

2,831,803

ELECTRO-DEPOSITION OF ALLOYS

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No Drawing. Application November 30, 1956
Serial No. 625,208

Claims priority, application Great Britain
December 2, 1955

9 Claims. (Cl. 204—43)

The use of chelating or sequestering agents to inhibit the normal reactions of metal ions in solutions has become known in recent years, more particularly for preventing precipitation of magnesium and calcium compounds in water softening. Application of such agents has been proposed for reduction of the activity of undesirable metal ions in plating solutions, whereby deposition of relatively pure metals may be effected even in presence of small quantities of other metals which otherwise would contaminate the deposit. In U. S. Patent No. 2,751,341 it has been proposed to effect electrodeposition of lead or a lead alloy, or of antimony or an antimony alloy, from a solution containing an alkali metal salt of ethylenediaminetetraacetic acid, which is said to give a smooth, lustrous, even, bright deposit of metal; electrodeposition of lead-indium alloys from such a solution is said to give most satisfactory results when the bath is operated with a cathode current density of 10-20 amperes per square foot.

The present invention is concerned with electrodeposition of alloys of lead and indium particularly at high cathode current densities, up to 120 amperes per square foot.

We have found that the deposition of indium and lead together proceeds relatively smoothly in the presence of substances to which we refer as "controlling agents." One such controlling agent is ethylenediaminetetraacetic acid which for the sake of brevity is hereinafter sometimes called "enta." Other controlling agents suitable for our purpose are the propylenediaminetetraacetic acids and cyclohexane 1.2 diaminotetraacetic acid.

The baths in which these controlling agents are used are preferably neutral, or nearly neutral, the controlling agents being then in fact present in the form of salts, which may be the sodium, potassium or ammonium salts, or mixtures of such salts.

When baths containing a controlling agent are operated with soluble anodes and when the anode efficiency exceeds the cathode efficiency, particularly at high current densities, the metal ion content steadily increases as a result of the difference between the anode and the cathode efficiencies. This increase not only causes variations in the composition of the deposit, but makes working cumbersome and expensive, because of the necessity of drawing off the electrolyte at frequent intervals and recovering the metal values. If in order to reduce the metal concentration in the electrolyte insoluble anodes are employed, oxidation of the controlling agent occurs with the production of formaldehyde and certain nitrogen compounds. These substances act as cathode inhibitors in respect of the deposition of indium. The use of insoluble anodes therefore results in destruction of the controlling agent and a severe decrease in the indium content of the alloy.

We have now found that the oxidation of the controlling agent which occurs when insoluble anodes are employed can be very greatly reduced if the electrolyte contains in addition hydrazine. For example, hydra-

zine in a solution containing enta is preferentially oxidised by an insoluble anode, thus minimising the destruction of enta. Furthermore, the decomposition products of hydrazine are not harmful in any way in contrast to the case when enta alone is oxidised. Hydrazine also destroys any formaldehyde which would otherwise gradually accumulate in the electrolyte, despite the greatly retarded oxidation of enta. It is therefore possible by the addition of hydrazine to our electrolytes to maintain the metal ion concentration at the desired value by the periodic use of insoluble anodes without excessive loss of controlling agent by oxidation.

In addition we prefer to have present in the bath either citric or tartaric acid to promote good anode dissolution, as is well known in the prior art. In addition, especially where high current densities are employed, we add a small proportion of gelatin to the bath. The use of gelatin in electrolytes is well known, but deposits from our freshly prepared electrolytes are in general not as smooth as is desired even with gelatin present. This is particularly so at high current densities, and we find it desirable in order to obtain smooth dense deposits at the cathode to add a small quantity of triethylenetetramine, or alternatively of diethylenetriamine, or of ethylenediamine. The baths in general will be improved by the addition of ammonium chloride.

Electrolytes used in the practice of the present invention thus contain compounds of lead and indium, one of the above mentioned controlling agents, and also hydrazine. With advantage they also contain citric acid (or alternatively tartaric acid), a small proportion of gelatin, triethylenetetramine (or alternatively diethylenetriamine or ethylenediamine), and ammonium chloride.

As an example of such an electrolyte, the following may be used for codeposition of indium and lead:

	Gms./litre
Pb (added as chloride)	20
In (added as chloride)	12.5
Enta	100
Citric acid	50
Hydrazine	11.0
Gelatin	1.0
Triethylenetetramine	5.0
Ammonium chloride	20.0

The precise amounts of the constituents in the bath may of course be varied but we prefer to operate within the following limits:

	G./l.
Pb	15-25
In	10-15
Enta	85-115
Citric acid	45-55
Hydrazine	9.5-62.5
Ammonium chloride	5-30
Gelatin	0.2-2.0
Triethylenetetramine	1-10

If tartaric acid is employed in place of citric acid, the amount used is preferably 35-45 g./l. The lead and indium may be introduced into the electrolyte as the hydroxide, sulphate, acetate, chloride or carbonate. Lead and indium nitrates may also be used but we prefer to exclude the presence of the nitrate ion from our electrolytes because of its action as a cathode inhibitor with respect to the deposition of indium.

The bath is adjusted to have a pH value in the range 5.0 to 7.0, 6.0 being preferred, and is operated with an insoluble anode (and preferably also with a soluble anode) at a temperature in the range 45° to 70° C., about 60° C. being preferred, and with a current density in the range 60 to 120 amperes/square foot. The lead-

indium alloy deposited contains from about 7% to about 10% indium, depending upon the precise operating conditions used. For example, raising the temperature will decrease the indium content of the alloy deposited. An increase in pH value will increase the indium content of the alloy deposited, as also will an increase in current density. Provided that the hydrazine concentration is maintained by additions during operation, the constituents of the bath other than lead and indium need only be added as often as is necessary to combat the effects of "drag-out." The rate of decomposition of the controlling agent is reduced to a very small value.

In order to maintain the metal content of the bath, it is preferable to use soluble anodes together with the insoluble anodes. The soluble anodes may be of pure indium and pure lead, or of the appropriate indium-lead alloy. The insoluble anodes are preferably of graphite. Instead of using both soluble and insoluble anodes connected to the busbars of the cells throughout the process, very good results are obtained by connecting soluble and insoluble anodes alternately for very short periods. For this purpose a rotating or other type of commutator may be employed, which is adjustable so that the times for which the respective anodes are connected and the frequency with which they are changed over may be varied as desired, to maintain the correct metal balance in the bath.

Our process is particularly valuable for the manufacture of bearings by codeposition of indium and lead on a suitable backing, whereby a layer of alloy is provided on the face of the bearing. By the practice of the invention smooth, dense, and coherent deposits of uniform composition and of suitable thickness for bearing faces are obtained.

We claim:

1. In a process for the codeposition of lead and indium by electrolysis of an aqueous bath containing soluble compounds of lead and indium and a controlling agent selected from the group consisting of the water-soluble salts of ethylenediaminetetraacetic acid, propylenediaminetetraacetic acids and cyclohexane 1,2-diaminotetraacetic acid, and employing an insoluble anode, the improvement which consists in minimizing oxidation of the

controlling agent by maintaining in the bath a significant concentration of hydrazine sufficient to effect said minimizing of oxidation.

2. The process defined in claim 1, in which the bath contains also a polyamine selected from the group consisting of triethylenetetramine, diethylenetriamine and ethylenediamine.

3. The process defined in claim 1, in which the bath contains the following constituents in quantities within the respective ranges stated, in grams per litre: lead 15 to 25; indium 10 to 15; a water-soluble salt of ethylenediaminetetraacetic acid 85 to 115; an organic acid selected from the group consisting of citric acid 45 to 55 and tartaric acid 35 to 45; hydrazine 9.5 to 62.5; ammonium chloride 5 to 30; gelatin 0.2 to 2 and triethylenetetramine 1 to 10.

4. The process defined in claim 1 in which the bath contains the following constituents in approximately the respective amounts stated in grams per liter: lead 20, indium 12.5, a water-soluble salt of ethylenediaminetetraacetic acid 100, citric acid 50, hydrazine 11, gelatin 1, triethylenetetramine 5, ammonium chloride 20.

5. The process defined in claim 1 in which the concentrations of lead and indium in the bath are maintained by using a soluble anode in addition to an insoluble anode.

6. The process defined in claim 5, in which the soluble and insoluble anodes are brought into circuit alternately.

7. The process defined in claim 1, in which the bath is maintained at a pH between 5.0 and 7.0 and in which the water-soluble controlling agent salts are selected from the group consisting of the sodium, potassium and ammonium salts and mixtures thereof.

8. The process defined in claim 1, in which the bath is maintained at a temperature between 45° and 70° C.

9. The process defined in claim 1, in which the cathode current density is in the range 60 to 120 amperes per square foot.

References Cited in the file of this patent

UNITED STATES PATENTS

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