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The Crystal Structure of $TiCuHg_2$

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X-Ray studies in the ternary system Ti—Cu—Hg revealed the existence of a new phase of the composition $TiCuHg_2$. The cubic unit cell has a lattice parameter a = 6.155 Å and contains appr. 3 formula units. The crystal structure was determined from x-ray powder diffraction data and found to belong to the ordered B 32 structure type. The density measurements indicate that the structure is only 71% filled.

INTRODUCTION

In the intermetallic systems Ti—Cu, Ti—Hg and Cu—Hg, at the equiatomic ratio, three binary phases exist. All of them are structurally related to the B 2 (CsCl) structure type: CuHg(γ-brass), TiHg (CsCl) and δ-TiCu(AuCu). We felt the study of the system TiHg—CuHg could give some interesting results mainly because of the well known potential sequence of crystal structures, found whenever a basic structural unit is a body centered cube, as for example in the system Fe—Al.[1]

The idea proved to be fruitful and the results of this investigations are presented in this paper.

EXPERIMENTAL

Materials and Methods

Titanium powder (Johnson Matthey) 2 N, copper fillings (electrolytic copper) and high purity mercury (TOS, Ljubljana) were weighed and enclosed in Vycor tubes filled with purified argon under reduced pressure.

The tubes were heated for 1 hour up to 700 °C and then slowly cooled down to room temperature. If components did not react completely, the same treatment was repeated.

X-ray patterns were taken on General Electric XRD-6 diffractometer using nickel filtered CuK radiation. DTA data were obtained on a G. Netsch differental thermal analyzer. The density was determined picnometrically with decalin and methylen iodide.

RESULTS AND DISCUSSION

X-ray powder patterns of both terminal binary phases on the TiHg—CuHg tie line agree very well with literature data[2,3]. If a mutual solid solubility exists it is less than 5% on both sides, because the strongest reflection belonging to the new phase appears to be visible beyond this value. The exact solubility limit is very difficult to determine because of the relatively poor quality of the X-ray diffraction patterns and due to the fact that in this case metallo-

graphy can not be used. A pure phase is obtained within the composition interval ranging from $Ti_{0.8}$ $Cu_{1.2}$ Hg_2 to $TiCuHg_2$. The phase decomposes above 200° C, and forms TiHg and CuHg. Above 300° C mercury starts to evaporate, leaving Ti and Cu as a residue (Fig. 1). We ascribe the exothermic effect at

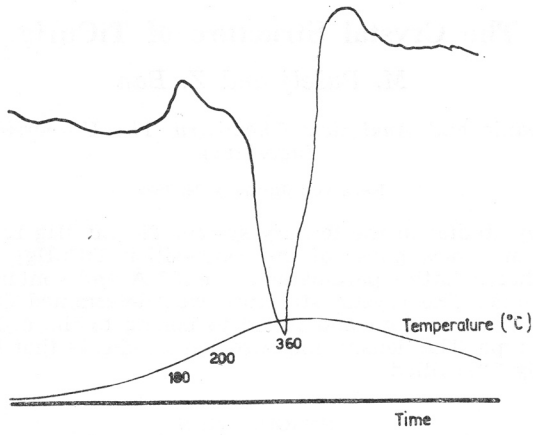

Fig. 1. A typical DTA curve for $TiCuHg_2$ (shortened form).

180° C to the stabilization (final ordering of atoms in the structure) or to the stress relief, because it varies in shape and area. No significant changes of the x-ray diffraction patern were found below and above this temperature.

The indexing of the reflections showed that the unit cell is cubic with the lattice parameter a = 6.155 Å.

Only those reflections were present where h, k and l indices are all odd or even, which determines a face centered arrangement of heavy atoms.

At first, chemical composition, together with the value of the lattice parameter and the type of extinct reflections suggested that we were dealing with a Heussler type alloy[4]. Trial calculations of some intensities immediatelly eliminated this assumption. If this were the case the ratio of the intensities for reflections 111 : 220 would be 1 : 400 which does not fit the experimental data. Later on we postulated three other possibilities with the atomic positions shown on Table I. The intensity calculations for all three possibilities are given in Table II.

As it is easily noticeable from the data presented in Table II, the assumption No. II, where titanium and copper atoms are statistically distributed over the set of positions, is unacceptable, simply because the reflection 200 would in that case have zero intensity.

Between the other two possibilities, we chose the one where the Ti-atoms occupy the positions within the unit cell and the copper atoms those on cube edges. In this way we obtain an ordered ternary structure belonging to B 32 structure type[5]. (Fig. 2). Some earlier papers mention the existence of ternary phases crystalizing in this structure type. The first of them[6] is not conclusive but an excellent article, recently published by Pauly *et al.*,[8] shows that a great number of intermetallic compounds tends to assume the same structure. These compounds are of the general composition Li_2EX (E = Cu, Ag, Au; X = Al, Ga,

TABLE I

Three Alternative Possibilities for the Atomic Arrangement in the Structure of $TiCuHg_2$

I

Hg_I	000 1/2, 1/2, 1/2 1/2, 0 , 1/2 0 , 1/2, 1/2	Hg_{II}	1/4, 3/4, 1/4 3/4, 1/4, 1/4 1/4, 1/4, 3/4 3/4, 3/4, 3/4
Ti	1/4, 1/4, 1/4 3/4, 3/4, 1/4 1/4, 3/4, 3/4 3/4, 1/4, 3/4	Cu	1/2, 0 , 0 0 , 1/2, 0 0 , 0 , 1/2 1/2, 1/2, 1/2

II

Hg_I and Hg_{II} the same position as in I; Ti and Cu statistically.

III

Hg_I and Hg_{II} the same position as in I; Cu and Ti change their positions.

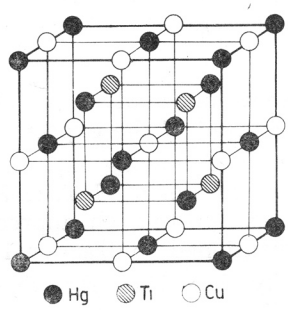

Fig. 2. The illustration of the atomic arrangement in the crystal structure of $TiCuHg_2$.

TABLE II

Diffractometer Data for $TiCuHg_2$ (Cu K α radiation)

hkl	d_o	d_c	I_o		I_c	
				I	II	III
111	3.559	3.559	25	23	24	31
200	3.076	3.079	2	0.05	0	0.05
220	2.179	2.179	100	100	100	100
113	1.856	1.844	15	13	16	18
222	1.776	1.777	5	0.5	0	0.5
004	1.536	1.540	13	16	17	16
224	1.257	1.257	37	35	35	35
333	1.187	1.187	5	2	1	4
602	0.970	0.971	15	16	16	16

$$I \sim F^2 \cdot p \cdot LP$$

where F = structure amplitude
p = multiplicity factor
and LP = Lorentz-polarization factor

In, Tl, Si, Ge, Sn, Pb, Sb, Bi). Therefore the crystal structure of $TiCuHg_2$ is the first defined and ordered ternary compound containing mercury having the structure of the B 32-type. The most unusual result was obtained by measuring the density of the compound. The calculated x-ray density amounts 14.90 g/cm³. This would correspond to a structure denser than mercury itself. However, the table of the interatomic distances (Table III) for the postulated

TABLE III

Interatomic Distances in $TiCuHg_2$

Atom	Neighbours	Distance (A)
Hg_I	6 Cu	3.08
	4 Ti	2.67
	4 Hg_{II}	2.67
Hg_{II}	4 Cu	2.67
	2 Ti	3.08
Cu	4 Ti	2.67

crystal structure does not show unusually short contacts, except perhaps the Hg_I—Hg_{II} distance (2.67 Å) instead of the expected value 3.0 Å.

For this result, we offer the following explanation. It is a matter of common knowledge that in the structures of NaTl (B 32) type, a very pronounced bond contraction is present[7], suggesting an appreciable degree of ionicity. A typical value for the aforementioned contraction is 13%.

In our case, the unusually short Hg_I—Hg_{II} distance is 13.8% shorter than the expected one (the metallic radius of mercury was not corrected for the coordination 8; R_{Hg} for C.N12 = 1.512).

Therefore, we assume a partially unfilled structure which, although not very common among intermetallic compounds, seems to be the only reasonable explanation for the apparent disagreement between the observed and the calculated densities.

The average experimental value for the density is 10.61 g/cm³. In other words the unit cell is only 71% filled with all atoms comprising the structure and also in a statistical manner.

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IZVOD

Kristalna struktura $TiCuHg_2$

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Rendgenografskim istraživanjem presjeka TiHg—CuHg u sistemu Ti—Cu—Hg ustanovljeno je postojanje ternarne faze $TiCuHg_2$. Struktura je kubična s parametrom elementarne ćelije a = 6,155 Å. Od tri moguća rasporeda atoma u strukturi, na osnovi rezultata računanja intenziteta, odabran je onaj koji predstavlja strukturu tipa NaTl (B-32) sa sređenim rasporedom svih atomskih vrsta. Mjerenjem gustoće ustanovljeno je da se radi o djelomično popunjenoj kristalnoj strukturi, jer elementarna ćelija sadrži približno tri formulske jedinice.

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