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(54) **Electrodeposition of aluminium alloys.**

(57) The invention is directed to a process for the electrochemical deposition of aluminium alloys on a substrate, said process comprising the deposition of aluminium/metal alloys from a solution of an electrolyte comprising aluminium halogenide and a quaternary ammonium compound, and at least one metal other than aluminium, as well as to a substrate coated therewith.

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The present invention is directed to the electrodeposition of aluminium alloys, more in particular the low temperature electrodeposition of aluminium alloys on a substrate.

The electrodeposition of aluminium on conductive substrates is well-known. Some processes are practised commercially. The main aim of electrodeposition is to provide a protection of the substrate against corrosion.

Electrodeposition of aluminium alloys is also known, but due to the rather unattractive properties of the chemicals to be used, it has not been employed at great scale.

An important advantage of alloys over the pure aluminium coatings is the possibility to provide coatings having "tailored" properties, i.e. specifically designed for a particular purpose.

In the article of Platis et al in J. Electrochem. Soc. (Oct. 1987, 134(10) PP 2425-2429) the electrochemical deposition of Al-Sn alloys from alkylbenzene, AlBr_3 -HBr electrolytes is disclosed. The use of these types of electrolytes is rather unattractive due to the presence of bromides. In addition thereto this process requires the presence of a solvent that has to be recovered and that restricts the amount of active component in the electrolyte.

It is an object of the invention to provide a simple and easy to handle method for electrodeposition of aluminium alloys.

According to the invention this object is reached by the deposition of aluminium/metal alloys on a substrate from a solution of an electrolyte comprising aluminium halogenide and a quaternary ammonium compound, and at least one metal other than aluminium.

The present invention is based upon the surprising fact, that it is very easy to deposit an alloy from a solution of an electrolyte composed of a quaternary ammonium salt and an aluminium halogenide, and at least one metal other than aluminium. Provided a suitable ratio of aluminium to quaternary ammonium salt is used, the electrolyte is liquid at low temperatures, i.e. as low as 10°C . This makes it possible to carry out the process at a temperature between about 20°C and the decomposition temperature of the electrolyte, i.e. about 150°C . Generally it is preferred to use temperatures of 20 to 100°C , as higher temperatures offer no advantages with regard to deposition rate, and are less economical. Lower temperatures than 20°C result in too low deposition rate.

The essential components of the electrolyte are the aluminium halogenide, preferably chloride, and the quaternary ammonium compound.

The at least one metal encompasses metal cations and complexes of metal ions. As the electrolyte is of course neutral, the electrolyte will also contain sufficient anions corresponding to the metal ions.

Suitable complexing agents for the metal ions are halogenides, preferably chlorides. According to a preferred embodiment the metal is used in the form of a salt, such as a chloride, that is soluble in the electrolyte.

According to another embodiment the metal is brought into the electrolyte by way of anodic dissolution. In case the metal is not easily dissolved in large amounts in the electrolyte, it can be advantageous to use an anode of the metal to be codeposited with the aluminium. During the process this anode dissolves and the metal ions obtained are transported to the cathode, i.e. the substrate, and are deposited.

The quaternary ammonium salt is usually a three-alkyl, or a dialkyl-phenyl compound, the alkyl being lower alkyl, such as 1-5 C-atoms, methyl being preferred.

According to a preferred embodiment the quaternary ammonium compound is an N,N,N-trimethylanilinium chloride (TrManCl) or tetramethylammonium chloride (TMACl).

It is an object of the invention to provide an electrolyte having a high concentration of active components, i.e. metals. In view thereof preferably no solvent is used.

In this respect it is remarked, that the use of lithium salts in an aluminium halogenide/tetra hydrocarbyl ammonium halide melt is disclosed as levelling agent in European patent application No. 87202328.8. No codeposition of lithium occurs in said process.

The metal of the alloy can in principle be any metal that can be introduced in the electrolyte system and that can be electrochemically codeposited therefrom with aluminium.

Suitable metals are those which are not less noble than aluminium. This generally excludes the alkali- and earth-alkali-metals, i.e. the metals of groups 1a and 2a of the Periodic table of elements, as published in Handbook of Chemistry and Physics, 54th Ed.

Preferably a metal is used of which the salt is soluble in the electrolyte. Suitable metals include manganese, lead, tin, hafnium, niobium, zirconium, chromium, tungsten, tantalum, gallium, iron, molybdenum and mixtures of two or more of these metals.

According to a preferred embodiment, the salts used are chlorides, both for the aluminium and the metal, as these salts provide the best results, in combination with their ease of use.

The relative amounts of aluminium halogenide and quaternary ammonium compound are in the first

place determined by the fact that the electrolyte should be liquid. Optimal ratio's are 2:1 molar ratio's of aluminium to quaternary ammonium compound, although ratio's of between 1:1 to 4:1, preferably 1.5:1 to 3:1 are also possible.

The electrodeposition can be carried out in a manner known for electrodeposition, such as bulk deposition. The apparatus suitable therefor and the conditions to be used therein are known to the person skilled in the art, or can be determined by routine experimentation.

The process can be continuous, semi continuous or discontinuous depending on the requirements.

In the process the cathode is generally the substrate to be coated, or the substrate remains in direct conducting contact therewith. The type of anode will depend on the situation. In the case a salt of the other metal is dissolved in the electrolyte, an inert anode is used, such as a platinum or a carbon anode.

Suitable carbon anodes are made from glassy carbon or graphite.

The invention is also directed to substrates coated with aluminium alloys obtained by the process of the invention.

A specific embodiment of the invention is directed to a substrate coated with a substantially amorphous aluminium alloy.

It has surprisingly been found that it is possible to obtain amorphous coatings of aluminium alloys on a substrate. More in particular aluminium-zirconium alloys can suitably be in the form of amorphous coatings. It is very advantageous, and up to now unknown, to have such amorphous aluminium coatings. Advantages are especially to be found with respect to corrosion resistance.

The composition of the coating depends on the required properties. However, it is also limited by the solubility of the metal compound, being the metal or metal salt, in the electrolyte. Generally the atomic ratio of aluminium to other metal ranges between 99:1 and 1:99, preferably between 98:2 to 50:50.

The thickness of the coating layer can vary between wide limits.

The invention is now elucidated on the basis of the following, non limiting examples.

Example 1

A number of plating experiments was carried out with zirconium as the metal to be alloyed with the aluminium.

The electrolyte consists of AlCl_3 and TMA^+Cl^- in the molar ratio 2:1. The electrolyte is liquid at ambient temperatures. Preparation is carried in a glove box system under argon. ZrCl_4 (Merck, purity >98%, solid) is added to the liquid. A 100 ml glass cell is filled with the electrolyte and brought out of the glove box where it is operated under a purified argon stream.

A copper wire is used as cathode, a platinum gauze as anode and an aluminium wire as reference electrode. The copper electrodes are etched in 50 (v/v) % HNO_3 and dried with acetone. Aluminium electrodes are etched in hot 1 M NaOH and also dried with acetone. Glassy carbon and platinum are rinsed with bi-distilled water and dried with acetone.

A deposit with thickness 20 μm is applied to the cathode. The E_{cathode} and E_{cell} are measured during the plating and are recorded.

The deposit is characterized by scanning electron microscope (SEM). Both surface and polished cross-section are examined. The composition of the deposit is measured by an energy dispersive analysis system (EDX).

The phases present were determined with X-ray diffractometry. The lattice constants a and Bragg angles 2θ , being well-known properties for those skilled in crystal analysis, were determined if possible. The results are given in tables I and II.

TABLE I

Composition of aluminium/zirconium alloys from deposition
of $\text{AlCl}_3/\text{TMA} \text{ nCl}$ electrolyte (mol ratio 2:1)

Exp.	current density, mA/cm^2	conc. ZrCl_4 , mol/l	temperature, $^{\circ}\text{C}$	Al/Zr wt. ratio
a	2	10^{-2}	70	1.9
b	5	10^{-2}	70	1.7
c	10	10^{-2}	70	4.4
d	15	10^{-2}	70	11
e	20	10^{-2}	70	12
f	50	10^{-2}	115	13-18.5
g	5	10^{-1}	70	1.4
h	15	10^{-1}	70	1.4
i	50	10^{-1}	115	1.4-1.7
j	15	$3 \cdot 10^{-1}$	70	1.3-1.5
k	50	$3 \cdot 10^{-1}$	115	1.0-1.5
l	5	10^{-2}	45	6.8-9.3
m	5	10^{-2}	70	1.8-2.0
n	5	10^{-2}	115	1.4-1.5

TABLE II

5 X-ray diffraction data of the aluminium/zirconium sample

		Al/Zr ratio	Al-phase lattice const. a (Å)	Amorphous phase 2θ °
	b	1.7 and 3.4	4.0744	38.8
15	d	11	4.0604	absent
	g	1.4 and 2.1	4.0617	38.3
	k	1.0-1.5	absent	38.7
20	l	6.8-9.3	4.0698	absent
	REFERENCE	Al with 2% Zr	4.051	
	REFERENCE	Al pure	4.0488	

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Example 2

30 In a manner comparable to example 1, a number of experiments were carried out using different metals. The results are given in table III, whereby it is remarked that in a number of experiments the anode was replaced by an anode of the material to be codeposited.

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TABLE III

	Metal (M)	potential, mV vs Al	Al, (m/m) %	M, (m/m) %	Al/M wt. ratio
5	Ti*	-100	72.6	11.7	6.2
	Ti*	-200	41.4	3.8	10.9
10	Ti*	-300	91.6	4.8	19.1
	Ti*	-400	55.1	2.0	27.6
	Cr*	-150	68.7	5.5	12.5
15	Cr*	-250	89.9	4.1	21.9
	Cr*	-350	92.5	4.1	22.6
	Fe	-180	5.5	5.3	1.0
20	Fe	-240	6.3	1.6	3.9
	Zn	-200	78.1	6.6	11.8
	Zn	-300	83.5	7.8	10.7
25	Zr	-200	67.5	21.4	3.2
			61.7	14.5	4.3
			11.8	5.5	2.1
30	Zr	-300	86.4	11.2	7.7
			73.9	10.6	7.0
	Mo	-250	84.1	6.9	12
35	Hf	-100	58.0	24.5	2.4
	Hf	-200	66.2	25.1	2.6
	Hf	-300	77.1	18.8	4.1
40	Hf	-400	76.9	20.9	3.7
	W (WCl ₆)	-75	72	6	12
	W (WCl ₆)	-175	85.6	2.0	43
45	W (WCl ₆)	-275	92.1	33.7	25
	W (WCl ₆)	-375	96.4	1.0	96
	W (WCl ₄)	-250	90	<4	<22

* The metal is supplied by anodic dissolution.

55 Claims

1. Process for the electrochemical deposition of aluminium alloys on a substrate comprising the deposition of aluminium/metal alloys from a solution of an electrolyte comprising aluminium halogenide, and a

quaternary ammonium compound, and at least one metal other than aluminium.

2. Process according to claim 1, wherein the quaternary ammonium compound is an N,N,N-trimethylanilinium chloride or tetramethylammonium chloride.
- 5 3. Process according to claim 1 or 2, wherein the at least one metal other than aluminium is chosen from the group of manganese, lead, tin, hafnium, niobium, zirconium, chromium, tungsten, tantalum, gallium, iron and molybdenum.
- 10 4. Process according to claims 1-3, wherein the at least one metal is comprised in a metal salt, preferably a chloride.
5. Process according to claims 1-3, wherein at least one anode is used consisting of the at least one metal to be codeposited with the aluminium.
- 15 6. Process according to claims 1-5, wherein the molar ratio of aluminium salt to quaternary ammonium compound is between 1 to 1 and 4 to 1.
7. Process according to claims 1-6, wherein the temperature is between 20 and 100 ° C.
- 20 8. Process for the electrochemical deposition of aluminium alloys as claimed in claim 1, substantially as described hereinbefore, especially with reference to the examples.
9. Substrate coated with aluminium alloy prepared in accordance with the processs of claim 1-7.
- 25 10. Substrate coated with substantially amorphous aluminium alloy.

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