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MAGNESIUM ELECTRODEPOSITION

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ABSTRACT OF THE DISCLOSURE

The method of electrodepositing a coherent, microcrystalline layer of magnesium and the bath used in such method. The method and bath initially consist essentially of an alkyl magnesium halide, preferably ethyl magnesium bromide, in the concentration range of about 1 to 3 molar in a solvent consisting essentially of tetrahydrofuran. After starting electrodeposition, an alkyl halide, preferably ethyl bromide, is added at a rate sufficient to maintain a concentration slightly above about 0.001 molar, and the alkyl magnesium halide is added at a rate sufficient to maintain a constant concentration. The method is adaptable in the electroforming of magnesium structures.

BACKGROUND OF THE INVENTION

Field of the invention

The field to which the present invention pertains is the field of electroforming structures which involves the electrodeposition of relatively thick, uniform metal coatings having excellent structural characteristics in low or no internal stress.

Description of the prior art

In the development of modern technology, a need has developed for large, dimensionally accurate structures such as, for example, parabolic reflectors used for solar collectors and antennas. Preferably, such structures are both strong and lightweight, particularly, for various space applications. However, such structures must be capable of being built relatively inexpensively and quickly in order to be economically useful. To meet such needs, a variety of fabrication processes have been developed including expanding plastics, stretch-forming metals, explosive-forming metals, and electroforming metals. However, to date, the electroforming process has been found to achieve the highest dimensional accuracy of any available fabrication process. Consequently, large dimensionally accurate metal structures have been formed out of metals such as nickel and copper. While such structures have been suitable for certain applications, it has been found that they have certain disadvantages for other applications. For example, if it is necessary to have a nonmagnetic structure to be compatible with magnetometers, then the use of nickel is practically ruled out. Likewise, where reasonably high strength-to-weight ratios are required, copper has not been found suitable. Consequently, substantial efforts have been directed to the electroforming of metals such as aluminum, magnesium, and beryllium. In the case of magnesium, it is common to produce magnesium by the electrolysis of a fused salt system including magnesium chloride, i.e., the Dow precess. However, the electroforming of a structure using a fused salt system has to date encountered insuperable difficulties. For example, normally magnesium is recovered from such systems in liquid form and yet the bath inherently requires high operating temperatures. If aqueous systems or inorganic, non-aqueous systems including ammonia, nitrosyl chloride, and borazine, are considered, again

process limitations preclude their use for the electroforming of magnesium structures. Consequently, the use of organic systems has appeared to be the most desirable approach to the electrodeposition of magnesium. However, to date when magnesium has been electrodeposited using an organic system, the resulting magnesium deposit had a powdery sponge form which lacks structural strength. An example of such prior electrodeposited magnesium would appear to be the unwanted magnesium deposition in the production process for tetraethyl lead described in Chemical & Engineering News, Dec. 7, 1964, pp. 52–53.

SUMMARY OF THE INVENTION

Consequently, the present invention is a method of electrodepositing a structurally strong coherent microcrystalline layer of magnesium and the bath used in such method. Such bath consists essentially of an alkyl magnesium halide in a concentration range of 1 to 3 molar and an alkyl halide in the concentration of about 0.001 molar in a solvent consisting essentially of tetrahydrofuran. The method involves forming the bath of the alkyl magnesium halide solution and electrodepositing magnesium from said bath. Simultaneously with such electrodeposition, the alkyl halide is added to such bath to achieve the desired concentration and to dissolve magnesium sponge deposit but not corrode the magnesium layer deposit. Likewise, alkyl magnesium halide is added at a rate sufficient to maintain its concentration in the solution substantially constant.

Consequently, an object of the present invention is the production of a large, lightweight, dimensionally accurate, magnesium structure by electroforming. Another object of the present invention is to electroform a structurally strong large magnesium structure.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The magnesium electrodeposition bath used in the method of the present invention consists essentially of an alkyl magnesium halide in the concentration range of about 1 to 3 molar and an alkyl halide in the concentration of about 0.001 molar in a solvent consisting essentially of tetrahydrofuran. The alkyl portion of the alkyl magnesium halide used in such bath may contain 1 to 6 or more carbon atoms as long as the compound remains sufficiently soluble in the bath; however, the ethyl radical is preferred. The halide portion of the alkyl magnesium halide may be any member of the halide group. For example, while the use of chloride achieves a more efficient use of the electrical power input, the use of bromide produces a somewhat better quality magnesium layer. Consequently, the use of bromide for the halide is preferred. The concentration range of the alkyl magnesium halide in the bath is in the range of about 1 to 3 molar. At concentrations below such concentration range the quality of the resulting magnesium layer substantially decreases, i.e., becomes spongy and loses its structural strength. At concentrations above such concentration range, the resistance of the bath increases so that the overall efficiency of the process decreases.

Similar to the alkyl magnesium halide, the alkyl portion of the alkyl halide used in the bath has 1 to 6 or more carbon atoms with the ethyl radical preferred. Similarly, the halide portion of the alkyl halide may be any member of the halide group with bromide being preferred. The concentration of the alkyl halide is about 0.001 molar. At alkyl halide concentrations substantially below such concentrations, the quality of the magnesium layer deposited substantially decreases. On the other hand, at concentrations substantially above such concentrations,

the quality of the magnesium layer again decreases, i.e., the layer of magnesium deposited becomes corroded. Although it is preferred to use the same alkyl and halide portions for both the alkyl magnesium halide and the alkyl halide, a different member of these groups may be utilized for the different compounds. For example, an ethyl radical may be utilized with the alkyl magnesium halide while the methyl radical is used in the alkyl halide and chloride may be used in the alkyl magnesium halide while bromide is used in the alkyl halide.

As set forth above, the solvent for the bath consists essentially of tetrahydrofuran; however, such compound may be diluted by one or more other ethers. Thus, an alkyl ether containing 1 to 6 or more carbon atoms such as ethyl ether, isopropyl ether, butyl ether, and hexyl ether may be added to the concentrations up to about 4 volumes to each volume of tetrahydrofuran. In addition, the evaporation losses of the bath solvent can be reduced by decreasing the bath vapor pressure by addition of solvents with high boiling points. Such additives must also be chemically inert to the bath constituents, be completely miscible, and have no adverse effects on the mode and quality of the electrodeposit. An example of such additive is bis(2-butoxy ethyl) ether which can be added in quantities up to equal volume to the tetrahydrofuran. In operation, the method of the present invention involves forming initially a bath consisting essentially of an alkyl magnesium halide in the concentration range of about 1 to 3 molar in a solvent consisting essentially of tetrahydrofuran. Then, magnesium is electrodeposited by passing electric current through said bath. Any clean, inert electrode may be utilized in such electro-depositing step for either the anode or cathode. Thus, silver electrodes were used for both anode and cathode in the method of the present invention. In addition, a separator such as a cellulosic membrane may be utilized to form anolyte and catholyte compartments during such electrodepositing step. Also, the bath may be agitated and portions of the bath circulated through a filter to remove particles suspended in the bath. Such techniques may improve the quality of the magnesium layer deposited. The current density during such electrodepositing step is up to about 40 amps per square foot. Above such current density, the quality of the magnesium layer deposited is substantially decreased. However, it should be noted that at the higher current densities, a higher concentration of alkyl magnesium bromide should be utilized to prevent a decrease in the quality of the magnesium layer deposited. Also, the quality of the magnesium layer deposited may be improved by reverse current cycling, although this substantially decreases the rate of deposition. Thus, at current densities of about 10 amps per square foot, if the time period for the forward direction of the current to the time period for the reverse direction of the current is in the ratio of about 12 to 1, a greater thickness of magnesium layer may be deposited without a decrease in its quality.

Simultaneously with the electrodepositing step, two constituents are added to the bath. One constituent is the alkyl magnesium halide present in the bath which is added at the rate sufficient to maintain a substantially constant concentration of said magnesium halide in the bath. In the present invention, such rate is one electrochemical equivalent of the alkyl magnesium halide, i.e., one-half its molecular weight, for each Faraday of electricity passed through the bath. The second constituent added to the bath is the alkyl halide at a rate sufficient to maintain a concentration of about 0.001 molar and to dissolve the magnesium sponge deposit but insufficient to corrode the magnesium layer deposit. Such rate in the present invention is about one-fourth the electrochemical equivalent weight, i.e., the molecular weight, of the alkyl halide for each Faraday of electricity passed through the bath. At a current density of about 10 amps per square foot, the proper rate of addition of the alkyl halide was achieved by adding a 0.1 molar solution of ethyl bromide in diethyl ether.

A flat magnesium plate was electroformed utilizing a bath containing a concentration of 1.5 moles of ethyl magnesium bromide in a solvent formed of equal volumes of tetrahydrofuran and diethyl ether. Simultaneously with the electrodepositing at a current density of 12 amps per square foot, ethyl bromide was added in the form of a 0.1 molar solution in diethyl ether at the rate of 10 ml./hr./ampere and ethyl magnesium bromide was added in the form of a solution of 1.5 molar in diethyl ether at the rate of 11 ml./hr./ampere. Under such conditions magnesium was deposited at the rate of approximately one mil per hour to form a 14 mil thick plate whose physical properties were tested. Such plate was found to have a yield strength with 2% offset of 9,855 p.s.i. with an ultimate yield strength of 10,400 p.s.i., the hardness (vicker) of 240, a density of 0.065 pound per cubic inch, and a relative yield strength-to-weight ratio of 1.95 (as compared to electroformed aluminum with a yield strength of 7,700 p.s.i. and a density of 0.100 pounds per cubic inch).

It should be noted that at present there is no theoretical basis for explaining a substantial portion of the operation of the present invention. Thus, the necessity of using an alkyl magnesium halide at its proper concentration as well as the use of tetrahydrofuran in the solvent at its proper concentration were empirically determined. Similarly, the necessity of adding the alkyl magnesium halide and the alkyl halide and the rates of such addition were also empirically determined. However, the following theory may explain a portion of the operation of the present invention. Such theory should be regarded as merely a probable explanation for the unusual and unexpected results achieved by the present invention and not as a limitation upon the invention.

A significant factor in determining the quality of the magnesium layer deposited is the sequence of addition of the alkyl halide. Thus, if the alkyl halide is present in the bath in the recommended concentration before the electrodepositing step is started, the resulting magnesium layer deposited has a poor quality. On the other hand, if such alkyl halide is added simultaneously with the electrodepositing step, the desired structurally strong magnesium layer is achieved. The proposed explanation for such phenomena is that the initial presence of the alkyl halide before any magnesium is deposited results in the alkyl halide attacking the coherent microcrystalline magnesium layer as it is deposited. On the other hand, if such layer is formed initially before the alkyl halide is present, the alykyl halide attacks substantially only the sponge magnesium deposit which occurs along with the desired coherent microcrystalline magnesium deposit.

There are several features in the present invention which clearly show the significant advance the present invention represents over the prior art. However, only the most outstanding feature will be pointed out to illustrate the unexpected and unusual results obtained by the present invention. The main feature of the present invention is that the invention makes possible the electroforming of structurally strong magnesium structures. All known prior processes for the electrodeposition of magnesium resulted in a spongy or powdery deposit which lacked structural strength. The present invention produces a microcrystalline coherent magnesium layer which has a substantial tensile strength.

What is claimed is:

1. A magnesium electrodeposition bath adapted to deposit a coherent microcrystalline layer of magnesium consisting essentially of an alkyl magnesium halide in the concentration range of about 1 to 3 molar and an alkyl halide in the concentration of about 0.001 molar in the solvent consisting essentially of tetrahydrofuran.

2. A magnesium electrodeposition bath as stated in

claim 1 wherein said alkyl magnesium halide is an ethyl magnesium halide.

3. A magnesium electrodeposition bath as stated in claim 2 wherein said ethyl magnesium halide is ethyl magnesium bromide.

4. A magnesium electrodeposition bath as stated in claim 1 wherein said alkyl halide is ethyl halide.

5. A method of electrodepositing a coherent, microcrystalline layer of magnesium comprising:

(a) forming a bath consisting essentially of an alkyl magnesium halide in the concentration range of about 1 to 3 molar in a solvent consisting essentially of tetrahydrofuran;

(b) electrodepositing magnesium by passing an electric current through said bath; and

(c) Simultaneously with said electrodepositing step, adding to said bath (i) an alkyl halide at a rate sufficient to maintain a concentration of about 0.001 molar and to dissolve magnesium sponge deposit but insufficient to corrode magnesium layer deposit and (ii) said alkyl magnesium halide at a rate sufficient to maintain a substantially constant concentration of said alkyl magnesium halide in said bath.

6. A method of electrodepositing magnesium as stated in claim 5 wherein said alkyl magnesium halide is an ethyl magnesium halide.

7. A method of electrodepositing magnesium as stated in claim 6 wherein said ethyl magnesium halide is ethyl magnesium bromide.

8. A method of electrodepositing magnesium as stated in claim 5 wherein said alkyl halide is ethyl bromide.

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