ACTA CHEMICA SCANDINAVICA 24 (1970) 611–617

X-Ray Determination of the Structure of the Primitive Cubic Gamma Ni,Cd Phase

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The primitive cubic γ-$NiCd_6$ phase has a structure which differs from those of other γ-brass like alloys in that the Inner Tetrahedral (IT) position of one atomic "cluster" is totally unoccupied. The same cluster contains, at the Outer Tetrahedral (OT) and OctaHedral (OH) positions, all the nickel atoms in the structure. The unit cell content can be written Ni_8Cd_{40}.

Hansen[1] summarizes the somewhat discrepant results of earlier phase analysis work on the nickel-cadmium system. The authors quoted agree upon placing a cubic phase, similar to gamma brass, in the vicinity of 16 atomic % Ni. The phase is reported to be stable up to 495 ± 5°C.

Lihl and Buhl[2] prepared this type of alloy with 18.5 atomic % Ni content ($a=9.773$ Å, recalculated from kX) whereas Ekman[3] obtained a single phase sample ($a=9.781$ Å) at 17.5 atomic % Ni. Ekman assumed an "ideal composition" of 19.23 atomic % Ni (Ni_5Cd_{21} stoichiometry, based on the Hume-Rothery rule) which, however, seems to lie outside the homogeneity range of the phase.

Neither the complete crystal structure nor even the number of atoms per unit cell have so far been determined and reported in the literature. Therefore, the present investigation was undertaken. It is part of a program aimed at establishing the atomic ordering in different types of gamma brass like structures.

EXPERIMENTAL

Nickel (Kebo *puriss.* powder 99.8 % carbonyl nickel) and cadmium (sticks, specially pure) were weighed out to match several different compositions around 16 atomic % Ni. The starting materials were heated together at 450 ± 10°C in sealed, evacuated silica capsules for 3 weeks. Specimens which had not reached complete equilibrium were then ground and re-heated in the same manner another 3 weeks, whereupon the temperature was slowly lowered to 400°C. During this time the capsules were inverted every other day. The heat treatments were interrupted by quenching of the capsules in water.

The nickel content of these preparations was determined analytically by dimethyl glyoxime precipitation.[4]

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

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

Single crystal X-ray data for the γ-Ni,Cd phase have been collected with a Weissenberg camera (Cu$K\alpha$ radiation) employing multiple film technique. The diffracted intensities were estimated visually by comparison with an intensity scale and put on a common basis by intercomparison of symmetry equivalent reflexions from photographs of several layer lines. No absorption correction was attempted since the crystal was a tiny (max. diameter 0.04 mm), irregular fragment.

It is in fact quite difficult to find a good single crystal. Most fragments picked out of the powder were aggregates consisting of several extremely small randomly oriented crystals.

A second set of more accurate data was collected with Mo$K\alpha$ radiation on an SAED (Siemens Automatisches Einkristalldiffraktometer) automatic diffractometer from the same crystal. In this manner 78 independent structure amplitudes were obtained.

X-Ray scattering factor tables were taken from Cromer and Waber [5] and corrected for dispersion according to Cromer.[6]

The initial structure refinement runs were performed on the IBM 1800 computer at this Institute with the least-squares program SFLS (World list [7] No. 6023), using the block diagonal matrix approximation. The final refinement was carried out with the full matrix program LALS (World list [7] No. 384) on the Stockholm IBM 360/75 computer. A weighting scheme according to Cruickshank, with $w = (150 + |F_o| + 0.1|F_o|^2)^{-1}$ was used at this stage.

RESULTS AND INTERPRETATIONS

A single gamma-brass like phase was observed to be present in alloys of weighed-in compositions of 16 and 17 atomic % Ni. The composition, lattice parameter and density of the 16 % alloy were determined and, from these data, the number, Z, of atoms per unit cell:

$$Ni_{0.162}Cd_{0.838}$$
$$a = 9.7878 \pm 3 \text{ Å}$$
$$d_{obs} = 8.90 \pm 4 \text{ g cm}^{-3}$$
$$Z = 48 \text{ atoms/cell}$$

This is definitely less than the 52 atoms per cell encountered in the ordinary gamma phase structures. With Z equal to precisely 48, the cell content can be written as Ni_8Cd_{40}.

The Weissenberg record obtained from a single crystal out of this alloy batch showed that the crystal structure is primitive cubic, and quite similar to *e.g.*, Cu_9Al_4. Consequently, attempts were made to refine variously ordered models with atomic parameters borrowed from earlier gamma phase structure determinations. The space group, thus, was assumed to be $P\bar{4}3m$ (No. 215), and the atomic designations (see Figs. 1 and 2) and coordinates as follows.[8]

All attempted refinements converged very poorly (or not at all). In particular, the individual thermal parameters of the IT and OT positions tended to become very high and their x parameters were shifted to values yielding impossibly small interatomic distances.

A more definite indication of how the starting structure model must be modified was obtained with the set of diffractometer data which had been

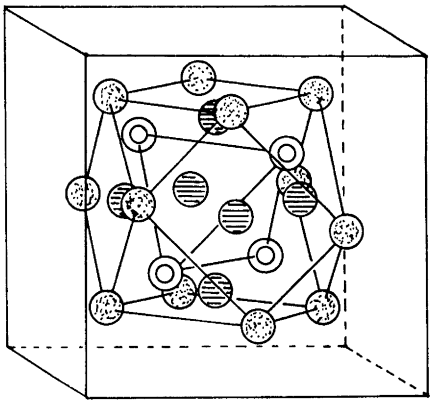

Fig. 1. Cluster A around the origin 0 0 0. OT and OH occupied by 4/5 Ni+1/5 Cd, CO by Cd.

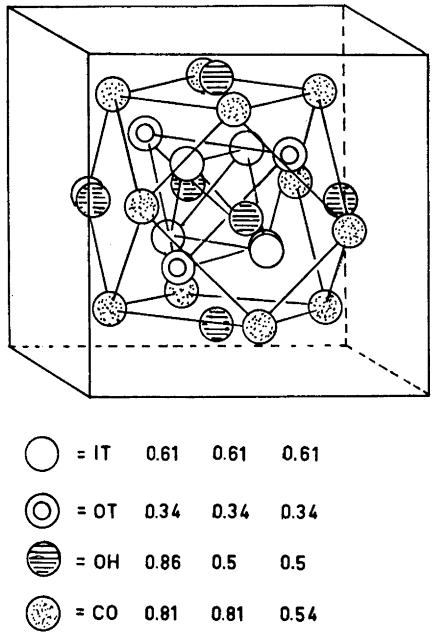

Fig. 2. Cluster B around ½ ½ ½. All atoms are Cd.

					Cluster A	Cluster B
Inner Tetrahedral	IT	4(*e*)	*x x x*	*etc.*	$x \approx 0.10$	$x \approx 0.60$
Outer Tetrahedral	OT	4(*e*)	*x x x*	*etc.*	$x \approx -0.17$	$x \approx 0.33$
Octa-Hedral	OH	6(*g*)	*x* 0 0	*etc.*	$x \approx 0.35$	
		6(*f*)	*x* ½ ½	*etc.*		$x \approx 0.85$
Cubo-Octahedral	CO	12(*i*)	*x x z*	*etc.*	$x \approx 0.30$	$x \approx 0.80$
					$z \approx 0.05$	$z \approx 0.55$

collected at this stage, The temperature factor value of the IT(A) position alone increased very sharply and the corresponding x decreased toward 0 in one refinement run.

Consequently, a model without atoms in the IT(A) position and with Cd in all other positions was tried. The refinement converged to a value of $R=100 \cdot \sum||F_o|-|F_c||/\sum|F_o|=8.2\%$. Remarkably high, but stable after convergence, were $B_{OT(A)}=5.6$ Å^2 and $B_{OH(A)}=5.5$ Å^2 compared to the other thermal parameter values around 1 Å^2.

Next, nickel atoms were introduced into the OT(A) and OH(A) positions and the resulting structure models refined. The best agreement between observed and calculated structure factors was obtained with 4Ni in 4(*e*) OT(A) and 4Ni+2Cd in 6(*g*) OH(A). The refinement converged to $R=7.7$ %.

Another refinement, with 8 nickel atoms statistically distributed over the 10 sites of OT(A)+OH(A) yielded a slightly higher $R=8.0$ %, which is, with 25 % probability, not significantly worse.[9] The Ni temperature factors improved considerably, however. Thus, it could be established that Ni is distributed over OT(A) and OH(A); whether the distribution is ordered or not remains in doubt.

The structure factors for the final, disordered, model are given in Table 1, the parameters in Table 2, and interatomic distances in Table 3. The structure is depicted in Figs. 1 and 2 (clusters A and B).

It must be remarked, finally, that the R and the thermal parameters are not extremely sensitive to substitution of Ni for Cd in the model. One also observes, in Table 2, considerable remaining scatter of B values. It is therefore not possible to state definitely that Ni occurs only at the OT(A) and OH(A) sites. On the basis of the present data, however, further attempts at locating partially Ni-substituted positions seems unwarranted.

Table 1. X-Ray structure factors from final model of γ-Ni,Cd. $R=8.0$ %

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*hkl*	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*hkl*	$\lvert F_o\rvert$	$\lvert F_c\rvert$
222	319	290	652	100	87	852	121	130
311	168	126	653	97	91	853	257	270
321	214	209	660	326	237	854	117	120
330	878	947	661	143	147	865	106	99
332	271	288	662	245	253	880	332	338
333	157	176	663	102	105	900	224	206
400	304	247	666	242	270	932	103	90
410	331	309	710	126	138	933	88	91
411	508	591	720	81	80	941	133	123
422	223	207	721	353	349	950	140	107
442	227	245	722	179	160	954	109	115
443	212	214	730	137	135	963	182	174
444	603	616	731	108	114	10.00	170	183
544	155	158	732	112	101	10.11	163	176
550	367	410	740	125	131	10.20	97	105
551	154	149	741	319	324	10.22	300	301
600	501	402	742	128	127	10.41	154	143
611	150	135	744	129	149	10.51	204	201
622	212	192	752	204	204	11.10	119	108
630	185	197	771	149	168	11.22	169	161
631	239	225	774	293	265	11.32	125	129
632	165	168	775	103	110	11.33	100	106
633	391	318	800	210	222	11.50	185	194
642	101	106	820	234	241	11.63	127	119
644	138	155	821	132	136	11.65	100	93
651	120	137	833	148	151	12.44	121	108

DISCUSSION

The main difference between the γ-$NiCd_5$ structure and other gamma-brass like structures is the absence of the Inner Tetrahedron in one of the "clusters" (A). The only position parameter value drastically affected by this

Table 2. Atomic distributions, positional and thermal parameters of the refined structure.

		$NiCd_5$	
	$a \pm \sigma$ Å	9.7878 ± 3	
		Cluster A	Cluster B
IT	Atom		Cd
	$x \pm \sigma$		0.6066 ± 15
	$B \pm \sigma$ Å²		2.9 ± 5
OT	Atom	4/5Ni + 1/5Cd	Cd
	$x \pm \sigma$	−0.1831 + 22	0.3361 ± 14
	$B \pm \sigma$ Å²	2.0 ± 7	0.7 ± 3
OH	Atom	4/5Ni + 1/5Cd	Cd
	$x \pm \sigma$	0.2508 ± 30	0.8631 ± 17
	$B \pm \sigma$ Å²	2.8 ± 7	0.9 ± 2
CO	Atom	Cd	Cd
	$x \pm \sigma$	0.2948 ± 7	0.8096 ± 9
	$z \pm \sigma$	0.0526 ± 11	0.5403 ± 14
	$B \pm \sigma$ Å²	1.0 ± 2	2.6 ± 3

Table 3. Coordination, number and type of contacts, interatomic distances (Å), with standard deviations. Ni means a distribution of 4/5 Ni + 1/5 Cd at the site.

3	OT(A)−OH(A)	Ni−Ni 2.619 ± 25	3	−CO(B)	−Cd 2.884 ± 21
3	−CO(A)	−Cd 2.777 ± 10	3	OT(B)−CO(A)	Cd−Cd 2.832 ± 20
3	−CO(B)	−Cd 2.709 ± 26	3	−IT(B)	−Cd 2.763 ± 20
			3	−OH(B)	−Cd 2.991 ± 12
2	OH(A)−OT(A)	Ni−Ni 2.619 ± 25	3	−CO(B)	−Cd 2.839 ± 13
4	−OH(A)	−Ni 3.471 ± 41	2	OH(B)−CO(A)	Cd−Cd 2.957 ± 11
4	−CO(A)	−Cd 2.962 ± 9	2	−IT(B)	−Cd 2.912 ± 15
2	−CO(B)	−Cd 3.336 ± 22	2	−OT(B)	−Cd 2.991 ± 12
1	CO(A)−OT(A)	Cd−Ni 2.777 ± 10	4	−CO(B)	−Cd 3.100 ± 8
2	−OH(A)	−Ni 2.962 ± 9	2	−CO(A)′	−Cd 3.391 ± 14
2	−CO(A)	−Cd 3.352 ± 18	1	−OH(B)′	−Cd 2.679 ± 34
1	−OT(B)	−Cd 2.832 ± 20	1	CO(B)−OT(A)	Cd−Ni 2.709 ± 26
1	−OH(B)	−Cd 2.957 ± 11	1	−OH(A)	−Ni 3.336 ± 22
2	−CO(B)	−Cd 2.938 ± 13	2	−CO(A)	−Cd 2.938 ± 13
1	−OH(B)′	−Cd 3.391 ± 14	1	−IT(B)	−Cd 2.884 ± 21
2	−CO(B)′	−Cd 3.050 ± 12	1	−OT(B)	−Cd 2.839 ± 13
3	IT(B)−IT(B)	Cd−Cd 2.950 ± 29	2	−OH(B)	−Cd 3.100 ± 8
3	−OT(B)	−Cd 2.763 ± 20	2	−CO(A)′	−Cd 3.050 ± 12
3	−OH(B)	−Cd 2.912 ± 15			

is the $x_{OH(A)}$ which here takes the value 0.25. (In other gamma phases it is approximately $x=0.35$).

Counting all distances listed in Table 3 (<3.5 Å) as interatomic contacts, the coordination numbers in the two different clusters are affected as follows:

	γ-brass	γ-$NiCd_5$(A)	γ-$NiCd_5$(B)
IT	12	—	12
OT	12	9	12
OH	13	12	13
CO	13 *	12	10

* Sometimes given as 11 when the long CO(A)—CO(A) contacts are not counted.

Each OT(A) naturally lacks the three contacts with IT(A), which reduces the coordination number from 12 to 9. Every CO(A) similarly loses its one IT(A) contact and, in consequence, obtains C.N. =12 instead of 13.

The OH(A)—OH(A)′ contact between adjacent clusters is furthermore lengthened to more than 3.50 Å as are also two long OH(A)—CO(B)′ contacts for each OH(A) atom. The two usual contacts every OH(A) makes with IT(A) have disappeared. These five contacts are replaced by four from OH(A) to OH(A) within the cluster, bringing the coordination down from 13 to 12.

These last being mainly Ni—Ni distances are, as such, very long (3.47 Å) and ought to be disregarded in a discussion of the bonding. Thus, the number of Ni—Ni bonds within one unit cell is limited to a fraction (determined by the Ni occupancy) of the 12 OH(A)—OT(A) contacts. The result is a total of approximately 8 bonds per cell between atoms of the minor component. These bonds are, as they should be, the shortest in the structure (2.619 Å). Even so, they are appreciably longer than the interatomic distance (2.49 Å) in the element.

Finally, as has been touched upon above, one contact from each CO(B) to OH(A) is lost. The B cubo-octahedron is also expanded so that the lengths of the CO(B)—CO(B) distances within the cluster increase to more than 3.50 Å. The coordination is thus decreased from 13 to 10.

There is one remarkably short Cd—Cd distance, *viz.* OH(B)—OH(B)′ (2.679 Å) in the structure. This is but a single contact, however, the others around OH(B) ranging in length from 2.91 to 3.39 Å, *i.e.* from a little less than normal short distances in Cd metal (2.97 Å) to somewhat more than normal long distances (3.29 Å) in the element.

Acknowledgements. This investigation has been carried out within a research program sponsored by the *Swedish Natural Science Research Council.*

We wish to express our gratitude to Professor A. Magnéli, for providing us with research facilities, for his continued interest in this work and for critical reading of the manuscript.

We are very grateful to Mr. A. Johansson and T. Lindahl who have been very helpful with the computer programs.

We also wish to acknowledge the technical assistance of Mrs. G. Winlöf, who took the Guinier photographs.

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Received August 15, 1969.