

- [54] **METHOD FOR ETCHING ALUMINIUM ALLOYS**
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[56] References Cited			
UNITED STATES PATENTS			
2,441,300	5/1948	Vande Bunte	156/22
2,719,781	10/1955	Hesch	156/21
2,796,334	6/1957	Robinson	156/22
3,039,910	6/1962	Zelley	156/21

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- [57] **ABSTRACT**
- An etching solution for etching aluminium alloys which contain copper comprises an aqueous solution of copper ions, together with a source of hydrogen ions and nitrate ions. The normality of the nitrate ions is arranged such that it is less than the normality of the hydrogen ions.
- 4 Claims, No Drawings**

METHOD FOR ETCHING ALUMINIUM ALLOYS

This is a division of application Ser. No. 288,308, filed Sept. 12, 1972, now abandoned.

This invention relates to solution for etching aluminium alloys.

Aluminium alloys are normally difficult metals to chemically etch as a result of the relatively unreactive layer of aluminium oxide present on their surfaces. In order that aluminium alloys may be successfully etched, alkaline etching solutions which are based on free metal hydroxides are normally utilized. Unfortunately when aluminium alloys which contain such metals as copper or zinc are etched by conventional alkaline etching solutions, a pebbly or nodular etched surface is obtained. It is believed that this effect is caused by the aluminium grains being attacked in preference to the copper or zinc rich grain boundaries. A nodular surface is undesirable as it has a detrimental effect on fatigue properties and also may lead to areas of localised thinning which may be outside manufacturing requirements.

The addition of various sulphur compounds such as polysulphides, sulphur mercaptans and thioureas to the etching solution have been proposed to achieve a smoothly etched surface, although the use of such additives has only been described with reference to alkaline solutions.

It is an object of this invention provide an aluminium alloy etching solution which is acid based and which achieves a relatively smooth etched surface when used for etching aluminium alloys containing copper.

According to the present invention, an etching composition for etching aluminium alloys which contain copper comprises an aqueous solution of copper ions together with a source of hydrogen ions and nitrate ions, the normality of said nitrate ions being arranged such that it is less than the normality of said hydrogen ions.

Preferably the concentration of hydrogen ions in said etching composition is within the range 1.5 to 6.0 Normal

Preferably the concentration of nitrate ions in said etching composition is within the range 0.5 to 5.0 Normal.

Preferably the concentration of copper ions in said etching composition is within the range 0.5 to 100 g/l.

Said hydrogen and nitrate ions may be derived from a mixture of hydrochloric and nitric acids.

Alternatively said nitrate ions may be derived from a nitrate salt.

The present invention also relates to a method of etching aluminium alloys which contain copper comprising treating said alloy surface with an aqueous solution of copper ions, together with a source of hydrogen ions and nitrate ions, the normality of said nitrate ions being arranged such that is less than the normality of said hydrogen ions, rinsing the surface of said alloy with water, treating said etched surface with aqueous dilute nitric acid solution in order to substantially remove the copper layer deposited thereon, repeating said water rinse of said etched surface, treating said etched surface with a dilute aqueous sodium hydroxide solution in order to substantially remove any porosity thereon and finally repeating said water rinse of said etched surface.

Preferably a 10% aqueous nitric acid solution is used for removing said deposited copper layer. Preferably a

15% aqueous sodium hydroxide solution is used for substantially removing said porosity.

When copper is added to aluminium as an alloyed agent, its presence is instrumental in altering the electrode potential of the alloy. More specifically as more copper is added to the alloy, then the more electronegative the alloy becomes with reference to a particular system.

We have discovered that an aqueous mixture of nitric and hydrochloric acids which contains copper ions is suitable for etching aluminium alloys of this type. In particular we have found that etching solutions of the following compositions are suitable:

H⁺ concentration 1.5 to 6.0 Normal

NO₃⁻ concentration 0.5 to 5.0 Normal

Cu concentration 0.5 to 100 g/l

The H⁺ concentration being greater than the NO₃⁻ concentration.

Although in the above compositions, the nitrate ions are derived from nitric acid, it will be appreciated that they could equally effectively be derived from a nitrate salt, for example the nitrate could be added in the form of copper nitrate.

Whilst we do not wish to be bound by any theory of the reaction or mechanism of these solutions we nevertheless believe the following mechanism to take place:

When an aluminium alloy workpiece is exposed to an etching solution according to the present invention, hydrogen ions present in the solution migrate through the protective aluminium oxide layer and react with the aluminium surface thereunder to form soluble aluminium hydride ALH₃. As aluminium is taken into solution, then by virtue of the relative positions of aluminium and copper in the electrochemical series, copper already present in the solution is deposited on the surface of the workpiece, thus displacing the protective oxide thereon. The deposited copper layer is gradually attacked by the etching solution until it eventually becomes porous and exposes the original aluminium workpiece surface to acid attack. As the grains and grain boundaries of the workpiece surface are no longer protected by a layer of aluminium oxide, they are etched at approximately the same rate as each other. As the reaction proceeds, a copper sponge builds up on the workpiece until it is eventually flushed away by the evolving hydrogen gas. The copper sponge re-dissolves in the solution and, together with copper which has been dissolved from the grain boundaries is re-deposited on the workpiece surface as the reaction proceeds. The copper present in the solution is thus continuously deposited and re-dissolved throughout the reaction.

After etching, the workpiece is removed from the etching solution and the copper layer deposited thereon is removed by immersion in dilute nitric acid. The resulting etched surface is somewhat porous is appearance. In order to remove this porosity, the workpiece is given a short rinse in an alkaline aluminium etching solution.

The following examples will serve to illustrate the invention: Examples 1, 3, 4 and 6 are in accordance with the present invention while Examples 2 and 5 also illustrate prior art processes.

EXAMPLE 1

An aqueous solution is accordance with the invention was prepared by dissolving copper chloride in a mix-

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ture of hydrochloric acid, nitric acid and water to give a solution of the following composition:

H⁺ - 2 Normal
NO₃⁻ - 1 Normal
Cu - 5 g/l

A sample of a forged aluminium alloy (2.4% Cu 1.5% Mg 1.2% Ni 1% Fe the balance being Al and impurities) was etched in the aforementioned solution for a period of 1 hour whilst air-agitating the solution and maintaining the temperature at 45°C. The sample was then withdrawn from the solution water washed, and the deposited copper removed by immersion in a 10% aqueous solution of nitric acid. After a further water wash the sample was treated for 3 minutes in a 15% aqueous solution of sodium hydroxide maintained at 80°C. The resulting surface finish was smooth and the depth of etch uniform.

EXAMPLE 2

A test piece of forged aluminium alloy (6% Cu 0.2% Mg 0.2% Si 0.25% Mn 1.5% Ti; the balance being Al and impurities) was immersed in a conventional 5% aqueous etching solution comprising 97 parts sodium hydroxide and 3 parts sodium sulphide. The solution was maintained at a temperature of 90°C and the exposed surface etched to a depth of approximately 0.200 inch, after which the test piece was then washed and dried. The etched surface obtained was coarse and nodular with a variation in depth of etch of 0.080 inch.

An aqueous etching solution according to the invention was prepared by dissolving copper chloride in a mixture of hydrochloric acid, nitric acid and water to give a solution of the following composition:

H⁺ - 2.5 Normal
NO₃⁻ - 1.3 Normal
CU - 20 g/l

A sample of the same aluminium alloy was etched to a depth of approximately 0.200 inch in this solution, the solution being air agitated and maintained at a temperature of 45°C. After treatment in nitric acid as described in Example 1 a further 0.003 inch was removed from the exposed surface by immersion in a 15% solution of sodium hydroxide maintained at 80°C. The resulting surface finish was smooth with no discernable nodules and a variation in depth of etch of 0.015 inch.

EXAMPLE 3

An aqueous solution was prepared by dissolving copper nitrate in hydrochloric acid and water to give a solution of the following composition:

H⁺ - 2.0 Normal
NO₃⁻ - 1.0 Normal
CU - 29 g/l

An aluminium alloy similar to that described in Example 1.

EXAMPLE 4

The etchant composition quoted in Example 1 give similar results to those obtained in that Example when used to etch an aluminium alloy containing 4% Cu 0.6% Mg, 0.8% Si, 0.8% Mn plus various impurities.

EXAMPLE 5

The acid etchant composition described in Example

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2 was used to etch the aluminium alloy described in Example 1. On a depth of etch of 0.200 inch the conventional sodium hydroxide/sodium sulphide etching solution gave a variation of depth of etch of 0.080 inch, the acid solution a variation of 0.020 inch.

EXAMPLE 6

An aqueous etching solution was prepared by dissolving copper chloride, hydrochloric acid, nitric acid and water to give a solution of the following composition:

H⁺ - 4 Normal
NO₃⁻ - 3 Normal
Cu - 15 g/l

A sample of the aluminium alloy quoted in Example 1 was etched in this solution, the solution being air agitated and maintained at a temperature of 15°C. The exposed surface was etched to a depth of 0.150 inch. The sample was removed from the etching solution, water washed, and immersed in a 10% aqueous solution of nitric acid in order to remove the deposited copper. The sample was then water washed and a further 0.003 inch was removed from the exposed surface by immersion in a 15% aqueous solution of sodium hydroxide maintained at 80°C. The resulting surface finish was smooth with discernable nodules and a variation in depth of etch of 0.010 inch.

It will be appreciated that although the present invention has been described with reference to copper-containing aluminium alloys, the invention is theoretically equally applicable to zinc-containing aluminium alloys. In this particular case however, the etching solution would, of course, contain zinc ions, not copper.

I claim:

1. A method of etching an aluminum alloy which contains copper comprising treating the surface of said alloy with an aqueous solution containing copper ions, hydrogen ions and nitrate ions, the concentration of said copper ions being within the range 0.5 to 100 grams per litre, the concentration of said hydrogen ions being within the range 1.5 to 6.0 Normal and the concentration of said nitrate ions being within the range 0.5 to 5.0 Normal, the normality of said nitrate ions being arranged such that it is less than the normality of said hydrogen ions.

2. A method of etching as claimed in claim 1 wherein after said alloy surface has been treated with said etching solution, it is rinsed with water, treated with dilute aqueous nitric acid solution in order to substantially remove any copper deposited thereon, rinsed for a second time with water, treated with a dilute sodium hydroxide solution in order to substantially remove any porosity thereon and finally rinsed for a third time with water.

3. A method of etching as claimed in claim 2 wherein a 10% aqueous nitric acid solution is used for removing said any deposited copper layer.

4. A method of etching as claimed in claim 2 wherein a 15% aqueous sodium hydroxide solution is used for substantially removing said any porosity.

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