THE ELECTROLYTIC CORROSION OF THE COPPER-ALUMINUM ALLOYS

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B. E. Curry¹ has determined the constitution of the aluminum bronzes. He has shown that on annealing to equilibrium at 500°, the alloy from pure copper to pure aluminum consists of five phases. The five phases are four solid solutions and one compound CuAl_2 , as appears from the concentration-temperature diagram, Fig. 1.

From 100 percent to 91 percent copper there exists the α phase; from 91 percent to 84 percent copper a mixture of the α and γ phases; from 84 percent to 79.5 percent pure γ ; from 79.5 percent to 75.5 percent γ and ϵ ; from 75.5 percent

Fig. 1

to 73 percent ϵ ; from 73 percent to 54 percent a mixture of ϵ and the compound CuAl_2 ; from 54 percent to 10.75 percent CuAl_2 and η ; and from 10.75 percent to 0 percent copper the pure η phase.

¹ Jour. Phys. Chem., 11, 425 (1907).

Annealed to 610° , the α phase exists from 100 percent copper to 91 percent. From 91 percent to 87.5 percent there is a mixture of the α and β phases, and from 87.5 percent to 84 percent the field is made up of the β and the γ phases. Below 84 percent the γ phase exists alone until 79.5 percent copper is reached.

Up to the present time very little has been done in commercial practice with these bronzes. They have remarkably fine properties in some percents of copper but the practical metallurgists seem to be very slow in taking advantage of them. This is partly due to the great variety of physical properties which are met with in the varying percents of copper, owing to the changes in the nature of the phases. Certain alloys are extremely brittle, almost crumbly, so that it requires the greatest care in handling them. Other alloys are extremely tough. Throughout the field the greatest variety of ductility can be obtained.

In a paper on the tensile strengths of the aluminum bronzes B. E. Curry¹ has given some very interesting data on the physical properties of the alloys.

Another difficulty up to the present time which seems to stand in the way of commercial work with the copper-aluminum alloy, has been in the casting, but it would seem that if the proper kind of moulds were used and care be taken not to "burn" the metal, little trouble should be encountered.

In the following pages it is hoped that some idea may be given of the relative solubility of the different phases of the aluminum bronzes in solutions of some of the more common sodium salts.

At first it was intended to make corrosions with the following percents of copper, 5, 10, 15, 25, 35, 45, 50, 55, 60, 65, 73, 79, 84, 85, 87, 88, 89, 90, 91 and 96, annealed at 500° , but as the work progressed it was found necessary to run other percents than those mentioned above in order more clearly to describe the corrosion of the various phases.

¹ Curry and Woods: Jour. Phys. Chem., 11, 461 (1907).

Alloys with 84, 85, 87, 88, 89 and 90 percent of copper were annealed at 610° to show the comparative corrosion in the $\alpha + \beta$ and $\beta + \gamma$ fields. It was found impossible to quench alloys below 83 percent of copper from 610° on account of the great brittleness of the γ phase and therefore corrosion of pieces, annealed at 610° and containing less than 83 percent copper, had to be omitted.

The alloys were made of electrolytic copper and 99.99 percent aluminum.¹ An ordinary gas blast furnace was used. The crucibles were made from Acheson graphite. Up to about 50 percent the aluminum was first melted under powdered carbon and the copper then added. With higher percents of copper, the copper was melted first. Powdered graphite was kept upon the surface of the melt. The castings were made in graphite moulds containing places for about five test pieces. Usually about 12 pieces were made from each cast. Working with graphite moulds and crucibles kept the alloy from contamination and there was seldom any difficulty experienced in getting clean and homogeneous castings. The crucibles were made by boring out a solid rod of graphite, about five inches in diameter, leaving a wall about one-half inch in thickness and a base of about three inches in height. This solid base allowed the blast to heat the crucible in a very satisfactory manner, without being driven directly against the walls, and thus considerably prolonged its life.

In the annealing, a nickel wire resistance furnace was used in which the temperature could be maintained very accurately at the degree desired by means of varying external resistance. At 610° about two hours time was sufficient to bring the phases to equilibrium. These pieces were quenched from that temperature in ice water. The pieces annealed at 500° were held at that temperature for five hours after repeated trials. It was found impossible to quench alloys of from 84 percent to 54 percent copper, and keep them from

¹ Presented by Aluminum Co. of America.

breaking, either as they were being quenched or as they were being cleaned. The γ and ϵ and the pure CuAl_2 phases are extremely brittle and test pieces containing these crystals can easily be fractured with a slight blow. Test pieces with the above percents of copper were therefore slow-cooled in the furnace after which they could be handled fairly satisfactorily, although still very brittle.

Curry's diagram does not cover temperatures below 400° but it is doubtful if any phase changes take place below that temperature and therefore slow-cooling from 500° probably answers the purpose. The work had to be done in this way or the corrosions from 54 percent to 84 percent copper omitted altogether.

Pieces containing from 100 percent to 84 percent and from 54 percent to 0 percent were quenched from 500° .

After annealing, the test pieces were cleaned on a carborundum wheel, care being taken to remove all oxide films. If necessary, they were afterwards smoothed off with a carborundum paper.

The test pieces were about 8 cm long and 0.8 cm in diameter. They were rotated during the corrosion at a rate sufficiently rapid to prevent any hydroxide film from adhering to them. This was accomplished by using small Ajax motor frames, so arranged that they could be rotated uniformly from a main shaft, which in turn was belted to a motor. The test pieces were attached to the motor shafts by binding posts. Each machine held five test pieces.

Later a machine was devised along the above lines and built by Messrs. Thomas and Grant, of Ithaca, N. Y. The whole apparatus was made heavier and more stable, and is arranged so that the speed may be varied. It is driven by a Westinghouse A. C. fan motor. As with the first machine used, the five sets are wired in series, but each set has a two-way switch attached so that any one of them may be cut out of the series without interrupting the current in the others. This was found of great convenience in cases where any one

test piece became aluic¹ and had to be cut out of the circuit.

A current of 35 milamperes was passed through the solutions for from seven to nine hours. At first an attempt was made to maintain the current constant throughout the entire time so that on each corrosion 280 milamp. hours would be used, but this was found very difficult to accomplish and therefore the 280 milamp. hours was in most cases only approximated. This is in reality of little moment for all the efficiency calculations are based upon the gain in weight of the cathode in a copper coulometer solution which is assumed to have 100 percent current efficiency.

The current efficiency curves which follow were obtained in the following manner with the one exception as noted under the corrosion in the sodium sulphate solution. A copper coulometer solution with copper electrodes was placed in series with each set of corrossions. The gain in weight of the cathode was taken as representing 100 percent current efficiency, and the efficiencies of the corrossions with the various percentage test pieces were obtained by using an electrolytic equivalent for each particular percentage and comparing it with the cathode coulometer gain. In these calculations aluminum was taken as trivalent while copper was made bivalent, except in the NaCl solution where it was taken as univalent, for it is well known that in chloride solutions copper dissolves in the cuprous form.

Inasmuch as in practically every case where there is the formation of hydroxides which are precipitated, there is a

¹ Up to the present the word "passive" has been used to signify a condition such that a metal as anode did not dissolve, even although the current continued to flow. A case of this is that of iron going passive in concentric nitric acid. The term has also been applied to an aluminum anode in a sulphuric acid solution but here the aluminum not only does not dissolve but also, by the formation of an oxide film, prevents the further flow of the current. To differentiate between these two conditions the word aluic will be used for the second case, that is, where the metal neither dissolves nor allows the passage of a current. Aluic is from the Greek word *ἄλω* meaning to flow, with the α signifying the negative, that is, non-flowing.

certain amount of acid occluded in the precipitate, there was a tendency in all such instances for the solution to turn alkaline at some time during the run.¹ Theoretically, in a case for instance, where there is little solution taking place at the anode, there is formed at that electrode free acid, as

and at the cathode, in a Na_2SO_4 solution,

and then as the acid and the base diffuse through the solution they again unite to neutralize each other. But with the electrolysis of a solution which attacks the anode, the NaOH from the cathode precipitates the hydroxide of the metal dissolved and there is a certain amount of the acid radical occluded in this precipitate. This of course leaves a certain amount of free base for which there is no acid radical, with the result that the solution becomes alkaline.

Looking ahead to Table 1 of the corrosion in NaOH it will be seen that both the CuAl_2 and the η phases are soluble, and therefore the values for the corrosion of those phases may be raised very considerably in the cases where the solutions have turned alkaline. The amount of solution in the sodium hydroxide depends of course upon its concentration which in turn depends upon the amount of acid occluded in the hydroxides precipitated. It further depends upon the time of the run, the speed of rotation, etc., etc., and as it was impossible to keep these factors absolutely constant, the points obtained in the efficiency curves below 73 percent copper cannot be absolutely comparable. It was deemed wise, however, to draw the curves as best possible with the data obtained, and in some cases dotted lines have been drawn to show the direction of the actual current efficiency values.

The corrosions were done in heavy beakers, containing about 200 cc of the solution. Platinum wire was used for the cathodes.

¹ Cf. Pickering: *Jour. Chem. Soc.*, 91, 1981 (1907).

Corrosions of pieces annealed at 500° were done in the following solutions: 7 percent NaOH, 7 percent Na_2SO_4 , 7 percent NaCl, 7 percent NaNO_3 , 7 percent Na_2CO_3 , 7 percent CH_3COONa , 3 percent $(\text{COO})_2\text{Na}_2$ + 3 percent $(\text{COOH})_2$, and 7 percent $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2$ + 3 percent NaOH. Corrosions of pieces annealed at 610° were done in the chloride, sulphate and nitrate solutions.¹

After the run the test pieces were removed and cleaned of any adherent oxide or film. This was accomplished by a few minutes work with a rubber-tipped glass rod. In certain cases it was found very difficult to remove all of the oxides without also scraping off some of the uncorroded portions.

In cases where there were non-removable oxides left on the test piece or where the finely divided copper which was left on a copper-rich surface had been oxidized by the air, reduction was effected by heating the pieces in a combustion tube through which a stream of hydrogen was passed.

With test pieces containing two phases, one of which is present in greater proportion than the other (and this, of course, occurs on the border of certain fields), and where one phase is soluble and the other insoluble or comparatively so, there is apt to be a solution of the more soluble phase such that it is completely dissolved from around the other phase and then that less soluble phase is mechanically dislodged from the test piece by the rotating motion. In this case one of two things may happen. The dislodged crystals may remain undissolved in the bottom of the beaker or they may after a time go into solution by chemical action independent of the electrolysis. Further, if they are dissolved, they may go into solution either quantitatively, or the copper or the aluminum be dissolved out and the remainder, being left in a very finely divided state, may be precipitated as the hydroxide, if the solution has turned alkaline during the run. This "falling off" tendency is most apt to take place near

¹ The greater part of the corrosions in the chloride, sulphate, nitrate and hydroxide solutions were made by R. B. Roe.

the edge of a field, and unless care is taken in the work, it may cause results which are higher than the actual efficiency values.

When the efficiency values run over 100 percent there is evidence of one of three things having happened. Either there has been a "falling off" of a relatively insoluble phase, or there has been chemical action upon the test piece in addition to that produced by the electrolysis, or possibly the copper or aluminum or both are dissolving with some valence lower than that upon which the efficiency is being calculated. It is very unlikely that this last case would occur. Unfortunately, with all percents of copper below 73 percent, and "falling off" could not be detected unless it were the ϵ phase, for both the CuAl_2 and the η phases are soluble in the alkaline solution, which is in most cases formed when there are hydroxides precipitated.

As a matter of experiment no cases were noted where there was any apparent dislodgement of crystals, except in some of the most brittle alloys and here it was due more to their crumbly nature. The runs in these cases were repeated and if the second time unsuccessful the data were omitted.

Any deposit on the platinum cathode was dissolved in nitric acid upon completion of the run and the whole solution made slightly acid with HNO_3 and H_2SO_4 . These solutions were then electrolyzed, the copper being deposited upon rotating platinum electrodes. The machine which was used for the corrosion was also used for the analyses. With the solutions of the organic compounds, it was found very difficult to get good deposits from acid solutions. It was found necessary first to deposit the copper from an ammoniacal solution and then to redissolve in and redeposit from a nitric-sulphuric acid solution. In this way very good deposits were obtained.

During the runs the presence of precipitates, oxide films, cathode deposits, etc., etc., was carefully noted and this was found of great use in explaining certain of the data which appeared abnormal.

Electrolytic Corrosion in Sodium Hydroxide Solution

In Table I are given the data obtained from the corrosion in a 7 percent solution of NaOH. The first column represents the percent of copper in the test piece, the second the corrosion in grams, which is obtained by weighing the test piece before and after the corrosion. The third column contains the amounts of copper corroded including that, if any, which was deposited upon the cathode, and the fourth column contains the percentage of copper dissolved to the total corrosion.

TABLE I
Corrosion in 7 percent sodium hydroxide solution

Percent of Cu in test piece	Corrosion in gram	Copper corroded in gram	Percent of copper corroded
0.0	0.1855	0	0
4.5	0.2439	0.0089	3.64
10.0	0.2168	0.0161	7.43
15.1	0.2862	0.0382	13.32
25.0	0.2406	0.0473	19.66
35.2	0.2873	0.0816	28.40
45.6	0.3739	0.1446	38.67
50.5	0.3410	0.1149	33.69
51.9	0.3526	0.1138	32.27
58.8	0.0920	trace	—
72.3	0.0062	0.0013	—
74.3	0.0053	0.0022	—
77.2	0.0050	0.0025	—
83.6	0.0063	0.0023	—
84.2	0.0020	0.0007	—
86.4	0.0019	0.0007	—
87.4	0.0016	0.0010	—
89.5	0.0019	0.0010	—
90.1	0.0022	0.0016	—
96.0	0.0031	0.0023	—

The principle item of note in this corrosion is the fact that the η and the CuAl_2 phases are the only ones which dissolve in NaOH. The corrosion practically reaches a maximum at 54 percent copper, where CuAl_2 exists alone. With the introduction of the ϵ phase it drops off very considerably

and from then on through the higher percents of copper the corrosion is practically zero.

From the fact that no copper is obtained from the corrosion in the $\epsilon + \text{CuAl}_2$ field, it would appear that the copper corroded comes entirely from the η phase, and yet the percentage of copper to the total corrosion increases with the amount of copper in the test piece. This makes it impossible for the copper to come entirely from the η phase for two reasons. First the η phase has only 10.75 percent of copper in it throughout the $\text{CuAl}_2 + \eta$ field and say in a 52 percent test piece, there would not be enough copper in the η phase present at that percent to furnish 32 percent of copper in the entire amount corroded, which is the result obtained experimentally. Secondly to have the percentage of copper in the solution constantly increasing across a field consisting of two phases where each has a constant composition but vary in ratio to each other, the phase from which the copper is dissolved must be the one which is constantly increasing. The amount of this last phase dissolved will also increase proportionately to the increase in copper in the test piece. The test piece would then be copper-rich at the end of the run while all the test pieces from 4.5 percent to 58.8 percent were corroded copper-rich in the sodium hydroxide solution.

It seems then that the copper must come from the CuAl_2 phase although no copper was obtained from that phase in the field of $\epsilon + \text{CuAl}_2$. The only explanation is that the presence of the η phase permits the solution of the CuAl_2 from which the copper must have come.

The fact that only the CuAl_2 and η phases are soluble in NaOH gives considerable aid in explaining the data obtained in the corrosion of the bronzes by the alkaline tartrate solution and also in other solutions where the occlusion of acid by the precipitated hydroxides caused the solutions to go alkaline during the run.

There was no coulometer solution run in series with these corrosions and therefore no current efficiency curves can be drawn.

Electrolytic Corrosion in Sodium Sulphate Solution

The curves shown in Figs. 2 and 3 represent the current efficiency of the corrosion of the bronzes obtained by two different methods of calculation. The data from which these efficiencies are calculated is given in Table 2.

In this table, as in all following tables, with one omission mentioned later on, the first column represents the percent of copper in the test piece corroded. The second column gives the corrosion in grams and the third column contains the gain in weight of the cathode in the coulometer solution upon which, taken as 100 percent, is based the efficiency of the corrosion. The next two columns give the efficiencies as described in the following paragraphs. The sixth column gives the amount of copper in the solution after the corrosion together with that, if any, which was deposited on the cathode, and the last column gives the percent of copper to the total corrosion.

TABLE 2
Corrosion in 7 percent sodium sulphate solution

Percentage copper in test piece	Corrosion in gram	Coulom. cathode gain in gram	Percent efficiency by composition of test piece	Percent efficiency by analysis of solution	Copper corroded in gram	Percent of copper corroded
10.0	0.0451	0.3453	36.74	26.99	0.0125	27.71
15.1	0.0408	0.3453	29.76	24.31	0.0114	27.94
25.0	0.0364	0.3453	22.72	20.01	0.0123	33.79
35.2	0.0352	0.3149	20.78	20.07	0.0134	38.08
45.6	0.0401	0.3149	20.84	22.26	0.0161	40.14
55.0	0.0430	0.3023	20.95	24.03	0.0196	43.00
65.4	0.0703	0.3068	30.00	31.30	0.0460	63.00
72.3	0.1334	0.3337	49.78	51.39	0.0908	68.08
74.8	0.1200	0.3068	45.9	50.00	0.0892	74.30
76.0	0.1082	0.2638	49.47	56.55	0.0667	61.70
78.9	0.1210	0.2661	53.43	59.28	0.0815	67.30
80.0	0.0854	0.2213	45.00	46.21	0.0660	77.28
83.6	0.1877	0.3480	61.09	61.71	0.1545	82.31
84.2	0.2945	0.3888	85.49	84.35	0.2523	85.67
86.4	0.3154	0.3888	89.83	90.04	0.2713	86.01
89.5	0.3209	0.3888	89.13	89.94	0.2884	89.87
90.1	0.2933	0.3480	90.53	90.04	0.2658	90.62
96.0	0.3426	0.3480	103.0	102.9	0.3220	94.0

Fig. 2 represents the efficiency as calculated similarly to the remaining efficiency curves shown in this paper and previously described. While this curve represents the change in the corrosion with the changes in the phases, it is based upon the percentage of copper in the alloy involved. That is to say an electrochemical equivalent has been calculated in each case for each percentage. In Fig. 3 the electrochemical equivalent is calculated from the percentage of copper in the solution and on the cathode at the end of the run.

Fig. 2—Sodium sulphate solution

Fig. 3—Sodium sulphate solution

Both curves have practically the same turning points. It so happened that the percents of copper to the total corrosion held a fairly constant relation to the actual percentage of copper in the test piece corroded and only where there is a marked variation in the two percents, will the curves vary.

While in reality the current efficiency curves should be based upon the composition of the solution after corrosion, which is, of course, the composition of that part of the alloy which is dissolved, it would be difficult to get the correct efficiencies by this method due to the variations in the percents of copper corroded to the total corrosion. For this reason the curves which follow are obtained upon the basis of the actual composition of the alloy. The data for the other calculation are given and the efficiencies may be calculated if desired.

In the sulphate solution, Fig. 2, the α phase is the most soluble, with a decreasing efficiency with the decrease in its percent of copper. The efficiency gradually falls through the $\alpha + \gamma$ field with the disappearance of the α phase. With pure γ it is 60 percent. It continues to fall with the decreasing amount of copper in the γ phase.

The alloy dissolves almost according to its composition through the α , $\alpha + \gamma$ and γ fields. The appearance of the ϵ phase increases the efficiency, it being more soluble than the γ . It might be expected that changing on to pure γ might still further increase the efficiency, but in reality it drops off. This is probably due to the increasing aluminum content through the pure ϵ field.

The fact that the ϵ phase dissolves slightly copper-rich tends to increase the efficiency when based upon the analysis of the solution after corrosion. This is the only place where the two curves differ materially and here the difference is small.

Whenever there is the formation and precipitation of hydroxides, this is accompanied by the occlusion of acid, as explained before and the consequent formation of an alkaline solution with the NaOH produced at the cathode. In the NaOH both the CuAl_2 and η phases are soluble, the pure η probably more so than the pure CuAl_2 and for some reason not yet determined, the mixture of the two is more soluble than either. It is therefore impossible to do much more than to plot the results obtained and to state that the percents of copper in the solutions are influenced by the chemical corro-

sion of the sodium hydroxide as well as by the solution by the acid ion. However, it is made quite certain, by a comparison with Table 1 for the NaOH, that there is a solution of the CuAl_2 phase and also possibly of the η phase from the $\text{CuAl}_2 + \eta$ field in the sulphate solution. The high percents of copper obtained in the solution from the corrosion of the 10 percent, 15 percent and 25 percent copper pieces shows that the CuAl_2 must form the major part of the dissolved portion, and it is problematical as to whether the η phase is dissolved in the sulphate solution. Its solution in these runs may have been entirely due to action of the unneutralized NaOH.

At 45 percent the curve begins to decline less rapidly and at 35 percent reaches a minimum. From then on to the 10 percent composition in the η field it continues to rise, but it was impossible to any data on a 5 percent piece as it became aluic and no current could be sent through. The true electrolytic efficiency curve, if the alkalinity had been avoided, would probably go as indicated by the dotted line, running down to 0 percent with pure aluminum.

Electrolytic Corrosion in Sodium Nitrate Solution

Table 3 and Fig. 4 show the data and efficiency curve for the corrosion of the aluminum bronzes in a 7 percent solution of sodium nitrate. The α phase has the greatest solubility. This decreases slightly with the decrease in the amount of copper present. The γ and ϵ phases are considerably less soluble as shown by the rapid drop in the efficiency across the γ and the $\gamma + \epsilon$ fields. With the disappearance of the γ phase, the efficiency rises slightly and remains almost constant across the $\epsilon + \text{CuAl}_2$ field. Here the efficiency values first curve downward, reaching a minimum at 35 percent copper and then rapidly rise to 95 percent efficiency with the 5 percent copper. As in other cases, the great increase in the efficiency is largely due to the chemical corrosion of the NaOH after the solution has gone alkaline. The actual current efficiency would probably go as indicated by the dotted line.

The phases throughout dissolve almost quantitatively, with the exception of the γ phase which dissolves copper-rich.

TABLE 3
Corrosion in 7 percent sodium nitrate solution

Percent of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percentage current efficiency	Copper corroded in gram	Percent of copper corroded
4.5	0.0996	0.3336	94.03	0.0072	7.22
10.0	0.0759	0.3336	64.0	0.0123	16.21
15.1	0.0653	0.3336	49.3	0.0129	19.75
25.0	0.0591	0.3336	38.18	0.0141	23.86
35.2	0.0640	0.3336	35.66	0.0217	33.91
45.6	0.0805	0.3562	36.99	0.0242	30.06
50.5	0.0941	0.3562	40.83	0.0476	50.58
55.0	0.0822	0.3023	40.05	0.0460	55.90
72.3	0.1253	0.3733	41.80	0.0908	72.46
74.3	0.1367	0.3733	44.82	0.0979	71.61
74.8	0.1220	0.3068	50.00	0.0831	68.10
76.0	0.0876	0.3253	32.48	0.0642	73.29
77.0	0.0697	0.2936	28.40	0.0519	74.40
78.9	0.1002	0.2661	44.24	0.0652	65.00
80.0	0.0733	0.2213	38.63	0.0572	78.00
83.6	0.1881	0.3733	57.06	0.1573	83.60
84.2	0.2180	0.2985	82.43	0.1838	84.30
85.8	0.2298	0.3023	84.45	0.1964	89.90
86.4	0.2409	0.2985	89.38	0.2151	89.29
89.5	0.2741	0.3345	88.58	0.2458	89.67
90.0	0.2912	0.3480	89.82	0.2649	90.97
96.0	0.2498	0.3480	93.17	0.2440	97.60

Fig. 4—Sodium nitrate solution

Electrolytic Corrosion in Sodium Chloride Solution

In Table 4 are given the results obtained from corrosion in a 7 percent solution of sodium chloride.

TABLE 4
Corrosion in 7 percent sodium chloride

Percentage of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent current efficiency	Copper corroded in gram	Percent copper corroded
4.5	0.1000	0.3808	72.5	0	0
10.0	0.0943	0.3808	54.3	0	0
15.1	0.0316	0.3808	15.4	0	0
26.0	0.0265	0.3808	9.6	0	0
35.2	0.0579	0.3808	24.1	0	0
45.6	0.0511	0.2734	17.7	trace	—
50.5	0.0337	0.2734	6.4	trace	—
51.9	0.0207	0.2734	10.9	trace	—
58.8	0.0555	0.2734	15.6	trace	—
74.8	0.1222	0.3068	25.4	0.0323	26.4
78.9	0.1084	0.2661	24.8	0.0345	31.8
80.0	0.1049	0.2213	28.5	0.0400	38.1
82.0	0.1257	0.2768	26.8	0.0442	35.1
83.6	0.1607	0.3194	29.2	0.0766	47.7
86.4	0.2124	0.3665	32.7	0.1291	60.78
87.4	0.2648	0.3665	40.4	0.1895	71.56
89.5	0.4422	0.3665	66.2	0.3885	87.85
90.0	0.4544	0.3487	71.1	0.4126	90.8
96.0	0.5623	0.3487	83.4	0.5345	95.1

As shown in Fig. 5, the α phase dissolves with the highest efficiency. Its solubility decreases with the decrease in the copper content of the bronze. The γ phase is relatively insoluble and from pure α to pure γ in the $\alpha + \gamma$ field the efficiency drops from 70 percent to about 28 percent. Throughout the γ , the $\gamma + \epsilon$ and ϵ fields the efficiency drops off slightly and continues to fall through the $\epsilon + \text{CuAl}_2$ field. From here on and even in the $\epsilon + \text{CuAl}_2$ fields the efficiency is problematical, for the solutions going alkaline had a chemical effect upon the CuAl_2 and η phases. A dotted line represents what is probably the actual current efficiency.

The α phase dissolves practically quantitatively, but the γ and ϵ phases dissolve copper-rich and the copper in the CuAl_2 and η phases does not dissolve at all.

From 0 percent copper to where the ϵ phase exists pure, the corroded pieces were left at the end of the run with the copper very finely divided, on account of the aluminum having been dissolved out. On standing a short time the copper was oxidized in the air. The copper oxide then

Fig. 5—Sodium chloride solution

powdered and was inclined to fall off of the test piece. In each case the test piece and the oxide were reduced in order to obtain the exact weight of the test piece as it was immediately after the corrosion.

It is interesting to note the following losses in weight of certain test pieces which had been allowed to stand three days until the copper was completely oxidized. At the end of that time the oxides were scraped off, leaving the test piece clean. In some cases a very considerable portion of the test piece had been corroded.

Percent of copper in test piece	Actual loss in gram	Loss with copper cleaned off
35.1	0.0579	0.1133
45.5	0.0511	1.5433
50.5	0.0337	1.0895
51.9	0.0207	1.0601
58.8	0.0555	0.8231

The actual loss was obtained from weighings made immediately after the test pieces were removed from the corroding solutions.

The efficiencies given for the sodium chloride solution are based upon the copper dissolving as cuprous chloride.

Electrolytic Corrosion in Sodium Carbonate Solution

Starting at 100 percent aluminum the efficiency of the corrosion of the aluminum bronzes in a 7 percent sodium carbonate solution is practically zero until the ϵ phase is reached. The solutions do not go alkaline at any stage of the corrosion and there is consequently no chemical action by NaOH. The efficiency as shown by Table 5 remains constant at about 10 percent through the $\gamma + \epsilon$ phase. The α phase is somewhat more soluble, the maximum efficiency being 20 percent at pure γ .

The CuAl_2 and η phases become aluic and it was impossible to pass any current through the test pieces having composition in the $\text{CuAl}_2 + \eta$ and the η fields.

TABLE 5
Corrosion in 7 percent sodium carbonate solution

Percent of copper in test piece	Total corrosion in grams	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
4.5	0.0019	0.0172 ¹	—	0	—
10.0	0.0035	0.0172 ¹	—	0	—
15.1	0.0006	0.0172 ¹	—	trace	—
25.0	0.0045	0.0172 ¹	—	0.0018	—
35.2	0.0011	0.2350	—	0.0015	—
45.6	0.0045	0.0172 ¹	—	0.0032	—
50.5	0.0054	0.2930	—	0.0043	—
58.8	0.0065	0.2930	—	0.0052	—
72.0	0.0108	0.2930	4.60	0.0055	—
73.0	0.0121	0.2084	7.19	0.0079	65.29
75.3	0.0206	0.2985	8.55	0.0149	72.32
84.2	0.0272	0.3162	9.71	0.0167	81.07
84.5	0.0243	0.2985	9.16	0.0197	61.40
86.4	0.0277	0.2350	13.04	0.0275	99.28
85.6	0.0485	0.3192	16.49	0.0371	76.50
90.1	0.0515	0.3192	17.33	0.0485	94.06

¹ Impossible to get more current through, using entire battery voltage of 28 volts.

There was no hydroxide precipitated in any of the runs, the copper dissolving as sodium copper carbonate, giving a clear blue color to the solution.

The efficiency curve was not of enough importance to be shown.

Electrolytic Corrosion in Sodium Acetate Solution

From Table 6, showing the results obtained by the corrosion of the aluminum bronzes in a 7 percent solution of sodium acetate, and from the efficiency curve, Fig. 6, it can be seen that the ϵ , CuAl_2 and η phases are practically insoluble, the efficiency running between zero and 7 percent by experiment. With the introduction of the γ phase, however, it rises to about 12 percent or 13 percent increases to 19 percent with nearly pure α . With the increase in the copper in the α phase, the efficiency continues to rise, reaching about 50 percent with the 96 percent bronze.

TABLE 6
7 percent sodium acetate solution

Percent copper in test piece	Total corrosion in gram	Coulometer cathode gain in gram	Percent current efficiency	Copper corroded grams	Percent copper corroded
4.5	0.0014	0.1684	2.6	0	0
10.0	0.0047	0.2930	4.5	0	0
15.1	0.1508	0.3426	11.1	0.0187	12.4
35.2	0.0038	0.2930	2.4	0.0027	—
45.6	0.0024	0.2975	1.3	0.0010	—
50.5	0.0084	0.1684	7.7	0.0050	—
58.8	0.0055	0.2975	2.6	0.0093	—
65.4	0.0145	0.3426	3.8	0.0016	—
72.0	0.0035	0.3162	1.4	0.0000	0
73.0	0.0100	0.2084	4.0	0.0014	—
77.2	0.0196	0.3162	7.9	0.0012	—
78.9	0.0098	0.2936	3.9	0.0048	—
80.0	0.0075	0.2936	3.0	0.0048	—
82.0	0.0089	0.2768	3.6	0.0065	—
85.8	0.0321	0.3023	11.8	0.0291	90.0
87.4	0.0327	0.2602	13.9	0.0288	88.1
89.5	0.0346	0.2602	14.35	0.0256	74.0
90.1	0.0442	0.2602	18.25	0.0377	85.3
96.0	0.1181	0.2350	51.67	0.1056	89.4

As in the carbonate solution, the test pieces with a high percent of aluminum had a tendency to become aluic and no current could be passed through some of them. Where the efficiency runs very low, the total amounts corroded are too

Fig 6—Sodium acetate

small to make the figures much more than indicative of the fact that there is a general tendency in all but the α phase not to dissolve in the acetate solution.

The solutions in all but the 96 percent test piece and those which became aluic early in the run, were all colored blue by the presence of the copper acetate. There was a slight hydroxide precipitate with the 96 percent copper piece.

The high result for the 15.1 percent piece is unaccounted for.

Electrolytic Corrosion in Acid Ammonium Oxalate Solution

Fig. 7 represents the efficiency curve of the solution of the aluminum bronzes in a solution of 7 percent ammonium

Fig. 7—Acid oxalate solution

oxalate and 3 percent oxalic acid, which was obtained from data in the following table.

TABLE 7
Corrosion in 7 percent sodium oxalate and 3 percent oxalic acid

Percent copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent of current efficiency	Gram of copper corroded	Percent of copper corroded
11.0	0.0054	0.2213	6.7	0.0013	—
15.1	0.0115	0.2638	11.2	T ₂	—
35.2	0.0310	0.3151	18.29	0.0053	—
45.6	0.0234	0.1648	23.24	0.0026	—
58.8	0.0394	0.3154	17.7	0.0077	19.5
65.4	0.0455	0.3154	19.1	0.0261	57.4
71.8	0.0306	0.2795	13.7	0.0119	38.9
73.0	0.0479	0.3154	19.4	0.0216	45.1
76.0	0.0371	0.2638	17.0	0.0246	66.3
77.0	0.0422	0.2936	17.2	0.0278	65.9
78.9	0.0651	0.2661	28.8	0.0444	68.2
80.0	0.0486	0.2213	25.6	0.0338	73.7
83.6	0.1906	0.2792	77.3	0.1542	80.9
84.2	0.2576	0.3154	90.1	0.2022	78.5
86.4	0.2454	0.2792	97.3	0.2069	84.3
87.4	0.2457	0.2792	96.9	0.2041	83.1
89.5	0.2526	0.2792	97.7	0.2155	85.3
90.1	0.2833	0.3147	98.1	0.2464	87.0
96.0	0.2762	0.3147	90.7	0.2558	92.6

The α crystals dissolve more easily than the others and with a composition of 91 percent have an efficiency of 98 percent. With an increase in the copper content, the α crystals are slightly less soluble.

With the introduction of the γ phase the efficiency falls off until pure γ of 84 percent copper composition is reached and across the γ field it continues to decrease with the decrease in the copper content. Across the $\alpha + \gamma$ and the γ fields the bronzes corrode copper-rich to a slight extent. Compared with the α and γ phases, the ϵ phase is considerably less soluble, with a resulting drop in the efficiency across the $\gamma + \epsilon$ field. In the ϵ and $\epsilon + \text{CuAl}_2$ fields the efficiency is about constant, although the points across this field are not

very well in line with the curve as drawn. The ϵ phase dissolves copper-rich, while in the $\epsilon + \text{CuAl}_2$ field the copper goes into solution almost entirely from the ϵ phase as evidenced by the fact that no copper to speak of dissolves from the $\text{CuAl}_2 + \eta$ field.

It was found very difficult to get any current through the test pieces containing the higher percents of aluminum, as there was a general tendency to become aluic. These pieces seemed to have a slight oxide film on them at the end of the run.

The total corrosion below the $\epsilon + \gamma$ field is so slight that the percentage of efficiency and the percent of copper corroded vary considerably. Experimental difficulties, coupled with the extreme brittleness of the ϵ and CuAl_2 phases make work in these fields rather open to error. At the same time the results are indicative of the general solubility of these bronzes.

There were some high efficiency values obtained for the 5, 10, 15 and 25 percent pieces but they have been omitted.

Electrolytic Corrosion in an Alkaline Tartrate Solution

The results obtained from the corrosion in the alkaline tartrate solution, 7 percent sodium tartrate and 3 percent of sodium hydroxide, are interesting. They were at first rather difficult to interpret but were finally made clear by use of the data obtained from the corrosion in sodium hydroxide, a few runs in a neutral tartrate solution and a large number of runs in the alkaline tartrate itself. The data in Table 8 and the efficiency curve in Fig. 8 show a gradual increase in the

Fig. 8—Alkaline tartrate solution .

efficiency through the α - and $\alpha + \gamma$ fields, reaching a maximum at pure γ . With the introduction of the ϵ phase, the efficiency drops off very rapidly and goes down to a bit less than 20 percent with the disappearance of the γ phase.

TABLE 8
7 percent sodium tartrate, 3 percent NaOH solution

Percent of copper in test piece	Corrosion in grams	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
0.0	0.3588	0.2147	> 100	0	0
4.5	1.6828	0.2147	> 100	0.0530	3.15
10.0	1.8280	0.2147	> 100	0.1511	8.30
15.1	1.3492	0.2147	> 100	0.1642	12.17
25.0	1.4226	0.2147	> 100	0.3457	24.30
35.2	1.1507	0.2147	> 100	0.3901	33.90
50.5	1.3668	0.2148	> 100	0.6120	44.77
51.9	1.4707	0.2147	> 100	0.6490	44.13
55.0	0.5314	0.3253	> 100	0	0
60.0	0.1811	0.3078	82.28	0	0
63.0	0.0883	0.2638	45.48	0	0
74.0	0.0480	0.3078	19.13	trace	—
76.0	0.0958	0.2638	43.81	0.0571	59.5
76.9	0.1731	0.3078	67.27	0.1284	74.1
80.0	0.2228	0.3078	84.42	0.1687	75.8
82.0	0.2086	0.2768	85.34	0.1543	73.90
84.5	0.2508	0.2795	95.47	0.1872	74.62
85.8	0.2283	0.3023	83.91	0.1815	79.50
86.4	0.2011	0.2350	94.96	0.1671	82.92
87.4	0.2916	0.5270	60.93	0.2230	76.47
89.5	0.2928	0.5270	60.00	0.2029	69.30
89.5	0.2887	0.5270	59.16	0.2085	72.22
90.1	0.2793	0.5270	56.91	0.2281	81.67
96.0	0.2483	0.5270	48.47	0.2444	98.45

By reference to Table 1, in the corrosion by sodium hydroxide, it will be seen that there is practically no corrosion of the α , γ or ϵ phases in that solution, and that the corrosion reaches a maximum at about pure CuAl_2 . Therefore the total corrosion in the fields above 73 percent copper is due to the tartrate and not to the sodium hydroxide. Below 73 percent copper, however, as shown by Table 1 the solution

of the aluminum out of the CuAl_2 phase takes place in the $\epsilon + \text{CuAl}_2$ field, and both copper and aluminum are dissolved from the $\text{CuAl}_2 + \eta$ and η fields. This causes the efficiency as actually determined in the alkaline tartrate solution to rise to over 100 percent at 54 percent copper. The greater part of the solution taking place below 73 percent is also due to the action of the sodium hydroxide upon the CuAl_2 and this, of course, increases with the increase of that phase through the $\epsilon + \text{CuAl}_2$ field.

The percentage of copper to the total weight corroded below 73 percent and above 54 percent copper, is very small, and therefore the majority of the corrosion in these fields is the solution of the aluminum alone. As seen by the table there was only a trace of copper dissolved in the field of pure ϵ . Again comparing with the sodium hydroxide corrosions, it is worthy of note that the tartrate is able to dissolve the aluminum out of the ϵ phase but that the sodium hydroxide has no effect upon it. The copper of the ϵ phase seems to be oxidized to cuprous oxide. In each case this was scraped off and taken as copper corroded.

From 54 percent to 0 percent copper the efficiency in the alkaline tartrate solution continues with over 100 percent efficiency. This is due entirely to the sodium hydroxide. To prove this, runs were made with test pieces containing 49 percent, 35 percent and 11 percent copper and in each case there was no corrosion though the test piece did not become aluic, the coulometer cathode gain being 0.3154 gram.

The dotted line from 73 percent copper (20 percent efficiency) is what would be obtained were it not for the chemical action of the sodium hydroxide. This was determined from the efficiency of the 73 percent test piece and from the fact that the pure CuAl_2 and η phases have been shown to be insoluble in the neutral tartrate solution.

Attention is called to the fact that the curve as actually determined has a gradual increase from 73 percent to 54

percent copper which is due altogether to the chemical action of the sodium hydroxide upon the CuAl_2 phase.

The α phase dissolves aluminum-rich and the γ phase almost according to its composition, the solution after corrosion being a little low in copper. The ϵ phase dissolves with no loss of copper.

Electrolytic Corrosion of Bronzes Annealed at 610°

Corrosions were made with the following test pieces: 83.6, 84.1, 86.4, 87.4, 98.5, 90.1 percent of copper in the chloride, sulphate and nitrate solutions. It was originally intended to run corrosions of test pieces containing copper down to 73 percent, so as to include the $\gamma + \Delta$ field but the test pieces with lower than 84 percent copper almost invariably broke on quenching.

No current efficiency curves have been given in these corrosions but a brief summary of the results follows.

TABLE 9
7 percent sodium chloride solution

Percentage of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
83.6	0.0639	0.1525	24.0	0.0082	12.8
84.2	0.0471	0.1525	17.7	0.0282	59.9
86.4	0.1542	0.1525	57.1	0.1358	88.1
87.4	0.1730	0.1525	63.0	0.1397	80.8
89.5	0.1954	0.1525	70.8	0.1757	89.9
90.1	0.2014	0.1525	72.0	0.1700	84.4

As seen in Table 9, in the sodium chloride solution the efficiency gradually decreases through the $\alpha + \beta$ and $\beta + \gamma$ fields from 72 percent to 17 percent at nearly pure γ , where the efficiency is similar to the efficiency of the pieces annealed at 500° . The β phase is nearly as soluble as the α and much more so than the γ phase. The α and β phases dissolve practically quantitatively, but the γ phase dissolves copper-rich.

TABLE 10
7 percent sodium sulphate solution

Percentage of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
83.6	0.0570	0.0743	86.9	0.0504	84.4
84.4	0.0565	0.0743	85.8	0.0428	75.8
86.4	0.0586	0.0743	87.3	0.0508	86.7
87.4	0.0583	0.0743	86.5	0.0511	88.0
89.6	0.0685	0.0743	99.6	0.0572	83.5
90.1	0.0725	0.0743	104.0	0.0633	87.3

In the sulphate solution the corrosion in the $\alpha + \beta$ field takes place with a higher efficiency than that of the $\beta + \gamma$ field, the first with 100 percent efficiency and the second at about 87 percent. The value of 104 percent for the 90.1 percent test piece is probably due to the mechanical dislodgement of either α or β crystals. By comparison with the sulphate solution (Table 2) it will be seen that there the α phase dissolves with slightly over 100 percent efficiency.

TABLE 11
7 percent sodium nitrate solution

Percentage of copper in test piece	Corrosion in gram	Coulometer cathode gain in gram	Percent of current efficiency	Copper corroded in gram	Percent of copper corroded
83.6	0.1267	0.1684	85.1	0.1028	81.2
84.2	0.1817	0.2619	78.5	0.1535	84.5
86.4	0.1809	0.2619	76.5	0.1552	85.8
87.4	0.1820	0.2619	76.5	0.1579	86.8
89.6	0.1941	0.2619	80.0	0.1664	85.7

In the nitrate solution the current efficiency through the $\alpha + \beta$ and $\beta + \gamma$ fields is about constant, the β phase being slightly less soluble than the α phase, while the γ phase is the most soluble of the three.

The fields here are rather narrow and yet the relative solubility of the α , β and γ phases is brought out fairly well. All of these phases in the three solutions used dissolve according to their composition with the exception of the γ phase in the sodium chloride solution, which dissolves copper-rich.

Summary

The corroding effects of the more common sodium salts and of sodium hydroxide upon the aluminum bronzes have been determined.

The organic acid salts, with the exception of the tartrate dissolve the α phase most easily. In the tartrate the γ phase is considerably more soluble. The CuAl_2 and η phases are practically insoluble in the organic acid salts used.

In the tartrate and sulphate the α is the most soluble, followed by the ϵ and γ while in the chloride the γ is slightly more soluble than the ϵ .

The α , γ and ϵ phases are practically insoluble in NaOH but the CuAl_2 and η phases are very readily soluble.

The bronzes practically do not corrode in the carbonate solution.

Unless caused by some additional chemical action, the changes in the rates of corrosion only occur upon the appearance or disappearance of a phase as shown in the equilibrium diagram.

There is a general tendency, except in the chloride and nitrate, and especially in the organic acid salt solutions for the bronzes high in aluminum to become aluic. This is accompanied by the formation of a thin film of aluminum oxide.

Unfortunately, the phases which have the greater resistance to corrosion are those which have the poorer physical properties. Were it not for the alkalinity of the solution as previously mentioned the efficiency curves in the $\text{CuAl}_2 + \eta$ and the η -fields would run very low. If that be true the alloy containing from 10 to 20 percent copper should be very serviceable for metal parts which are subject to the weather.

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