X-RAY INVESTIGATIONS ON COPPER-ARSENIC ALLOYS.

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Earlier Investigations. According to the thermal and microscopic investigations of Hiorns⁽¹⁾ there should exist no less than three intermediate phases in the copper-arsenic system within the range 0–44% As, corresponding to the formulas Cu_3As, Cu_5As_2 and Cu_2As. Friedrich⁽²⁾ using the same methods of investigation, claims to have found Cu_3As and Cu_5As_2, but he did not confirm the existence of Cu_2As.

The electrical properties of these alloys were first studied by Matthiessen and Holzmann.⁽³⁾ Friedrich⁽⁴⁾ observed an abrupt change of direction in the conductivity curve at the limit of the saturation, of arsenic in the copper phase. Puschin and Dischler⁽⁵⁾ measured the conductivity of a series of alloys containing up to 43% As. This investigation have only confirmed the existence of one intermediate phase, namely Cu_3As.

By passing arsenic vapour over hot copper Koenig⁽⁶⁾ succeeded in producing macroscopic crystals of Cu_3As which have been subjected to cryst-

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(1) A. Hiorns, "Electro-chemist and Metal," (1904).
(2) K. Friedrich, *Metallurgie*, **5** (1908), 529.
(3) A. Matthiessen and Holzmann, see *Metallurgie*, **5** (1908), 529.
(4) K, Friedrich, ibid.
(5) N. A. Puschin and E. Dischler, *Z. anorg. Chem.*, **80** (1913), 65.
(6) G. A. Koenig, *Z. Kryst.*, **38** (1903), 529.

allographic measurements. According to Stevanoic⁽¹⁾ they crystallize in orthorhomic system with axial ratios 0.5771 : 1 : 1.0206, while Wright⁽²⁾ describes the symmetry as hexagonal with an axial ratio 1 : 1.539.

Quite recently Ramsdell⁽³⁾ found that crystals of Cu_3As produced by Koenig's method and material produced by fusion give the same X-ray pattern, a result which has been confirmed by the present author. Although the crystals are quite well developed, the powder photograms show that their composition is not uniform. Ramsdell made no attempt to determine the structure.

By melting the theoretical quantities of the components in an evacuated quartz tube, Machatschki⁽⁴⁾ prepared alloys of the compositions Cu_3As and Cu_5As_2, and subjected them to an X-ray investigation. All interferences of Cu_3As were accounted for by a quadratic form of the hexagonal type, and the lattice dimensions were found to be the following:

$$a=7.200\text{Å}, \qquad c=7.478\text{Å}.$$

The axial ratio is $c:a=1.039$.

Machatschki also made a goniometoric determination of the axial ratio of crystals obtained by Koenig's method, The following table shows the result obtained by him compared with those which he has calculated from the data of Stevanoic and of Wright.⁽⁵⁾

	c : a
Machatschki	1.023
Stevanoic	1.0206
Wright	1.0259

The alloy with the composition Cu_5As_2 was found by Machatschki to be inhomogeneous but to consist mainly of a phase with the same structure as Cu_3As but with slightly different lattice dimensions.

Preparation of Samples and their Chemical Analysis. The alloys with less than 30% As were prepared in a high frequency induction furnace in nitrogen atmosphere,⁽⁶⁾ 20 grams of electrolytic copper were first melted in a magnesia crucible. The arsenic (Kahlbaum) was then dropped

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(1) S. Stevanoic, *Z. Kryst.*, **37** (1903), 246.

(2) F. E. Wrignt, *Z. Kryst.*, **38** (1903), 509.

(3) L. S. Ramsdell, *The American Mineralogist*, **14** (1929), 188.

(4) F. Machatschki, *Neues Jahrbuch für Mineral.*, **59**, Bl. Bd. (1929), 137; *Centralblatt für Mineralogie*, A, (1930), 13–19.

(5) Loc. cit.

(6) G. Hägg, *Nova Acta Regiœ Soc. Scient. Ups.*, Ser. IV, 7, No. 1 (1929).

into the melt. The alloys with higher content of arsenic were prepared by melting copper and arsenic together in an evacuated quartz tube, as described by Thomassen.(1) In order to obtain a uniform product, the tube was turned after fusion, allowing the melt to flow down along the wall of the tube. Samples of 6 to 7 grams were prepared in this way.

The composition of the samples could be estimated by weighing the product obtained and assuming that no copper was lost during the melting process.(2) The content of copper was, however, also determined analytically by one of the following methods.

All samples were dissolved in warm nitric acid and evaporated with sulphuric acid. When the arsenic content was low, a copper sulphate solution free from arsenic was obtained by evaporation with hydro-fluoric acid. Copper was then determined electrolytically in the presence of nitric acid.(3) The samples with higher content of arsenic were treated according to a method described by Jannasch and Biedermann.(4) The sulphate solution was made strongly alkaline and the copper was reduced by hydrazine sulphate. The copper was then dissolved in acid and determined iodometrically.

X-ray Analysis. The X-ray tube used was of the Hadding-Siegbahn type and was run at 45 kv. and 10 ma. Three cameras of the focussing type(5) covering together the whole diffraction range, were used. The time of exposure varied from 5 to 8 hours. The cameras were constructed by G. Phragmen and were calibrated with sodium chloride. The K-radiation of chromium was used throughout the work.

The α Phase. According to Friedrich,(6) copper dissolves about 4% As at room temperature. The dimensions of the face-centred cubic copper phase (α) increase with the arsenic content. While the edge of the elementary cube is for pure copper 3.608Å, it was found to be 3.629Å for an alloy with 2.0% As. At the limit of solubility at room temperature the edge was found to be 3.640Å.

The β Phase. Friedrich found the β phase to have a homogeneity range extending from 28.6 to 29.6 % As. This was confirmed by the present author. As already mentioned, Machatschki succeeded in finding the ele-

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(1) L. Thomassen, *Z. physik. Chem.*, **135** (1928), 385.

(2) Puschin, loc. cit.

(3) A. Classen, "Quantitative Analyse durch Elektrolyse," (1927).

(4) P. Jannasch and K. Biedermann, *Ber.*, **33** (1900), 631.

(5) H. Bohlin, *Ann. der Physik*, **61** (1920), 422; A. Westgren and G. Phragmen, *Phil. Mag.*, **50** (1925), 318.

(6) Loc. cit.

mentary dimensions of this phase. Before Machatschki's work was published, the present author had also found the quadratic form. The following dimensions were determined by the author.

	a	c	c : a
Cu-limit of homogeneity range	7.121 Å	7.293 Å	1.024
29.1 % As	7.118 Å	7.279 Å	1.023
As-limit of homogeneity range	7.095 Å	7.267 A	1.024

The density of Cu_3As was determined by several authors as follows:

Stevanoic	7.02–8.10
Weisbach	7.0–7.5
Machatschki	7.88
Calculated from Koeing	7.94

The most probable number of molecules in the unit cell is 6, which according to the X-ray data of the author would give the theoretical density 8.22.

Table 1 gives the X-ray data of an alloy within α–β two phase range. Table 2 shows the data of a slowly cooled alloy with 30.9% As, only faint lines appear besides those belonging to the β phase. When the same specimen was quenched from 630°C., however, a number of new lines appeared (Table 3). This might also expected from Friedrich's diagram. The lines of the β phase occupy exactly the same positions in both photograms, which shows that the limit of the homogeneity range is not appreciably influenced by the temperature.

Alloys with higher content of arsenic will be subjected to continued investigations. An alloy with the composition Cu_5As_2 was tempered at 700°C. for 7 days and quenched from 670°C. The photogram was not homogeneous but showed lines belonging to the β phase. A quenched alloy containing 38.7% As contains no more β phase. It was found to consist of primary crystals in an eutectic. The author confirmed Friedrich's observation that these primary crystals slowly decompose into two new phases.

Table 1.

Powder Photogram of a Cu-As Alloy with 19.6 % As.

Chromium-K-radiation.

Intensity	$\sin^2\theta/2_{obs.}$	Radiation	h k l	$\sin^2\theta/2$	h k l	$\frac{\sin^2\theta/2}{\Sigma h^2}$
w	0.0995	α	002	0.0982		
w	0.1042	α	110	0.1029		
w	0.1289	α	111	0.1275		
w	0.2020	α	112	0.2011		
m	0.2361	α	202	0.2354		
St	0.2453	β			111	.0818
m	0.2555	β	300	0.2558		
w	0.2642	α	211	0.2647		
w	0.2686	β	113	0.2683		
v. St	0.2958	α			111	.0986
St	0.3088	α	300	0.3088		
St	0.3238	α	113	0.3239		
v.w	0.3380	α	212	0.3384		
v.w	0.3465					
St	0.3946	α			200	.0987
v.w	0.4070	α	302	0.4070		
m	0.6323	α	223,214	0.6328, 0.6331		
v.w	0.6540	β			200	.0818
St	0.7889	α_1			220	.09861
m	0.7919	α_2			220	.09899
w	0.9000	β			311	
w	0.9254	α_1	330	0.9254		
w	0.9285	α_2	330	0.9285		
w	0.9408	α_1	404	0.9408		
w	0.9436	α_2	404	0.9442		

Table 2.

Powder Photogram of a Slowly Cooled Cu-As Alloy Containing 30.86 % As. Chromiun K-radiation.

Intensity	$\mathrm{Sin}^2\,\theta/2_{\mathrm{obs.}}$	h k l	$\mathrm{Sin}^2\,\theta/2_{\mathrm{calc.}}$
m	0.0987	(002)	0.0998
w	0.1035	110	0.1037
w	0.1296	(111)	0.1284
w	0.1716		
w	0.1968	β 202	0.1966
w	0.2032	(112)	0.2025
St	0.2378	202	0.2371
m	0.2569	300	0.2579
w	0.2656	211	0.2667
v. St	0.3106	300	0.3111
v. w	0.3176		
v St	0.3253	113	0.3261
m	0.3399	212	0.3408
m	0.4089	(302)	0.4099
w	0.4290	104	0.4299
v. w	0.4385	(221)	0.4395
v. w	0.4735	311	0.4741
v. w	0.4990	(114)	0.4991
w	0.5279	β 214, β 223	0.5284, 0.5284
St	0.6371	α_1 214, α_1 223	0.6372, 0.6374
w	0.6386	α_2 214, α_2 223	0.6396, 0.6394
v. w	0.6822	321	0.6815
w	0.7506	(411)	0.7508
m	0.7557	205, 322	α_1 0.7560, α_1 0.7556
w	0.7583	205, 322	α_2 0.7587, α_2 0.7583
m	0.8449	314	0.8448
w	0.8481	314	0.8481
v. w	0.8594	215	0.8598
m	0.8897	501, 006	α_1 0.8889, α_1 0.8896
w	0.8938	501, 006	α_2 0.8921, α_2 0.8928
St	0.9334	330	α_1 0.9334
w	0.9363	330	α_2 0.9366
St	0.9485	404, 413	α_1 0.9485, α_1 0.9484
m	0.9522	404, 413	α_2 0.9518, α_2 0.9517
w	0.9635	502	0.9631

Table 3.

Powder Photogram of an Cu-As Alloy with 30.86 % As Quenched from 630°C. Chromium K-radiation.

Intensity	$\sin^2 \theta/2_{\text{obs.}}$	Radiation	h k l	$\sin^2 \theta/2_{\text{calc.}}$
w	0.0988	α	002	0.0988
w	0.1185	α		
w	0.1289	α	111	0.1284
w	0.1860	α		
w	0.2129	α		
m	0.2195	α		
m	0.2369	α	202	0.2371
m	0.2492	β		
v. w	0.2566	β	300	0.2579
w	0.2632	β		
m	0.2707	β	113	0.2705
m	0.2796	α		
St	0.3018	α		
w	0.3106	α	300	0.3111
St	0.3193	α		
St	0.3259—0.3302	α	113	0.3261
m	0.3391	α	212	0.3408
m	0.4115	α	302	0.4099
w	0.4302	α	104	0.4299
St	0.6365	α_1	214, 223	0.6373, 0.6372
w	0.6394	α_2	214, 223	0.6396, 0.6394
m	0.6933	α		
v. w	0.7232	α	115	0.7215
m	0.7464	α		
m	0.7572	α	205, 322	0.7560, 0.7556
m	0.7744	β	330	0.7738
w	0.7867	β	404	0.7864
w	0.8241	α	412	0.8248
w	0.8454	α	314	0.8448
v. w	0.8912	α	501, 006	0.8921, 0.8919
St	0.9133	α_1		
w	0.9158	α_2		
w	0.9340	α	330	0.9334
St	0.9436	α_1		
w	0.9456	α_2		
St	0.9488	α_1	404, 413	0.9485, 0.9484
w	0.9514	α_2	404, 413	0.9518, 0.9517

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