[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF CINCINNATI]

The Crystal Structure of Precipitated Copper–Tin Alloys

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It has been shown by Mylius and Fromm[1] that tin added to a neutral or slightly acid 1% aqueous solution of copper sulfate produces a precipitate whose composition approximately agrees with that of Cu_3Sn. It was the purpose of this investigation to determine whether the crystal structure of the precipitated alloy is the same as that of a fused alloy of like composition. During the investigation it was found that the composition of the alloy could be varied from nearly pure copper to nearly 40% tin by changing the amount of acid in the solution. These percentages include the α-phase as well as the one containing Cu_3Sn, so that the structure of the precipitated α-bronze was also compared with that of fused α-bronze.

The crystal structures of fused Cu_3Sn and α-bronze have been carefully investigated by Jones and Evans,[2] Weiss[3] and Westgren and Phragmén,[4] so that it was unnecessary to prepared fused alloys for comparison.

Experimental

The x-rays were supplied by a gas tube[5] having a copper target and equipped with a reflection spectrograph.[6] The tube was operated at about 25 kv. and 30 ma.

The samples were prepared by adding 5 g. of lead-free tin foil to beakers of hot (80°) 1% aqueous solutions of $CuSO_4{\cdot}5H_2O$ containing various quantities of sulfuric acid. These were kept at 80° for five hours and then allowed to cool gradually to room temperature. It was found that the same alloys could be produced with smaller quantities of tin foil as well as at other temperatures, but that at the lower temperatures a longer time was required for the alloys to form, especially in the case of the less acid solutions. During the time the alloys were being precipitated, the solutions were stirred occasionally. After the solutions had cooled to room temperature, the liquid was decanted and the precipitate washed several times to get rid of a white sediment which had formed, and which tended to remain suspended in the liquid more easily than the alloy. The precipitate was dried at 120° and cooled in a desiccator before the chemical and crystal structure analyses were made.

Results

The percentages of tin and copper in the precipitated alloys are plotted

(1) Mylius and Fromm, *Ber.*, **27**, 630 (1894).

(2) Jones and Evans, *Phil. Mag.*, [7] **4**, 1302 (1927).

(3) Weiss, *Proc. Roy. Soc.* (London), **A108**, 643 (1925).

(4) Westgren and Phragmén, *Z. anorg. allgem. Chem.*, **175**, 80 (1928).

(5) Kersten, *Rev. Sci. Inst.*, **3**, 145 (1923).

(6) Kersten, *ibid.*, **3**, 384 (1923).

as functions of the number of cc. of concentrated sulfuric acid per liter of solution in Fig. 1.

The curves show that there is a preferred tendency to precipitate either α-bronze or Cu_3Sn. All the precipitated alloys contained sulfur in addition to tin and copper. This probably makes up the difference between 100% and the total per cent. of metal.

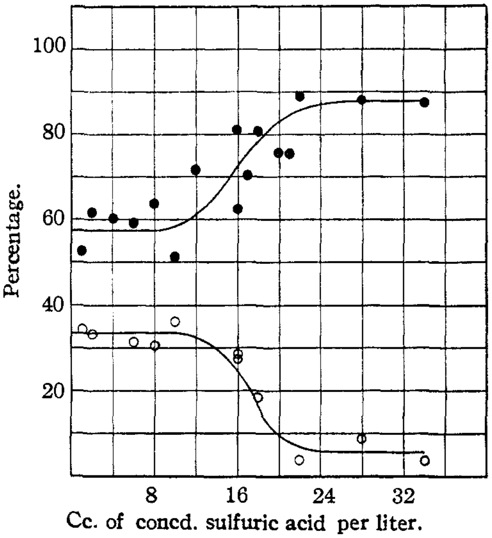

Fig. 1.—Percentages of tin and copper in the precipitated alloys as a function of the number of cc. of sulfuric acid per liter: upper curve, copper; lower curve, tin.

In column 3 of Table I are given all the observed values of 2Θ for precipitated Cu_3Sn. Column 2 gives the corresponding α-lines observed by Jones and Evans[2] for fused Cu_3Sn, as well as values for several β-lines. The β-lines were computed from the theoretical spacings given by the authors just mentioned.

Table II shows a similar comparison of the lines of precipitated α-bronze with those computed, assuming a face-centered cube whose side is equal to 3.623 Å. as given by Weiss.[3]

No lines, other than those listed, were observed. For each phase the agreement is sufficiently close to show that precipitated α-bronze and precipitated Cu_3Sn have the same structure as the corresponding alloys prepared by fusion.

TABLE I

1 Planes	2 Lines for fused Cu_3Sn	3 Lines for precipitated Cu_3Sn
. .	. . . . .	30° 50′
100β	33° 54′	35°
100α	37° 44′	39°
101β	38° 56′	39° 50′
101α	43° 28′	44°
102β	51° 2′	52°
. .	. . . . .	63° 40′
102α	57° 34′	58° 20′
110α	68° 2′	69°
201α	84° 28′	84°
203α	114° 24′	114° 40′
210α	117° 52′	117° 50′
211α	122° 16′	122°
114α	130° 56′	131° 10′

TABLE II

Planes	Computed 2Θ	Observed 2Θ
111β	38° 42′	38° 50′
111α	43° 12′	43° 30′
200α	50° 18′	50°
220α	73° 52′	74°
311α	89° 40′	89° 50′
222α	94° 48′	94° 40′
331α	135° 40′	136° 10′
420α	144°	144° 10′

Summary

Tin added to a dilute, aqueous, hot, 1% solution of $CuSO_4{:}5H_2O$ containing less than 12 cc. of concentrated sulfuric acid per liter precipitates an alloy corresponding in composition and crystal structure to that of the Cu_3Sn phase prepared by fusion. When the solution contains more than 20 cc. of concentrated sulfuric acid per liter, an alloy corresponding in composition and crystal structure to that of the α-phase of the copper–tin system is precipitated.

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The Heat of Dilution and the Partial Molal Heat Capacity of Zinc Sulfate from the Electromotive Force of Galvanic Cells

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I. Introduction

Although the use of the Gibbs–Helmholtz equation has been recognized for many years as a reliable procedure for calculating changes in heat content in chemical processes from the e. m. f. measurements of galvanic cells, the applications have been restricted almost exclusively to processes involving displacement reactions between metals and their salts.

In spite of the renewed interest in the theoretical interpretation of the caloric properties of electrolytes in the region of high dilution, little use has been made of the method for the determination of heats of dilution of electrolytes in this important region.[2]

The paucity of galvanic cells which will yield reversible e. m. f.'s at the low concentrations necessary for an unambiguous extrapolation to infinite dilution is undoubtedly one reason for the neglect of the method. Skepticism of the reliability of methods involving differentiation for their numerical solution is another. The latter objection, however, is not peculiar to the e. m. f. method, for in the calorimetric method it is necessary to differentiate the measured integral heat of dilution in respect to concentration to calculate the partial molal quantity which is obtained in the e. m. f. method by differentiating the e. m. f. values with respect to temperature.

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(1) This is a second paper constructed from a dissertation submitted in December, 1930, by Irving A. Cowperthwaite to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. This paper was presented at the Buffalo (1931) meeting of the Society. The first paper appeared in THIS JOURNAL, **53**, 4333 (1931).

(2) Recently Harned and Nims [THIS JOURNAL, **54**, 423 (1932)] have computed the partial molal heat of dilution and partial molal heat capacity of sodium chloride solution from 0.05 *m* to 4 *m* against the reference state of the 0.1 *m* solution from e. m. f. measurements through the temperature range of 0–40°. See also Harned and Murphy, *ibid.*, **53**, 8 (1931); Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 392; Ellis, THIS JOURNAL, **38**, 737 (1916).