

ELECTROLYTIC CORROSION OF BRASSES IN SYNTHETIC SEA WATER.

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In a previous paper¹ there was presented the results of our investigation on the electrolytic corrosion of brasses in normal solutions of a number of simple salts, including sodium chloride, sodium sulphate, sodium acetate, sodium nitrate, sodium carbonate, ammonium nitrate, ammonium oxalate and acid ammonium oxalate. It was our intention to determine the corrosion in solutions of mixtures of various salts and particularly in sea water. In this paper we shall present the results obtained in the electrolytic corrosion of a number of brasses in synthetic sea water and in solutions of commercial bath salt.

The brasses employed were those prepared for the previous work and represented practically all of the stable solid solutions of copper-zinc alloys at 400° C, at which temperature they were annealed for several weeks, in order to insure equilibrium of these phases. For the preparation of these brasses, as well as for the details of the method employed in carrying out the electrolytic corrosion, reference must be had to the previous articles.²

In general, the method consisted in arranging the thirteen test pieces so that they could be corroded simultaneously. The brasses were the anodes and were rotated about 800 revolutions per minute, thus keeping the electrolyte thoroughly mixed. A current of about 0.03 ampere was passed through the solutions for about six to seven hours, and two copper coulometers were placed in series, and from these the current employed was ascertained. Platinum cathodes were used.

¹ Trans. of the Amer. Elec. Chem. Soc., **11**, 43 (1907). Jour. Phys. Chem. **11**, 501 (1907).

² I. c.

Corrosion in Bath Salt Solution

Solutions of commercial West India bath salt were prepared of approximately the concentration of sea water, *i. e.*, about 3.5 percent solution. The corrosion was run in triplicate and the data presented in Table 1 are characteristic. In the first column is given the percentage of copper in the test pieces; in the second column the number of grams the test pieces lost during corrosion; in the third column, the number of grams of copper in the corrosion product; in the fourth, the percent of copper found is of the total corrosion; while in the last column is given the so-called current efficiency, *i. e.*, the percent of copper and zinc dissolved was of the quantity that should have been dissolved by the current that was used.

TABLE 1

Percent Cu in test pieces	Gram of corrosion	Gram Cu in corrosion	Percent Cu in corrosion	Current efficiency
3.08	0.2155	0.0017	0.8	92.0
10.5	0.2096	0.0034	1.6	89.1
22.6	0.2083	0.0050	2.5	87.8
47.6	0.2026	0.0125	6.7	84.4
51.3	0.2565	0.0654	25.9	96.3
56.8	0.2827	0.0990	34.2	100.0
60.3	0.3302	0.2055	62.3	98.7
66.5	0.3420	0.2287	66.9	98.9
73.4	0.3595	0.2718	75.6	97.5
76.3	0.3664	0.2838	77.4	98.0
83.3	0.3901	0.3295	84.4	98.5
86.6	0.4019	0.3525	87.7	98.7
93.6	0.4249	0.4003	94.1	98.7

Copper deposited in coulometer = 0.2269 gram.

These results are represented diagrammatically in the figure by the curves designated Bath Salt. The amount of corrosion decreases with the decrease of copper content until brasses of about 53 percent copper are reached, when the corrosion remains practically constant for the remainder. The curve representing the copper in the corrosion shows

that the corrosion product from the brasses containing less than about 53 percent of copper consists practically of pure zinc. This accounts for the film of pure copper which appears on the 51.3 percent copper brass and which scales off readily. The percent of copper in the corrosion as represented in the next to the last column for the brasses containing α , β , and α and β crystals is practically the same as in the test pieces; but with the appearance of the γ solid solutions, the copper apparently ceases to dissolve and the corrosion consists almost exclusively of the solution of zinc. The current efficiency as given in the last column for the brasses high in copper, represents that the copper and zinc dissolve almost quantitatively. Where the corrosion consists chiefly of zinc, the current efficiency is low. The current efficiency is calculated upon the basis that the copper dissolves as cuprous copper and this has been confirmed in a series of experiments which we have carried out.

Corrosion in Synthetic Sea Water

According to Dittmar¹ the average of the total solids in the 160 samples of sea water collected by the Challenger expedition is 3.5 percent. He gives² the following average composition of the solids dissolved in sea water:

Chloride of sodium.....	77.758
Chloride of magnesium.....	10.878
Sulphate of magnesium.....	4.737
Sulphate of lime.....	3.600
Sulphate of potassium.....	2.465
Bromide of magnesium.....	0.217
Carbonate of lime.....	0.345
Total solids.....	100.000

This combination of acids and bases is an arbitrary one and in the preparation of our sample of synthetic sea water, the same combinations were retained except that the car-

¹ Geol. History of Lake Lahontan, U. S. G. S. Monograph, XI, Russel, p. 178.

² The Voyages of H. M. S. Challenger: Physics and Chem., 1, 204.

bonate was potassium carbonate instead of calcium carbonate, while the calcium was introduced as additional calcium sulphate, the potassium required for the potassium carbonate being deducted from the potassium sulphate and the calcium sulphate substituted. Otherwise the sample of sea water was prepared by employing the salts listed, and the quantities taken sufficient to make a solution containing 3.5 percent of solids, the concentration of sea water.

The electrolytic corrosion was carried out in the manner previously described, and the data given in Table 2 are the results of one of the duplicate determinations. The headings of the columns are the same as in the other tables and are self-explanatory.

TABLE 2

Percent Cu in test pieces	Gram of corrosion	Gram Cu in corrosion	Percent Cu in corrosion	Current efficiency
3.08	0.2140	0.0009	0.45	92.2
10.5	0.1858	0.0012	0.65	80.0
22.6	0.2057	0.0015	0.73	88.6
47.6	0.2118	0.0031	1.5	90.8
51.3	0.2513	0.0405	16.1	100.0
56.8	0.3040	0.1428	46.9	101.4
60.3	0.3295	0.2044	62.0	99.4
66.5	0.3424	0.2243	65.6	100.8
73.4	0.3619	0.2660	73.5	100.5
76.3	0.3679	0.2720	76.1	101.8
83.3	0.3917	0.3251	83.0	100.9
86.6	0.4020	0.3459	86.0	101.0
93.6	0.3485	0.3239	93.0	82.5

Copper deposited in coulometer = 0.2253 gram.

The curve marked Synthetic Salt No. 1 in the figure represents diagrammatically the data given in Table 2. These curves, as well as the others, have been smoothed and while no values were obtained for brasses of compositions between 47 and 22 percent copper, the curves have been drawn continuous.

Another series of corrosions was run in a synthetic sea

water wherein iodine was substituted for bromine. The iodine was introduced as potassium iodide and the other necessary adjustments of the quantities of the constituents calculated so that a 3.5 percent solution was prepared. The data obtained from the results of these corrosions in this solution are represented by the series given in Table 3.

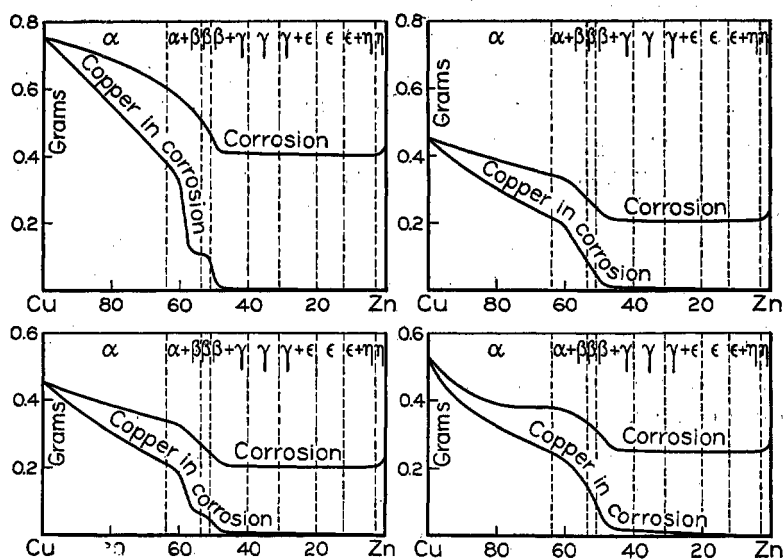
TABLE 3

Percent Cu in test pieces	Gram of corrosion	Gram Cu in corrosion	Percent Cu in corrosion	Current efficiency
3.08	0.2647	0.0016	0.62	98.3
10.5	0.2173	0.0028	1.3	80.4
22.6	0.2538	0.0083	3.5	93.1
47.6	0.2613	0.0260	9.9	86.6
51.3	0.3488	0.1438	41.2	103.8
56.8	0.3535	0.1888	53.6	97.5
60.3	0.3804	0.2420	63.6	97.9
66.5	0.3774	0.2520	66.8	95.0
73.4	0.3781	0.2845	75.3	89.3
76.3	0.3805	0.2835	76.6	90.4
83.3	0.4081	0.3450	84.5	89.5
86.6	0.4092	0.3585	87.6	87.5

Copper deposited in coulometer = 0.2612 gram.

The curves labeled Synthetic Salt No. 2 represent diagrammatically, as do the other curves, the relation of the grams of corrosion, the grams of copper in the corrosion product and the variation of these with the change in the concentration of the brasses. The vertical dotted lines represent the boundaries of the different solid solutions.

The upper curve in these diagrams represents a decrease in the amount of corrosion with the decrease in the copper content of the brasses. In some of the determinations there seemed to be a tendency for the amount of corrosion of the sample of brass of the highest copper content to be lower than that found for brasses of lower copper content. In order to determine whether this was real or not, a number of determinations of the amount of corrosion of the three highest copper brasses were made in the two synthetic salts and the



Upper figure, left : Sodium Chloride.

Upper figure, right : Synthetic Sea Salt, No. 1.

Lower figure, left : Bath Salt.

Lower figure, right : Synthetic Sea Salt, No. 2.

bath salt. The data given in Table 4 represents the results of these numerous determinations.

TABLE 4

Percent Cu in test pieces	Gram of corrosion		
	Synthetic salt No. 1	Synthetic salt No. 2	Bath salt
93.6	0.3681	0.3564	0.3713
86.6	0.3613	0.3483	0.3448
83.3	0.3460	0.3447	0.3379

These values show conclusively that the amount of corrosion increases with the increase in the copper content of the brass.

In the figure the curves for the corrosion of the brasses as determined in normal sodium chloride solutions are given

for comparison. It will be readily observed that the general form of the curve representing the grams of corrosion in the sodium chloride solution is the same as that for the synthetic sea waters and for the bath salt solutions. The curve representing the grams of copper in the corrosion product is similar in all four cases. With the appearance of γ crystals, the copper in the corrosion product drops nearly to zero; and for the brasses, the copper content of which is less than about 53 percent copper, the corrosion product is practically pure zinc. Therefore, we may conclude that the corrosion of these samples of brasses is practically the same in the synthetic sea water and in solutions of bath salt as in pure sodium chloride solutions.

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