ELECTRODEPOSITION OF MAGNESIUM AND BERYLLIUM FROM ORGANIC BATHS

by Abner Brenner and John L. Sligh

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ABSTRACT

Solutions that are feasible for electrodepositing magnesium were prepared from Grignard reagents with the addition of boranes in ether solutions. A typical bath consisted of methylmagnesium chloride, 3-molar, (dissolved in tetrahydrofuran) and 1-molar in triethylboron. The deposits were white, ductile and contained at least 99% of Mg. Cathode and anode current efficiencies were 100%. A similar beryllium plating solution, prepared with beryllium dimethyl and decaborane, yielded dark grey, coherent deposits containing 85% to 90% beryllium.

KEY WORDS: Magnesium, electrodeposition of; Beryllium, electrodeposition of; nonaqueous plating baths; Grignard reagents; Beryllium dimethyl; Beryllium azide; Beryllium thiocyanate, decaborane; triethylboron; Organic plating baths.

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I. INTRODUCTION

The chief interest in electrodepositing the light structural metals, beryllium, magnesium, and aluminum is for the purpose of electroforming light-weight engineering components of complex shape or precise dimensions that are needed in satellites. These metals are too active to be electrodeposited from aqueous solutions, hence, organic baths must be used. Of the three metals, aluminum is the only one that has been successfully electrodeposited and used in pilot-scale investigations. Recently, it has been utilized for plating fasteners used in the construction of aircraft.

Thus far, the literature contains no reports of feasible processes for depositing beryllium or magnesium. Our investigation has led to the development of an organometallic magnesium-boron plating system which is feasible for electroforming magnesium. We did not succeed in developing a beryllium plating bath, but some advances were made in the electrodeposition of the metal.

There is special interest in the possibility of electroforming beryllium because of its unusual properties. Electroforming would be all the more valuable for its utilization, because beryllium is hard and brittle, hence, difficult to fabricate by conventional metal-working procedures. Compared to the other light structural metals, aluminum and magnesium, beryllium has a surprisingly high modulus of elasticity $(42 \times 10^6$ psi) which is more than four times that of aluminum, six times that of magnesium, and larger than that of steel. The coefficient of linear thermal expansion of beryllium (11.6×10^{-6}) is less than half that of aluminum or magnesium. These outstanding properties of beryllium coupled with its low density $(1.85$ g/cm^3, about 2/3 that of aluminum) make it a valuable structural material in applications requiring a high strength to weight ratio, especially at elevated temperatures. (Aluminum and magnesium melt at 660°C and 650°C, respectively. Beryllium melts at 1277°C.) In spite of the advantages offered by beryllium it should be noted that the oxide is toxic and certain work codes should be observed in processing the metal and its compounds.

The literature up to about 1965 on the electrodeposition of beryl-
lium and magnesium from organic solutions was given in a recent publica-
tion [1] by one of the authors, hence, there is need only to call atten-
tion to articles subsequently published. Strohmeier and coworkers [2]
electrodeposited beryllium from mixtures of organometallic beryllium
compounds and quaternary ammonium salts. The baths were more in the
nature of fused salts than an organic solution. The deposits were con-
taminated with organic matter and/or alkali metal. An advance in the
electrodeposition of magnesium was reported by one of the authors in a
recent note [3]. The bath consisted of an organometallic magnesium com-
pound in conjunction with decaborane in an ether or tetrahydrofuran (THF)
solution. The deposits were white, smooth and ductile. The investiga-
tion of magnesium plating reported herein is an extension of this work.

All electrolyses were conducted in small vessels provided with an
prepurified
atmosphere of   argon. The electrolytic cell most used had a capacity
of 50 ml and is shown in figure 1. A smaller cell with a capacity of
10 ml is shown in figure 2. Transfer of air-sensitive materials to the
vessels was usually done in an inert atmosphere chamber (or glove box)
filled with argon. For storing stock solutions of air-sensitive mater-
ials, the vessel shown in figure 3 was used. Transfer was made in the
open from this vessel to the electrolytic cell with a pipette. Filtra-
tion in an argon atmosphere was done with the apparatus shown in
figure 4.

II. ELECTRODEPOSITION OF BERYLLIUM FROM ORGANIC SOLUTIONS

Although pure beryllium deposits were not obtained in our investigation, some advances were made in that baths were developed for producing smooth, sound deposits containing 85% to 90% beryllium. The remainder of the deposit was probably boron.

In an investigation [4] which was carried on in this laboratory about 15 years ago, the only system that showed any promise for beryllium deposition was beryllium borohydride dissolved in ethers. Although these solutions on electrolysis yielded sound, coherent coatings, these deposits were not pure beryllium, but a boron alloy containing about 70% beryllium. In the current investigation a 6-molar solution of beryllium borohydride in diethyl ether was electrolyzed. The few analyses gave a beryllium content of 55% which is lower than that reported earlier. This difference is probably bona fide, as experiments with another plating bath showed considerable variation in beryllium content with composition of solution. The apparent cathode current efficiency of deposition (assuming that the deposit was all beryllium) was in all cases much above 100%, in some instances being almost 200%./ This anomaly indicated the impurity of the deposit. The deposits were black, smooth, and chemically reactive. Most of them reacted with water vigorously to liberate hydrogen, and the dry deposits sparked like a lighter flint when struck with a hard, sharp object. Some of the deposits ignited and were completely consumed. None of the variants introduced into the plating operation, or into the composition of the baths, as given in Table I (No. 15-18), led to any appreciable improvement in the quality of the deposits.

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Most of the subsequent experiments involved the reaction of beryllium dimethyl with various compounds and the effect of variation of the solvent (Table I, No. 1-14). In the further search for an improved beryllium plating process we electrolyzed solutions of some different kinds of beryllium compounds, which had recently been prepared in non-aqueous systems, such as the azide and thiocyanate (No. 22-26). None of these experiments were successful and they are placed in Table I only for the purpose of record.

The most promising plating bath was prepared from beryllium dimethyl and decaborane, $B_{10}H_{14}$. The best deposits contained between 85% and 90% beryllium and were dark grey, smooth and coherent. Unlike the deposits obtained from the borohydride bath, they were stable in air and could be left indefinitely immersed in water. They did not spark when struck. However, they were brittle and did not lend themselves, therefore, to electroforming. Sound deposits 2 mils thick were obtained. No investigation was made of the greatest thickness obtainable.

The deposits were obtained over a wide range of operating conditions. Current densities ranged from 1 to 20 mA/cm^2. The best deposits were obtained at the lower current densities. The voltages in the plating cells of figure 1 with a cathode area about 5 cm^2 ranged from about 3 to 15 volts for this range of current density. An elevated temperature improved the conductivity of the bath, but did not improve the quality of the deposit appreciably.

Beryllium chloride etherate added to the bath in moderate quantity produced a slight improvement in the quality of the deposit and in the conductivity of the bath, but in large concentrations was deleterious. An optimum bath composition was: beryllium dimethyl, 2 molar; decaborane, 0.65 molar; and beryllium chloride, 0.65 molar. The solvent was diethyl ether. The bath could also be prepared with THF as solvent, and this had the advantage that THF has a higher boiling point than ether. However, the $BeCl_2$ had to be omitted as it forms an insoluble etherate in THF.

The most critical factor in obtaining stable, nonreactive deposits was the ratio of boron to beryllium in the bath. It may be noted that the ratio of boron to beryllium in the suggested bath composition is about 1:3 on a molar basis. An increase in the ratio of boron to beryllium, for example to 1:1, resulted in deposits which had lower percentages beryllium, reacted with water, and sparked when struck. These results explain the high reactivity of the deposits from the borohydride bath in which the ratio of boron to beryllium is 2:1.

A complete assay of the deposit was not performed but analysis revealed it to be of considerable beryllium content. The gross weight of the coating ranged from 140 to 180% that expected for pure beryllium, based on the number of coulombs passed. Even the beryllium content determined by analysis exceeded by 105 to 115% that calculated using the latter. Thus, these results suggest a complex ion reaction rather than the simple reduction of beryllium ion.

The decaborane bath was prepared by adding a solution of decaborane in ether to an ethereal solution of beryllium dimethyl. A very small addition of decaborane produced a large increase in conductivity of the solution (although decaborane by itself has a very low conductivity). For example, beryllium dimethyl in ether (in a small bath as noted above) required about 25 volts to pass a current of 10 mA and about 120 volts for a current of 35 mA. On adding decaborane equivalent to 1/30 of the moles of beryllium, the conductance of the system improved considerably: 10 mA required only 4 volts and 50 mA about 15 volts. Further additions of decaborane increased the conductivity slightly. A bath with only a small content of boron compound was not feasible to operate, however, as the voltage increased during operation, probably because of polarization. It was expedient, therefore, to have larger concentrations of boron, such as 1:6 or 1:3 of boron to beryllium (in moles).

The phenomena occurring during the preparation of the bath are interesting. The addition of decaborane to the beryllium dimethyl solution caused evolution of a gas, which was probably methane. The first small addition resulted in a clear solution, but as more was added, so as to produce a bath of the indicated composition, two layers formed. The lower layer had a much higher conductivity than the upper layer. However, similar appearing deposits were obtained from both layers, and the compositions of the deposits were not far different. Further additions of decaborane decreased the conductivity of the upper layer so that plating from it was no longer feasible. In the preparation of the indicated plating solution, it was expedient to evaporate off most of the upper layer, as a cathode contacting both layers received a nonuniform deposit.

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Since decaborane is still a rare compound (the current price of small quantities is about $3.00 a gram) the investigation was to some extent duplicated with triethylboron, which is commercially available at about $17.00 a pound. As with decaborane, a suitable bath was 2.0 molar in beryllium dimethyl and between 0.35 and 0.65 molar in triethylboron. The latter compound is much less pleasant to work with than decaborane, because it is spontaneously inflammable and cannot be handled in the open, but must be measured out in an inert atmosphere. The solutions in ether are less sensitive to the air and can be transferred in the air by pipette from a stock solution (preserved under argon) to a bath. The solution of triethylboron in THF is less likely to spontaneously inflame than the diethyl ether solution.

The phenomena involved in the preparation of the bath from beryllium dimethyl and triethylboron differed somewhat from those with decaborane as no gas evolution occurred on adding the boron compound and only a small amount of heat was produced indicating formation of a less tight complex. An interesting sidelight on the reaction of triethylboron with dimethyl beryllium is that the latter (which is a solid) did not react with the boron compound (which is a liquid) but remained undissolved and unreacted for a day. However, on adding ether the beryllium dimethyl quickly dissolved, presumably with formation of a complex, although there was no appreciable heat evolution.

In the triethylboron baths there was evidence that the boron compound was not as tightly complexed as in the decaborane bath, as on distilling out some of the ethereal solvent, the resultant solution had a somewhat lower conductivity, indicating volatilization of the boron compound.

With regard to the choice between THF and ether in forming a bath, THF may be advantageous as it formed a tighter complex with triethylboron than did ether, and this may be an advantage in reducing the escape of the boron compound and the flammability of the bath. Also, THF yielded slightly better conducting baths. However, the characteristics of the deposits from baths prepared from the two different ethers have not been compared.

As with the decaborane bath, the cathode efficiency of beryllium deposition was about 115%. The anode current efficiency varied between 80% and 100%. Deposits from a bath in which the boron to beryllium ratio was 1:1 in moles contained only 60% beryllium, and thus, were comparable to the deposits from the borohydride solutions. After distilling off some of the ether and presumably some of the triethylboron, the deposits then contained about 75% beryllium.

Some variations of the alkyl boron plating process were investigated (Table I, No. 12-14). Substitution of tributylboron for triethylboron had no advantage, except a lower flammability of the bath. Operation of the triethylboron bath in a closed system under pressure so as to attain a bath temperature of 90°C did not lead to any obvious improvement in the quality of the deposit or its beryllium content.

Since both dimethyl beryllium and triethylboron are not easy to obtain and are difficult to use because of their spontaneous inflammability, some effort was directed toward producing them in solution from simpler starting materials without isolating them. Production of beryllium alkyl was attempted by reacting an ethereal solution of beryllium chloride with lithium methyl in ether or lithium ethyl in benzene. By metathesis, lithium chloride precipitated out readily, but not completely. The precipitate was difficult to filter and the operation had to be done under argon pressure. It was found more expedient to pack the precipitate by centrifuging and pouring off the clear solution. Best results were obtained with beryllium chloride in excess. With nearly stoichiometric quantities, too much lithium remained in solution, and on electrolysis either deposited in preference to beryllium or co-deposited, thus resulting in mossy deposits. The experiments on the in situ production of the beryllium alkyl did not lead to satisfactory deposits and more work needs to be done.

The attempt to produce the boron compound in situ was more successful. An ethereal solution of beryllium dimethyl was treated with an ethereal solution of boron trichloride (freshly prepared). Provided that the content of boron was kept below the 1:3 molar ratio, the bath seemed to operate very much like the one prepared from triethylboron, but no detailed investigation was made of it.

The nonaqueous beryllium baths should all be protected from moisture. The baths containing alkyl boron compounds should also be protected from the air. The decaborane bath is not spontaneously inflammable, but no investigation was made as to the necessity of preserving it from the air. The triethylboron bath catches on fire if poured out into the open in any quantity. To dispose of the bath (volume 25-50 ml) it was poured into a metal vessel which was quickly covered with a metal plate. The solution absorbed oxygen and became hot, but combustion was prevented by the limited access of air.

One of the difficulties in enlarging the variety of compounds for the investigation of the electrodeposition of beryllium was the preferential deposition or codeposition of alkali metals involved in the preparation, for example, in Table I, No. 6,8,19,21, and 25. On the basis of the chemical reactivity of the metals, one would not expect this to happen.

The electrodeposits were assayed only for their beryllium content. Because of the small electrochemical equivalent of beryllium, the amount of deposit available for assaying was often only 5 or 10 milligrams, and the determination of the small amount of boron in the deposit would have been difficult. The beryllium content was determined by a simple procedure. The deposit was dissolved from the copper basis metal with dilute hydrochloric acid and the solution transferred to a platinum crucible. Ammonia was added to precipitate beryllium hydroxide, the contents of the crucible were evaporated to dryness in an oven and ignited. Ammonium salts, boron oxide, and organic matter were volatilized and only BeO remained.

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III. ELECTRODEPOSITION OF MAGNESIUM FROM ORGANIC SOLUTIONS

A. From Grignard Reagents

The early work on the attempts to electrodeposit magnesium was discussed and referenced in a recent publication [1], hence, these investigations need not be discussed in detail. One aspect of the early work, however, is perplexing. The reports on the electrolysis of Grignard solutions were to the effect that the conductivity of the solutions was low and that the deposits were mossy or crystalline and could not be removed intact from the bath. For example, Overcash and Mathers [9] used an ethylmagnesium iodide solution and stated that,

"The Grignard reagent, without dimethylaniline, gave loose, crystalline deposits of magnesium and extending "trees" formed so rapidly that cathodes could not be removed from the bath without loss. .....

"The Grignard reagent made from ethyl bromide instead of ethyl iodide gave a bath that had a higher resistance and was less stable.

"The anode current efficiency was zero, but the cathode efficiency was approximately 55 percent.

"The bath was not easy to operate and any commercial operation would seem impossible.

"The really great difficulty was due to the failure of the magnesium anodes to dissolve or corrode during electrolysis. This caused a gradual decrease in the concentration of the magnesium in the bath until, at last, no electrodeposit could be obtained."

Connor, Reid, and Wood [10] had a similar experience with treeing with a 2.5 molar ethylmagnesium bromide solution.

The following discussion shows that these early observations are at variance with our experience with commercial Grignard reagents, some of which yielded smooth, white deposits without trees and required only about 5 volts for the above current density.

Table II lists 15 organometallic compounds of magnesium which were electrolyzed in ether solutions. Unless otherwise indicated the solutions were 2 to 3 molar in magnesium and were chlorides. All solutions, except the one with the cyclopentadiene derivative yielded fairly smooth, sound deposits of magnesium ranging in color from white to dark grey. The voltages required for a given current density of deposition varied widely, for example, 5 mA/cm^2 required a voltage of 6 with t-butylmagnesium chloride in THF (No. 8 in Table II), whereas t-butylmagnesium chloride in ether (No. 7 in Table II) required 43 volts, and cyclohexylmagnesium chloride in ether (No. 9) required over 120 volts. A solution of magnesium diethyl (prepared by precipitating magnesium chloride from the Grignard reagent with dioxane) had a still lower conductivity (see No. 1 No. 15). Hence, the presence of the halide ion is important in conferring conductivity.

Since there are available a large number of Grignard reagents with widely different electrochemical characteristics, a large variation in the characteristics of electrodeposition from the various solutions is to be expected. On the one hand, a solution can be very well behaved. For example, the methylmagnesium chloride solution in THF yielded a magnesium deposit, at least 99% pure, at cathode and anode current efficiencies of 100%. The methylmagnesium iodide solution gave similar efficiencies and, judging form the ductility of the deposits, these also were pure magnesium. On the other hand, anode efficiencies ranging from 75% to 100% and cathode current efficiencies ranging from 75% to 115% were obtained for other Grignard solutions, and it is likely that the high cathode efficiency represented codeposited nonmetallic material.

The 3-molar methylmagnesium chloride solution in THF and the 3-molar methylmagnesium iodide solution in ether, without modification, are both satisfactory baths for electrodepositing magnesium. At the lower range of current densities they yielded smooth, white deposits 1 mil thick without treeing. The only drawback was the low conductivity of the solutions. The conductivity of the chloride solution was 0.0010 mho or about 2/3 that of a 1/100 molar KCl solution. Some of the other Grignard solutions also might be satisfactory for depositing thin coatings of magnesium. The ethyl magnesium bromide bath, as reported in the literature, did start to give treed deposits after several minutes of electrolysis. Despite the variation in the performance of the various Grignard solutions on electrolysis, we did not encounter the extreme difficulties reported by others for the common Grignard reagents and are unable to explain them. The difficulties may be a composite of a number of slightly unfavorable factors, such as exposure of the Grignard to the oxygen of the air, use of a bromide instead of a chloride, presence of excess alkyl halide in the reagent, use of ether instead of THF, and a lower concentration of Grignard in the solution.

The passage of dry air through a Grignard reagent (ethylmagnesium bromide in ether) did not destroy the ability of the solution to yield magnesium on electrolysis. However, a higher current density was required and the deposit was less sound.

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B. From Grignard Reagents with Boron Additives

A great improvement in the electrodeposition of magnesium was obtained by complexing the magnesium organometallic compound with a borane type compound. The first successful bath consisted essentially of a magnesium alkyl halide complexed with decaborane [3]. Subsequently, it was found, as the case with beryllium deposition, that the more accessible alkyl boranes could be used in place of decaborane. The following report deals mainly with Grignard reagents to which triethylboron had been added.

As was the case with beryllium dimethyl, the addition of triethylboron to the solution of the organometallic magnesium compound greatly increased the conductivity. Table II shows that although some of the Grignard reagents had widely different conductivities, as evidenced by the widely different voltages required for a given current (compare No. 1 with No. 9 or with No. 14) after addition of triethylboron, in the ratio of about 1/3 mole to 1 mole of magnesium, the conductivities were as much as ten-fold higher and very much alike for all the Grignards. The conductivity of methylmagnesium chloride in THF with added triethylboron was 0.004 mho or about the same as that of 1/30 molar KCl solution.

With respect to the composition of the bath, those prepared from the lower molecular weight Grignards gave the whiter deposits and had a more constant voltage on continued operation. Also, a higher current density could be used in these baths. For example, a current density of 20 mA/cm^2 was feasible with the methylmagnesium iodide bath, but not with the cyclohexyl or phenyl baths. The effect of the solvent is shown by comparison of bath No. 7 with No. 8 and of bath No. 9 with No. 10. The Grignard reagents made up with THF (without the boron compound being present) were more highly conductive than those made up with diethyl ether. However, after the boron complex had been formed, there was less difference, or the situation could even be reversed. Note that the boron complex of methylmagnesium iodide in ether (bath No. 4) had the lowest operating voltage of any of the baths, a current density of 20 mA/cm^2 requiring less than 3 volts.

The ratio of boron to magnesium was not as critical as with the beryllium baths. A ratio of 1:3 moles of boron to magnesium gave good results. A ratio beyond 1:2 was no advantage. It might even lower the conductivity of the solution and it increased the inflammability.

The anode and cathode efficiencies were determined in only a few instances. They were both about 100% and the assay of the deposits indicated that they were at least 99% magnesium.

Sensitivity to oxygen is not an essential characteristic of the bath for magnesium deposition. Our experience with the decaborane bath [3] was that it could be operated in the presence of air although, as is the case with all nonaqueous plating baths, moisture had to be excluded. Also, bath No. 12 in which o-carborane was used instead of triethylboron should not be oxygen-sensitive, inasmuch as o-carborane is highly oxidation resistant. To test the effect of oxygen on a triethyl-boron-magnesium bath, dried air was bubbled through the cyclohexylmagnesium chloride bath (Table II, No. 9) for 30 minutes. The reaction caused the bath to heat up to about 45°C. On electrolysis a satisfactory appearing deposit of magnesium was still obtained, although the voltage of deposition was several volts higher.

Perhaps the optimum baths for electrodepositing magnesium are 3-molar solutions of methylmagnesium chloride in THF or iodide in diethyl ether, which are 1-molar in triethylboron. Current densities of 2 to 10 mA/cm^2 may be used. Although the anode corrosion is 100% efficient, the piling up of anode products around the anode at the higher current density may result in an increase in the operating voltage.

In one experiment boron trifluoride was added to the ethylmagnesium chloride solution instead of triethylboron. The conductivity of the solution increased. The electrodeposit was not as white as the one obtained with triethylboron, but it was sound. This experiment indicates that with further investigation, inorganic boron halides might be used for preparing the baths in place of triethylboron.

An alloy was electrodeposited from a bath produced by adding one of the beryllium plating baths, prepared from triethylboron and beryllium dimethyl, to an analogous magnesium plating bath. The white deposit was analyzed qualitatively and found to contain beryllium.

The magnesium content of the deposits was assayed by dissolving the coating from the copper cathode with dilute acetic acid, evaporating to dryness in a platinum crucible, and igniting. Magnesium was weighed as MgO.

IV. DISCUSSION

Although the best beryllium-containing electrodeposits contained only 85% to 90% of metal, the prognosis for further improvement in the plating process is good. Deposits with higher beryllium contents might be obtained by developing baths with a lower boron to beryllium ratio than the ones used in this investigation. There are a host of derivatives of decaborane, carborane, and the alkyl boranes to choose from in formulating a bath. The plating process that we developed is not suitable for electroforming because the deposit is too brittle.

The magnesium plating process should have some applicability for electroforming light-weight components, and might even displace aluminum plating for the purpose. One advantage of magnesium is its lower density, 1.74 as compared with 2.7 for aluminum. Thus, an object formed from magnesium instead of aluminum would be reduced in weight by one-third. Another advantage of the magnesium plating process over aluminum plating is the greater economy of the materials. Aluminum plating from the hydride-ether system requires the use of lithium aluminum hydride, which is still an expensive reagent. Magnesium plating can be done from Grignard reagents which are commercially available in quantity and the boron can be introduced into the bath in the form of the relatively inexpensive boron trichloride or trifluoride instead of using an organic borane. However, before magnesium plating can become commercially feasible, much more investigation needs to be done: to select the best composition of bath from the innumerable Grignard reagents, ethers, and borane derivatives, which have been prepared; to investigate the behavior of the bath over a long period of operation; and to determine the properties and composition of the deposits obtained over a range of operating conditions.

Another possible future application of magnesium is as coatings for the protection of steel. The metal is now used in the massive state for the cathodic protection of steel. As a coating, magnesium would have to compete with the much cheaper zinc. However, if sacrificial protection were the only criterion, magnesium could compete with zinc because of its much smaller equivalent weight (12.2 as compared with 32.7 for zinc) which is a little more than a third of that of zinc. Stating this in a more concrete fashion, if magnesium cost 35 cents per pound, 13 cents worth of magnesium would yield the same electrochemical protection as a pound of zinc (which costs about this amount). Another consideration is that magnesium is the third most abundant structural metal (after aluminum and iron) and about 200 times more abundant than zinc in the earth's crust. A cubic mile of sea water, from which magnesium is easily obtainable, contains 6 million tons of magnesium. Thus, at some future date, coatings of magnesium may displace zinc. In the atmosphere and in various solutions, magnesium corrodes at a rate comparable to that of zinc [12].

The codeposition of a few percent of beryllium with magnesium may be of interest for increasing the strength of the magnesium deposit. Beryllium is not appreciably soluble in magnesium in the solid state, hence, if codeposited, it might yield an alloy amenable to precipitation hardening. Beryllium-magnesium alloys are difficult to produce by simple metallurgical techniques.

V. ACKNOWLEDGMENT

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TABLE I

BERRYLLIUM PLATING SOLUTIONS WHICH WERE CURSORILY EXAMINED

Bath No.	Solvent	System Composition	Variant or Purpose of Experiment	Notes
1	Diglyme	Beryllium dimethyl	Solvent	At room temperature, mossy deposit, reactive with water. At elevated temperatures, smooth and adherent. System not promising.
2	Sulfolane	Beryllium dimethyl	Solvent	Thin, Black deposit. Not promising.
3	Ether	Beryllium dimethyl + Tributylphosphine	Phosphine derivative	Deposit like that from dimethyl beryllium alone. Not promising.
4	Ether	Beryllium dimethyl + Thiocyanogen	Thiocyanogen	No deposit.
5	Ether	Beryllium dimethyl + HCN	HCN	Solution: low conductivity. Deposit similar to that from $Be(CH_3)_2$ alone.
6	Ether	Beryllium dimethyl + Sodium hydride	To prepare beryllium methyl hydride.	Deposit was probably sodium.
7	Dimethyl Ether	Beryllium dimethyl	To compare dimethyl with diethyl ether.	Much better conductivity than either diethyl ether or THF.
8	THF	Beryllium dimethyl + alkali metal fluorides (KF,RbF,CsF)	Presence of fluorides to form a complex.	Deposit was reactive with water and was mainly alkali metal.
9	None	Beryllium dimethyl + $POCl_3$	Reaction with $POCl_3$	Violent reaction with flame.
10	THF	Beryllium dimethyl + $H_2(B_{12}H_{12})$	To prepare beryllium-boron salt by metathesis.	Mixed solutions gelatinized, probably because of precipitation of the beryllium-boron salt.
11	Ether	Beryllium dimethyl + o-Carborane	Boron compound	Deposit obtained, but no advantage over bath prepared with decaborane or triethylboron.
12	Ether	Beryllium dimethyl + Boron trichloride	To use the more accessible BCl_3 in place of triethylboron.	Black, adherent deposit. Promising bath, which might replace that of triethylboron. Too much BCl_3 is deleterious to deposition.
13	Ether	Beryllium dimethyl + Boron trifluoride	To use BF_3 instead of triethylboron.	Precipitation of BeF_2. Electrodeposit not satisfactory.
14	THF	Beryllium dimethyl + Tributylboron	Substitution of ethyl by butyl.	Deposit similar to, but less satisfactory than that with triethylboron.
15	Ether	Beryllium Borohydride + $BeCl_2$ etherate	Borohydride instead of beryllium dimethyl and addition of $BeCl_2$.	Conductivity increased by $BeCl_2$, but deposit similar to that from borohydride bath alone.
16	Ether	Beryllium Borohydride + triethylamine	Addition of triethylamine to borohydride bath.	No improvement in deposit.
17	Ether	Beryllium chloride etherate + $LiBH_4$	To prepare $Be(BH_4)_2$ in solution by metathesis.	Electrolysis of bath and nature of deposit similar to bath prepared from solid $Be(BH_4)_2$.
18	Ether	Beryllium Borohydride + HCN	Effect of HCN on Borohydride bath.	No improvement over borohydride bath alone.
19	Ether	$BeCl_2$.etherate + Li methyl + triethylamine	To prepare $Be(CH_3)_2$ in solution by metathesis. Then add $B(C_2H_5)_3$.	Deposit unsatisfactory. Reactive with water. Probably contained lithium.
20	Ether	$BeCl_2$.etherate + Li ethyl in benzene + triethylboron	To prepare $Be(C_2H_5)_2$ in solution and then add $B(C_2H_5)_3$.	If half the stoichiometric amount of Li ethyl is used (Excess $BeCl_2$ is then present) electrodeposit is obtained after addition of $B(C_2H_5)_3$ to bath.
21	Ether	$BeCl_2$.etherate + $LiB(C_2H_5)_2$ prepared from Li ethyl + triethylboron	To prepare bath without using beryllium dimethyl.	Deposit reactive. Probably mostly lithium.
22	Ether	Beryllium cyclopentadiene, 0.5 M [5]	Different beryllium organometallic compound.	Conductivity very low. Less than 1 mA at 115 V. On addition of $BeCl_2$, small amount of black electrodeposit. Unsatisfactory.
23	Ether	Beryllium Thiocyanate [6]	Different beryllium inorganic compound.	Solution conducted, but no electrodeposit.
24	THF	Beryllium Azide [7]	Different beryllium inorganic compound.	Electrodeposit reactive with air.
25	Ether and THF	Beryllium Azide + $Na_2B_{10}H_{10}$	Prepare beryllium boron salt by metathesis.	Incomplete metathesis. Electrodeposit reactive with air and was probably mostly sodium.
26	THF	Beryllium metal reacted with acetyl chloride [8]	Different beryllium compound.	No electrodeposit obtained.

TABLE II

COMPARISON OF THE VOLTAGES REQUIRED TO PRODUCE A RANGE OF CURRENT DENSITIES

IN SOLUTIONS OF VARIOUS ORGANOMETALLIC MAGNESIUM COMPOUNDS.

(Unless otherwise noted, all solutions were between 2 and 3 molar and were chlorides.
In the boron-containing baths, the ratio of boron to magnesium was 1/3:1 in moles.)

Solution No.	Organometallic Compound of Magnesium	Solvent	MAGNESIUM COMPOUND ALONE Voltage to Produce Current Density				COMPOUND WITH TRIETHYLBORON Voltage to Produce Current Density			
			2 mA/Cm^2	5 mA/Cm^2	10 mA/Cm^2	20 mA/Cm^2	2 mA/Cm^2	5 mA/Cm^2	10 mA/Cm^2	20 mA/Cm^2
1	Methyl	THF	2	5	9	17	0.6	1.0	2.0	4.0
2	Methyl[†]	THF	2	5	9	17	1.3	2.7	5.3	10.5
3	Methyl[π]	Ether	5	16	34	55	0.3	0.6	1.1	2.0
4	Methyl[*]	Ether	3.7	8	14	30	0.3	0.7	1.2	2.2
5	Ethyl	THF	5	10	16	26	1	2	4.3	6
6	Ethyl[π]	Ether	10	21	44	—	1.4	2.7	4.8	9
7	t-Butyl	Ether	18	43	58	—	1.0	2.1	4.0	7.3
							Solution evaporated and THF added:			
							0.7	1.3	2.3	4.0
8	t-Butyl	THF	2.8	6	12	21	0.7	1.4	2.6	4.5
9	Cyclohexyl	Ether	38	>120	—	—	0.5	1.0	1.9	3.5
							Evaporated and THF added:			
							0.8	1.6	3.4	6.5
10	Cyclohexyl	THF	3.8	9.5	22	—	0.8	1.5	3.0	8.4
11	Vinyl	THF	2.7	6.6	16	—	1.4	3.5	10	—
12	Allyl[**]	THF	3.7	8.0	16	30	1.0	2.0	4.5	7.0
13	Phenyl	THF	5	12	28	50	1.3	3.3	6.5	13
14	Ethyl[***]	THF	>120	—	—	—	0.7	1.4	3.5	6.4
15	Cyclopentadiene[***] [11]	THF	#̸	—	—	—	—	—	—	—

[†]Methyl magnesium chloride complexed with decaboron (instead of triethylboron) with addition of magnesium chloride in THF.

[π]Bromide instead of chloride.

[*]Iodide instead of chloride.

[**]o-Carborane used instead of triethylboron.

[***]No anion present

#̸Conductivity less than 0.1 mA at 10 volts for a 0.2 Molar solution. No deposit obtained. After addition of magnesium chloride in THF to the bath an electrodeposit of magnesium was obtained.
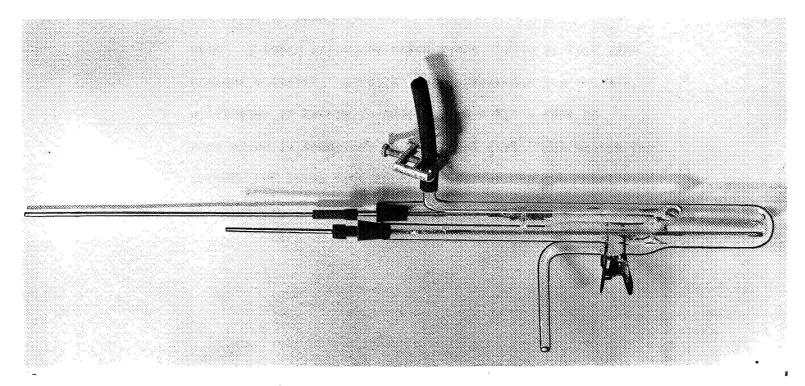
FIGURE 1. Electrolytic cell with a capacity of 50 ml. Argon enters
cell through tube on left and passes out through tube on
right, which is connected to a mercury trap. When an
electrode is removed from the cell, a vigorous stream of
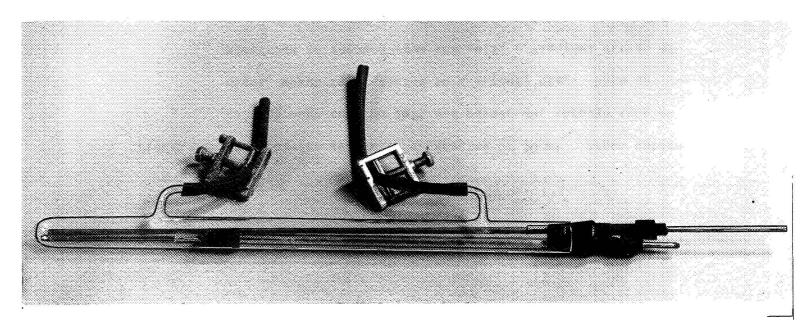argon flows upward through the glass chimney and prevents
ingress of air.

FIGURE 2.   Electrolytic cell with a capacity of 10 ml.   Argon passes

through the lower side tube and out through the upper side

tube which is connected to a mercury trap.   One of the two

electrodes is partially enclosed in a glass tube to

prevent shorting.   Usually, both electrodes are removed at

once.   A rapid stream of argon flows upward at this time
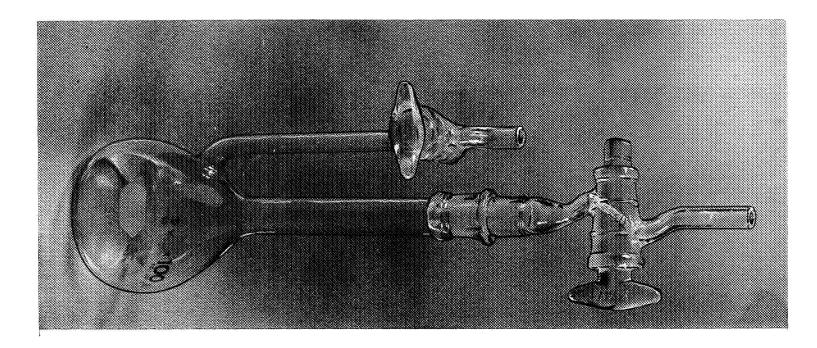
and prevents ingress of air.

FIGURE 3. Flask for storing spontaneously inflammable or air-
sensitive stock solutions. A current of argon flows
into the side tube on the left and out through the
upper stop-cock. The latter is removed, while a rapid
stream of argon flows upward through the neck of the
flask. The atmosphere protects the solution while a
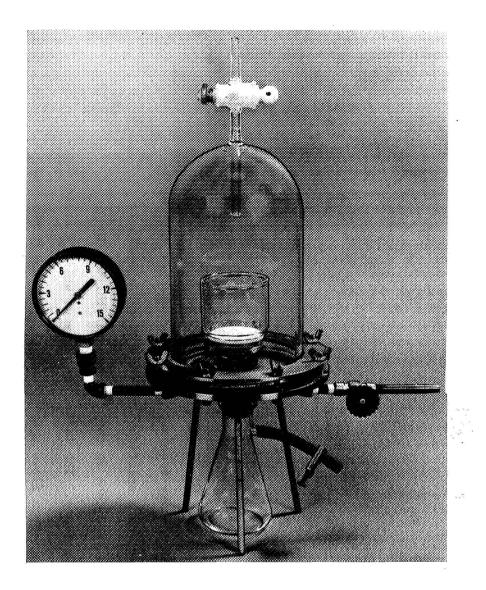pipette is lowered into it for a sample.

FIGURE 4. Apparatus for filtration under pressure of an inert
atmosphere. The solution to be filtered is forced by
pressure of an inert gas through the upper stop-cock
into the filter. Next, an inert gas is applied through
the valve on the right which is connected to a tank
of argon. Packing of a precipitate by centrifuging
usually was more rapid than filtration under pressure.