

[54] SURFACE TREATMENT OF ALUMINIUM AND ALUMINIUM ALLOYS

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[58] Field of Search 204/37 R, 44

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[57] ABSTRACT

The surface of aluminium or an aluminium alloy is treated by electrolytic deposition of a copper-indium alloy surface layer followed by the diffusion heat treatment of the coated surface. Electrolysis is carried out in a bath containing, in an aqueous alkaline solution, monovalent copper ions, trivalent indium ions, an alkali metal hydroxide, an alkali metal cyanide, an alkali metal gluconate, gluconic acid, and oxalic acid, and the heat treatment is carried out at between 120° and 155°C.

10 Claims, No Drawings

SURFACE TREATMENT OF ALUMINIUM AND ALUMINIUM ALLOYS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the treatment of surfaces of aluminium or aluminium alloys to improve their frictional properties and resistance to wear and seizure by forming on their surface, by diffusion, intermetallic or semi-metallic compounds.

2. Description of the Prior Art

Various processes are known for forming coatings of this kind on the surface of a metal. This is in particular true of French Patent No. 1530 of the 6th May 1967 and its five certificates of addition, which describe processes for forming composite anti-friction layers by depositing a metal coating on a metal surface and then subjecting it to a suitable heat treatment. Two techniques have been proposed:

1st technique

First, the deposition of successive layers of metals on the metal parts to be treated;

then diffusion in a preferably neutral or reducing atmosphere, in accordance with a thermal cycle comprising two separate phases: first heating to a temperature at least 20°C below the melting point of the most readily fusible of the metals present, then heating to a temperature between the said melting point and 800°C.

2nd technique

First, deposition on the part of a layer of an alloy of two or more metals,

then the baking of the part coated in this manner, optionally in a single stage.

In comparison with the first technique, the second technique permits the use of a lower diffusion temperature and a shorter temperature holding time.

After diffusion using either technique, the treated part presents from inside to outside:

the base metal;

a layer of residual metal;

a layer formed of metallic compounds of a thickness greater than 10 microns and of a hardness above 500 Vickers;

a residual surface layer of a thickness less than 4 microns of one of the metals present.

The preceding technique is applicable to aluminium alloys and an example is described in the previously mentioned French Patent, in which the diffusion coating is produced from copper and indium, the temperature of the last stage of the heat treatment being indicated as equal to 200°C. In this case the part presents after treatment, from inside to outside:

the aluminium base alloy,

a residual layer of copper,

a layer of compounds of copper and indium,

a residual surface layer of indium.

These techniques for producing diffused coatings based on copper and indium, when applied to aluminium and its alloys, nevertheless have the following disadvantages: (a) the heat treatment temperature, which must be higher than 155°C (melting point of indium), is too high and results in a deterioration of the mechanical properties of the aluminium alloys, particularly those subjected to substantial structural hardening, such as for example the aluminium-zinc alloys, whose mechanical properties start to fall at a temperature close to 130°-135°C; in addition, since the heat treat-

ment temperature is higher than the melting point of indium (155°C), the coatings formed have great porosity.

When subjected to friction, this coating morphology results in rapid wear of the porous zone and a substantial, progressive increase of the coefficient of friction; at a certain degree of wear there may even be epidermic sticking and seizure.

b. the presence of a layer of copper having poor mechanical characteristics under a layer of fragile compounds having good mechanical characteristics results in pronounced overall fragility of the composite layer, which prevents it from following any substantial deformations of the substrate without fracturing.

In the above mentioned known process the alloy of copper and indium originally deposited on the metal part was obtained from known baths, for example baths based on sulphamates.

Nevertheless, these baths have the following main disadvantages:

a. the composition of the alloy deposited varies from one point to another on the treated part, and this variation is considerable. When the copper content of the mixed coating is above 50 percent by weight, the alloy, when subjected to friction, becomes covered with copper, which in practice is incompatible with the usual mechanical parts, particularly steels, which have to rub against parts of the treated aluminium alloys. When the indium content exceeds 65 percent by weight the hardness of the alloys formed decreases very rapidly and the mechanical characteristics of the layer of alloy become insufficient to prevent the phenomenon of surface creep when friction occurs.

b. These baths are chemically unstable, that is to say they rapidly change in the course of time and it is not possible for an alloy of a constant given composition to be deposited on successive parts.

An object of the present invention is to provide a process by which it is possible, under industrial large-scale production conditions, to obtain on surfaces of aluminium and aluminium alloys a coating having good frictional properties without seizing and without reduced wear, which is capable of following without fracturing any deformation, even substantial deformation, of its substrate, which is not subject to surface creep, and which has a hardness several times greater than that of the uncoated aluminium alloy, while the mechanical properties of the latter are not affected.

SUMMARY

The present invention proposes a process for the treatment of surfaces of aluminium or aluminium alloys by depositing a layer of a copper-indium alloy followed by diffusion heat treatment, characterised in that this deposition is effected galvanically in a bath containing, in an aqueous alkaline solution, monovalent copper ions, trivalent indium ions, an alkali metal hydroxide, an alkali metal cyanide, an alkali metal gluconate, gluconic acid, and oxalic acid, these products being used in accurately defined proportions which, according to the original feature of the invention, must be concurrently respected, and in that the diffusion heat treatment is effected at a temperature between 120° and 155°C.

In order to obtain a friction coating having the properties indicated above, after being subjected to degreasing and pickling treatments known per se the part

is electrolytically coated with a copper-indium alloy in a bath according to the invention, the operating conditions of which are controlled within the undermentioned limits:

mass ratio of indium metal to copper metal between 2 and 8;
 content of alkali metal gluconate above or equal to 0.5g per gram of indium metal in the bath;
 pH between 12 and 14 and kept between those values by adjusting the content of alkali metal hydroxide;
 content of free alkali metal cyanide between 1.1 and 1.8g per gram of copper metal in the bath;
 temperature of the bath between 30° and 60°C;
 cathodic current density between 3 and 8 A/dm²;
 anodic current density between 1.5 and 4 A/dm²;
 concentrations of gluconic acid and oxalic acid between 1 and 10 mg/litre.

After deposition of the desired thickness, the part is rinsed and dried and subjected to the diffusion heat treatment at a temperature between 120° and 155°C for a time between 2 and 6 hours.

By this process it is possible to form a friction coating which does not have the disadvantages of those obtained by the previously mentioned known processes, that is to say which is non-porous, of constant composition throughout its thickness and at any point on the treated surface, and is capable of deformation without fracturing, while the diffusion treatment temperature does not affect the mechanical characteristics of the base aluminium alloy and does not bring about local fusion.

Furthermore, the friction coating produced according to the invention is a good conductor of heat and electricity, while in addition possessing the unexpected property of providing a friction surface having a low coefficient of friction without unalloyed indium appearing on the surface, which occurs in the above mentioned prior art processes.

Micrographic examination of a section made in a part of this kind shows the presence of the surface of a layer which is perfectly homogeneous and regular whatever part of the surface is examined, which has perfect adhesion and a hardness between 300 and 450 Vickers under 0.15 N. This coating contains copper and indium in the proportion of from 35 to 50 percent by weight of copper in indium, and is composed of hard but non-fragile Cu/In compounds.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

First Example

This relates to the rubbing of a bearing of aluminium alloy against a shaft of hardened cemented steel, the mechanism being kept in an oil bath and the temperature being that of the ambient air. The characteristics of the parts are as follows: shaft diameter: 40 mm; clearance between shaft and bearing: 0.08 mm; sliding speed: 2 metres per second; specific load: 140 bars.

Under these conditions a bearing of aluminium alloy of the AU4G type containing 94.5 percent of aluminium, 3.8 percent of copper, and 1.5 percent of magnesium cannot undergo friction for more than 5 seconds, at the end of which time there is an abrupt seizure with the transfer of aluminium to the shaft of cemented hardened steel.

On the other hand, a bearing treated by the process described in the present invention can operate for several hours with a coefficient of friction of 0.03.

In this example, given without limitation, the aluminium alloy bearing has undergone the treatment of the invention in the following manner:

a. the part was first degreased and pickled;
 b. the part was thereupon rinsed and then immersed in a galvanic bath to receive a mixed deposition of copper and indium of a thickness of 20 microns; the bath had the composition previously indicated in the description of the invention and the following conditions were adopted:

ratio of indium metal to copper metal in the bath equal to 2.7;

content of alkali metal gluconate, in this case potassium gluconate, equal to 2.5 g of this gluconate per gram of indium metal in the bath;

gluconic acid content equal to 2 mg per litre of bath;
 oxalic acid content equal to 1.5 mg per litre of bath;
 bath temperature 50°C;

pH of bath equal to 13.3;
 cathodic current density 4 A/dm²;
 anodic current density 2 A/dm²;

c. finally, the part coated in this manner was washed and dried and then kept for 4 hours at a temperature of 150°C in an atmosphere of air.

By way of comparison, a bearing of aluminium alloy AU4G treated by thick anodic oxidation can operate for no more than 2 minutes, after which time there is an abrupt transfer of aluminium to the steel shaft.

Second Example

This relates to a test of friction between two plane surfaces, carried out under the following experimental conditions: plane cursor of a length of 20 mm with two longitudinal bearing surfaces of a width of 4 mm; reciprocating movement on a plane track with a stroke of 60 mm; load: 30 daN; speed of movement 1 cm/s; time delay: 1 second stoppage at the end of each stroke; atmosphere: interposition of grease at beginning and then operation in ambient air without additional supply of lubricant.

Under these conditions, when the cursor and the track are of untreated aluminium alloy of the AS₇G type, that is to say containing 91.2 percent of aluminium, 7.2 percent of silicon, 1.1 percent of magnesium, the movement is halted by sticking and seizure at the end of 180 cycles.

On the other hand, when the cursor and the track are treated as in the preceding example by the process described in the present invention, the test is voluntarily stopped at the end of 5,000 cycles, the mean coefficient of friction then being 0.10.

By way of comparison, when thick anodic oxidation is effected on the track of AS₇G, the movement is stopped with the emission of numerous particles at the end of 320 cycles.

I claim:

1. A process for the treatment of the surface of aluminium or an aluminium alloy, comprising the steps of
 a. depositing a copper-indium alloy layer on the said surface by electrolysis in a bath containing, an alkaline solution, monovalent copper ions, trivalent indium ions, an alkali metal hydroxide, an alkali metal cyanide, an alkali metal gluconate, gluconic acid, and oxalic acid, and

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b. subjecting the coated surface to a diffusion heat treatment at a temperature between 120° and 155°C.

2. A process according to claim 1, characterised in that the mass ratio of indium metal to copper metal in the bath is between 2 and 8.

3. A process according to claim 1, characterised in that the alkali metal gluconate content in the bath is higher than or equal to 0.5 g of this gluconate per gram of indium metal in the bath.

4. A process according to claim 1, characterised in that the pH of the bath is between 12.5 and 14, this pH being maintained between these values by adjusting the alkali metal hydroxide content of the bath.

5. A process according to claim 1, characterised in that the free cyanide content of the bath is between 1.1 and 1.8 g of the said alkali metal cyanide per gram of

copper metal in the bath.

6. A process according to claim 1, characterised in that the temperature of the bath is between 30° and 60°C.

7. A process according to claim 1, characterised in that the cathodic current density is between 3 and 8 A/dm².

8. A process according to claim 1, characterised in that the anodic current density is between 1.5 and 4 A/dm².

9. A process according to claim 1, characterised in that the gluconic acid and oxalic acid contents are between 1 and 10 milligrams per litre.

10. A process according to claim 1, characterised in that the heat treatment is effected in air for between 2 and 6 hours.

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