5-1-1940

The Electrolytic Recovery of Copper and Zinc from Scrap Brass with Special Reference to Lead-Bearing Brass.

Frederick A. Hames

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THE ELECTROLYTIC RECOVERY OF COPPER AND ZINC FROM SCRAP BRASS
WITH SPECIAL REFERENCE TO LEAD-BEARING BRASS

By
Frederick A. Hames

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
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INTRODUCTION

Several methods have been investigated, with some success, for treating scrap brass to recover copper and zinc, either as pure metals or as salts of the metals. (1,2,3,4,5,6,7,8,9,) One of the more promising of these methods is electrolysis in sulfate solution for the recovery of pure copper and zinc. The starting electrolyte is copper sulfate solution, and a brass anode and copper cathode are used during copper deposition. Both copper and zinc dissolve at the anode. When the zinc concentration in the electrolyte has built up to a suitable strength, the copper is stripped from solution and the zinc is recovered by electrolysis with a lead anode and aluminum cathode. The spent zinc electrolyte is charged with copper sulfate and the cycle repeated. (9)

One of the problems encountered, and reported by Swank (10), was the formation of a film of lead peroxide during electrolysis on anodes of lead-bearing brass, which protects the underlying brass from further anodic solution. As scrap brasses would undoubtedly contain some lead, this factor is to be considered.
It was the purpose of the present research to study the anodic solution of lead-bearing brasses, to determine if the lead peroxide film renders the anodes insoluble, and if so, to try and discover a means of combating this hindrance.

THEORY

In general, the anodic dissolution of an alloy (11,12) depends on the variation of electrode potential with composition. The structure of the alloy is also a factor.

When an alloy is used as an anode, the least noble phase (the one with the more negative potential against the electrolyte) dissolves first. Apart from concentration and other polarization the potential remains constant until this phase has disappeared. The potential then rises to that of the more noble phase. During the dissolution of a two-phase alloy, the noble phase left undissolved may form a protective coating over the electrode and prevent the dissolution of the baser phase. The anode potential will then rise, the coating will dissolve and the potential may fall again as the less noble phase is exposed.
When the alloy is a solid solution, the metals will dissolve simultaneously as only one phase is present.

Brass consists of one or two solid solutions of copper and zinc, depending on the composition. The structure of brasses of various compositions can be determined by an examination of the copper-zinc equilibrium diagram.

The brasses investigated contained over 60% copper, so only alpha and beta solid solutions need be considered. Beta having the lower potential should dissolve first followed by alpha.

When the brass contains lead, its anodic behavior is somewhat complicated. Lead is less noble than alpha or beta solid solution so, on the basis of the above theory, should dissolve first. However, in sulfate solution lead does not go into solution but lead peroxide forms, which adheres to the anode as a film. Allmand (12) explains the behavior of a lead anode as follows. If lead is made an anode in dilute sulfuric acid, a film of sparingly soluble PbSO₄ soon forms a badly conducting layer over the electrode. In the pores of this layer the current density becomes very great and
can no longer be maintained by the original electrode process \( \text{Pb} - 2e \rightarrow \text{Pb}^{2+} \). The potential therefore rises until another reaction \( \text{Pb} - 4e \rightarrow \text{Pb}^{4+} \) can set in, giving \( \text{Pb}(\text{SO}_4)_2 \) which, however, readily undergoes hydrolysis in dilute \( \text{H}_2\text{SO}_4 \) according to

\[
\text{Pb}(\text{SO}_4)_2 + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 2\text{H}_2\text{SO}_4.
\]

The result is that \( \text{PbO}_2 \) is deposited on the anode and still further reduces the size of the pores in the original film. Since, however, \( \text{PbO}_2 \) adheres tightly to the metal and is a good conductor, anions can be discharged at its surface when a sufficiently positive potential has been reached. Eventually the electrode will become covered with \( \text{PbO}_2 \) and behave as a practically insoluble electrode, the anode process being simply the evolution of oxygen.

**MATERIALS**

Anode #1 was cast from Anaconda electrolytic copper and zinc; #2 from Anaconda electrolytic copper and zinc and test lead; #3 from commercial scrap brass with test lead added; and #4 was cut from a commercial rolled brass sheet. Casting was carried out by melting
about 250 grams of the metals in the desired proportions in an assay crucible covered with an inverted scorifying dish in an electric furnace. The melt was stirred with a carbon rod and poured into a previously heated graphite mold to give an anode two inches by three inches by one-quarter inch. The anodes were trimmed on a mechanical shaper and smoothed with emery cloth.

The copper sulfate used was of technical grade. All other reagents were C.P.

Analysis of brass was made by determining copper and lead by the electrolytic method and obtaining zinc by difference. The electrolyte was assayed for copper by the electrolytic method.

Electrolyses were carried out in 250 cc. beakers. E.M.F. was supplied by a small laboratory sub-station and current was controlled by a rheostat.

EXPERIMENTAL

The first experiment was conducted to illustrate the fundamental processes. An electrolysis was carried out with a 70Cu-30Zn brass anode, a copper cathode,
and a starting electrolyte containing 40 grams per liter of Cu as CuSO₄ and 10 cc. per liter of H₂SO₄. The current density was 15 amps. per square foot. A good deposit of copper was obtained on the cathode. The solution was next stripped down to a trace of copper with a copper cathode and lead anode at a current density of 30 amps. per square foot. At this current density, the copper "burned" and was obtained as a dark spongy deposit. The last trace of copper was precipitated with zinc dust and the resulting ZnSO₄ solution electrolysed with a lead anode and aluminum cathode at a current density of 30 amps. per square foot. A good quality zinc deposit was obtained at the cathode.

The next experiment was designed to study film formation during electrolysis on brass anodes containing various amounts of lead. The electrolytic cell, consisting of a brass anode and copper cathode in CuSO₄ solution acidified with H₂SO₄, was operated at a current density of 15 amps. per square foot in series with a copper coulometer. During the experiment the following data were obtained: source of anode; analysis of anode; volume of electrolyte; Cu content of starting electrolyte; Cu content
of electrolyte after electrolysis; weight of Cu deposited; weight of brass corroded; time of electrolysis; current density; and weight of Cu deposited in coulometer.

The data for each anode are listed on the next four pages.
Source: cast from pure copper and zinc
Analysis of anode: Cu 64% Zn 36% Pb 0%
Volume of electrolyte: 170 cc.
Cu content of starting electrolyte: 38.76 gr./liter
Cu content of final electrolyte: 21.26 gr./liter
Weight of Cu deposited: 11.70 grams
Weight of anode corroded: 11.36 grams
Time of electrolysis: 24 hours
Current density: 15 amps./sq. ft.
Weight of Cu deposited in coulometer: 11.72 grams

There was a slight colored film on the anode which tended to fall to the bottom of the beaker rather than accumulate on the anode. On washing off the film, the anode was found to be covered with a thin copper colored skin of metal.
Anode #2

Source: cast from pure copper, zinc, and lead
Analysis of anode: Cu 60.2% Zn 38.9% Pb 0.9%
Volume of electrolyte: 170 cc.
Cu content of starting electrolyte: 38.76 gr./liter
Cu content of final electrolyte: 22 gr./liter
Weight of Cu deposited: 8.90 grams
Weight of anode corroded: 9.38 grams
Time of electrolysis: 17.5 hours
Current density: 15 amps./sq. ft.
Weight of copper deposited in coulometer: 8.91 grams

A thick, spongy, reddish-brown deposit, consisting mainly of lead peroxide, but containing small amounts of copper and zinc, formed on the anode. Beneath the peroxide film was an adherent thin skin of copper colored metal on the surface of the anode. This skin could not be washed off, but had to be removed by scraping.
Anode #3

Source: cast from commercial scrap brass with Pb added

Analysis of anode: Cu 60.1% Zn 34.6% Pb 5.3%

Volume of electrolyte: 200 cc.

Cu content of starting electrolyte: 38.76 gr./liter
Cu content of final electrolyte: 28.88 gr./liter

Weight of Cu deposited: 8.56 grams

Weight of anode corroded: 9.29 grams

Time of electrolysis: 17 hours

Current density: 15 amps./sq. ft.

Weight of Cu deposited in coulometer: 8.57 grams

A reddish-brown film was found on the anode similar to the film on anode #2. As on anodes #1 and #2 a copper colored skin was found.
Anode #4

Source: commercial rolled sheet brass
Analysis of anode: Cu 64.20% Zn 35.67% Pb 0.13%
Volume of electrolyte: 200 cc.
Cu content of starting electrolyte: 41.26 gr./liter
Cu content of final electrolyte: 10.10 gr./liter
Weight of Cu deposited: 20.81 grams
Weight of anode corroded: 21.15 grams
Time of electrolysis: 44 hours
Current density: 15 amps./sq. ft.
Weight of Cu deposited in coulometer: 20.83 grams

The film on this anode was darker than the previous films. It was also flakey and brittle and tended to fall off the anode to the bottom of the beaker without accumulating on the anode. The copper skin noticed on anodes 1, 2, and 3 was not noticed on this anode.
CALCULATIONS

From the above data it should be possible to calculate the theoretical weight of brass that should be corroded and compare this figure with the weight of brass actually corroded as found by experiment. Two methods of calculation were resorted to. Method 1 is based on the assumption that copper and zinc dissolve in the same proportions as they appear in the alloy so is applicable only to brasses containing one of the solid solutions. From the copper content of the electrolyte before and after electrolysis the amount of copper going into solution from the brass can be calculated. Knowing the analysis of the brass, the amount of brass that would have to be corroded to yield this copper can be calculated. Anodes 1, 2, and 4 contain copper and zinc in the proportions to form alpha solid solution so this method applies. Anode #5 contains a mixture of alpha and beta solutions so method 1 cannot be used on this alloy.

Method 2 of calculation is used to determine the theoretical weight of brass that should be corroded by a given quantity of electricity irregardless of the proportions
in which the metals dissolve. The quantity of electricity passed is determined from the copper coulometer.

The two methods are illustrated by the calculations for anode #4.

**Method (1)**

### Analysis of Brass

<table>
<thead>
<tr>
<th>Metal</th>
<th>Weight %</th>
<th>Equivalent %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>64.20</td>
<td>64.93</td>
</tr>
<tr>
<td>Zn</td>
<td>35.67</td>
<td>35.03</td>
</tr>
<tr>
<td>Pb</td>
<td>0.13</td>
<td>0.04</td>
</tr>
</tbody>
</table>

One "equivalent" of brass

\[
= 0.6493 \times 31.78 + 0.3503 \times 32.69 + 0.0004 \times 103.6 = 32.09 \text{ grams}
\]

Cu in 200 cc. at start

\[
= \frac{41.26}{1000} \times 200 = 8.25 \text{ grams}
\]

Cu in 200 cc. at finish

\[
= \frac{10.10}{1000} \times 200 = 2.02 \text{ "}
\]

Cu removed from solution

6.23 "

Cu deposited = 20.81 grams

Cu from solution = 6.23 "

Cu from brass = 14.58 grams = 0.459 equivalents

Brass theoretically corroded

\[
= \frac{0.459}{0.6493} = 0.706 \text{ equivalents}
\]

\[
= 0.706 \times 32.09 = 22.65 \text{ grams}
\]

**Method (2)**

Equivalents of Cu deposited in coulometer

\[
= \frac{20.83}{31.78} = 0.655
\]

The same number of equivalents of brass should have corroded = 0.655 x 32.09 = 21.02 grams.
The results for the four anodes are summarized in the table below.

<table>
<thead>
<tr>
<th>Method of Determination</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated by Method (1)</td>
<td>13.63</td>
<td>9.45</td>
<td>--</td>
<td>22.65</td>
</tr>
<tr>
<td>Calculated by Method (2)</td>
<td>11.85</td>
<td>9.05</td>
<td>8.97</td>
<td>21.02</td>
</tr>
<tr>
<td>Actually, by experiment</td>
<td>11.86</td>
<td>9.38</td>
<td>9.29</td>
<td>21.15</td>
</tr>
</tbody>
</table>

In the belief that the effect of the lead peroxide film would be manifested by a variation in anode potential, an attempt was made to measure the anode potential during electrolysis. A normal calomel half-cell was used as a reference electrode but this was unsatisfactory. Potassium chloride solution from the half-cell diffused into the electrolyte and reacted with the anode coating it with a white film, thus masking the true condition of the anode. This difficulty could probably be solved by using a copper reference electrode using a copper sulfate solution of approximately the same composition as the electrolyte.
DISCUSSION OF RESULTS

On comparing the results of the calculations by Method (1) and the actual weights of brass corroded, it is seen that in every case less brass corroded than is theoretically required, which would seem to indicate that the anodes had been rendered insoluble by the anode films. However, it must be remembered that the calculations were based on copper assays alone without regard to how much zinc dissolved. Unfortunately, the electrolyte was not assayed for zinc. This would have been very useful in studying the anode process.

On comparing the figures of Method (2) with the actual weights of brass corroded, it is seen that sufficient brass has corroded to meet the requirements of the theoretical calculations. From this it may be inferred that the proportion of zinc to copper dissolving was greater than the proportion of zinc to copper in the alloy.

The copper skin found on anodes 1, 2, and 3 is significant. This same feature has been found by other investigators. Lincoln (13) discovered it in his study of the electrolytic corrosion of brasses. It is interesting to note that Lincoln found that the amount of copper in the corrosion
product decreases very rapidly with the decrease in the copper content of the test piece, becoming practically zero for brasses containing 50% and less copper. In his study of the dezincification of brass, Abrams (14) observed a copper film on brass that had been corroded. He explains this by showing that copper after dissolving from the brass is replaced in solution by brass with the result that copper is redeposited on the alloy surface. This would cause a depletion of copper in solution and may explain the discrepancies between observed values and values calculated by method (1) for weight of brass corroded. This explanation would also substantiate the inference made above that the proportion of zinc to copper dissolving was greater than the proportion of zinc to copper in the alloy. Abrams reports that redeposition is favored by an artificial membrane placed around the test specimen. It is possible that in the present experiments the lead peroxide film acted as a membrane and so the copper skin on the anodes is accounted for.
CONCLUSIONS

When a lead-bearing brass is used as an anode in a sulfate solution, the lead is converted to lead peroxide, which adheres as a film to the anode. Under the conditions of the present experiments, the lead peroxide film did not render the anode insoluble. This was possibly due to the fact that the electrolyses were not carried out for a sufficient length of time for the lead peroxide film to build up thick enough to protect the underlying brass from anodic solution.

The lead peroxide film seems to promote the reposition of copper on the anode with the net result that the ratio of zinc to copper dissolving is greater than the ratio of zinc to copper in the brass.

SUGGESTIONS FOR FURTHER WORK

The anode processes, including the behavior of lead, need to be studied further and a means of preventing lead peroxide formation discovered. In this connection, it is suggested that the effect of such salts nitrates, acetates, and chlorates, which form soluble lead salts, be investigated.
as addition agents in the electrolyte.

The flow sheet for treating brass electrolytically as suggested by Barker (9) needs adjusting. The supply of copper sulfate to the electrolyte for copper electrolysis is not entirely satisfactory. No provision for the disposal of $\text{H}_2\text{SO}_4$ in the spent zinc electrolyte is provided, so under the present flowsheet it will continually build up during repeated use in the cycle.
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ACKNOWLEDGEMENT

The guidance and assistance of Dr. A.E. Koenig, Dr. Curtis L. Wilson, and Dr. E.A. Peretti during this investigation are gratefully acknowledged.