The 16th William Blum Lecture
Presented at the 62nd AES Annual Convention in Toronto, Ontario, Canada
June 23, 1975

Theoretical and Practical Aspects of Alloy Plating

by

Ernst Raub
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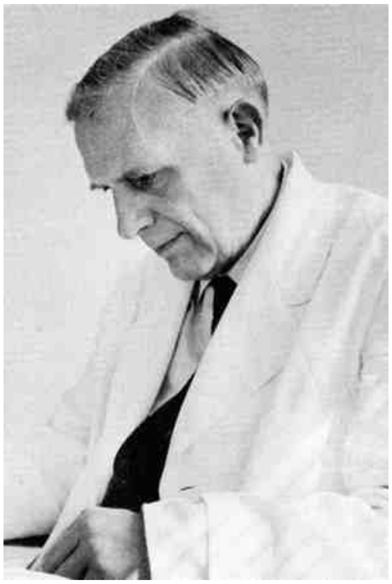

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ABSTRACT

The enormous literature on alloy plating is mostly restricted to alloys in the strict sense which contain metallic components with at least some per cent of a second metal. For practical purposes, codeposition of a second metal and also of non-metallic elements, e.g. sulfur or selenium, in small amounts is often interesting. Hydrogen as an alloying element has been known for a long time, but only incompletely investigated. The same is true for the activity of hydrogen ions in the electrolyte. The influence of electrodepositing conditions, e.g. of specific inhibition, cathodic adsorption and incorporation and of the effects of complexing agents present, is discussed. Properties of electrolytic deposits, their changes by heat treatment, and alloy formation between deposit and underlying metal or between two or more electrolytic layers are mentioned.

Introduction and background

William Blum and George B. Hogaboom[1] wrote in 1949, in the third Edition of their book *Principles of Electroplating and Electroforming* on alloy deposition, "In a strict sense every plating bath of a single metal is an alloy bath, since both metal and hydrogen may be discharged and the hydrogen may dissolve in or form compounds with the metal deposited."

In the same publication the authors mentioned the existence of an enormous amount of literature on alloy deposits. Abner Brenner[2] gives an extensive description on the *Electrodeposition of Alloys*, which comprises two volumes with 1370 pages. Therefore it is a hazardous enterprise to talk about alloy deposition in a short paper. And yet I will try to do so because the electrodeposition of alloys holds problems of general interest for electroplating, which even today are only partially cleared. Furthermore the practical importance of alloy plating has grown during recent years, especially for various new applications in modern industry.

For a long time brass and gold-alloy deposits have been employed as decorative deposits, but for some decades brass plating has also been used for technical purposes to improve bonding of rubber to steel or to enhance the deep drawing properties of steel sheet. Gold-alloy deposits are used in the modern electronic industry as tarnish resistant surface layers with low contact-resistance. Tin-lead deposits are employed to guarantee good solderability of printed circuits in electronics. For the same purpose nickel-tin deposits are applied.

They also find rising interest in other industries. Tin-lead and to a certain degree tin-indium deposits have been used for many years as linings for friction bearings. At present electrodeposited magnetic alloys, which contain as main components iron and nickel or cobalt with different additional elements, serve as memory elements in the electronics industry.[3] Electrolytic alloy plates have been used for many years as wear resistant materials. Nickel-cobalt alloys serve for the production of tools by electroforming. Other metal deposits with small amounts of alloying metals are used for bright and / or hard deposits. Some so called hard-bright silver layers contain antimony. Gold alloys with gold contents as low as possible while still yielding sufficient chemical resistance, are not only deposited in all colors for decorative purposes but also for industrial use to minimize the use of the expensive gold. For the same reason the deposition of palladium alloys, such as palladium-nickel and palladium-copper, find rising interest.

Generally in practice deposits with small amounts of a second metal or of non-metallic elements are no longer considered to be alloys, but they often have such significant properties that it is impossible to neglect them.

It may be mentioned that electrolytically produced compound materials, to which dispersion hardened deposits also belong, are only mixtures of metals and non-metallic substances with quite different properties, and therefore will not be discussed here.

Of special relevance to alloy deposits in the strict sense is the molecular inclusion of non-metallic, organic or inorganic substances. Not only is their influence on the properties of the deposited metal similar to that of a codeposited second metal, but quite often alloy deposition is connected with molecular inclusion. Therefore it is necessary to discuss it with alloy deposition.

The formation of alloys by diffusion between deposit and basis metal or double and triple layers is of practical interest. Occasionally an annealing of alloy deposits is necessary to promote diffusion and to achieve certain properties. Another class of alloy deposits, formed by autocatalytic chemical reduction without an external current source, will not be discussed in this paper.

Since up to now electrolytic deposition of alloys has been carried on for the most part in aqueous solutions, this report will be restricted to the cathodic reactions in aqueous solutions, and the properties of the deposits dependent upon the deposition conditions, including the influence of subsequent heat treatment.

During the passage of current the cathode reacts with all the substances contained in the electrolyte. Besides cathodic reduction, chemical reactions in the electrolyte and physical adsorption on the cathode surface are of importance. Often the adsorbed substances do not exist in the original electrolyte. They are formed by cathodic reduction and subsequent chemical reactions. Cathodic adsorption and inhibited crystallization were investigated by H. Fischer.[4-7] For electrodeposition of metals and alloys partial coating by physical adsorption is most important. Chemisorption or chemical reactions with the cathode surface may cause surface layers which exhibit an unfavorable influence.

The cathodic reduction reactions not only include metals and hydrogen, but also involve non-metallic elements which are present as oxides, or as sulfur, selenium or phosphorous compounds. They may be cathodically reduced to negatively charged ions, such as S^{+4} to S^{-2} ions. Since the solubility of heavy metal sulfides is small, cathodic adsorption and inclusion takes place readily. Sulfonic acids and other organic sulfur compounds used as addition agents also undergo cathodic reduction and sulfide formation. Adsorption and inclusion of non-metallics as elements or insoluble compounds, *e.g.*, heavy metal sulfides, do not necessarily presume a cathodic reduction of oxidic compounds. They take place too when soluble compounds present as addition agents chemically decompose in the electrolyte, *e.g.*, by hydrolysis, during formation of elements or negative ions.

Cathodic reduction is not limited to simple cations, but also extends to neutral molecules and anions.

Metals which exist in several valences may be reduced under proper conditions by cathodic reduction to a lower valence without metal deposition. When the bath contains a component which forms an insoluble compound with a metal ion of lower valency, this may be of decisive influence on the deposition of alloys.

For the discharge of ions, their migration in the electric field is not critical as is the transport of the dischargeable mass particles to the cathode by diffusion and convection. At sufficiently high concentrations of reducible mass particles in the cathodic diffusion layer, their reduction potentials are the controlling factor for the reactions actually taking place on the cathode surface. Concerning the discharge of metal ions one has to keep in mind that in most practical cases electrolytes are used which contain the metals to be discharged, as complex ions, quite often as anions. Normally in these electrolytes the discharge step does not result from the predominant complex, but from a lower coordinated complex, or from a totally different compound. Our knowledge of the mechanism of discharge from complex cyano ions is due largely to the work of H. Gerischer.[8,9] The discharge of zinc in cyanide electrolytes proceeds via $Zn(OH)_2$ and not via the $Zn(CN)_4^{-2}$ complex predominant in the electrolyte. In the cyanide cadmium bath the discharge of the cadmium goes via $Cd(CN)_3^-$ or $Cd(CN)_2$, dependent on the cyanide concentration of the bath as the discharge controlling step. In fact, especially in cyanide electrolytes mass particles which exist only in small amounts control the cathodic discharge. They are formed by chemical reactions of the predominant complexes. So it is possible to influence the discharge potential of a metal in an extremely wide range by changing the concentration of complexing agents in the electrolyte. The stability of the predominant complex ion in the cyanide solutions of many metals can be changed to a great extent, but differing for every metal, by merely varying the cyanide concentration of the electrolyte. The stability of the predominant complex controls the formation of the lower coordinated dischargeable complex, and thus the discharge potential of the metals. It is possible to achieve similar discharge potentials of metals, or to reverse potentials, by altering the concentration of the complexing agent.[10] In cyanide brass-plating, the zinc content of the deposits increases with increasing cyanide content of the electrolyte because the stability of the copper cyanide complex $Cu(CN)_3^{-2}$ or even $Cu(CN)_4^{-3}$ is much stronger at higher cyanide concentration. The discharge of copper in the cyanide bath is controlled by the $Cu(CN)_2^-$ complex. Its formation depends on the stability of the predominant higher coordinated complex.

Addition of sodium hydroxide to the electrolyte favors codeposition of zinc because it shifts the equilibrium,[8]

$$Zn(CN)_4^{-2} + 4OH^- \Leftrightarrow Zn(OH)_4^{-2} + 4CN^-$$

to the right, and facilitates the formation of the dischargeable $Zn(OH)_2$. Many other examples of the influence of the complexing agent concentration on alloy plating can be given, especially when several complexing agents are present.

The total quantity of the complexing agents and their ratio to the metal in the electrolyte may be much more decisive for the composition of the deposited alloys than the concentration ratio of the metals to be deposited. This is valid as long the limiting current density of one of the metals is not exceeded.

Furthermore, due to the formation of complexes with low solubility, the discharge of the more noble metal may be inhibited by cathodic adsorption, so that the codeposition of the less noble metal is facilitated.

During electrodeposition a steady state occurs at the cathode, which is controlled by several factors, *e.g.*, the ratio of the dischargeable or reducible mass particles in the cathodic double layer, their average concentration in the electrolyte, the convection and diffusion processes, the number of mass particles reduced per unit of time, and the replacement of substances included during electrodeposition.

As a rule of thumb it may be stated that under normal conditions the discharge of the most noble metal is favored, causing deposits to be richer in this metal than could be expected from its relative concentration in the electrolyte. All changes of electrolysis conditions which increase polarization, such as rising cathodic current density, decreasing temperature, unstirred electrolyte, do shift the composition of the deposit in direction to the less noble metal. All changes of the depositing conditions which diminish the polarization, such as decreasing current density, rising temperature and stirred electrolyte, increase the content of the more noble metal in the alloy. This rule is only applicable as long as the limiting current density is not surpassed. Above the limiting current density the cathodic discharge is diffusion-controlled since the concentration of dischargeable particles at the cathode surface is zero. As soon as the limiting current density for the deposition of one metal is obtained any further increase of the current density has no additional influence on the electrodeposition of this metal. If the current density is higher than the limiting current density for both metals then the ratio of the metals in the deposit will not change with increasing current density. Any current rise will only produce a third cathodic reduction reaction, *e.g.*, hydrogen evolution.

Molecular inclusion of chemical compounds

The influence of the inclusion of non-metallic substances has been investigated long ago, and has been thoroughly discussed by A. Brenner.[2] In spite of this, I want to mention the main points. The molecular inclusion of non-metallic substances may cause changes of properties which are more pronounced than those resulting from the codeposition of an alloying metal. Indeed, by inclusion the real properties of the alloy may be masked completely.

Such changes of properties are only proportional to the included substances in the lower range of inclusion. At high inclusion levels, no clear relationship upon the quantity of the included substance exists.

By molecular inclusion the hardness of copper can reach about 300 kp/mm², of silver nearly 200 kp/mm² and of iron up to 800 kp/mm².

Hard iron layers attain the hardness of chromium deposits, and their wear resistance equals that of chromium.

Table 1 shows the abrasion resistance of deposits with different hardnesses.

Table 1 - Wearing with emery powder of different electrolytic coatings (load, 50 g; path length, 1000 m).

Coating	**Vickers-hardness kp/mm^2**	**Wear mg**
Iron	512	3.9
	904	1.0
Chromium	832	3.9
	997	0.9
Bright Nickel	560	7.6
Mat Nickel	286	10.2
Nickel-Tin	565	33.6

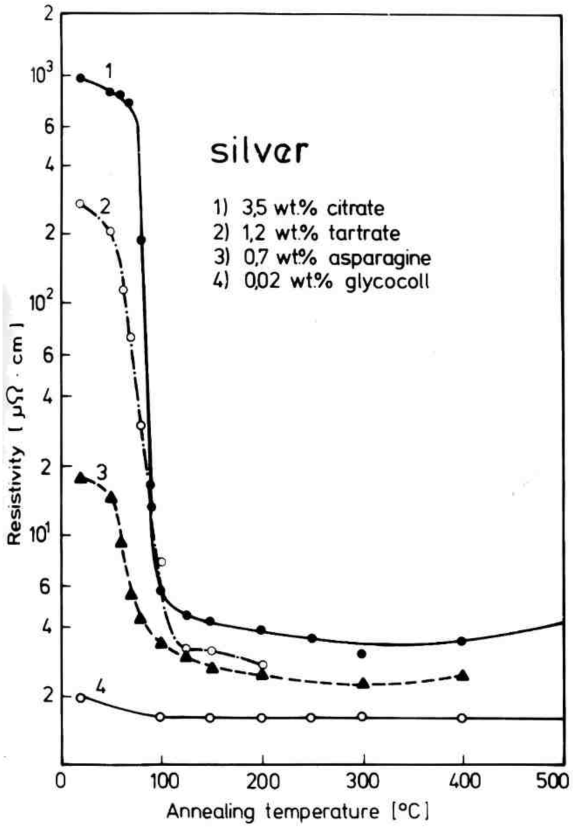


Figure 1 - Resistivity changes of silver deposits with included non-metallics during heat treatment.

As seen from the table, under the abrasive conditions used, the harder chromium and iron deposits investigated had reduced wear. At corresponding hardnesses of both metals, the abrasion resistance is nearly the same. However, the decrease of abrasion with increasing hardness is not a general rule. Quite often high hardness resulting from inclusion is associated with high embrittlement, causing a decrease in abrasion resistance as can be seen from Table I for tin-nickel alloys.

Higher inclusion rates influence the electrical resistance in a very pronounced way. Due to the formation of isolating films or filaments in the electrocrystallized metal, the resistivity may be higher by three orders of magnitude than that of the pure metal. Also the chemical properties change significantly.[11]

Heat treatment of deposits with included non-metallic substances effects characteristic changes of their properties as shown for the electrical resistivity of silver in Fig. 1. At a certain relatively low temperature (the decomposition temperature of the non-metallics) resistivity drops suddenly.[11]

Figure 2 shows the influence of non-metallic inclusions on the hardness of iron deposits and its change by heat treatment at different temperatures. The low hardness of pure iron deposits changes only very little by heat treatment. In the presence of more inclusions hardness reaches higher values. But no clearcut relationship with the amount of included substance is known. Again, during heat treatment hardness quickly decreases at a distinct temperature. In Fig. 2 the hardness curve for the iron deposit with 95.5 wt% iron shows a peak at 700°C. This iron sample contained citrate, which decomposed with the segregation of carbon. At temperatures of about 700°C the incorporation of this carbon again increases hardness.[12]

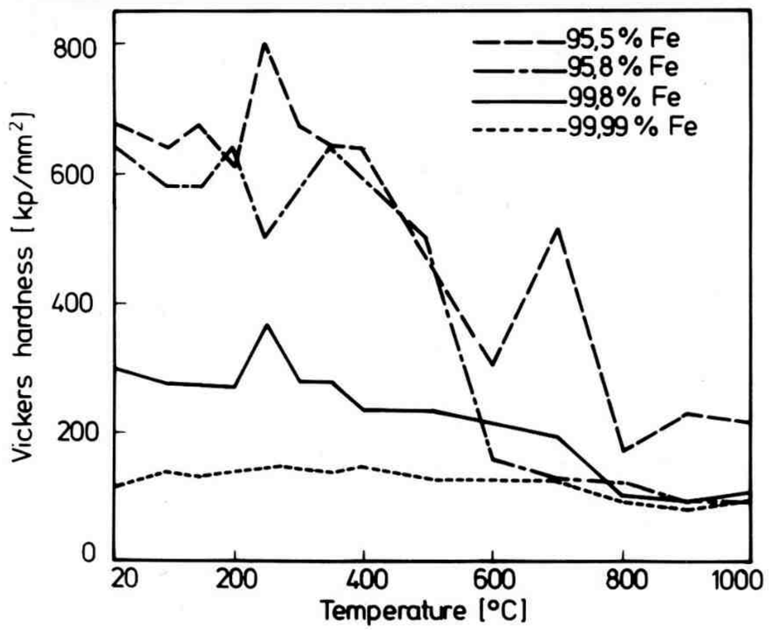


Figure 2 - Hardness changes of iron deposits during heat treatment.

Deposits with included substances have a lamellar structure, which may be coarse or very fine. Partially they show, by x-ray investigations, a characteristic fibre texture but they may also be completely disordered. The interference lines of the Debye-Scherrer diagrams are indistinct and may completely disappear at high diffraction angles. With high quantities of incorporated material the x-ray structure may approach that of the amorphous state. The classic example is the so called explosive antimony. According to x-ray studies the molecular inclusion of non-metallic substances in the metal lattice causes an extremely high amount of lattice defects, and finally only very small coherent lattice ranges exist.

Concerning their properties, electrodeposited pure metals are comparable to hard worked metal if the deposition temperature is much lower than the temperature at which lattice defects heal quickly. Electrodeposited metals with incorporated non-metallic substances are comparable to extremely age hardened supersaturated solid solutions. A difference exists insofar as, in age hardened alloys, by diffusion and agglomeration at a longer heat treatment, the normal properties of the alloy are regained. The influence of non-metallic inclusions in the lattice of an electrodeposited metal cannot be lost in this way as non-metallic compounds do not diffuse in the metal lattice. It is lost only by decomposition of the included material. The decomposition is mostly combined with gas evolution, so that the remaining metal will show gas porosity, and therefore the properties of the annealed pure metal are not completely equaled (see Fig. 1).

An age hardening effect of metal deposits with only low non-metallic inclusion, as shown in Fig. 3 for gold,[13] is caused by the greater thermal expansion of the included non-metallic substance compared to that of the metal before its decomposition. The same age hardening effect was also observed during tempering of other metals with only very low inclusion, *e.g.*, silver.[14]

The close relationship between alloy and single metal deposits with inclusion of non-metallic substances explains why under certain circumstances it is not possible to examine the influence of the alloying metal separately from that of an inclusion. It can only be discerned when incorporation remains small, and no coherent films or filaments of included substances exist. Under such conditions it is possible to investigate those properties which are only slightly structure sensitive, such as lattice constant and electrical resistance, which are controlled by the ratio of the metallic components in the electrodeposited alloys.

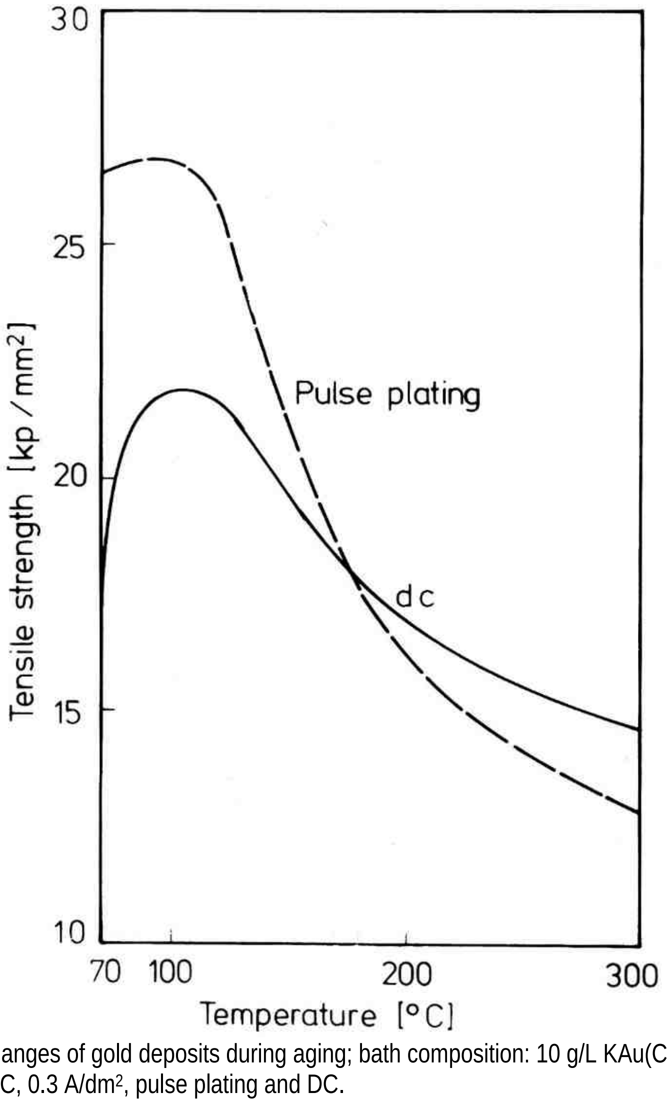


Figure 3 - Tensile strength changes of gold deposits during aging; bath composition: 10 g/L $KAu(CN)_2$, 30 g/L KH_2PO_4, 30 g/L K_2HPO_4, pH 6, 70°C, 0.3 A/dm^2, pulse plating and DC.

Hydrogen and alloy deposition, hydrolysis and abnormal alloy deposition

The co-discharge of hydrogen is in many aspects of great importance in the deposition of alloys.

In acid solutions hydrogen is discharged via protons. In alkaline electrolytes the proton concentration is very small, and the discharge of hydrogen occurs immediately by decomposition of water molecules. The earlier assumption that the first step is a discharge of alkali metal ions is now considered to be wrong.

Deposition of quite a number of metals is only possible because of the high hydrogen overvoltage on their surface. The importance of hydrogen for the deposition of alloys of metals such as tungsten and molybdenum, together with iron group metals, which cannot be deposited in the unalloyed state from aqueous solutions, was thoroughly discussed by A. Brenner.[2] The generally known discharge of sodium ions on mercury cathodes is not only due to the high hydrogen overvoltage, but is also due to the formation of a diluted sodium-mercury alloy, which equals the electrochemical properties of mercury. The hydrogen ion activity of the electrolyte is not only of interest for the amount of hydrogen codeposition, but often determines the properties of the alloy-electrolyte. In weak acid solutions the pH will rise in the cathodic diffusion layer by hydrogen discharge, and hydrolysis of metal salts may occur. The hydroxide compounds formed in this way are adsorbed on the cathode surface and influence the electrodeposition of alloys.

During metal deposition under conditions which do not lead to significant cathodic hydrogen evolution hydrolysis may occur by changes in the average pH of the electrolyte. Normally, by hydrolysis, the cathodic potential curve will be shifted to higher overvoltages. This is shown in the upper part of Fig. 4 for cadmium, a metal which electrocrystallizes from sulfate solutions with very low overvoltage. At pH values between 1 and 6, the overvoltage of cadmium changes very little. But at a pH of 7, at which hydrolysis and adsorption of $Cd(OH)_2$ on the cathode surface take place, the overvoltage is significantly higher.[15]

Zinc sulfate solutions show hydrolysis and cathodic adsorption of hydrolysis products at rather low pH values. The influence of pH on the overvoltage of zinc is much stronger and quite different from what it is for cadmium. As seen from the lower part of Fig. 4 for zinc, rising pH lowers the overvoltage. This points out that the discharge or zinc via $Zn(OH)^+$ and $Zn(OH)_2$ takes place more readily than via Zn^{+2}.

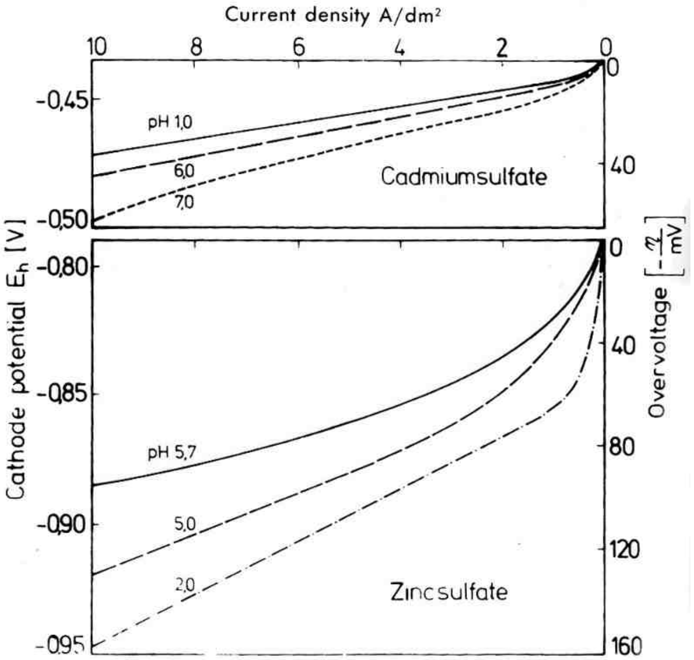


Figure 4 - Potential- and overvoltage-current density curves in 0.5M cadmium- and zinc-sulfate solution at different pH values.

In contrast the deposition of nickel is strongly inhibited by the presence of even small quantities of zinc in the electrolyte, as seen in Fig. 5.[16] By additions of zinc to the nickel electrolyte, the cathodic potential shifts to that of zinc. In pure sulfate solutions the deposition potential of zinc is, under comparable conditions, 200 to 300 mV more negative than that of nickel. The striking slope of the potential curves in the alloy baths is due to zinc hydroxide adsorption on the cathode surface.

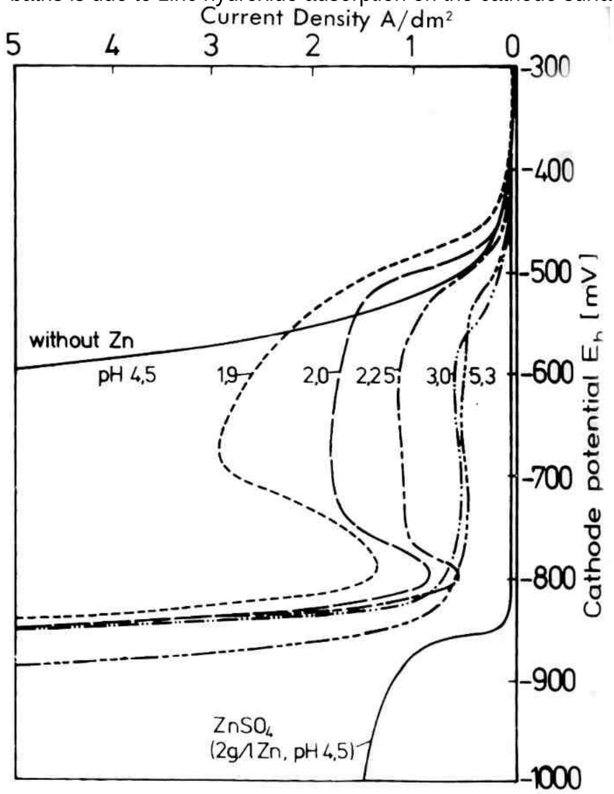


Figure 5 - Influence of 30 m mole/L Zn on the cathode potential current density curves of a Watts nickel bath at different pH values.

In a Watts bath containing zinc the electrochemical behavior of the cathode is just the same as in the presence of organic inhibitors, such as Butindiol, N-Methylphthaleneimid a.o.[17] Figure 6 shows curves for the zinc content of nickel-zinc alloys from a Watts bath with small additions of zinc. As can be seen, the zinc to nickel ratio of the deposits at lower current density is much greater than that in the solution. With rising current density it decreases very rapidly as a result of the depletion of zinc in the cathodic diffusion layer.[18] The preferred deposition of zinc compared to nickel is remarkable, because in sulfate solutions of the pure metals, nickel is the more noble metal (Fig. 5). But in a bath containing nickel and zinc, zinc assumes the behavior of the more noble metal. This is caused by the strong inhibition of the zinc hydrolysis products on nickel deposition, and their depolarization on zinc deposition. This is an example of the so-called abnormal electrodeposition of alloys which is characterized by preferred deposition of the less noble metal.

Cobalt and iron deposition is also strongly inhibited by zinc hydroxide so that abnormal alloy deposition can be observed.[19]

The importance of pH for brass plating has been discussed. Other examples are acid gold plating baths which contain gold as $Au(CN)_2^-$. The pH value of these baths must be kept in relatively close limits. If the pH is too low the cyanoaurate complex decomposes and gold cyanide segregation begins. If the pH is too high, alloying metals may segregate as insoluble compounds; for instance as ternary phosphates. On the other hand, the stability of the complexes may be raised so much at a higher pH that they are no longer discharged with the gold; *e.g.*, in the presence of EDTA. The pH value is of special importance to the stability of the sulfite gold alloy baths.[20]

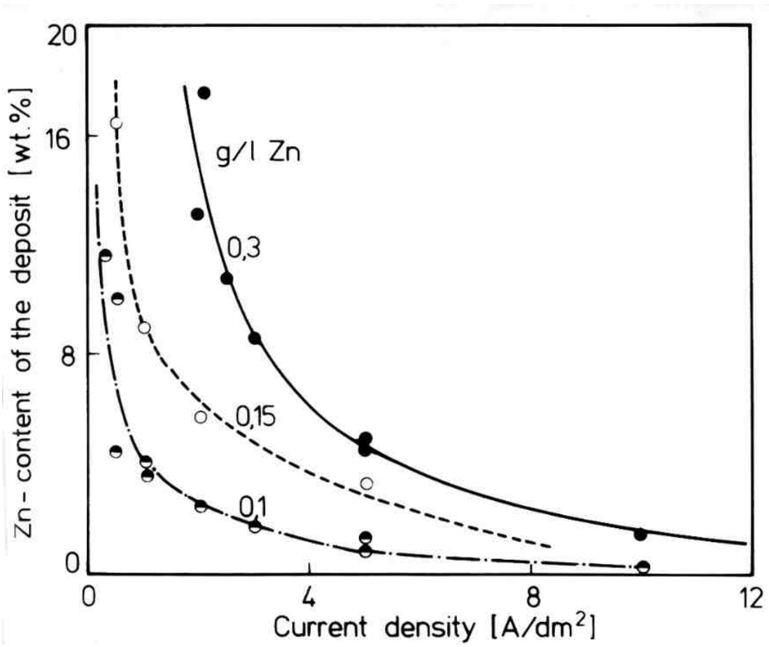


Figure 6 - Zinc content of nickel deposits from a Watts bath with 1 g/L p-toluol sulfonamide and small additions of zinc at 50°C and stirred electrolyte.

Sulfur and selenium in alloy deposits

Up to the present time solid solutions of sulfur in metals during electroplating have not been conclusively proven. Iron deposits with higher sulfur contents have some lattice changes which indicate a certain solubility of sulfur in electrodeposited iron.[21] The influence of sulfur on the properties of the metal deposits is equal to that in melted or sintered alloys of corresponding composition.

In general, sulfate is not cathodically reduced under normal electroplating conditions. In alkaline plating solutions also sulfite cannot be reduced. Figure 7 shows the strong influence of current density on the sulfur content of nickel deposits from electrolytes with additions of sodium hydrogen sulfite (left) and aromatic sodium sulfonic acids (right). In the presence of sodium hydrogen sulfite, the sulfide contents of the deposits are much higher than in the presence of aromatic sulfonates. In the latter the sulfite ion is formed at first by cathodic reduction from the aromatic sulfonate. This sulfite is then reduced to sulfide, and cathodic adsorption and inclusion of nickel sulfide take place.[22,23] The inclusion of nickel sulfide is diffusion controlled. Sulfur and sulfide contribute to depolarization in the deposition of nickel. In plating practice aromatic sulfonates and related compounds are generally used as stress reducers in bright nickel baths, a disadvantage being the lower corrosion resistance of these deposits. Potentiostatic anodic potential current density curves in 0.1N sulfuric acid (Fig. 8) show that nickel deposits produced in electrolytes with sulfur-free addition agents have only a very narrow current density range in which active solubility appears. Sulfur-containing nickel deposits are actively dissolved over a wide range of current density, and show no real passivity. Figure 9 shows that between sulfur-free and sulfur-containing nickel in weakly acid sodium chloride solution, a galvanic element is formed in which the sulfur-free nickel is about 200 mV more noble than sulfur-containing nickel. Sulfur-free addition agents have no significant influence on the potential of nickel deposits. Sulfur-containing nickel is more susceptible to contact corrosion than sulfur-free nickel, which must be remembered for practical applications. The poorer corrosion resistance of sulfur-containing nickel is due to the fact that sulfide prevents passivation by formation of nickel sulfide on the corroding surface. Therefore the difference in the corrosion resistance of sulfur-containing and sulfur-free nickel is only existent in corrosion media free from sulfurous acid. In the presence of sulfurous acid, nickel sulfide forms on the surface of sulfur free nickel deposits according to the reaction:

$$4\,SO_3^{-2} \Leftrightarrow 3SO_4^{-2} + S^{-2}.$$

Therefore a difference in corrosion mechanism can no longer be observed.[24,25]

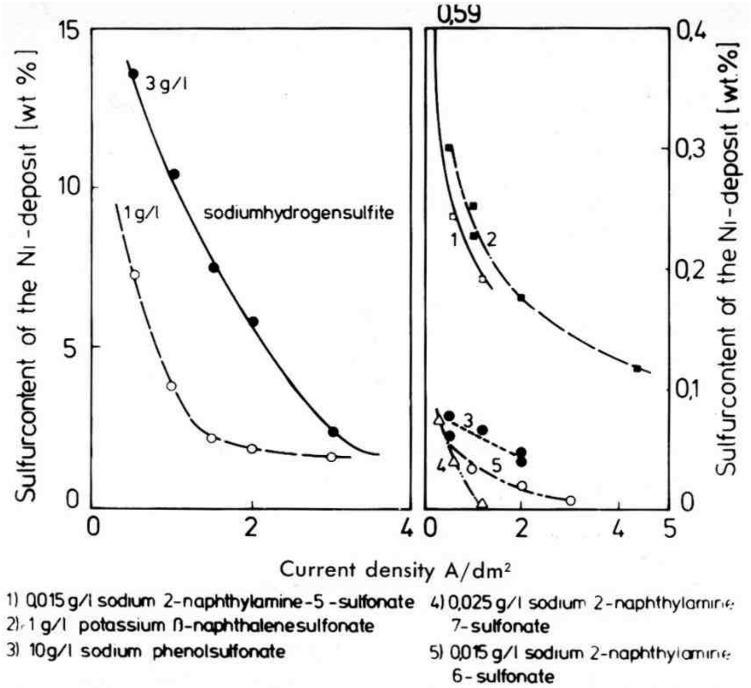


Figure 7 - Sulfur content of nickel deposits from nickel baths with additions of sodium hydrogen sulfite or aromatic sulfur compounds.

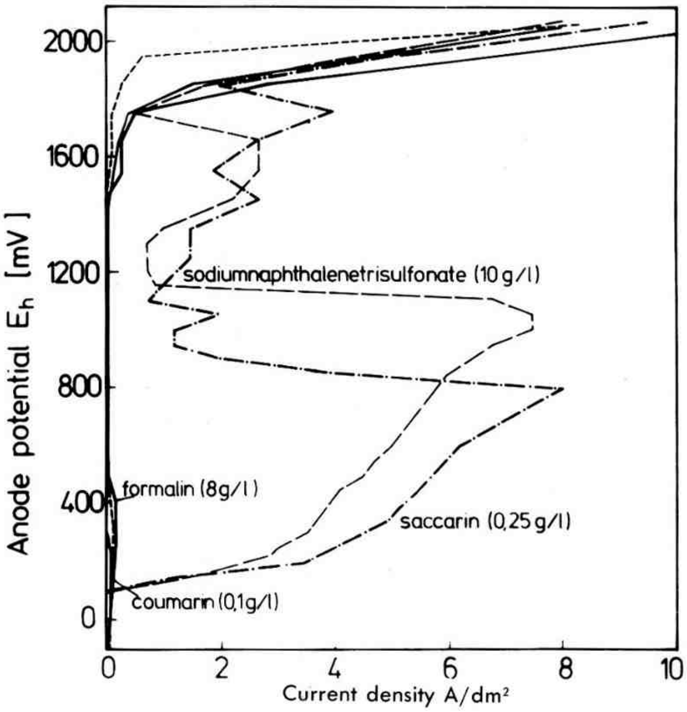


Figure 8 - Potentiostatic anode potential current density curves of electrolytic nickel from a Watts bath with different addition agents.

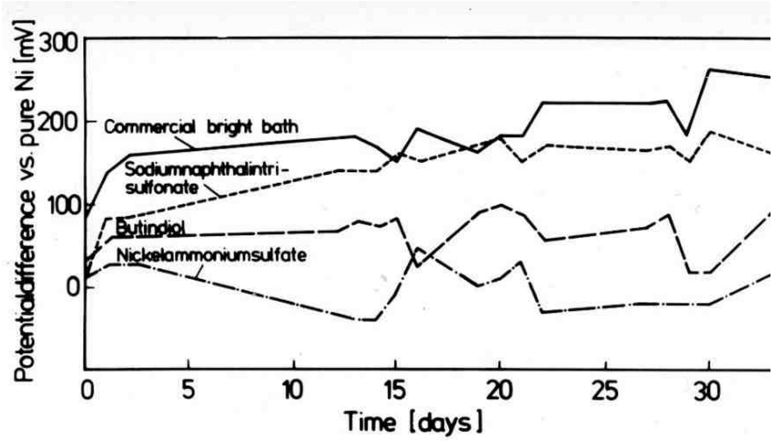


Figure 9 - Potential difference between pure electrolytic nickel and nickel from baths with different addition agents in 3% sodium chloride solution with a pH of 3 at room temperature.

In baths where the sulfite ions are not cathodically reduced, the effect of sulfur or sulfide may be achieved by addition of a soluble sulfur compound. From this a metal sulfide or elementary sulfur may be formed by a chemical reaction. Substances of this kind are thiourea and thiosulfate.[26-28]

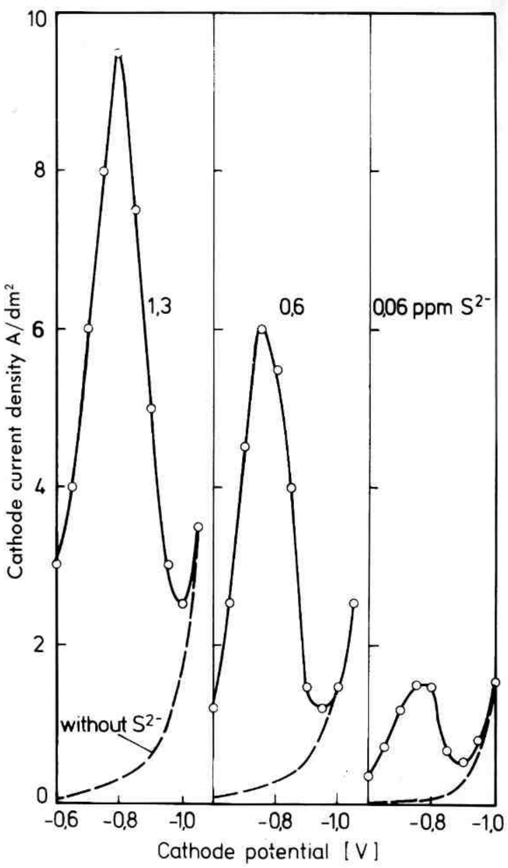


Figure 10 - Potentiostatic potential-current density curves in a cyanide silver electrolyte with and without additions of S^{-2} ions. Electrolyte composition 200 g/L KCN and 80 g/L Ag as $KAg(CN)_2$.

The interesting influence of very small amounts of S^{-2} ions on silver deposition from the cyanide bath may be discussed here.[29] Figure 10 shows potentiostatic cathode potential curves for an electrolyte with 80 g/L Ag and 200 g/L free KCN under nitrogen. As cathode, a silver sheet was used. At as low a concentration as 0.06 ppm S^{-2} a discontinuous increase in current density is observed between -0.6 and -0.8 V. Above -0.9 V the potential current density curves for the S^{-2}-free and the S^{-2}-containing electrolyte are equal. The influence of the S^{-2} concentration in the electrolyte is also shown in Fig. 10. This behavior can be used to determine very small S^{-2} quantities between 2 and 0.01 ppm. The influence of such small sulfur amounts on the cathodic potential curve in cyanide silver solutions is caused by the extremely low solubility of silver sulfide. As a consequence the reaction,

$$2Ag(CN)_2^- + S^{-2} \Leftrightarrow Ag_2S + 4CN^-$$

takes place.

The silver sulfide is adsorbed on the cathode surface and is included by the crystallizing silver. It depolarizes the discharge of silver. Its influence on the slope of the cathode potential curve lasts until all S^{-2} present is included as silver sulfide by the crystallizing silver.

To a certain extent, selenium shows an influence similar to sulfur, but the selenate and selenite ions are much more easily reduced than the corresponding sulfur compounds. Selenous-and selenic acids are chemically reduced in acid solutions by most metals under formation of elemental selenium. In general, soluble selenides decompose under segregation of selenium. Cathodic reduction of selenates also occurs in acid solutions. In alkaline electrolytes investigated, cathodic reduction of selenates was observed only in the cyanide copper bath. Selenites are electrolytically reduced in acid and some alkaline baths.[30,31] The codeposition of selenium in acid solutions is diffusion controlled.

The selenite ion is simultaneously reduced in the alkaline cyanide gold electrolyte, but not in the cyanide silver bath. Therefore the properties of silver, such as its brightness, are not improved by addition of selenium dioxide. To influence silver deposition, it is necessary to use selenide compounds which chemically decompose in the electrolyte, *e.g.*, selenocyanate or selenourea.

As seen from the pulse rates of gold deposits from a gold bath with additions of doped selenium dioxide (Fig. 11) the codeposition of selenium is small and drops relatively quickly with increasing current density. Over 0.3 A/dm² it is nearly independent of the current density. When selenium dioxide is used as brightener for gold baths it is to be noted that oxidation of the selenite to the selenate ion on insoluble anodes must be prevented.

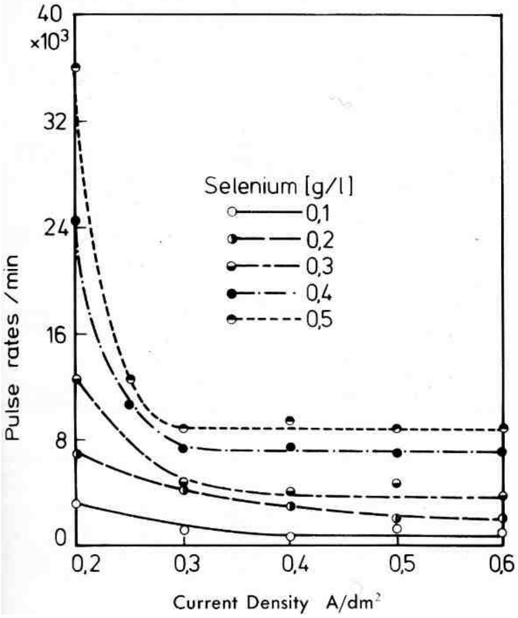
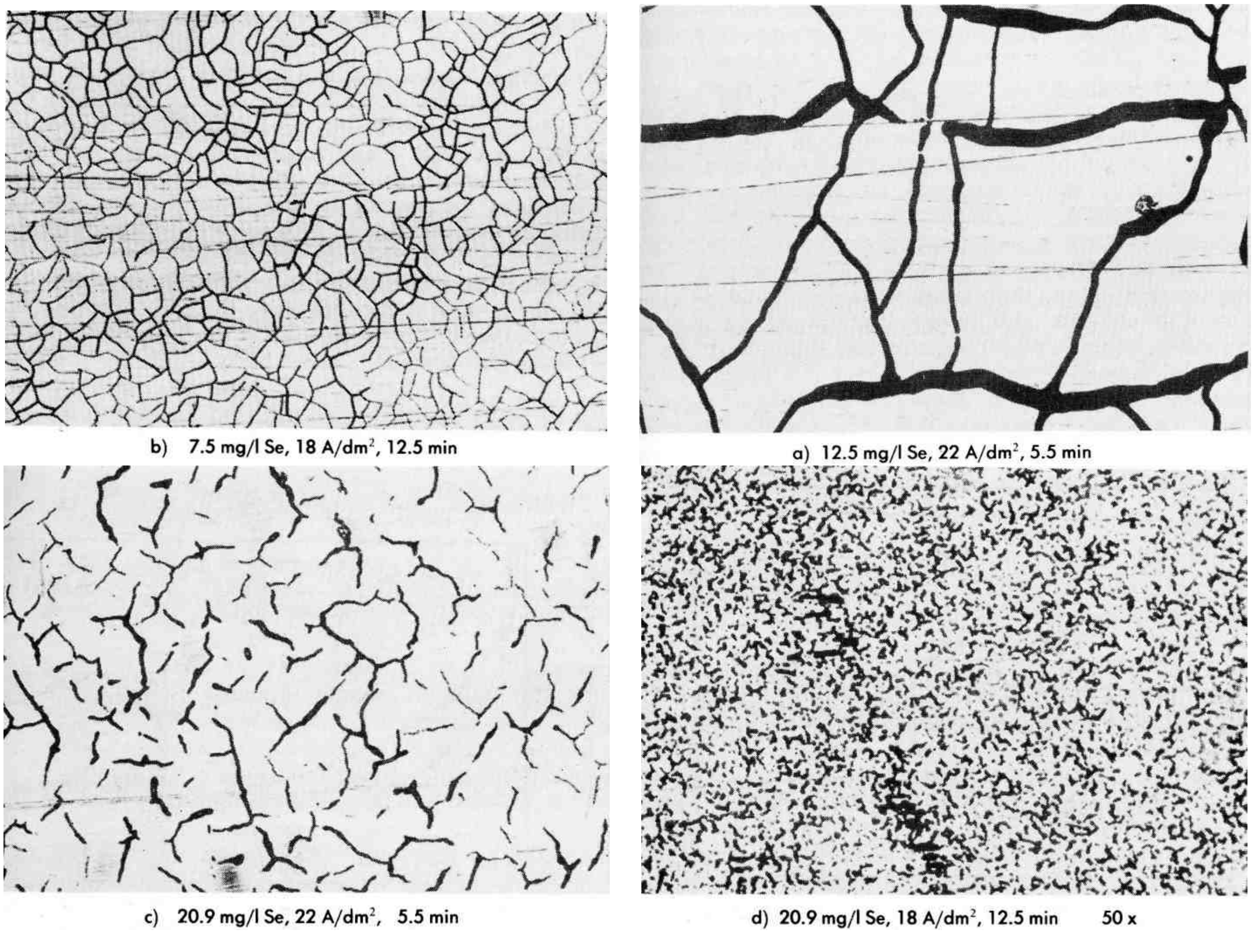


Figure 11 - Pulse rates of gold deposits from a stirred bath with 2 g/L Au as $KAu(CN)_2$ and 4 g/L KCN with additions of sodium selenite doped with ^{75}Se (bath temperature 55°C).

In the chromium bath selenic acid is stable, and is reduced simultaneously with chromium. Selenite in the chromium plating bath is slowly oxidized to selenate. As long as selenous acid is present it is impossible to get reproducible results.

Selenic acid cannot be used in place of sulfuric acid as a catalyst for chromium deposition; it is reduced preferentially with formation of grey amorphous selenium. The codeposition of selenium in the chromium plating solution is controlled by the penetration polarization. From Fig. 12, it can be seen that by codeposition of selenium, macro- and microcracked as well as microporous chromium may be deposited.



b) 7.5 mg/l Se, 18 A/dm², 12.5 min

a) 12.5 mg/l Se, 22 A/dm², 5.5 min

c) 20.9 mg/l Se, 22 A/dm², 5.5 min

d) 20.9 mg/l Se, 18 A/dm², 12.5 min 50 x

Figure 12 - Influence of selenium on the surface structure of chromium deposits (electrolyte: 250 g/L CrO_3; 2.5 g/L H_2SO_4; 44°C.

Alloy deposition from simple cations

In a few cases, deposition potentials are so close together that simultaneous discharge of two or more metals can be achieved from simple ions without difficulties. It is possible for the deposition of iron, nickel and cobalt alloys. The same is true for tin-lead alloys. Figure 13 shows a 50 mV difference between pure tin versus pure lead and only 2 or 3 mV between different alloy compositions.[32] Table 2 shows that in alloy plating the deposition of lead is favored over tin. This is in agreement with the slope of the cathodic potential curves in solutions of the single metals. The behavior during the simultaneous discharge of lead and tin in fluoborate solution corresponds to the values of the standard potentials, Pb/Pb^{+2} = -0.126 V and Sn/Sn^{+2} = -0.140 V. This is one of the few cases in which the standard potential of two metals permits a prediction of the deposition of alloys. A prerequisite for this is that the controlling step is the discharge of metals from simple, and not from complex ions. Furthermore it is necessary that the deposition polarization in the electrolyte employed is nearly equal for both metals.

Table 2 – Lead-tin deposition characteristics.

Bath Composition				Current density	Sn-content of the deposits wt per cent
Lead g/l	Normality	Tin g/l	Normality	A/dm^2	
154	0.74	17	0.14	0.5	0.15
				1.5	0.35
				3.0	0.83
				5.0	1.28
68	0.33	68	0.57	0.5	3.32
				1.5	14.52
				3.0	21.48
				5.0	29.91

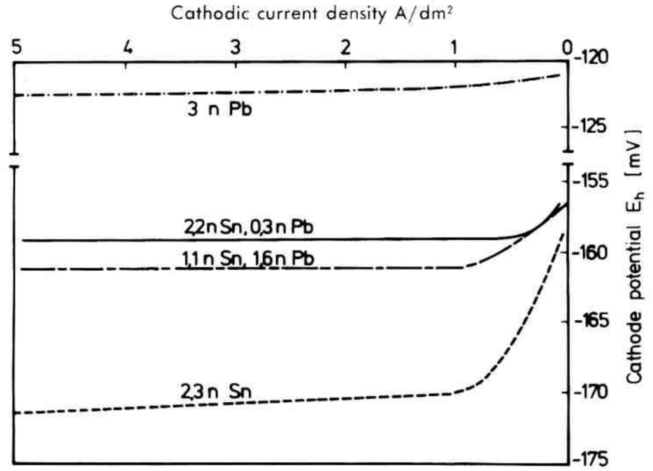


Figure 13 - Cathode potential-current density curves of lead and tin in fluoborate solutions.

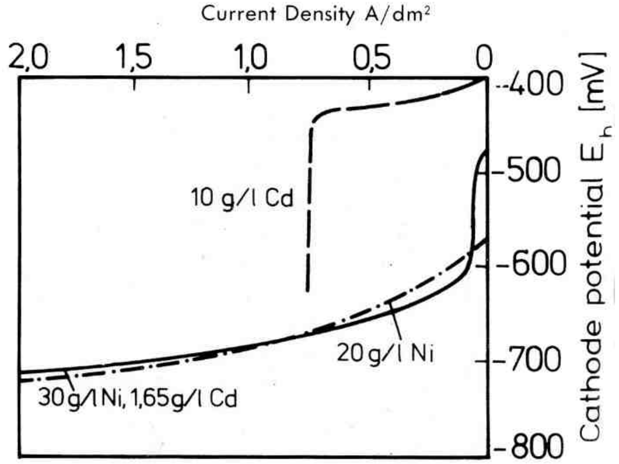


Figure 14 - Cathode potential-current density curves in quiescent cadmium and nickel sulfate solutions at 20°C.

In this aspect codeposition of cadmium and nickel is interesting. Standard potential of Ni/Ni^{+2} is -0.23 V and of Cd/Cd^{+2} -0.402 V. Therefore one might assume that during simultaneous discharge nickel is favored. This is wrong. As already discussed, cadmium is discharged in sulfate solutions with very low and nickel with very high polarization. This causes cadmium to be discharged in sulfate solutions at a potential 0.2 to 0.3 V more noble than nickel,[33] which explains why cadmium behaves more noble than nickel (Fig. 14). The limiting current density of cadmium is reached in an electrolyte with 2.5 g/L Cd at about 0.7 A/dm². In a nickel electrolyte with 30 g/L Ni and 1.65 g/L Cd, the deposition potential of cadmium turns to more negative values but it is still very significantly more noble than nickel. Figure 15 gives the composition of cadmium-nickel alloy deposits from baths with varying cadmium concentrations as a function of the current density. At low current density (dependent on the cadmium concentration) only cadmium is deposited. At current densities higher than the limiting current density of cadmium, codeposition of nickel begins. This different behavior of cadmium and nickel ions during the cathodic discharge makes possible a quantitative electrolytic separation of the two metals by operating at current densities below the limiting current density of cadmium. The mechanism of the preferred deposition of zinc in zinc-containing nickel baths is quite different from that of cadmium-containing solutions and has already been discussed. In sulfate solutions cadmium behaves as a more noble metal because of its very low overvoltage during discharge compared to nickel with its high penetration polarization.

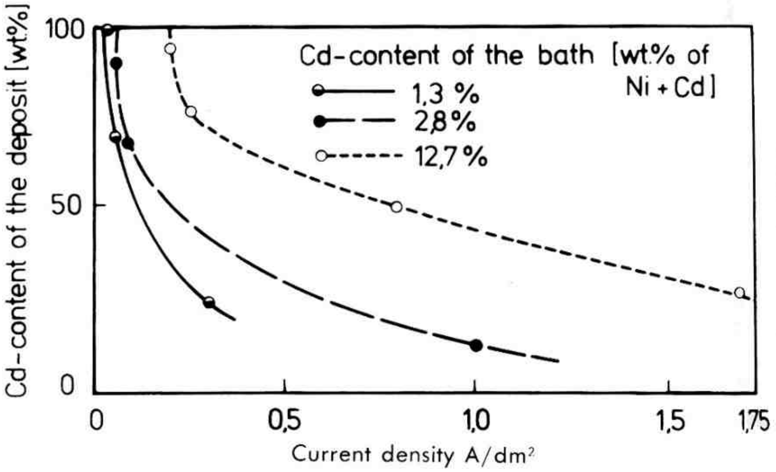


Figure 15 - Cadmium content of cadmium-nickel alloy deposits from sulfate solutions at different cadmium contents of the electrolyte.

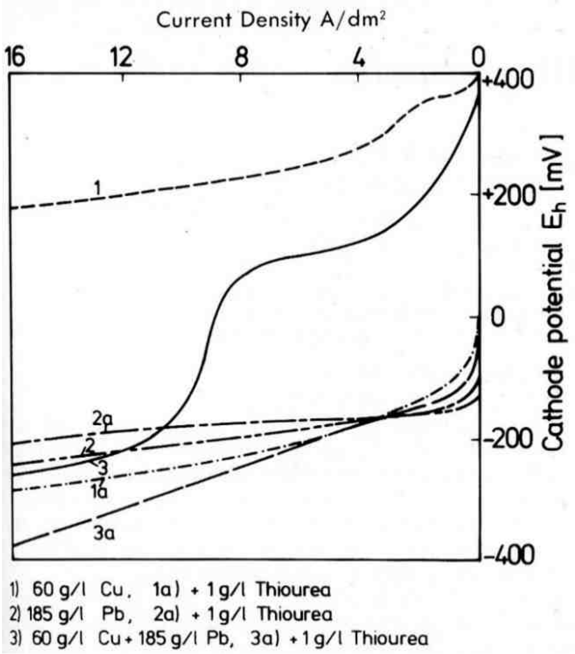


Figure 16 - Cathode potential-current density curves of copper and lead in acid perchlorate solutions with and without thiourea, at 25°C and quiescent electrolyte.

Specific inhibition and alloy plating

The inhibition of nickel, cobalt and iron by zinc hydroxide is one case of specific inhibition. In other alloy plating baths specific inhibition may be achieved by addition agents which form a complex of low solubility with the more noble metal, and thereby inhibit its discharge by cathodic adsorption. The behavior of thiourea in acid copper solutions may be discussed here.[27,34-37] Thiourea is oxidized by Cu^{+2} to dithioformamidine with formation of copper(I) ions and hydrogen. Under proper experimental conditions, separation of an insoluble copper(I) thiourea complex can be observed. This complex, a strong inhibitor for copper deposition, is adsorbed on the cathode surface and incorporated. The preceding chemical reduction of copper with thiourea is not just assumed. During passage of current in an acid copper electrolyte, besides metal deposition, small quantities of Cu^{+} ions are formed. These react immediately on the cathode with thiourea and the formation of the complex. This reaction is of interest, *e.g.*, in the codeposition of lead and copper from acid solutions. In Fig. 16, cathode potential-current density curves in a perchloric acid solution[21] are given. The deposition potential of copper is about 0.4 V more noble than that of lead, and in the mixed solution only copper is deposited as long as its limiting current density is not exceeded. But when only 1 g/L thiourea is added to the electrolyte, the potential curve of copper is shifted by about 0.45 V to more negative values, whereas the lead potential remains unchanged. From the thiourea-containing electrolyte, lead is codeposited with copper at the lowest current densities. In this electrolyte, lead still shows the properties of the less noble metal. The lead-to-copper ratio in the deposits is lower than that in the bath. It rises with the current density, a characteristic of less noble metals. To summarize, the influence of thiourea on copper deposition in acid solutions is not that of a normal complexing agent, but of an inhibitor by cathodic adsorption, and therefore its influence can be observed at small concentrations in the electrolyte.

Alloy deposits from complex compounds

As an example, cyanide complexes are widely used in commercial practice to approach deposition potentials of the metals to be simultaneously deposited. The classical example, copper-zinc, has already been mentioned.

Stability of cyanide complexes differs strongly and the complex from which discharge occurs changes with metal-to-cyanide ratio of the electrolyte.

The deposition potentials in cyanide solutions are not always close enough together to permit the codeposition desired. Simultaneous deposition of zinc and cadmium happens equally in acid sulfate and alkaline cyanide solutions.[38] In Fig. 17 the potential curves in the acid and in the alkaline cyanide bath are shown. They are nearly 0.4 V apart, and codeposition of zinc with cadmium occurs only when the limiting current density of cadmium is exceeded. In the cyanide alloy bath at higher current densities a second limiting current density is observed which relates to the deposition of zinc. As in the acid bath, in the alkaline cyanide bath also, zinc deposition does not take place until the limiting current density for cadmium is exceeded. The often described simple method to transform a cadmium electrolyte into a zinc electrolyte just by substituting cadmium anodes for zinc anodes relies on the preferred cathodic discharge of cadmium and the anodic dissolution of zinc. Using this method one has to keep in mind that at current densities above the limiting current density for cadmium separate crystallization of both metals easily leads to the deposition of alloys with insufficient properties. It is better to work during the conversion of a cadmium into zinc bath at current densities below the limiting current density of cadmium.

In cyanide solutions silver behaves as the most noble metal. Gold dipped into a cyanide silver plating bath dissolves without application of external current, and silver is deposited onto gold by electron exchange. Under normal conditions of practical silver electroplating, metals which form stable cyanide complexes are not discharged simultaneously with the silver. Gold and mercury are exceptions. In cyanide solutions gold is codeposited with silver at low current densities. If traces of sulfide ions are present, no codeposition of gold with silver will occur as long as the depolarization of the sulfide ion on silver is effective. As soon as the incorporation of the sulfide ion as silver sulfide in the silver deposit is complete and the cathodic potential has reached that of the sulfide free electrolyte, codeposition of gold begins as normal.

For the simultaneous deposition of other metals with silver from cyanide solutions it is of importance that the deposition potential of silver depends to a high degree on the molar ratio of silver to cyanide. At high cyanide concentration the predominant complex ion is $Ag(CN)_3^{-2}$; discharge of silver goes over to $Ag(CN)_2^{-}$ as the discharge determining step at a relative high potential. At lower cyanide concentration the normal $Ag(CN)_2^{-}$ exists, and the discharge of silver AgCN is decisive.[9]

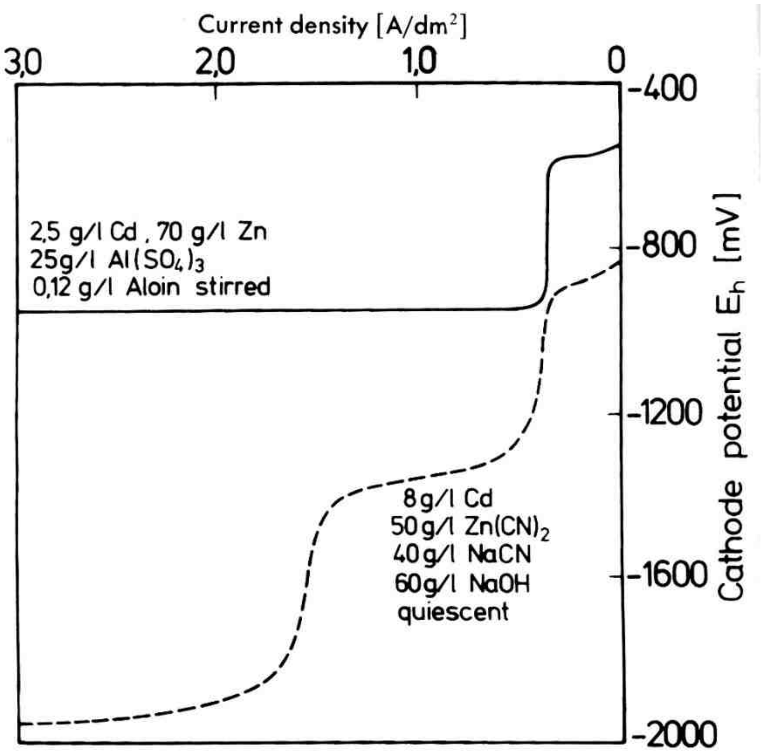


Figure 17 - Cathode potential-current density curves in quiescent acid and cyanide cadmium-zinc electrolytes at 20°C.

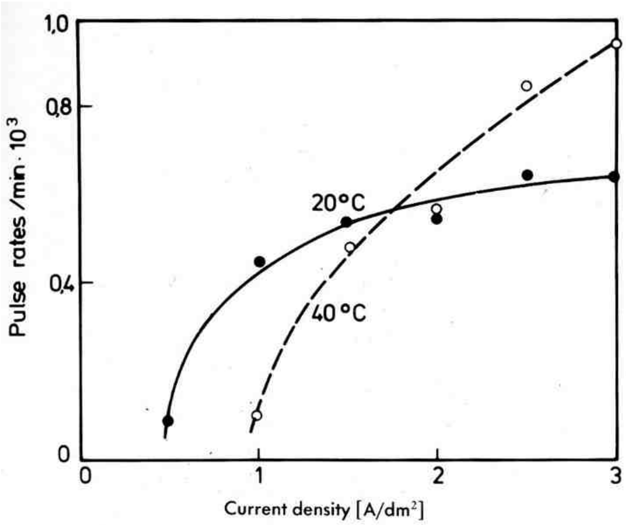


Figure 18 - Impulse rates of silver deposits from a cyanide electrolyte with 5 g/L Ag and 30 g/L Ni doped with ^{63}Ni.

Also under extreme conditions codeposition of less noble metals, which form stable cyanide complexes, such as iron, nickel and cobalt, is practically impossible.

This is shown in Fig. 18 for an electrolyte containing 5 g/L silver, 30 g/L nickel as cyanide complexes and 80 g/L free potassium cyanide.[39] Only at relatively high current densities can a very small amount of nickel be detected in the deposit by radioactive tracer method. It is not certain whether this nickel is really discharged or if it only results from electrolyte occluded by the rough surface of the silver deposited.

In electroplating practice nickel was used erroneously for a long time as a hardener for silver deposits. (It was proved that additions of nickel to the silver plating bath have no influence on the hardness of the deposits). But any codeposition of nickel must be excluded from consideration under normal conditions. Also, codeposition of copper and silver in a cyanide bath is possible only under extreme conditions, since the copper cyanide complex is much more stable than that of silver. In addition the influence of the cyanide concentration on copper is stronger than on silver. Therefore it is impossible to achieve codeposition of copper and silver at high cyanide concentration.

Zinc, cadmium and indium were repeatedly proposed as alloying metals for silver deposits to obtain tarnish resistant silver. Apart from the fact that these metals indeed prevent reaction of silver with sulfur, and thus tarnishing, they cause discoloring by the formation of oxide in a humid atmosphere. In cyanide alloy plating baths it is difficult to control deposition closely enough to get deposits with reproducible properties. It is possible to obtain deposits with zinc or cadmium content[40] as shown in Fig. 19 for silver-zinc. The zinc content of the deposits rises very quickly when the limiting current density of silver is surpassed. At very low silver concentration of the electrolytes used this occurs at low current densities. As soon as the limiting current density of the zinc deposition is reached (between 1 and 2 A/dm^2) a further increase of current density has no more significant influence on the composition of the alloy deposits. Only silver deposits with a low zinc content can be deposited in a usable form to higher thicknesses. Codeposition of silver and indium in cyanide solutions is possible too, if indium in the electrolyte is stabilized by dextrose which prevents indium hydroxide separation. In these baths indium shows the typical behavior of the less noble metal compared to silver. Besides problems in bath control silver-indium deposits tend to be discolored. They often show a typical spiral growth structure on the surface.[41]

The problem of tarnish resistant silver deposits by alloying metals is still unsolved.

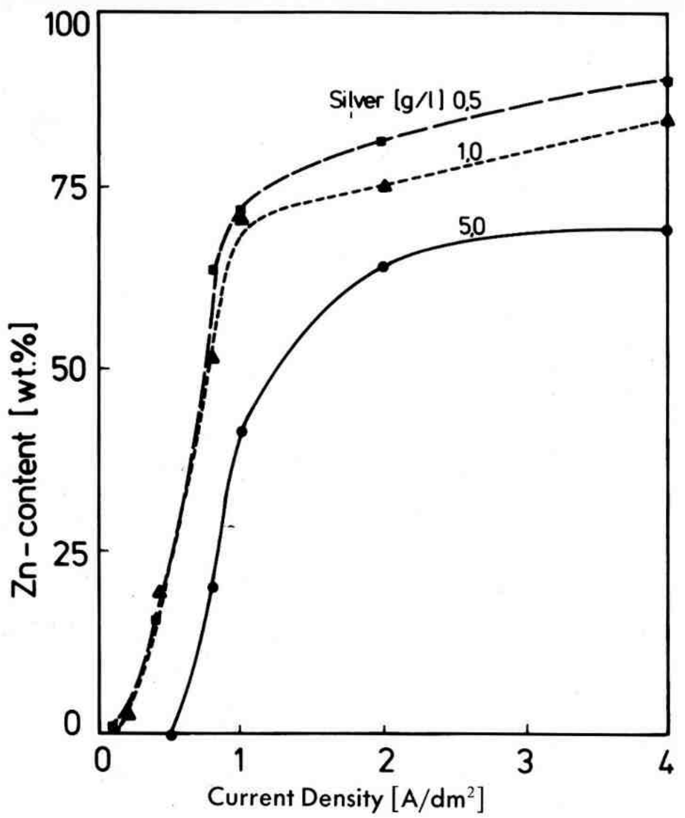


Figure 19 - Zinc content of silver-zinc deposits from on electrolyte with 100 g/L Zn(CN)$_2$, 100 g/L NaOH, 160 g/L NaCN with silver contents of 0.5, 1.0 and 5.0 g/L.

Simultaneous deposition of other metals with silver can be achieved best with metals which form no stable complex cyanide ions, as lead, tin (as Sn^{+2} ion), antimony, bismuth or arsenic. To stabilize these metals in the alkaline cyanide solution, organic complexing agents, *e.g.*, oxy-acids as citric or tartaric acid and other complex formers partly with alkaline hydroxide contents, are used.

Silver-lead alloys were proposed as friction bearings but in practice air craft engine bearings have successive layers of different metals deposited and then diffused by heat.

The advantage of silver bearings with lead-tin or lead-indium linings compared to cast copper-lead bearings is due to the fact that molten lead dissolves in silver during runs under extreme conditions. The microstructure of such a friction bearing shows lead segregations in the silver matrix. When copper-lead friction bearings are overheated the lead, not having alloyed with the copper, melts and collects at the overheated area, and blocks oil channels or holes.

Silver-antimony alloys with small amounts of antimony are generally used as hard and bright deposits. For electrotechnical purposes it must be kept in mind that the resistivity is considerably increased by the presence of antimony in solid solution with silver. By codeposition of arsenic it is easy to get bright silver deposits with a very good appearance but arsenic in these deposits is not quite insoluble in dilute acetic acid. A difficulty in the practical use of silver-tin baths is the tendency of Sn^{+2} in the electrolyte to oxidize to Sn^{+4}. The latter cannot be codischarged.

In silver electrolytes which contain an alloying metal which does not form a stable cyanide, the composition of the alloy deposit can be influenced over a wide range by changing the cyanide content. Figure 20 shows curves of the bismuth content of deposits from silver-bismuth baths with equal silver and bismuth contents (25 g/L), and potassium cyanide concentrations between 22 and 150 g/L. At cyanide concentrations of 22 and 44 g/L, the bismuth content of the deposited alloys is very small. During electrolysis bismuth behaves as the less noble metal. With cyanide concentrations of 70 g/L and higher at low current densities silver-free bismuth is deposited. With rising current density the bismuth content of the deposits decreases quickly at first. After the limiting current density of the silver deposition is reached, it remains nearly constant. By changing the metal ratio in the electrolyte to higher silver contents the potassium cyanide concentration at which codeposition of bismuth is strongly favored, is changed to higher values.[42]

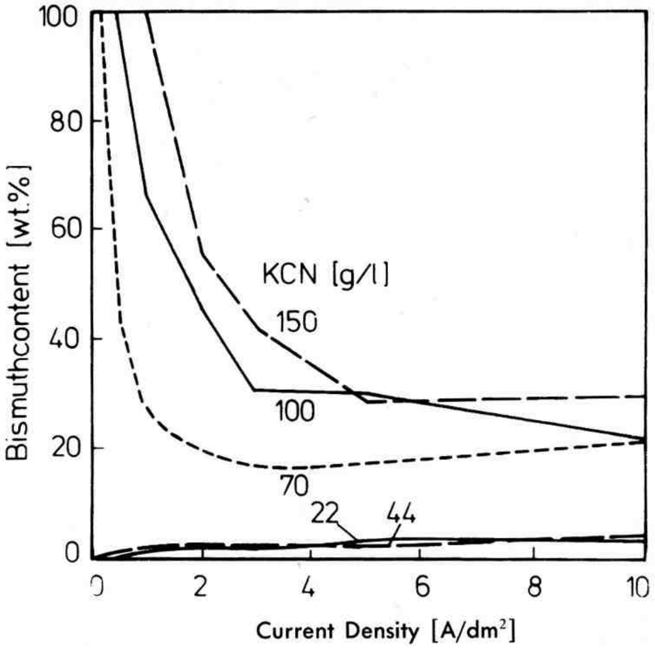


Figure 20 - Bismuth content of silver-bismuth deposits from a bath with 25 g/L Ag, 25 g/L Bi, 35 g/L potassium tartrate, 25 g/L potassium hydroxide and different cyanide concentrations, 25°C, stirred electrolyte.

Gold forms only one very stable cyanide complex of the composition $Au(CN)_2^-$. In acid solutions the $Au(CN_4)$ complex of the Au^{+3} ion is relatively stable; in alkaline solutions it decomposes to $Au(CN)^{-2}$, the complex of the Au^+ ion, according to the equation.[43]

$$Au(CN)_4^- \Leftrightarrow Au(CN)_2^- + (CN)_2$$

As far as is known, gold is the only metal to be discharged immediately via the $Au(CN)_2^-$-complex predominant in the electrolyte. In comparison to other metals the influence of the cyanide concentration on the deposition potential is minor and the aforementioned stability in weak acid solutions is characteristic. From this many possibilities result, which influence the codeposition of other metals.

Gold alloy deposits of different compositions are used for jewelry and wares of daily use, as well as for technical applications, especially in the electronics industry. Not only binary but also ternary and even quaternary alloys are deposited.

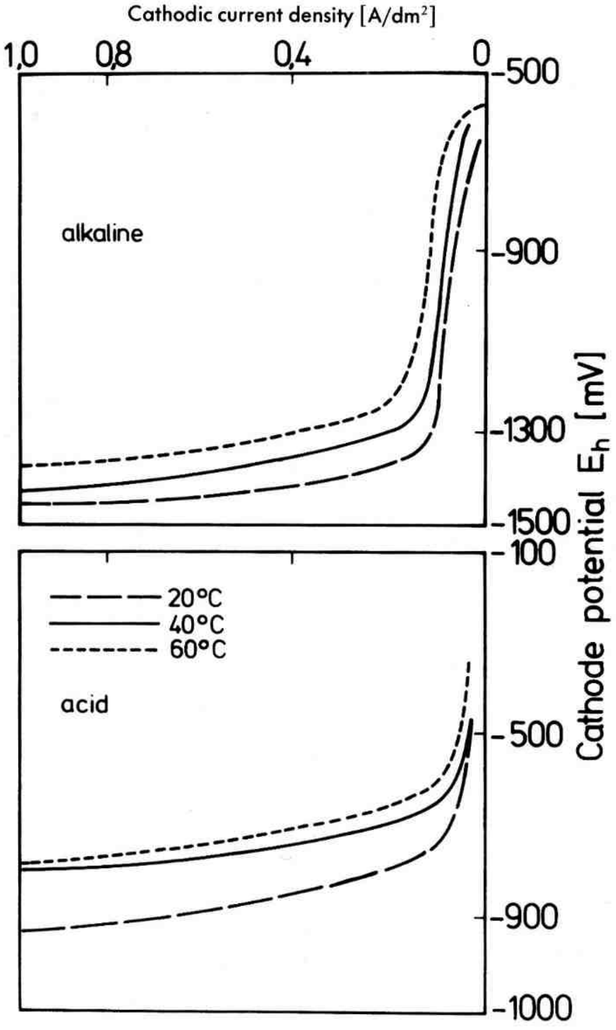


Figure 21 - Cathode potential-current density curves in gold electrolytes: Alkaline: 2 g/L Au as $KAu(CN)_2$, 8 g/L KCN; Acid: 2 g/L Au as $KAu(CN)_2$, 40 g/L citric acid, 60 g/L sodium citrate, pH = 4.2.

As Fig. 21 shows, the potential-current density curves for the alkaline cyanide baths are in general more negative than those in a weak acid bath, disregarding low current densities beneath the limiting current density range in the alkaline bath.[44] Generally, current efficiency in acid electrolytes is much lower than in alkaline electrolytes, highly efficient acid solutions may exceed 55%. That in alkaline baths a limiting current density for the gold deposition exists is due to the mentioned fact that hydrogen is discharged in alkaline solutions immediately from the water molecule at a more negative potential; in acid solutions protons are discharged at a less negative potential.

The cathodic potential curves of a cyanide copper bath (Fig. 22) show a very strong dependence upon the cyanide concentration, and copper is finally no longer discharged. The codeposition of copper with gold therefore takes place much more readily in electrolytes in which the ratio of copper to cyanide is as high as possible. Figure 23 shows cathodic potential curves (upper part) and the metal contents of the deposits in relation to the current density (lower part) of a cyanide gold-copper electrolyte.

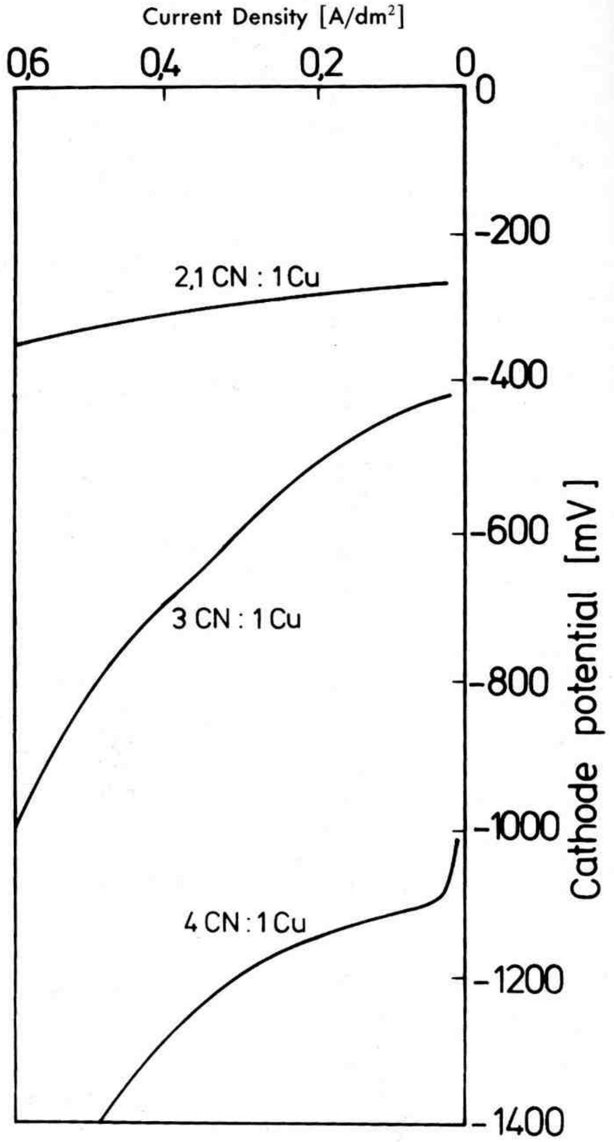


Figure 22 - Cathode potential-current density curves in potassium-cyanocuprate solutions with different ratios of CN:Cu; copper concentration 20 g/L, 60°C, quiescent electrolyte.

The potential curves show a marked limiting current density for gold deposition. As soon as this is exceeded codeposition of copper rises with the current density, at first very fast but soon levels out as a consequence of the exhaustion of the cathodic diffusion layer in dischargeable $Cu(CN)_2^-$ ions.

In acid baths, where only gold is present as a cyanide complex, codeposition of copper can be observed at very low current densities.

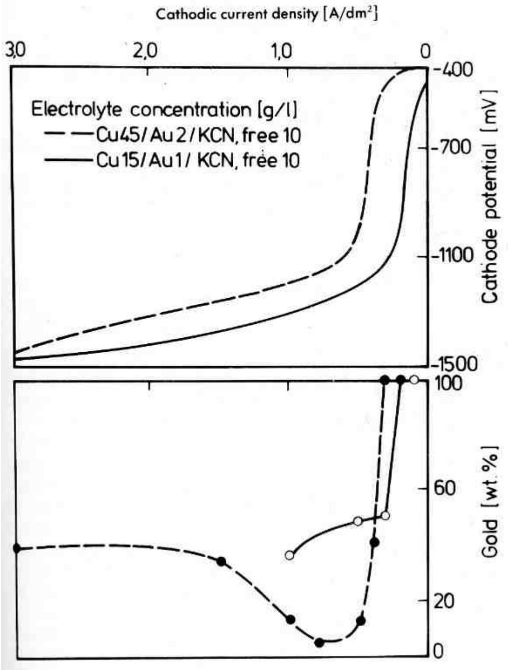


Figure 23 - Cathode potential-current density curves and gold content of gold-copper alloy deposits in stirred alkaline cyanide baths, 50°C.

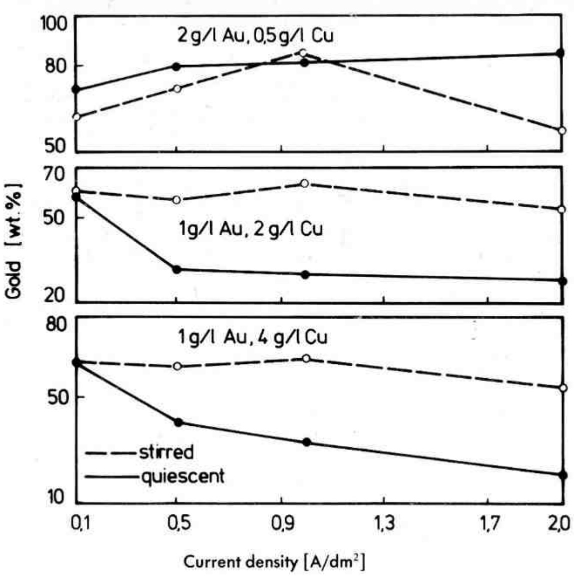


Figure 24 - Gold content of gold-copper alloy deposits from acid baths with different gold to copper ratio at 40°C and a pH of 5.5 (Au as $KAu(CN)_2$, Cu as $CuSO_4$, 60 g/L, sodium citrate, 40 g/L citric acid).

Figure 24 shows the changes of the gold content in deposits from acid solutions. In an electrolyte with low copper and higher gold concentration, the gold content of the alloys increases with increasing current density. At higher copper concentrations the gold content decreases with increasing current density. In these baths gold behaves as the more noble metal, and one might expect with rising polarization by higher current density the gold content of the deposits to get smaller. This contradiction can be explained by the fact that the electrolytes have relatively small concentrations of dischargeable mass particles. Therefore exhaustion will soon take place at the cathode, so that the discharge of gold or copper or both is diffusion controlled. In an electrolyte with only 0.5 g/L copper and 2 g/L gold, diffusion control for copper deposition starts at low current densities. At a copper concentration of 2 to 4 g/L and 1 g/L gold the diffusion control for gold begins at lower current densities. Therefore the gold content of the deposits decreases with rising current density.

Cobalt cannot be simultaneously discharged with gold in alkaline cyanide electrolytes.[39] From an acid gold bath simultaneous discharge of cobalt with gold presents no difficulties (Fig. 25).[45] At very low cobalt concentrations of the electrolyte codeposition of cobalt occurs. According to Fig. 25, cobalt content of the alloys decreases very quickly with rising current density due to the fact that cobalt concentration in the electrolyte is very small as compared to gold. This causes a diffusion controlled deposition.

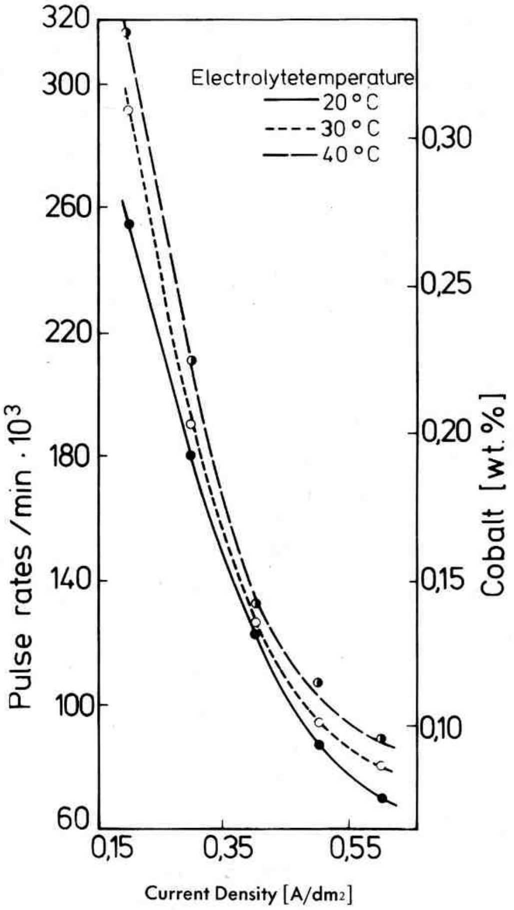


Figure 25 - Pulse rates and cobalt content of gold-cobalt deposits from a weak acid phosphate electrolyte with 120 g/L KH_2PO_4, 8 g/L Au as $KAu(CN)_2$, 0.0136 g/L Co (doped with Co-60) as $CoCl_2$, pH 4.5; 40°C.

Nickel may be codeposited with gold from alkaline and acid plating solutions. As shown in Fig. 26, the codeposition of nickel and gold in an alkaline cyanide bath starts as soon as the limiting current density of gold is reached. As seen from the right-hand part of Fig. 26, the codeposition of nickel is forced back to higher current densities[45] by an addition of 1 g/L silver to the electrolyte. In an acid electrolyte which contains nickel, no longer as a cyanide complex, codeposition with gold starts at very low current densities (Fig. 27). As shown for an electrolyte with 2 g/L gold and 10 or 20 g/L nickel, alloy deposits with high nickel contents can be obtained. In acid electrolytes gold behaves as the more noble metal as compared to nickel.

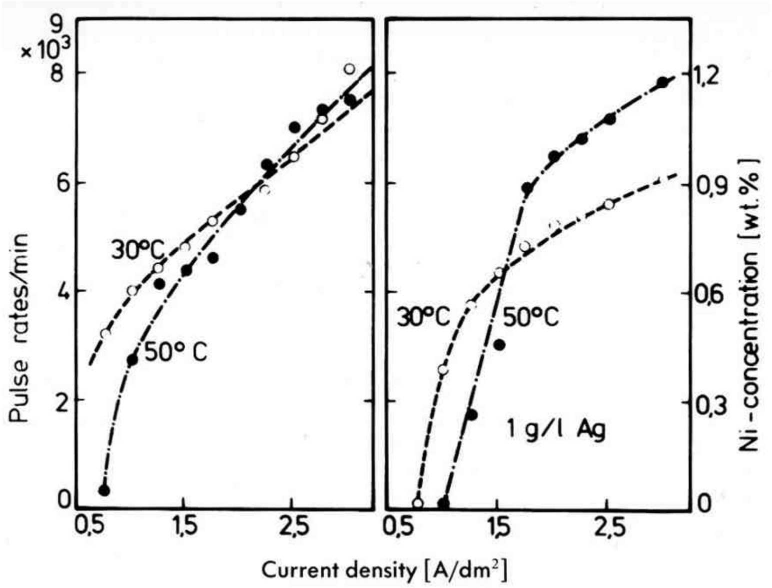


Figure 26 - Nickel content of gold-nickel deposits from an alkaline cyanide bath (10 g/L Au, 3 g/L Ni doped with ^{63}Ni, 150 g/L KCN).

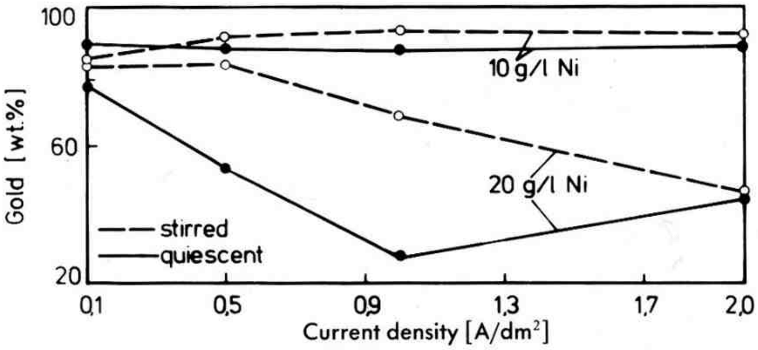
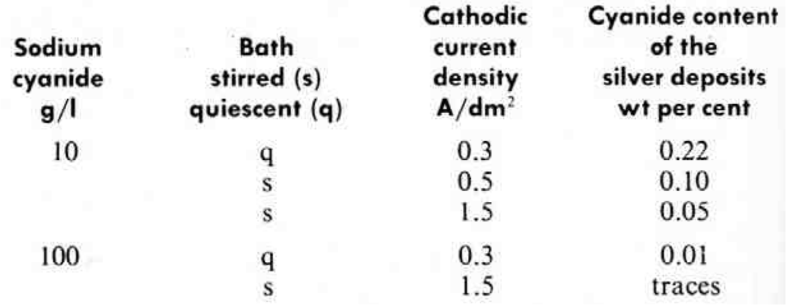


Figure 27 - Gold content of gold-nickel deposits from a citric acid bath with 2 g/L Au as $KAu(CN)_2$, 10 or 20 g/L Ni as $NiSO_4$, 60 g/L sodium citrate and 40 g/L citric acid; pH 4.2; 40°C.

For the production of the so-called hard gold alloys with only low concentrations of nickel or cobalt, alloy baths with relatively low concentration of the alloying metal are used. Cobalt- or nickel-containing hard gold alloys from acid baths sometimes show difficulties in soldering and contact problems in service caused by included non-metallic substances. Numerous investigations have been made into this problem.[46-53]

Inclusion is always associated with the codeposition of nickel or cobalt and gold. Even today it is not possible to fully explain the source of the inclusion. According to studies by Munier and others a polymer is codeposited. Quantity and ratio of carbon, nitrogen, oxygen, hydrogen and alkali metals in hard gold deposits make it probable that rather than a homogenous substance a mixture of different substances from the electrolyte is included. Among these, cyanides of low solubility are important. Interesting but not yet explained is the presence of hydrogen. Evidently it is contained as supersaturated solid solution, made possible by high lattice defects of the hard gold, or as occluded molecular hydrogen. Only part of it can be present in the form of chemical compounds. According to G.B. Munier,[46] gold-silver deposits from an electrolyte with a pH of 11 show the same content of non-metallics as hard-gold deposits with nickel or cobalt from acid baths. This behavior can be explained by the fact that at low cyanide contents, the deposition of silver is connected with inclusion of AgCN as shown in Table 3.[54] The danger of inclusion is not present when a sulfite bath is used, but this bath causes other difficulties, among them instability and often insufficient corrosion resistance of alloy deposits.[20]

Table 3 - Cyanide content of silver deposits from an electrolyte with 20 g/L silver at a temperature of 20°C.



Sodium cyanide g/l	Bath stirred (s) quiescent (q)	Cathodic current density A/dm^2	Cyanide content of the silver deposits wt per cent
10	q	0.3	0.22
	s	0.5	0.10
	s	1.5	0.05
100	q	0.3	0.01
	s	1.5	traces

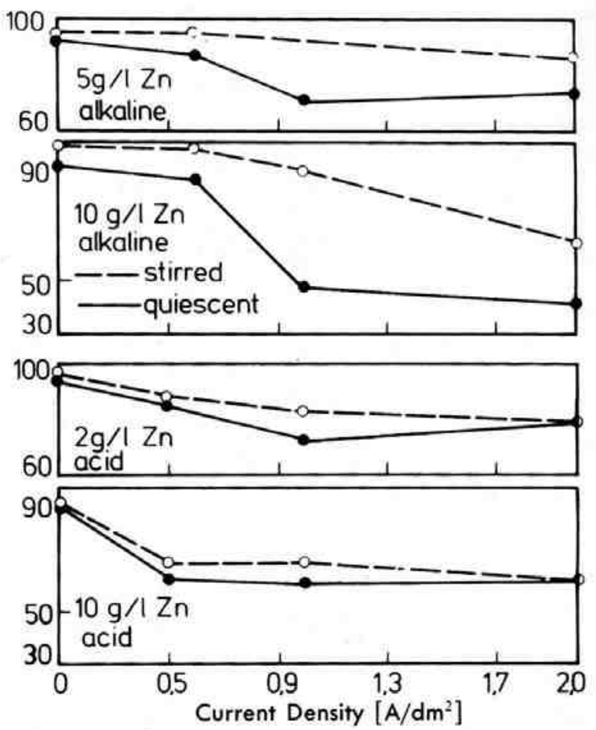


Figure 28 - Gold content of gold-zinc deposits: Alkaline bath: 2 g/L Au as $KAu(CN)_2$, zinc as $K_2Zn(CN)_4$, 43 g/L KCN, 42 g/L KOH; Acid bath: 2 g/L Au as $KAu(CN)_2$, Zn as $ZnSO_4$, 60 g/L sodium citrate, 40 g/L citric acid, pH value 4.2; 40°C.

Figure 28 shows the gold content of alloy deposits as related to the current density for alkaline and acid gold-zinc alloy baths. Independent of the composition of the electrolyte and other working conditions, gold content decreases with rising current density.

The influence of the zinc content in the electrolyte, and of the transition from alkaline to acid bath on the composition of the alloys is slight. In alkaline and acid solutions gold is, at the investigated bath compositions, always the more noble metal. The zinc content in the deposits increases with increasing current density.[44]

Cadmium is of great interest as an alloying metal for gold; also for ternary and quaternary alloys. Contrary to zinc it is codeposited with gold at very low current densities below the limiting current density of gold alkaline cyanide electrolytes. As shown in Fig. 29, in the alkaline bath cadmium behaves as the less noble metal, the gold content in the deposits decreasing with rising current density. In an acid bath cadmium is more noble than gold. Its ratio to gold in the deposits is higher especially at low current densities.[44] In alkaline as well as in acid baths it is possible to deposit gold-cadmium alloys in nearly every composition desired.

Metals such as lead and bismuth which form no stable cyanide complexes in alkaline solutions behave more nobly than gold. Their deposition is strongly preferred as shown for bismuth gold alloys in Fig. 30.[55]

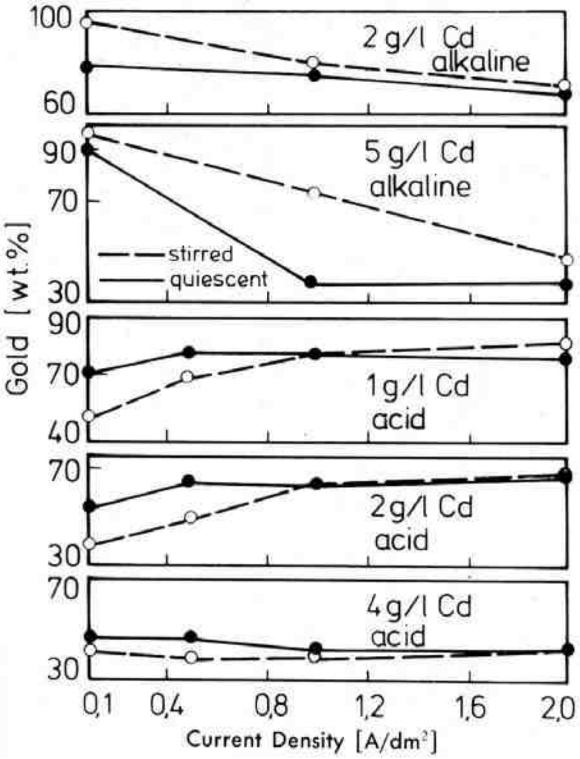


Figure 29 - Gold content of gold-cadmium deposits: Alkaline bath: 2 g/L Au as $KAu(CN)_2$ and Cd on 5 g/L Cd as $K_2Cd(CN)_4$, 18 or 34 g/L KCN, 4 or 10 g/L KOH; Acid bath: 2 g/L Au as $KAu(CN)_2$, Cd as $CdSO_4$, 40 g/L citric acid and 60 g/L sodium citrate, pH = 4.2, 40°C.

In acid cyanide baths besides cyanide which is present only in amounts enough to form the $Au(CN)_2^-$ complex a further complexing agent, such as citric acid, is added. Also ethylendiamintetraacetic acid (EDTA) is a stronger chelating agent for heavy metals, but the constant is different for various metals. It depends on the pH value of the solutions, as is also true of other complex compounds. The $Au(CN)_2^-$ complex itself is not influenced by EDTA significantly. The cathode potential curve is shifted to more noble values, but this is due to the depolarization of hydrogen deposition and not to that of gold.[56] Nickel- and cobalt-EDTA complexes are very stable, and to discharge nickel it is necessary to keep the molar nickel to EDTA ratio above 1. For iron special conditions exist. The EDTA complex of the Fe^{+3} has a very high complex constant compared to that of Fe^{+2} so that in the presence of oxygen Fe^{+2} is quickly oxidized to Fe^{+3}. Bright gold alloys with iron, nickel and cobalt may be deposited from acid baths in presence of EDTA as a third complexing agent in addition to cyanide and citrate. The optimum conditions for good deposits from such a solution are very limited.[57] Of special importance is the molar ratio of metal to EDTA. The very narrow limits of the metal to EDTA ratio for crack free gold-iron alloys are shown in Fig. 31. The range of the optimum ratio of metal to EDTA changes with the metal codeposited with gold as given in Fig. 32.[45]

The current density range in which bright and crack-free deposits are obtained rises from nickel via cobalt to iron. For iron it is very high because it is necessary to exceed the limiting current density for the redox reaction Fe^{+3}/Fe^{+2}.

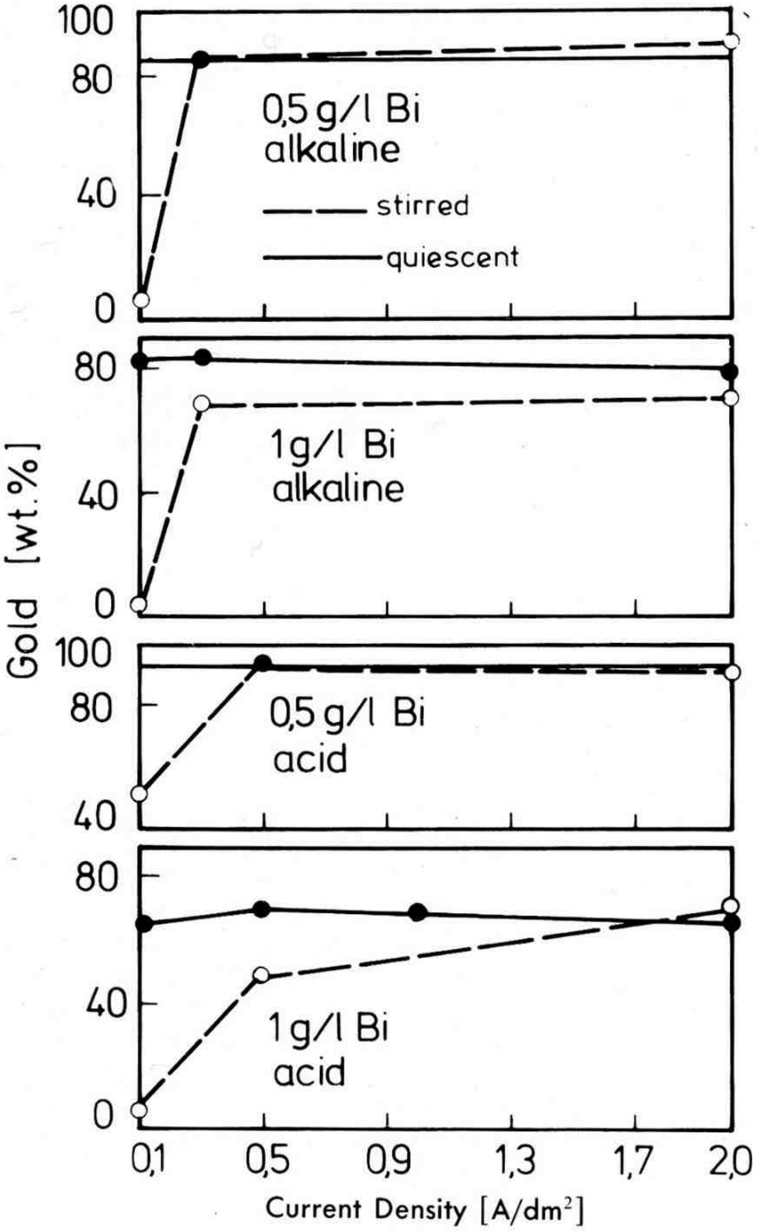


Figure 30 - Gold content of gold-bismuth alloy deposits from an alkaline cyanide both with potassium hydroxide and potassium tartrate to keep bismuth in solution and from a citric acid bath, gold content of both baths 2 g/L.

To possess sufficient chemical resistance gold alloy deposits should contain at least 75% gold. Often it is difficult to deposit alloys with controlled properties and at the same time keep their gold content within the desired tolerances. In alloys for decorative purposes with definite colors copper and cadmium are preferred to achieve yellow (Cd) or red (Cu) gold in different shades. Furthermore silver, zinc and in small amounts nickel are used. Nickel, cadmium and silver are generally contained in binary white gold deposits. For technical purposes binary gold-silver alloys are of interest. For special applications in the electronic industry other alloying metals, *e.g.*, antimony, are employed.

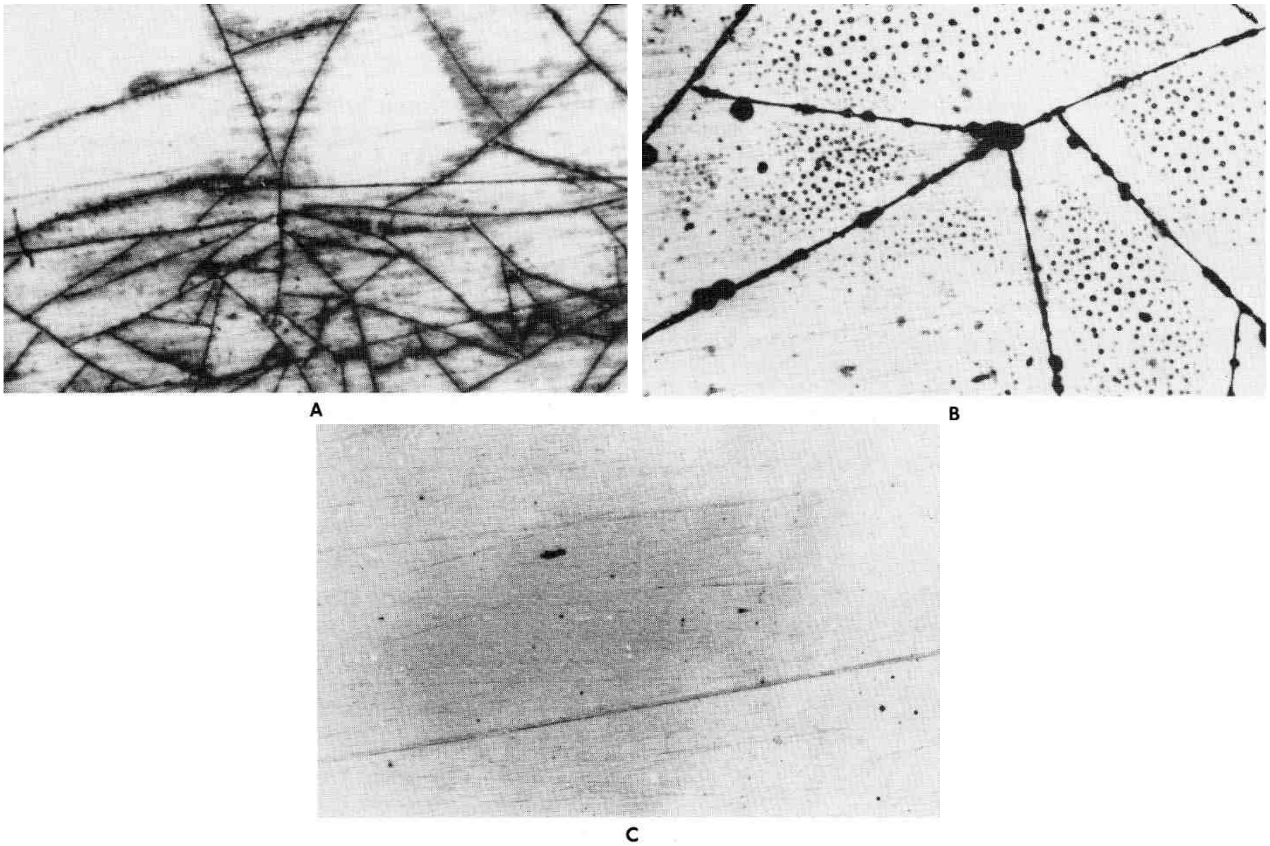


Figure 31 - Gold-iron alloy deposits from a citric acid bath with EDTA as third complexing agent; molar ratio Fe; EDTA (a) 1:0.95, (b) 1:0.8, (c) 1:0.7.

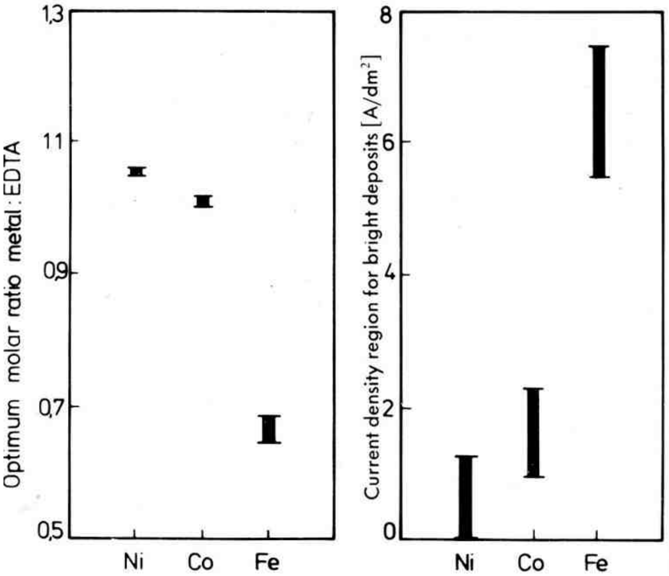


Figure 32 - Optimum conditions for the deposition of gold-alloy deposits with Fe, Co and Ni from the citric acid bath with addition of EDTA.

A comparison of properties of alloys, electrodeposited and melted and recrystallized

Electrodeposited alloys are usually not in a state of thermo-dynamical equilibrium.[21,58] Electrocrystallization takes place in aqueous solutions at temperatures far below the temperatures at which detectable diffusion takes place. But if the deposition temperature is higher than that at which diffusion begins, stable structures are obtained. This occurs for alloys of low melting metals, such as tin-lead, tin-indium, zinc-cadmium and tin-zinc. Other alloys deviate in their properties more or less from cast alloys. This is due not only to the fact that they are not in equilibrium, but that their structure sensitive properties are often strongly influenced by inclusion of non-metallic substances. The structures of electrodeposited and cast alloys correspond inasmuch as, nearly always, only phases which exist in the phase diagram are formed. During electrocrystallization of alloys and crystallization of the casting, the components may crystallize separately, in the form of solid solutions or intermetallic phases. Great differences often exist in the concentration ranges of phases formed. Phases present in the phase diagram may be absent in electrocrystallized alloys, or phases which are unstable at the temperature of electrocrystallization may appear. Figure 33 gives, based upon x-ray studies, several more complicated phase diagrams of electrodeposited alloys in comparison to equilibrium diagrams. It can be seen that in part greater differences exist, but that on the other hand during electrocrystallization as well as luring solidification true alloys crystallize.

The differences in composition are of high importance to solid solutions. In spite of complete solid solubility between two metals, under certain circumstances very small or even no solid solution at all is observed in the electrodeposited alloys. On the other hand it is possible to electrodeposit alloys with an extended solid solution range when the phase diagram shows no remarkable mutual solubility of the bordering phases.

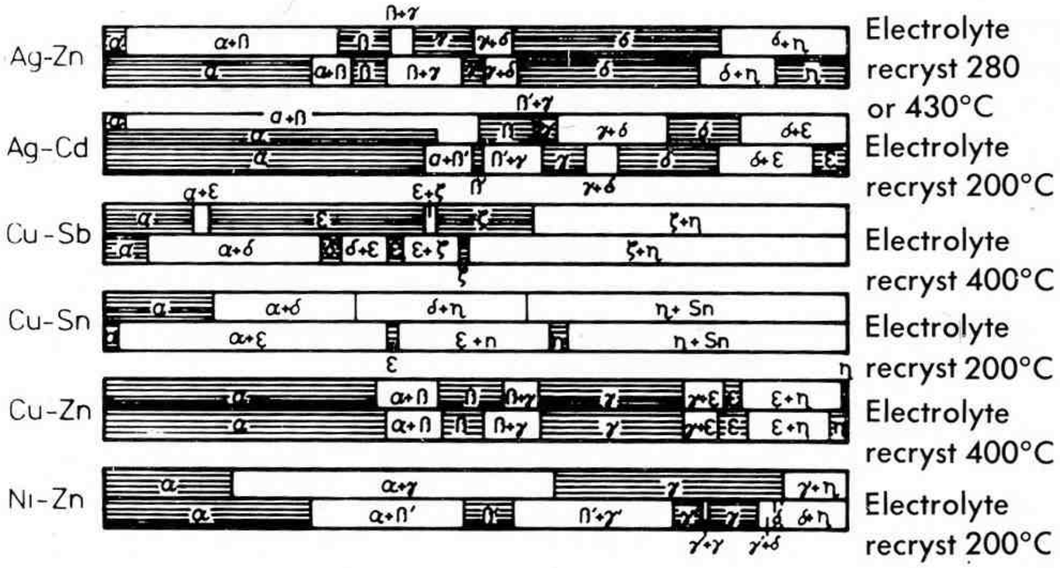


Figure 33 - Phase ranges of electrolytic and recrystallized alloys.

One must keep in mind that the structure of electrodeposited alloys may vary considerably with deposition conditions.

Microscopically, alloy deposits often show a characteristic structure. Solid solutions may have a laminar structure which can be caused either by periodic concentration changes of the soluted metal or by inclusion of non-metallic substances during electrocrystallization. Intermetallic compounds formed by electrocrystallization often show typical structures (Fig. 34).

When a heterogenous mixture of two phases is formed during electrodeposition it may result in a very fine dispersion. The phases can also crystallize in a very coarse form as shown by Fig. 35. Coarsely crystallized deposits are of no practical interest unless the intercrystalline cohesion is strong.

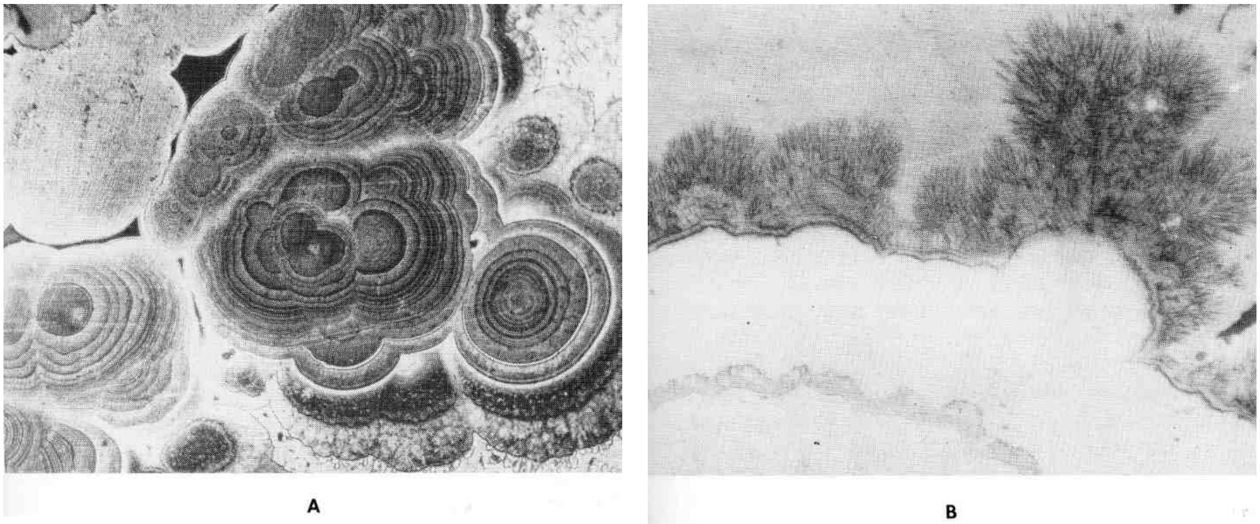


Figure 34 - Structure of brass deposits: (a) β-brass, 56.3% Cu, (b) η-brass, 11.7% Cu.

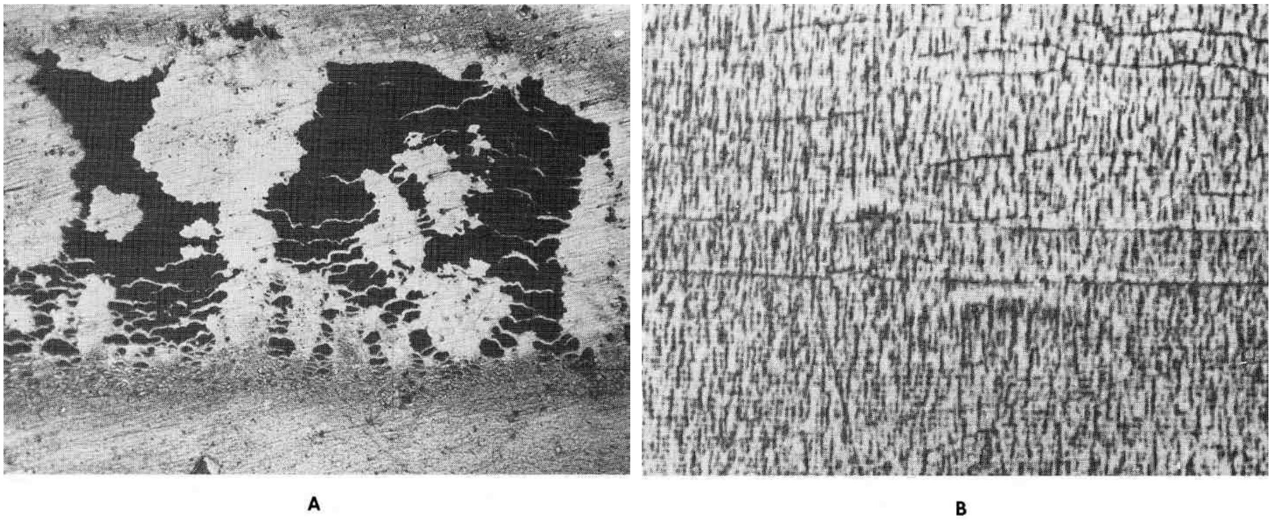


Figure 35 - Structure of cadmium-silver deposits: (a) 37% Cd (deposited from a simple cyanide electrolyte), (b) 40% Cd (deposited from a silver containing bright-cadmium electrolyte).

The different behavior of two metals during simultaneous electrocrystallization may be explained on the basis of the cathodic potential current density curves.

Dependent on the electrolyte composition and the metals present, codeposition of the less noble metal may occur only after exceeding the limiting current density of the more noble metal. In this case either a mixture of both metals or of the more noble metal and an intermetallic compound is formed. The intermetallic compound must approach the electrochemical properties of the less noble metal. However, if no limiting current range separates the simultaneous discharge of both metals then crystallization by formation of solid solutions may occur during electrodeposition, even when no solid solution in the phase diagram exists. In this way, highly supersaturated solid solutions form, which normally cannot be produced in cast alloys or only by very fast quenching. One disadvantage is that electrolytic crystallization of these highly supersaturated solid solutions is nearly always associated with inclusions of non-metallics.

An influence by inclusion upon the extreme supersaturation achieved during electrodeposition of alloys cannot be denied. It is known that soluted atoms concentrate at sites with high lattice defects. By inclusion, extremely high lattice distortions are produced which facilitate supersaturation.

Hydrogen as an alloying element

In discussing the structure of electrodeposited alloys hydrogen is often forgotten despite the fact that it is the most common alloying component, stated by Blum and Hogaboom 25 years ago. On cadmium and zinc surfaces the overvoltage of hydrogen is very high. In the baths of these metals codeposition of hydrogen occurs after the limiting current density is exceeded.[38] Electrodeposited cadmium and zinc do not contain hydrogen in supersaturated solution. All hydrogen discharged escapes as molecular hydrogen. The hydrogen in electrodeposited zinc is formed by a reaction between zinc and water or zinc hydroxide, which is occluded in the deposits, according to:[59]

$Zn + H_2O \Leftrightarrow ZnO + H_2$ and

$Zn + Zn(OH)_2 \Leftrightarrow 2ZnO + H_2$

These reactions proceed very slowly at room temperature. As hydrogen does not diffuse in zinc, it is enriched during longer storage at room temperature, as shown in Fig. 36.

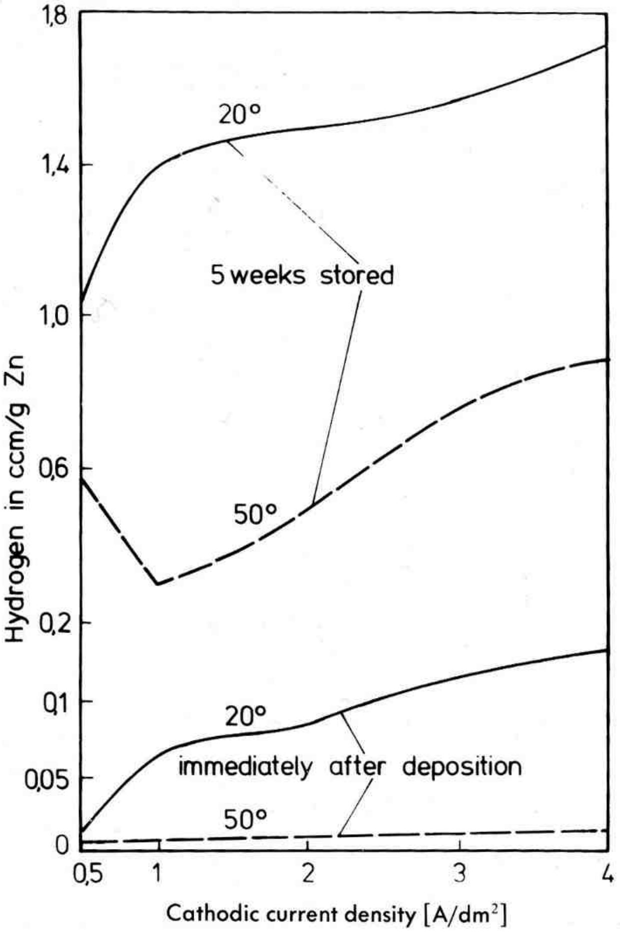


Figure 36 - Hydrogen content of zinc deposits determined by cold extraction.

To investigate this behavior of zinc deposits it is necessary to use the method of cold extraction of hydrogen by amalgamation. During hot extraction the reaction of zinc with water or zinc hydroxide is very fast, so that at a sufficiently high extraction temperature it will be completed in a short time. The total hydrogen evolved by these reactions is easily determined by high temperature extraction. Figure 37 gives the ZnO content after extracting, the hydrogen evolved and the molar ratio of zinc oxide to hydrogen plotted against current density for zinc deposits from cyanide baths. The slopes of the curves for zinc oxide and hydrogen evolution are equal. The pronounced minimum in the curves is caused by the limiting current density of zinc. The molar ratio of zinc oxide to hydrogen increases continuously from a value of nearly 1.0 at low current densities to about 1.75 at a current density of 4 A/dm². If the total amount of hydrogen were formed with water according to the first equation the molar ratio would be 1:1 and in the case of the second reaction with $Zn(OH)_2$ it would be 2:1. In no case is the ratio less than 1, which would make possible the conclusion that at least a certain part of hydrogen evolved during crystallization is trapped in voids as molecular hydrogen. The proportion to which each of the two possible reactions of zinc and water or zinc hydroxide participates in the formation of hydrogen changes with current density. At increasing current densities the inclusion of zinc hydroxide increases. Zinc cyanide is not included by zinc from cyanide solutions. This confirms that the deposition does not take place via a cyanide complex as the discharge determining step but via zinc hydroxide.

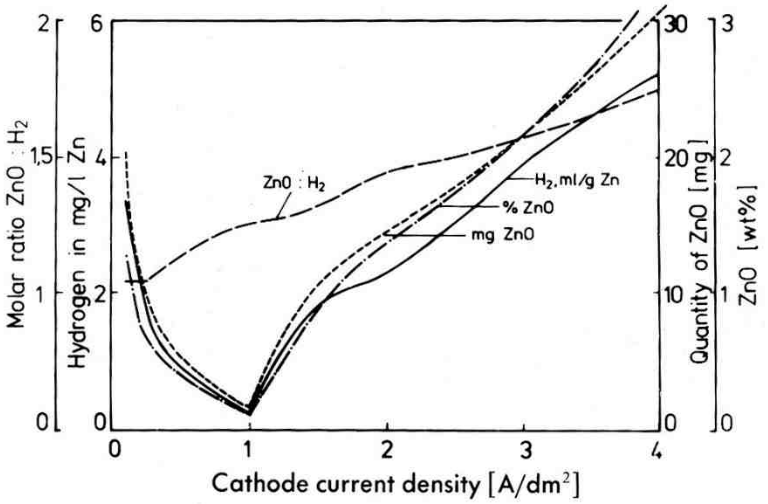


Figure 37 - Hydrogen and zinc oxide contents of zinc deposits from a cyanide electrolyte as determined by hot extraction.

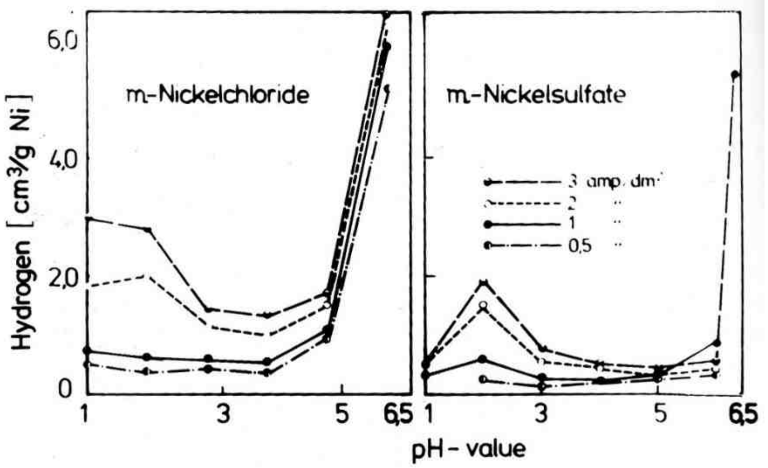


Figure 38 - Relationship of the hydrogen content of nickel deposits to the pH value of the electrolyte. Electrodeposition temperature 20°C.

Very high supersaturation of dissolved hydrogen is observed in metals which are not deposited without simultaneous hydrogen discharge, such as iron, cobalt, nickel, chromium and platinum metals. Figure 38 shows the influence of pH value on the supersaturation of nickel with hydrogen deposited in chloride and sulfate solutions.[60] The hydrogen content is low at a low pH, where the current efficiency for the discharge of nickel is lowest, and where the hydrogen discharge is the highest. But at high pH-values where the simultaneous hydrogen discharge is lowest, hydrogen supersaturation is very high, as seen from Fig. 38. At very high values, over a pH of 5.0 in the chloride bath and over a pH of 6.3 in the sulfate bath, the hydrogen content of the nickel jumps. The reason for the extreme increase in the hydrogen content is the hydrolysis of nickel salts at these pH values. The nickel chloride hydrolysis constant is higher than that of nickel sulfate, therefore hydrolysis followed by adsorption and inclusion of basic nickel chloride occurs at a lower pH. The high lattice defects caused by inclusion of the hydrolysis products lead to very strong enrichment of hydrogen. Strains in the nickel lattice causing high hydrogen supersaturation may also be formed by codeposition of a second metal, which enters into a solid solution with nickel. But it is not certain that adsorption and inclusion of other non-metallic substances do not co-operate, which is absolutely possible, *e.g.*, in nickel-zinc or nickel-thallium alloys. Figure 39 shows the influence of the zinc concentration in electrodeposited zinc-nickel solid solutions on their hydrogen content. The hydrogen supersaturation limit of the face-centered cubic nickel-zinc solid solutions increases very fast till the saturation limit of the zinc is reached. At higher zinc concentrations, hydrogen content of alloys again decreases and reaches zero at about 80 wt% zinc.

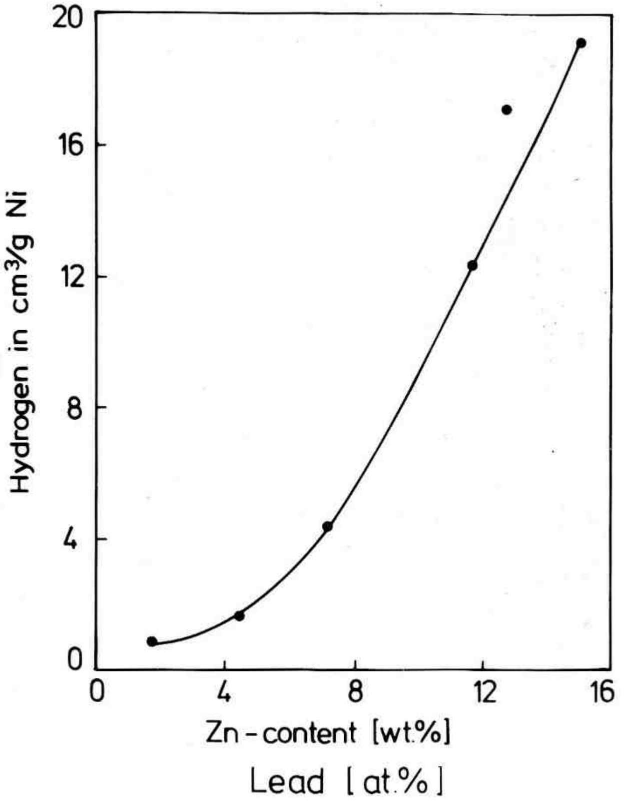


Figure 39 - Hydrogen content of electrolytic face centered cubic zinc-nickel solid solution in relation to the zinc content of the alloys.

Detailed x-ray structure analysis showed that in chloride solutions hexagonal nickel by hydrogen codeposition[61] is not formed.[62] In contrast a chromium hydride of the composition CrH with hexagonal structure has been confirmed.[63] The formation of this hydride during the electrocrystallization of chromium depends on the electrolysis conditions. It can be deposited in pure state with pulsating DC at temperatures below 25°C. The formation of chromium hydride is favored by high current densities and high chromic acid concentrations. The hexagonal hydride possesses only a small homogeneity range from $CrH_{0.95}$ to $CrH_{1.00}$. The existence of a hydride with face-centered cubic structure is confirmed, yet it has not been possible to establish its composition. It is believed that the face centered cubic hydride is formed from the hexagonal hydride by an alteration of the stacking order of the more densely packed lattice planes. In chromium hydrogen alloys the body-centered cubic chromium lattice along with the hexagonal lattice is seen in a wide concentration range from $Cr\text{-}H_{0.04}$ to $CrH_{0.95}$.

Supersaturated hydrogen-nickel solid solutions decompose in air at room temperature slowly with the evolution of hydrogen. CrH too, is an unstable compound, but in air it does not decompose at room temperature. This stability occurs in the same way as the passivity of chromium, by the formation of a pore-free atmospheric oxide layer which prevents hydrogen evolution. Chromium hydride decomposes in vacuum at room temperature slowly; in a few minutes in air slow deposition begins at 100°C. The chromium remaining after low temperature decomposition of the hydride is very active. In air it forms a thicker oxide layer with accompanying heats, yet oxidation soon stops.[63] This type of chromium has a more noble potential than electrolytic chromium.[64] The properties of chromium hydride are similar to those of normal electrolytic chromium.

Properties of electrodeposited solid solutions

As has been discussed, included non-metallic substances are of high importance to the formation of highly supersaturated nickel-hydrogen alloys. The same behavior was observed in the formation of some highly supersaturated binary solutions of two metallic components. As examples, alloys of silver with lead, bismuth or thallium and of copper with lead may be mentioned. In these systems very highly supersaturated silver or copper rich alloys are deposited from electrolytes of appropriate composition. Probably complexes with organic oxy-acids; *e.g.*, tartrate, citrate or, in the case of copper-lead alloys, a copper(I)-thiourea complex, are included. That true solid solutions are formed may be seen from the lattice constants of the solvent metal. The lattice constant is a property of low sensitivity to lattice strains and it is possible to hold the inclusion of foreign substances during electrocrystallization low enough, so that the x-ray interferences do not fade into the background too much. As long as no films or filaments of the included substances exist, only a very small increase in the resistivity by lattice defects will be observed. Normally in solid solutions it increases very fast. As shown in Fig. 40, the resistivity of electrolytic copper-lead alloys rises very quickly in the range of copper rich alloys up to about 12 wt% Pb. Since copper does not dissolve in lead, the resistivity changes continuously from pure lead to the supersaturated copper rich solid solution. According to the phase diagram the maximum of the solid solution of lead in copper, 0.1 wt%, is reached at 900°C and 0.04 wt% at 500°C.[65]

The solid solubility may be different for the same metals, depending on the composition of the electrolyte. This has been stated for silver-cadmium[40] and copper-gold[44,65] alloys. Depending upon the bath composition, these alloys crystallize in a wide range as solid solutions or in two phases. In the alkaline cyanide electrolyte, simultaneous discharge of copper and gold begins above the limiting current density of gold. In nearly neutral, or more so in weakly acid solutions in which codeposition of copper with gold occurs at lowest current densities, copper crystallizes in the formation of solid solutions with gold.[44,66]

The supersaturated electrodeposited alloys show strong deviations from supersaturated solid solutions of cast and recrystallized alloys after quenching.

Supersaturated quenched silver alloys of lead or bismuth have only a hardness of about 40 kp/mm^2. Electrodeposited alloys of silver-lead or silver-bismuth have hardnesses of 140 to 190 kp/mm^2, depending on the plating conditions. Copper-lead alloys may reach a hardness of 300 kp/mm^2. It is striking that there is no significant hardness relationship with the concentration of the soluted metal. Furthermore the hardness equals that of metals with inclusion of non-metallics without the codeposition of a second metal.

The electrodeposited alloys can be brought into thermodynamic equilibrium by heat treatment. Changes of their properties during annealing are different from those of recrystallized supersaturated alloys.

Characteristic changes in resistivity are given in Fig. 41. Electrodeposited supersaturated solid solutions show no age hardening. Segregation temperature and rate are independent of the atomic supersaturation. The fact that, as shown in Fig. 41, for silver-lead and silver-bismuth alloys resistivity passes through a minimum, and increases at higher temperatures, is due to the increase in solubility with increase in temperature.

Hardness, caused by lattice defects independent of dissolved metals, shows another behavior. It does not change during the segregation process. This is shown in Fig. 42 for a silver-bismuth alloy. The same behavior was observed much earlier for solid solutions of hydrogen in nickel and chromium.[67] Hydrogen can be evolved without any change in hardness of the metal under consideration.

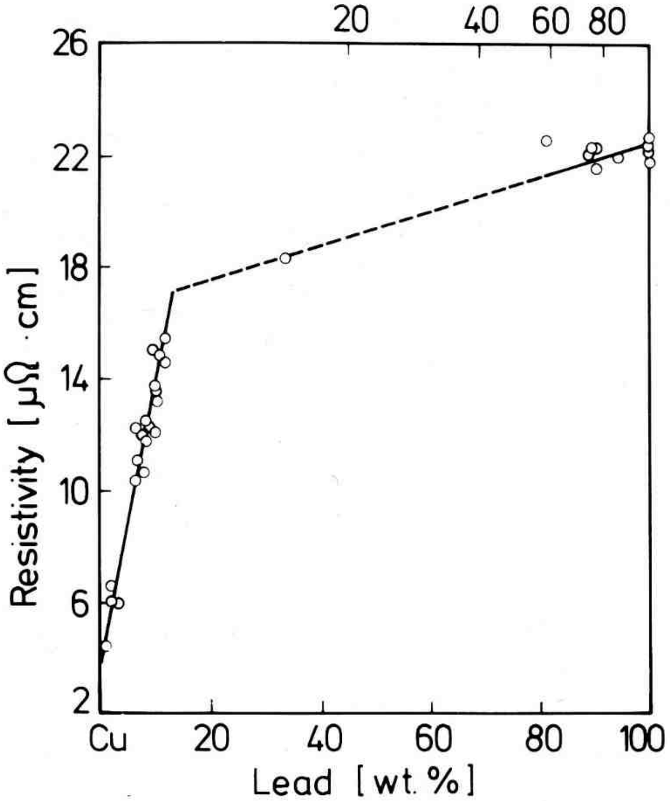


Figure 40 - Resistivity of lead-copper deposits.

Heat treatment of electrodeposited alloys

By heating it is possible to achieve equilibrium conditions in all electrodeposited alloys. Included inorganic or primarily organic compounds are decomposed during heating, and develop gases which lead to porosity. At higher inclusion levels, *e.g.*, electrolytic lead-copper alloys can decompose to powder) during heating. At lower inclusion levels, they get porous and brittle.

Hard gold alloys from acid gold baths contain inclusions as already discussed. After heating at higher temperatures such deposits show a surface with blisters and craters as shown in Fig. 43. Generally it can be stated that alloys with inclusions are not suitable for technical applications at elevated temperature. Thus it is not possible to get from copper-rich lead-copper alloys with a hardness of about 300 kp/mm^2, an alloy with an as-cast hardness of about 40 kp/mm^2 through heat treatment. Electrodeposited lead-copper alloys treated in this way are brittle and not suited for friction bearings. In contrast copper-poor lead alloys are well suited for linings of aluminum friction bearings, since no solid solution and no troublesome inclusion occurs.

Electrodeposited alloys free from detectable amounts of inclusion show no formation of pores or blisters during heating. When their structure corresponds to that of the phase diagram, all properties behave normally during annealing. After a critical temperature is reached a sudden decrease in hardness and tensile strength connected with a discontinuous increase in elongation occurs, as shown for an 18-carat gold-copper-cadmium alloy by F.I. Nobel, D.W. Thomson and J.M. Feibel.[68] Such electrodeposited alloys offer the same problems as cast alloys of the same composition for use at higher temperatures.

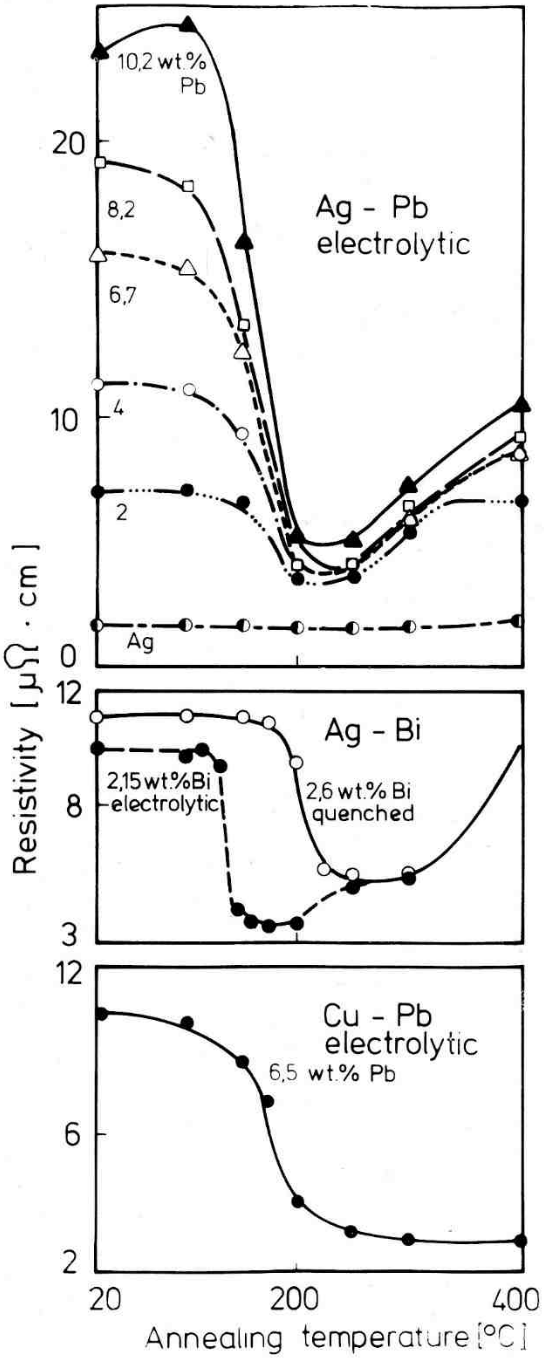


Figure 41 - Resistivity changes of supersaturated alloy deposits during aging.

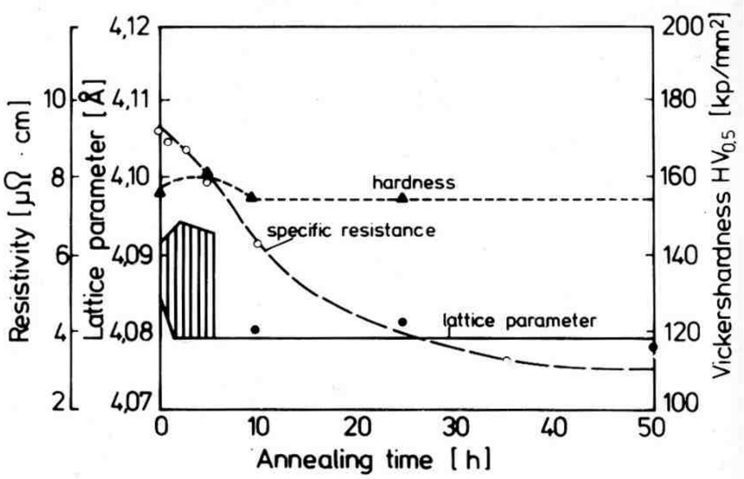


Figure 42 - Changes of the properties of a bismuth-silver alloy deposit with 2.15 wt% Bi during aging at 140°C.

A heat treatment is often of special value for practical use when during simultaneous electrocrystallization little or no solid solutions are formed. Electrodeposited gold alloys are only chemically resistant when all components, at a high enough gold content, are present in solid solution with gold. This is significant for white and colored gold alloys, containing metals like copper, cadmium or nickel, when these metals are not or are only partially in solid solution and crystallize as less noble metals or gold compounds. If in these alloys the second phase is present as small particles, it is easy to bring them into solid solution with gold at adequate temperatures. The necessary temperature depends on the specific metals to produce solid solution with gold. The heat treatment should be in vacuum or in a neutral or reducing atmosphere to prevent oxidation. At most in colored gold alloy deposits from alkaline cyanide baths the inclusion of non metallics is so slight that no difficulties will occur during heat treatment.

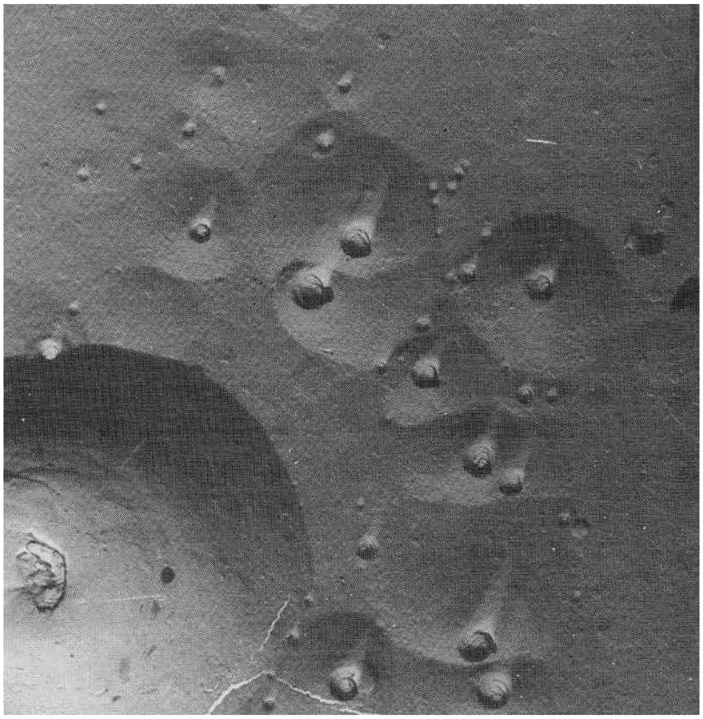


Figure 43 - Crater formation on the surface of a hard gold deposit (Ni-Au) from the acid bath after heating at 500°C for 15 min. Original magnification 10,000×.

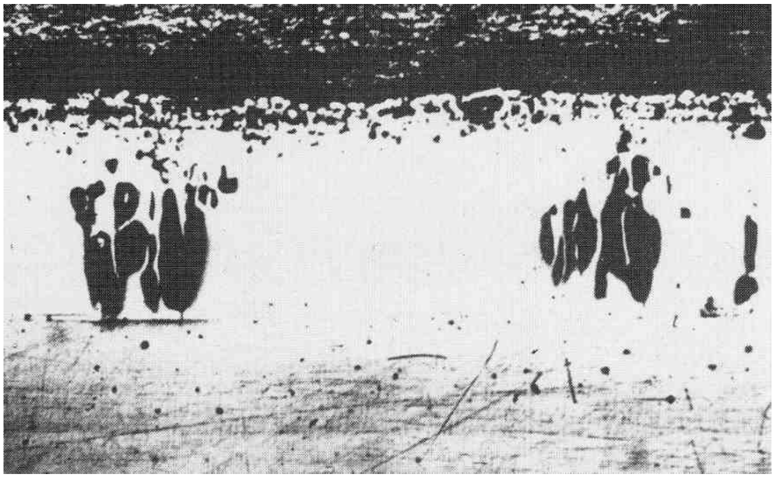


Figure 44 - Diffusion in copper-plated zinc after annealing at 400°C for 24 hr.

Diffusion properties are of interest to the electroplating industry from other points of view too. Diffusion in the solid state takes place only when the components form solid solutions or intermetallic compounds. Low-melting metals in which diffusion occurs at room temperature or lower are able to form alloys at rather low temperatures. The so called "sink in" of brass deposits on zinc is caused by diffusion of zinc to the surface, which assumes the color of zinc. Also between silver or copper deposits and underlying zinc, diffusion is fast at relatively low temperatures. This property was utilized for the production of brass deposits with controlled composition by electrodepositing copper and zinc successively on iron with a subsequent heat treatment. Using this method one has to keep in mind that first copper must be deposited on iron, because during heating, diffusion and alloy formation between zinc and iron occurs as well as between copper and zinc. If zinc is first deposited it is impossible to get a brass layer with desired properties. When one of the components diffuses faster than the other, holes may form in the diffusion zone (Kirkendal effect). This is shown in Fig. 44 for copper deposits on zinc after annealing at 400°C.

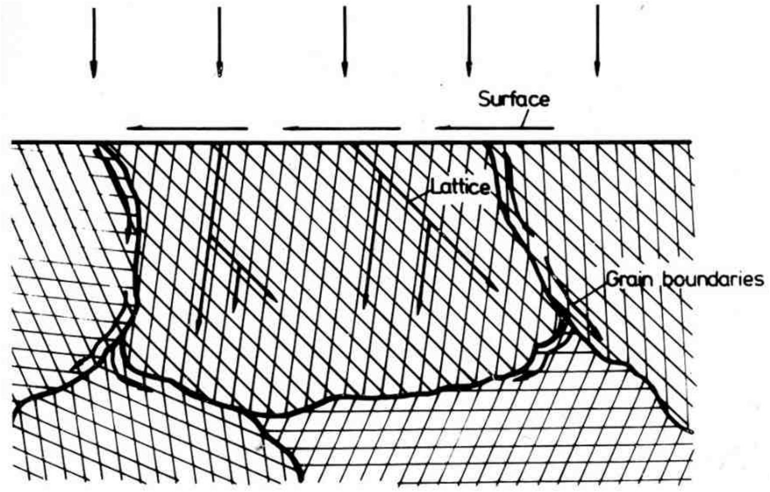


Figure 45 - Schematic representation of the diffusion types.

The diffusion between surface layer and underlying metal is of great interest. Under certain circumstances it can be of practical advantage, in other cases it is disadvantageous. One has to distinguish between surface, lattice and grain boundary diffusion, as shown in Fig. 45. Surface diffusion is characterized by atoms diffusing along the surface. During lattice diffusion they move uniformly along within the crystal lattice. Grain boundary diffusion along the grain boundaries is generally undesirable. Figure 46 shows grain boundary diffusion for a pure gold deposit on silver. By this type of diffusion the effective layer becomes thinner. The effect of diffusion of gold on alpaca, a nickel-copper-zinc alloy, is quite different. Figure 47 shows in the left portion gold plated alpaca prior to diffusion annealing. In the right portion the same sample is shown after diffusion treatment. In this case a thicker alloy plate has formed by lattice diffusion, which is still corrosion resistant. Only small grain boundary diffusion occurred. A sharp distinction between the three types cannot be made. In general, all three types of diffusion can be observed simultaneously, *e.g.*, in chromium-iron samples.

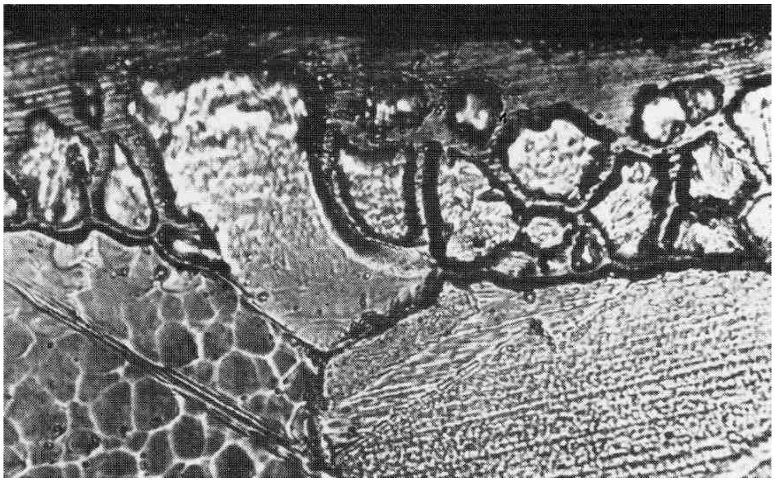


Figure 46 - Diffusion of gold and silver in gold-plated silver during annealing.

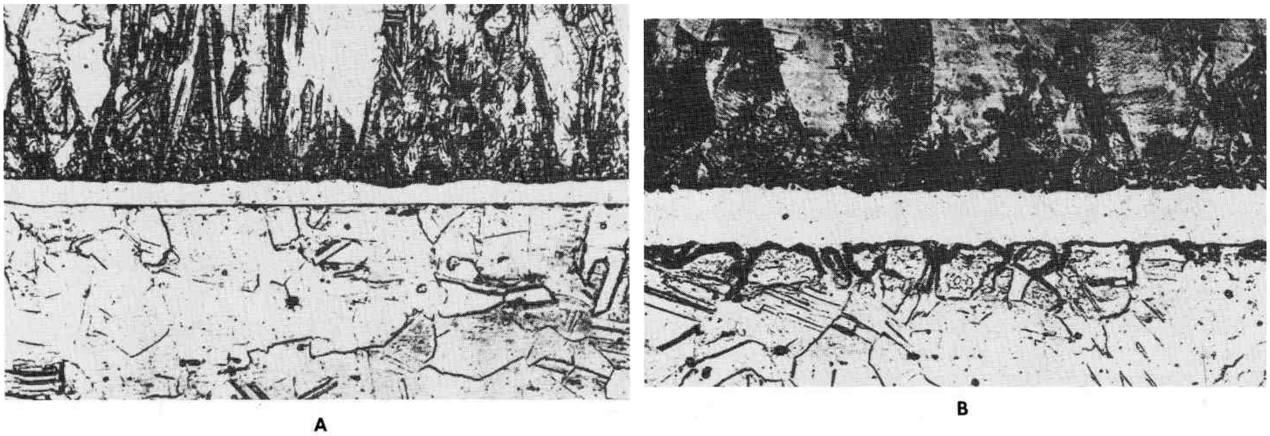


Figure 47 - Gold-plated alpaca with 13% Ni: (a) prior to diffusion annealing, (b) after diffusion annealing.

As an example of surface diffusion, the diffusion of chromium and iron, may be mentioned. Figure 48 shows the edge of an iron sheet chromium plated on one side after annealing at 850°C and 1000°C. On the original chromium-free edge a thin chromium-iron alloy has been formed at 850°C. Annealing at 1000°C has caused a relatively thick chromium-iron alloy layer on the unplated surface. Surface diffusion of chromium on iron depends on the atmosphere. In the presence of only small amounts of oxygen, surface diffusion is nearly zero. Trace amounts of volatile chlorides, such as chromium (II) or iron (II) chloride in the atmosphere strongly intensify surface diffusion. An intermediate layer of copper retards the diffusion of the chromium and iron as long as the temperature is below the melting point of copper. Most influential is the carbon content of iron because of the formation of ternary chromium-rich carbides. These act as a barrier layer and prevent further diffusion.

The pronounced surface diffusion of chromium on iron is sustained by the relatively high vapor pressure of chromium at high temperatures.

To prevent diffusion, nickel is used under gold layers on silver or copper and copper alloys. But for very thin layers of gold, nickel as barrier layer is not sufficient since at temperatures high enough the gold-nickel diffusion has to be considered.

According to J.C. Turn and E.L. Owen,[69] chromium and nickel with 8 to 10% P are the most effective barriers for the copper-electrodeposited gold system.

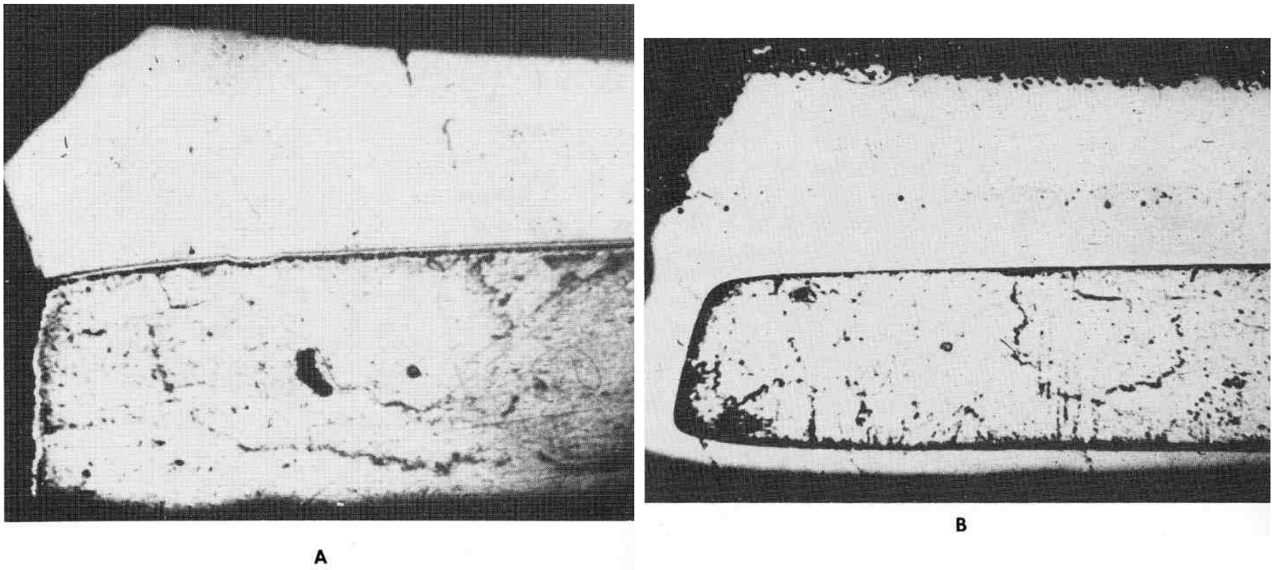


Figure 48 - Surface diffusion in sheet steel, chromium plated on one side: (a) annealed at 850°C, 24 hr., (b) annealed at 1000°C, 24 hr.

High melting point metals, such as molybdenum, tungsten, tantalum and others react readily with gases, especially oxygen, at high temperatures. This behavior restricts their usage. To prevent these reactions electrolytic surface layers of precious metals have been proposed. As protective coatings, silver deposits cannot be used because oxygen diffuses in silver at elevated temperatures at a very fast rate, so that oxidation of the underlying metal occurs even if the silver layer is free from pores. Gold and platinum are the only metals which are impermeable for gases at high temperatures. Gold does not alloy with molybdenum or tungsten. With other high melting metals, such as vanadium, niobium and tantalum alloy formation takes place at relatively low temperatures and the function as barrier layer is lost. Gold can be used in an extended temperature range only on molybdenum and tungsten, but a disadvantage is that pores in the gold deposit on these metals cannot be sealed by heat treatment. Furthermore, at temperatures near the melting point of gold very coarse grains are formed and at the grain boundaries of the gold layer pores show up through which oxygen reacts with the underlying metal. Platinum reacts with all high melting metals in the solid state, and intermetallic phases are formed.

Since gold does not diffuse into molybdenum or tungsten, it was of interest to investigate the influence of an intermediate layer of gold before electroplating with platinum. Platinum and gold diffuse at high temperatures very rapidly with the formation of mutual solid solutions. The affinity of platinum to the high melting metals to be protected is higher than it is to gold. Platinum diffuses through gold and reacts with molybdenum forming the hexagonal close packed ε-phase of the platinum-molybdenum phase diagram.[70] At high enough temperatures, the cubic A-15 phase is formed which exists only as a high temperature phase. Its presence causes embrittlement and crack formation in the alloy layers. After annealing long enough, all of the platinum migrates through the gold, so that finally a pure gold layer is on the surface and beneath it molybdenum-platinum phases are formed. The structures of these phases depend on annealing temperature and time. Therefore platinum and gold-platinum double layers, as protection for high temperature use of high melting metals, are restricted by temperature and time.

As shown, the formation of alloys by diffusion of a deposited metal with the underlying metal, or by mutual diffusion of two or more electrolytic layers may be useful in some cases but in others it is detrimental.

Summary

In the present paper only some aspects of alloy plating could be discussed. In a broader sense the problems of the electrodeposition of alloys are very complex and touch nearly all questions of electrodeposition. In the past years alloy plating has grown fast, especially for functional purposes. It must be understood that alloy plating, sometimes in connection with diffusion treatment, is only used when it gives advantages over pure metals. In spite of enormous research and development work, not all possibilities of alloy deposition for practical use have been exhausted. The properties of electrodeposited alloys are quite often different from those of melted alloys of the same composition. This is sometimes a disadvantage and prevents immediate industrial use but shows new directions for further scientific and practical work.
Not all alloys in technical use can be electrodeposited. On the other hand electrolytic deposits of alloys which have no importance in the cast and recrystallized state are used technically, *e.g.*, nickel-tin.

Abner Brenner, in his book *Electrodeposition of Alloys*, on page 256 called me "a protagonist of the idea that the properties of even the bimetallic alloys are largely determined by the presence of inclusions." You will understand that living up to this reputation in my paper, non-metallic inclusions were discussed extensively.

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#16 - Ernst Raub - 1975

About the author

This piece was written at the time Dr. Raub was announced as the recipient of the 1974 Scientific Achievement Award:

Dr. Ernst Raub has been chosen by the AES Scientific Achievement Award Selection Committee as the 1974 recipient. The announcement was made at the opening session of the 61st Annual Technical Conference of the American Electroplaters' Society in Chicago on June 17, 1974.

Dr. Raub was born on April 5, 1905 in Klotingen/Westphalia. He obtained his Ph.D. at the University of Münster and immediately afterwards started his work as a research assistant at the fledgling Forschungsinstitut für Edelmetalle in Schwäbisch Gmünd. The wide scope of his interests already shows up in his first papers in 1928, "On the Behavior of Natural and Cultured Pearls in UV Light," "Investigations on the Ag-Cu Eutectic" and "Equilibrium Studies in the Systems Co-S-O and Ni-S-O."

His first paper on an electroplating problem appeared in *Mitteilungen des Forschungsinstituts* in 1930, dealing with the analysis of chromium plating solutions. From this time on, papers from Dr. Raub and coworkers appeared in various German and international journals at an average rate of about seven per year.

In 1934, Dr. Raub was appointed director of the Forschungsinstitut für Edelmetalle and in the same year he started giving lectures on plating and precious metals technology at the University of Stuttgart. From 1930 on, the Forschungsinstitut arranged highly esteemed two-week training courses of electroplating. These courses grew into classes for electroplating engineers in the later Fifties and formed the basis for the electroplating branch of the Staat-liche Ingenieurschule Aalen, of which Dr. Raub became the founding director in 1962. He retired from this position in 1970.

Dr. Raub has published more than 300 papers, about half of which are concerned with electroplating problems. He is author or coauthor of several books on noble metals and electroplating. His book, *Die Edelmetalle und ihre Legieurungen*, is the first book covering this subject from scientific and technical aspects. From 1955 to 1967, Dr. Raub was an editor of *Metalloberfläche* and the founding president of the Deutsche Gesellschaft für Galvanotechnik, of which he has been honorary president since 1968. He is an active member of numerous German and international societies.

He received the AES Bronze Medal in 1959 and the Grosse Verdienstkreuz der Verdienstorden of the Federal Republic of Germany. He has many personal friends all over the world and has been to the United States several times. Many foreign visitors have spent an enchanted evening in his home.

His son, Dr. Christoph J. Raub, succeeded him as head of the Forschungsinstitut. He has three grandsons, the oldest a resident of California. Together with his wife he is interested in painting, his specialty being animal paintings of various styles and periods. In addition to this hobby, he likes to go swimming and walking and to grow his own fruits and vegetables in what spare time he has left while still arriving at the Institute regularly at 6:30 A.M.