

THE BINARY SYSTEMS CALCIUM-COPPER, STRONTIUM-COPPER AND BARIUM-COPPER

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SUMMARY

The calcium-copper, strontium-copper and barium-copper systems have been examined by thermal and differential thermal analysis and the intermediate phases studied by X-ray diffraction.

Compounds corresponding to the following compositions were observed: CaCu_5 (950°C), CaCu (567°C), Ca_2Cu (488°C); SrCu_5 (845°C), SrCu (586°C); BaCu_{13} (670°C), BaCu (570°C). Only CaCu_5 and BaCu melt congruently.

INTRODUCTION

The alloying behaviour of calcium, strontium and barium with copper has been investigated by several authors. The calcium-copper system was studied by Baar¹, but the suggested phase diagram appeared to be thermodynamically impossible and a reinvestigation of the system was considered desirable². The occurrence of intermediate phases was examined by Haucke³ and by Nowotny⁴, and recently by Myles⁵ in the course of an investigation on the ternary magnesium-calcium-copper system.

For the strontium-copper system, only the existence of the SrCu_5 phase (CaCu_5 -type) has so far been reported⁶.

The barium-copper system has been partially studied by Braun and Meijering⁷.

EXPERIMENTAL

The alkaline-earth metals used in this investigation were commercial products of Fluka Co. (Switzerland). Calcium and strontium were purified by distillation using the procedure reported by Peterson *et al.*^{8,9}. The melting points and lattice constant values found for these metals are given in Table I and are in good agreement with the known data¹⁰.

Alloys containing from 100 to 60 at. % of alkaline-earth metal were prepared in iron crucibles soldered under an argon atmosphere, while molybdenum was used as container material for the compositions richest in copper.

The calcium-copper system was examined by direct thermal analysis on

TABLE I

Metal	Melting point (°C)	Lattice constant (Å)
Ca	839	5.585 ± 0.002 (A_1 type)
Sr	773	6.082 ± 0.002 (A_1 type)
Ba	710	5.019 ± 0.002 (A_2 type)
Cu	1084	3.615 ± 0.002 (A_1 type)

samples of about 20 g. Cooling was carried out at the rate of 2–4°C/min after stirring the melt, the temperature being recorded with a chromel–alumel thermocouple connected to a Leeds and Northrup Speedomax (Type G) potentiometer.

The strontium and barium alloys were examined by differential thermal analysis, using samples of about 2.0 g against an equal amount of molybdenum as reference material. The oxidation of these alloys increases continuously with the alkaline-earth content, making metallographic examination of the specimens difficult. Polishing was carried out under paraffin oil.

In all three systems temperature measurements were accurate to $\pm 1.0^\circ\text{C}$.

Powders and single crystals for X-ray examination were kept in glass capillaries under vacuum or inert-gas atmosphere.

The alloys were chemically analysed, alkaline earths being determined with EDTA solution and copper by electrochemical deposition.

THE CALCIUM–COPPER SYSTEM

The equilibrium phase diagram developed is plotted in Fig. 1. Agreement with

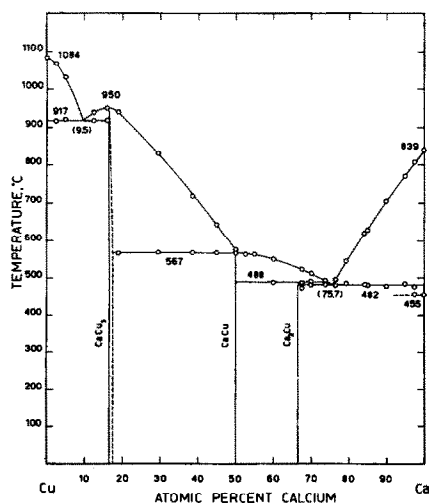


Fig. 1. The yttrium–cadmium phase diagram.

Baar's¹ results applies only in the part of the system richest in copper, namely between 0.0 and 20.0 at. % calcium.

The thermal arrest at 482°C, observed by Baar over the composition range 16.0–100.0 at. % calcium, was found only over the range 66.7–100.0 at. % calcium, corresponding to a eutectic formed by calcium with the Ca_2Cu phase, which melts incongruently at 488°C. The existence of the compound CaCu reported by Nowotny⁴ and by Myles⁵ was confirmed.

Calcium showed a transformation in the solid state, a change from b.c.c. to f.c.c. occurring at 455°C.

THE STRONTIUM-COPPER SYSTEM

Two phases, SrCu_5 and SrCu , exist in this binary system, as shown in Fig. 2.

Unlike the copper-calcium system, the compound richest in copper melts incongruently at 845°C. The cooling curve for the strontium metal gave a thermal arrest at 610°C, which agrees with the observations of Rinch¹¹ and Peterson⁹ on the allotropy of this element.

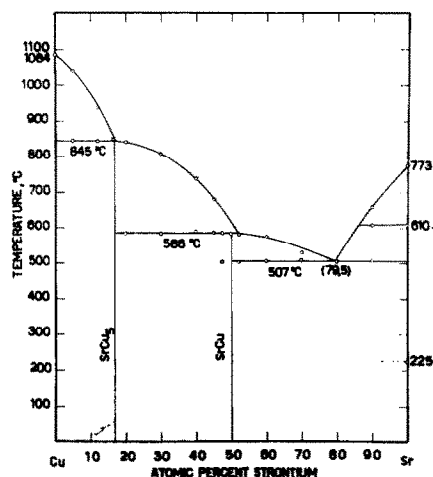


Fig. 2. The copper-strontium phase diagram.

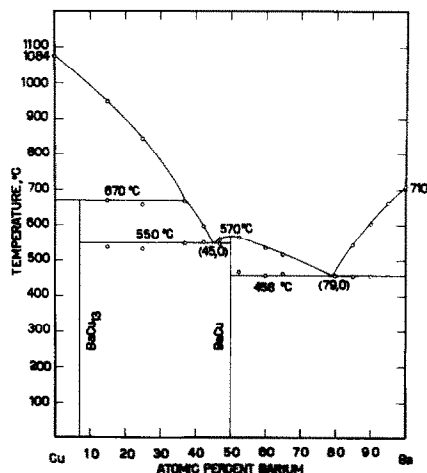


Fig. 3. The copper-barium phase diagram.

THE BARIUM-COPPER SYSTEM

Barium forms the compounds BaCu_{13} and BaCu with copper. The equilibrium phase diagram is given in Fig. 3.

The part richest in copper agrees with the previous data obtained by Braun and Meijering⁷. The addition of barium lowers the solidification temperature of copper to 550°C, corresponding to a eutectic point (45.0 at. % barium). The phases forming this eutectic are BaCu_{13} and BaCu . The latter compound melts congruently at 570°C and gives another eutectic (at 458°C; 79.0 at. % barium) with barium metal.

INTERMETALLIC COMPOUNDS

Structural data for the intermediate phases formed by calcium, strontium and barium with copper are listed in Table II.

TABLE II

Compound	System and structure type	Space group	lattice constants (\AA)		
			a_0	b_0	c_0
CaCu ₅	hexag.- $D2_d$	$P6_3/mmm$	5.074 (± 0.002)	—	4.074 (± 0.002)
CaCu	orthorhombic	$Pnma$	15.520 (± 0.003)	4.270 (± 0.003)	5.867 (± 0.003)
Ca ₂ Cu	unknown	—	—	—	—
SrCu ₅	hexag.- $D2_d$	$P6_3/mmm$	5.261 (± 0.002)	—	4.058 (± 0.002)
SrCu	hexag.	$P6_3/mmc$	4.346 (± 0.003)	—	15.566 (± 0.003)
BaCu ₁₃	cubic- $D2_3$	$Fm3c$	11.754 (± 0.002)	—	—
BaCu	hexag.	$P6_3/mmc$	4.495 (± 0.003)	—	16.230 (± 0.003)

For the CaCu₅ phase, whose crystal structure is known ($D2_d$ -type), differing values of the lattice constants are reported in the literature, *viz.*, $a_0 = 5.092 \text{ \AA}$, $c_0 = 4.086 \text{ \AA}$, according to Haucke³, who used alumina crucibles in its preparation, and $a_0 = 5.107 \text{ \AA}$, $c_0 = 4.073 \text{ \AA}$, according to Nowotny⁴, who used graphite containers.

The extent of solid solubility around the 1:5 composition was examined with the results shown in Table III.

TABLE III

Calcium content (at. %)	Formula	Thermal treatment	Lattice const.		$V_{\text{cell}} (\text{\AA})^3$
			$a_0 (\text{\AA})$	$c_0 (\text{\AA})$	
14.0	CaCu _{6.1}	Annealed at 800°C and quenched	5.078	4.076	91.09
16.6	CaCu _{5.0}	Furnace cooled	5.074	4.074	90.90
19.0	CaCu _{4.3}	Furnace cooled	5.109	4.050	92.16
20.0	CaCu _{4.0}	Annealed at 800°C and quenched	5.110	4.046	92.24

The observed variation of lattice constant values agrees with a small increase in the volume of the unit cell on the calcium side.

Single crystals of 1:1 composition were isolated. Rotating and Weissenberg photographs showed orthorhombic symmetry with the characteristic extinctions of

the *Pnma* space group. The following lattice constant values were obtained from powder patterns by the least-square method:

$$a_0 = 15.520 \text{ \AA}; b_0 = 4.270 \text{ \AA}; c_0 = 5.867 \text{ \AA}.$$

Two parameters (b_0 and c_0) are quite similar to those of YbCu, whose FeB type of structure was determined by Iandelli and Palenzona¹²; the third parameter (a_0) is about twice the value found for YbCu ($a_0 = 7.568 \text{ \AA}$). The study of the CaCu crystal structure is in progress.

Single crystals of the compound Ca_2Cu were not obtained and the powder photographs were not indexed. The d -spacings agree with those reported by Myles⁵ who also established the 2:1 stoichiometry of this phase.

Evidence of isomorphism between SrCu and BaCu was found from powder patterns. Owing to the extreme oxidation potential and softness of the Sr and Ba alloys around this composition, many attempts had to be made before results from single crystals could be obtained. Eventually, a plate-formed fragment of SrCu gave fairly good rotating and Weissenberg patterns. The observed Laue symmetry and extinctions (hkl reflections present only for $l = 2n$) correspond to the $P6_3/mmc$ space group. The lattice constant values reported in Table II for SrCu and BaCu were obtained by the least-squares method. As for CaCu, the crystal structure of SrCu and BaCu will be the object of further study.

Lattice constant values obtained in the course of this work from SrCu_5 specimens are in agreement with those reported by the author in a previous paper⁶.

The crystal structure of BaCu_{13} (NaZn_{13} -type) was already known. Although this phase is peritectically formed much below the liquidus temperature, large and well grown single crystals can be obtained by cooling 16.0–25.0 at. % barium alloys. Any solid solubility around the 1:13 composition has been excluded.

CONCLUSION

The equilibrium diagrams for the three systems studied show that the 1:5 phase loses stability on passing from calcium to strontium and does not exist for barium. A rough relationship between the atomic dimensions of the alkaline-earth component and the stoichiometry of the phase richest in copper could be discerned: It is well known that the crystal structure of CaCu_5 (and SrCu_5) is largely controlled by the size factor, and hence, the greater atomic dimensions of barium could explain the non-existence of an isomorphous BaCu_5 phase. In the 1:13 compound (with the NaZn_{13} type of structure), barium is surrounded by 24 copper atoms (instead of 20 as for calcium and strontium in the CaCu_5 type of structure), while the coordination number of copper is the same in both structures.

The 1:1 phase exists for all the alkaline-earth metals, but isomorphism is only found in the cases of strontium and barium.

The 2:1 phase exists only for calcium.

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