Rhombohedrally Distorted Gamma Phases in the Copper-Mercury and Chromium-Aluminium Systems

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The rhombohedrally distorted, body-centered pseudo-cubic unit cells of two gamma-brass like phases have been established by X-ray powder diffraction.

The phase with the proposed composition $Cu_{15}Hg_{11}$ has the cell parameters:

$$a = 9.4067 \pm 7 \text{ Å}, \qquad \alpha = 90.413 \pm 10°$$

and the phase with the probable stoichiometry Cr_9Al_{17}:

$$a = 9.1031 \pm 4 \text{ Å}, \qquad \alpha = 90.326 \pm 6°$$

Previous crystallographic investigations of the Cu—Hg system have been summarized by Hansen.[1] The only intermediate phase found is of gamma-brass type and has been reported to be cubic, with a lattice parameter of approximately 9.42 Å. Its composition, according to Lihl,[2] is Cu_4Hg_3. It decomposes into its constituent elements at 96°C.

The very complex phase diagram of the Cr—Al system has been analyzed by Bradley and Lu[3] and, more recently, by Köster, Wachtel and Grube.[4] The above authors agree upon placing one pair of gamma-brass like phases, γ_1 (high temperature), γ_2 (low temperature) at the composition Cr_5Al_8 and another pair, γ_3 (high temperature) and γ_4 (low temperature) at Cr_4Al_9. There are marked differences between the two investigations in the assessment of the thermal stabilities of the various phases. Both references, however, fix the transformation temperature of γ_4, with which substance the present investigation is concerned, at 700°C. The composition range of γ_4 is fairly restricted, and has not been uniquely established.

In a separate investigation, Bradley and Lu[5] solved the structure of γ_2 from powder data and proved it to be rhombohedral, with space group $R3m$ (No. 160). The lattice parameters given are:

$$a' = 7.8054 \text{ Å}, \qquad \alpha' = 109.127°$$

The relationship to the gamma brass structure is more clearly brought out by reference to the pseudo-cubic body-centered cell:

$$a = 9.0512 \text{ Å}, \qquad \alpha = 89.273°$$

(The above values have been recalculated from the published data given in kX units).

Thus, the distortion away from cubic symmetry implies an elongation of the remaining threefold axis with respect to the other body diagonals of the unit cell. The direction of distortion is the same as in γ_2-Cu,Al:[6]

$$a = 8.6899 \text{ Å}, \qquad \alpha = 89.782°$$

In the present investigation it is shown that both Cu_4Hg_3 and low-temperature γ_4-Cr,Al possess pseudo-cubic gamma-brass like structures, the distortion of which can be described instead by a foreshortening of the threefold axis.

EXPERIMENTAL

Cu_4Hg_3 was prepared electrolytically according to the procedure described by Lihl.[2] As a modification, a copper anode was used so that the Cu^{2+} concentration in aqueous solution was held approximately constant during the electrolysis. The starting materials were Hg (metal, Kebo), Cu (foil, *pro analysi*, Analar) and $CuSO_4 \cdot 5H_2O$ (*pro analysi*, Merck).

Several alloy specimens of chromium (pellets, Mattheys, spectrographically standardized) and aluminium (ribbon, Merck, *puriss* > 99.99 % Al) were prepared by arc-melting together, in an argon atmosphere, of different proportions of the components. The weight loss in the process was generally $3-5$ mg for a 1000 mg sample. Compositions reported in the text and in the tables are synthetic. The arc-melted pellets were crushed and portions of the powder heated at 600°, 800°, 900°, and 1000°C for a period of about two weeks in sealed, evacuated silica capsules. At the end of the heating period the capsules were quenched in water.

X-Ray powder diffractograms of all preparations were taken in a Guinier camera with strictly monochromatized $CuK\alpha_1$ radiation, $\lambda = 1.54050$ Å, and with KCl, $a = 6.2919$ Å,[7] as an internal standard.[8]

The density of the Cu_4Hg_3 preparation was measured by weighing of a sample in air and in chloroform.

RESULTS AND DISCUSSION

Powder photographs of several different preparations of the γ-Cu,Hg phase were identical except for the fact that some of the very weak reflections were not visible on all films. Table 1 lists the averages of measurements from 6 such films. Twenty-two of the powder lines were easily measurable and uniquely indexable, and from these (for which $\Delta \sin^2\theta$ are given in the table) the following, pseudo-cubic unit cell was derived:

$$a = 9.4067 \pm 7 \text{ Å}, \qquad \alpha = 90.413 \pm 10°$$

(Standard deviations of the last figure are given here and elsewhere in the text and tables.)

The corresponding primitive rhombohedral cell has the dimensions:

$$a' = 8.1660 \text{ Å}, \qquad \alpha' = 109.66°$$

(if the cell were truly cubic, α' would be $= 109.47°$).

The measured density was 12.6 ± 1.0 g cm^{-3}. Assuming that the cell contains 52 atoms, the composition CuHg which has also been proposed in the literature [9] yields a calculated density of 13.7; the composition Cu_8Hg_5, a calculated density of 12.0; and $Cu_{15}Hg_{11}$, which approximates most closely to the analytical Cu_4Hg_3 formula, a calculated density of 12.6, thus constituting the best agreement with the measured value.

Table 1. Guinier powder pattern of γ-Cu,Hg. Pseudo-cubic indexing; $a = 9.4067 \pm 7$ Å, $\alpha = 90.413 \pm 10°$; $\sin^2\theta = (0.0067048 \pm 1)\cdot(h^2+k^2+l^2)+(0.0000968 \pm 2)\cdot(hk+kl+lh)$.

I	h k l	sin²θ_obs	sin²θ_calc	10⁵·Δsin²θ
m	$\bar{1}$ 1 0 1 1 0	0.01336	0.01331 0.01350	
vw	2 $\bar{1}$ 1	0.04015	0.04013	+ 2
m	2 2 0	0.05415	0.05403	+ 12
s	$\bar{3}$ 1 0	0.06678	0.06676	+ 2
s	3 1 0	0.06741	0.06737	+ 7
m	$\bar{2}$ 2 2	0.08013	0.08007	+ 6
m	2 2 2	0.08163	0.08162	+ 1
vs	3 $\bar{2}$ 1	0.09344	0.09339	+ 5
m	3 2 1	0.09498	0.09493	+ 5
m	4 0 0	0.10735	0.10727	+ 8
vs	$\bar{3}$ 3 0 $\bar{4}$ 1 1	0.11970	0.11982 0.12001	
vs	4 $\bar{1}$ 1	0.12055	0.12059	− 4
vs	4 1 1 3 3 0	0.12162	0.12156	+ 6
m	$\bar{3}$ 3 2	0.14672	0.14664	+ 8
diffuse	$\bar{4}$ 2 2	0.15961	0.15976	
»	4 3 1	0.17598	0.17616	
w	5 2 1	0.20280	0.20279	+ 1
w	4 $\bar{3}$ 3	0.22712	0.22709	+ 3
m	4 4 $\bar{2}$ 6 0 0	0.24143	0.24137	+ 6
vw	4 4 2	0.24449	0.24447	+ 2
m	$\bar{6}$ 1 1	0.25375	0.25372	+ 3
m	6 1 1	0.25582	0.25604	−22
vw	$\bar{6}$ 2 0	0.26688	0.26703	−15
vw	6 2 0	0.26893	0.26935	−42
vw	$\bar{5}$ 4 1	0.27943	0.27957	
vw	5 4 $\bar{1}$	0.28213	0.28266	
m	$\bar{6}$ 2 2	0.29295	0.29307	−12
m	$\bar{6}$ 3 1 6 $\bar{3}$ 1	0.30666	0.30639 0.30697	
m	$\bar{4}$ 4 4	0.32025	0.32028	− 3
m	$\bar{5}$ 5 0	0.33265	0.33282	
w	6 4 0	0.35080	0.35097	
m	7 $\bar{2}$ 1 6 $\bar{3}$ 3	0.36117	0.36119	
diffuse	6 4 $\bar{2}$	0.37608	0.37586	
»	7 $\bar{3}$ 2	0.41445	0.41444	
»	6 5 $\bar{1}$	0.41778	0.41754	
»	8 1 1	0.44431	0.44417	
»	8 2 0	0.45421	0.45438	
»	6 $\bar{5}$ 3	0.46657	0.46673	

Table 2. Phases present in alloys Cr_xAl_{1-x} at 660°C. Phase designations as in Refs. 3 and 4.

x	Phases
0.204	ε
0.257	$\varepsilon + \gamma_4$
0.328	γ_4
0.351	γ_4
0.388	$\gamma_4 + \gamma_2$
0.408	γ_2
0.491	$\gamma_2 + (\beta)$
0.598	$\gamma_2 + \beta$

The stoichiometry $Cu_{15}Hg_{11}$ may be derived from a hypothetical Cu_8Hg_5 ($D8_2$-type) structure by substitution of Hg for Cu in the only one-fold Cu position in the primitive rhombohedral cell. A single crystal investigation of the structure is in progress.

Among the chromium—aluminium preparations, those containing 40.8 mole % Cr consisted of well crystallized single phase rhombohedral γ_2, whatever the temperature of heat treatment ($\leq 1000°C$). This observation appears

Table 3. Guinier powder pattern of γ_4-Cr,Al. Pseudo-cubic indexing: $a = 9.1031 \pm 4$ Å, $\alpha = 90.326 \pm 6°$; $\sin^2\theta = (0.0071597 \pm 6)\cdot(h^2+k^2+l^2)+(0.0000820 \pm 13)\cdot(hk+kl+lh)$.

I	$h\,k\,l$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	$10^5\cdot\Delta\sin^2\theta$
m	$\bar{1}\,1\,0$	0.01430	0.01424	+ 6
vw	$1\,1\,0$	0.01442	0.01440	+ 2
w	$2\,0\,0$	0.02867	0.02864	+ 3
s	$\bar{2}\,1\,1$	0.04274	0.04271	+ 3
m	$2\,1\,1$	0.04338	0.04337	+ 1
vw	$3\,\bar{2}\,1$	0.09984	0.09983	+ 1
vs	$\bar{3}\,3\,0$ $\bar{4}\,1\,1$	0.12811	0.12814 0.12830	
s	$4\,\bar{1}\,1$	0.12870	0.12879	− 9
vs	$3\,3\,0$ $4\,1\,1$	0.12954	0.12961	− 7
w	$3\,\bar{3}\,2$	0.15672	0.15677	− 5
vw	$3\,3\,2$	0.15939	0.15923	+ 16
w	$\bar{4}\,2\,2$	0.17082	0.17085	− 3
w	$4\,\bar{2}\,2$	0.17148	0.17150	− 2
vw	$\bar{4}\,4\,2$	0.25642	0.25644	− 2
m	$4\,4\,\bar{2}$ $6\,0\,0$	0.25752	0.25775	− 23
w	$\bar{4}\,4\,4$	0.34228	0.34235	− 7
vw	$4\,4\,4$	0.34752	0.34760	− 8
vs	$6\,\bar{3}\,3$	0.38599	0.38588	+ 11
w	$7\,2\,1$	0.38849	0.38851	− 2
vw	$5\,5\,2$ $6\,3\,3$	0.39033	0.39031	+ 2
vw	$\bar{5}\,5\,4$	0.47063	0.47049	+ 14

to substantiate the corresponding findings of Köster *et al.*[4] who place the transformation $\gamma_2 \rightleftharpoons \gamma_1$ at 1125°C. It contrasts with the phase diagram published by Bradley and Lu.[3] According to these authors the gamma phase is decomposed into α (Cr phase) and δ (CrAl$_3$) at 900°C.

The only heat-treatment series comprising preparations of crystallized, identifiable γ_4 phase was that at 600°C. This is in agreement with both previously published phase diagrams. Table 2 lists the result of the present phase analysis at 600°C. Single phase γ_4 was observed in preparations containing 32.8 and 35.1 mole % Cr, respectively. This is a somewhat higher Cr content than previously reported for this phase, namely around 31 mole % Cr.

Starting from the γ_2 structure, which can be formulated $Cr_{10}Al_{16}$ (38.5 mole % Cr), one obtains Cr_9Al_{17} (34.7 mole % Cr) by substitution of Al for Cr in a one-fold position in the primitive cell. One more such substitution would yield the postulated Cr_8Al_{18}, or Cr_4Al_9 (30.8 mole % Cr) stoichiometry. However, no one-fold Cr position remains in the structure and the substitution must be more or less random to achieve the above composition. The Cr_9Al_{17} formula agrees fairly well with the γ_4 composition range observed in this investigation.

In Table 3 is listed the Guinier powder pattern of a sample containing 35.1 mole % Cr. The pseudo-cubic cell derived from it is:

$$a = 9.1031 \pm 4 \ \text{Å}, \qquad \alpha = 90.326 \pm 6°$$

The dimensions of the primitive cell are:

$$a' = 7.8984 \ \text{Å}, \qquad \alpha' = 109.62°$$

A single crystal structure investigation is in progress.

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