



The William Blum Lectures

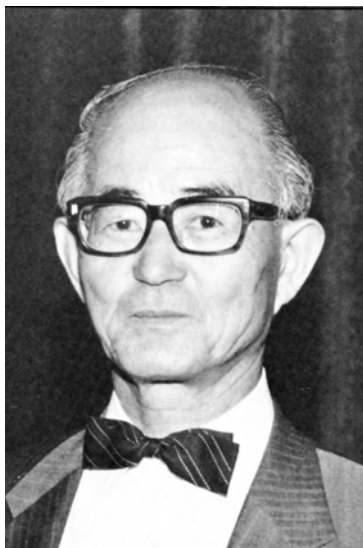
#32 - Tadao Hayashi - 1991



**The 32nd William Blum Lecture
Presented at the 78th AESF Annual Convention (SUR/FIN 1991)
in Toronto, Ontario, Canada
June 24, 1991**

From Art to Technology: Developments in Electroplating in Japan

**by
Dr. Tadao Hayashi
Recipient of the 1990 William Blum
AESF Scientific Achievement Award**





The William Blum Lectures

#32 - Tadao Hayashi - 1991



The 32nd William Blum Lecture

Presented at the 78th AESF Annual Convention (SUR/FIN 1991)
in Toronto, Ontario, Canada
June 24, 1991

From Art to Technology: Developments in Electroplating in Japan

by

Dr. Tadao Hayashi

Recipient of the 1990 William Blum
AESF Scientific Achievement Award

Editor's Note: Originally published as *Plating & Surface Finishing*, **78** (9), 30-34, 39-41 (1991), this article is re-publication of the 32nd William Blum Lecture, presented at the 78th AESF Annual Convention, SUR/FIN 1991, in Toronto, Ontario, Canada on June 24, 1991.

ABSTRACT

During the past 20 to 25 years, the development of electroplating in Japan has been linked with the automotive and electronics industries. Basic research in academic institutions has led to the establishment of new plating systems in Japanese industry. New plating processes and technologies, such as alloy plating, dispersion coatings, electroless Cu, Ni, and Au plating, super-hard Cr deposits, aluminum plating and others will be discussed.

The origin of plating (Mekki) in Japan can be traced back to 757 A.D., when a statue of Buddha was treated with gold amalgam to decorate the body. (A historical survey on plating in Japan is summarized in Table 1.) The first electroplating process was introduced in southern Japan (Kyushu Island, Satsuma District) in 1855. Gold and silver plating were applied for decorative purposes, by using a Daniel cell as the electric source. The Daniel cell had been presented to Tokugawa shogunate by Admiral Perry, when he landed at Shimoda in 1854, as an American envoy sent to conduct trade negotiations between the U.S. and Japan.

As early as 1870, there were three electroplating job shops in Tokyo, and their main products were ornaments plated with silver and gold. Sometime around 1883-1884, the Bunsen battery was introduced to the plating industry in Japan. By 1880, there were 31 electroplating job shops in Tokyo; and in 1889, the number had increased to 66. In 1887, Mr. Miyagawa opened his shop in that city, also plating with silver and gold. Nickel plating became commercially available in 1892.

In 1894, a motor generator, powered by a gasoline engine, was first used to operate a nickel plating factory. Soon, more of these generators were installed in other shops, where decorative objects, such as silverware, medical instruments, bicycle parts, watch cases and jewelry were plated.

Spurred by a textbook written by William Blum and George Hogaboom in 1924, electroplating with chromium was introduced in Japan in 1925. Since that time, the number of job shops in Tokyo and Osaka dealing with chromium plating has grown steadily, where such products as knives and forks, automobile parts, and bicycles are made. Textile machines and drums were plated with so-called "hard chromium" to get wear-resistant coatings. In 1929, it was popular in Japan to use a new process, plating thin chromium on bright nickel, and two years later this process was used to make many ornamental and practical items.

In 1936, the Japan Industry Standards (JIS), similar to the ASTM guidelines in the U.S., were proposed and authorized. Since 1937, there has been strict government regulation of the importing of nickel, and its use is tightly controlled. This has prompted ongoing efforts to develop a new method of plating without nickel. In fact, direct chromium on copper was used for many products in the 1930s. Electroplating of multi-layered Ni-Cr coatings was introduced in 1947.

Table 1 - History of plating in Japan

Year	Processes
757	Au plating by amalgamation
1855	First electroplating of Au and Ag
1884	Daniel cell was brought by Perry
1892	Nickel plating was commercially available in Tokyo
1894	Motor generator operated by gas engine was used for Nickel plating
1925	First Cr plating Cd plating
1929	Thin Cr coating on Ni plating
1931	Application of Ni-Cr coatings on commercial products
1933	Bright Cd plating
1936	Japan Industry Standards (JIS)
1937	Cyanide Zn plating
1937-1940	Strict regulation of nickel usage
1945	Dull Ni, Acid Cu, Acid Zn, Hard Cr
1950	Cyanide Cu
1952	Fluosilicate Cr bath
1955	Bright Ni
1957	Leveling Ni
1960	Multi-layered Ni-Cr coatings Pyrophosphate Cu Tin Free Steel
1965	Bright acid Cu Micro-cracked or micro-porous Cr Non-cyanide Zn Plastic plating (Electroless Ni or Cu)
1966	High speed plating process Pollution control problems
1970	PWB production Low concentration baths (Cr and Ni)
1972	Dispersion coatings Non-aqueous Al plating bath
1975	Pulsed current electrolysis Solar selective black coatings
1980	Hard magnetic films (Electroless Co-P, Co-P alloys)
1981	Automatic bath analyzer and controller
1982	Zn alloy coatings for steel strips
1984	Laser enhanced metal deposition
1988	Amorphous alloy deposition

A new era dawns

Electroplating in Japan has been evolving from art to technology since 1950, when much of the latter was brought in from England and the U.S., and chemicals and equipment were imported from the U.S. and Europe. Japanese shops are eager to master new skills in the industry. In Osaka, a new organization was established to help surface finishers to master the processes and meet the varied demands from the auto industry, and the new challenges coming from the electronics field. According to the records of the Electroplaters Technical Association in Osaka, members of the group used to meet regularly, every two months, to discuss the new techniques coming from abroad.

The increased demand for plated parts from both the automobile and electronics industries has created a healthy climate in which Japanese plating shops have enjoyed growth and prosperity. Figures 1 and 2 show the production of electroplating shops in Japan between 1970 and 1988.¹

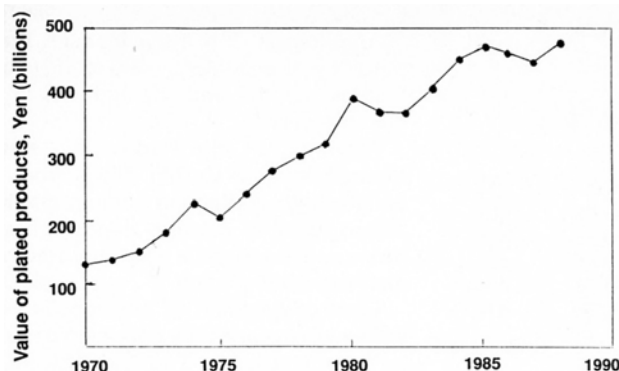


Figure 1 - Production of plated items in Japan, 1970-1988.

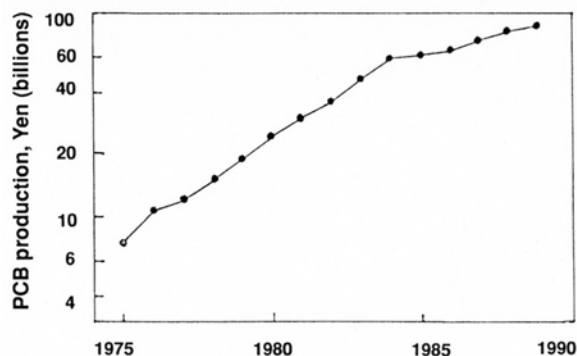


Figure 2 - PCB production in Japan, 1975-1989.

Research

Many universities and governmental institutes work on plating projects and cooperation among those organizations and private industry is on the rise. The outcome of the research often results in profitable new processes, such as alloy plating, dispersion coatings, pulse plating and electroless plating. The evolution of these processes, and their use in Japan during the last 10 years, follows.

Alloy plating

The formation of amorphous alloy deposits has received much attention in the past two to three years. The Surface Finishing Society of Japan published a special issue, *Preparation and Application Of Amorphous Plating Films*, in March 1989. Table 2 shows the commercial alloy plating available in Japan. Tin alloy coatings, such as Sn-Ni, Sn-Co and Sn-Cu-Ni have been used as final finishes for plating plastics. A Sn-Co alloy deposit has been promoted as a replacement for decorative chromium coating, with the advantage of better throwing power, covering power and color, resembling that of chromium.

Table 2 - Commercial alloy plating in Japan.

I. Decorative Coatings	
1. Cu-Zn	(Zn, 30-40%)
2. Au-Ni	(Ni, 5%)
3. Sn-Co	(Co, 20-30%)
4. Sn-Ni	(Ni, 45-50%)
5. Sn-Cu	(Cu, 30%)
6. Sn-Ni-Cu	(Sn, 70, Ni, 25.5, Cu, 4.5%)
7. Cu-Ni	(Ni, 10%)
8. Cu-Ni	(Ni, 30%)
9. Sn-Co-W	(Co+W, 20%)
II. Decorative and Corrosion Protective Coatings	
1. Ni-Fe	(Fe, 20-40%)
2. Sn-Ni	(Ni, 40-50%)
3. Sn-Cu	(Cu, 50%)
4. Cu-Zn-Sn	(Cu, 65, Zn, 30, Sn, 5%)
5. Ni-P	(P, 5%, Electrolytic)
III. Corrosion Protective Coatings	
1. Zn-Ni	(Ni, 8%)
2. Zn-Fe	(Fe, 0.2-0.8%)
3. Sn-Co	(Co, 20-30%)
4. Sn-Zn	(Zn, 30%)

Enomoto, *et al.*, conducted extensive studies on the electrodeposition of tin alloy coatings, and pyrophosphate baths were found to produce high-quality Sn-Ni, Sn-Co and Sn-Cu-Ni deposits.² The Sn-Ni alloy coating also proved to be suitable for electric contact applications.

Fracture strain and structure of Sn-Ni alloys electrodeposited from a pyrophosphate bath were studied by Izaki, *et al.*³ Dohi, *et al.*, established electrodeposition of semi-bright and bright Sn-Pb alloy deposits from a phenol sulfonate bath, and these solder coatings were found to be suitable for printed circuit board (PCB) production.⁴ Hayashi and his school performed electrodeposition of Ni-Fe alloys.⁵ The effect of an addition agent on the formation of Ni-Fe alloy deposits was analyzed by polarization measurements and by the ductility of the deposits. Nakamura, *et al.*, discussed temperature and pH effects on the anomalous codeposition of Ni-Fe alloy from a sulfate-chloride bath.

A Ni-Fe alloy deposit, containing about 11% iron, obtained from a sulfamate bath, was found to be stress-free. This type of alloy plating can be used for electroforming.⁶ Figure 3 illustrates the effect of iron content on the stress of those deposits. Furukawa and Hayashi studied the electrodeposition of bright Ni-Fe alloys, using a soluble alloy anode.⁷

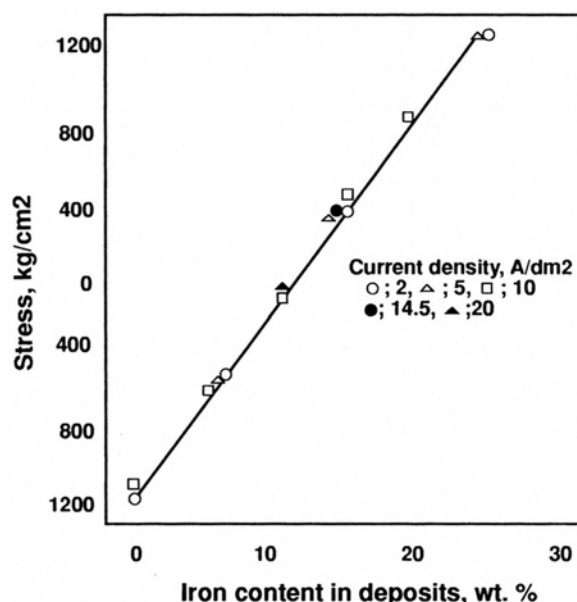


Figure 3 - Effect of iron content on internal stress of Ni-Fe alloy deposits.

By using a trivalent chromium bath, Cr-Ni, Cr-Fe and Cr-Ni-Fe alloy deposits were prepared. A Cr-Ni-Fe alloy deposit, containing 18% Cr - 8% Ni, prepared by the pulsed current method, has higher hardness and better corrosion resistance than those obtained by the DC method as shown in Table 3.⁸

Yasuda, *et al.*, investigated electrodeposition of Fe-Cr-Ni ternary alloys from a mixed solution of metal chlorides and glycine at pH 2.4.⁹

Ni-Ti alloy coatings, with approximately 20% Ti, were prepared by electrolysis of an aqueous solution containing $(\text{NH}_4)_2\text{TiF}_6$ (0.1-0.2 M), NiSO_4 (0.1 M) and glycine (0.2 M) with pH 3.5-4.5, at a current density of 1-2 A/dm² at 20°C. Deposition of titanium was confirmed to occur above -1.05 V, with an increase in hydrogen evolution. The deposition of titanium increased sharply above the limiting current of the reduction of Ti^{+3} . Ni-Ti alloy deposits obtained from the $(\text{NH}_4)_2\text{TiF}_6$ - NiSO_4 -glycine bath seemed to consist of metallic nickel and TiO_2 , with a small portion of metallic titanium.¹⁰

Pulsed current, with short on-time and longer off-time, has been applied to the electrodeposition of Au-Ni and Pd-Ni alloys.¹¹ Changes in the metal ratio of alloy deposits. Table 4 shows the effect of average current density on the grain size of Au-Ni and Pd-Ni alloy deposits, respectively.

Table 3 - i_{corr} , E_{corr} and microhardness of alloy deposits.

Plating condition C.D. (A/dm ²)	Composition of alloys (%)			I_{corr} (mA/dm ²)	E_{corr} (V vs. SCE)	Hv
	Cr	Ni	Fe			
dc 7.5	13	8	79	10.0	-0.57	452
pc i_p 20, i_a 10	13	8	79	3.2	-0.58	503
dc i_p 15	18	8	74	0.25	-0.35	440
pc i_p 100, i_a 8	18	8	74	0.17	-0.48	453
dc i_p 30	24	8	68	0.34	-0.56	404
pc i_p 100, i_a 15	24	8	68	0.05	-0.56	414

Electrolyte:
0.6 M CrCl₃, 0.05 M NiCl₂, 0.2 M FeCl₂, 1 M HCOONa,
0.5 M NH₂CH₂COOH, 0.15 M NH₄Br, 1 M NH₄Cl, 0.6 M H₃BO₃,
pH 2.8, 30°C.

Table 4 - Grain size of Au-Ni and Pd-Ni alloy deposits.

i_a A/dm ²	Grain size/ μ m			
	Au-Ni		Pd-Ni	
	dc	pc 1:49	dc	pc 1:99
0.2	1	0.3		
0.3			5	1
0.5		0.2		
1		0.2	1.5	0.3
2	0.5	0.1	0.5	0.2
3			0.2	0.1
4	0.2	0.1		

Amorphous Ni-S alloy deposits, prepared by pulse plating, were found to be suitable for the cathode material in a chlorine cell.¹²

Akiyama, *et al.*, studied the electrodeposition of Zn-Mn alloys from a sulfate bath containing sodium citrate. These types of zinc alloy deposits have been applied to steel strip, as a corrosion-resistant coating.¹³

Electrodeposition of amorphous Fe-Mo alloy films and their corrosion behavior were studied by Yao and Kowaka.¹⁴ They also studied the corrosion resistance of electrodeposited Cr-Mo.¹⁵

Dispersion coatings

Hayashi, *et al.*, have electrodeposited Ni-Al₂O₃, Ni-TiO₂ ZrO₂ dispersion coatings.¹⁶

Masuko, *et al.*, have studied the mechanism of electrodeposition of Ni-Al₂O₃ composite, by using a rotating-cylinder electrode. They analyzed the size distribution of Al₂O₃ particles in the composite coatings.¹⁷

Suzuki Motor Co. Ltd. developed the new Ni-P-SiC dispersion coatings by an electrolytic method, and these coatings have been applied to aluminum cylinders of motorcycles, outboard motors and snowmobiles. An actual machine test of the chassis of an air-cooled, two-cylinder (125 cc displacement) engine revealed that the wear of the Ni-phosphorus-SiC dispersion coatings plated on a cylinder is about 70% of that of a cast-iron cylinder.¹⁸ Omi, *et al.*, studied the mechanism of the adherence of SiC to the nickel matrix in the dispersion coating, finding that heat treatment of dispersion coatings, at 600°C, increased adherence between the metal matrix and the dispersoid.¹⁹

Uyemura & Co. Ltd. developed a process for electrodeposition of self-lubricating dispersion coatings, such as Ni-(CF)_n, Cu-(CF)_n and Ni-(PTFE), and a Ni-(CF)_n composite coating was used as the molds for plastics and metals. Ni-(PTFE) dispersion coatings were applied for soft vinyl-chloride molding.²⁰

Hiramatsu, *et al.*, studied Zn-SiO₂ dispersion coatings, using silane coupling for the dispersion coatings. These types of dispersion coatings were found to have excellent characteristics for bonding to the organic polymers.²¹

Furukawa, *et al.*, did research on the electrodeposition of zinc dispersion coatings.²² Nickel, aluminum or chloride ion in the zinc sulfate bath promoted the codeposition of particles with zinc. Incorporated fine particles, such as silicate, seemed to enhance the corrosion resistance of the zinc dispersion coatings in a 3% NaCl solution. Figure 4 illustrates the corrosion resistance of zinc dispersion coatings in a 3% NaCl solution.

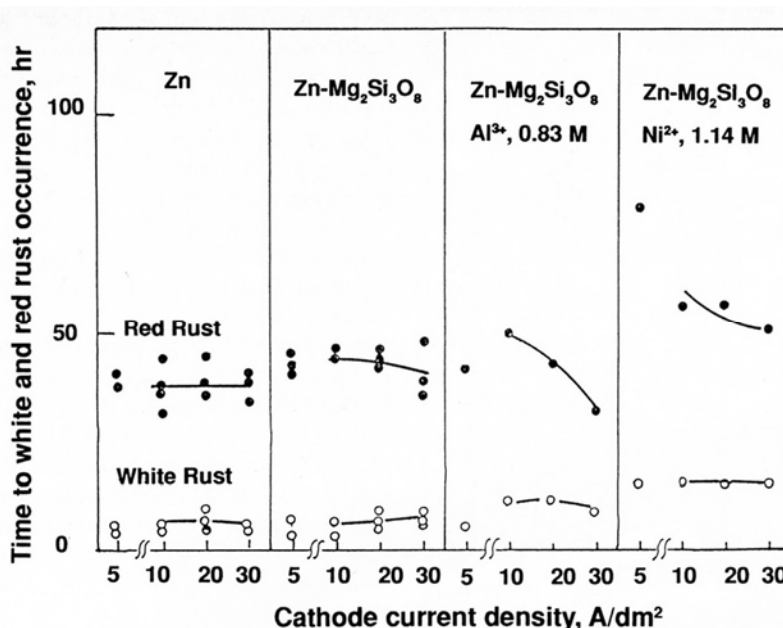


Figure 4 - Corrosion resistance of zinc dispersion coatings by immersion test in aerated 3% NaCl solution at 30°C. Coating weight, 20 g/m².

Hayashi prepared a new, colored nickel plating by using fluorescent organic pigments* (mean particle size 3.5 - 4.5 μm) as a dispersing agent.²³

As-plated nickel dispersion coatings, containing fluorescent organic pigment, have a matte surface, with a different color tone specific to the color of the pigments used. Under the irradiation with UV light in the dark, the colored nickel plate gave a strong fluorescence, derived from the organic pigments.

Furukawa, *et al.*, have used Ni-Al-Co-Al₂O₃, Ni-Co-SiC and Ni-Mn-S-SiC dispersion to develop wear-resistant coatings.²⁴

Takaya and coworkers studied the electrodeposition of Cr-SiC and Cr-diamond composite coatings from a trivalent chromium bath.²⁵ They also studied the deposition of Cr-diamond composite coatings from a hexavalent chromium bath.²⁶

Matsuoka, *et al.*, studied the electroless deposition of a Ni-B-SiC dispersion coating, to achieve corrosion resistance.²⁷

Chromium plating

Eguchi, *et al.*, developed a super-hard chromium plating.²⁸ Chromium deposits obtained from the Cr⁶⁺ + Cr³⁺ bath, containing 200 g/L CrO₃, 640 g/L H₂C₂O₄ and 75 g/L (NH₄)₂SO₄ have the hardness of 1000-1200 Hv. Carbon content in the chromium

* Sinloihi Color FZ, Dainippon Teryo-Sinloihi Co., Japan.

deposit was found to be 2 - 4 wt%, and part of the carbon codeposited formed Cr-C alloys. Upon heat treatment at 600°C, hardness of the deposit increased to give a maximum value of about 2000 Hv. However, a further increase in temperature resulted in a decrease of the hardness of the deposits. The hardness of super-hard chromium seemed to be attributable to the formation of Cr-carbide in the deposits.

Figure 5 shows the effect of heat treatment on the hardness of chromium deposits obtained from an oxalate bath and Sargent's bath.

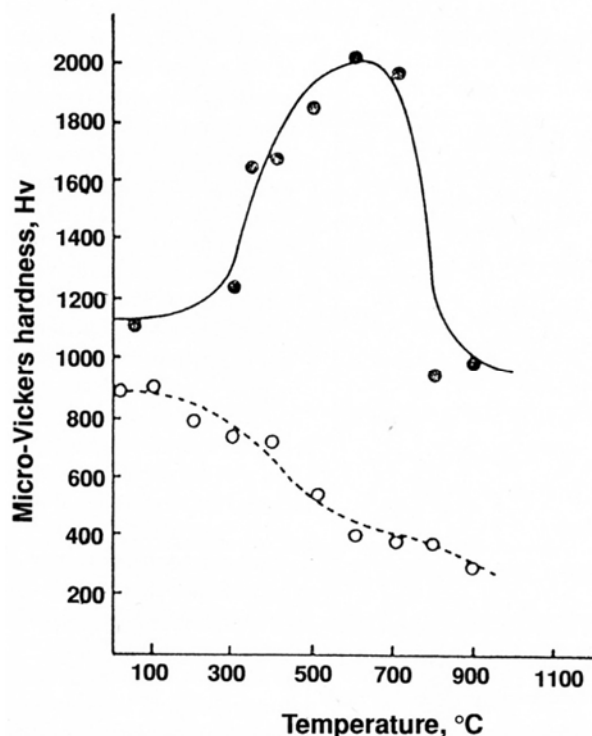


Figure 5 - Effect of heating on hardness of chromium deposits. Heating time 1 hr; Oxalic acid bath: 200 g/L CrO_3 , 640 g/L $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 75 g/L $(\text{NH}_4)_2\text{SO}_4$, current density 20 A/dm², 60°C, pH 2.0; Sargent's bath: 250 g/L CrO_3 , 2.5 g/L H_2SO_4 , current density 50 A/dm², 50°C.

Hoshino, *et al.*, also electrodeposited a super-hard chromium coating from a CrO_3 -HCOOH bath, containing 100 g/L CrO_3 , 5 g/L H_2SO_4 and 20 g/L HCOOH, at 30°C, at a current density of 10 -100 A/dm². The chromium deposits obtained have an amorphous structure and the hardness was 950-1050 Hv.²⁹

Electroless plating

In the past 20 years, a number of papers have been published on the electroless plating of copper, nickel, cobalt and Co-alloys. The technology of electroless copper plating has been focused on the development of a new, high-speed plating bath, suitable for the fully additive process in the production of PCBs.

In fully additive processes for the fabrication of the PCBs, stability of the bath, high-speed plating and ductility of the copper deposits were claimed to be essential.

Matsuoka, *et al.*, studied the effect of addition agents on the mechanical properties of copper deposits, obtained from EDTA and Quadrol baths. The ductility of the copper films obtained was evaluated (Fig. 6) by a fatigue ductility tester.³⁰ (The composition of the test bath is given in Table 5.) They also studied the role of dissolved oxygen in the electroless copper plating bath,

monitoring the concentration of the dissolved oxygen with the aid of a galvanic-cell type analyzer.³¹ It was learned that the high content of dissolved oxygen in the plating bath resulted in an induction time for copper deposition and decreased the ductility of the copper deposits.

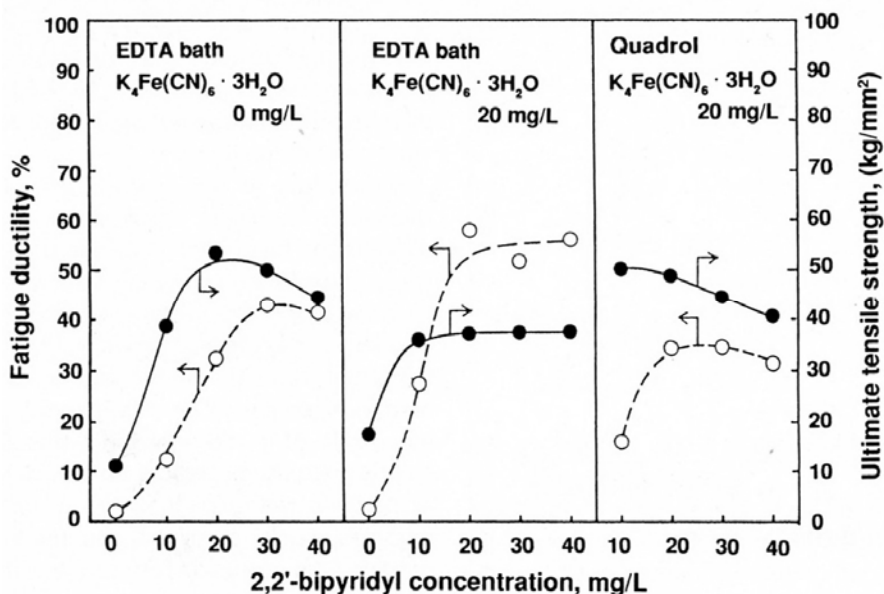


Figure 6 - Effect of additives on fatigue ductility and ultimate tensile strength.

Table 5 - Composition of electroless plating bath and plating conditions.

Composition and conditions	EDTA bath		Quadrol bath	
$CuSO_4 \cdot 5H_2O$	0.04	M	0.04	M
EDTA · 4Na	0.08	M		
Quadrol			0.08	M
NaOH	6	g/L	5	g/L
2,2'-bipyridyl	0-40	mg/L	0-40	mg/L
$K_4Fe(CN)_6 \cdot 3H_2O$	0-40	mg/L	0-40	mg/L
HCHO	0.1	M	0.1	M
Bath temp.	70	°C	70	°C

It is important to control the dissolved oxygen with optimum concentration (3 - 4 ppm), depending on the activity of the bath. Mizumoto, *et al.*, studied mechanical properties and conducted a thermal-shock test of electroless copper films deposited from an EDTA bath, containing a large amount of glycine and potassium hexacyanoferrate (II). Electroless copper obtained from that bath had high ductility, and the PCB fabricated by the fully or partly additive process (using the bath) yielded excellent reliability in the thermal-shock test, comparable to the PCB prepared by the subtractive method.³²

A new type of electroless nickel plating bath, using pyridine borane as a reducing agent has been developed by Matsuoka, *et al.*³³

Okamura, *et al.*, have studied thermal stability of the electroless Ni-Cu-P films. As the undercoat, an electroless Ni-Cu-P coating was also applied to prepare the hard disk.³⁵

The crystallization process of the electroless Ni-Mo-P alloys has been studied by thermal analysis.³⁶

Osaka, *et al.*, has researched the effect of molybdenum content on the thermal stability of the electroless Ni-Mo-P alloy films.³⁷ Factors affecting the structure of electroless Ni-Mo-B alloys have also been a subject for Osaka and associates.³⁸

Nickel- or copper-coated mica was prepared by the electroless plating method, and these products were used as a filler for EMI shielding.³⁹ Mica or non-conducting powder was treated with an alcohol or water solution, containing aminosilane, then activated with palladium chloride solution to give an adherent electroless deposit.

Takano and his school have carried out extensive studies of the electroless cobalt and Co-alloy coatings.⁴⁰ Recently, there has been much attention paid to magnetic properties of the Co-alloy deposits as a perpendicular recording medium. Starting with Co-W-P and Co-Mn-P alloy films, Osaka and his research groups developed various types of the alloy coatings, such as Co-Ni-Mn-P, Co-Mn-Re-P and Co-Ni-Re-P. They found that Co-Ni-Re-P film is most effective in perpendicular magnetic recording.⁴¹ They also studied the mechanism of initial deposition of the Co-Ni-Re-P films used for the hard disk.⁴² Matsuda, *et al.*, studied the magneto-optical properties of the electroless Co-alloy films.⁴³

Matsuoka, *et al.*, developed a new autocatalytic gold plating bath, using $\text{KAu}(\text{CN})_4$ as a main constituent and KBH_4 as a reducing agent. The deposition rate of gold increased sharply with an addition of PbCl_2 , up to 1.5 mg/L, and then decreased gradually with further increase of PbCl_2 .⁴⁴

Kubota, *et al.*, developed electroless silver plating as the undercoat of alumina ceramics.⁴⁵

Electroless tin plating, based on disproportionation from Sn^{+2} -NaOH solution, has been studied by Koyano, *et al.*⁴⁶ The same authors have tried the Sn^{+2} -KOH bath for electroless deposition of tin.⁴⁷

Galvanized steel

Many types of zinc alloy coatings have been developed for corrosion-resistant coatings of steel strip. Table 6 shows typical zinc alloy coating systems developed by steel companies in Japan.⁴⁸

Table 6 - Zinc alloy coatings for steel strips.

Alloy systems	Composition (Manufacturer*)
Zn-Co-Mo	Co 0.3%, Mo 0.1-0.5% (TKC)
Zn-Co-Cr	Co 0.3%, Cr 0.05% (NKK)
Zn-Ni	Ni 13%, (SMI, KSC, NKK, KBS)
Zn-Ni-Co	Ni 13%, Co 0.3% (NSC)
Zn-Fe	Fe 10-25% (NKK, NSC, KBS, KSC, SMI)
Zn-Al	Al 10-15% (KSC)
Zn-Mn	Mn 30-80% (NKK)

* TKC, Toyo Kohan Co., Ltd.
NKK, Nippon Kokan K.K.
SMI, Sumitomo Metal Industries, Ltd.
KSC, Kawasaki Steel Corp.
KBS, Kobe Steel, Ltd.
NSC, Shin Nippon Steel Corp.

Among the zinc alloy coatings on steel strip, Zn-Ni and Zn-Fe deposits seemed to have excellent corrosion resistance when combined with organic coatings.

Electrodeposition of aluminum

In recent years, the electrodeposition of aluminum has attracted much attention in the industry in Europe. Electrodeposition of aluminum from an $\text{AlCl}_3\text{-LiAlH}_4\text{-THF}$ bath has been studied by Yoshio, *et al.* They have developed a low-temperature, fused-salt bath, suitable for aluminum plating with high current density, using benzene as a solvent.⁴⁹

Kato, *et al.*, have developed a new aluminum plating bath, containing $\text{AlCl}_3\text{-butylpyridinium chloride}$.⁵⁰

Electrocatalysts obtained from plating processes

Electrodeposited metals and alloys can be used as the electrocatalyst in various electrode reactions. Fukumoto, *et al.*, prepared a platinum-plated tungsten electrode which can be used as an anode in the formation of peroxydisulfate.⁵¹ The same method was also applied for the formation of a platinum-plated tantalum electrode, which was used as an anode in many anodic reactions.

Another electrocatalyst prepared by Fukumoto's group is a Ni-Sn alloy deposit.⁵² Such deposits, containing 17 at% tin, electrodeposited from a pyrophosphate bath, were found to have high electrocatalytic activity in the hydrogen evolution reaction. Therefore, these Ni-Sn alloy deposits can be used as a cathode in a water electrolysis cell for the production of hydrogen. Changes in catalytic activity with heat treatment of the Ni-Sn alloy deposits revealed that the metastable Ni-Sn phase structure plays an important role in the hydrogen evolution reaction. Figure 7 shows typical polarization curves for hydrogen evolution reaction on Pt, Ni, Sn and Ni-Sn alloy deposits.

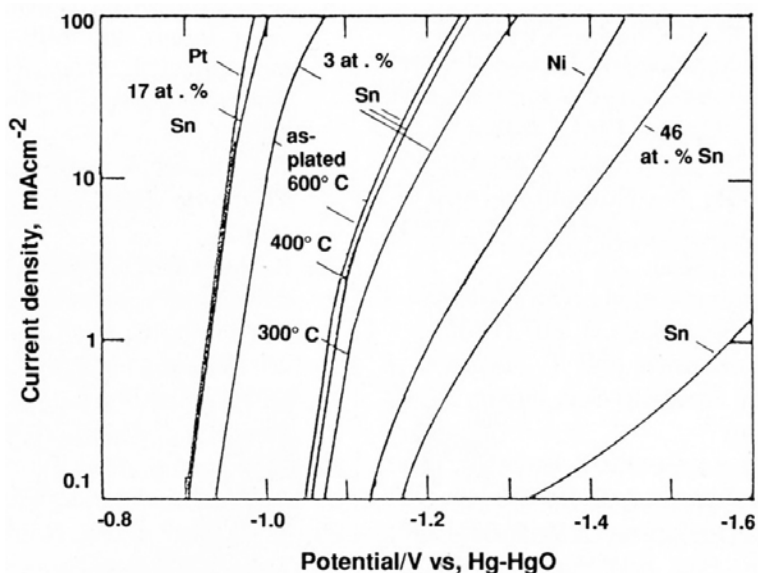


Figure 7 - Polarization curves for hydrogen evolution reaction on Pt, Ni, Sn, as-plated Ni-Sn, and heat-treated Ni-Sn alloy (3 at% Sn). The Ni-Sn alloy deposit was obtained from the following bath: 0.25M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.5M $\text{K}_4\text{P}_2\text{O}_7$, 3.6 - 16mM $\text{SnCl}_2 \cdot 2\text{H}_2$, 1M $\text{NH}_4\text{CH}_2\text{COOH}$, current density 0.5 A/dm², pH 8.0, 50°C.

Conclusion

Plating is the only method by which relatively inexpensive metals and plastics can be transformed into valuable products, with improved function and usefulness. This fact makes the plating industry fascinating, as well as important to our industrialized civilization.

Japan's somewhat slower economy, along with the fluctuation of the rate of exchange of the world's currency, has caused some difficulties for the plating industry in that country. However, cooperation among science, industry and government is expected to result in technological improvements of the many processes, restoring profitability.

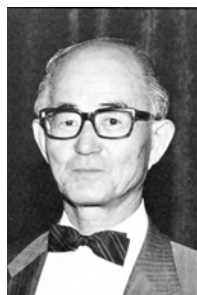
References

1. Industry Statistics; Ministry of International Trade & Industry, Japan (1990).
2. H. Enomoto, *et al.*, *J. Metal Finishing Soc. Japan*, **32**, 23, 555 (1981); **33**, 332, 341, 369 (1982).
3. M. Izaki, E. Enomoto and T. Omi, *ibid.*, **38**, 189 (1987).
4. N. Dohi, *et al.*, *ibid.*, **26**, 309 (1975); **27**, 282 (1976); **27**, 596 (1976).
5. N. Nakamura and T. Hayashi, *Met. Finish.*, **84** (5), 49 (1984); *idem*, *Bull. Univ. Osaka Pref.*, **A32** (1), 27 (1983); *idem*, *ibid.*, **A32** (2), 127 (1983); N. Nakamura and T. Hayashi, *Plating and Surf. Fin.*, **72**, 42 (Aug. 1985).
6. K. Iwahara, *et al.*, *New Materials & New Processes*, **3**, 287 (1985).
7. N. Furukawa and T. Hayashi, *J. Metal Finishing Soc. Japan*, **37**, 67 (1986).
8. A. Ishihama and T. Hayashi, *Proc. Interfinish '80*, 118 (1980); *idem*, *Bull. Univ. Osaka Pref.*, **A29** (2) 83 (1980); *idem*, *Plat. and Surf. Fin.*, **66**, 36 (Sept. 1979).
9. M. Yasuda, *et al.*, *J. Metal Finishing Soc. Japan*, **39**, 19 (1988); *idem*, *ibid.*, **39**, 70, 282 (1988).
10. Y. Fukumoto, *et al.*, *Bull. Univ. Osaka Pref.*, **A34** (2), 197 (1985).
11. Y. Fukumoto, *et al.*, *Proc. AESF 3rd International Symposium*, Washington, DC (Oct. 1986).
12. K. Yamakawa, *et al.*, *J. Metal Finishing Soc. Japan*, **38**, 285, 324 (1987).
13. T. Akiyama, *et al.*, *ibid.*, **39**, 730 (1988).
14. S. Yao and M. Kowaka, *ibid.*, **39**, 736 (1988).
15. L. Zhao, S. Yoa and M. Kowaka, *ibid.*, **39**, 772 (1988).
16. T. Hayashi, *et al.*, *Proc. Interfinish '76*, (1976); N. Furukawa and T. Hayashi, *J. Metal Finishing Soc. Japan*, **28**, 527 (1977).
17. N. Masuko and K. Mushiake, *ibid.*, **28**, 534 (1977); *idem*, *ibid.*, **29**, 646 (1978); **33**, 337 (1982).
18. S. Ishimori, *et al.*, *J. Metal Finishing Soc. Japan*, **28**, 508 (1977); S. Ishimori, *et al.*, *Proc. SUR/FIN* '84, Session O*, AESF, Orlando, FL (1984).
19. T. Omi and H. Yamamoto, *J. Metal Finishing Soc. Japan*, **34**, 416 (1983).
20. K. Naito and T. Otaka, *New Materials & New Processes*, **1**, 178 (1980); F. Yamaguchi, *et al.*, *Denki Kagaku*, **43**, 57, 106 (1975).
21. M. Hiramatsu, *et al.*, *J. Metal Finishing Soc. Japan*, **37**, 87 (1986).
22. T. Hayashi, *et al.*, *Proc. SUR/FIN* 67*, AESF, Orlando, FL (1987).
23. T. Hayashi and N. Nurukawa, *New Materials & New Processes*, **2**, 213 (1983); *Proc. 12th World Congress on Surface Finishing*, 119, Paris (Oct 1988).
24. N. Furukawa, *et al.*, *Denki Kagaku*, **51**, 171 (1983); *idem* *Proc. SUR/ FIN '84, Session Q*, AESF, Orlando, FL (1984).
25. M. Takaya, *et al.*, *J. Metal Finishing Soc. Japan*, **37**, 671 (1986).
26. M. Takaya, *et al.*, *ibid.*, **38**, 185 (1987).
27. M. Matsuoka, *et al.*, *J. Surface Finishing Soc. Japan*, **40**, 831 (1989).
28. T. Morikawa, *et al.*, *ibid.*, **42**, 95 (1991); S. Eguchi, *et al.*, *J. Metal Finishing Soc. Japan*, **33**, 272 (1982); T. Morikawa, *et al.*, *ibid.*, **37**, 341 (1986).
29. S. Hoshino, *et al.*, *J. Electrochem. Soc.*, **133**, 681 (1986).
30. M. Matsuoka and T. Hayashi, *Metal Finishing*, **85** (6), 85 (1985).
31. M. Matsuoka, *et al.*, *Kinki Chem. Soc. Japan*, **1** (4), 205 (1986).
32. S. Mizumoto, *et al.*, *J. Metal Finishing Soc. Japan*, **37**, 121 (1986); *idem*, *ibid.*, **36**, 64 (1985).
33. M. Matsuoka and T. Hayashi, *Plat. and Surf. Fin.*, **68**, 66 (July 1981).
34. Y. Okamura, *et al.*, *J. Metal Finishing Soc. Japan*, **38**, 424 (1987).
35. F. Matsui and M. Saito, *ibid.*, **38**, 446 (1987).
36. I. Koiwa, *et al.*, *ibid.*, **38**, 488 (1987).
37. T. Osaka, *et al.*, *ibid.*, **39**, 717 (1988).
38. T. Osaka, *et al.*, *ibid.*, **39**, 778 (1988).
39. T. Kambe, *et al.*, *J. Metal Finishing Soc. Japan*, **37**, (3), (iii) (1986).

40. O. Takano, *et al.*, *J. Metal Finishing Soc. Japan*, **34**, 278, 359 (1983); O. Takano and M. Matsuda, *ibid.*, **35**, 440 (1984); *idem.*, *ibid.*, **37**, 753 (1986).
41. T. Osaka and N. Kasai, *ibid.*, **32**, 309 (1981); T. Osaka, *et al.*, *Denki Kagaku*, **49**, 792 (1981); *idem.*, *ibid.*, **52**, 197 (1984); T. Osaka, *et al.*, *J. Electrochem. Soc.*, **130**, 568, 790 (1983); H. Matsubara, *et al.*, *J. Metal Finishing Soc. Japan*, **37**, 708 (1986).
42. I. Koiwa, *et al.*, *ibid.*, **38**, 434 (1987).
43. H. Matsuda, *et al.*, *ibid.*, **38**, 524 (1987).
44. M. Matsuoka, *et al.*, *Proc. 2nd Asian Metal Finishing Forum*, 121 (1985).
45. A. Kubota and N. Koura, *J. Metal Finishing Soc. Japan*, **37**, 131 (1986).
46. H. Koyano and M. Ichikawa, *ibid.*, **38**, 240 (1987).
47. H. Koyano, *et al.*, *ibid.*, **39**, 440 (1988).
48. T. Inui and T. Adaniya, *Iron & Steel*, **71**, 520 (1985).
49. N. Ishibashi and M. Yoshio, *Electrochim. Acta*, **17**, 1343 (1972); M. Yoshio, *et al.*, *Denki Kagaku*, **49**, 794 (1981).
50. Y. Kato and S. Takahashi, Japan Pat. S62-70592, S62-70593 (1987); Y. Kato, *et al.*, *Preprint 78th Technical Conference, Metal Finishing Soc. Japan*, 180 (Oct. 1988).
51. Y. Fukumoto, *et al.*, *Denki Kagaku*, **41**, 132 (1973); **43**, 258, 463 (1975).
52. Y. Fukumoto, *et al.*, *Chemistry Express*, **3** (9), 575 (1988).

About the author:

This piece was written at the time Dr. Hayashi was announced as the recipient of the 1990 Scientific Achievement Award.



One of the highlights of AESF's SUR/FIN® Conference is the announcement of the recipient of AESF's most prestigious award for scientific achievement. The award recognizes an individual who has made outstanding contributions that have raised the theory and practice of electroplating and the allied sciences, raised the quality of products or processes, and enhanced the dignity of the profession.

For 1990, that honor has been bestowed upon **Dr. Tadao Hayashi**, Professor Emeritus of Applied Chemistry, University of Osaka Prefecture, Osaka, Japan. His research interests have been concentrated in the theoretical field of electrodeposition of metals and alloys, as well as electroplating technology.

Dr. Hayashi received his B.S. in chemistry from the Tokyo Institute of Literature and Science in 1948, and was awarded his doctoral degree in engineering from the Tokyo Institute of Technology in 1961. His doctoral thesis involved the effect of addition agents on the electrodeposition of metals.

Prior to joining the University of Osaka Prefecture as a research associate in 1955, Dr. Hayashi was a research associate in the Department of Chemistry at Ohio State University for two years. He was promoted to Assistant Professor at the Prefecture in 1967 and became Professor in 1969. Upon his retirement in 1986, he was awarded the honor of Professor Emeritus.

Dr. Hayashi has been a member of the AESF since 1970, and has served as an international liaison of the Research Board since 1982. He is also a member of the Metal Finishing Society of Japan (served as vice president in 1981-1982), the Chemical Society of Japan, the Institute of Metal Finishing (England), the Electrochemical Society (USA), and the International Society of Electrochemistry. In 1980, he was chairman of the technical committee for INTER-FINISH '80, which was held in Kyoto.

Dr. Hayashi has been a president of the Electroplater's Technical Association (Japan), which is well-known for its promotion of the science and technology of electroplating.

Dr. Hayashi has published more than 130 scientific papers on electroplating and related fields and has directed more than 20 doctoral theses at the University of Osaka. He is co-editor of the book, *Properties of the Functional Platings* (Japanese) and also co-author of several other books published in Japan. In 1986, he received the Silver Medal Award from AESF for a paper published in *Plating and Surface Finishing*. In addition, he has received Outstanding Paper Awards (1966 and 1984) from the Metal Finishing Society of Japan, as well as the 1977 Gold Medal Award from the Electrochemical Society of Japan.

Dr. Hayashi's research activities have traversed a wide scope in surface finishing:

Electrodeposition of metals

Dr. Hayashi's first research (1955-1958) involved the study of the electrodeposition of aluminum from an organic solvent. He also carried out the electrodeposition of aluminum from a fused-salt bath to develop the feasible process for the preparation of aluminum-coated steel strip.

The inhibition of organic additives in the mechanism of the electrodeposition of metals is difficult to understand, because the electrode surface is always changing during the deposition of metals. It is preferable, therefore, to use a single crystal plane as a substrate for the electrodeposition of metals. Dr. Hayashi prepared the single copper crystals which have been used for the electrodeposition of copper from a copper sulfate bath in the presence of organic addition agents. Effect of addition agents in the copper deposition and also nickel deposition on the copper single crystal was evaluated by the electrochemical method and x-ray diffraction analysis.

Evaluation of brightener components

Dr. Hayashi introduced a new technique for the evaluation of the action of the brightener component in the electrodeposition of copper and nickel from acid baths by using a tracer method in which thiourea and naphthalene sulfonic acid are labeled with a radioactive ^{15}S . His results confirmed that the diffusion-controlled adsorption of these additives in the electrodeposition of copper from an acid sulfate bath was observed. In the electrodeposition of nickel from a Watts bath, the adsorption of thiourea was found to be controlled by the diffusion process, as with the deposition of copper. However, potential dependent adsorption phenomena was noticed when the concentration of thiourea was increased.

Plating with copper acid sulfate

Dr. Hayashi also proposed a new mechanism for the electrodeposition of copper from an acid sulfate bath, especially the role of the intermediate (Cu^+) in the electrode reaction. Adsorption of the polyoxyethylene-glycol, component of the brightener in the copper sulfate bath was also analyzed by the potentiostatic polarization method. Cooperative action of the small amount of chloride anion with the organic additives was found to be essential in the formation of bright deposits.

Chromium plating

As for chromium plating, Dr. Hayashi studied the mechanism of the formation of chromate film through which the metallic chromium is formed in the electrolysis of chromic acid solution containing various types of inorganic anion, such as chloride, nitrate, perchlorate and sulfate. Inclusion of sulfate anions in the chromate films was analyzed by using the tracer method in which the labeled sulfate (S-35) was added to the plating bath.

Alloy plating baths

In collaboration with Dr. Ishihama, Professor Hayashi developed a new type of Cr-Ni-Fe alloy plating bath. Based on the study of the Cr-Fe alloy deposition from trivalent chromium baths, alloys containing 18% Cr-8% Ni and a balance of Fe were obtained with 5-20 A/dm² in the formate-glycine baths with a current efficiency of ca.55% when the pH and temperature of the bath were adjusted to 2.8-3.0 and 20-30°C. The Cr-Ni-Fe alloy deposits obtained by the pulsed current electrolysis were found to have better hardness and corrosion resistance compared to those plated with DC current.

Dr. Hayashi analyzed the phenomena of anomalous codeposition of Ni-Fe alloys. The mechanical bulge-type instrument for the measurement of ductility of the deposits was constructed and the ductility of the Ni-Fe alloy deposits was evaluated. The internal stress was barely affected by the current density, and a linear relationship between the internal stress and the Fe content of the alloy was observed. Stress in the Ni-Fe alloy deposits changed from compressive to tensile with an increase in the Fe content of the alloy deposits. Stress-free Ni-Fe alloy deposit was obtained when the Fe content of the alloy was 11.0 wt% and this type of Ni-Fe coating has been applied for electroforming.

Dispersion coatings

Dr. Hayashi has consistently been a leader in research activities in Japan. In 1972 he began an extensive study on the formation of various dispersion coatings. His first paper on this subject was presented at INTERFINISH 76 (Ni-Al₂O₃, Ni-TiO₂ and Ni-ZrO₂ dispersion coatings).

Dr. Hayashi invented a new process for the preparation of a colored nickel coating by using the dispersion coating method, in which fluorescent pigment was used as a dispersoid in the electrodeposition of nickel from a Watts bath. The organic pigment used in this study was a melamine resin organic fluorescent pigment - lemon yellow, orange, green and pink. Each sample had a different color pigment as a dispersoid. Therefore, the color tone of the dispersion coating was quite specific for the color of the pigment combined with the original color of the nickel deposits. Under the irradiation by UV light, each sample had a strong fluorescence derived from the organic pigment codeposited. The colored nickel coatings containing organic fluorescent pigment prepared by the dispersion coating process have many practical uses in the preparation of fluorescent metal plates as well as decorative color coatings.

Pulse plating

In collaboration with his co-workers at the electrochemistry laboratory at the University of Osaka Prefecture, Dr. Hayashi conducted an extensive study on the pulse plating of Pd, Pd-Ni, Au-Ni, Ag, Zn and Cu. A paper published on this subject in 1986 in P&SF earned him a Silver Medal Award.

Electroless plating

Dr. Hayashi extended his research into electroless plating when Dr. Matsuoka joined his laboratory in 1974. His main interest was to develop a new electroless nickel plating bath using various reducing agents other than sodium hypophosphite. He thus conducted an extensive study on the electroless plating of Ni, Ni-Co, and Ni-Fe by using NaBH_4 and DMAB as reducing agents.

Dr. Hayashi invented a new low pH acid-type electroless nickel plating bath using a pyridine borane as a reducing agent. These results were published in P&SF in 1981.

In connection with printed circuit board production, Dr. Hayashi carried out high speed electroless copper plating using an EDTA bath. He and his co-workers explained the role of dissolved oxygen in the electroless plating of copper by using the ductility measurement of copper deposits obtained from the EDTA bath.

Another study concerned the effect of addition agents in the electroless plating of gold from a trivalent gold cyanide bath using a KBH_4 as a reducing agent. When a small amount of PbCl_2 was added to the bath, the autocatalytic reaction of $\text{Au}(\text{CN})_4$ was found to be accelerated by the adsorbed Pb on the electrode.

Corrosion resistance

Corrosion resistance of electroplated coatings is one of the important problems encountered in the practical application of multi-layered Cu-Ni-Cr coatings. Dr. Hayashi tried to evaluate the corrosion resistance of metal coatings, such as copper, nickel or chromium by using the electrochemical polarization method as well as the contact corrosion behavior in Ni-Cr electroplates. Results obtained from his study made the significant contribution to the application of these multi-layered coatings to industrial products.

Electrodeposited metals and alloys can be used as the electrocatalyst in various electrode reactions. In collaboration with Dr. Fukumoto, Dr. Hayashi established the formation of the platinum-plated tungsten electrode, which can be used as an anode for the formation of peroxydisulfate. This study has been extended to the preparation of the platinum-plated tantalum electrode, which was used as an anode in the anodic reactions.

Another example of the electro-catalyst prepared by Dr. Hayashi and his co-workers is Ni-Sn alloy deposits. Ni-Sn alloy coatings containing 17 wt% Sn electrodeposited from a pyrophosphate bath were found to have high electrocatalytic activity in the hydrogen evolution reaction. Therefore, these Ni-Sn alloy deposits can be used as a cathode material in a water electrolysis cell for the production of hydrogen. Changes in the electrocatalytic activity with a heat treatment of the Ni-Sn alloy deposits revealed that the metastable Ni-Sn phase structure plays an important role in the hydrogen evolution reaction.