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METHOD AND COMPOSITION FOR THE ELECTROLYTIC ETCHING OF BERYLLIUM-COPPER ALLOYS

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The present invention relates to a method and electrolyte composition for electrolytically etching metal alloys. In particular, the invention is concerned with the electrolytic etching of beryllium-copper alloys, especially beryllium-copper alloys containing cobalt in the form of cobalt-beryllide.

Many beryllium-copper alloys contain cobalt. When such alloys are precipitation-hardened, grains of the intermetallic compound cobalt beryllide are formed in a matrix of copper. The resulting two-phased system is difficult to smooth or polish by conventional elcetrolytic etching techniques. The major difficulty is that the anodic potentials established at the surfaces of the two phases result in a preferential dissolution of one of the phases. The other phase protrudes at surfaces and edges and this results in a rough surface, rather than the desired smooth surface.

Accordingly, the objective of the present invention is to provide an electrolyte composition and method for smoothly etching beryllium-copper alloys, especially beryllium-copper alloys containing cobalt beryllide.

A further specific objective of the invention is to provide a composition and method for electrolytically smoothing beryllium-copper alloys containing grains of copper beryllide.

The manner in which the above objectives and many other highly desirable objects and advantages are achieved in accordance with the present invention will be apparent in view of the following detailed description of preferred embodiments thereof.

In general, the present invention comprises anodically etching an article of a beryllium-copper alloy containing cobalt-beryllide grains to provide a smooth surface on the article by connecting the article as anode in an electrolytic system including an electrolyte containing the following constituents:

hydrofluosilicic acid, H_2SiF_6,
ethylene glycol,
hydroxylamine hydrochloride,
isopropyl alcohol, and
2,2′ diquinoline.

Hydrofluosilicic acid, considering, for example, a bath of about 105 ml. volume, comprises the major portion by volume of the composition, generally over 50% and usually on the order of about 60% by volume. The hydrofluosilicic acid is used as 30% by weight aqueous H_2SiF_6. Ethylene glycol is present in a substantial but minor proportion, generally on the order of about 20% by volume of the composition. The hydroxylamine hydrochloride is present in a small amount, generally on the order of 1 gm. and preferably about 0.5 gm. The 2,2′ diquinoline also is present in a small amount, usually less than 1 gm. and preferably about 0.2 gm. and is dissolved in the isopropyl alcohol. The isopropyl alcohol is present in minor proportions which may comprise about 20% by volume of the composition.

The anodic current density on the surface of the part etched with this composition is preferably in the range of from about 500 to 1000 amperes per square foot (a.s.f.).

The invention will be more fully appreciated in the light of the following example which illustrates a preferred embodiment of the composition.

EXAMPLE 1

A part of beryllium-copper alloy which has been precipitation-hardened to form grains of cobalt-beryllide in a matrix of copper was anodically connected in an electrolytic cell which also included a stainless steel cathode plate opposite the part. An electrolyte of the following formulation was introduced into the cell:

Hydrofluosilicic acid (30% by weight H_2SiF_6)	ml.	60
Hydroxylamine hydrochloride	gm.	0.5
Ethylene glycol	ml.	20
Isopropyl alcohol containing 0.2 gm. 2,2′ diquinoline	ml.	25

The electrolyte was employed at a temperature of about 30° C. and a current density of 500 a.s.f. was applied for 30 seconds. The pH of the electrolyte was maintained between 4 and 5. A smooth surface was produced on the metal part.

The distribution of current over the surface of the part electrolytically etched can be adjusted to effect overall uniform attack. This is accomplished by the use of shaped cathodes, current shields and current thieves. Addition agents can be included in the bath formulation to alter electrical conductivity and solution viscosity as well as the composition of the film at the anode surfaces. The above factors are determined experimentally for each system and part configuration.

An electrolyte comprising a major portion of hydrofluosilicic acid and a minor portion of ethylene glycol, not including the other above-described additives, has also been found to be useful for through-etching of Be-Cu alloys and for etching Ni-Fe-P magnetic alloy films.

Beryllium-copper alloys have been found to be useful in the production of substrates for electrical components. In one application, the metal sheets are suitably masked and etched through their entire thicknesses to form chain-like structures. Generally, the conventional process for accomplishing the etching has involved exposure to aqueous chemical solutions, such as acidified ferric chloride or ammonium persulfate. The rate of dissolution, however, in such chemical etchants is influenced by the concentration of the solution, the presence of dissolved copper salts, and the temperature of the solution, as well as the degree of agitation of the solution. Thus, in the same period of time, one part may be etched properly and another part over-etched or under-etched due to slight variation in conditions.

Where the part to be etched is a piece of beryllium-copper alloy which is to be etched completely through at one or more points, the part is first provided with a coating of a suitable masking or resist material to confine the etching to the desired portions of the base metal. The part is then positioned between two cathodes which may be copper or stainless steel sheets and is connected as the anode in the system. The electrolyte is then introduced into the cell and an anodic current density of at least 50 a.s.f. is applied.

Where the part to be etched is nickel-iron-phosphorus alloy, the preferred electrolyte is an aqueous solution of hydrofluosilicic acid and ethylene glycol. For this embodiment, the preferred cathode material is stainless steel sheet or foil and the anodic current density on the part is preferably in the range of from 500 to 2000 a.s.f.

The following two examples, Examples 2 and 3, illustrate the above-described electrolytic etching of Be-Cu and Ni-Fe-P alloys.

EXAMPLE 2

A piece of beryllium-copper alloy 0.003 inch thick is anodically connected between two stainless steel cathodes. The sheet is provided with resist coated areas on those portions of the surface which are not be to etched. An anodic current density of 500 a.s.f. is applied to the part for two minutes in an electrolyte comprising 125 ml. (30% by weight of H_2SiF_6) and 25 ml. of reagent grade ethylene glycol.

There is no substantial attack on the beryllium-copper alloy in the absence of passage of the direct current through the part.

The extent and rate of removal of the base metal is not influenced by small changes in solution temperature. The amount of metal removal can be ascertained and controlled through the use of Ampere-hour meters. The rate of penetration is directly related to the current density selected.

EXAMPLE 3

A thin film of nickel-iron-phosphorus magnetic alloy was deposited on a palladium coated beryllium-copper alloy. Magnetic alloy bits, in a density of 36 bits to a word line, were protected with a resist material. The necks between the covered or protected bits were then etched by immersing the part as an anode in an electrolytic cell containing a stainless steel sheet cathode. The electrolyte contained 125 ml. hydrofluosilicic acid (30% by weight H_2SiF_6) and 25 ml. ethylene glycol. An anodic current density of approximately 1000 a.s.f. was applied for about 40 seconds with a current of 200 milliamperes. The total exposed area of a 36 bit word line is approximately 0.03 square inch. The electrolyte temperature was maintained at from 20 to 30° C. Satisfactory etching of the necks was achieved without corrosion cracking of adjacent bit areas.

It will be apparent to those skilled in the art that various changes may be made in the compositions and procedures described above without departing from the spirit or scope of the invention as expressed in the following claims.

What is claimed is:

1. A method for smoothly etching the surface of a Be-Cu alloy part containing grains of cobalt beryllide comprising anodically etching said part in an electrolyte of the following composition:

a major portion of hydrofluosilicic acid, as 30% by weight H_2SiF_6,
a minor portion of ethylene glycol,
a small amount of hydroxylamine hydrochloride, and
a minor portion of isopropyl alcohol containing dissolved therein a small amount of 2,2′ diquinoline.

2. The method of claim 1 wherein said hydrofluosilicic acid is on the order of about 60% by volume of said composition, said ethylene glycol is on the order of about 20% and said isopropyl alcohol is on the order of about 20% by volume.

3. The method of claim 1 wherein the electrolyte has the following composition:

Hydrofluosilicic acid as 30% by weight H_2SiF_6	ml	60
Hydroxylamine hydrochloride	gm	0.5
Ethylene glycol	ml	20
Isopropyl alcohol containing dissolved therein 0.2 gm, 2,2′ diquinoline	ml	25

4. The method of claim 1 wherein a current density of from 500 to 1000 a.s.f. is applied to the surface of said part.

5. An electrolyte composition for smoothly etching a Be-Cu alloy part containing cobalt beryllide grains when said part is immersed as an anode in said electrolyte comprising:

a major portion of hydrofluosilicic acid, as 30% by weight H_2SiF_6,
a minor portion of ethylene glycol,
a minor portion of isopropyl alcohol having dissolved therein a small amount of 2,2′ diquinoline, and
a small amount of hydroxylamine hydrochloride.

6. An electrolyte as described in claim 5 wherein said hydrofluosilicic acid is on the order of about 60% by volume of said composition, said ethylene glycol is on the order of about 20% and said isopropyl alcohol is on the order of about 20% by volume.

7. An electrolyte as described in claim 5 having the following composition:

Hydrofluosilicic acid as 30% by weight aqueous H_2SiF_6	ml	60
Hydroxylamine hydrochloride	gm	0.5
Ethylene glycol	ml	20
Isopropyl alcohol containing dissolved therein 0.2 gm. 2,2′ diquinoline	ml	25

8. A method for etching an alloy selected from the group consisting of Be-Cu and Ni-Fe-P comprising immersing the alloy as anode in an electrolyte consisting essentially of a major portion of hydrofluosilicic acid as 30% by weight H_2SiF_6 and a minor portion of ethylene glycol.

9. The method of claim 8 wherein the composition contains 125 ml. of hydrofluosilicic acid as 30% by weight aqueous H_2SiF_6 and 25 ml. ethylene glycol.

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