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Electrolytic Recovery of Copper and Zinc from Brasses

Thomas Barker Jr.

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Barker, Thos. Jr.

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by
THOMAS BARKER, Jr.

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

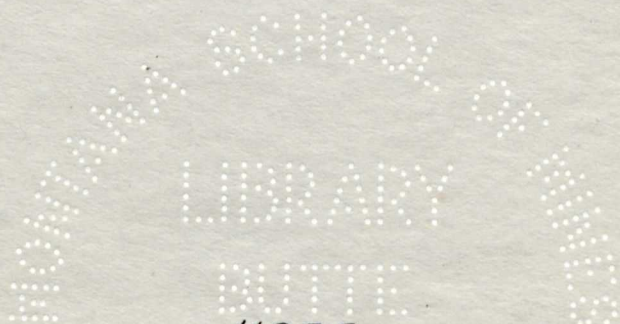
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INTRODUCTION

Reclaimed metals, or as they are known in the Metallurgical Industry, secondary metals, are becoming of very great importance in the metal industries of the world. As far back as 1913, secondary metals were an important factor in production, for scrap copper in that year amounted to 17 per cent of the total copper production in the United States; in 1923, 35 per cent was recovered as scrap; during 1934, 57 per cent of copper was produced from scrap.

The increase in the secondary production of copper is due to many factors. One of these may be its permanence; that is, the metal does not corrode very readily. It is electronegative to most metals and, if in contact with them, will not dissolve before all the other metals above it in the electromotive series have gone into solution. Also, oxide coatings that are formed are adherent and protect the metal from further chemical attack. Another reason for the increase in secondary production of copper is the high price paid for it. The price received for the metal depends on its purity, so if the metal can be electrolytically refined, the price received will be the same as that for virgin electrolytic copper.

Most of the secondary copper is refined pyrometallurgically and used for making brass or mixed metals without separation from its alloys. A great deal of the scrap that is collected is old brass which is recast into lower grade material. If the

brass could be treated to recover the copper and zinc, each in a pure state, the price received for these metals would be much higher than that received for the brass.

Brasses may be treated for the recovery of copper only, by adding them to the charge of a matting furnace for treating copper concentrates. The copper present will unite with sulfur in the charge to form matte which may be processed by standard methods for the recovery of the metal of electrolytic grade. In this furnace treatment, the zinc will oxidize and be lost in the slag. However, this can be done only by large copper producing companies which have the facilities for the recovery of copper from sulfide ores. The brass would have to be shipped from the large cities where it is collected to the smelters which are usually considerable distance from them. If some direct method could be devised for the recovery of both metals from brass, not involving such an elaborate process as above described, small recovery plants could be situated in important cities all over the country, thus saving expense on freight, and recovering the zinc as well as the copper.

In this investigation, laboratory tests were conducted to study the possibility of electrolytic recovery of the pure metals from scrap material. The method of procedure which was studied was that of using anodes of brass and electrolyzing in a sulfate solution.

SCOPE OF INVESTIGATION

To determine the limiting copper concentration at which good deposits of the metal could be obtained at definite current

densities.

To study the deposition of copper from made-up anodes of pure brass, that is, brass containing only copper and zinc.

To study the deposition of copper from commercial brasses.

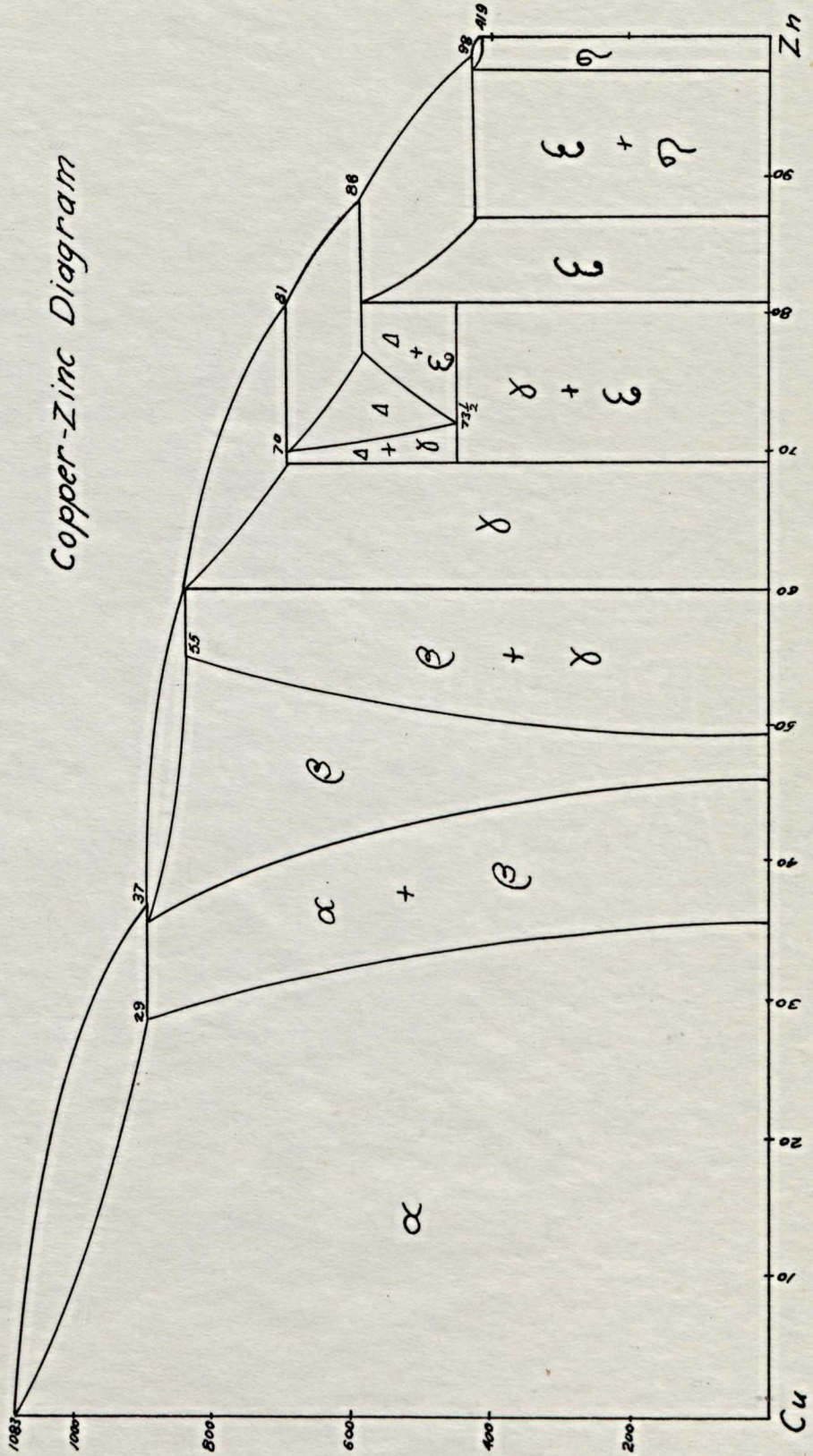
To study the effect of impurities on made-up brasses.

THEORY

There are many so called "regular" brasses used today.¹ The amount of copper in them is between ninety and thirty-five per cent, but the most important alloys are those containing from eighty to fifty-five per cent copper. Alloys of more than sixty-four per cent copper are composed solely of alpha solution. Those with copper between sixty-four and fifty-five per cent are made up of alpha and beta solution when quenched above 470°C; and of alpha and gamma when cooled slowly. In electrolyzing brass then, either one of two phases will be present but no more unless the brass contains metals other than copper and zinc. This has an important bearing on the amount of anode scrap that will be formed by dissolving the brass by electrolysis. To show this it will be necessary to discuss the theory of anodic dissolution of alloys. The discussion deals only with alloys in which all of the constituents are soluble in the electrolyte under the action of electric current.

For example copper, if electrolyzed in a sulfuric acid solution, and zinc, if electrolyzed in the same solution, will do the same. In the anodic dissolution of an alloy meeting these conditions, if more than one phase is present, the least noble phase

Copper-Zinc Diagram



(the phase with the more negative potential to the electrolyte) will dissolve first.² The solution potential will be constant until the least noble phase disappears. The potential will raise to that of the next nobler phase. It is seen that in alloys of this nature the phase is the determining factor and not the constituents under the electrolyzing conditions given. Therefore if alloy consists of a solid solution, both of the metals will dissolve simultaneously for the solution consists of only one phase. The potential of the anode will depend on the protective effect of any undissolved phase. If much of a nobler phase is present, it may completely cover the less noble phase and the potential will raise until this outer crust dissolves. The voltage will then drop to that of the less noble phase. If very little of the more noble phase is present or it is separated into isolated crystals, the dissolution of the less noble phase will cause the electrode to disintegrate and more noble phase will fall to the cell bottom.

The pure brasses to be studied will not contain any impurities to complicate the study of anode dissolution. As gamma solid solution is very seldom found in brasses it need not be discussed. Only alpha and beta have to be considered. In the electrolysis the beta solution will dissolve before the alpha for it is the less noble of the two.

As the alloy dissolves ions of copper and zinc are formed. In a solution containing these two ions, the copper will be deposited almost entirely before any zinc will plate, unless the

discharge potentials are made the same.

The discharge potential of copper is $.34 + 0.0285 \log C_{Cu}$ and the same for zinc is $-.76 + 0.0285 \log C_{Zn}$. If these two are equated the composition of the solution to plate the two metals simultaneously can be found.

$$E = .34 + 0.0285 \log C_{Cu}$$

$$E = -.76 + 0.0285 \log C_{Zn}$$

$$.34 + 0.0285 \log C_{Cu} = -.76 + 0.0285 \log C_{Zn}$$

$$1.1 = 0.0285 \log \frac{C_{Zn}}{C_{Cu}}$$

$$38.6 = \log \frac{C_{Zn}}{C_{Cu}}$$

$$\frac{C_{Zn}}{C_{Cu}} = 4 \times 10^{38}$$

This shows that the concentration of the zinc ions would have to be 4×10^{38} times that of copper. Due to the limited solubility of the zinc salts in aqueous solutions, the concentration of copper ions will reach an extremely low value before any zinc will be deposited unless other phenomena occur at the cathode.

It was shown above that the dissolution of brass would be on the phase as such and not on the constituents present in the phase. On this basis if a brass consisted of 70 per cent copper and 30 per cent zinc, the highest that the anode efficiency of copper electrolysis could be is 70 per cent (consider molecular weights of the two metals equal). If the current efficiency of

deposition of copper at the cathode exceeds 70 per cent the solution would have more copper removed than would be replaced at the anode, therefore the copper concentration of the electrolyte would gradually diminish.

When the copper concentration of the solution had become so low that the efficiency of deposition was not economical, zinc dust could be added to eliminate the remaining copper from the solution. The solution could then be purified if need be and then electrolyzed with insoluble anodes to recover the zinc from the solution.

At the outset of the study a search of the available literature revealed very little reference to any brass metal recovery. One abstract on work by W. W. Stender³ discussed the recovery of powdered copper from brass cuttings by electrolyzing in hydrochloric acid and recovery of zinc chloride as a by product.

In this investigation, attempts were made to obtain the copper as a strongly adherent, sound, cathodic deposit and not in the form of a powder.

APPARATUS

The electrolyses were conducted in 250 cubic centimeter breakers with electrode holders for spacing as required.

Copper cathodes were used in all tests involving copper precipitation. Brass was the anode in all runs except where stated to the contrary.

Operations were conducted at room temperature, and no stirring was used except in one test when mechanical stirring

was used.

REAGENTS

Copper used in this problem was Anaconda electrolytic copper wire. Anaconda electrolytic zinc was used for alloying with the copper to make brass. The fusions were made in graphite crucibles and the brass was cast in carbon molds.

Solutions of sulfuric acid were made by diluting concentrated C.P. sulfuric acid with distilled water. Recrystallized copper sulfate was used in the preparation of solutions containing that salt.

Analyses were made with potassium ferrocyanide for zinc and sodium thiosulfate for copper.

Commercial brass castings were collected from junk piles and cast into suitable shapes for electrolysis.

EXPERIMENTAL

STRIPPING OF SOLUTION OF COPPER

As a preliminary experiment to determine the extent to which copper can be extracted from solution, a test was run on a copper sulfate solution. Six cells were set up, the anodes and cathodes of such size that, with a current of .3 amperes, the current density of the solutions would be eighteen, fifteen, twelve, nine, six, and three amperes per square foot. The solutions were not stirred except by oxygen evolution at the lead anodes. The electric circuit was closed by placing the electrodes in all the cells at one time to prevent the precipitation of copper on the lead anode which would occur if the lead

were not under action of the electric current. When the cathode deposit in a cell became "burned," the cell was disconnected from the circuit and the electrodes removed. The solution was then analyzed for its copper content. The acid content was calculated by difference.

Results:

The 18 amperes per square foot cathode turned black very soon after the electrolysis was started. The strength of the solution was found to be less than the limiting strength of the 15 amperes per square foot cathode. It must be explained here that the volume of the solution of the 18 amperes cell was about one half that of the 15 amperes cell so the former would be depleted much sooner. The results of the first cell was then discarded. The table shows acid and copper content of the various solutions.

Current Density	Copper	H ₂ SO ₄
15 amps/ "	12.02g/L	5.00g/L
12 " "	11.26g/L	6.16
9 " "	6.89g/L	12.89
6 " "	6.61g/L	13.31
3 " "	2.65g/L	19.42g/L

In work conducted by Sawyer,⁴ a solution containing:

Copper	21.1 grams per liter
Zinc	85.9 grams per liter
Iron	0.9 grams per liter
Acid	6.5 grams per liter

was electrolyzed. The current density was ten amperes per square foot at the start and then lowered to 7.5 and, as the copper con-

tent was lowered to 12 grams per liter, to 5.0 amperes per square foot. The resulting solution was as follows;

Copper	6.2 grams per liter
Zinc	87.9 grams per liter
Sulfuric Acid	45.0 grams per liter

He suggests that to decrease the current density in practice, longer tanks could be used with larger anodes and cathodes, the tanks being in series in the same electrolyzing circuit.

ELECTROLYSIS OF PURE BRASS

A brass containing approximately 80 per cent copper was made up by heating the materials in a graphite crucible in a muffle, until the metals were molten, and pouring into carbon molds. The castings were melted and recast to get a uniform product. The castings were then rolled until they were about three millimeters thick. This was done so that duplicate samples of each brass could be tested. No cracking occurred in these samples. The samples were then cut to desired length and used as anodes.

One sample was electrolyzed with a copper sulfate solution containing 40 grams copper per liter. Potential readings were taken at regular intervals to determine any variations. After 45 minutes of running the anode showed signs of peeling. It was shaken, and strings of metal glided from it and settled to the bottom of the cell. The operation was continued for nineteen hours. The anode corroded evenly. No zinc was present in the cathode. However, the solution was much lower in copper at the end of the operation than at the start. Duplicate experiments

were made with identical results.

The resulting solution from one of these runs was depleted of copper by the addition of zinc dust and electrolyzed with lead anodes for the recovery of zinc. A very adherent, clean deposit of zinc was collected showing that impurities that may have been present did not affect the deposition.

ELECTROLYSIS OF COMMERCIAL BRASS

Scrap material was collected from junk piles and cast into molds. Attempts were made to roll the castings without success. Several were annealed and then rolled, but none were successfully reduced to the thinness of the previous samples. Using the thick casting as anodes, the same experiments were conducted as with pure brass, and the results were the same except that more peelings settled beneath the anode.

These operations were considered successful but created a problem. The starting solution was copper sulfate and in a plant operation this salt could not be continually added to replenish the solution.

To attempt to get around this difficulty, a cast sample was electrolyzed for twenty hours in a sulfuric acid solution. Copper collected at the cathode in the form of a powder. The same solution was re-run with a different anode. The solution built up slightly in copper, probably due to low mobility of the copper ions in the solution and thus deposition of hydrogen in its stead.

Copper collected as a powder would not be desirable for

the dust loss in casting would be great, so search was begun for a more adherent deposition. The same solution used in the previous attempt was electrolyzed with much agitation by means of an electrical-mechanical stirrer. A very adherent deposit was obtained. The test was tried again with a pure sulfuric acid solution and the copper plated out as a powder. These tests show that sulfuric acid could not be used unless copper was present in solution, and agitation was used.

ELECTROLYSIS OF BRASS CONTAINING TIN

To study the influence that tin would have on the solution of the anodes, two tests were conducted with brass containing this element. Anodes were poured containing copper and zinc with tin added. One sample had one-fourth of one per cent tin, and the other had four per cent tin.

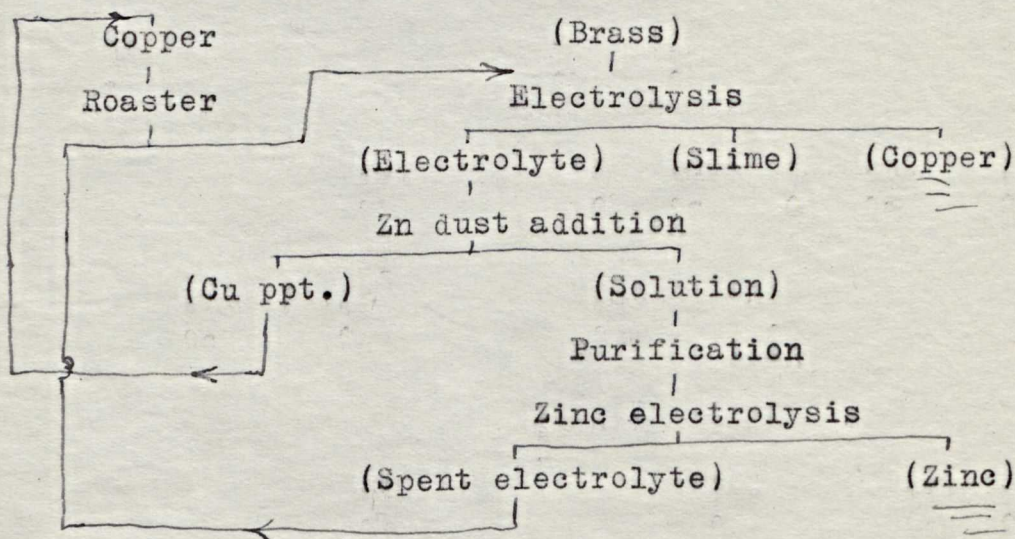
The anodes were electrolyzed in a copper sulfate solution containing forty grams copper per liter. The copper went into solution as before leaving a shell the same shape as the anode. As long as the cell was left undisturbed the shell held its shape, but when the anode was tapped it fell to pieces and collected at the bottom of the beaker. The only difference in action of the two anodes was in the amount of waste produced; the slime from the four-per-cent tin-brass being greater than that from the one-fourth-of-per-cent tin-brass.

CONCLUSIONS

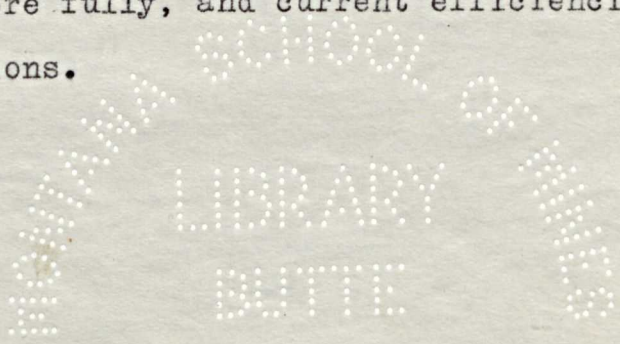
The tests conducted show that copper and zinc can be re-

covered from brass, the copper either in the form of a powder or as a coherent bright deposit. Tin present does not hinder the electrolysis but increases the amount of waste collected. A problem which must be overcome in practical recovery is the supplying of a copper sulfate solution for the copper electrolysis. This probably could be supplied by roasting copper shavings and fine copper from the cleaning operation, to copper oxide and dissolving with spent electrolyte from the zinc deposition.

A general flow sheet for recovery would then be as follows:



Further study on this subject should be conducted to perfect this flow sheet in detail. The anode processes need to be investigated more fully, and current efficiencies should be taken for all operations.



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