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ALUMINUM ELECTROFORMING

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This invention relates to coating with aluminum. More particularly, it relates to an improved process and bath for depositing aluminum on metal, or other electrically conductive surfaces, and to a bright, smooth aluminum coating produced thereby.

The physical properties of aluminum, particularly its resistance to corrosion, tend to make it highly desirable for use as a structural material. However, the low tensile strength prevents widespread usage in pure form. Accordingly, many attempts have been made to form a coating of aluminum on steel or other suitable construction materials, wherein the aluminum coating will serve to protect the surface of the base material. Because of the physical properties of aluminum, it is also useful as a decorative, corrosion-resistant coating.

This improved process for electrodepositing aluminum is also useful in electroforming articles of complex shape. A low-melting alloy can be cast, or otherwise formed, into the desired shape, and then coated with aluminum. The base material is melted out, leaving a light-weight shell. This procedure is particularly useful for manufacturing radar wave guides and comparable electronic equipment. It has not been possible to make such articles by prior-art methods of electrodepositing aluminum.

Although several processes for electrodepositing aluminum have been described in the prior art, it has not been possible to produce dense coatings thicker than about 0.002 inch, since any excess of deposited metal consisted entirely of nonadherent powder, sponge or trees. As a result, the surfaces were not smooth and "bright" as the term is commonly used in the art.

Another difficulty encountered in prior-art methods of electrodepositing aluminum is the extremely short life of the bath. After only a few days' use, the bath deteriorates causing nonadherent deposits that are completely sponge-like.

In Patent No. 2,446,331, Hurley has disclosed an electrolyte for use in the electrodeposition of aluminum. This bath comprises an anhydrous aluminum halide and a N-alkyl pyridinium halide. Wier and Hurley, in Patent No. 2,446,349, show the addition to this electrolyte of a liquid aromatic hydrocarbon, such as benzene, toluene, xylene, and the like. Also, Wier, in Patent No. 2,446,350, discloses the further improvement of superimposing an alternating current on the direct current used in the plating bath.

In the process of Patents Nos. 2,446,349 and

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2,446,350, a finite amount of toluene was miscible with the aluminum halide-alkyl-pyridinium halide fusion, and any excess amount of hydrocarbon floated in a layer on top of the fusion. Copending application, Serial No. 254,655, filed November 2, 1951, discloses that if an excess amount of a liquid aromatic hydrocarbon is added, and if the bath is continuously agitated so that the excess hydrocarbon is dispersed throughout the electrolyte, a thicker plate having better properties can be deposited.

It has now been found that the addition of certain organic addition agents will result in the deposition of thick, dense and ductile aluminum coating which also has a greater hardness than prior-art coatings. In addition, this coating is "bright" and has a high degree of crystal orientation.

It is accordingly one of the objects of this invention to provide a "bright" aluminum coating which is dense and ductile.

Another object is to provide an aluminum coating having a high degree of crystal orientation.

It is a further object to provide an improved method of depositing aluminum on a metal, or other electrically conductive surface.

Yet another object is to provide an improved, long-life electrolyte for depositing aluminum on a metal, or other electrically conductive surface.

In general, the bath for depositing the aluminum coating comprises a nonaqueous solution of a fusion of an aluminum halide and a quaternary salt of nitrogen. This fusion is dissolved in an excess of a liquid aromatic hydrocarbon, an organic addition agent is added, and the bath is agitated continuously during the plating operation.

In preparing the fusion mixture for the bath, any aluminum halide may be used. The aluminum halide is fused with a quaternary salt of nitrogen, preferably a pyridinium salt. Very satisfactory results have been obtained by using a N-alkyl pyridinium halide, such as methyl or ethyl pyridinium halide. Proportions of about two mols of the aluminum halide to about one mol of the nitrogen salt will form a low-melting eutectic.

The solvent for the fusion mixture is a liquid aromatic hydrocarbon mixture, such as toluene or benzene. A sufficient amount of solvent is used to completely dissolve the fusion product and also form a layer of excess solvent on top of the fusion solution. Although any excess of solvent will aid in imparting desired properties to the bath, an excess of less than 23 per cent

per volume of the total bath will result in a plating which is less smooth, dense and ductile, than when a larger excess is used. If over about 45 per cent excess is used, it cannot be completely dispersed. The bath also tends to become nonconductive when more than about 45 per cent solvent is used. The most satisfactory platings were formed from baths having an excess of solvent in the range of from 35 to 40 per cent.

Suitable organic addition agents, which aid in giving desired properties to the bath, include methyl tert-butyl ether, ethyl ether, diphenyl oxide, dimethyl aniline, di-o-tolylurea, di-o-tolylthiourea and dichloroethylene.

The introduction of a small amount of the organic addition agent is sufficient to produce improved coatings. Although the exact amount will, of course, vary with the size and composition of the bath, current densities, placement of electrodes, amount of agitation, etc., very good results were obtained by an amount equal to about 1.0 to 2.2 per cent by volume of the bath.

The plating cells may be constructed of glass, ceramics, plastics, or any other suitable material which will not react with the bath. It is also desirable to provide a cover for the cell whenever possible in order to prevent the entry of impurities into the bath.

As has been heretofore disclosed, it is important that the bath be agitated during the plating operation in order to disperse the excess hydrocarbon solvent. Although any suitable means may be used for this agitation, the most satisfactory results have been obtained by bubbling an inert gas through the bath. Nitrogen, argon, or any other inert gas, may be used. However, care must be taken that no oxygen is present, since this causes the bath to degenerate. It is desirable to remove any oxygen present in the gas before passing it into the bath.

The flow rate of the gas depends, to a great extent, on the surface area of the plating bath. However, best results are obtained when the rate is slightly greater than the minimum flow needed to disperse the excess solvent. A rate of about 0.2 cu. ft. per hour per sq. in. of surface area provides satisfactory dispersion.

Dispersion of the excess hydrocarbon may also be accomplished by means supersonic vibration from a quartz crystal.

The base material to be coated forms the cathode in the bath. Materials suitable for coating include steel, copper, silver, lead-, zinc-, and cadmium-base alloys, and similar materials. The anodes are aluminum. High-purity aluminum, such as 99.9% or 99.99%, forms better coatings than, for example, 2-S aluminum. These anodes dissolve with a current efficiency nearly equal to 100 per cent.

During the coating process, the bath should be maintained within a temperature range of about 80° F. to about 100° F. At temperatures appreciably lower than 80° F., it has been found that the resulting coating tends to be brittle and cracked. The optimum temperature for coating is from about 83° F. to about 87° F.

For best results in coating, an alternating current should be imposed on the direct current passed through the bath. Successful results have been obtained with cathode densities of 5 to 25 amp. per sq. ft., D. C., and 2.5 to 50 amp. per sq. ft., A. C. Preferred current densities are in the range of 8 to 10 amp. per sq. ft. D. C., and 10 to 20 amp. per sq. ft. A. C. Less than 6 volts are needed.

The high finish on both surfaces of the aluminum coating also makes it desirable for use in forming hollow articles of complex shapes, such as wave guides. A low-melting alloy is cast in the shape desired for the finished hollow article. This mandrel is surface-finished, and preferably coated with a copper plate to facilitate deposition of a smooth aluminum plate. Aluminum is then electrodeposited, utilizing the process and bath heretofore disclosed. The mandrel is melted out and the copper plate dissolved from the inner surfaces of the hollow article. The resulting article has a uniform thickness, is light in weight, and compares favorably in physical properties to a heavy metal electroform.

Alternatively, a cast or machined nonmetallic solid, such as a plastic, can be used as a base by surfacing it with silver by any of the well-known chemical reduction methods and electrodepositing aluminum thereon. The plastic is then dissolved by means of a suitable solvent. If desired, the silver liner need not be removed from the inner surface of the electroformed aluminum article.

The following examples will serve to illustrate the invention with greater particularity:

Example I

A mixture in the ratio of 2 mols of aluminum chloride and 1 mol of ethyl pyridinium bromide was fused at 400° F. 3000 grams of this fusion product were added to 7000 cc. of toluene. About 3700 cc. of toluene were required to dissolve the fusion product, leaving an excess of 3300 cc. of toluene. 96 cc. of methyl tert-butyl ether were added. The total volume of the bath was about 9100 cc.

The bath was placed in a glass plating tank. A current was passed through the bath between a copper-base material, as the cathode, and an aluminum anode. The base material was a waveguide mandrel having a rectangular cross section. A source of direct current was connected from the anode to the cathode, and a source of 60-cycle alternating current was connected in series with the direct current. The cathode density was 10 amp. per sq. ft. for the D. C. current and 20 amp. per sq. ft. for the A. C. current. Anode densities were 2.0 and 4.0 amp. per sq. ft. for the D. C. and A. C. currents, respectively. During the plating the bath was maintained at a temperature of 85° F. The excess toluene was dispersed by bubbling high purity nitrogen through the bath at a rate of 7.5 cu. ft. per hour. After 49 hours, an electroplate about 0.028-inch thick was formed on the base material. The coating was smooth, ductile and bright, and had a high degree of crystal orientation with the (110) crystal planes being parallel to the plane of the surface. The hardness of the electro-deposited aluminum was about 70 Knoop. When the base material was removed, the resulting wave guide had a smooth inner surface with square corners.

Example II

75 grams of the fusion product in Example I were dissolved in 200 cc. of toluene, resulting in an excess of toluene of about 95 cc., or 38 per cent of the total volume which was 250 cc. 2.5 cc. of ethyl ether were added to the bath and it was placed in a glass plating tank. Using a current source similar to Example I, the current was passed from an aluminum anode to a copper-base material serving as a cathode. The cathode current density was 10 amp. per sq. ft. for both A. C. and D. C. current, and the anode current density

was 2 amp. per sq. ft. for both A. C. and D. C. current. The bath temperature was maintained at 85° F., and the excess toluene was dispersed by a nitrogen flow of 1 cu. ft. per hour. After 36 hours, an electroplate 0.020-inch thick was formed. This foil was tough, ductile and dense.

Example III

A bath similar to that used in Example II was prepared, except that 2.5 cc. of diphenyl oxide were used as the organic additive. The same plating equipment and electrical circuit were used as in Example II. The current densities were 10.0 and 13.0 amp. per sq. ft., respectively, for the D. C. and A. C. at the cathode, and 5.0 and 6.5 amp. per sq. ft., respectively, for the D. C. and A. C. at the anode. After plating for 12.5 hours at a bath temperature of 100° F. and using a flow of 3 cu. ft. per hour of nitrogen to disperse excess toluene, an electroplate 0.006-inch thick was formed. This deposit was dense, smooth, and bright, and had good ductility.

Example IV

A mixture of 551 g. of ethyl pyridinium bromide and 752 g. of aluminum chloride were fused at 400° F. for 30 minutes. 80 g. of the fusion product were added to 200 cc. of toluene. 2.6 cc. of dimethyl aniline were added. The same plating equipment and electrical circuit were used as in Example II, except that the cathode was a copper-coated wave-guide mandrel. The current densities were 27 amp. per sq. ft. for both D. C. and A. C. at the cathode and 5 amp. per sq. ft. for both D. C. and A. C. at the anode. The voltage was about 2.3 volts. After plating for 42 hours at a bath temperature of 100° F., and using a flow of 1.3 cu. ft. per hour of nitrogen to disperse the excess toluene, an electroplate 0.018-inch thick was deposited. When the mandrel was removed the wave-guide segment was found to have a smooth, dense surface, free of cracks or other discontinuities. It also possessed good ductility. The hardness of the electrodeposited aluminum was 33 to 54 Knoop. The crystals were highly oriented with the (100) planes parallel with the cathode surface.

Example V

The same bath was used as in Example IV except that 2.5 g. of di-o-tolylthiourea were substituted as the organic additive. The current densities were 10 amp. per sq. ft. for D. C. and A. C. at the cathode and 5 amp. per sq. ft. for D. C. and A. C. at the anode. By the same procedure as in Example IV, a 0.017-inch thick electroplate was formed on a copper-base material after 72 hours plating time. The coating was a dense, smooth, bright deposit, having good ductility.

Example VI

The same procedure and apparatus was used as in Example IV, substituting 2.5 cc. di-o-tolylurea as the organic additive. Current densities used were 10 amp. per sq. ft. D. C. and 12 amp. per sq. ft. A. C. at the cathode and 5 amp. per sq. ft. D. C. and 6 amp. per sq. ft. A. C. at the anode. After approximately 40 hours plating time, a 0.010-inch thick electroplate was formed on a copper-base material serving as the cathode. This coating was dense, smooth and had good ductility.

Example VII

The same bath and apparatus were used as in Example IV, except that 5 cc. of dichloroethylene were used as the organic additive. Using current densities of 11 amp. per sq. ft. D. C. and A. C. at the cathode, and 5 amp. per sq. ft. D. C. and A. C. at the anode, an electroplate 0.019-inch in thickness was formed on a copper-base material serving as the cathode. The coating was found to have excellent ductility.

As can be seen from the preceding examples, by utilizing the process and bath of this invention, it is possible to form aluminum coatings in thicknesses greater than 0.002 inch without treeing or forming nonadherent powders or sponge. The improved coatings have superior properties of hardness and ductility. Hollow articles of complex shapes can be formed by applying this coating to a low-melting metal base, and subsequently melting out the base. The bath is long-lived and can be used over long periods of time without appreciable change in the quality of the coatings produced thereby.

What is claimed is:

1. The method of electrodepositing a thick, dense aluminum coating on an electrically conductive surface which comprises the steps of forming a fusion of about 2 mols of aluminum chloride and about 1 mol of ethyl pyridinium bromide, making a bath by dissolving said fusion in toluene, said toluene being present in an amount sufficient to provide an excess layer in volume equal to about 23 to about 45 per cent of the total volume, adding an organic material selected from the group consisting of methyl tert-butyl ether, ethyl ether, and diphenyl oxide, in an amount sufficient to achieve said thickness and density, bubbling an inert gas through said bath, whereby the excess solvent is continuously dispersed throughout said bath, and simultaneously passing an electric current through the bath between an aluminum anode and the electrically conducting surface serving as a cathode.

2. An electrolyte for electrodepositing thick, dense aluminum on an electrically conducting surface, said electrolyte comprising toluene in which is dissolved an organic additive selected from the group consisting of methyl tert-butyl ether, ethyl ether, and diphenyl oxide, in an amount sufficient to achieve said thickness and density, and a fusion of about 2 mols of aluminum chloride and about 1 mol of ethyl pyridinium bromide, said toluene being present in an amount sufficient to provide an excess layer in volume over that required to dissolve said fusion equal to about 20 to about 45 per cent of the total volume of the electrolyte.

3. The method of electroforming a thick, dense aluminum article which comprises the steps of forming an electrically conductive base in a desired configuration, immersing said article in a bath, said bath comprising a solution of a liquid aromatic hydrocarbon solvent in which is dissolved an organic additive selected from the group consisting of methyl tert-butyl ether, ethyl ether, and diphenyl oxide, in an amount sufficient to achieve said thickness and density, and a fusion of an aluminum halide and a quaternary salt of nitrogen, said solvent being present in sufficient quantity to form a layer of excess solvent, continuously dispersing said excess solvent throughout the bath, passing an electric current between an aluminum anode and said conductive base as a cathode until an aluminum coating is deposited thereon, removing said coated base from the bath, and separating said conductive base from said aluminum coating.

4. The method of electroforming a thick, dense

aluminum article which comprises the steps of forming a solid nonmetallic base in a desired configuration, making the surface of said solid base conductive, immersing said surface in a bath, said bath comprising a solution of a liquid aromatic hydrocarbon solvent in which is dissolved an organic additive selected from the group consisting of methyl tert-butyl ether, ethyl ether, and diphenyl oxide, in an amount sufficient to achieve said thickness and density, and a fusion of an aluminum halide and a quaternary salt of nitrogen, said solvent being present in sufficient quantity to form a layer of excess solvent, continuously dispersing said excess solvent throughout the bath, passing an electric current between an aluminum anode and said conductive base as a cathode until an aluminum coating is deposited thereon, removing said coated base from the bath, and separating said conductive base from said aluminum coating.

5. The method of electrodepositing a thick, dense aluminum coating of an electrically conductive surface, which comprises the steps of forming a fusion of an aluminum halide and a quaternary salt of nitrogen, making a bath by dissolving said fusion in a liquid aromatic hydrocarbon solvent, said solvent being present in sufficient quantity to form a layer of excess solvent separate from said solution, adding an organic material selected from the group consisting of methyl tert-butyl ether, ethyl ether, and diphenyl oxide, in an amount sufficient to achieve said thickness and density, maintaining the excess solvent dispersed throughout the bath, and passing an electric current through the solution between an aluminum anode and an electrically conductive surface serving as a cathode.

6. The method according to claim 5 wherein the nitrogen salt is a N-alkyl pyridinium halide.

7. An electrolyte for electrodepositing thick, dense aluminum on an electrically conductive surface, said electrolyte comprising a liquid aromatic hydrocarbon solvent in which is dissolved an organic additive selected from the group consisting of methyl tert-butyl ether, ethyl ether, and diphenyl oxide, in an amount sufficient to achieve said thickness and density, and a fusion of an aluminum halide and a quaternary salt of nitrogen, said solvent being present in sufficient quantity to form a layer of excess solvent separate from said solution.

8. The bath according to claim 7, in which the nitrogen salt is a N-alkyl pyridinium halide.

References Cited in the file of this patent

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