

1

3,692,644

SELF-COLORING ANODIC OXIDATION OF ALUMINUM AND ITS ALLOYS

Giancarlo Paolini and Ciro Micheletti, Novara, Italy, assignors to Società per l'Esercizio dell'Istituto Sperimentale dei Metalli Leggeri, Milan, Italy
No Drawing. Filed Aug. 12, 1969, Ser. No. 849,503
Claims priority, application Italy, Aug. 14, 1968, 20,177/68

Int. Cl. C23b 9/02

U.S. Cl. 204—58

1 Claim

ABSTRACT OF THE DISCLOSURE

Improvements are obtained in the anodic oxidation of aluminum or its alloys by electrolytic treatment in aqueous solutions in which the aluminum acts as an anode, by separating the electrolytic cell into an anodic compartment and a cathodic compartment with a porous separator. Formation of precipitates in the electrolyte solution with subsequent clogging and other disadvantages are minimized. Further improvement is obtained by using different electrolytes in the two compartments.

The present invention concerns an improvement in the self-coloring anodic oxidation of aluminum and its alloys. The improvement permits reduction of the consumption of the components of the electrolytic system used and elimination or reduction of the precipitates of said system.

It is known that aluminum and its alloys may be coated with layers of oxide which have a substantial thickness and which are very resistant, by means of an electrolytic treatment in aqueous solutions in which the aluminum acts as an anode.

It is known, for instance, that by using as electrolytes, solutions based on carboxylic acids of the aliphatic series, it is possible to obtain self-coloring layers through the transformation and incorporation into said layers of the constituents and alloying materials present in the material to be oxidized.

All the processes of anodic oxidation so far suggested (amongst which may be mentioned in particular the MS process based on a binary mixture of maleic and sulfuric acid, the MOS process based on a ternary mixture of maleic-oxalic-sulfuric acid as, for instance, described in Italian Pat. No. 793,929 and in Belgian Pat. No. 660,867, and the TOS process based on a ternary mixture of tartaric-oxalic-sulfuric acid, as described, for instance, in Italian Pat. No. 720,028) have in common one serious drawback: that is, they produce in the course of the oxidation, by-products of cathodic and/or anodic decomposition of the aliphatic carboxylic acids used, thereby causing a high consumption of the components involved, an increase in the cost of the method and considerable variations in the reproducibility of the coloring.

The above mentioned decomposition reactions lead in some instances to the complete fission of the carboxylic acid or to its transformation into soluble products as is the case with oxalic acid in the TOS and MOS processes, which acid at the anode breaks down into CO_2 and H_2O , while at the cathode it is transformed into different products such as acetic aldehyde, glycolic acid, ethylene glycol, etc.; in other cases, on the contrary, there occurs a transformation of the involved acid into difficultly soluble products (as is the case of the maleic acid in the MOS and MS processes, which, through the primary cathodic reaction, converts into succinic acid which subsequently, through secondary anodic reactions, is probably transformed into adipic acid) with the consequent formation of precipitates in different parts of the plant thus causing

2

clogging (particularly in the perforated pipes used for the compressed-air stirring of the electrolyte) and causing the reduction of the heat-exchange capacity of the cooling apparatus and of the resin columns used for the elimination of the Al from the bath.

Thus, an object of this invention is to provide an improvement in the self-coloring anodic oxidation of aluminum, and its alloys, by which all the above listed drawbacks may be eliminated or at least considerably reduced.

More particularly, an object of this invention is to provide a process which will eliminate, or at least reduce to a minimum, the formation of precipitates from the electrolytic solution and consequently prevent the damaging clogging phenomena occurring in the plant and the reduction of the exchange capacity of the cooling apparatus and of the ion-exchanging resin columns.

Another object of this invention is that of eliminating or at least reducing the consumption of the components of the electrolytic system used, with considerable practical and economical advantages, while also obtaining a better uniformity of the composition of the electrolytic system and therefore a better reproducibility of the coloring obtained in the anodic coating, without having to revert to frequent and expensive refillings of electrolyte.

These and still other objects will appear more clearly to a person skilled in the art from the following detailed description. According to the present invention, a self-coloring anodic oxidation of aluminum and its alloys by means of electrolytic baths comprises placing into the electrolytic cell a porous baffle immersed in the electrolytic solution used, which baffle subdivides said cell into two compartments: the anodic one and the cathodic one.

The electrolytic system used for the anodic oxidation may be identical into the two compartments or with further advantages for the above cited objects, may be different, by preferably using in the cathodic compartment an electrolyte that will not decompose or which will not produce difficultly soluble decomposition products, or also by adding to the cathodic compartment oxidizing substances or substances inhibiting the decomposition reactions of the electrolyte used.

The electrolytic system generally used in the anodic compartment, which may be the same as that used in the cathodic compartment, is based on at least one aliphatic carboxylic acid, preferably a dicarboxylic acid.

The carboxylic acid may be chosen from amongst: maleic, oxalic, tartaric acid, either alone or in binary or ternary combination and generally with the presence of sulfuric acid.

Preferably the electrolytic system used in the cathodic compartment is different from that used in the anodic compartment and it is constituted by an alkaline hydroxide or by sulfuric acid or an alkaline sulfate or by an electrolyte such as, for instance, oxalic acid which will not yield insoluble products due to a cathodic decomposition.

The porous baffle is made out of a material resisting the corrosive action of the electrolytic system used. For this purpose it has been found to be convenient to use porous baffles made of plastic material, for instance of polyethylene or of glass or of a ceramic material.

The porous baffle which subdivides the electrolytic cell into two compartments or zones, the anodic and the cathodic one, may have a varying porosity and pore diameter, depending on different situations. It has been found that the best results are obtained with a porosity of the baffle comprised between 10% and 50% of the surface and with the diameter of the pores comprised between 0.1 and 50 μ .

Preferably the porosity of the baffle is comprised between 20% and 40%, and more particularly between 25%

3

and 35%, and the diameter of the pores between 1 and 10μ , and more particularly between 3 and 8μ .

In fact, in order to study the mechanisms of formation of the above mentioned decomposition products, there have been carried out anodic oxidation tests with porous baffles immersed into the electrolytic solution, so as to be able to separate the anodic zone from the cathodic one and thus permit evaluating separately the reactions at the two electrodes.

These tests proved surprisingly that the adoption of these porous baffles, by hindering the diffusion phenomena, especially in the case of the MS and MOS processes, offers considerable advantages without involving on the other hand, due to the introduction of a new resistance, a substantial increase, in the voltage, required by the method.

These advantages may be thus summarized as follows:

elimination of the precipitates (in the case of MS and MOS processes) from the anodic zone and the consequent elimination of the drawbacks due to the precipitates;

reduction (in the case of all the cited processes) of the consumption of the components involved by secondary reactions at the electrodes.

Further tests, in particular carried out on the MS process, have shown furthermore that by using at the cathode an electrolytic solution different from the anodic one, it is possible to eliminate, or at least considerably reduce, the formation of difficultly soluble products also in the cathodic compartment. More particularly, the results mentioned above have been achieved by using in the cathodic compartment an electrolyte which will not decompose (e.g. H_2SO_4 , NaOH) or which will not produce difficultly soluble decomposition products (e.g. oxalic acid). Analogous effects may furthermore be attained by adding to the cathodic zone oxidizing substances which will preferably bind the hydrogen, thus hindering the reduction of the maleic acid to succinic acid, or by adding suitable inhibitors of such reduction.

In order to provide a clearer description of the scope and advantages of this invention, the following examples of various embodiments of the invention are provided, which are of a purely illustrative character.

EXAMPLE 1

The anodic oxidation was conducted at 1.5 a./dm^2 , at 20° C. for 45 minutes in a self-coloring bath of the MS type having the following compartment:

Anodic compartment:

Maleic acid—300 g./lt.

Sulfuric acid—3 g./lt.

Cathodic compartment:

Sodium hydroxide—N/2

The anodic compartment was separated from the cathodic one by a porous baffle with a 25% porosity and the diameter of the pores equal to 3μ (mean value); the baffle was made of non-corrodible material (polyethylene).

In the bath were subsequently oxidized a number of samples (the colorings obtained, under equal conditions of oxidation and with the same material treated, were analogous to those obtained by the normal MS process, that is without using the porous baffle and with the same electrolytic bath based on maleic and sulfuric acid in both electrode compartments), until the bath had aged about 50 ah./lt.

After this aging it could be observed that the use of the baffle and of different electrolytic solutions in the anodic and cathodic compartments resulted in the following advantages:

in the anodic compartment there was no formation of precipitates, while in the normal MS process used without the porous baffle such formation of precipitates

4

equalled 1 to 1.5 g./ah. after about 10 ah./lt. aging of the bath (in the initial phase the transformation of maleic acid into succinic acid was equal to about 7 g./ah);

in the cathodic compartment the formation of precipitates is practically negligible, while using the MS solution in both compartments separated by the porous baffle there was production of precipitates of about 0.5 g./ah.

Consequently, the total consumption of maleic acid may be considered as exclusively due to losses by dragging and incorporation of this component into the anodic layer; this consumption is about 40% less than that found for the normal MS process.

Of course there are also practically eliminated all the drawbacks connected with the precipitates in the bath (clogging of the different parts of the plant with the consequent drawbacks in the stirring of the electrolyte and thus with the reduction of the exchange capacities of the cooling apparatus and of the ion-exchanging resin columns).

EXAMPLE 2

The anodic oxidation was carried out at 1.5 a./dm^2 , at 20° C. for 45 minutes in a self-coloring bath of the MOS type, having the following composition:

Anodic compartment:

Maleic acid—300 g./lt.

Oxalic acid—3 g./lt.

Sulfuric acid—1 g./lt.

Cathodic compartment:

Sodium hydroxide—N/2.

The anodic compartment was divided from the cathodic one by a porous baffle as in the preceding example.

Also in this case after aging of the bath about 50 ah./lt., advantages analogous to those described in the preceding example with regard to the decomposition of the maleic acid were obtained. Further advantages were furthermore obtained with regard to the consumption of oxalic acid which appears to be reduced by 40% in comparison to that which would occur if the same electrolyte were used in the cathodic zone and the anodic zone using the same porous baffle.

EXAMPLE 3

The anodic oxidation was carried out at 1.5 a./dm^2 , at 20° C. for 45 minutes, in a self-coloring MOS bath of the following composition:

Anodic compartment:

Maleic acid—300 g./lt.

Oxalic acid—15 g./lt.

Sulfuric acid—3 g./lt.

Cathodic compartment:

Sodium hydroxide—N/2.

The anodic compartment was divided from the cathodic one by a porous baffle (porosity=30%, diameter of pores (mean value)= 4μ). The baffle was made of non-corrodible material (glass).

Also in this example, after aging of the bath about 50 ah./lt., results analogous to those described in the preceding examples were obtained, both as far as the decomposition of the maleic acid is concerned as well as with regard to the destruction of the oxalic acid.

EXAMPLE 4

The anodic oxidation was carried out at 1.5 a./dm^2 , at 20° C. for 45 minutes in a self-coloring TOS bath having the following composition:

Anodic compartment:

Tartaric acid—150 g./lt.

Oxalic acid—15 g./lt.

Sulfuric acid—0.5 g./lt.

Cathodic compartment:

Sodium hydroxide—N/2.

5

The anodic compartment was divided from the cathodic one by a porous baffle (porosity of 35%; diameter of pores of 8μ (mean value)); the baffle was made of non-corrodible material (ceramic).

Also in this example, after aging of the bath 50 ah./lt., results analogous to those described in the preceding examples with regard to the destruction of the oxalic acid were obtained.

EXAMPLE 5

The anodic oxidation was carried out at 1.5 a./dm.² at 20° C. for 45 minutes in a self-coloring bath of the MS type, having the following composition:

Anodic compartment:

Maleic acid—300 g./lt.

Sulfuric acid—3 g./lt.

Cathodic compartment:

Sodium hydroxide—N/2.

The anodic compartment was divided from the cathodic one by a porous baffle having a porosity of 10% and a diameter of pores of 5μ (mean value); the baffle was made of non-corrodible material (polyethylene).

Also in this case, after aging of the bath about 50 ah./lt., advantages analogous to those described in the preceding examples with regard to the decomposition of maleic acid were obtained.

EXAMPLE 6

The tests of the preceding Examples 1, 2, 3 and 5 were repeated under the same conditions of said examples but using a porous baffle having a porosity of 15% and a diameter of pores of 0.8 to 1μ (mean value).

Also in this case, after aging of the baths about 50 ah./lt. or higher, advantages analogous to those described in said above examples with regard to the decomposition of the maleic acid were obtained.

In these tests only an increase of the voltage required by the method was necessary.

EXAMPLE 7

The tests of Example 6 were repeated using a porous baffle having a porosity of about 30% and with a diameter of pores of 10–20 μ (mean value).

Also in this case, after aging of the baths about 50 ah./lt. or higher, advantages analogous to those described in said above example were obtained without the said increase of the voltage.

In these tests only an increase in the production of precipitates per ah. was observed in the cathodic compartment, using the MS or MOS solution in both compart-

6

ments; the production of precipitates was about 0.6 to 0.8 g./ah.

EXAMPLE 8

The tests of Example 6 were repeated using a porous baffle having a porosity of about 35% with a diameter of pores of 30 to 50 μ (mean value).

Also in this case, after aging of the baths about 50 ah./lt. or higher, advantages analogous to those described in said above example were obtained without said increase of the voltage. In these tests only an increment in the production of precipitates per ah. was observed in the cathodic compartment using the MS or MOS solution in both compartments, the production of precipitates was about 0.9 to 1.1 g./ah.

In the above examples, as a cathodic electrolyte, a NaOH solution preferably N/2 was used, but NaOH solution from 0.01 to 1 N may be advantageously used. Substantially equivalent results are obtained by replacing the NaOH by other alkaline hydroxides (for instance LiOH, KOH, etc.) at the same concentration, or by H₂SO₄ or alkaline sulfates preferably at a SO₄⁻ concentration of 3 g./lt. (but also concentrations from 0.1 to 10 g./lt. may be advantageously used) or else by electrolytes that will not produce insoluble decomposition products (for instance oxalic acid).

What is claimed is:

1. In the process for self-coloring anodic oxidation of aluminum and its alloys by means of an electrolytic bath consisting of an aqueous solution of maleic and sulfuric acid, the improvement comprising

placing a porous baffle immersed in the electrolytic solution used into the electrolytic cell, said baffle having pores of a diameter between 0.1 and 50 μ and subdivides the cell into an anodic compartment and a cathodic compartment and applying direct current between the workpiece as the anode and the cathode.

References Cited

UNITED STATES PATENTS

687,386	11/1901	Schwerin	204—131
2,540,602	2/1951	Thomas et al.	204—58
2,370,463	2/1945	Herrick	204—58
2,331,071	10/1943	Halvorsen	204—58
1,323,236	12/1919	Abernethy et al.	204—252
590,826	9/1897	Darling	204—260

JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner