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SURFACE TREATMENT OF ZINC/ALUMINIUM ALLOYS

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ABSTRACT OF THE DISCLOSURE

In a method for the surface treatment of an alloy consisting predominantly of zinc and aluminium, and containing 60–85% by weight of zinc by immersing a surface of the alloy in dilute aqueous sulphuric acid, comprising subjecting the alloy to anodic oxidation at a current density of from 50 to 200 milliamperes per square centimetre of surface. The alloy may include up to 0.5% by weight of copper or magnesium as a third metal.

This invention relates to the surface treatment of zinc/aluminium alloys to produce thereon a protective and/or decorative surface finish.

It is well known that zinc can be anodically oxidised, using conventional DC techniques and electrolytes based on sodium hydroxide or sodium carbonate, to give a white film at high current densities and a black film at low current densities. It is also known that alloys of zinc containing 4 to 12% aluminium can be similarly anodised in similar electrolytes again to give white or black films. However, with zinc or the low-aluminium alloys mentioned these films produced have not been found useful for practical application since they comprise mainly zinc oxide.

It is standard practice in the aluminium industry to anodise high purity or even commercial grade aluminium in 15 to 25% (w./v.) solutions of sulphuric acid to produce films of aluminium oxide which can confer corrosion resistance or decorative appearance to articles made of the metal so treated. It is also known that aluminium alloys containing a few percent of zinc by weight can be anodised in a 15% solution by weight of sulphuric acid to produce aluminium oxide films containing zinc values in approximately the alloying proportions. It has been found impossible to anodise zinc in any sulphuric acid solution or a 55/45 zinc/aluminium alloy in 4 N sulphuric acid solution at a current density of 10 ma./sq. cm.

The invention consists in a method for the surface treatment of an alloy consisting predominantly of zinc and aluminium, and contaiining 60–85% by weight of zinc, comprising immersing a surface of the alloy in dilute aqueous sulphuric acid and subjecting it to anodic oxidation at a current density of from 50 to 200 milliamperes per square centimetre of the surface.

It will be apparent that the current density employed in the present method is considerably higher than that used in conventional aluminium anodizing operations, which is typically 10–20 milliamperes per square centimetre.

Thus zinc/aluminium alloys containing 60–85% by weight of zinc may be anodically oxidised in aqueous solutions of sulphuric acid to produce films which are basically aluminium oxide with only a small content of zinc, probably as oxide, of about 5–10% by weight of the anodised film. Moreover an accelerated corrosion test has indicated that this film confers corrosion protection on the alloy and that sealing treatment of the type

applied to anodised films on aluminium also has a beneficial effect on these films.

The alloy is usually either an alloy of high-purity zinc, or commercial-purity zinc (i.e. containing only incidental impurities, as well known to the man skilled in the art) with correspondingly high-purity or commercial-purity aluminium. While the alloy can have a composition containing up to 85% by weight of zinc, i.e. as little as 15% by weight of aluminium, in practice it is most preferred to use compositions containing 60–80%, or even 60–70% of zinc by weight. Although the alloys to be treated in the present method consist predominantly of zinc and aluminium it is possible to include minor amounts of a ternary metal as deliberate additions, e.g. up to 0.5% of copper or magnesium may be added.

The microstructure of the alloy is usually that produced by casting and mechanical working, and will generally comprise alternate regions, e.g. of approximately 1μ diameter (i.e. 10^{-6} metres) of zinc-rich and aluminium-rich phases.

Zinc may be removed from the surface of the alloy prior to anodizing e.g. by evaporation in vacuo. However, it is a valuable feature of the present method that by suitable control of the anodizing conditions the preferential leaching of a zinc phase and the anodizing of an aluminium-rich phase may be carried out simultaneously in the same bath of sulphuric acid.

The sulphuric acid concentration is preferably between 1% and 40% (w./v.) and the most preferred range is between 10% and 20% (w./v.) H_2SO_4 in water. The anodizing is preferably carried out at a temperature within the range 0°–30° C. Above 30° C. the anodized layer becomes less adherent.

It is preferred to anodise in the constant current mode, although possible to operate in the constant voltage mode.

It is further envisaged to carry out an optional sealing treatment on the anodised films produced. Sealing can be effected in boiling distilled water.

The invention will be further described with reference to the following examples which describe anodising treatments carried out on commercial-purity and high-purity zinc/aluminium alloys. Six samples of alloy were treated as summarised below.

Sample	Description	Current densities used (ma./cm.^{2})
A	Commercial purity zinc and 30% aluminium.	150, 100, 50 and 25.
B	Commercial purity zinc and 40% aluminium.	150, 100, 50 and 25.
C	High purity zinc and 30% aluminium	150, 100, 50 and 25.
D	High purity zinc and 40% aluminium	150, 100, 50 and 25.
E	Commercial purity zinc and 15% aluminium.	150, 100 and 50.
F	Commercial purity zinc and 22% aluminium.	150, 100 and 50.

Anodic films could be formed on all six alloys in 15% w./v. sulphuric acid at 20° C. at 150, 100 and 50 ma./cm.^{2}, and additionally on high purity zinc with 40% aluminium at 25 ma./cm.^{2}. All films were grey and had a sheen, most visible in films of the high-purity alloys, which made them quite attractive in appearance.

The following description shows that leaching and anodising can be carried out in one operation.

(a) ALLOYS A AND C

At 150 ma./cm.^{2}, voltage/time curves for both commerical-purity and high-purity alloys (A and C) initially exhibited a region of very low voltage (about 1–2 volts) which lasted for about 30 seconds. This was followed by a sharply rising voltage/time curve region which was less steep in the case of the high-purity alloy C. At about 8 v. this subsided into a region in which the voltage rose more gradually, then the gradient of this region also in-

creased giving a peak of 30 v. after 7 minutes for both alloys. Both alloys then exhibited a further short but steep voltage increase which terminated in a region of gentle voltage fluctuation at about 34 v. for commercial-purity alloy A and about 35 v. in the case of high-purity alloy C.

At 100 ma./cm.^{2}, similar features in the voltage/time curve were observed but the various regions took longer to become evident. A peak of 30 v. was reached after 14 minutes for the high-purity alloy C.

At 50 ma./cm. the various regions of the voltage/time curve appeared as before although the final peak took up to 2 hours to form.

(b) ALLOYS B AND C

At 150 ma./cm. alloys B and D exhibited a sharp voltage increase starting as soon as the current was switched on. This region terminated at 15 v. for both alloys although this was reached after 10 seconds by the high-purity alloy D and 40 seconds by the commercial-purity alloy B. There was no initial low voltage region for alloys B and D as there has been for the zinc-30% aluminium alloys A and C. A region of more gradual voltage increase followed peaking at 49 v. after 4.5 minutes for the commercial-purity alloy and 35 v. after 2.5 minutes for the high-purity alloy. This was followed for both alloys B and D by a gently fluctuating voltage region, similar to that for the zinc-30% aluminium alloys A and C though with larger fluctuations in the case of the high-purity alloy D.

At 100 ma./cm.^{2} similar behaviour occurred. The peaks were at 49 v. after 7 minutes for commercial-purity alloy B and 37 v. after 5 minutes for the high purity alloy D.

At 50 ma./cm.^{2} both alloys B and D exhibited an initial period of low voltage (about 1 v.) which terminated after 1.5 and 0.5 minutes for the commercial-purity alloy B and high purity alloy D respectively. Commercial-purity alloy B then exhiibted a voltage plateau of about 3 v. which was still evident after 12 minutes. High-purity alloy D exhibited a sharp voltage increase reaching 10 v. after 3 minutes, easing off to reach 14 v. after 8 minutes, and rising steeply again to give a peak of 30 v. after 12.5 minutes, before entering region of gentle voltage fluctuation.

(c) ALLOY E

At 150 ma./cm.^{2} alloy E exhibited a sharp voltage increase to 5 v. after 7.5 minutes after a region of very low voltage (1–2 v.) lasting 5 minutes. This voltage was maintained until a further sharp rise started at 12.5 minutes to give a peak of 40 v. after 17.5 minutes. The voltage then dropped slowly to 15 v. after 26 minutes, increased again slowly to 40 v. at 40 minutes and dropped once again to 25 v. at 42 minutes. Thereafter the voltage gently fluctuated about this last value up to 60 minutes.

At 100 ma./cm.^{2} the voltage began to rise slowly after a region of very low voltage (1–2 v.) lasting 5 minutes, and then more steeply to give a peak of 50 v. after 25 minutes. The voltage then dropped slowly to give 15 v. after 34 minutes, and then rose slowly to give 35 v. after 60 minutes.

At 50 ma./cm.^{2} a very gradual rise in the voltage to about 3 v. after 60 minutes occurred.

(d) ALLOY F

At 150 ma./cm.^{2} alloy F exhibited a region of very low voltage (1–2 v.) lasting 2 minutes followed by a voltage rise to a plateau of 8 v. after 3 minutes. This value was maintained until a sharp rise started after 7.5 minutes to give 30 v. after 12.5 minutes. The voltage then rose more gradually to 45 v. after 22.5 minutes. At this stage a voltage surge to over 100 v. occurred at about 25 minutes. The voltage then dropped sharply to 30 v. and thereafter fluctuated gently about this value.

At 100 ma./cm.^{2} the voltage rose to a plateu of 4 v. after 6 minutes after an initial low voltage region of about 1–2 v. lasting 5 minutes. After about 16 minutes a sharp rise occurred reaching 30 v. after 22.5 minutes. The voltage then rose more gradually to about 45 v. after 35 minutes. It then dropped gradually to about 40 v. after 47.5 minutes and then more sharply to 25 v. after 50 minutes. Thereafter the voltage remained approximately at this value.

At 50 ma./cm.^{2} a very gradual rise in voltage to about 3 v. after 60 minutes occurred.

Tests were also carried out on commercial purity zinc/aluminium alloys containing small amounts of magnesium and copper. Two alloy samples were treated as summarised below.

Sample	Description	Current densities used (ma./cm.^{2})
G	Commercial purity zinc, 22% aluminium, and 0.01% magnesium.	150, 100 and 50.
H	Commercial purity zinc, 22% aluminium and 0.15% copper.	150, 100 and 50.

(e) ALLOY G

At 150 ma./cm.^{2} alloy G exhibited a voltage rise to a plateau of 4 v. at 4 minutes after an initial low voltage region (1–2 v.) lasting 3 minutes. At 10 minutes the voltage rose sharply to give 30 v. after 17.5 minutes. This value was maintained until 32.5 minutes. The voltage then dropped gradually to a minimum of 22 v. after 42.5 minutes and then rose again to 30 v. after 60 minutes.

At 100 ma./cm.^{2} the voltage rose gradually to 3 v. after 20 minutes. This rise steepened to 30 v. after 35 minutes. The voltage then dipped to 28 v. after 42.5 minutes and rose again to 37 v. after 60 minutes.

At 50 ma./cm.^{2} the voltage rise was very slow giving 2–3 v. after 60 minutes.

(f) ALLOY H

At 150 ma./cm.^{2} alloy H exhibited a voltage rise to 25 v. after 12.5 minutes after an initial region of very low voltage (1–2 v.) lasting 2 minutes. Thereafter the voltage fluctuated between 25 v. and 35 v. until 60 minutes (the duration of the investigation) had elapsed.

At 100 ma./cm.^{2} the voltage rose to 4 v. after 6 minutes after an initial low voltage region of 1–2 v. lasting 5 minutes. The voltage then rose increasingly sharply to give 26 v. after 25 minutes. It then rose gradually to 35 v. after 52.5 minutes and then dropped to 25 v. after 60 minutes.

At 50 ma./cm.^{2} the voltage rose very slowly giving about 3 v. after 60 minutes.

There is given below corrosion test results carried out on anodised commercial grade 60:40 zinc/aluminium alloy.

CORROSION TEST DATA

Specimens of 60:40 Zn:Al (commercial grade) were treated as follows in 15 w./v. H_2SO_4 at 20° C.:

Specimen No.	Current density (ma./cm.^{2})	Terminal voltage (v.)	Treatment time (min.)
1	Untreated—merely degreased with acetone		
2	150	35	3.5
3	As 2 and sealed in boiling distilled water for 30 minutes		
4	125	35	5
5	As 4 and sealed as before		
6	100	35	9.5
7	As 6 and sealed as before		
8	75	35	17
9	As 8 and sealed as before		

Test-results (using the "salt-fog" test):

Specimen No.	120 h. salt fog: Rating (white rust)	120 h. salt fog: Percent staining	200 h. salt fog: Rating	200 h. salt fog: Percent staining
1	2	70	2.5	90
2	7	30	6	90
3	9.5	0.1	8.5	15
4	7	30	6	60
5	7	20	6.5	80
6	7	20	6	60
7	9	1	7.5	50
8	7	30	6	80
9	9	1	7.5	40

Rating is on a scale 10—perfect to 0, and staining (i.e. loss of uniformity of coating colour) is on a scale 0 (perfect) to 100%. These give an order of merit of:

Best	120 h., No. 3	200 h., No. 3	Overall, No. 3	Best
	9	7, 9	9	Little difference.
	7	5	7	
Worst	2, 4, 5, 6, 8	2, 4, 6, 8	5	Little difference.
	1	1	2, 4, 6, 8	
			1	Worst.

From these tests it appears that all anoidized specimens, whether sealed or unsealed, are more corrosion-resistant then the non-anodised control specimen, and that sealing has a beneficial effect. The most resistant film was produced by anodising at the highest current density and sealing.

There is now given below data relating to the film thickness of the anodised film produced on zinc/22% aluminium at 100 ma./cm.^{2}.

SPECIMEN FILM THICKNESS-TIME DATA

The figures in the table below refer to the thickness of the anodic film (in microns) formed during anodising of Zn-22% Al at 100 ma./cm.^{2} in 15 w./v. sulphuric acid at 20° C. for various times.

Time (min.):	Film thickness (micron)
1.0	10
2.0	16
3.0	28
4.0	32
5.0	40
6.0	44
7.0	50
8.0	52
9.0	52
10.0	56

The figures tabled are approximate.

We claim:

1. In a method for the surface treatment of an alloy consisting predominantly of zinc and aluminium, by immersing a surface of the alloy in dilute aqueous sulphuric acid, the improvement in combination therewith comprising subjecting the alloy containing 60 to 85% by weight of zinc to anodic oxidation at a current density of from 50 to 200 milliamperes per square centimetre of the surface.

2. A method as claimed in claim 1 wherein the alloy includes up to 0.5% by weight of a third metal selected from the group consisting of copper and magnesium.

3. A method as claimed in claim 1 wherein zinc is removed from the surface of the alloy prior to anodizing by evaporation in vacuo.

4. A method as claimed in claim 1 wherein leaching of the zinc phase and the anodizing of the resulting aluminium-rich phase are carried out simultaneously in a common sulphuric acid bath.

5. A method as claimed in claim 1 wherein the sulphuric acid concentration is between 1% and 40% (w./v.) in water.

6. A method as claimed in claim 5 wherein the sulphuric acid concentration is between 10% and 20% (w./v.) in water.

7. A method as claimed in claim 1 wherein the anodizing is carried out at a temperature between 0 and 30° C.

8. A method as claimed in claim 1 further comprising sealing the anodized film produced in boiling distilled water.

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