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Cu_xHg_y: a puzzling compound

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Abstract

The Cu–Hg system has been re-examined focusing on the only intermediate phase. Our results are not in agreement with the accepted literature data: both decomposition temperature and composition have been discussed. The structural determination performed on a single crystal is already in progress and, although it shows a trigonal cell, the reflection conditions seem to exclude the diffraction symbol *R*, rejecting the space group of the structure Cu_7Hg_6, *R3m*. The existence of a small compositional range of stability has been pointed out. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cu–Hg phase diagram; Crystal structure

1. Introduction

Hansen [1] and Massalski [2] have summarized previous crystallographic investigations into the Cu–Hg system. In short, only one intermediate phase was found in this system [1,2] although, to date, the existence of one or more metastable intermediate phases cannot be excluded [2].

A long debate had been set up on the structure of this phase whose composition ranges from 50 to 60 at.%Cu [3].

Lindahl et al. [4] have carried out a detailed examination of the possible composition: CuHg, Cu_7Hg_6, Cu_4Hg_3, and $Cu_{15}Hg_{11}$ even in the absence of a single phase sample for density measurement and chemical analysis [5].

The debate eventually ended in favour of the Cu_7Hg_6 composition [3] instead of the earlier composition Cu_4Hg_3 proposed by Katoh [6].

The shape of the phase diagram changed too. The main modifications are essentially limited to the peritectic reaction isotherm, practically ranging from pure copper to pure mercury. In fact, earlier results gave a lower decomposition temperature for this phase: 96°C [7].

The temperature of 128°C was determined by Lugscheider and Jangg [3], whereas we propose the slightly higher temperature of 140°C [8].

Recently, two new copper amalgams with the formula Cu_7Hg_6 obtained from mineral deposits were described: kolymite by Markova et al. [9] and Cipriani and Mazzetti [10], and belendorffite by Bernhardt and Schmetzer [11]. The first was indicated as cubic, with unit cell dimension of $a = 9.414(2)$ Å [10], the second as pseudo-cubic, $a = 9.4082(4)$ Å and $\alpha = 90.472(5)°$; for this reason, Bernhardt and Schmetzer concluded that Cu_7Hg_6 is dimorphous [11].

2. Experimental details

The intermediate phase was prepared starting from the elements, Cu deoxidized powder (min. 99.7%, Merck) and Hg (min. 99.6%, Merck) put into an evacuated pyrex glass ampoule.

The reaction was performed at 350°C for 24 h, to obtain enough Hg vapor pressure to attack the surface of Cu. Then the ampoule was kept in an oven at 90°C for 1 week, and then kept at room temperature (RT) for another week before performing any measurement.

Six different samples with nominal composition of 53.05, 55.1, 56.2, 57.1, 58.3 and 59.5 at.%Cu were prepared changing the copper content from slightly lower than Cu_7Hg_6 to slightly higher than Cu_4Hg_3 stoichiometry.

The decomposition temperature of different samples was investigated by differential scanning calorimetry (DSC, Mettler), operating with a constant nitrogen flow of 100 $cm^3\ min^{-1}$. The crucibles were made suitably from tantalum foils with gold lids.

All samples started to decompose at around 140°C. Each analysis showed a prior endothermic effect occurring at a

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different temperature from one another. The two peaks could not be deconvoluted unambiguously, so the respective thermal contribution could not be ascertained.

Low temperature (LT) DSC analyses were performed using a Mettler DSC apparatus.

All the alloys were metallic silver color and apparently homogeneous to visual inspection. Conventional polishing performed on the samples failed to provide suitable specimens for metallographic analysis.

Scanning electron microscope (SEM) and microprobe analyses were performed on all samples focusing on the composition and morphology of the crystals.

The LT X-ray analyses were performed at ten different temperature from 15 to 295 K using a Huber LT Guinier camera.

The crystal structure of the phases were investigated by the X-ray powder method using a Philips diffractometer and by single-crystal analysis (Nonius CAD-4 diffractometer) using MoKα, CuKα and CoKα radiations. The intensity calculations for the powder patterns were performed using the Lazy Pulverix program.

The high temperature (HT) X-ray measurement were carried out using a Rigaku-Denki high temperature powder chamber.

Resistivity tests were performed by the conventional four wire technique in which the wires were fixed onto the sample by conductive silver paste.

3. Results

Analysing the samples with a composition between 53.1 and 59.5 at.% Cu by X-ray diffraction at room temperature, we always found the same pattern and, in some cases, traces of Cu.

By the Guinier method (CuKα radiation, in the range $0° < \theta < 45°$) we obtained a film with 32 single reflections, as reported in Table 1. All reflections could be indexed starting from a monoclinic cell performed by TREOR software [12] with $a=7.633(1)$, $b=13.364(1)$, $c=4.706(1)$ Å and $\beta=90.70(1)°$.

As powder indexing can sometimes be ambigous, we have compared the pattern of our film with the spectrum of the rhombohedral cell Cu_7Hg_6, $a=13.346$ and $c=16.166$ Å, given by Lindahl [4,13] after a structural determination from a single crystal quickly decayed. We observed that the indexing as *R3m* [13] obtained using the Lazy-Pulverix software, v.4 (1984) [14] showed various blanks, the most important for $d_{calc}=9.402$ Å ($I_{rel}=1000$) and $d_{calc}=3.134$ Å ($I_{rel}=280$). Nevertheless, the patterns were in good agreement as regards the values of theta and interplanar distance d for all the reflections that have $l=2n$, but the intensities were very different. Notwithstanding these important differences, we tried to index our film using the output of the Lazy-Pulverix: the result was a rhombohedral cell with $a=13.355(1)$ and $c=16.178(2)$ Å, in agreement with the values reported in literature [4,13].

Table 1
Comparison between this work Guinier film and the published data by Lindahl [5][a]

Guinier film this work			Cu_4Hg_3 pseudo-cubic, [5] $a=9.4067(7)$ Å, $\alpha=90.413(10)°$					
d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	h	k	l
6.652	6.670	mw	6.669	6.682	m	−1	1	0
3.850	3.859	vw	3.847	3.846	vw	2	−1	1
3.308	3.315	w+	3.313	3.317	m	2	2	0
2.978	2.985	w+	*2.983*	2.984	s	−3	1	0
2.966	2.972	w+	*2.969*	2.970	s	3	1	0
2.719	2.724	w+	2.723	2.724	m	−2	2	2
2.693	2.698	w	2.698	2.698	w+	2	2	2
2.517	2.522	mw	*2.519*	2.523	s	3	−2	1
2.496	2.501	w−	2.501	2.502	m	3	2	1
2.349	2.354	w−	2.353	2.354	m	4	0	0
2.222	2.226	m	*2.228*	2.227	vs	−3	3	0
2.215	*2.219*	*s*	*2.220*	*2.220*	*vs*	*4*	*−1*	*1*
2.206	2.210	mw	2.210	2.211	vs	4	1	1
2.008	2.012	mw	2.013	2.013	m	−3	3	2
1.925	1.929	w−	1.930	1.929	diffuse	−4	2	2
1.850	1.853	vw	1.838	1.837	diffuse	4	3	1
1.840	1.843	vw						
1.832	1.835	w−						
1.719	1.722	vw						
1.708	1.711	w	1.712	1.712	w	5	2	1
1.614	1.617	w	1.618	1.618	w	4	−3	3
1.566	1.568	w	1.569	1.569	m	4	4	−2
1.555	1.558	w−	1.559	1.559	vw	4	4	2
1.528	1.531	w	1.530	1.530	m	−6	1	1
1.520	1.522	w	1.524	1.524	m	6	1	1
			1.491	1.492	w−	−6	2	0
			1.485	1.485	w−	6	2	0
1.455	1.457	vw	1.457	1.458	w−	−5	4	1
			1.450	1.450	w−	5	4	−1
1.421	1.423	w+	1.424	1.424	m	−6	2	2
1.389	1.392	w+	1.392	1.393	m	6	−3	1
1.359	1.361	w+	1.362	1.362	m	−4	4	4
1.334	1.336	w+	1.337	1.336	m	−5	5	0
1.298	1.300	vw	1.302	1.301	w	6	4	0
1.279	1.282	mw	1.283	1.283	m	7	−2	1

[a] The d_{obs} in italics are the six strongest reflections reported by Ref. [11].

On the other hand, if the comparison is effected with the pseudo-cubic cell, $a=9.4067(7)$ Å and $\alpha=90.413(10)°$, previously obtained from powders by Lindahl [5] and reported as γ-brass Cu_4Hg_3, the agreement is better (see Table 2 and Fig. 1). It is to observe that the standardization of the pseudo-cubic cell produces a rhombohedral cell with $a=13.351$ and $c=16.175$ Å, very similar to our result.

To resolve the intriguing problem of the structure of this compound, we proceeded with the X-ray analyses at low (from RT to −260°C) and high (from RT to 200°C) temperature.

Table 2
Powder pattern of t.w. Guinier film indexed as *R3m* [4,13][a]

Guinier film this work			Cu_7Hg_6 Space group. *R3m* [4,13] a=13.346 Å; c=16.166 Å; γ=120° from Lazy-Pulverix				
d_{obs}	D_{calc}	I_{obs}	d_{calc}	I_{calc}	h	k	l
			9.402	**1000**	**1**	**0**	**1**
6.652	6.670	mw	6.673	28.5	1	1	0
3.850	3.859	vw	3.853	1.5	3	0	0
3.308	3.315	w+	3.312	39	0	2	4
			3.134	**280**	**3**	**0**	**0**
2.978	2.985	w+	2.978	31.9	1	3	−2
2.966	2.972	w+	2.966	25.1	2	1	4
2.719	2.724	w+	2.721	25.6	0	4	2
2.693	2.698	w	2.694	27.8	0	0	6
2.517	2.522	mw	2.522	4.6	4	1	0
2.496	2.501	w−	2.498	12.4	1	1	6
2.349	2.354	w−	2.350	10.7	4	0	4
2.222	2.226	m	2.224	108.7	3	3	0
2.215	*2.219*	*s*	2.217	67.9	2	3	−4
2.206	2.210	mw	2.208	149.6	0	3	6
2.008	2.012	mw	2.011	19.9	5	1	−2
1.925	1.929	w−	1.926	12.3	6	0	0
1.850	1.853	vw	1.851	2.3	5	2	0
1.840	1.843	vw	1.841	3.1	4	1	6
1.832	1.835	w−	1.834	6.8	1	2	8
1.719	1.722	vw	1.722	2.9	6	1	2
1.708	1.711	w	1.709	7.6	1	3	−8
1.614	1.617	w	1.618	0.5	0	7	2
1.566	1.568	w	1.567	12.2	6	0	6
1.555	1.558	w−	1.557	14.9	0	2	10
1.528	1.531	w	1.531	0.8	7	1	0
1.520	1.522	w	1.521	24.2	5	0	8
1.455	1.457	vw	1.456	5.5	3	6	0
1.421	1.423	w+	1.422	17.9	8	0	2
1.389	1.392	w+	1.390	10.9	5	4	4
1.359	1.361	w+	1.360	25.3	0	8	4
1.334	1.336	w+	1.335	18.8	5	5	0
1.298	1.300	vw	1.299	5.7	2	4	10
1.279	1.282	mw	1.281	13.5	6	3	6

[a] Only the most important blanks for d_{calc}=9.402 Å and d_{calc}=3.134 Å are reported.

The result showed that there is no phase transition at low temperature [8], and the same structure remains stable till 140°C, when the decomposition starts to occur. At about 130°C a clearing of mercury is evident both under optical microscope and by DSC (Fig. 2).

The high temperature photogram performed at 140°C shows clearly the simultaneous presence of both copper and the intermediate phase.

Resistivity measurements (Fig. 4) show metallic behavior, small change in slope at about 240 K, no occurrence of superconductivity till 4.2 K, and ρ_{298}=31 (±30%) μΩcm. Structure and overall compositions were determined by powder X-ray diffraction, micrography and SEM analyses.

To define the structure of this compound definitely, it is necessary to find a single crystal big enough to be analysed by a diffractometer with strong reflections for determining a cell.

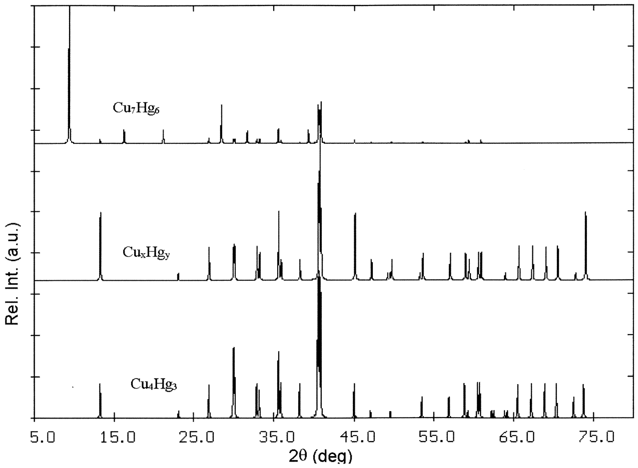

Fig. 1. Cu_xHg_y experimental spectrum (this work) compared with the structures proposed in literature: Cu_7Hg_6 (*R3m* [13]) calculated using the Lazy-Pulverix software and Cu_4Hg_3 (pseudo-cubic), sperimental, reported by Lindahl [4,5].

So far, this important step has been too difficult to achieve, because the crystals are very small or imperfect, as shown by SEM (Fig. 3). By breaking a piece of sample under nitrogen, we have obtained a truncated pyramid-like crystal of dimensions 0.10×0.11×0.07 mm that was used to collect data on a Nonius CAD-4 diffractometer with graphite-monochromatized MoKα radiation. A preliminary cell was obtained from 18 reflections of medium intensity, θ range 6.8–16.5°: the more probable lattices, with the same FOM, were monoclinic C and rhombohedral H. Comparing the powder pattern of our compound obtained by the Guinier camera with the simulated spectra starting from the above-mentioned cells, only the rhombohedral lattice included all the reflactions. At the end of the data collection carried out using the trigonal cell in the hexagonal setting, 5949 reflections were picked up. The check on the equivalent symmetry reflections excludes the Laue class $-31m$, but the ambiguity between -3 and $-3m1$ remains. The extinction rules of lattice rhombohedral R ($-h+k+l=3n$) are not verified for all of the reflections, but only for the $hk0$: this leads to considering the lattice P as correct. Various attempts to solve the structure in all the possible space groups P gave uncertain results owing to the imperfection of the crystal.

4. Discussion

Thermal analysis reveals that the first thermal effect in Fig. 2 starting in most cases at 128°C is due to mercury clearing as observed by optical high temperature micro-

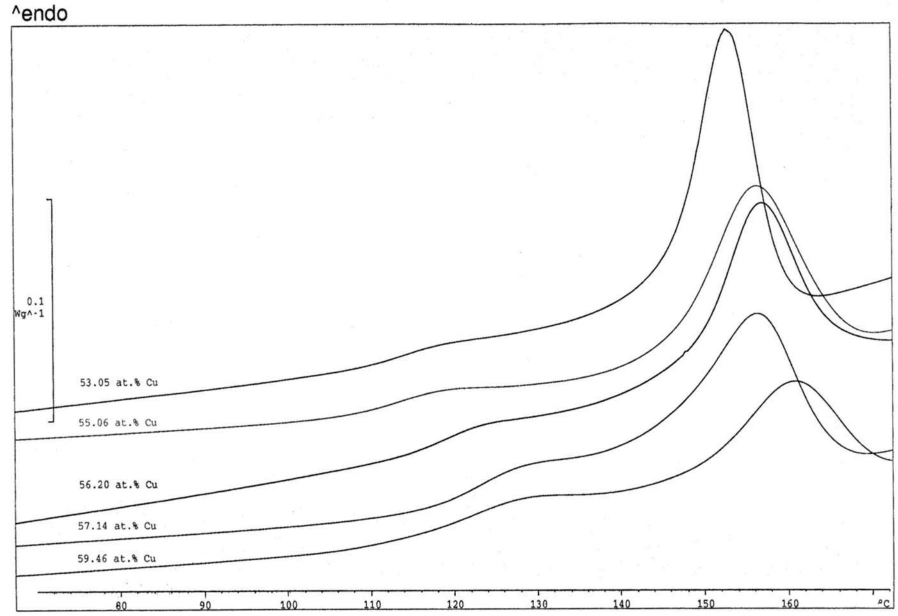

Fig. 2. Examining the HT DSC graphs, two thermal effects are evident for all samples: the beginning of mercury purging (near 128°C) and the decomposition (near 140°C).

scopy. The decomposition of the phase starts at a temperature higher than 140°C as confirmed by HT X-ray analysis. This was performed at the following temperatures: 25, 85, 110, 140, 175, 195 and again at 25°C. The simultaneous presence of Cu and the intermediate phase at 140°C and the presence of the thermal effect at 128°C suggest that a certain solubility exists in Cu_xHg_y, or that the defected crystals shown in Fig. 3 start melting at lower temperature.

Conversely the presence of a phase (Hg?) undetected by RT X-ray diffraction, but that can be revealed easily by LT DSC analysis is ascertained. The amount of this phase is reduced by RT prolonged annealing of Cu_xHg_y, but to date could not be nulled even if an annealing as long as 6 months is performed. A possible explanation could be improper annealing or out of stoichiometry of the alloys.

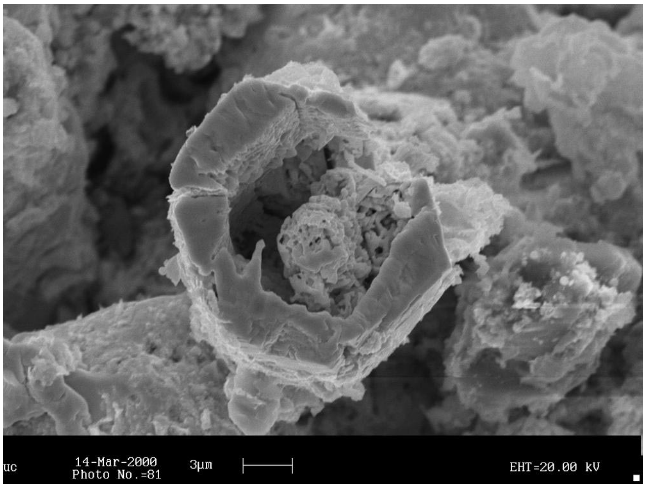

Fig. 3. SEM photograph of Cu_xHg_y copper amalgam: the crystals are small or imperfect. The mercury purging seems to destroy the crystal internally starting from its core.

Notice, however, that presence of free Hg is also detected in belendorffite [11].

The temperature corresponding to this thermal effect, about −38°C, is practically the melting temperature of pure Hg. Moreover no phase transition of Cu_xHg_y could be detected by LT X-ray diffraction [8], only a faint diffraction line appears that could be due to solid Hg. So we are confident that this phase is effectively Hg. The resistivity test of Fig. 4 is a further confirmation of this as no sharp resistivity change is detected.

Provided that this secondary phase is effectively pure Hg or nearly pure Hg, it is possible, taking into account the ΔH of melting of Hg, to calculate the amount of free mercury in the sample. For the samples annealed for 6 months, whose thermal effects are reported in Fig. 2, the free mercury was found to range from 5 to 12 wt.%. It should be considered that at the proper composition of Cu_xHg_y and for a proper homogeneization annealing, the thermal effect should disappear. This could not be obtained for the samples of Fig. 5, although the thermal effect is greatly reduced in respect of freshly prepared samples. However, the effect of composition is clearly visible. ΔH diminishes towards a possible compositon for Cu_xHg_y: the hint is Cu_4Hg_3. This is not in agreement with the thermal

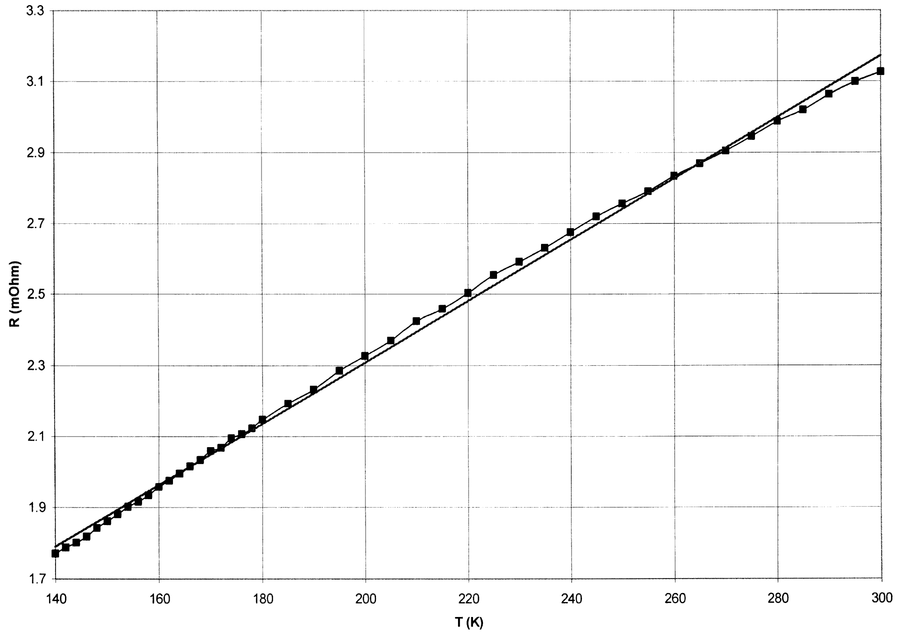

Fig. 4. The behaviour of the resistence vs. temperature for Cu$_x$Hg$_y$ sample. Straight line is $y=0.0086x+0.5811$, $\xi^2=0.9982$.

data of Ref. [3] where the enthalpy of decomposition in function of the alloy composition suggested the Cu$_7$Hg$_6$ stoichiometry.

We have already pointed out the presence of the pretransitional effect before the decomposition, so that it would be very difficult to calculate the net thermal effect due to the decomposition. Moreover, the effect of ageing on the first thermal effect was never investigated.

Several SEM analyses performed on the crystals of the samples revealed a nominal composition of about 55% Cu in atoms but this result is not sufficient enough to determine the exact stoichiometry of the phase.

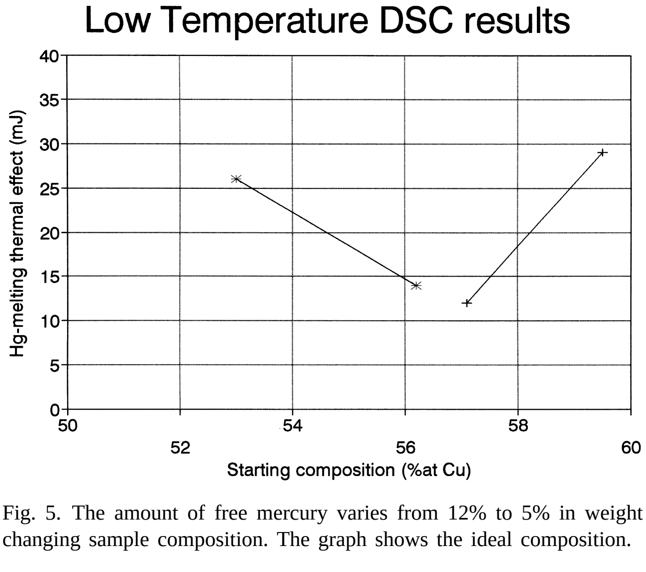

Fig. 5. The amount of free mercury varies from 12% to 5% in weight changing sample composition. The graph shows the ideal composition.

Now we have found a small crystal and, for the moment, we can say that the cell derived from X-ray analysis is trigonal *P* with $a=13.327(9)$ and $c=8.071(3)$ Å: these parameters are very similar to literature results previously seen [4,13], but *c* is half.

This explains the good indexing of our films in *R3m* space group only for *hkl* with $l=2n$.

The good agreement with the powder pattern of Lindahl above mentioned [5] induces us to think that this result could also be applied to the pseudo-cubic structure.

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