

연구논문 초록 (1967~1978)

各種 鍍金液의 迅速分析法 (第 1 報)

康 熙 澤

Rapid Determination of Electroplating Solutions

(1) (Copper from Copper Plating Solutions)

H. T. Yum

ABSTRACT

Up to this date, numerous methods of analysis of electroplating solutions are published. Some, however, need lots of works before reaching final results, or require high technique and special instruments, and also some are unaccurate due to unclearness of end point. Like our undeveloped countries, technicians of electroplating shops are most high school graduates or under, and have not much knowledge on chemistry. Furthermore, those technicians have to control their plating solutions by themselves without having enough analytical laboratory equipment.

Therefore, in this paper the simplest, besides accurate method is investigated after comparing numerous methods published.

Among the methods of copper determinations from acid and alkaline copper plating baths, EDTA titration method are chosen, due to these methods are the simplest and fastest for the evaluation of metal content, without requiring any special instrument. For acid copper solutions, chelate titrations were accurate enough. Since the end point of titration of chelate method is variable according to the kind of indicators and other metal's coexistence as well as solution component, many difficulties were encountered from cyanide copper, on the contrary of acid copper bath. PAN, PV, and MX indicators were tried, but it is found that MX is the best. In cyanide solution, due to cyanide is the masking reagent, elimination of this component is essential, and finally found that elimination CN^- by precipitation with AgNO_3 solution was the simplest and the most accurate way among others. This method was very accurate for the new plating solutions even coexistence with organic brighteners. However used solutions for long months

running have to be predetermined the accurate copper value by thiosulfate method from time to time, before chelate titration by means of AgNO_3 precipitation. Always some constant deviations will be seen according to the solutions nature. Therefore those deviation values have to be compensated each time.

Al의 陽極處理에 關한 研究 (第 1 報)

(電解條件이 皮膜에 미치는 影響)

李鍾南 · 李成柱 · 金會楨

Anodizing of Aluminium (Part 1)

(The effects on film by electrolytical conditions)

C. N. Lee, S. J. Lee and H. J. Kim

The characteristics of sulfuric acid anodized layer was studied under various conditions, acid concentration: 5-20%, temperature: 5-25°C, bath voltage: 16 volts, bath agitation: mechanical.

The Al^{+++} ion increase in anodizing bath, the film thickness under microscope, the comparative porosity and the thickness were determined. It was found that film thickness and the porosity which are the main factors of determining anodized layer quality, rule the *corrosing and abrasion resistance* of the film, and that the porosity is increasing in the outer layer.

The formation mechanism was assumed as follows:

The film thickness-increase is due to OH^- ion diffusion into compact non-conductive layer and $\text{Al}^+ + \text{OH}^- \rightarrow \text{Al}(\text{OH})$, $\text{Al}(\text{OH})^+ + \text{OH}^- \rightarrow \text{Al}(\text{OH})_2$, $\text{Al}(\text{OH})^+ + \text{OH}^- \rightarrow \text{Al}(\text{OH})_3$. the strong adhesion force is also due to $\text{Al}(\text{OH})$ or $\text{Al}(\text{OH})_2$ in transition layer. And the pore-nucleation is produced by volume change between Al and Al_2O_3 and activated H_2O gas created by large reaction heat of $\text{Al}^{+(x)} + \text{OH}^- \rightarrow \text{Al}(\text{OH})_x$.

니켈鍍金液中的 硼酸 迅速定量法

廉 熙 澤

Rapid Analysis of Boric Acid in Nickel Plating Solutions

H. T. Yum

Only mannitol or glycerine is generally used for the determination of boric acid in a nickel plating solution in order to make its acidic property so strong that it can be titrated with NaOH. However, these solutions give very ambiguous color change of indicator due to the precipitation of nickel salts. Therefore, only experienced chemists or well trained workmen can accurately confirm the actual end point of the titration. For eliminating such interference of nickel salts and easily confirming the end point by any persons, the author attempted to find out a solution which produces no precipitates during the titration in these experiments, and also he tried to turnish the reason for ambiguousness in titration.

The following results were obtained after many experiments.

(1) In any titrations which produce nickel salts such as $\text{Ni}(\text{OH})_2$, the salt is formed until very approximate to the end point, which shows some error by the consumption of titrant (NaOH). Then, the pink color of phenolphthalein is absorbed by $\text{Ni}(\text{OH})_2$ and the pH jumping at the end point is also diminished to as little as less than 15% of the total phenolphthalein pH range.

(2) Known methods by complex salts of citrate, which do not produce precipitates of $\text{Ni}(\text{OH})_2$, are also not very satisfactory, because, the pH jumping at the end point is only about 35% and the color change of phenolphthalein is from blue-green to purple-blue.

(3) New method by complex salts of oxalate were attempted in these experiments. They also did not produce Precipitates of $\text{Ni}(\text{OH})_2$ and were very satisfactory in color change at the end point, because the pH jumping at the end point was about 65% and the color change was from blue-green to purple-red. In these methods, analytical cost was minimized by the use of less amounts of cheaper chemicals than the conventional citrate complex methods. The mixture of chemicals used was composed of 37g/l of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$), 2g/l of phenolphthalein, and 400ml/l of glycerin. The accuracy of analysis was within the error of 0.5%.

(4) The procedure of analysis was as follows. One ml of nickel plating solution was taken out and to it were added 20ml of water and 20ml of the above

mixture for the indicator. The solution was titrated with 0.1N NaOH. The quantity of boric acid was calculated by the following equation.

$$\text{Boric acid(g/l)} = 6.184 \times F \times \text{ml}$$

Vol. 3, No. 1 1970. 4

니켈鍍金液의 硼酸分析에 關한 研究

廉 熙 澤*

Theoretical Study of Boric Acid Determination In Nickel Plating Solution

H. T. Yum

ABSTRACT

“Rapid Determination of Boric Acid in Nickel Plating Solution¹⁾” by the addition of $\text{Na}_2\text{C}_2\text{O}_4$ and thus preventing the precipitation of $\text{Ni}(\text{OH})_2$ during titration, has previously been reported. In this paper, the exact amount of glycerine and the complexing possibility of oxalate with nickel has been determined by means of conductivity titrations. This experimental work has been supported by the mathematical application of the Debye-Huckel and mass action equations as well as statistical analysis. The results were: (1) For determining boric acid in nickel plating solution, 20ml of 400ml/l glycerine was sufficient, since 97% of the H_3BO_3 was dissociated by this addition. (2) In the absence of $\text{Na}_2\text{C}_2\text{O}_4$, the continuous precipitation of $\text{Ni}(\text{OH})_2$ during titration with NaOH even past end-point for boric acid determination resulted in considerable analytical error. (3) In the presence of $\text{Na}_2\text{C}_2\text{O}_4$ during titration, Ni^{++} combined with $\text{C}_2\text{O}_4^{--}$ to form NiC_2O_4 . The solution with this precipitate of very fine, colloidal, transparent particles, remained quite clear for approximately 2 hours. Therefore it was shown that the presence of $\text{Na}_2\text{C}_2\text{O}_4$ prevents the formation of gross $\text{Ni}(\text{OH})_2$ precipitation by forming NiC_2O_4 instead of a complex salt with Ni^{++} , which did not interfere with the visible determination of the end-point for boric acid with NaOH titration. This observation may be interpreted in the light of the previously published solubility ratio for NiC_2O_4 and $\text{Ni}(\text{OH})_2$, 0.3mg/100g H_2O (25°C), and 1.3mg/100g H_2O (25°), respectively. Precipitation of the less solu-

ble, albeit transparent salt, NiC_2O_4 precluded therefore the precipitation of the $\text{Ni}(\text{OH})_2$ salt.

Vol. 4, No. 1 1971. 4,

鉛-朱錫-銅系 合金鍍金에 關한 研究

康 卓·趙鍾琇·康熙澤

A Study of Electro-Deposition for Pb-Sn-Cu Alloy System

T. Kang, C.S. Cho and H.T. Yum

ABSTRACT

In this study, fluoborate solution consisting of lead fluoborate, tin fluoborate and cupric acetate was used. By addition of small amount of Cu^{++} ion to the solution, the Cu content of deposition layer was almost controlled less than 5%. The amount of Cu in deposition layer was almost constant without any influence of Pb^{++} & Sn^{++} quantities in the solutions. The amount of Sn, however, was decreased by the increase of total concentration of Pb^{++} Sn^{++} in the solution, and the amount of Pb was increased by the increase of total concentration of Pb^{++} Sn^{++} in the solution. Agitation of plating solution & low current density resulted in the increase of Cu content. Analyzing of microscopic structures and etching tests of the deposited alloy, it was believed that the alloy had a lamellar structure consisting of copper rich lamellar and lead rich layers.

Vol. 4, No. 1, 1971. 4,

印刷配線用 電解銅箔의 製造에 關한 研究

尹容九·李震亨

Fabrication & Evaluation of Electroplated Copper Foils for Printed Circuit Board Applications

Y.K. Yoon and J.H. Lee

Abstract

Copper-clad laminate(CCL) was fabricated and evaluated by bonding $35 \pm 5\mu$ thick electroplated copper foils with a suitable adhesive to an insulating base such as phenolic resin laminate. In this study, electroplating methods and conditions were studied to produce good quality copper foils for printed circuit board applications. The electroplating bath solutions used were a copper sulfate solution and a concentrated copper fluoborate solution. A surface roughening treatment that improves the adhesive strength of copper foils with an insulating laminate was also developed. A conventional copper sulfate solution containing sulfuric acid was used for the roughening treatment.

Vol. 5, No. 1, 1972. 2,

ABS 樹脂上的 化學鍍金에서의 最適 Etching 條件에 關한 研究

金 源 澤 · 金 仁 培

The Optimum Etching Condition of the Chemical Plating on ABS Plastics

W. T. Kim and I. B. Kim

Abstract

We have studied about the optimum chemical etching and sensitizing conditions of the plating on plastics. As specimen "Mitsubishi Nobren MM2A" was used. The results were as follows.

1) The optimum chemical etching conditions.

Etched the specimens for 10 ~ 40 minutes at $70 \sim 80^\circ\text{C}$ with the etching solution table 1, and for 10 ~ 15 minutes at $65 \sim 70^\circ\text{C}$, with the etching solution of table 2,

Table 1. Etching solution (I)

Composition	Component
H ₂ SO ₄ (95%)	250 ml
H ₃ PO ₄ (85%)	75 "
K ₂ Cr ₂ O ₇	12.5g
Water	175 ml

2) The optimum sensitizing conditions.

Sensitized the specimens for 60 ~ 90 seconds at 25°C with the sensitizing solution of table 3

Table 2. Etching solution (II)

Composition	Component
H ₂ SO ₄ (95%)	22.5 ml
H ₃ PO ₄ (85%)	15 ml
CrO ₃	105 g
Water	150 ml

Table 3. Sensitizing solution

Composition	Component
SnCl ₂	9 g
HCl (35%)	36 ml
Water	300 ml

Vol. 3, No. 2, 1972. 6,

산성 황산등 용액 내에서 동판 위에 녹청 형성에 관한 기초적 조사

尹 勝 烈

An Investigation on the Patination of Copper in Acidic Copper Sulfate Solution

S. R. Yoon

Abstract

A method of preparation of synthetic inorganic coating on copper (patina) has been presented. An Eh-pH diagram was constructed for the present Cu-H₂O-SO₄ system using the most recently available thermodynamic data. In the path of the patination at room temperature the general behavior of copper in acidic cop-

per sulfate solutions with potassium chlorate as an oxidizing agent appeared to follow those predictable in this Eh-pH diagram. In the presence of 0.05 molar cupric sulfate at a temperature of about 28°C a green brochantite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$) layer was formed on copper sheet in 20 days. In a solution having an initial pH of 3.5 the development of a brochantite coating has been observed to take place in two stages. In the first, a layer of cuprous oxide formed on the copper at a relatively rapid rate. In the ensuing step the outer layer of cuprite was oxidized at much slower rate to form brochantite. The synthetic coatings appeared to consist of crystallites of brochantite growing perpendicular to the cuprous oxide surface. The outer tips of the crystallites were easily broken off and gave to the layer a rather chalky character. Underneath, at the brochantite Cu_2O interface, however, the green layers were firmly attached. The effect of reagent concentration, solution agitation, and moderate temperature increase were investigated to improve the quality of coating. So also in a qualitative way were the effect of light.

Vol. 5, No. 3, 1972. 10,

AgI 결정면에 물의 흡착에 관한 이론적 고찰

백 영 현

Interaction of Water with Silver Iodide

Y. H. Paik

Abstract

The interaction energy of water molecule over the surfaces of basal planes of silver iodide has been calculated, assuming 1-4-6-12 type potentials between the gas molecule and lattice ions in the silver iodide lattice. The heat of adsorption ranges from 12.25 to 12.75 kcal/mole at low coverage such as around the level of the latent heat of sublimation of water.

Vol. 7, No. 1, 1974. 4,

古代新羅의 金屬技術 研究

姜 聖 君 , 趙 鍾 琇

A Study of Metal Technology in Ancient Silla Dynasty

S. G. Kang and J. S. Cho

Abstract

The corrosion film of gilt bronz, silver and iron objects, which were excavated from Ancient Tomb of Silla Dynasty, was removed by the electrolytic reduction process. These metallic objects were mainly investigated for microstructure, designs and gilding film etc. Most iron objects might be made by hot forging process. The cold extrusion technique might be used for gold and silver objects, in addition to an amalgam method might be applied for the gilding of Au film on Cu-alloy surface. For the gilding on glass surface, first, a Cu alloy was cladded on glass, next, Au-film was obtained on the Cu-alloy by the amalgam method.

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Strip 형 반도체 부품상에 회전음극 방법에 의한 주석도금에 관한 고찰

이 완 구

Rotary Cathode Tin Plating on Strip Type Semiconductors

W. K. Lee

Abstract

A novel electroplating process is described and effect of anode lay-out on thickness distribution and on plating rate are discussed. Microphotographic

analysis indicates deposits are compact and less "POROUS" than of barrel and rack. With this process production cost reduction and capacity increase could be achieved by a rate of 60% and 97% respectively, as compared to our present barrel plating process. This process disclose a number of beneficial processes such as color coding system on TO-92 package and development of a new tin bath formula.

Vol. 8, No. 2, 1975. 7,

Ag-Au 合金의 光學的 特性研究

盧 平 植 金 顯 男

Optical Properties of Ag-Au Alloys

P.S.Re and H.N.Kim

ABSTRACT

To study optical properties of Ag-Au alloys as the simplest homogeneous disordered alloys, the dependence of the reflectivity of Ag-Au alloys on their composition has been measured with the wavelengths ranging from $700m\mu$ to $900m\mu$.

Measurements were made on mechanically polished bulk samples and the experimental results are discussed in terms of the Drude-Zener theory. The distributions of the reflectivity for various wavelengths are also discussed.

Vol. 8, No. 3, 1975. 10,

혜로보론과 NaBF_4 에 의한 鋼材의 浸 硬化處理에 關하여

呂 運 寬 金 文 一

Study on the Boriding of Steel in Ferroboron and NaBF₄ Powder Mixture

Mi M.I. Kim and W.K. Yeo

ABSTRACT

The boronizing method using ferroboron and NaBF₄ powder mixture was studied for surface hardening of medium carbon steel.

This boride layer was compared with a boride layer that was formed in ferroboron and KBF₄ powder mixture.

The frequency factor and activation energy were discussed in this paper. The main results obtained can be summarized as follow.

- 1) The optimum range of NaBF₄ content is 10 to 15% of weight to obtain a thick and dense boride layer.
- 2) The depth of the boride layer d was approximately expressed by the following equation: $d=100 \exp(-18,000/RT) \sqrt{t}$
- 3) The oxidating resistance of boronized steel proved to be good at 800°C but almost unacceptable near at 900°C.
- 4) The NaBF₄ effect was the same as that reported for KBF₄.

Vol. 8, No. 3, 1975. 10,

固體鐵-熔融亞鉛의 溶解反應

尹秉河 鄭潔相 朴景采

The Dissolving Reaction of Solid Iron with Molten Zinc

B. H. Yoon, I. S. Chung and K. C. Park

Abstract

The dissolving and growth kinetics of intermetallic compounds for the reaction between solid iron and molten zinc were studied under nitrogen atmosphere over the temperature range between 470°C and 680°C. The rates of dissolution

of solid iron into molten zinc were obtained under a static condition. The amount of dissolution of solid iron and the width of intermetallic compounds could be determined by means of microscopy.

The thickness of intermetallic compound at a given temperature increases with increasing time, whereas for a given time decreases with increasing temperature. The rate of dissolution is controlled by the diffusion process of iron in the effective boundary layer of molten zinc over the temperature range $470^{\circ} \sim 530^{\circ}\text{C}$, $570^{\circ} \sim 620^{\circ}\text{C}$, and $650^{\circ} \sim 665^{\circ}\text{C}$, while by the surface reaction over the range $530^{\circ} \sim 570^{\circ}\text{C}$ and $620 \sim 650^{\circ}\text{C}$.

Vol. 9, No. 2, 1976. 7.

電子 部品上의 金鍍金에 關한 研究 (第二報)

廉 熙 澤

Gold Alloy Plating on Electronic Parts (II)

H. T. Yum

Abstract

In order to get high wear-resistant gold alloy plating on electronic parts, an attempt has been made, in which Cu, Ni, and Zn EDTA salts were added in gold plating solution.

The results obtained on the wear resistance are as follows:

1. The addition of 0.5g/l or over Cu in plating solution, showed 1.5 times more wear resistance than in case of no addition.
2. The addition of 1.5g/l or over Ni, showed 3.5 times more wear-resistance.
3. The additions of 1.5g/l and 4.0g/l Zn, showed 3.5 times and 6.8 times more wear resistance, respectively.
4. The additions of 1.5g/l Ni and 1.0g/l Zn simultaneously, showed about 10 time more wear resistance than in case of no addition.

Vol. 9, No. 3, 1976. 10,

水壓에 의한 Epoxy 수지 被覆膜의 破斷強度에 관한 硬 관한 研究

白 英 男 · 金 冕 燮 · 趙 鍾 琇

A Study of Rupture Strength of Epoxy Resin Film by Water Pressure

Y. N. Paik, M. S. Kim and J. S. Cho

Abstract

In this study, a rupture strength of epoxy resin film coated on the leaking spot in waterpipe line was determined, using water pressure, without interrupting water supply. This results could be used for the sealing of water leakage in large size waterpipe lines. An experimental equation $P=Kt^m/R^n$ ($m=2$, $n=3.5$) was also obtained, where P is the rupture pressure, K is a const, t is the thickness and R is the radius of the resin film. From this results, the safety thickness of the film for a domestic use was calculated with various radii against the maximum pressure.

Vol. 10, No. 1, 1977. 3,

도금액 관리에 관한 조사연구

신종철 · 박광자 · 이성주 · 이종용

Studies on Control of Gilding Liquid

J. C. Shin, K. J. Park, S. J. Lee and J. Y. Lee

Abstracts

To support the domestic plating industry concerning localized products, survey was conducted in connection with chemicals and properties of plating solution. Collected samples from 55 factories throughout the country were investigated

by spectigated by spectrograph, Hull cell test and chemical analysis method to find major chemical components of the plating solution.

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저농도 크롬도금에 관한 연구

이경진·박광자·이성주·이종용

A study on the chromium plating from low concentrate bath

K. J. Lee, K. J. Park, S. J. Lee and J. Y. Lee

Abstract

In decorative chromium plating, highly concentrated conventional baths (CrO_3 150~400g/l) have been used. Because of the problems of heavy metal pollution and the saving of raw materials, chromium plating from dilute bath has been developed recently.

The present study was performed to determine the effects of all the variables in the low concentrated chromium plating bath, such as brightness, appearance, current efficiency, and plating rate with regard to the bath composition and plating conditions.

Vol.10, No. 3, 1977. 12,

3價크롬鹽에 의한 크롬鍍金

高錫水·朴柄珏

A Study on Chromium Plating from Trivalent Chromium Salts

S. S. Ko and B. K. Park

Abstract

The trivalent chromium plating process have been studied by several group of orkers in the recent years.

In the plating process, Alecra 3 process is the most familiar one.

Potassium formate and potassium chloride of the bath compositions in the above process, are exchanged for sodium formate and sodium chloride, and then they have been examined characteristics of the electrodeposition using above bath solution and a few optimum conditions. The results are as follows,

(1) The characteristics of the electrodeposition; that is, throwing power, covering power, appearance, and deposition rate are most satisfied when concentration of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is 0.4 mol/l, and mol ratio of HCOONa to Chromium (III); $\text{HCOONa}/\text{Cr}^{+3}$, is 2 to 3.

(2) Throwing power, covering power, color and deposit rate show a similiar tendency to Alecra 3 process.

Vol.10, No. 3, 1977. 12,

용융아연 (熔融亞鉛) 도금공정 (鍍金工程)에서 아연부착량 (亞鉛附着量)에 관한 연구

金完哲 · 姜聖君 · 南勝義

A Study of Zn-coating Weight in Hotdip Galvanizing Process.

W. C. Kim, S. K. Kang and S. E. Nam

Abstract

This experiment intends to study Zn-coating weight through galvanixing process.

A through examination has been carried out on the change of steel-composition, galvanizing-temperature, dipping-time, Fe-loss when other factors were regular.

Activation energy needed for Fe-loss was obtained and within this sample,

the best condition which has influence on coating weight was found so as to reduce Fe-loss.

As Fe-loss was diminished, the amount of product of Dross and Zn-using amount per total products could be reduced.

The results of experiments are as follows.

1. Zn-coating thickness was increased by the rising Zn-bath temperature and was the maximum at 8-minutes dipping time.
2. The coating weight was greatly influenced by Si. As in other samples, the proportion of increasing was very rare after 20 minutes. If the dipping time prolonged, the increasing amounts of Fe-loss are more greatly.
3. Activation Energy needed for Fe-loss was as follows

Such numerical values were most equal to those of the activation energy which had influences on the growth of γ -phase.

Sample - I = 18,500 Cal/mole

Sample - III = 22,000 Cal/mole

Sample - V = 42,300 Cal/mole

Vol. 11, No. 1. 1978. 3,

시안화亞鉛浴中에 있어서의

有機化合物添加劑의 影響 (第一報)

李柱性·朴正一

Effects of Organic Additives in Cyanide Zinc Electroplating Bath (I)

J. S. Lee and J. I. Park

Abstract

Organic compounds, such as aldehydes, amines, amides, sulfur compounds of polymers, have been added to cyanide Zinc electroplating bath to achieve in improvement of the brightness and of the current efficiency.

It was found that the addition of only one compound of these organic compounds in the bath were unsuitable to be used for brightener, but mixture of aldehyde and reaction products obtained from epoxides and amines and/or amides were suitable for brightener in cyanide zinc electroplating baths.

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