8	103	97
4	4	4	704	726	4	4	8	114	116
0	1	5	56	44	1	5	8	169	162
1	2	5	118	122	3	5	8	370	356
0	3	5	257	258	5	5	8	149	126
2	3	5	183	184	0	6	8	248	235
1	4	5	179	172	2	6	8	164	156
3	4	5	59	40	4	6	8	104	103
0	5	5	478	462	1	7	8	131	132
2	5	5	176	160	0	3	9	378	336
4	5	5	212	203	2	3	9	108	100
0	0	6	677	643	1	4	9	176	171
1	1	6	92	92	3	4	9	83	89
0	2	6	126	139	0	5	9	151	161
1	3	6	179	165	2	5	9	50	49
3	3	6	615	583	4	5	9	121	119
2	4	6	77	62	1	6	9	154	161
4	4	6	179	172	3	6	9	331	362
1	5	6	133	131	0	0	10	181	187
3	5	6	203	198	1	1	10	361	337
5	5	6	116	106	0	2	10	114	104
0	6	6	563	548	2	2	10	302	309
2	6	6	220	208	0	4	10	73	61
4	6	6	139	138	2	4	10	266	279
1	2	7	440	448	1	5	10	254	283
2	3	7	131	124	0	1	11	208	206
1	4	7	512	483	0	3	11	277	301

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

		Zn – Zn	
3	IT(A) – IT(A)	2.686 ± 27 Å	
		Zn – Ir	
3	– OT(A)	2.679 ± 7 Å	
		Zn – Zn	
3	– OH(A)	2.667 ± 10 Å	
		Zn – Zn	
3	– CO(A)	2.672 ± 16 Å	
		Ir – Zn	
3	OT(A) – IT(A)	2.679 ± 7 Å	
		Ir – Zn	
3	– OH(A)	2.791 ± 7 Å	
		Ir – Zn	
3	– CO(A)	2.618 ± 8 Å	
		Ir – Zn	
3	– CO(B)	2.595 ± 9 Å	
		Zn – Zn	
2	OH(A) – IT(A)	2.667 ± 10 Å	
		Zn – Ir	
2	– OT(A)	2.791 ± 7 Å	
		Zn – Zn	
1	– OH(A)	2.598 ± 23 Å	
		Zn – Zn	
4	– CO(A)	2.861 ± 5 Å	
		Zn – Zn	
2	– CO(B)	2.643 ± 8 Å	
		Zn – Zn	
2	– CO(B)′	3.004 ± 10 Å	
		Zn – Zn	
1	CO(A) – IT(A)	2.672 ± 16 Å	
		Zn – Ir	
1	– OT(A)	2.618 ± 8 Å	
		Zn – Zn	
2	– OH(A)	2.861 ± 5 Å	
		Zn – Ir	
1	– OT(B)	2.595 ± 9 Å	
		Zn – Zn	
1	– OH(B)	2.643 ± 88 Å	
		Zn – Zn	
1	– OH(B)′	3.004 ± 10 Å	
		Zn – Zn	
4	– CO(B)	2.749 ± 8 Å	
		Zn – Zn	
(2	– CO(B)	3.401 ± 14 Å)	

Several low-angle F_c's which were at this stage not adequately matched by corresponding F_o's were definitely improved in the subsequent refinement of the correct model thus indicated. The thermal parameters became much less scattered and the final R value obtained was $R = 5.8$ %.

The small excess of iridium that can be dissolved in the phase has not been experimentally located in the present case. In analogy with the Pd – Zn phase,[2] though, it may reasonably be supposed to enter in the OH position.

In Table 2 are given observed and calculated structure factors for the final refined model, the parameters of which are listed in Table 1. Finally, Table 3 gives the interatomic distances in the coordination shells around the four different atomic sites.

A general discussion of the structures of the gamma brass like phases will shortly appear elsewhere.

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