

THE PREPARATION OF METALLIC BORON



by

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TABLE OF CONTENTS

I	Summary	page	1
II	Introduction		3
III	Procedure		6
IV	Results		13
V	Discussion of Results		16
VI	Recommendations		21
	APPENDIX		22
	Details of Procedure		23
	Bibliography		31

I SUMMARY

It was the object of this thesis to investigate the possibility of preparing metallic boron by electrolytically plating or depositing the metal from a solution of a boron halide. Other methods of preparing boron either result in a poor product or are too expensive to industrial application.

The source of boron used was boron fluoride ethyl ether. This was electrolyzed alone and with glacial acetic acid and sodium chloride added. Electrodes were used in the following combinations: carbon and copper; palladium and copper; and palladium and nickel. Potentials used were 13 volts and 116 volts. Two types of cells were used, the vertical type (Fig. 1) and the U-tube type (Fig. 2). After electrolysis, the cathodes were washed in boiling water, alcohol, and ether, in that order.

It was found that: using boron fluoride ethyl ether alone, a loose black deposit could be obtained which was non-adherent and gave a positive green flame test for boron; adding glacial acetic acid to this solution increased the current flow but gave similar results; adding glacial acetic acid saturated with sodium chloride to the boron fluoride ethyl ether solution gave about the same current flow as the addition of the glacial acetic acid alone, but that a closely adherent plate could be obtained which could be polished to

a gun-metal lustre with a soft cloth, one of these cathodes taking on a chromium-like finish when buffed with a cloth wheel; the plate obtained analysed spectrographically to show the presence of boron, copper, aluminum, and calcium; the amount of aluminum in the plate was negligible because the coating did not deteriorate in hot concentrated caustic; the coating on the plated cathodes came off upon dipping the cathode in fused boric acid; indications are that the deposit obtained is boron, however positive chemical proof has yet to be established.

It is recommended that further experimentation be carried out on these lines to definitely determine the valence state of the boron deposited and to determine optimum current density for plating this metal.

II INTRODUCTION

It is the object of this thesis to investigate the possibility of preparing metallic boron by electrolytically plating or depositing the metal from a solution of a boron halide.

Boron was first prepared, in the early nineteenth century by the fusing of boric oxide, B_2O_3 , with potassium. The resulting product was a highly impure form of metallic boron. At the same time, H. Davy claimed to have prepared the metal by electrolyzing moist boric oxide. This latter experiment has never been successfully duplicated and it is probable that Davy had actually worked with fused boric oxide, which method will yield impure boron. Techniques for preparing boron by reduction of the fused anhydride with potassium, sodium, magnesium, and aluminum have been thoroughly investigated. For the most part these techniques result in a product which contains too much impurity or which, in some cases, is a definite high boron-containing compound, such as $Al_3B_{48}C_2$ (W. Hampe) or $Al_3B_{44}C_2$ (H. Blitz).

Boron, as it has been obtained, has appeared usually as an amorphous powder, varying in color from gray to maroon. E. Weintraub, of General Electric Laboratories, succeeded in fusing this powder to obtain highly pure boron which resembled black diamonds and exhibited a conchoidal fracture. Within the last ten years, considerable has been

done on the preparation of boron by reducing boron halides in the alternating current arc. Boron prepared in this way will take a high polish (to resemble chromium) and, although not appearing crystalline under the microscope, does exhibit a crystalline structure when subjected to x-ray analysis.

Although the recorded characteristics of boron are based to a large extent on impure samples, the following seem to be well substantiated:

- 1) Boron will not react with air at temperatures below 700 C.
- 2) Boron is attacked only by HF, hot concentrated sulfuric and nitric acids at nominal temperatures.
(It is claimed that the pure, crystalline boron prepared by the A. C. arc method described above is not attacked by any acid, even aqua regia.)
- 3) Boron is second to the diamond in hardness. Its addition to steels results in higher tensile strength.
- 4) Boron is a non-conductor at room temperature but becomes a good conductor when heated (when heated to red heat).

Also recorded in the literature, but not so well substantiated is the fact that boron is located just above lead in electromotive series. These properties suggest many prospective uses for boron if a cheap, commercially practical

method for the preparation or plating of this metal could be devised

Based on the theory that boron can exist as a positive ion in solution, it was decided to work with a boron compound that would conceivably furnish such an ion. This suggested the use of a boron halide. Since boron fluoride is at present the cheapest commercially available halide of boron, it was investigated in this thesis.

Boron fluoride is a gas at ordinary temperatures (B.P. 101 C) and like the other halides had never been shown to exhibit any tendency to ionize in solution, or otherwise exhibit typical salt characteristics. Consequently, the major problem to be solved was how to make a solution of boron fluoride conduct and decompose without getting decomposition of the solvent first.

The use of water as a solvent was out of the question, since boron fluoride reacts with water to give hydrofluoric acid and boric acid. A non-aqueous solution consequently must be used. Ethyl ether was chosen as the first solvent to be used in this thesis and results showed others to be unnecessary. Boron fluoride ethyl ether (45% BF_3) was obtained from the Eastman Kodak Company for initial experimentation. It was considered best to use boron fluoride since the pure compound being a readily hydrolyzed gas would entail additional apparatus and more difficulty in handling.

III PROCEDURE

I Boron Fluoride Ethyl Ether Solution

A. Copper and Carbon Electrodes

Using a vertical electrolytic cell of the type pictured in Fig. 1, copper cathode and carbon anode, and a potential of 13 volts across the cell, an immeasurably small (measured by a three-ampere ammeter) current was passed through boron fluoride ethyl ether solution for nineteen hours. A loose black deposit was obtained which easily washed off. There was no noticeable adherent plate left on the cathode.

B. Copper and Palladium Electrodes

Using a U-cell of the type pictured in Fig. II, copper cathode and palladium anode, and a potential of 116 volts across the cell, a current of 20 milliamperes (using a 500 milliamperere ammeter) was passed through boron fluoride ethyl ether solution for 5 hours. The cell was kept at constant temperature by immersing in a bath of running water. A loose black deposit was obtained which was easily removed upon washing in ether. This powder after cleaning and drying gave a green flame when heated on clean

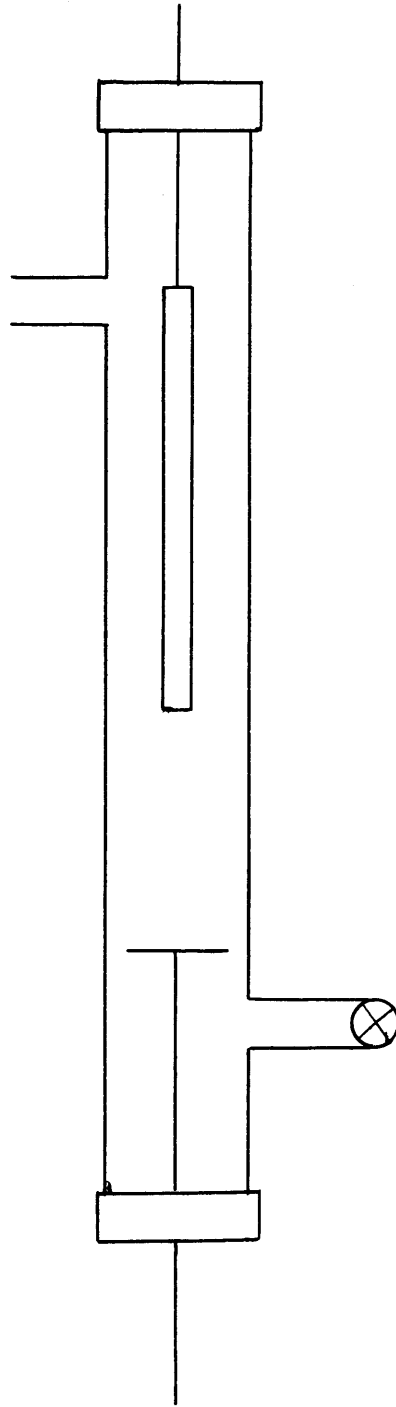


Fig. I Vertical Cell

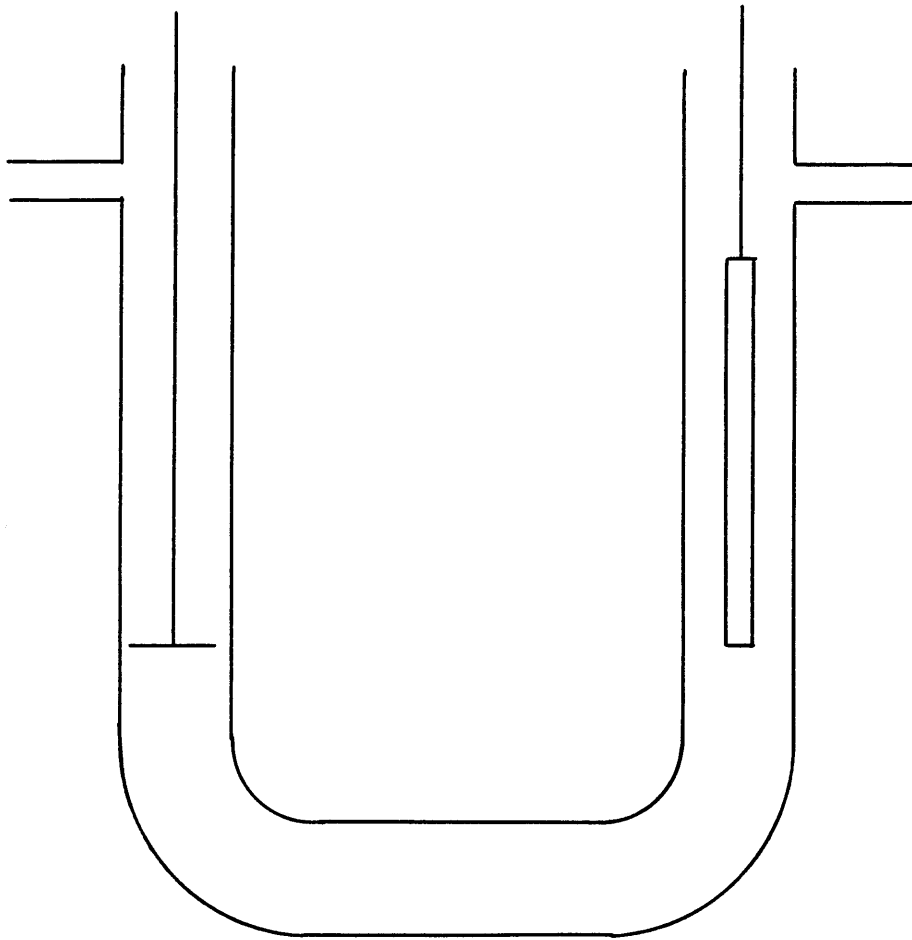


Fig. II U-type Cell

nickel and palladium in a bunsen flame.

II Boron Fluoride Ethyl Ether Solution and Glacial Acetic Acid

A. Copper and Carbon Electrodes

Using a vertical electrolytic cell (Fig. I), copper cathode and carbon anode, and a potential of 13 volts, a current of .03 amperes was passed through a mixture of boron fluoride ethyl ether solution and glacial acetic acid for nineteen hours. A loose black deposit was obtained which rubbed off easily. There was no noticeable adherent plate on the copper.

III Boron Fluoride Ethyl Ether Solution and Glacial Acetic Acid Saturated with Sodium Chloride

A. Copper and Carbon Electrodes

1. 13-volt potential

Using a copper cathode and a carbon anode with a mixed solution of boron fluoride ethyl ether and glacial acetic acid saturated with sodium chloride, it was found that a current of .03 amperes could be passed through this solution in a vertical cell (Fig. 1), when the electrode separation was three

inches. Upon reducing this separation to one inch a current value of .07 amperes was obtained. This process resulted in a black, closely adherent plate being produced on the cathode. Upon washing in boiling water, alcohol and ether, and polishing with a soft cotton cloth, this plate took on a gray metallic lustre. One of these cathodes was analyzed spectrographically and found to contain boron, aluminum, copper, and calcium.

2. 116-volt potential

Using a U-cell (Fig. 2) with the same type electrodes and solution as above, it was found that a 100 to 110 milliamperes current could be passed through the solution. In every case, the cathode was washed in boiling water, alcohol, and ether at the end of the run and polished with a cotton cloth to a metallic lustre. One plate was sufficiently adherent to withstand the action of a cloth buffing wheel and a chromium like finish was obtained. This particular cathode was immersed in hot concentrated caustic of sufficient strength to rapidly dissolve aluminum but no deterioration of the plate was observed. The cathodes coated in this manner were dipped into fused boric acid but the coating did not remain.

B. Nickel and Palladium Electrodes

Two runs were made with U-cells containing nickel cathodes and palladium anodes. In each case the potential used was 116 volts and the electrolytic solution was made up of boron fluoride ethyl ether and glacial acetic acid saturated with sodium chloride. One was run for four hours, and the other for 10 hours. In each case it was found that the height of the liquid in the cathode side was higher than that in the anode side. The four-hour run resulted in the nickel cathode being coated with a dark deposit similar in appearance to that previously obtained on copper. This dark deposit disappeared when the cathode was dipped into fused boric acid. The ten hour run resulted in the coating of the cathode with a fine brown powder similar in appearance to amorphous boron. This powdery coating was easily removed and no adherent coat was left after polishing with a soft cotton cloth.

C. Copper and Palladium Electrodes

Here the same setup was used as described in the foregoing paragraph excepting in that copper was substituted for the nickel cathode. In every case, using a voltage of 116, it was found that the cathode had become coated with a thin adherent plate

that polished to a gun-metal gray lustre. None of these coatings remained after dipping in fused boric acid, but when two of the plated cathodes were dissolved in concentrated nitric acid and treated with methyl alcohol and sulfuric acid, the distilled vapors burned with a green-rimmed flame, indicating the presence of boron. When in some cases the current was left on longer than necessary (more than six or seven hours) in an attempt to produce a thicker plate it was found that some of the deposit came off on the polishing cloth as a dark brown powder.

IV RESULTS

I Boron Fluoride Ethyl Ether Solution

A. Copper and Carbon Electrodes

Electrolyzing boron fluoride ethyl ether solution alone resulted in the copper cathode becoming coated with a loose black powder which was non-adherent.

B. Copper and Palladium Electrodes

Using this solution a black deposit was obtained on the copper. This deposit came off as a black powder. It was not soluble in cold concentrated nitric acid but did dissolve in the hot acid. This also gave the green flame test for boron.

II Boron Fluoride Ethyl Ether Solution and Glacial Acetic Acid

A. Copper and Carbon Electrodes

Addition of glacial acetic acid to the boron fluoride ethyl ether solution resulted, upon electrolysis, in the copper cathode becoming coated with a loose, black, non-adherent deposit.

III Boron Fluoride Ethyl Ether and Glacial Acetic Acid
Saturated with Sodium Chloride

A. Copper and Carbon Electrodes

Using this setup runs were made with thirteen and one hundred and sixteen volts, cell potential. In both cases black deposits were obtained which took a high polish when the cathode was rubbed with a cloth. One of these was analyzed spectrographically and showed that boron, copper, aluminum, and calcium were present. On dipping one of the plates in fused boric acid the black deposit was removed. The fused boric acid was hot enough to melt the copper and it would have removed anything that could not insulate the copper from it. The plate which was used in this test did not have a heavy enough deposit on it to protect the copper. One of these plates, when polished with a cloth buffing wheel, took a high polish which resembled a chromium finish. This plate was placed in hot concentrated sodium hydroxide, but the finish was not noticeably deteriorated.

B. Nickel and Palladium Electrodes

With these electrodes only the one hundred and sixteen volt circuit was used. Two runs were made and in the first a black plate, similar to that which

came out on the copper, was obtained. This disappeared when dipped in fused boric acid. On the second run, which was considerably longer, a brown powder was deposited on the cathode. This powder corresponds to the description of amorphous boron given in the literature.

C. Copper and Palladium Electrodes

Several runs were made using these electrodes on the one hundred and sixteen volt circuit. Each time a black plate was obtained, which on polishing, took on a gray metallic lustre. One of these was dissolved in concentrated nitric acid, sulfuric acid and methyl alcohol were added and the solution distilled. The vapors burned with a green flame. This is another boron test which gives a positive result.

V DISCUSSION OF RESULTS

Since it was the purpose of this thesis to attempt to prepare metallic boron, the question is whether or not the results show this attempt to be a success or a failure. The results do show, first of all, that the cathodes used in this experimentation have in every case been affected. Some were coated with an adherent plate, some with a non-adherent powder, and others with both the adherent deposit and the powder upon that. Ignoring for the moment the various factors that influenced the character of this deposit, let us inquire into the composition of the deposit.

Spectrographic analysis was resorted to when the first adherent deposit was obtained. In this type of analysis the presence of elements can be ascertained but the valence state of these elements can not be determined. In other words if the spectrograph showed boron to be present, it would not show whether the metal existed there in its elementary form or as BF_3 or H_3BO_3 for example. The analysis of a plated cathode which had been thoroughly washed in boiling water, alcohol, and ether did show that boron was present, and copper, calcium, and aluminum as well. The presence of copper was of course to be expected since the deposit was on a copper disc. Calcium was evidently present as an impurity in the copper since any calcium in the deposit would have been removed by the boiling water. Metallic aluminum did

not make up an appreciable part of the deposit since the polished surface of the cathodes did not deteriorate when immersed in hot concentrated sodium hydroxide solution.

That the deposit might have been boric oxide or a boron suboxide seems out of the question since it was plated out on the cathode, which is the reducing electrode. The confirmatory test was not positive however. This test consisted in dipping the plated cathode in fused boric acid which should theoretically dissolve off any metallic oxide (including oxides of boron) but not affect the elementary metal. Copper cathodes dipped into fused boric acid completely lost their adherent coating, but the temperature of the bath was sufficiently high to dissolve copper itself hence would remove any thin deposit along with some copper. When this test was tried with a nickel cathode, the deposit seemed to disappear but this did not indicate anything since it had been previously found that these deposits, when polished, would make a nickel-like finish. Consequently any boron on the nickel would be invisible after cleaning in fused boric acid.

Methods of positive chemical identification of metallic boron all involve conversion of the boron into boric acid. The fact that cathodes dissolved in nitric acid gave a green flame test upon addition of sulfuric acid, and methyl alcohol and ignition of the distilled vapors again show that boron was present in the deposit. Another method involves

weighing the cathode before and after deposition, dissolving plated cathode in nitric acid, and titrating with standardized sodium hydroxide solution, first to a methyl orange end point, and finally after addition of mannitol, to a phenolphthalein end point. Since the weight gained by the cathode was only of the order of .00045 grams on .200 grams of copper, it was out of the question to attempt this method since at least one milligram must be present to get any results and these of poor quantitative significance when so little is present.

Results show that a deposit of powder can be obtained by electrolysis of the boron fluoride ethyl ether solution alone, and that the addition of glacial acetic acid does not seem to change the character of the deposit. When the glacial acetic acid added is saturated with sodium chloride, however, an adherent plate is obtained. Thus it would seem necessary for sodium chloride to be present if an adherent plate is desired, at least under the voltage conditions (13 and 116 volts) used in this experimentation. Even with sodium chloride present there is apparently a definite limit to the thickness of adherent deposit to be obtained since it was found that if current was allowed to flow through the cells for more than a certain length of time (6-7 hours with 100-110 milliamperes at 116 volt potential) the adherent deposit was further coated with a non-adherent powder. This can be explained by the fact that boron does not conduct electricity at room

temperature. Evidently the boron (if it is boron) has affinity for the copper under the right conditions and will adhere to it, but ~~has~~ not any affinity electrolytically for itself. In other words, as long as the copper surface is free, boron will adhere to it, but when coated with a deposit, more boron cannot reach it and hence deposits on itself as a fine non-adherent powder. Results further showed in substantiation of this theory that in those long runs when both types of deposit were obtained, the current had substantially dropped off at the end.

One possibility which should not be overlooked is that this electrolysis might have been a colloidal phenomenon involving deposition of a resinous boron-containing colloid. The boron fluoride does have a high-boiling fraction ~~which in-~~ seems to be of a resinous nature and imparts the dark color to the solution. This possibility could be qualitatively ruled out by the fact that the deposits obtained had a definitely metallic appearance and took a chromium-like polish, but of course such evidence is not chemical proof.

The deposits obtained resembled boron in that: they did not dissolve in HCl or in cold nitric acid but did dissolve in hot nitric acid; they resemble boron in appearance (brown, amorphous powder - takes a high polish to resemble chromium - see introduction); they burn with a green flame and give a green flame borate test after oxidation. They do

not resemble boron in hardness, but this might be attributed to the fact that the adherent deposits were so thin, they could not be expected to be any harder than the copper on which they were deposited.

Summing up, this experimentation has uncovered a method to deposit electrolytically a substance which contains boron, has the characteristics of boron, has exhibited the properties to be expected of a thin plate of boron, but which has yet to be positively identified as metallic boron.

VI RECOMMENDATIONS

We recommend that:

These experiments be repeated and the valence state of the boron be determined definitely.

Experimentation be carried out to find the optimum current density for plating the boron.

Experiments be made using other boron halides as the source of boron, and using other organic solvents in an attempt to find better conditions for plating boron.

A larger cell be used so that a cathode having a larger area could be used.

The electromotive potential of the boron ion in the solution be determined.

APPENDIX

EXPANSION OF PROCEDURE

Preliminary Testing

The source of boron first considered was the Eastman Kodak product, boron fluoride ethyl ether (45% BF_3) which is a dark-colored liquid that fumes strongly in air. It reacts with water to form hydrogen fluoride and boric acid. We first prepared a vertical electrolytic cell as shown in Fig. 1, using a carbon rod for anode and a small copper plate for a cathode. Cell was then filled with boron fluoride ethyl ether solution and a potential of 13 volts impressed across its terminals. No current was registered on the 3-amp. ammeter which had been connected in the line.

Glacial acetic acid and sodium chloride were then added to the cell in rough quantities and a current of three hundredths of an ampere resulted. Bubbles arose from the anode very slowly. After half an hour the cell was disconnected. There was no deposit on the cathode.

Run # 1

Cleaned the copper cathode thoroughly with emery cloth, HCl, alcohol and ether and again prepared the cell with HAc, NaCl, and BF_3 solution. Thirteen volts impressed across this solution only gave three hundredths of an ampere current. After four hours the current was turned off and the cathode found to be still clean. The electrode separation was reduced

from three inches to one inch and the cell allowed to run for fourteen hours at seven hundredths of an ampere. The cathode was removed and washed in ether. It appeared to be covered with a black plate on which there were minute white crystals (probably sodium chloride). Washing with boiling water removed these crystals which did not reappear when the cathode was subsequently washed in alcohol and ether. The black surface of the copper was then polished lightly with a cotton cloth which removed some of the black deposit as a fine powder. The surface of the cathode had now acquired a gun-metal grey surface of metallic lustre. The deposit was not hard enough to withstand rubbing with emery cloth as was attempted on one corner. The cathode was analyzed spectrographically -- copper, boron, aluminum, and calcium were shown to be present.

Run # 2

Made another cell similar to the first (Fig. 1) and connected the two cells in parallel to a thirteen volt source (two storage batteries). Filled the first cell with the boron fluoride solution alone, the second with boron fluoride solution and acetic acid. The boron fluoride solution carried practically no current, but the second cell carried three-hundredths of an ampere. Both cells were allowed to run for nineteen hours. In each case, at the end of the run

the solutions were muddy, the anode eroded and the cathode was covered with a loose black deposit which came off easily on washing and burned quickly on gentle ignition. There was a slight discoloration of the cathode in each case, but nothing to compare with the black plate obtained in run # 1.

Run # 3

In order to avoid interference of carbon particles falling on the cathode as the anode slowly eroded in previous runs a U-cell was made as in Fig. II. The same type of cathode and anode were used as in the other runs. Thirteen volts potential was impressed across the cell giving a current of .01 amp. (decreased current probably due to increased electrode separation). Bubbles of gas were given off at the anode. The cell was disconnected after nine hours and the cathode washed in boiling water, alcohol and ether. The plate obtained was adherent and gave a gun-metal gray lustre with rubbing. This cathode was then dipped in fused boric acid. The coating was removed and only minute globules of silvery appearance were left on the surface of the copper. These were quite possibly from the solder which had been used to hold the plate to the wire. However, the boric oxide was not enough to melt the copper itself if it was submerged for more than a few seconds.

Run # 4

Two new U-cells were then connected in series to a 116 volt d.c. line. The current obtained was .08 ampere. The potential across the first cell was 57 volts and across the second, 59 volts. After four and one-half hours, the first cell was disconnected and the cathode found to have a black coating as in the previous runs. In both cells the dark color had migrated from the cathode portion into the anode portion. Connected second cell back into 116 volt line. Solution started to boil shortly afterwards and current went from 110 to 200 milliamperes. Placed cell in bath of continuous running water. Current went back to 110 milliamperes. Fourteen hours later found the anode had eroded so that there was no longer electrical contact, hence no current. Cathode had black very adherent deposit which after washing (as others were) buffed up to a chromium like finish on a buffing wheel. This plate did not dissolve in hot concentrated caustic as aluminum would have. Dissolved in conc. HNO_3 , added methyl alcohol and sulfuric acid and distilled mixture. Vapors burned with a green flame, indicating presence of boron.

Run # 5

Made palladium anod(of coiled wire) and nickel cathode for use in cell. Used no solder in order to avoid all possible extraneous effects. Filled U-cell with mixture of

BF_3 solution, glacial acetic acid, and small amount of NaCl. During the four-hour run, the dark color migrated to the anode as before and it was noticeable that flocculation took place in that arm of the water-cooled cell. There was a definite difference in the height of liquid in the two arms of the cell, that of the anode being $\frac{1}{4}$ inch lower than that of the cathode. Cathode showed a dark plate as had been obtained on the copper. Dipped nickel cathode in fused boric acid and dark plate disappeared.

Run # 6

Set up cell with same solution and electrodes as in run # 5 and allowed to run for 10 hours in bath of running water. Current was 110 milliamperes, voltage 116. Flocculation at anode again took place, a difference in height of the liquid in the two arms was again noted, this time amounting to about $\frac{1}{2}$ inch. Cathode was coated with a brown powder corresponding to the description of amorphous boron.

Run # 7

Set up cell similar to run # 6 except that a copper cathode was substituted for the nickel. It was noticed that bubbles were given off from both electrodes. Flocculation again took place at the anode, dark color migrated to the anode, and at the end, the level of the liquid was $\frac{1}{2}$ inch higher at the cathode than at the anode. Voltage 116, current 100 milliamperes. Copper cathode after washing and

polishing with a cotton cloth had a gun-metal plate on it.

Run # 8

Repeated run # 7 except that current was passed through cell for 18 hours in an attempt to get a thicker plate. Current decreased from 100 milliamperes to 60 milliamperes during the run, indicating that plate had electrically insulating properties. Found plate had brown amorphous powder on it which rubbed off to leave same gun-metal gray finish underneath. Since boron does not conduct electricity, it seems that there is a definite limit to the thickness of an electrolytically deposited plate of this substance. Probably powder was amorphous powder of boron indicating, as would be expected that the non-conducting boron has little electrolytic affinity for itself. The polished cathode was dissolved in concentrated HNO_3 , methyl alcohol and sulfuric acid added and the mixture distilled. The vapors burned with a green flame -- positive test for the presence of boron.

Run # 9

Cleaned a copper cathode in HNO_3 and HCl . Set up cell as in previous run with 116 volt potential. Current was 110 milliamperes. Removed cathode after 4 hours, washed and polished lightly. It had a very thin plate which lightened in HCl . Washed again in water, alcohol, and ether and returned

to cell for further electrolysis. Passed current (110 milliamperes) through cell for seven more hours. Obtained fairly good plate which after washing in water, boiling water, alcohol, and ether, and polishing had a gray fairly nonporous appearance.

Run # 10

Cleaned copper cathode in HNO_3 and HCl and weighed. Weight = 0.19800 g. Set up U-cell with palladium anode and weighed copper cathode and ran current (110 milliamps) through the cell for seven hours. Cathode had some loose powder on the plate which rubbed off on polishing. A gun-metal gray plate remained. Dried plate and weighed. Weight = 0.19845 g. Additional weight of 0.00045 g. was too small to justify running boric acid conversion and titration with NaOH to establish valence state of boron.

Run # 11

Using copper cathode and palladium anode in U-cell filled with boron fluoride ethyl ether alone, obtained current of 15 milliamperes with a potential of 116 volts. After running cell for 15 hours, found that cathode was covered with a loose black flaky deposit and the current had diminished to 8 milliamperes. Deposit came off readily on washing in ether. After heating a piece of nickel sheet and palladium in a flame until they gave no color to the flame, put some of this

washed powder on each, and in each case a green flame resulted upon heating -- fairly good proof of the presence of boron. This cathode had no adherent plate whatsoever, and it seems necessary for both NaCl and glacial acetic acid to be present before an adherent plate can be obtained.

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