

DESCRIPTION

Chemical Dissolution Treatment Liquid for Iron-Nickel Alloy

TECHNICAL FIELD

The present invention relates to a chemical dissolution treatment liquid for an iron-nickel alloy, which treatment liquid is capable of being easily controlled in composition thereof and of contributing to producing an iron-nickel alloy article having an excellent finish quality.

BACKGROUND ART

Iron-nickel alloys are known to be useful as materials for electronic parts of integrated circuits and the like. While iron-nickel alloy materials are processed from a starting material to a final product through, for example, pressing and cutting steps, undesirable land flashes (fins) and scales are generated. These flashes and scales affect a plating procedure applied to the iron-nickel alloy material, and thus should be removed by a chemical dissolution treatment.

Also, oxide film formed on the iron-nickel alloy material, which film obstructs the intimate adhesion of a plating layer to the iron-nickel alloy material, should be removed before plating.

As a conventional chemical dissolution treatment liquid for the iron-nickel alloy, a glacial acetic acid-nitric acid-hydrochloric acid mixture bath or a nitric acid-hydrofluoric acid mixture bath has been used. The conventional treatment liquid generates a harmful gas containing, for example, NO_x , hydrogen chloride and/or, hydrogen fluoride upon being applied to the iron-nickel alloy material, and therefore is not preferred in consideration of environment and safety for workers. Accordingly, the above-mentioned conventional treatment

liquid is often replaced by a new type of treatment liquid containing hydrogen peroxide as an oxidizing agent.

As chemical dissolution treatment liquids containing hydrogen peroxide, a hydrogen peroxide-hydrochloric acid composition is disclosed in Japanese Unexamined Patent Publication No. 54-100940, a hydrogen peroxide-hydrofluoric acid-nitric acid composition is disclosed in Japanese Unexamined Publication No. 51-91839, a hydrogen peroxide-oxalic acid-sulfuric acid composition and a hydrogen peroxide-ammonium hydrogenfluoride are disclosed in Japanese Examined Patent Publication No. 58-2748, and a hydrogen peroxide-ammonium hydrogenfluoride-sulfuric acid composition is also known. The dissolving treatment liquids which are now most widely used contain, as principal components, hydrogen peroxide, ammonium hydrogenfluoride and sulfuric acid.

However, when the hydrogen peroxide, ammonium hydrogenfluoride and sulfuric acid-containing treatment liquid is used for an iron-nickel alloy over a long period of time in one and the same treating bath, this treatment is disadvantageous in that (1) the dissolving rate of the iron-nickel alloy in the bath is significantly reduced, and (2) the degree of stability of hydrogen peroxide in the bath is significantly decreased. Therefore, the above-mentioned conventional treatment liquid has a low capacity of dissolution treatment for the iron-nickel alloy (which will be referred to as "a treatment capacity", hereinafter).

To compensate for the above-mentioned disadvantages, an attempt has been made to prevent a change in the composition of the treatment bath and to maintain the composition constant by very frequently supplementing the effective components in the bath. The control of the treating bath in the above-mentioned way is very troublesome and the control system or apparatus must be on a large scale.

Under the above-mentioned circumstances, there is a strong demand for a new type of chemical dissolution treatment liquid for the iron-nickel alloy, which has a large treatment capacity and does not need a specific complicated control to maintain the composition of the treatment liquid constant.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a chemical dissolution treatment liquid for an iron-nickel alloy, which provides easy control of the composition thereof and always exhibits a large treatment capacity for the iron-nickel alloy, without supplementing the effective components.

Another object of the present invention is to provide a chemical dissolution treatment liquid for an iron-nickel alloy, which is capable of producing a uniformly treated iron-nickel alloy article having a good finish appearance, without generating local pitting corrosion.

The inventors of the present invention found that by adding specific compounds to the dissolution treatment liquid containing, as principal components, hydrogen peroxide, ammonium hydrogenfluoride and sulfuric acid, the stability of the hydrogen peroxide in the treatment liquid is enhanced, and the iron-nickel alloy surface is uniformly treated without generating local pitting corrosion, and thus the above-mentioned objects can be attained.

The present invention was completed based on the above-mentioned finding.

The chemical dissolution treatment liquid of the present invention for an iron-nickel alloy, comprises (A) an acid aqueous solution containing hydrogen peroxide, ammonium hydrogenfluoride and sulfuric acid; and (B) a stabilizing agent comprising at least one member selected from sulfanilic acid, sulfanilamide, salicylic acid, benzoic acid, benzaldehyde and benzenesulfonic acid.

The treatment liquid of the present invention optionally further comprises (C) a local pitting corrosion-preventing agent comprising at least one aliphatic amine having 1 to 15 carbon atoms.

Also, the treatment liquid of the present invention optionally further comprises (D) a surface-smoothing agent comprising at least one member selected from mono- and polyhydric aliphatic alcohols and ammonium sulfate.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing a relationship between the concentration of metal dissolved in a chemical dissolution treatment liquid of the present invention and the dissolving rate of the metal, and

Fig. 2 is a graph showing a relationship between the concentration of metal dissolved in a chemical dissolution treatment liquid of the present invention and the retention of hydrogen peroxide in the treatment liquid.

BEST MODE OF CARRYING OUT THE INVENTION

The chemical dissolution treatment liquid of the present invention is used for surface treating an iron-nickel alloy material, for example, comprising 50 to 70% by weight of iron and 30 to 50% by weight of nickel. A typical iron-nickel alloy is a 42 alloy comprising 58% by weight of iron and 42% by weight of nickel.

The aqueous acid solution (A) for the chemical dissolving treatment liquid of the present invention comprises hydrogen peroxide, ammonium hydrogenfluoride and sulfuric acid. Preferably, hydrogen peroxide is present in a concentration of 30 to 150 g/liter, more preferably 50 to 150 g/liter, ammonium hydrogenfluoride in a concentration of 10 to 60 g/liter, more preferably 30 to 60 g/liter, and sulfuric acid in a concentration of 0.5 to 20 g/liter, more preferably 0.5 to 10 g/liter.

In the treatment liquid of the present invention, the stabilizer (B) comprises at least one member selected from sulfanilic acid, sulfanilamide, salicylic acid,

benzoic acid, benzaldehyde and benzenesulfonic acid.

The stabilizer effectively prevents the decomposition of hydrogen peroxide present in the treatment liquid and is employed preferably in a concentration of 1 to 10 g/liter.

The treatment liquid of the present invention optionally further comprises a local pitting corrosion-preventing agent comprising at least one aliphatic amine having 1 to 15 carbon atoms. The local pitting corrosion-preventing agent is contributory to preventing a local pitting corrosion of the iron-nickel alloy article, and to improving the finishing result of the surface of the iron-nickel alloy article. The aliphatic amine for the local pitting corrosion-preventing agent is preferably selected from mono-, di- and tri-alkyl amines having 1 to 15 carbon atoms, for example, diethylamine, mono- n-butylamine, tri-n-butylamine, and diisopropylamine.

Preferably, the local pitting corrosion-preventing agent is present in a concentration of 1 to 20 g/liter.

When salicylic acid, benzoic acid, benzaldehyde and/or benzenesulfonic acid is employed for the stabilizer, the local pitting corrosion-preventing agent comprising at least one aliphatic amine having 1 to 15 carbon atoms is preferably added to the treatment liquid. Also, when sulfanilic acid and/or sulfanilamide is employed as the stabilizer, the local pitting corrosion-preventing agent is also preferably used.

The treatment liquid of the present invention optionally further comprises a surface-smoothing agent (D) comprising at least one member selected from aliphatic mono- and polyhydric alcohols, preferably, water-soluble mono- and polyhydric aliphatic alcohols, and ammonium sulfate. The surface-smoothing agent is effectively contributory to uniformly smoothing the treated iron-nickel alloy article surface and to evenly improving the appearance of the article. The aliphatic

alcohols usable for the present invention include, for example, ethyl alcohol, propyl alcohols, ethylglycol, diethyleneglycol, and triethyleneglycol, and preferably employed, as the surface-smoothing agent, in a concentration of 0.2 to 10 g/liter. Also, ammonium sulfate is used as a surface-smoothing agent, in a concentration of 1 to 10 g/liter.

In the surface treatment with the chemical dissolution treatment liquid of the present invention, the surface of the iron-nickel alloy article is brought into contact with the treatment liquid by immersing the alloy article in the treatment liquid or spraying or coating the article surface with the treatment liquid. The surface treatment is carried out preferably at a temperature of 10 to 60°C, more preferably 20 to 50°C, for 10 seconds to 10 minutes, more preferably 20 seconds to 5 minutes. During the contact of the iron-nickel alloy article surface with the treatment liquid, a surface portion of the iron-nickel alloy article is uniformly chemically dissolved in the treatment liquid, and the resultant fresh surface of the iron-nickel alloy article exhibits a desired uniform appearance, for example, gloss, color and texture, without generating local pitting corrosion.

When the specific stabilizer (B) of the present invention is added, optionally together with the local pitting corrosion-preventing agent (C), to the aqueous acid solution (A), in an initial stage of the dissolution treatment in which stage, the concentration of the metal dissolved in the treatment liquid is low, the dissolving rate of the iron-nickel alloy is restricted to a proper level, and in a final stage of the dissolution treatment in which stage, the dissolved metal is in an increased concentration in the treatment liquid, a reduction in the dissolving rate of the iron-nickel alloy is also restricted. Therefore, the iron-nickel alloy can be chemically dissolved at an approximately constant

dissolving rate in the treatment liquid from the initial stage to the final stage of the treatment procedure. In other words, the stabilizer (B) of the present invention optionally combined with the local pitting corrosion-preventing agent (C), is contributory to minimizing the change in the dissolving rate of the iron-nickel alloy in the treatment liquid throughout the treatment procedure, without generating the local pitting corrosion of the iron-nickel alloy article.

Accordingly, the dissolution treatment liquid of the present invention has a specific composition which can be easily controlled during the treatment procedure without specifically supplementing the effective component in the treatment liquid. Also, the dissolution treatment liquid of the present invention has an excellent treatment capacity for the iron-nickel alloy article and can provide a beautiful and uniform surface on the treated article, while preventing the local pitting corrosion of the article.

The hydrogen peroxide contained in the treatment liquid can be stabilized over a long period of time and the dissolving rate of the iron-nickel alloy can be maintained approximately constant from the start to the finish of the treatment. Therefore, the dissolution treatment liquid has a long working life, and the deviation in the quality of the resultant treated article is very small. Also, even after the treatment liquid is employed for a long time, substantially no mist (precipitation) is generated in the treatment liquid and the working circumstances around the treatment liquid can be kept clean.

EXAMPLES

The present invention will be further explained by the following examples.

Examples 1 to 8 and Comparative Examples 1 and 2

In each of Examples 1 to 8 and Comparative Examples 1 and 2, a chemical dissolution treatment liquid

was prepared by mixing an aqueous acid solution of 85 g/liter of hydrogen peroxide, 42.5 g/liter of ammonium hydrogenfluoride and 2.5 g/liter of sulfuric acid, with the compound or compounds as shown in Table 1 and each in the amount as shown in Table 1.

A 42 alloy lead frame having a thickness of 0.3 mm was immersion-treated in the chemical dissolution treatment liquid at a temperature of 40°C, then rinsed with water and dried.

In each of the following stages ① to ③, the dissolving rate of the metal into the treatment liquid, the retention of hydrogen peroxide in the treatment liquid and the surface conditions of the 42 alloy lead frame were measured.

① The starting (initial) stage of the treatment.

② The stage at which the concentration of the metal dissolved from the 42 alloy lead frame into the treatment liquid reached 10 g/liter.

③ At the stage at which after the concentration of metal dissolved from the 42 alloy lead frame into the treatment liquid reached 10 g/liter, the 42 alloy lead frame was removed from the treatment liquid and left to stand in the air atmosphere at a temperature of 50°C for 24 hours.

The dissolving rate of metal was determined from a reduction in thickness of the frame due to the dissolution treatment with a gradual stirring and the treatment time. The thickness reduction was calculated from a reduction in weight of the frame by the dissolution treatment.

The retention of hydrogen peroxide in the treatment liquid was determined in such a manner that the 42 alloy lead frame was treated by the treating liquid until the concentration of the dissolved metal reaches a desired value, the frame was removed from the treating liquid, the remaining treating liquid was left to stand at a temperature of 50°C for 24 hours, the concentrations of

hydrogen peroxide in the treating liquid before and after the leaving procedure were measured, and the retention in concentration of hydrogen peroxide was represented by a ratio in % of the hydrogen peroxide concentration after the leaving to that before the leaving.

The surface condition of the treated 42 alloy lead frame was evaluated by a visual observation as follows.

Class	Evaluation	Surface conditions
3	Excellent	Uniform surface appearance, No local pitting corrosion
2	Satisfactory	Slightly uneven in surface appearance, No local pitting corrosion
1	Bad	Uneven surface appearance Local pitting corrosion occurred

The test results are shown in Table 1.

The relationships between the dissolved metal concentrations and the dissolving rate in Example 3 and Comparative Example 1 are shown in Fig. 1.

Also, the relationships between the retentions of hydrogen peroxide and the dissolved metal concentrations in Example 1 and Comparative Example 1 are shown in Fig. 2.

Fig. 1 shows that the change in the dissolving rate of metal in the treatment liquid of the present invention (Example 3) in response to the change in the dissolved metal concentration in the treatment liquid is significantly smaller than that of Comparative Example 1.

Also, Fig. 2 clearly shows that the reduction in the concentration of hydrogen peroxide in the treatment liquid of the present invention (Example 3) in response to the change in the dissolved metal concentration in the treatment liquid is significantly smaller than that in Comparative Example 1.

Table 1

Example No.	Additive compounds		Dissolving rate of metal at 40°C (μm/min)			Reten- tion of H ₂ O ₂ (%)	Metal surface conditions			
	Type	Amount (g/l)	①	②	③		①	②	③	
Comparative Example	1	None	-	6.7	3.0	0.9	30	2	1	1
	2	n-butylamine	5	4.8	0.5	-	0	3	2	-
Example	1	Sulfanilic acid	2.5	5.1	1.5	1.3	90	2	2	-
	2	Sulfanilamide	2.5	7.0	4.2	2.4	92	2	2	2
	3	Sulfanilic acid n-butylamine	2.5 5.0	4.5	2.3	2.0	91	3	3	2
	4	Benzoic acid di-isopropylamine	2.5 10.0	5.3	2.5	2.1	86	3	3	2
	5	Sulfanilic acid n-butylamine diethyleneglycol ammonium sulfate	2.5 5.0 1.0 2.5	4.4	2.2	2.0	81	3	3	3
	6	Sulfanilamide n-butylamine ethyl alcohol ammonium sulfate	2.5 5.0 5.0 5.0	6.0	3.5	1.8	94	3	3	3
	7	Salicylic acid benzaldehyde n-butylamine ethyl alcohol ammonium sulfate	1.0 1.0 7.5 4.0 5.0	4.4	2.3	2.1	80	3	3	3
	8	Benzenesulfonic acid n-butylamine diethyleneglycol ammonium sulfate	5.0 10.0 5.0 5.0	5.0	2.4	2.0	76	3	3	3

Example 9 and Comparative Example 3

In each of Example 9 and Comparative Example 3 a chemical dissolution treatment liquid was prepared by mixing an aqueous acid solution of 100 g/liter of hydrogen peroxide, 50 g/liter of ammonium hydrogenfluoride and 2.5 g/liter of sulfuric acid, with the compounds as shown in Table 2 in the amount as shown in Table 2.

A 42 alloy lead frame having a thickness of 0.3 mm was immersion-treated in the treatment liquid at a temperature of 30°C, rinsed with water and then dried. The same tests as in Example 1 were applied. The test results are shown in Table 2.

Table 2

Example No.	Additive compounds		Dissolving rate of metal at 40°C (μm/min)			Reten- tion of H ₂ O ₂ (%)	Metal surface conditions		
	Type	Amount (g/l)	①	②	③		①	②	③
Comparative Example 3	None	-	5.5	3.1	1.1	31	2	1	1
Example 9	Sulfanilic acid	2.5	4.3	3.1	3.3	92	3	3	3
	diisopropylamine	5.0							
	diethyleneglycol	1.0							
	ammonium sulfate	2.5							

INDUSTRIAL APPLICABILITY

The chemical dissolution treatment liquid of the present invention has an excellent treatment capacity for iron-nickel alloy materials, has a high working stability and life and can impart a uniform and good surface appearance, without generation of local pitting corrosion, to the article.

CLAIMS

1. A chemical dissolution treatment liquid for an iron-nickel alloy, comprising:

(A) an aqueous acid solution containing hydrogen peroxide, ammonium hydrogenfluoride and sulfuric acid; and

(B) a stabilizer comprising at least one member selected from sulfanilic acid, sulfanilamide, salicylic acid, benzoic acid, benzaldehyde and benzenesulfonic acid.

2. The chemical dissolution treatment liquid as claimed in claim 1, further comprising (C) a local pitting corrosion-preventing agent comprising at least one aliphatic amine having 1 to 15 carbon atoms.

3. The chemical dissolution treatment liquid as claimed in claim 1, wherein the stabilizer (B) comprises at least one member selected from salicylic acid, benzoic acid, benzaldehyde and benzenesulfonic acid and further comprises (C) a local pitting corrosion-preventing agent comprising at least one aliphatic amine having 1 to 15 carbon atoms.

4. The chemical dissolution treatment liquid as claimed in claim 1, 2 or 3, further comprising (D) a surface-smoothing agent comprising at least one member selected from mono- and poly-hydric aliphatic alcohols and ammonium sulfate.



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Fig.1

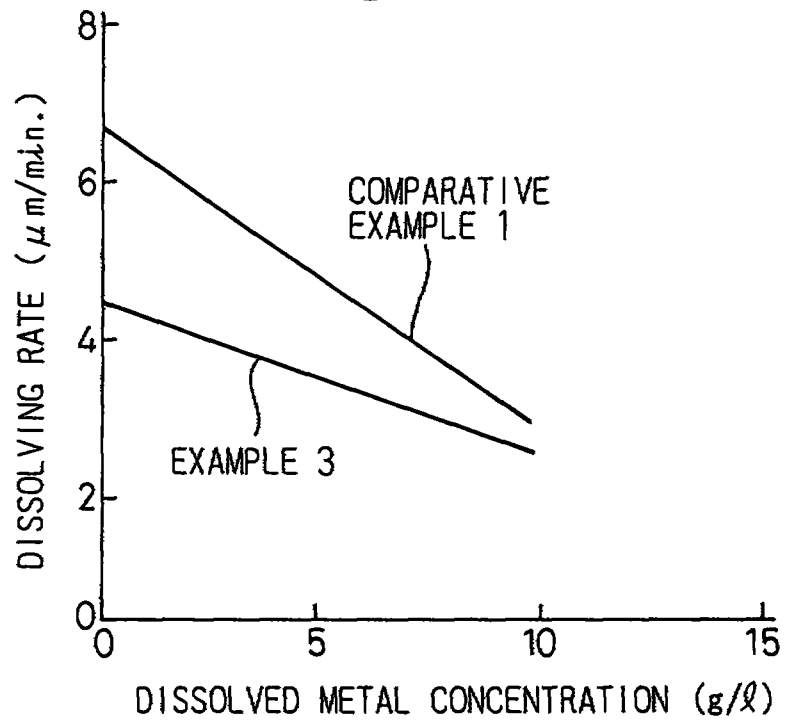
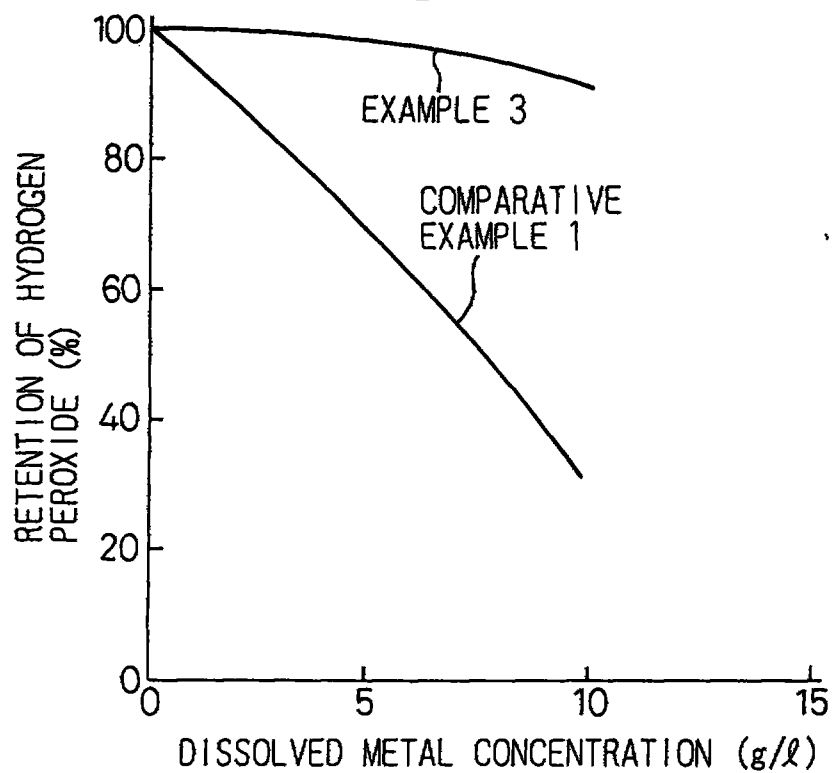


Fig.2



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Substitute sheet - 23 October 2000

ABSTRACT

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CHEMICAL DISSOLUTION TREATMENT LIQUID FOR IRON-
NICKEL ALLOY

5 An iron-nickel alloy can be uniformly surface
treated, without local pitting corrosion, with a chemical
dissolution treatment liquid including (A) an aqueous
acid solution of H_2O_2 , ammonium hydrogenfluoride and
sulfuric acid, (B) a stabilizer selected from sulfanilic
acid, sulfanilamide, salicylic acid, benzoic acid,
10 benzaldehyde and/or benzenesulfonic acid and optionally
(C) a local pitting corrosion-preventing agent selected
from aliphatic amines, and optionally (D) a surface-
smoothing agent selected from aliphatic alcohols and/or
ammonium sulfate.

(Figure 1)