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The electrodeposition of palladium–iron alloys

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THE ELECTRODEPOSITION OF PALLADIUM - IRON ALLOYS

by

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November 1998

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THE ELECTRODEPOSITION OF PALLADIUM-IRON ALLOYS

M. E. BAUMGAERTNER

SYNOPSIS

The main subject of the thesis is the investigation of palladium-iron alloy electrodeposition from aqueous solutions in general. Palladium-iron alloy deposits could be in principle a substitute for nickel or nickel-palladium deposits to avoid metal dermatitis. Nickel contact dermatitis is an especially sensitive allergy caused by decorative or functional use of nickel: it needs to be avoided in a number of applications.

Electrochemical and chemical experiments have been carried out on several solutions with variable pH, salts and metal complexes to design a chemical and electrochemical stable electrolyte for palladium-iron alloy electrodeposition. Electrochemical measurements, physical and chemical analysis techniques, mechanical, optical, chemical and electrochemical measurements methods as well as different corrosion tests were used to describe the electrochemical processes and the properties of the palladium-iron deposits.

Investigations have shown that from ammoniacal electrolytes electrodeposition in a wide range of composition is possible ($\text{pH} = 7.5 - 10.5$). Electrolyte consists of palladium as $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ and iron as iron(III)-citrate. Composition of the deposited alloys depends mainly on the ratio of the metal ions in the electrolyte, while the effect of current density and electrolyte temperature is slight. Current efficiency depends on iron concentration in the electrolyte and is a maximum of ca. 85 %. Palladium-iron alloys with a higher content of palladium ($\geq 80 \text{ wt.-%}$) show cracks because of the high internal stress (tensile stress) of those layers. Alloys with smaller content of palladium ($\leq 20 \text{ wt.-%}$) are less sensitive to cracking.

Wear resistance and corrosion resistance of the palladium-iron alloys are similar or sometimes better to palladium, palladium-silver, palladium-cobalt or palladium-nickel deposits. Hardness of the palladium-iron layers increases with increasing iron content from 200 to 600 VHN. Contact resistance is low in the range of 0.5 to 1.5 $\text{m}\Omega$ and barrier layer properties are excellent for gold and copper diffusion during services up to 160 °C for 240 hours.

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The FEM is gratefully acknowledged for giving me the opportunity, time and facilities to complete this work.

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**Ihre Entstehung verdanken
die Meisterwerke dem Genie;
Ihre Vollendung dem Fleiß.**

Joseph Joubert 1754 - 1824

**Creation of a masterpiece is a production of genius;
accomplishment is the product of diligence.**

**To my dear wife, Andrea,
for her encouragement and patience**

SUMMARY

The main subject of the thesis is the investigation of palladium-iron alloy electrodeposition from aqueous solutions in general. Palladium-iron alloy deposits could be in principle a substitute for nickel or nickel-palladium deposits to avoid metal dermatitis. Nickel contact dermatitis is an especially sensitive allergy caused by decorative or functional use of nickel: it needs to be avoided in a number of applications.

Electrochemical and chemical experiments have been carried out on several solutions with variable pH, salts and metal complexes to design a chemical and electrochemical stable electrolyte for palladium-iron alloy electrodeposition. Electrochemical measurements, physical and chemical analysis techniques, mechanical, optical, chemical and electrochemical measurements methods as well as different corrosion tests were used to describe the electrochemical processes and the properties of the palladium-iron deposits. Investigations have shown that from ammoniacal electrolytes (pH = 7.5 - 10.5) electrodeposition in a wide range of composition is possible. Electrolyte consists of palladium as $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ and iron as iron(III)-citrate. Ammonium citrate and ammonium sulphate were added as well as ammonia to adjust pH.

Bright layers without cracks up to a thickness of 2.5 - 3.5 μm can be deposited with current densities of 0.5 - 10.0 A/dm^2 in a temperature range from 25 - 75 °C. Composition of the alloys depends mainly on the ratio of the metal ions in the electrolyte, while the effect of current density and electrolyte temperature is slight. Current efficiency depends mainly on iron concentration in the electrolyte and is a maximum of ca. 85 %. Palladium-iron alloys with a higher content of palladium show cracks because of the high internal stress (tensile stress) of those layers. Alloys with smaller content of palladium are less sensitive to cracking. Hydrogen content of the layers depends on deposition parameters and is, at lower temperatures of the electrolyte and high cathodic current densities, the lowest.

Wear resistance under dry conditions is better than those of palladium, silver or gold-alloys and similar to palladium-nickel or palladium-cobalt layers. Hardness of the deposits depends on the iron content of the layer and increases with increasing iron content from 200 to 600 $\text{VHN}_{0.01}$. Contact resistance is low in the range of 0.5 to 1.3 $\text{m}\Omega$ and barrier layer properties are excellent for gold and copper diffusion during services up to 160°C for 240 hours. Corrosion resistance of the alloys depends on the kind of corrosive media and is therefore similar or sometimes better or reduced to palladium, palladium-silver, palladium-cobalt or palladium-nickel deposits.

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1. INTRODUCTION

Electrodeposited alloys from aqueous solutions have been developed and are used because of their not obtainable with pure metals [1,2]. Among the early objects for electrodeposited alloys was simply to reduce cost [3-5]. Today, electrodeposition of alloys is part of every industrial production from machinery to electronics. Examples range from magnetic layers on the basis of iron-nickel or cobalt-palladium and platinum alloys over gold-iron, gold-cobalt or gold-nickel alloys for electrical contacts to brass for metal, rubber or plastic items [6]. The mechanical properties of nickel-phosphorous and cobalt-phosphorous, both electroplated and autocatalytic, demonstrate not only excellent wear performance in many applications [7,8], but also corrosion performance surpassed only by some of the titanium or cast nickel super-alloys. For better corrosion protection of iron or steel, zinc based alloys, like zinc-nickel, zinc-cobalt or zinc-iron are reliable and well established elements in automobile manufacturing.

The most recent application of an alloy deposited from the beginning of alloy plating, is yellow or white bronze used today as an alternative for nickel in costume jewellery with more or less success. Because only few researches on palladium-iron electrodeposition have been reported [9-11], and no systematic investigations on the process parameters and deposit properties exist, the main subject of this thesis is the investigation of palladium-iron alloy electrodeposition from aqueous solutions in general. Substitute for nickel or palladium-nickel is an additional aim of the research.

There are nine metals in Group 8 of the periodic system. Iron is the first member of the first triad of Group 8 of the transition metals in the Periodic Table. The metals in Group 8 can be divided in two subgroups: 1. The three iron group metals, iron, cobalt and nickel and 2. the six platinum group metals, ruthenium, rhodium, palladium, osmium, iridium and platinum. Typical for these transition metals are multiple valences, coloured ions and the tendency to complex formation in aqueous solutions [12,13]. Iron, cobalt and nickel are very similar in physical and chemical properties. They are all magnetic: iron the most and nickel the least, chemically, iron is the most active, as evidenced by its great tendency to oxidise: rust as a typical surface state of iron is well-known! Nickel is the least active and under most conditions tends to become passive and to resist tarnish or oxidation. Cobalt is intermediate in chemical

properties. Electrochemically these three iron group metals are characterised by chemical polarisation. They are not deposited at an appreciable rate until potentials considerably more negative than their equilibrium potentials have been reached. This delay in deposition may be associated with the initial deposition of the metal in an unstable state, which slowly changes to the stable form. Each of these three metals has compounds with valences of II and III, with higher valences in some unusual compounds [14]. The divalent compounds of iron, i. e. the iron(II) compounds, are readily oxidised to the trivalent iron(III) compounds, which are the most stable [15,16]. With nickel and cobalt, the divalent compounds are most stable. Therefore, nearly all electrodeposition of these three metals is carried out from their divalent compounds.

The next six metals in Group 8 are the so-called platinum metals: ruthenium, rhodium, palladium, osmium, iridium and platinum. The platinum metals are among the scarcest of metallic elements, and thus their cost is high. Their most exceptional trait in the metallic form is their excellent corrosion resistance due to their nobility. The electroplating of the platinum metals from aqueous electrolytes for practical applications is limited principally to palladium, and to a much lesser extent to platinum, rhodium and thin layers of ruthenium. There are practically no electrolytes available for the electrodeposition of osmium or iridium and they have no commercial position at present.

Palladium is used as a gold substitute in the electronic industry for electrical contacts, especially those operating at low current and voltages. In many respects the properties of palladium are closely associated with those of platinum and gold. Because it resists oxidation and tarnish in most of the atmospheres, it enables reliable performance and low electrical noise. Several alloys of palladium have been developed to meet specific contact requirements. Palladium provides the required noble metal characteristics while additions of other metals improve hardness, wear resistance or reduce production costs. Primary alloys are palladium with 30 to 50 per cent silver, 30 to 50 per cent cobalt and palladium-nickel with 20 to 25 per cent nickel. Palladium-nickel is the most common palladium alloy today.

Chemically palladium, as a platinum metal, is characterised by the ease with which it forms stable complexes in solution [12,13]. Therefore, palladium can be electroplated

from a wide variety of systems, which can be broadly characterised as ammoniacal, chelated, or acid processes. Of these, today the most numerous used are the ammoniacal systems, in which palladium is present as an ammine complex such as palladosamine chloride $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ or diaminodinitrite, $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$, which is known as the P-Salt. Therefore, nearly all electrolytes in common use are of this nature, the metal being present either as an anionic or cationic complex ion like $[\text{Pd}(\text{NH}_3)_4]^{2+}$ or $[\text{Pd}(\text{NO}_2)_4]^{2-}$. Even in the nominally simple palladium salt electrolyte the metal is probably present as a simple hydrated anion $[\text{Pd}(\text{Cl})_4]^{2-}$ or cation or in some intermediate forms [3,14,17]. These complexities of the platinum metal chemistry causes sometimes difficulties in the production of reproducible performance, but enables otherwise noble metals to be reasonably easily processed [13].

Although iron is the cheapest metal available and easily electroplated from several types of electrolytes iron electroplating is not widely used. Iron has no decorative applications because of its low corrosion resistance. On the other hand palladium as a platinum group metal is more noble, with the disadvantage that electrodeposition from simple salts is difficult. Mechanical properties, like hardness, wear resistance, and stability of the plating solution can be improved by adding a metal from the iron group, like nickel.

Basis for the development of a palladium-iron alloy electrodeposition technology is therefore as follows. First the improvement of the properties of the single metals: in the case of palladium this could be a better wear resistance, better solderability, reduced brown powder effect, etc. and in the case of iron mainly a better corrosion behaviour is expected. But the first priority is that the metals' solution chemistry must produce deposits with acceptable physical properties at practicable plating rates and a minimum of stability of the electrolytes.

2. LITERATURE REVIEW

2. 1 Iron Electrodeposition

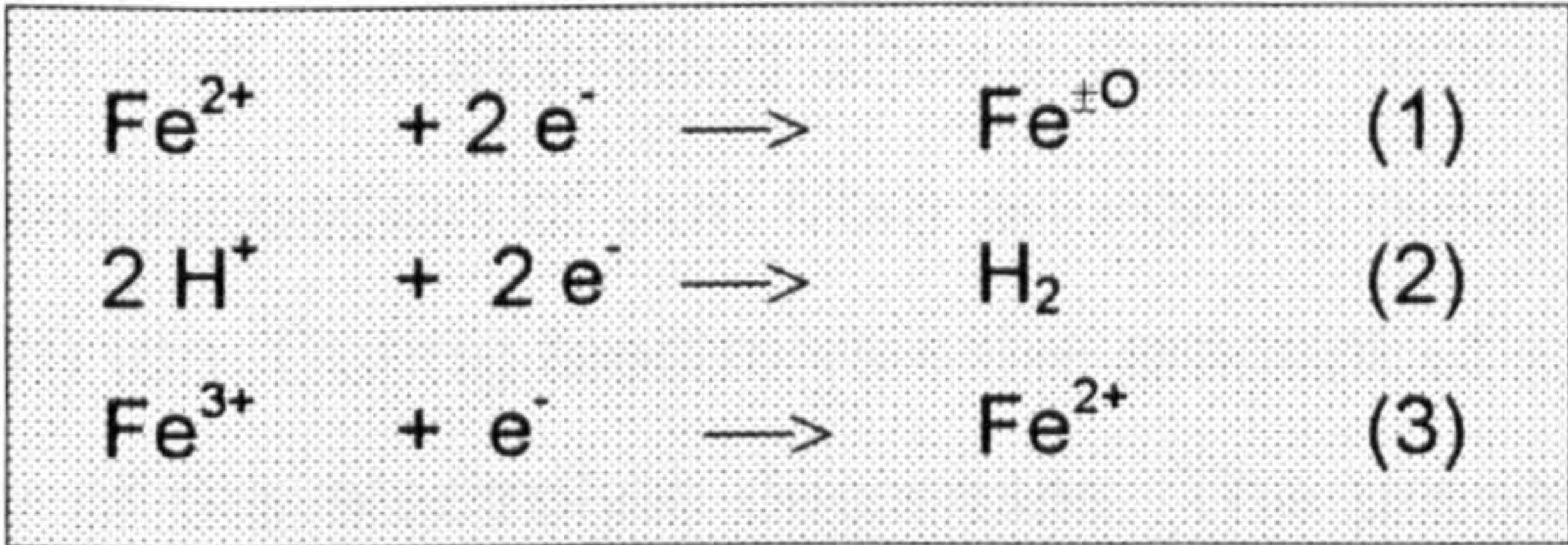
As mentioned above iron readily tarnishes and rusts in most atmospheres. Therefore, iron is not used as a protective coating for technical or decorative applications. The principal uses of iron deposition depend upon its advantageous physical properties and its cheapness [2, 3,14]. It is mainly employed in electroforming and in special instances because of its magnetic properties [12, 14]. It can also be used as a means of preparing pure iron in either a dense or a powdered form [12]. In fact, much of the deposition of other metals is done in order to cover and to protect iron or steel against corrosion. But one advantage of iron deposits is that they are soft enough to be machined or otherwise finished, after which they can be case-hardened [2,3,14]. The interest in iron electrodeposition was always connected with the availability and costs of other metals, like copper or nickel. In times when these metals were very expensive or not available a lot of research on iron electrodeposition has been carried out.

The electrochemical properties of iron, especially the anodic reactions, have been studied extensively over a long time, even because of the great importance of iron as a bulk material with the disadvantage of poor corrosion protection under most atmospheres [12,13]. In the case of cathodic reactions the two states of iron, the iron(II) state and iron(III) state is the most important. In the iron(II) state iron hydroxide is slightly amphoteric, dissolving easily in acids but also in concentrated sodium hydroxide. In an un-complexed form iron(II) is somewhat more stable than iron(III). Iron(II) salts are however easily oxidised to iron(III) state. Iron(II)-chloride for example is the salt of a weak base ($\text{Fe}(\text{OH})_3$) and a strong acid (HCl) and hence aqueous solutions suffer hydrolysis with the production of free acid which lowers the pH from the neutral value of $\text{pH} = 7$. Iron(III)-chloride on the other hand is a common impurity of iron(II)-chloride and is readily produced by atmospheric oxidation of the ferrous salt. In complex compounds, the iron(III) state is the more stable [15,16]. Iron(III) forms many complexes with inorganic and organic ligands. Nevertheless, the complex chemistry of iron(III) is almost as extensive as that of chromium [3,14].

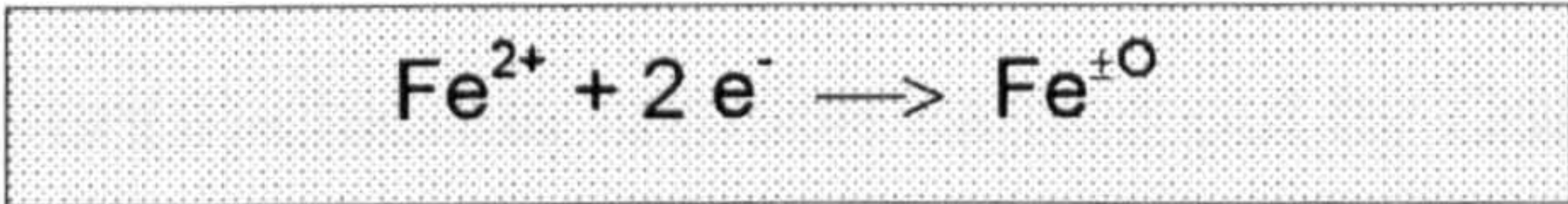
From the standard potentials it is seen that oxidation of iron in simple solutions is easier in the presence of groups that precipitate or complex the oxidation product. Iron(III) is quite easily reduced to iron(II), but under alkaline conditions iron(II)hydroxide is readily oxidised to iron(III). Since hydrated iron(III)-oxide is much more insoluble than iron(II), acidic pH is required in order to maintain a solution in the reduced form and to prevent the precipitation of Fe(OH)₃.

Nevertheless, the main problem of such electrolytes is the tendency of iron(II) salts to oxidise in the air to form iron(III) salts; in practice it is not yet solved. Different ways of solving the problem like covering the electrolyte with plastic balls, large an-ode area, addition of iron chips, etc. [4,14] were suggested and some are in use.

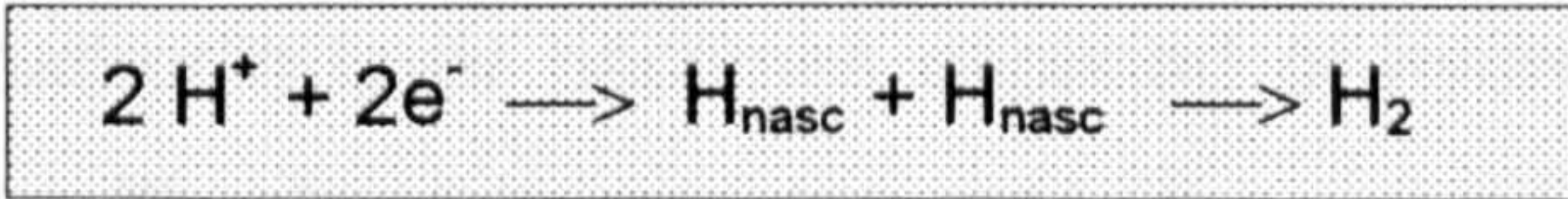
Additionally to the oxidation of iron(II) ions, caused by the chemistry of the solution or the oxygen in the air, iron(III) ions are also generated during the electroplating processes. Therefore, iron electrodeposition from iron(II) solutions is always a result of several reactions:



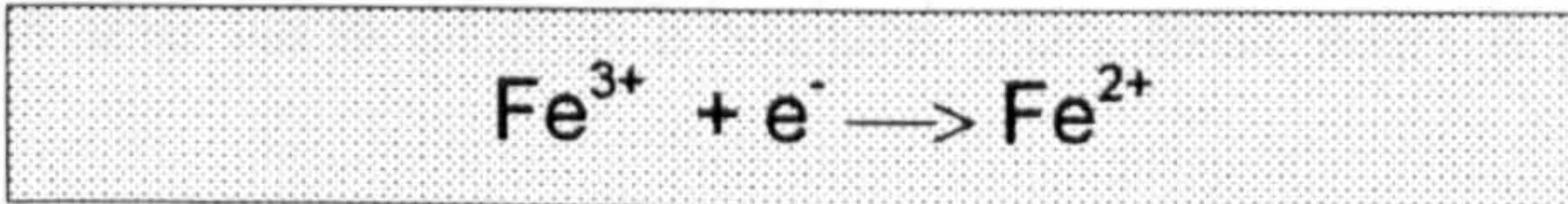
The cathodic half cell reaction is mainly metal deposition (1):



Cathode efficiency will depend to a large extent on the pH of the solution. As pH de-creases, efficiency is likely to drop as the side reaction (2) and hydrogen evolution



assume greater importance and more hydrogen is evolved. Cathode efficiency may also be lowered by the reduction of iron(III) ion at that electrode (3):



This reaction will be negligible if the concentration of iron(III) ion in solution is main-tained at a low level. But, in the case when iron(III) ion concentration in the solution

is high (several grams), reduction of iron(III) ion to iron(II) ion could become the main reaction. Similarly the reduction of iron(III) ion in cathodic film or in the nearness of the cathode surface by nascent hydrogen (H_{nasc}) will be negligible or dominant depending on iron(III) ion content and pH of the solution.

An examination of the standard oxidation potentials of the reactions possible at the anode shows that theoretically the reaction occurring will be oxidation of iron(II) ion to iron(III) ion.

H_2O	\longleftrightarrow	$\frac{1}{2} O_2 + 2 H^+ + 2 e^-$	$E^{\circ}_{25^{\circ}C} = + 1.230 \text{ V}$
Cl^-	\longleftrightarrow	$\frac{1}{2} Cl_2 + e^-$	$E^{\circ}_{25^{\circ}C} = + 1.360 \text{ V}$
Fe^{2+}	\longleftrightarrow	$Fe^{3+} + e^-$	$E^{\circ}_{25^{\circ}C} = + 0.770 \text{ V}$

Table 1
Standard Oxidation Potentials [16]

Practical experience in iron electroplating shows that in reality the anodic reaction occurring during electrodeposition of iron from an iron(II) electrolyte is the oxidation of iron(II) ion to iron(III) ion. During electrolysis the amount of iron(III) ions increases and current efficiency of the electrolyte decreases. The presence of iron(III) ion in the solution not only reduces current efficiency, iron(III) ions also affect the properties of the deposits even in relatively small concentrations [18].

Investigations on an iron(II)-chloride solution carried out by *Domnikov* [20] show the relationship between laminated structure of the iron deposits from electrolysis parameters of the plating solution. The results obtained indicate a direct connection between lamination and the formation of iron hydroxides in the cathodic layer. During electrolysis the cathodic layer becomes depleted of hydrogen ions which discharge on the cathode. This leads to a higher pH in the cathodic layer and results in the formation of practically insoluble iron hydroxides. Hydroxides begin to precipitate out and cause formation of laminated structure. Addition of ascorbic acid, as a reducing agent, reduces the ions of the trivalent iron and with it prevention from laminated structure [20].

Electrolyte Type	Chloride	Sulfate	Double Sulfate	Sulfate Chloride	Fluo-borate	Sulfa-mate
Iron Content (g/l)	80 - 125	48	36 - 51	60	55	75 ^{*)}
$\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$	250 - 450			36		
$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$		240		250		
$\text{Fe}(\text{SO}_4)(\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$			250 - 360			
$\text{Fe}(\text{BF}_4)_2$					227	
CaCl_2	100 - 300					
NaCl					10	
NH_4Cl				20		
$\text{NH}_4\text{S}_3\text{NH}_2$						30 - 38
pH	1.2 - 1.8	2.8 - 3.5	2.8 - 5.5	3.5 - 5.5	3.0 - 3.4	2.7 - 3.0
Temperature (°C)	85 - 95	30 - 65	20 - 65	30 - 70	55 - 65	50 - 60
Current Density (A/dm ²)	2 - 8	4 - 10	2 - 10	2 - 10	2 - 9	5
Current Efficiency (%)	95 - 100	95 - 100	95 - 100	95 - 100	60 - 90	95 - 100

^{*)} As sulfamate concentrate

Table 2
Common Electrolytes for Iron Electrodeposition [14]

It might appear desirable to use the more stable iron(III) compounds for plating solutions. However, the yield of iron for a given current at 100 per cent cathode efficiency would be only two-thirds as much from an iron(II) as from an iron(III). Even in iron(II) electrolytes the presence of iron(III) in more than trace concentrations (100 mg/l up to 3 g/l) cause a considerable reduction of current efficiency [21,22].

Moreover the iron(III) salts tend to hydrolyse in aqueous solutions and to precipitate as iron(III)-hydroxide, unless considerable free acid is present. On the other hand, further investigations turned out that reactions of iron with oxygen are too complicated to describe them with simple models. Presence or absence of moisture, for example, has a distinct effect, too. The exact mechanism is not known in detail even today [22].

The first authentic description of an iron electrolyte for the deposition of iron was probably that of *Böttger* published in 1846 [23]. *Böttger* used a plating solution containing sulfate and ammonium chloride. In 1869 *Jacobi* [24] described the results of electroplating with iron on copper for making dies and plates for notes by a process worked out by *Klein* in 1868 [25]. The plating solution was a cold sulfate electrolyte consisting of FeSO_4 and $(\text{NH}_4)_2\text{SO}_4$. In 1905 *Maximowitsch* also investigated a iron(II)-sulphate electrolyte for the electrodeposition of plates to print Russian bank notes [26].

Modern electroplating of iron nowadays is also mainly conducted from iron(II) salts, usually the chloride or sulfate or mixtures of the two [2,3,14]. Common electrolytes and the most commercial used solutions are summarised in table 2 (on page 7). From sulfate electrolytes smooth, bright and brittle deposits can be obtained [27-30]. Sulfate is not as soluble as chloride. Sulfate electrolytes work from room temperature to 65 °C, which is an advantage, however, plating rate is slower in comparison with chloride solutions [21]. Where plating speed is of no concern and lower operating temperatures are desired, the sulfate plating solutions are suitable. Chloride electrolytes have a good conductivity and are often used because of their relatively high deposition rate. The most commonly used chloride electrolyte is the iron(II)-chloride / calcium chloride solution [31-35]. Chloride electrolytes operate at temperatures from 85 °C to 95 °C and produce relatively strong, ductile, and smooth deposits [36-40]. The hot, acid solution is very corrosive and special equipment have

to be used. These electrolytes, however, present containment and environmental problems because of the high temperature, toxicity and acidity of the solution [41,42]. Fluoborate [43,44], sulfamate [45,46], and pyrophosphate [47] electrolytes were also developed, but their employment is limited to some special applications. The fluoborate electrolyte has a high conductivity and good stability. Increased operating temperatures permit higher metal content and higher current densities. Organic contaminations cause brittle and stressed deposits. The sulfamate electrolyte is similar to the sulfate electrolyte, but permits higher cathode current densities [46].

Levy and Hutton [48] investigated the electrodeposition and properties of high strength iron foils electroformed from a fluoborate chloride electrolyte. Under a variety of conditions they produced foil up to 1000 μm thick with practicable mechanical properties. The plating solution was very stable with respect to the effect of oxidation and changes in pH. *Farmer et al* [44] described iron plating from fluoborate electrolytes without organic additions. They investigated effects of impurities and their role in pit formation. In addition some comparisons with the iron(II)-chloride electrolyte were made. A ferrous sulphamate electrolyte suggested by *Barret* [45] has been examined in more detail by *Read* [49].

A detailed review covering main electrolyte types which surveys iron alloy deposition and discusses properties was published 1976 by *Walker and Irvine* [50]. A review of the publications from 1965 to 1993 about iron electroplating and their properties is given by *Zesch et al* [22] who summarised main parameters for commonly used iron electrolytes, like chloride, sulphate, fluoborate and ammoniacal solutions and described cracked and crack-free deposits produced under different plating conditions. According to them the properties of electroplated iron deposits are determined by the deposition parameters and by the impurities of the electrolyte. Deposits produced at room temperature are hard and brittle and have a high stress as indicated by a tendency to form cracks. Increase of temperature causes a decrease of brittleness. But the full benefits of higher temperature are not realised below about 90°C.

Hence, *Blum and Hogaboom* [12] suggested for very high current densities that it is desirable to operate at 105 °C and to have a fairly high acidity. Nearly pure iron or steel anodes dissolve readily, but there is some separation of solid particles that may cause rough deposits. From steel anodes this residue or sludge consists chiefly

of carbon, while from iron it may consist of iron oxide. In either case it is desirable to employ anode bags in order to prevent the sludge from becoming suspended in the electrolyte especially when working with sulfate electrolytes.

While most organic impurities cause hard and brittle deposits [42], iron electrolytes are not very sensitive to metallic impurities. Therefore, only few organic additions like wetting agents to prevent pitting are used. *Stoddard* [18] reported the effects of small amounts of manganese(II)-chloride which caused formation of finer grained and more ductile deposits. Aluminium, beryllium and chromium(II)-chloride have also been reported [14] to produce more ductile and softer deposits.

Other authors discovered the effect of organic additives and alternating current on internal stress of electrodeposited iron [32]. Effect of organic compounds and alternating current can be separated. Alternating current can be used to reduce internal stress. Internal stress is more sensitive to use of organic compounds than to over-voltage [51]. Optimisation of conductivity for the iron chloride electroforming solution by addition of other chlorides, e. g. potassium, magnesium, aluminium, calcium, and ammonium was discussed by *Moore and Gabe* [52,53].

A detailed and systematic study of the mechanical properties of electrodeposited iron from chloride electrolyte was carried out by *Max and van Houton* [54] on iron produced from a concentrated solution of iron(II)-chloride and calcium chloride. Specimens were deposited over a wide range of temperature and current densities and the effect of pH and iron(III) ion content were examined. As a result, a sufficiently low pH to maintain iron(III) ions in solution and high electrolyte temperatures are necessary to produce ductile deposits. At electrolyte temperatures less than 88 °C the internal stress was so high that the deposits were non-coherent. Mechanically stirring and ultrasonic agitation also lead to greater hardness value as *Walker and Perrins* [55] discovered from several iron plating solutions.

Liebscher [30] showed applications and problems in electrodeposition of iron and its alloys: applications include electroforming, build-up of worn machinery, wear resistant coatings, ferromagnetic layers and alloying layers. Polarisation plots revealed regions in which the structure of the iron deposits is either polycrystalline or monocrystalline. *Yoshimura et al* described in recent publications [56-58] the preferred orientation and morphology of electrodeposited iron from iron(II)-chloride solution as

well as the relationship between micro-hardness and crystal structure of iron deposits from iron(II)-chloride and iron(III)-chloride solutions. The corrosion properties of iron deposits as an intermediate layer are described by *Clarke* [59] who investigated bright iron deposits in salt spray tests. As a result, iron as an underlayer, with nickel and chromium above, are then more corrosion resistant.

2. 2 Palladium Electrodeposition

Palladium has been electroplated prior to the beginning of the 20th century. By the end of 1840 Smee [60] published a text book entitled: *Elements of Electrometallurgy*, in which he described his processes for both platinum and palladium plating, writing that: *Hitherto the reduction of these metals, in any other state than that of the black powder, has been always considered impossible*. For palladium plating Smee used an electrolyte with nitro-muriate of palladium, ammonia, and a palladium anode and he noticed: *This metal is whiter than platinum, but not so bright as silver. It might be used in the same cases, and with the same advantages as platinum; and we have, besides, twice the bulk of metal in the same weight*.

Pile and Carry, French patent 165,243 (1884) and US-Patent 330,149 (1885) deposited palladium from a chloride solution containing ammonium phosphate and potassium phosphate. Numerous investigations were carried out for palladium electrodeposits mainly for jewellery as a protective finish for silver in the 1930s [61]. But palladium was early displaced in this context by rhodium and thereafter relatively little interest aroused in palladium electroplating until the 1960s and 1970s, when the price of gold peaked, prompting a search for alternatives [62].

Since the first experiments on palladium electroplating many electrolytes have been proposed over all pH ranges [63]. An acid chloride electrolyte prepared by dissolving palladium chloride in hydrochloride acid was originally developed by *Wise* [64,65]. Other main plating solutions are those based on tetra-ammino-palladous chloride dissolved in $\text{NH}_4\cdot\text{OH}$ and NH_4Cl [66] and an electrolyte based on diammino-dinitrito palladium, from which good, bright, and adherent deposits could be obtained [67]. This salt has the valuable attribute of containing, other than metal, only volatile constituents and, as a medium of replenishment, avoids the build up of inert salts in the electrolyte.

Fatzer [68] recorded the production of bright, non-adherent and infinitely porous coatings from a tetrammino-palladous nitrate electrolyte operated at a pH of 9. These results do not accord to the results *Reid* [69] obtained from this electrolyte. At a current density of 0.5 A/dm^2 he obtained semibright deposits, virtually free from cracking. Increase of the electrolyte temperature from 60 to 80 °C resulted in increased porosity.

Attention focused on palladium in 1960s and 1970s as an alternative to gold because the advantages of palladium at that time were both technical and economic ones. Therefore, starting with the previous work in 1950s and 1960s from several research workers [70-77] on palladium plating, numerous papers were published in the years from 1975 to 1985, dealing with new electrolytes and new improved properties of electroplated palladium layers on mainly electrical contact materials [78-103].

Among the main alternatives for gold and hard gold considered were tin, tin-lead, silver, ruthenium, palladium and more recently palladium-nickel alloys and palladium-silver alloys. From the cost standpoint silver would have been an ideal alternative, however, the tendency to form sulfide tarnish films made it only an alternative as a lower cost finish for semiconductor applications. Tin and tin-lead deposits are less resistant to corrosion, fretting corrosion and wear resistance. In the case of ruthenium its use so far appears to be mainly in sealed reed contact applications. Rhodium is only employed in cases where high resistance to wear is a functional deposit requirement. The high cost of rhodium has not made it a serious contender. Therefore, palladium and palladium-nickel deposits are currently used for electrical contact applications, while decorative applications of palladium are limited due to the dark colour of the metal.

In 1965 *Reid* [104] published a comprehensive review of palladium processes and applications in the electronic industry of the United Kingdom and stating that in the United Kingdom it is evident that palladium plating is finding an established niche in the industrial precious metal plating field with prospects of expanding adoption with growing experience and confidence in electrolytes and processes. Today, more than 30 years later, palladium plating is a common plating process in the electronic industry and is a well-established technology. Amongst the platinum metals, palladium is perhaps the easiest to deposit. Currently the ammonia based electrolytes are the most common. In this electrolytes, palladium is based mainly on tetrammino-palladous complexes with different anions, like tetrammino-palladous nitrite $[\text{Pd}(\text{NH}_3)_4](\text{NO}_2)_2$, tetrammino-palladous nitrate $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$, tetrammino-palladous sulfate $[\text{Pd}(\text{NH}_3)_4](\text{SO}_4)_2$, tetrammino-palladous chloride $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and tetrammino-palladous carbonate $[\text{Pd}(\text{NH}_3)_4](\text{HCO}_3)_2$.

The palladium concentration (metal content) can vary from 5 to 35 g/l depending on the application [105]; see table 3 on page 15. Low speed processes such as barrel, rack, or vibratory plating use the lower metal content, whereas high speed plating technique use the highest concentrations [82,106,107]. Conductivity and buffer capacity are achieved by additions of ammonium hydroxide, ammonium chloride, etc., typical around 70 - 120 g/l. Phosphate ion is also used in this capacity from 70 - 100 g/l. The pH range of the electrolytes is pH 7 to pH 9 with operating temperatures from 35 °C to 70 °C, except the sulfite electrolyte working at pH < 1 and temperatures from 20 °C to 30 °C. Organic additives are common in these ammonia based chemistries. Several surfactants, brighteners, and stress reducers are typically used to obtain bright and low stress deposits [14,69,108,109].

A typical problem with palladium plating is plating close to or above the limiting current density. This can result in burnt deposits or in an increase of hydrogen incorporation, which leads to high internal stress and the formation of cracks even during plating of work-pieces with complicated design. Pulse plating technique may be used to solve these problems [110-112].

The ammonia based chemistries can also be problematic sometimes, and are subject to base metal contamination, like copper etching. Electrodeposition from these electrolytes on copper or copper based substrates therefore, requires a gold-, or palladium-strike intermediate layer [113]. However, ammonia gas evolution and connected change of the pH of the electrolyte, resulting from ammonia loss, must not be a compelling disadvantage for such types of electrolytes. Modern process control equipment guarantees exact process control and allows e.g. operating parameters at the lower end of the pH and temperature range, minimising the contrary influence of the ammonia species. Ammonia evolution on the other hand prevents gaseous cyanide incorporation in the electrolyte as well as an increase of the salt concentration in plating solutions.

An additional possibility for palladium solutions uses proprietary organic amines instead of ammonia to complex the palladium. *Morrissey* [114] described a chelated palladium complex based on a mildly acid phosphate electrolyte, which operates, depending on the choice of chelating agent, at pH values from pH 3 to pH 7. This permits direct deposition of palladium on copper, nickel, and copper based alloys

Electrolyte Type	Palladium as P-Salt	Palladium as Sulfate	Palladium as Nitrate	Palladium as Sulfite	Palladium-Nickel as Chloride	Palladium-Nickel as Sulfate
Components	$\text{Pd}(\text{NH}_3)_4(\text{NO}_2)_2$ NaNO_2 $\text{NH}_4(\text{NO}_3)$	$\text{Pd}(\text{NH}_3)_4(\text{SO}_4)_2$ $(\text{NH}_4)_2\text{SO}_4$ NH_4OH	$\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ NaNO_2 Na_2SO_4 KH_2PO_4 (NH_4OH)	$\text{PdSO}_4 \cdot x \text{H}_2\text{O}$ Na_2SO_3 H_2SO_4	$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ NiCl_2 NH_4Cl NH_4OH	$\text{Pd}(\text{NH}_3)_4(\text{SO}_4)_2$ NiSO_4 $(\text{NH}_4)_2\text{SO}_4$ NH_4OH
pH	7 - 9	7 - 9	6 - 7 and 7 - 9	< 1	7 - 9	7 - 9
Metal Content	Pd	Pd	Pd	Pd	Pd Ni	Pd Ni
Strip Plating Barrel / Rack	15 - 35 6 - 12	10 - 20 8 - 10	- 5 - 15	5 - 20 5 - 20 (Rack)	9 - 11 5.5 - 20	10 - 20 8 - 10
Temperature (°C)	50 - 70	35 - 60	45 - 70	20 - 30	25 - 60	35 - 60
Current Density (A/dm ²)						
Strip Plating Barrel / Rack	1 - 120 0.1 - 2.5	5 - 60 0.5 - 2.5	- 0.1 - 3.5	1 - 20 0.5 - 1.0	20 - 75 0.1 - 20.0	5 - 60 0.5 - 20
Current Efficiency (%)	70 - 75	85 - 95	60 - 85	97	90 - 95	85 - 95

Table 3
Common Electrolytes and most Commercial used Solutions for Palladium and Palladium-Nickel Electroplating [105]

without the use of a strike pre-treatment. The metal concentration is in the same range as in the case of the ammonia electrolytes, depending also on the application. Conductivity and buffering are achieved by the presence of phosphate ions in the range of 70 to 120 g/l, or similar conducting salts. The typical pH ranges from pH 9 to pH 12, with operating temperatures of 40 °C to 65 °C. Copper contamination does not seem to be a major problem. Unfortunately, there are some problems with the stability of the chelate complex and palladium deposits show micro-cracks.

A minor class of palladium electroplating solutions operate at low pH, generally in the range of pH 0 to pH 3.0. Based on palladium chloride these solutions use concentrated hydrochloric acid. Even these types of acid palladium electrolytes, like acid chloride electrolyte with 50 g/l PdCl_2 , 30 g/l NH_4Cl , and HCl, have been used to deposit thick layers of very low stress but their application is limited. Because the plating solution is very acid pH 0.1 to pH 0.5 and sensitive to contamination by copper, substrates have to be pre-plated with palladium or gold [14,105,108]. The deposits are dull or semibright. Recent developments of a new acid (pH < 1) sulfite electrolyte have also been carried out [115]. The new electrolyte contains palladium sulphate (PdSO_4), sodium sulfite (Na_2SO_3), and sulphuric acid (H_2SO_4) and produces bright deposits with current efficiencies of 97 %. While ammoniacal and acid systems tend to be more chemically aggressive toward substrates, particularly copper, the acid sulfate/sulfite system appears to be somewhat less chemically aggressive with respect to copper and its alloys than does the acid chloride system.

Friedrich and Raub [116] investigated the laser-enhanced palladium electrodeposition from several palladium electrolytes based on $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$. The results obtained, show that in principle the influence of a laser beam can support electrodeposition, but optimisation of deposition parameters is necessary for further experiments.

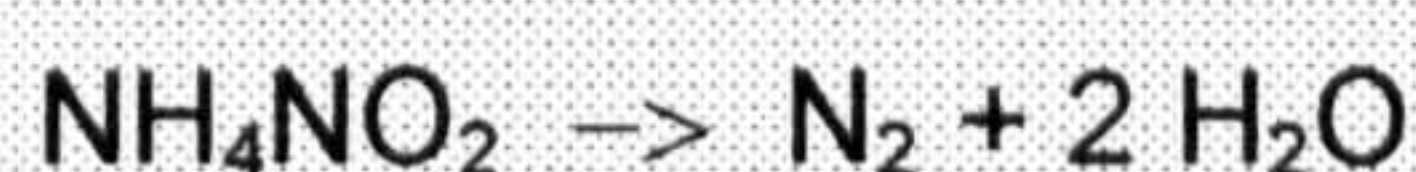
Even though the investigations on palladium electroplating were on a low level during the last years, recent developments on thin multi-layer palladium coatings for semiconductor packaging applications carried out at *AT&T Bell Laboratories* [117] as well as the opportunity of pure palladium deposits as a substitute for palladium-nickel deposits [118] as diffusion barrier layers, give rise to expect a renaissance of palladium electroplating and an increase of research on these types of electrolytes for the future.

The nitrate electrolyte can be simply prepared by dissolving the solid salt in water. Chloride, sulfate, nitrite and carbonate electrolytes are prepared by dissolving the diammino-palladous salt in strong ammonia and adding certain salts like sodium salt or ammonium salts of inorganic acids such as chloride, sulfamate, sulfate, phosphate, nitrate, nitrite or carbonates.

The products of electrolysis of a tetrammino-palladous salt solution are shown by the following equation [12]:



Palladium is anodically insoluble in this type of electrolyte which therefore, must run with insoluble anodes and replenishing the metal in the solution with palladium salt is necessary [119,120]. This practise leads to an accumulation of ammonium salt in the electrolyte. In the case of a tetrammino-palladous nitrate electrolyte the ammonium nitrate produced reduces the current efficiency from 95 to 50 %. If tetrammino-palladous nitrite is used instead of nitrate the lifetime of the electrolyte increases, because ammonium nitrite is unstable and salt accumulation is lessened:



In the palladium chloride / hydrochloric acid electrolyte deposition occurs from an equilibrium:



The palladium is rather loosely bound, so it deposits easily onto less noble metals in an blackish powdery form without external current [63]. At a current efficiency of between 97 and 100 per cent palladium is electrodeposited as a compact crack-free layer, even at higher thickness, with a microhardness of about 250 to 350 VHN.

As mentioned above palladium is a member of the transition metal group of the periodic system. Gold for example belongs to the non-transition metals. This is the cause for several basic differences in the behaviour of gold and palladium [62].

Palladium is catalytically very active both in solution and as metal, while under these circumstances gold is not. Therefore, palladium electrolytes tend to be much more sensitive to impurities or alterations in its composition than a gold electrolyte. Furthermore, palladium is well known for exhibiting the so-called "brown powder effect" which originates from the condensation or polymerisation of organic vapours, emanating from plastics and other sources in the surroundings [62].

A distinctive factor in palladium electroplating is the very high amount of hydrogen evolution parallel to metal reduction. While palladium is an excellent catalyst for hydrogenation reactions it also has a remarkable ability to absorb hydrogen [121]. An unstable thermodynamic phase resulting from high hydrogen in the lattice can cause cracking of palladium deposits during or after plating thus exposing the less noble substrate and significantly reducing corrosion performance [2,3,12-14,92].

The key is keeping the H : Pd ratio below 0.03 since in this range palladium hydride is present as a face centred cubic α -phase with a lattice constant close to that of pure palladium. Escape of hydrogen from this structure does not cause significant lattice contraction. When the H : Pd ratio is above 0.57 palladium hydride is present in a cubic face centred β -phase with a lattice constant which is about 3.8% higher than that of the α -phase [122,123].

These reactions are controlled by the electrochemical characteristics of the metal ions and hydrogen ions, stability of the metal complexes, kinetic of the anodic and cathodic reactions occurring, temperature of plating solution, concentration of the complexing ligands and hydrogen ion concentration in the electrolyte (i. e. pH). The hydrogen to palladium ratio in the deposits can be further controlled by increasing the relative concentration of Pd ions : H ions at the electrode surface. This can be accomplished by increasing the bulk concentration of palladium and the electrolyte agitation [123,124].

Therefore, the problems usually encountered in palladium electrodeposition are: hydrogen embrittlement, limited deposition rates, unstable chemical systems, unstable buffer (pH) systems, chemical attack of non-noble metal substrates and high cost of chemistries. In order to develop viable new palladium or palladium alloy electrolytes these problems must be considered and if possible, solved or their effects must be minimised at least.

2. 3 Palladium-Nickel Alloy Electrodeposition

One of the earliest patents dealing with the deposition of alloys of the platinum metals was the one issued to *Thomas and Burgum* in 1894 [126]. It dealt with the co-deposition of platinum, palladium, and iridium with the baser metals tin, cadmium, zinc, cobalt, and copper. The electrolytes were alkaline and contained cyanide ions. In view of the difficulty to deposit platinum metals from cyanide electrolyte, the utility of this patent is doubtful [2]. Similar to palladium electrodeposition, there has been always a considerable demand for palladium-alloy electrodeposition [2] despite the relative difficulty of electroplating an alloy with satisfactory physical properties. Since the first employment of a micro-cracked palladium-nickel deposit, numerous investigations on improved alloy coatings and electrolytes were carried out. Especially the substitute of gold or hard gold in view of an application in the electronic industry was the subject of the main research [127-137].

Nowadays palladium alloy electrolytes in the form of tetrammine, diamminedinitrite, ethylenediamine, or tetra-complexes are the basis of the commercially available chemistries. The plating solutions for commercial palladium alloy electrolytes are generally based on the same or similar complexes as the ones for palladium alone [62] and the chemistries can also be separated into two broad classes: those containing $\text{NH}_3/\text{NH}_4^+$ buffer ligands and those without $\text{NH}_3/\text{NH}_4^+$ ligands. In palladium-nickel electrolytes the nickel ion is typically present as $[\text{Ni}(\text{NH}_3)_4 \cdot 2 \text{H}_2\text{O}]^{2+}$. The nature of this ion is pH dependent and the number of ammonias can vary from two to six. Chloride, bromide or sulphate are used as the anions, see table 3 on page 15. Conductivity and buffer capacity are achieved by additions of ammonium hydroxide and ammonium chloride, typically from 60 g/l to 120 g/l. Operating temperatures are nearly the same as in the case of pure palladium electrodeposition (25 - 60 °C) as well as typical pH range from pH 7 to pH 9. The nickel concentration can vary from 2.5 g/l to 20 g/l, depending on the application and the specific alloy that is desired. For electronic applications the nickel content can vary from 10 wt.-% to 40 wt.-%. However, the most preferred alloy is 20 wt.-% to 25 wt.-% nickel. Organic additives are also used to obtain low internal stress and crack-free deposits.

As mentioned above the main application for palladium alloys, actually palladium-nickel, is for electrical connectors. The properties of palladium-nickel deposits are

generally similar to those of gold [62,77-84]. Soldering, crimping and wire wrapping present no serious problems and it has a higher hardness. The sliding and wear behaviour of palladium are similar to those of hard gold [77-82,86]. Palladium-nickel coatings may be slightly less porous than gold coatings and they resist tarnish and corrosion. *Morrissey* [97] found palladium-nickel alloy electrodeposits to be notably less sensitive to hydrogen-induced cracking than pure palladium deposits. They are, however, somewhat more susceptible than pure palladium to stress cracking upon deformation.

On the other hand, the chemical properties of palladium are quite different from those of gold, which may explain why an effective agent for stripping palladium and palladium-nickel deposits has not yet been developed. The lower price of palladium metal coupled with its lower density Pd 12.04 g/cm³ for pure palladium or palladium-nickel iron 9.5 - 11.5 g/cm³ versus Au 19.3 g/cm³ for pure gold or ~ 17.3 g/cm³ for hard gold (AuCo) implies considerable cost savings on utilised palladium to replace. Palladium-nickel alloys can be deposited as a homogeneous alloy over a composition range from 30 wt.-% to 90 wt.-%. Current practise favours an alloy composition from approximately 75 wt.-% to 85 wt.-% palladium. This alloy is notably less sensitive to hydrogen-induced cracking than are pure palladium deposits.

A very detailed paper, which distinguishes between low and high speed deposition processes for palladium-nickel electrodeposition, is given by *Abys et al* [138]. The authors show the dependence of deposit properties, like ductility, porosity, hardness, reflectance, density, electrical contact resistance, and hardness from electrolyte composition and deposit parameters.

Several authors [127,131-136] have compared palladium-nickel layers with gold in terms of its electrical contact resistance and wear resistance as plated and after ageing. As a result they found palladium-nickel deposits are equivalent to hard gold layers in terms of contact resistance, environmental corrosion resistance and wear resistance. For sufficient solderability a thin gold overcoat is required [132]. Palladium-nickel deposits are less porous than pure palladium coatings, and superior to hard gold layers in creep corrosion resistance and bend ductility [62]. *Baker* [139] also reviewed substitutes for gold, these being gold alloys, tin, tin-lead, ruthenium,

palladium, palladium-nickel, and palladium-silver and it is concluded that no one of these is a proper substitute though they may be used with gold to partially replace it.

Reid et al [140] and *Butz et al* [141] studied the palladium-nickel electrodeposition from ammoniacal electrolytes. Because of the un-noble potential where palladium-nickel deposition occurs, hydrogen co-deposition is always present. Internal stress of the alloy was analogous to pure palladium deposits from ammoniacal solutions.

Simon [142] also described the electrodeposition of palladium-nickel alloys from an ammoniacal electrolyte. A marked effect of sulfite concentration on hydrogen content of deposit was found. Working under commercial conditions palladium-nickel electrolytes must show stability in pH, be insensitive to impurities as possible, and should be able to co-deposit a constant amount of nickel over a large range of current density.

The effects of several organic additives to deposit bright, crack-free palladium-nickel alloys with good corrosion resistance from an ammoniacal electrolyte were investigated by *Schulze-Berge* [143,144]. With the help of current density potential curves he showed the different behaviour of brighteners of the first or second type. For a practicable electrolyte a mixture of both types is required. In the case of a pre-treatment with a bright nickel layer, the organic additives should be the same as those used in the alloy electrolyte or at least, they should not cause difficulties because of their chemistry in the palladium-nickel electrolyte.

From an acid chloride electrolyte with a simple synthesis, based on palladium chloride, nickel chloride, hydrochloric acid and organic ligands for the metals, palladium-nickel deposits were also obtained [145]. The pH of the solution for optimum conditions is about pH 4.5. Bright, fine grained palladium-nickel deposits up to a thickness of 2 μm can be deposited in a wide range of deposition parameters without using organic additives. Hydrogen evolution and incorporation is a problem, even at low electrolyte temperatures and current densities. However, an increase of temperature and current density leads to a decrease of the brightness of the layers.

PdCl_2 , NiCl_2 , NH_4Cl and $\text{NH}_4 \cdot \text{OH}$ are the compounds of an chloride ammoniacal electrolyte investigated by *Walz and Raub* [146]. Alteration of the composition of the electrolyte versus operation time results in a distinct change of the properties of the

deposited layers. Especially impurities from pre-treatment processes change hydrogen incorporation dramatically and from there mechanical behaviour of the deposits. Notice should also be taken of palladium and nickel salts, as an additional resource for impurities. During further research [147] palladium-nickel was deposited from an electrolyte containing ethylenediamine (EDTA) as a complexing agent. Employment of EDTA stabilises the pH of the electrolyte, reduces chemical attack on substrates, and enables the use of high current densities, which makes the deposition process faster. The disadvantage of using EDTA as an complexing agent is the increase of internal stress and environmental problems with waste water treatment.

Investigation of the electrodeposition of palladium-nickel from a pyrophosphate solutions has shown that solutions containing sodium pyrophosphate, palladium, and nickel compounds can be used without containing ammonia [148].

While several authors [149-151] have reported the use of low and high speed electrolytes for electrodeposition of palladium-nickel alloys with current densities up to 200 A/dm^2 , *Fukamoto et al* [152,153] described the alloy deposition using pulse current. At high overpotential deposition the deposits are bright and smooth, depending on pulse parameters. Pulse current density and duty ratio did not only affect nickel and hydrogen content of deposits but also influenced orientation index and lattice content. *Knödler et al* [154] and *Tebai et al* [155] also observed a decrease of nickel content if pulse plating technique was used, as well as decrease of hardness and electrical conductivity. While palladium-nickel layers deposited without pulse plating do not show preferred orientation of the crystallite, pulse plated palladium-nickel alloys display a preferred $\langle 220 \rangle$ orientation. Gold flashed palladium-nickel layers are a suitable alternative finish to hard gold [156-158] and porosity of electroplated palladium-nickel layers is today no longer a serious problem [159-161].

Bär and Rühlicke [162] reported on a successfully installed process for electronic applications. A layer combination: Ni/Pd-Ni/Au containing 80 wt.-% palladium is performed on previously punched contact strips in a continuous electroplating process by dip and spot plating. The annealing behaviour of palladium-nickel alloy deposits in the range of 85 - 15 wt.-% to 70 - 30 wt.-% palladium-nickel alloy can be utilised to produce a ductile electrodeposit amenable to stamping and forming of electronic contacts [163].

2. 4 Palladium-Silver Alloy Electrodeposition

Clad palladium-silver alloys have been in use in the electronic industry for 60 years and, because of their excellent hydrogen solubility, palladium-silver membranes with a high palladium content are widely used for hydrogen purification, separation, and detection [164,165]. Although there have been several attempts to develop practicable electrolytes, no available plating solution exists today which satisfies the requirements of a modern plating production. *Grube and Beichscher* [166] investigated as early as 1933 the electrodeposition of palladium-silver alloy from cyanide solution. The alloy produced, with a palladium content of 20 - 22 wt.-%, was of poor appearance and poor adhesion and cathode efficiency was below 1 %. Several years later *Domnikov* [167] also reported some experiments on silver-palladium alloys from cyanide electrolytes using potential reverse technique. Although he has same difficulties with palladium deposition from cyanides solutions, his X-ray data showed that solid solutions were formed with hardness twice that of pure silver. *Knödler et al* [154] tried to deposit palladium-silver from cyanide solutions using pulse plating technique. As a result the authors stated that the cyanide complex was too stable. Therefore, even at high current densities, no silver reduction in a technically interesting range was obtained.

Deposits from thiocyanate-based electrolyte showed a broader compositional range, up to 70 wt.-% palladium. The best coatings from this type of electrolyte contain from 2 wt.-% to 19 wt.-% palladium [166].

According to literature data [69,168] silver-palladium alloys with a higher content of palladium can be obtained from acid chloride solutions containing the metals and lithium chloride. While *Kubota* [169] studied the effect of electrolyte composition, pH, temperature and current density on the composition of silver-palladium alloy electrodeposition from electrolytes containing ethylenediaminetetraacetic acid (EDTA), *Kudrayavtsev et al* [170,171] investigated silver-palladium alloys from an electrolyte containing ammonia, ammonium carbonate, amino-hydroxides and Trilon-B (EDTA potassium salt). They showed alloy composition as a function of electrolyte composition, temperature, pH, agitation and current density. Hardness range of the silver-palladium was 220 - 280 VHN. *Luo et al* [172] deposited bright, fine grained palladium-silver coatings from an electrolyte containing methylsulphonic acid. The coatings were solid solutions containing 50 - 90 wt.-% silver.

Nobel et al [173] compared palladium-silver layers with pure palladium, palladium-nickel, silver, and gold-cobalt deposits. As a result they found the electrodeposited palladium-silver alloy is subject to fewer restrictions and is considerably superior to either palladium or palladium-nickel in overall performance. Electrodeposited palladium-silver with a gold flash can be a substitute for hard gold.

Morphological effects on electroplated palladium-silver alloy layers were investigated with X-ray diffraction diagrams as function of deposition conditions [174]. The layers were single or multiple phase depending on deposition conditions. Fine structures, with repeat distance as small as 0.05 μm , were obtained from a lithium chloride electrolyte.

Investigations on the structures of silver-palladium layers deposited in a wide range by cyclic multilayered alloy (CMA) deposition were carried out by *Cohen et al* [175]. This technique allows a control of thickness and composition of individual layers within the deposit in a precise and convenient manner. There are no significant changes in the properties between direct current and CMA deposition. The only noticeable difference was the increasing brightness of CMA deposits with the frequency of the square or triangle waveform.

Palladium-silver alloys were also electrodeposited from ammoniacal nitrate solutions by using pulse plating techniques [176]. Depending on the pulse parameters, cathode efficiency of the alkaline electrolyte (pH 11.5) as well as the properties of the layers, like hardness, ductility, and cracks can be influenced in a positive way [177]. The investigations demonstrated that silver co-deposition from an electrolyte containing $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ and $\text{Ag}(\text{NH}_3)_4(\text{NO}_3)$ occurs under mass controlled conditions. Unfortunately, bright silver-palladium deposits are only obtained up to a silver content of 25 wt.-% maximum. This behaviour is similar to direct current density deposition. Results from pulse plating of silver-palladium alloys from a bromide electrolyte were reported by *Shou-Jiang et al* [178]. The silver content of the alloy increased with an increase in the average current density, but this trend was less pronounced with pulse plating than with direct current plating. Pulse parameters leading to a high overpotential produced fine grained deposits. The formation of smooth and bright alloy deposits during pulsed current plating seems to be also attributed to a high overpotential.

2. 5 Palladium-Cobalt Alloy Electrodeposition

While the number of papers about electrodeposition of palladium-nickel alloys or palladium-silver alloys is large, only a few papers about the electrodeposition of palladium-cobalt alloys have been published. *Vinogradov and Kudryavtsev* [179,180] deposited palladium-cobalt alloys from ammino-chloride complexes. The deposits were dense and semibright, crack-free at lower thicknesses ($< 1\mu\text{m}$), but cracked above this. High wear resistance and low contact resistance make this alloy a candidate for coating contacts. *Vyacheslavov et al* [181] also reported about palladium-cobalt alloys as candidates for electrical contacts. The alloys were deposited from pyrophosphate electrolytes to which palladium chloride and cobalt sulphate were added. *Knödler et al* [154] found a decrease of hydrogen content in palladium-cobalt coatings when pulse plating technique was used.

Dense, bright, and fine grained deposits with up to 25 wt.-% cobalt and low internal stress were produced from an electrolyte containing palladium as $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ and cobalt as $\text{Co}(\text{NH}_3)_6\text{Cl}_2$. By X-ray analysis they showed a series of solid solutions to be formed plus a pure ϵ -Co-phase [182]. Increasing cobalt content in the deposits increased microhardness. Good corrosion resistance, hardness up to 575 VHN, excellent solderability and satisfactory optical properties were obtained. In the typical pH range from pH 9.5 to pH 10.0 smooth layers without pores were deposited.

Juzikis and Juskenas described the change in internal stress and magnetic coercivity of palladium-cobalt alloys deposited from ethylenediamine containing electrolyte [183]. Internal stress of the deposits depended on cobalt content of the layer. A maximum of coercivity force was reached at a palladium content of 87 wt.-%, while hydrogen content was at a minimum. Cobalt content of the layers decreased with increasing temperature, pH, and current density as well as agitation of the electrolyte. Current efficiency was in the range of 82 - 88 %. Deposits were crack-free up to a thickness of about $2\mu\text{m}$ [184]. From *AT&T Bell Laboratories* an electrolyte has been designed for the deposition of palladium-cobalt alloy on electronic components using high speed plating techniques [185]. The palladium-cobalt electrolyte is capable of producing plating rates in the range of $1.2 - 1.5\mu\text{m}/\text{min}$ at $100\text{ A}/\text{dm}^2$. The properties of the deposits are similar to palladium-nickel layers. Cobalt content is in the range of 20 - 25 wt.-%, hardness is about 600 VHN and contact resistance is below $4\text{ m}\Omega$.

2. 6 Palladium-Iron Alloy Electrodeposition

Although iron is the cheapest metal available and deposition is possible from several types of electrolytes, iron electroplating is not widely used. One reason may be the disadvantage that iron has no decorative applications because of low corrosion resistance, although electrodeposited iron is somewhat more corrosion resistant than iron as a bulk material because of its high purity. On the other hand palladium as a platinum group metal is very noble, with the disadvantage that electrodeposition from simple salts is difficult and deposits tend to show cracks, even at higher thicknesses. During a diploma work [9], carried out at the Forschungsinstitut für Edelmetalle und Metallchemie (FEM), Schwäbisch Gmünd, Germany in 1993, different palladium and iron compounds were investigated in view to design a stable solution for palladium-iron alloy electroplating. Some months later *Juzikis et al* [10,11] showed the first results obtained from an electrolyte based on palladium(II)-chloride, iron(III)-chloride, and sulfosalicylic acid as a complexing agent. Alloy layers, deposited with direct current, showed cracks while cracking could be reduced when pulse plating techniques were employed. Non-metallic impurities were in the range of a few 100 ppm, hydrogen content and coercive force displayed a maximum near 75 wt.-% palladium. The obtained layers were crystalline and coercive forces of the as-deposited alloy in the range of 100 - 1250 Oe.

Because only a few basic experiences on palladium-iron alloy electrodeposition are available, except for the results from the research carried out at the FEM [9-11], the possibility of a successful electrodeposition of iron and palladium together can only be judged from the behaviour of these metals in similar alloy electrolytes. At least the electrolyte must perform two tasks in order to be a viable manufacturing process. First, the chemistry must produce deposits with acceptable physical properties at desired amounts and plating rates. Second, the process must be stable enough that the electrolyte can be handled several times producing reproducible results.

Therefore, the physical and chemical properties of the ligand species complexing the palladium and iron ions, the counter ions, and the buffer system must be considered. The ligands should be electrochemically and thermally stable, have low activity with base metals, e.g. limited etching rate, be highly soluble and preferable non-volatile.

The same considerations also hold for the counter ion. The nature of the complex dictates the mechanism of reduction and hence the deposit structure and therefore the materials properties of the palladium-iron alloy deposits. The buffer system used is for the most part determined by the desired pH range. Other considerations are chemical stability, effective pH control, and effect on the deposited layers. For commercial use in industry additives like brightening agents, stress reducers etc. are common to influence the electrodeposition process and thus modify the properties by changing the structure of the layers. But, in this first step of investigations the aim is to understand the chemical and electrochemical reactions during palladium-iron electrodeposition and the presentation of alloy coatings, which allow a description of their properties. Therefore, the development of a complete commercial electroplating solution, including organic additives for bright deposits, etc. will be the aim of further investigations.

An important characteristic of palladium electroplating as well as palladium-alloy electroplating is the fact, that metal reduction is usually accompanied by hydrogen co-deposition and incorporation of hydrogen into the metal film [95,122]. The deposition of palladium and hydrogen leads to the formation of two types of palladium hydride phases, which can cause disastrous consequences for the final coatings.

In the case when incorporation of hydrogen is at a ratio $\text{Pd} : \text{H} < 0.03$, palladium hydride is present in an α -phase with a lattice constant close to that of pure palladium. Escape of hydrogen from this structure does not cause any dramatic lattice constriction. When the $\text{H} : \text{Pd}$ ratio is above 0.57 palladium hydride is present in a β -phase with a lattice constant which is about 3.8% higher than that of the α -phase. The unstable thermodynamic β -phase, resulting from high hydrogen in the lattice, causes cracking of palladium deposits during or after electroplating. The formation of the two phases are controlled by the electrochemical characteristics of the metal ions and hydrogen ions, stability of the metal complexes, kinetic of the anodic and cathodic reactions occurring, temperature of plating solution, concentration of the complexing ligands and hydrogen ion concentration in the electrolyte (i. e. pH). The hydrogen to palladium ratio in the deposits can be further controlled by increasing the relative concentration of Pd ions : H ions at the electrode surface. This can be accomplished by increasing electrolyte and substrate agitation.

Half Cell Reaction	Standard Potential E° , 25°C
$\text{Zn}^{2+} + 2 e^- \rightleftharpoons \text{Zn}$	- 0.760 [V]
$\text{Cr}^{3+} + 3 e^- \rightleftharpoons \text{Cr}$	- 0.740 [V]
$\text{Fe}^{2+} + 2 e^- \rightleftharpoons \text{Fe}$	- 0.440 [V]
$\text{Co}^{2+} + 2 e^- \rightleftharpoons \text{Co}$	- 0.280 [V]
$\text{Ni}^{2+} + 2 e^- \rightleftharpoons \text{Ni}$	- 0.250 [V]
$\text{Sn}^{2+} + 2 e^- \rightleftharpoons \text{Sn}$	- 0.140 [V]
$\text{Pb}^{2+} + 2 e^- \rightleftharpoons \text{Pb}$	- 0.130 [V]
$\text{Fe}^{3+} + 3 e^- \rightleftharpoons \text{Fe}$	- 0.040 [V]
$2 \text{H}^+ + 2 e^- \rightleftharpoons \text{H}_2$	0.000 [V]
$\text{Cu}^{2+} + 2 e^- \rightleftharpoons \text{Cu}$	+ 0.345 [V]
$\text{Cu}^+ + e^- \rightleftharpoons \text{Cu}$	+ 0.520 [V]
$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+ 0.800 [V]
$\text{Pd}^{2+} + 2 e^- \rightleftharpoons \text{Pd}$	+ 0.980 [V]
$\text{Pt}^{2+} + 2 e^- \rightleftharpoons \text{Pt}$	+ 1.190 [V]
$\text{Au}^{3+} + 3 e^- \rightleftharpoons \text{Au}$	+ 1.360 [V]

Table 4
Standard Reduction Electrode Potentials [15]

The table of standard reduction potentials, table 4, is a very rough guide for deciding if two metals may be co-deposited from a simple salt solution and transfer to the real conditions in a practical electrolyte may be difficult, but for a first indication the table is adequate. According to table 4 the standard electrode potential of palladium is in a noble range of about + 0,980 V/NHE. Therefore, from aqueous solutions containing palladium as a simple salt, like palladium chloride (PdCl_2), reduction of the metal occurs easily. In contrast, the standard electrode potential of iron in the iron(II) state is much less noble: $E^\circ_{25^\circ\text{C}} = - 0,44 \text{ V/NHE}$.

The marked difference in standard electrode potential causes reduction of the palladium ions corresponding to following disproportionation equation (1):



Alloy electrodeposition with palladium and iron together is not possible from this type of solution. Iron exists in iron(II) state and iron(III) state, this is in contrast to nickel or cobalt co-deposition. Therefore, iron(II) can reduce palladium ions to metallic palladium by oxidising iron(II) to iron(III):



Only deposition conditions preventing reduction of palladium ions and oxidation of iron ions will guarantee a palladium-iron alloy electrodeposition. With the exception of only a few examples of alloy deposition, good alloy plating does not occur if the difference between the electrode potential is too large [2]. Complexing agents can be vital to bring the deposition potentials of the two metals together. The most common complexing agents used in electroplating techniques are summarised in table 5 on page 30. Beside the standard potentials there is another type of important potentials: The potentials at which metals actually deposit, the dynamic potentials are even more important than the static potentials. Dynamic potentials of metal deposition are always more negative than the static potentials, because of the polarisation during electrodeposition [2].

**Dynamic potentials of two metals can be brought closer together
by**

- decreasing the content of the noble metal in the electrolyte -**
- increasing the current density -**
- using solutions in which the metals are present as complex ions -**
- using special addition agents in the electrolyte -**

If the polarisation of deposition of the noble metal is large compared to the polarisation of the less noble metal, the dynamic potential of the more noble metal may approach closely enough to the deposition potential of the less noble metal to make co-deposition possible.

Special addition agents are normally used in low concentrations which should not affect the static potentials of the metals. They are usually rather specific and increase the polarisation of the deposition [2]. Typical agents of this type are: caffeine, persulphate, formate, formic acid, gelatine, glue, thiourea, resorcin, salicylic acid, etc..

CYANIDE CN^-
AMMONIA $\text{NH}_4\cdot\text{OH}$
THIOSULPHATE $\text{M}^+_x(\text{S}_2\text{O}_3)^{2-}$
PERSULPHATE $(\text{S}_2\text{O}_7)^{2-}$
PHOSPHATE $\text{M}^+_4\text{P}_2\text{O}_7$ and $\text{M}^+_2\text{H}_2\text{P}_2\text{O}_7$
HYDROXYORGANIC ACIDS, CITRATES, TARTRATES malic acid, tartaric acid, citric acid
AMINES ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$) ethylenediaminetetraacetic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$)
ETHANOLAMINES $\text{C}_2\text{H}_7\text{NO}$
GLYCINES $\text{C}_3\text{H}_8\text{O}_3$
OXALATE ROOC-COOH
FLUORIDE HF_2^-

Table 5
Typical Complexing Agents for Electroplating Processes

Under practical process conditions the number of chemical constituents should be minimised. Stability and low volatility of the chemical components are a major advantage since it prolongs electrolyte lifetime and simplifies electrolyte maintenance procedures. Replenishment and recovery schemes for the electrolyte components are also extremely important, as are low toxicity and cost. Finally, control and maintenance techniques must be simple and straightforward in order to facilitate implementation.

One of the important factors in the electrodeposition of palladium is the need to substantially reduce deposit stress and minimise or eliminate the co-deposition of hydrogen. The selection of additional or complexing components must admit this, because otherwise deposits will not be sufficiently ductile and can crack, thereby reducing the corrosion resistance or destroy the complete plating system.

In the case of palladium or palladium-iron electrodeposition additives are generally not very desirable because these systems show the tendency that the kinetic inhibition effect of the additives force the palladium reduction to more negative potentials and therefore into the hydrogen evolution regime.

For the palladium-iron alloy electrodeposition an electrolyte is necessary producing smooth, bright to semibright, mechanically stable coatings. Using a simple chemistry to operate a stable electrolyte without other additives whenever possible, will be another object of the investigations.

$\text{Pd}(\text{CN})_4^{2-}$	$\beta = \frac{[(\text{PdCN})_4^{2-}]}{[\text{Pd}^{2+}] \cdot [\text{CN}]^4}$	$= 10^{51,6}$
$\text{Pd}(\text{NH}_3)_4^{2+}$	$\beta = \frac{[(\text{PdNH}_3)_4^{2+}]}{[\text{Pd}^{2+}] \cdot [\text{NH}_3]^4}$	$= 10^{29,6}$
H_2PdCl_4	$\beta = \frac{[(\text{H}_2\text{PdCl})_4]}{[\text{Pd}^{2+}] \cdot [\text{C}]^4 \cdot [\text{H}^+]^2}$	$= 10^{12,2}$

Table 6
Stability Constants of Three Typical Palladium Complexes [16]

Some of the complexing agents are excellent but possibly critical from the view of waste water treatment. Some years ago the author himself has carried out some experiments on platinum metals plating using ethylenediamine [182]. Ethylenediamine is an excellent complexing agent especially in electrolyte containing platinum metals and metals from the iron group [143,180], but nowadays an electrolyte with such a complexing agent will not be very successful. Similar problems will cause the employment of electrolytes based on pyrophosphate solution, because of waste water treatment, even though pyrophosphates are excellent complexing agents. Because of their dangerous and notorious history some people do not like cyanides; but in practice they are excellent, and easy and well-known to handle, even in the case of waste water treatment. Therefore, the most important complexes for practical alloy plating electrolytes are still cyanide complexes!

Unfortunately, for palladium plating cyanides are not practical. The stability of palladium-cyanide is too strong with $\beta = 10^{51}$ as shown in table 6 on page 31. Palladium-iron electroplating from $[\text{Pd}(\text{CN})_4]^{2-}$ and iron from $\text{Fe}(\text{SO})_4$, at a pH of 4.5, similar to a reliable gold-iron electrolyte [183] was possible only with a very low current efficiency of $\leq 5\%$ maximum. Comparable investigations on the electrodeposition of iron from cyanide solution [9] showed that the cyanide complexes of both the iron(II) state and iron(III) state were both extremely stable and had no applications in practical iron plating. The complex number of $[\text{Fe}(\text{CN})_6]^{4-}$ is $\beta = 10^{24}$.

In contrast to $\text{Pd}(\text{CN})_4^{2-}$, the complex number of $\text{H}_2(\text{PdCl})_4$ is $\beta = 10^{12.2}$. The hydrated chloride salt is not stable enough for a common iron electrodeposition. Between palladium chloride and palladium cyanide the tetrammino-palladous complex, $[\text{Pd}(\text{NH}_3)_4]^{2+}$, $\beta = 10^{29.6}$, is situated. Further investigations [9] showed that this complex was stable enough so that no reduction occurred in the presence of iron and electrodeposition was possible. A preferred pH range for this type of electrolyte is from 7.5 to 10.5. Electrolytes working at this pH need complexing agents for iron ions to prevail iron from precipitation.

Therefore, for a new electrolyte the first aim has to be to design an electrolyte containing metal salts and complexing agents to create stable metal complexes. The complexes must be stable enough to prevent metal reduction and oxidation and

electrochemically active enough to enable electrodeposition of the two metals on practical substrates. Typical metal compounds and their equilibrium potential for palladium and iron electroplating are shown in table 7.

Metal Compounds			Reduction Potential, 25 °C	
Pd^{2+}	$+ 2 e^-$	\rightleftharpoons	Pd	$+ 0.980 \text{ [V]}$
$[\text{PdCl}_4]^{2-}$	$+ 2 e^-$	\rightleftharpoons	$\text{Pd} + 4 \text{Cl}^-$	$+ 0.621 \text{ [V]}$
$[\text{PdCl}_6]^{4-}$	$+ 2 e^-$	\rightleftharpoons	$\text{Pd} + 6 \text{Cl}^-$	$+ 0.615 \text{ [V]}$
$[\text{PdBr}_4]^{2-}$	$+ 2 e^-$	\rightleftharpoons	$\text{Pd} + 4 \text{Br}^-$	$+ 0.560 \text{ [V]}$
$[\text{Pd}(\text{NO}_2)_4]^{2-}$	$+ 2 e^-$	\rightleftharpoons	$\text{Pd} + 4 \text{NO}_2^-$	$+ 0.340 \text{ [V]}$
$[\text{Pd}(\text{SCN})_4]^{2-}$	$+ 2 e^-$	\rightleftharpoons	$\text{Pd} + 4 \text{SCN}^-$	$+ 0.615 \text{ [V]}$
$[\text{Pd}(\text{OH})_2]$	$+ 2 e^-$	\rightleftharpoons	$\text{Pd} + 2 \text{OH}^-$	$+ 0.070 \text{ [V]}$
$[\text{Pd}(\text{NH}_3)_4]^{2+}$	$+ 2 e^-$	\rightleftharpoons	$\text{Pd} + 4 \text{NH}_3$	$+ 0.000 \text{ [V]}$
$[\text{Pd}(\text{CN})_4]^{2-}$	$+ 2 e^-$	\rightleftharpoons	$\text{Pd} + 4 \text{CN}^-$	$- 0.400 \text{ [V]}$
$[\text{Fe}(\text{CN})_6]^{4-}$	$+ 2 e^-$	\rightleftharpoons	$\text{Fe} + 6 \text{CN}^-$	$- 1.160 \text{ [V]}$
$\text{Fe}(\text{OH})_2$	$+ 2 e^-$	\rightleftharpoons	$\text{Fe} + 2 \text{OH}^-$	$- 0.877 \text{ [V]}$
$\text{Fe}(\text{OH})_3$	$+ e^-$	\rightleftharpoons	$\text{Fe}(\text{OH})_2 + \text{OH}^-$	$- 0.560 \text{ [V]}$
Fe^{2+}	$+ 2 e^-$	\rightleftharpoons	Fe	$- 0.447 \text{ [V]}$
Fe^{3+}	$+ 3 e^-$	\rightleftharpoons	Fe	$- 0.037 \text{ [V]}$
Fe^{3+}	$+ e^-$	\rightleftharpoons	Fe^{2+}	$+ 0.770 \text{ [V]}$
$[\text{Fe}(\text{CN})_6]^{3-}$	$+ e^-$	\rightleftharpoons	$[\text{Fe}(\text{CN})_6]^{4-}$	$+ 0.360 \text{ [V]}$

Table 7

Equilibrium Electrode Potentials of Palladium and Iron Compounds in Basic Solutions [16]

3. EXPERIMENTAL PROCEDURE

3. 1 Apparatus and Techniques

Palladium, iron, palladium-iron, and palladium-cobalt were deposited on copper, brass, silver, gold, palladium, and platinum substrates from different electrolytes. Sample size varied from 1 cm² to 1 dm². Insoluble titanium anodes (grids), platinum-coated (2.5 µm) from salt melting process, were used. (Platinodes, *Degussa*, Schwäbisch Gmünd, Germany). Prior to electroplating the samples were subjected to an alkaline decreasing procedure in a commercial cleaning solution (Cleaner1190, *Schlötter*, Geislingen, Germany) enhanced by ultrasonic agitation (SonorexSuper RK103H, *Bandelin*, Berlin, Germany) and following a cathodic electrolytic cleaning (CleanerKG, *Schlötter*, Geislingen, Germany). Sodium peroxodisulfate (Na₂O₈S₂, *Fluka*, Buchs, Switzerland) was used to activate copper substrates and potassium cyanide (KCN, *Merck*, Hohenbrunn, Germany) to activate silver samples. KCN was also used to investigate the critical CN⁻ concentration of the plating solutions.

After cleaning and rinsing procedures the samples were immersed either in an acid solution (H₂SO₄ 10 vol.-%, *Merck*, Hohenbrunn, Germany) or an ammonia solution (NH₄·OH 10 vol.-%, *Merck*, Hohenbrunn, Germany) depending on the pH of the following plating electrolyte. A linear power supply (Digistant6426, *Burster*, Gernsbach, Germany) was used to apply the necessary current to the plating cell. Voltage and cathodic current density were measured with various multimeters (Multimeter174A, *Keithley*, Germering, Germany). While the pH of the electrolytes was controlled continuously (pH-Meter761, *Knick*, Berlin, Germany) and adjusted by adding ammonia solution (NH₄OH 25 vol.-%, *Merck*, Hohenbrunn, Germany), electrolyte temperature was fixed by using a water bath with thermostat (IKA®TER2, *Jahnke & Kunkel*, Staufen i. Br., Germany). Electrolyte agitation was maintained by magnetic stirring (300 r/min) during experiment. Sample agitation was established by horizontal movement of the sample holder (1 m/sec). After electrodeposition the samples were rinsed in distilled water and ethanol (C₂H₅OH, *Riedel-de Haën*, Seelze, Germany) and dried in a desiccator at RT. Palladium-iron electrodeposition from electrolytes with a high iron content (1 : 10 or 1 : 100) were performed on substrates with a gold (flash gold) intermediate layer. Therefore, an almost addition-free gold bath was

used (Auruna[®] 551, *Degussa*, Schwäbisch Gmünd, Germany). The electrolyte work at RT, pH = 4, and current densities of 0.1 - 0.5 A/dm² with a cathodic current efficiency of ca. 20 %. A layer thickness of up to 0.1 µm was deposited. The intermediate palladium and nickel layers for diffusion barrier tests were also obtained from commercial solutions (Zodiac230[™], *Schlötter*, Geislingen, Germany, and Palladure150[™], *Lea Ronal*, Birkenfeld, Germany).

In most cases the samples were individually plated on both sides in a 1000 ml cell. Some experiments were carried out in a commercial 250 ml *Hull-Cell* (*Lea Ronal*, Birkenfeld, Germany) and for the electrodeposition on pins a small commercial barrel plating equipment was used (TG, *Degussa*, Schwäbisch Gmünd, Germany). Potentiodynamic measurements were carried out in a 500 ml solution using a rotating electrode (figure 1). Rotational speed to 10.000 r/min were obtained (Electrode Rotator Model 636, *EG & G*, Princeton/NJ, USA). Potentiodynamic polarisation measurements with the three-electrode techniques were made with a commercial potentiostat (273A, *EG & G*, Princeton/NJ, USA). Several experiments on carbon, iron, copper, palladium, platinum, and gold substrates were carried out. To isolate the reference electrode from the sample solution a salt bridge (*Haber-Luggin* capillary) containing non-interfering ions (saturated KCl gelled with agar) was used.

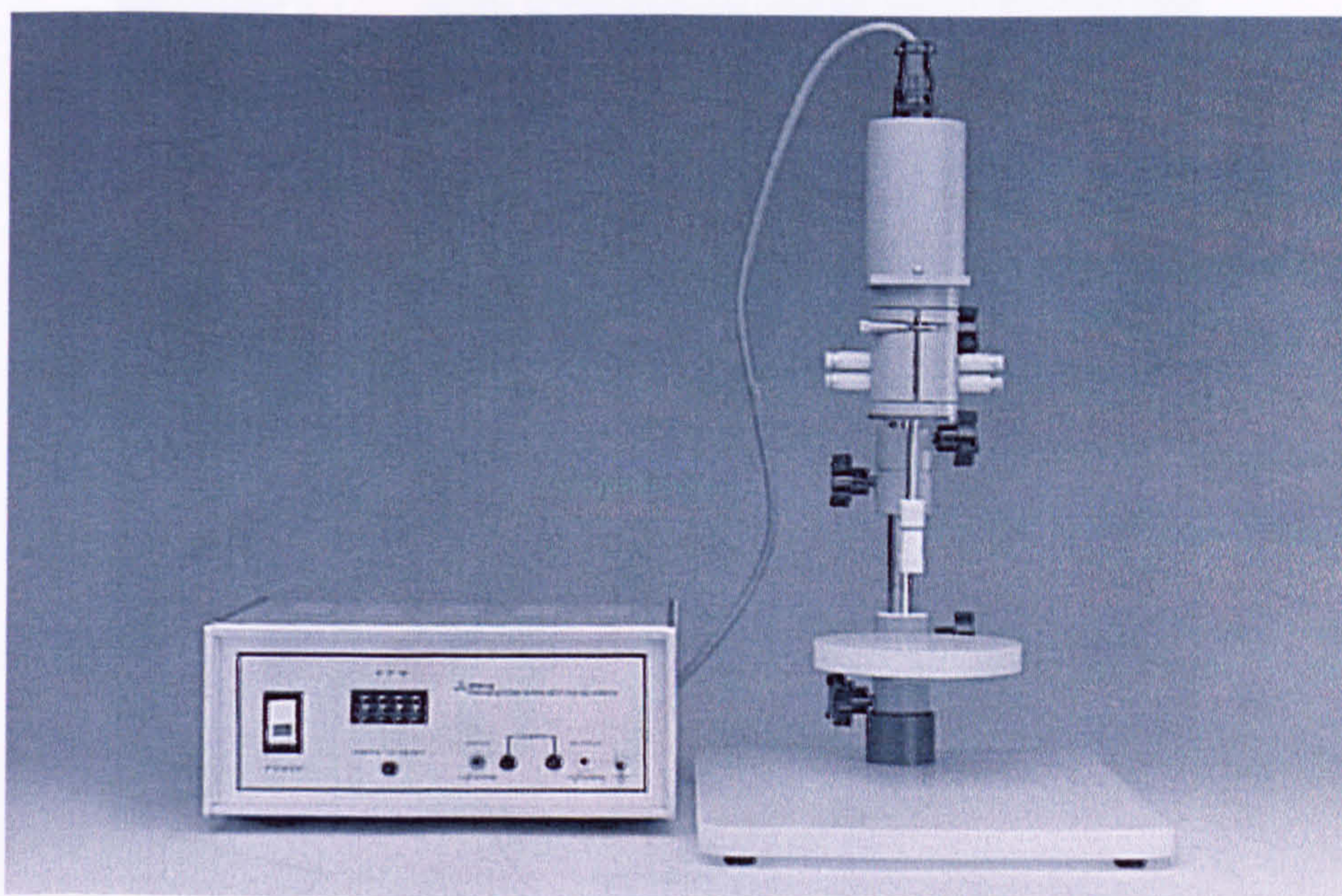


Figure 1
Rotating Disc Electrode (Model 636, EG & G, Princeton/NC, USA)

Reference electrode was a saturated calomel electrode (EG & G, Princeton/NJ, USA) SCE, $E^{\circ}_{25^{\circ}\text{C}} = + 241,5 \text{ mV}$, with respect to a normal hydrogen electrode (NHE). Counter electrode was either a glassy carbon (SigadurG, HTW, Thierhaupten, Germany) or a platinated ($2,5 \mu\text{m}$) titanium grid (Platinodes, Degussa, Schwäbisch Gmünd). Evaluation of the resulting curves was done with the support of commercial software (PAR M352 Rev.2.01, PAR M398 Rev.1.01, EG & G, Princeton/NJ, USA). Palladium salts were of commercial metal concentration in the range of 50 - 60 wt.-% palladium, manufactured by either Degussa, Schwäbisch Gmünd, Germany or Saxonia, Halsbrüche/Sachsen, Germany. Lea Ronal, Birkenfeld, Germany, and Engelhard-Clal, Cinderford, United Kingdom provided palladium electrolytes and some improved additives, like wetting agents (Palladure150TM and PallanicTM). Finally a commercial palladium-cobalt electrolyte (PallaTechTM) was provided by AT & T, Murray Hill, NJ, USA). The degree of purity of all other chemicals was "pro analysi" (p. a.) or better. Water used for solution preparation or rinsing was bi-distilled at the FEM with a conductivity below $3 \mu\text{S}$.

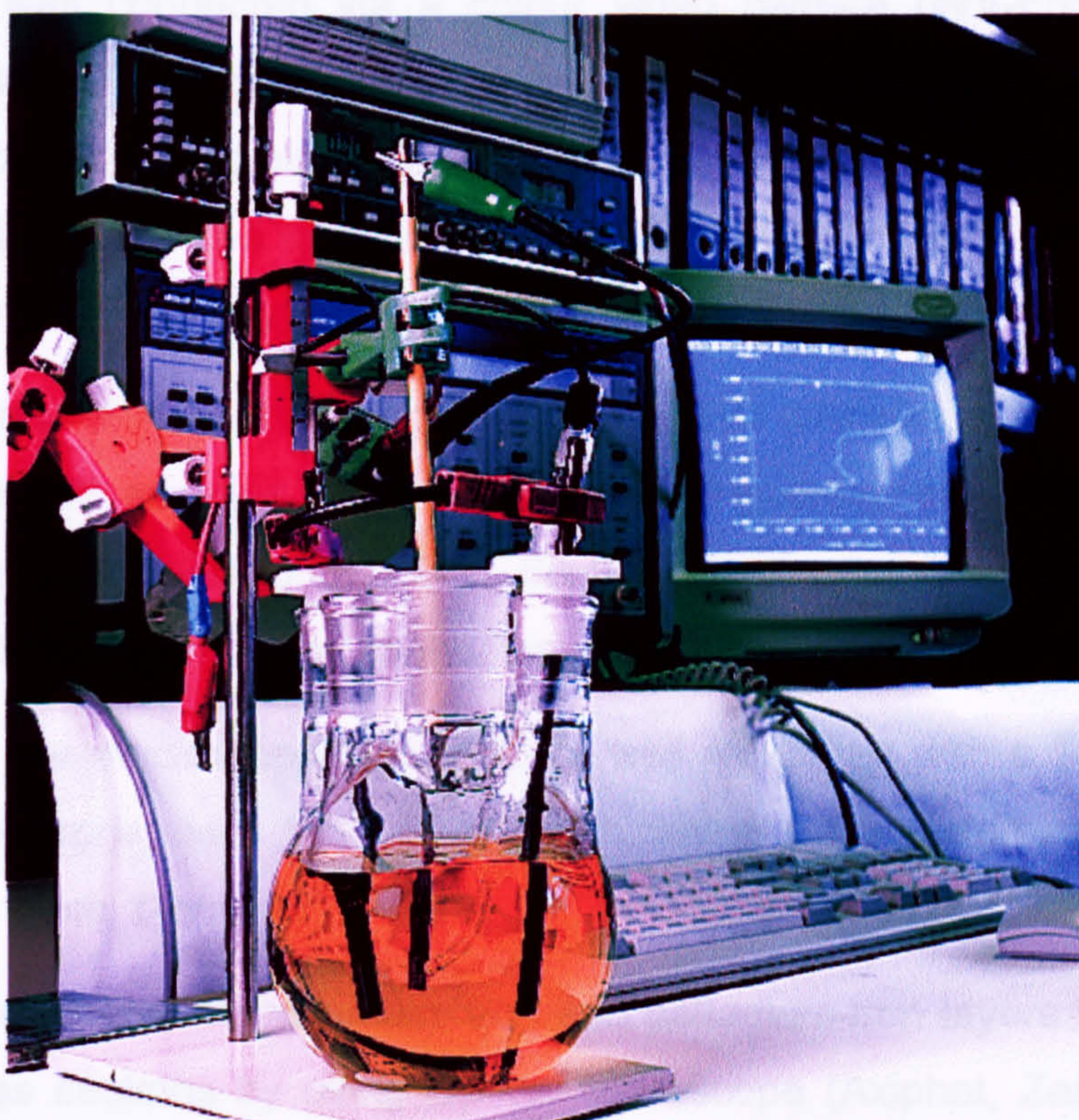


Figure 2
Electrolyte Cell, Potentiostat, and Personal Computer used for Electrochemical Measurements with the Three-Electrode Technique

Until a stable electrolyte was created each sample was deposited from an unused solution. For chemical analysis additional gold samples were plated together with the samples. After removing the layers from the substrate, palladium and iron both were examined by Inductively Coupled Plasma Spectroscopy ICP (Iris/AP, *Thermo Jarrel Ash*, Offenbach, Germany) and Atomic Absorption Spectroscopy AAS (AAS, *Unicam*, Offenbach, Germany). For that purpose the plated samples were first dissolved in concentrated nitric acid (Puratronic 65 %, *Merck*, Hohenbrunn, Germany). Then the acidic solution was diluted with distilled water to a concentration of about 1 M. Metal and ligand concentration in the electrolytes were determined with classical chemical analysis methods or in the case of very low concentration by Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma Spectroscopy (ICP).

Morphology Characterisation of the electroplated layers was performed by using Optical Microscope (Axiphot, *Zeiss*, Oberkochen, Germany) and Scanning Electron Microscope SEM (DSM940, *Zeiss*, Oberkochen, Germany) fitted with an Energy Dispersive X-ray Microanalyser EDX (HNU, *EG & G*, Princeton/NJ, USA). The Optical Microscope was connected via a colour video camera (WV-E550E, *Panasonic*, Kadom, Japan) with a personal computer for documentation. Grain structure was determined by examining etched cross sections. A reliable etching solution for palladium and palladium alloys was a commercial gold stripper (AuStripper645, *Degussa*, Schwäb. Gmünd, Germany) with an additional amount of potassium cyanide (KCN).

The characterisation of the deposit structure was performed by X-ray diffraction measurement with samples with a surface area of approximately 1 cm² using a Powder Diffractometer (KristalloflexD5000, *Siemens*, Karlsruhe, Germany) equipped with scintillation detector and using excited copper as the radiation source.

Hardness of the electrodeposited coatings was measured with a 1 g load on cross section of electrodeposits 15 to 50 µm in thickness (Microduromat4000E, *Reichert-Jung*, Heidenheim, Germany).

Coating thickness of the palladium, iron and palladium-iron layers were also measured on cross sections by using Optical Microscope (Axiphot, *Zeiss*, Oberkochen, Germany) and Scanning Electron Microscope SEM (DSM940, *Zeiss*, Oberkochen, Germany) since the X-ray fluorescent method, according to ISO 3497 (05/1990), was not accurate enough, especially for palladium-iron alloy coatings.

Internal stress of palladium and palladium-alloy coatings were measured with an apparatus working on the principle of *Hoar and Arrowsmith* [188] and constructed by *Stalzer* [189] at the *Forschungsinstitut für Edelmetalle und Metallchemie* (FEM), Schwäbisch Gmünd, Germany. This method is based on plating one side of a substrate strip while the back side is isolated. One end of the strip is clamped while the other is mounted via a movable glass stick on the apparatus. For deposits in tension, the free end of the strip tries to deflect towards the anode, while compressive stress is indicated by attempted deflection of the free end of the strip away from the anode. A potentiometer connected with the glass stick prevents movement of the strip continuously and allows determination of stress as a function of layer thickness.

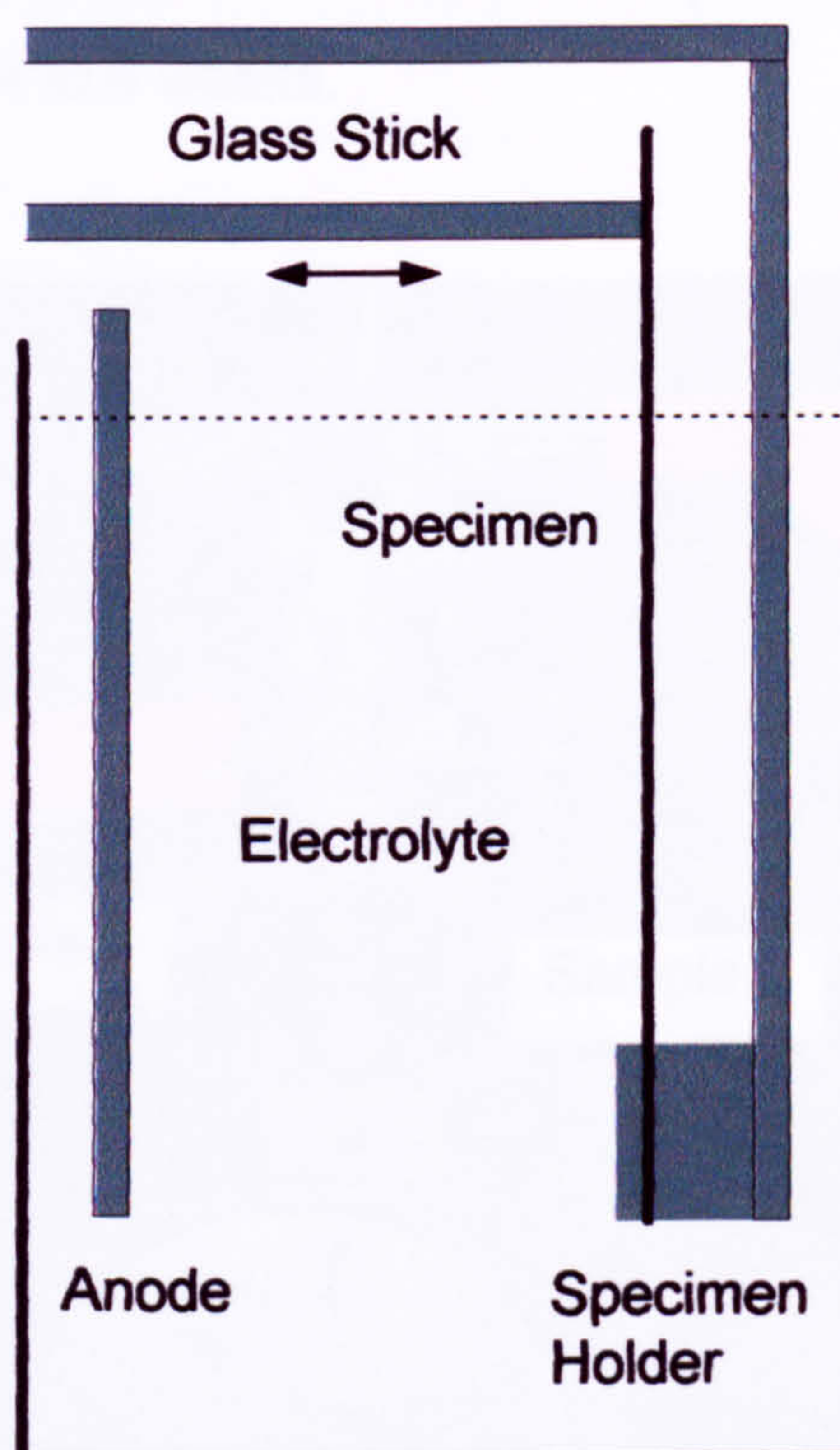


Figure 3
In-situ Measurement of Internal Stress (Macro Stress) during Electrodeposition

For thermal treatment, to observe diffusion properties and suitability of palladium-iron as barrier layers, experiments were carried out in an oven, which held the temperature within 160 ± 5 °C during test runs (*Heraeus*, Hanau, Germany). Diffusion behaviour of substrate material, intermediate layer, and coating was examined with etched cross sections with Scanning Electron Microscope SEM (DSM940, *Zeiss*, Oberkochen, Germany) and surface analysis by Glow Discharge Optical Spectroscopy, GDOS (GDS-750, *Spectrums-Analytik*, Seefeld-Dröbling, Germany).

To measure the contact resistance, brass pins (4 mm diameter x 25 mm) electroplated with 2.5 µm bright silver were cathodically cleaned, activated (KCN) and plated with approximately 1.0 - 5.0 µm palladium, iron, palladium-cobalt or palladium-iron with various palladium content. The contact resistance measurements were obtained by the four terminal bridge method (figure 4) at RT using 3 loads between 2 and 8 N. The samples were measured 24 hours after electrodeposition and after exposition at room temperature in laboratory atmospheres for 4 to 6 weeks.

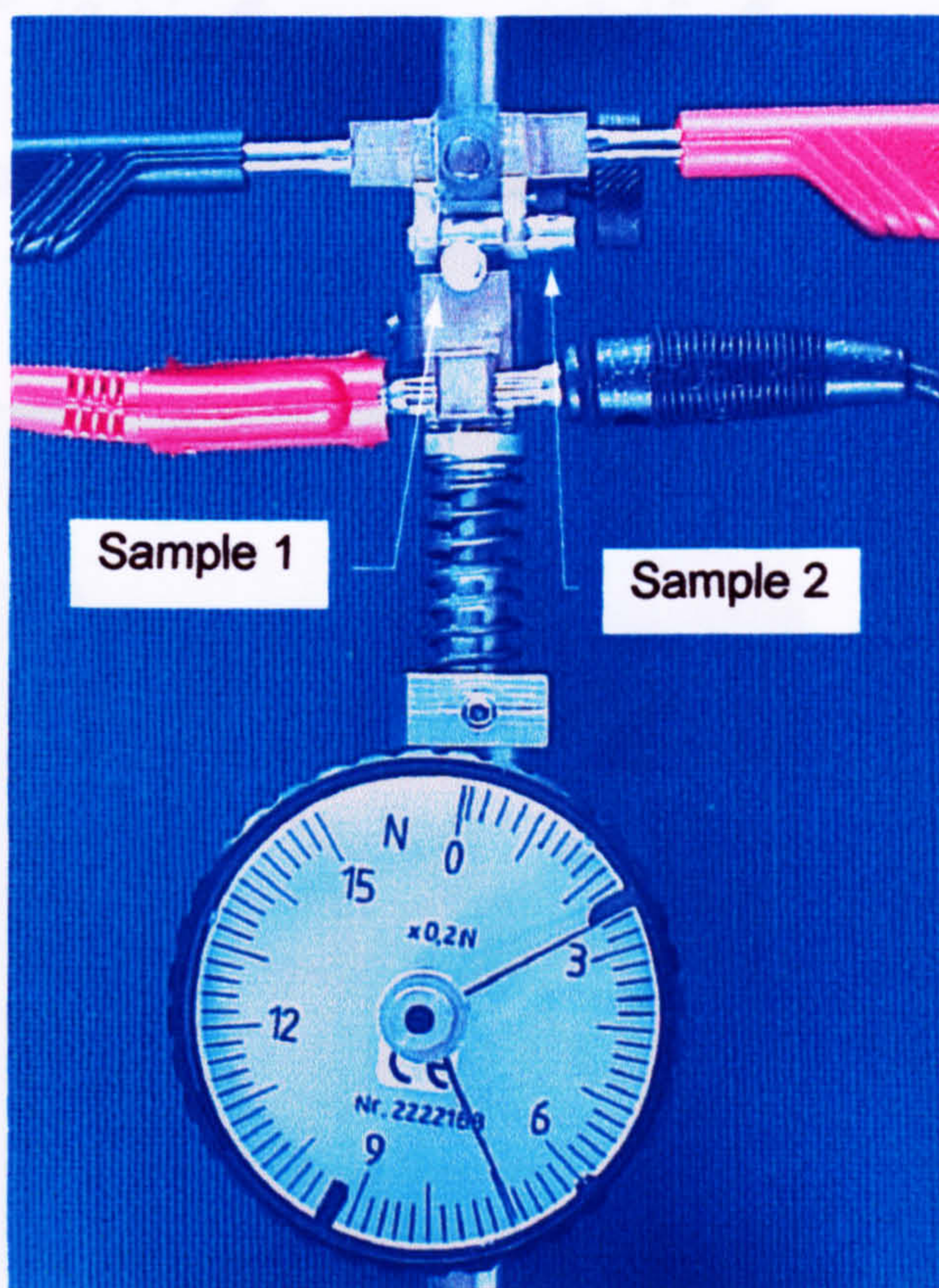
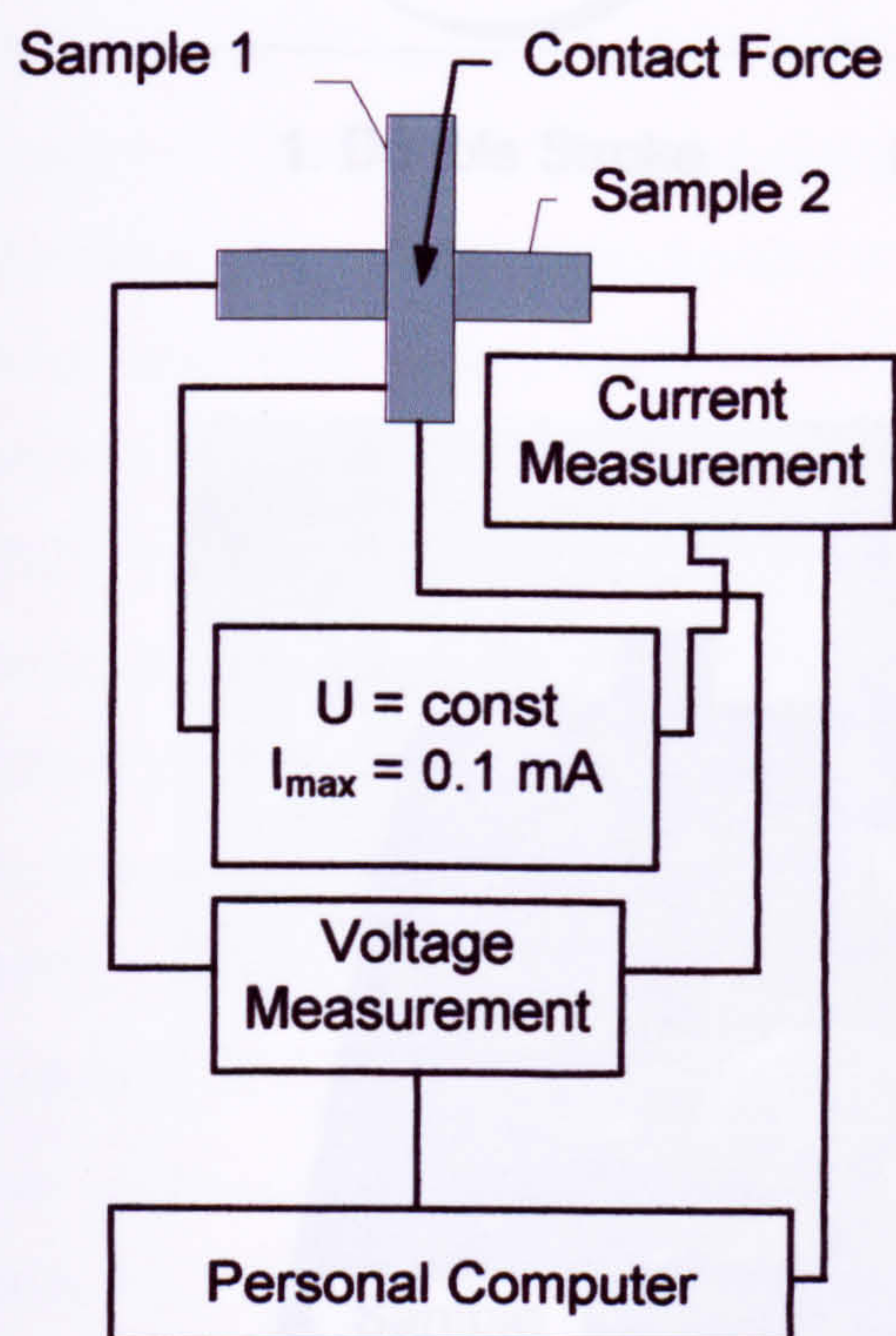


Figure 4
Contact Resistance Measurement

There are numerous tests for evaluating wear resistance with more or less defined test conditions. *Taber Abrader* wear test is a very common method but too aggressive for palladium and palladium alloys. The *Taber Abrader* test is excellent for hard materials like chromium, electroless nickel or anodised aluminium. Therefore, a less aggressive test method, the *Bosch-Weinmann Test* [191] was selected to investigate palladium, palladium alloys and similar coatings. Wear is produced by the sliding action of a cylinder with grinding paper. The cylinder moves with a constant force and a predetermined number of stokes over the sample (figure 5).

In order to guarantee constant test conditions of the grinding paper for every stroke, the cylinder is rotated by a predetermined amount after every double stroke. The weight loss in mg per 4×100 double strokes is measured.

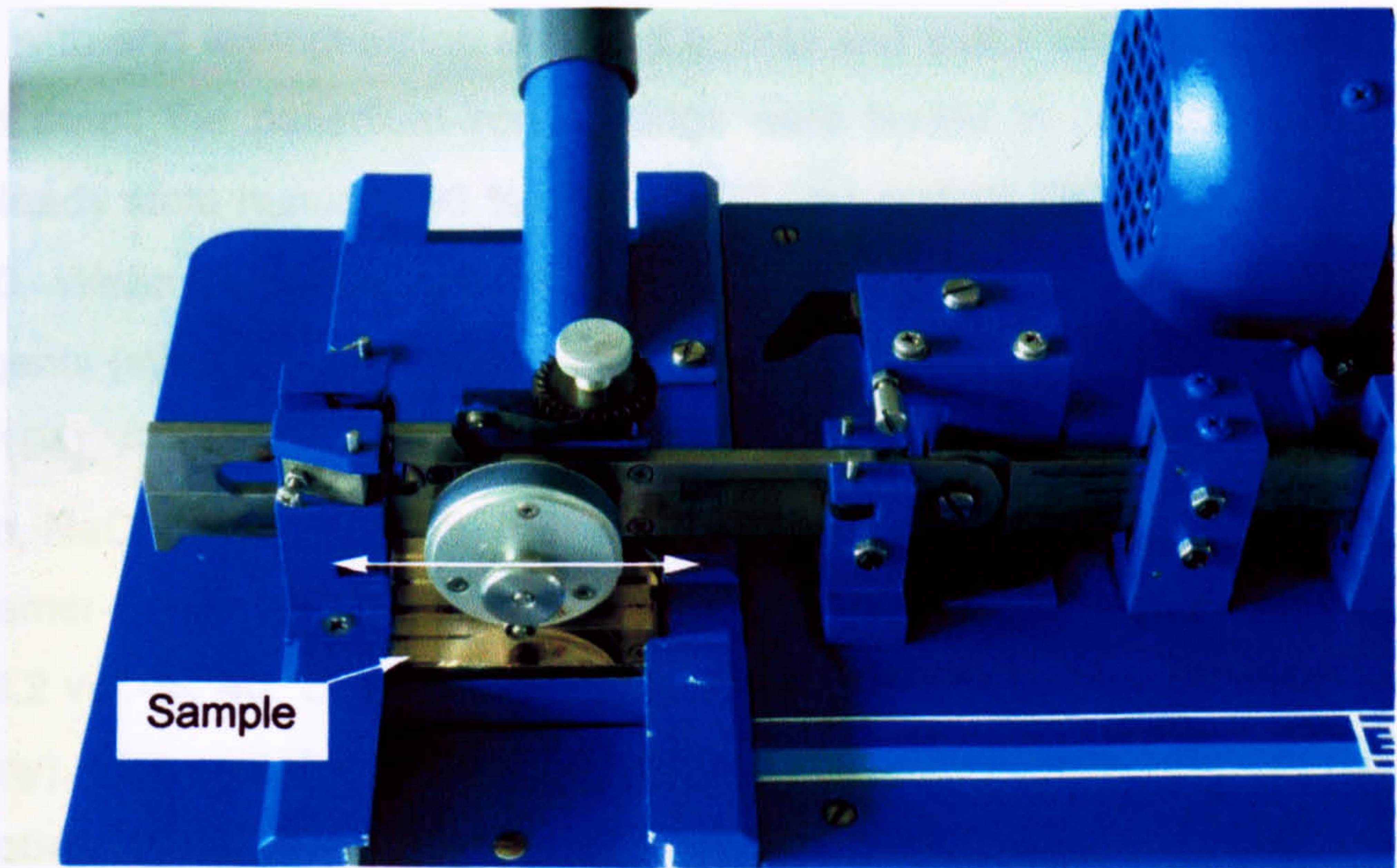
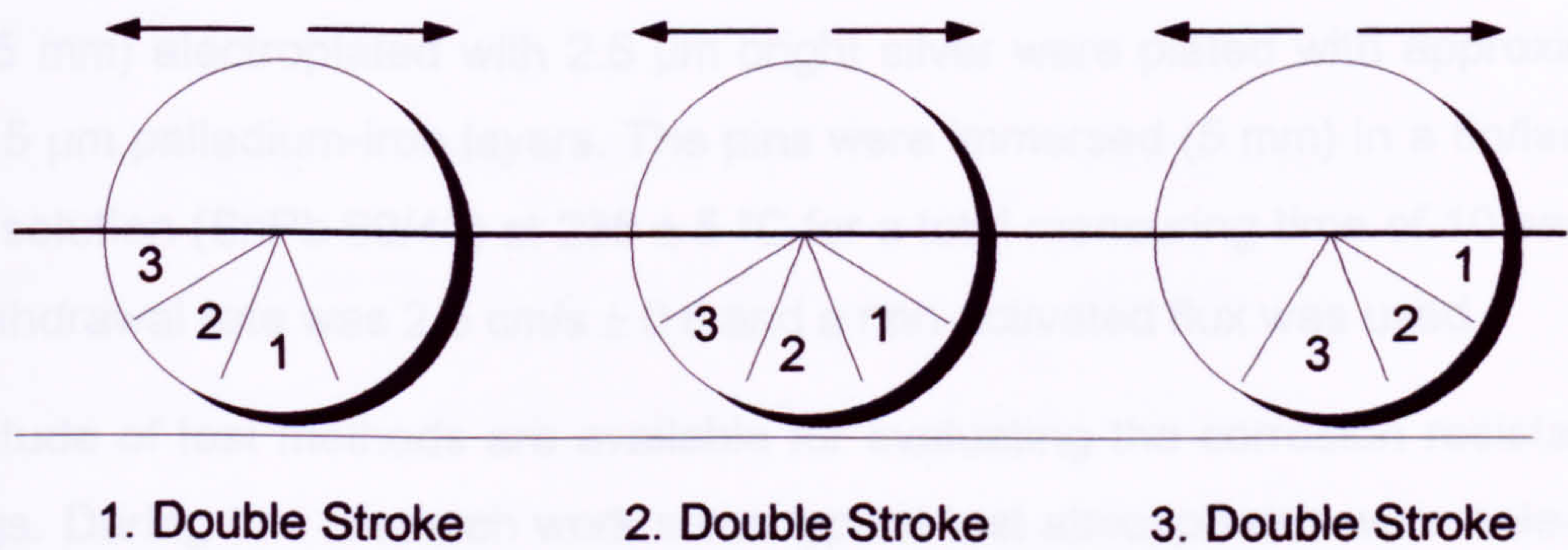


Figure 5
Bosch-Weinmann Wear Test Apparatus [191]

Determination of hydrogen was carried out by the established principle of the hot extraction method. Hydrogen from the samples was converted to a carrier gas flow and change in electrical conductivity was measured (H_2A2002 H-Analyser, *Rosemount*, Hanau, Germany). For this purpose the palladium and palladium alloy layers were electrodeposited on copper substrates with a very low amount of hydrogen.

Carbon and sulfur contents were determined using the analytical system of Leco Corporation (CS-125, *Leco*, St. Joseph/Michigan, USA). In this technique the amount of carbon dioxide (CO_2) and sulfur dioxide (SO_2) evolved by heating the sample in oxygen at $1200^\circ C$ in a high frequency induction furnace is measured.

Solderability tests of the palladium-iron layers were performed by the wetting balance method according to DIN 32 508 T3, T4, 1988 [192]. Brass pins (4 mm diameter x 25 mm) electroplated with $2.5\ \mu m$ bright silver were plated with approximately $2.0 - 3.5\ \mu m$ palladium-iron layers. The pins were immersed (5 mm) in a tin/lead soldering solution (SnPb 60/40) at $235 \pm 5^\circ C$ for a total measuring time of 10 seconds. Dip/Withdrawal rate was $2.5\ cm/s \pm 0.6$ and a non-activated flux was used.

A multitude of test methods are available for evaluating the corrosion resistance of coatings. During this research work some typical test atmospheres were selected to describe the corrosion behaviour of the layers with respect to decorative (jewellery) and functional (electronics) applications. Samples were tested in suitable atmospheres with and without saline and acid agents and sulfur dioxide according to DIN ISO. In detail the palladium-iron coatings were tested in constant climate, damp heat, steady state humidity 90 %, $60^\circ C$, 672 hours, (DIN IEC 68 T 2-3, 1986 [193], SB1300, *Weiss Umwelttechnik*, Reiskirchen-Lindenstruth, Germany), in saline and acid agents (synthetic perspiration test), $pH = 4.7$, $40^\circ C$, 12 - 48 hours (ISO 3160-2, 1992 [194], *FEM*, Schwäbisch Gmünd, Germany), spray test with sodium chloride solution, NaCl 50 g/l, $pH = 6.5 - 7.2$, $35^\circ C$, 24 hours (DIN 50 021, 1988 [195], *Erichsen*, Hemer-Sundwig, Germany), and sulfur dioxide with condensation of moisture, $SO_2 = 0.2\ vol.\%$, $40^\circ C$, 24 hours (DIN EN ISO 6988, 1997 [196], *Köhler*, Lippstadt, Germany). The samples were tested together with pure palladium, iron and palladium-cobalt layers. After the different tests the samples were examined visually for corrosion products under x 100 magnification. In addition the porosity of the samples was inspected under an Optical Microscope (Axiphot, *Zeiss*, Oberkochen, Germany).

3. 2 Selecting a Suitable Electrolyte for Palladium-Iron Alloy Electrodeposition

As discussed in chapter 2.6 standard electrode potential of palladium is very noble, while standard electrode potential of iron is un-noble. From aqueous solutions containing palladium and iron as simple salts alloy deposition will not be very practicable. Therefore, the first aim was to design an electrolyte containing metal salts and complexing agents to create stable metal complexes. The complexes must be stable enough to prevent metal reduction and oxidation and electrochemically active enough to enable electrodeposition of the two metals on practical substrates. From the experience and results of previous work carried out at the FEM [9] several salts and compounds were selected and their applicability was tested (table 8).

Palladium-(II)-chloride	PdCl_2
Palladium-(II)-diammino-dinitrite	$\text{Pd}(\text{NO}_3)_2(\text{NO}_2)_2$
Palladium-(II)-tetrammino-dinitrate	$\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$
Palladium-(II)-tetrammino-dichloride	$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$
Palladium-(II)-tetrammino-disulfate	$\text{Pd}(\text{NH}_3)_4(\text{SO}_4)_2$
Palladium-(II)-tetrammino-dicarbonate	$\text{Pd}(\text{NH}_3)_4(\text{HCO}_3)_2$
Palladium-(II)-sulfate-hydrate	$\text{PdSO}_4 \cdot \text{H}_2\text{O}$
Iron-(II)-chloride	$\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$
Iron-(II)-sulfate	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$
Iron-(II)-ammonium-sulfate	$\text{Fe}(\text{SO}_4)(\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$
Iron-(II)-fluoborate	$\text{Fe}(\text{BF}_4)_2$
Iron-(III)-chloride	$\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$
Iron-(III)-citrate	Fe-Citrate

Table 8
Iron and Palladium Compounds for Palladium-Iron Alloy Electrodeposition

The first part of the investigation covered the determination of pH range and primary components (type of solution for alloy plating, type and amount of complexing agent, etc.) from which it is possible to obtain stable solutions. Stability of the solutions was examined from pH 1 to pH 12 with variable palladium and iron concentration. A selected amount of „possible“ solutions were then checked to see if they were suited for electrodeposition (table 9).

Iron (II) Compound	Electrolyte Composition	Chemical Stability	Electro- deposition	Oxidation Fe²⁺ to Fe³⁺	Alloy Suitability
Fe(II)- cyanide	K ₄ [Fe(CN)] ₆	pH 12	NO	NO	NO
Fe(II)- oxalate	FeSO ₄ + 7 · H ₂ O NH ₄ Cl Oxalic acid	pH 12	YES	possible	YES
Fe(II)- pyro- phosphate	FeSO ₄ + 7 · H ₂ O K ₄ P ₂ O ₇ 3 · H ₂ O	pH 10	YES	possible	YES
Fe(II)- citrate	FeSO ₄ + 7 · H ₂ O NH ₄ Cl Na-Citrate	pH 10	YES	possible	YES
Fe(II)- succinate	FeSO ₄ + 7 · H ₂ O NH ₄ Cl Succinic acid	pH 5	NO	possible	NO

Table 9
Behaviour of Different Iron Compounds During Electrodeposition

The results showed that stable solutions, containing iron in the iron(II) state, from which electroplating of palladium and iron together is possible, could not be simply designed. For an application of iron(II) in acid solutions, non suitable complexing agent with the stability required could be obtained. Palladium ions oxidise the iron(II) to iron(III) while reduction of palladium to solid form occur. A shift of the pH to a more alkaline value is limited due to iron precipitation. To sum up, electrodeposition of palladium and iron together from such type of solutions is not realistic, at least with the complexing agents tested.

Electrolyte Composition	Stability of the Electrolyte during or after Electrodeposition	Possibility of Electrodeposition	Current Efficiency %
$[\text{Pd}(\text{CN})_4]^{2-}$ *) Fe(II)SO ₄ malic acid KOH	low	yes	< 10%
$[\text{Pd}(\text{CN})_4]^{2-}$ Fe(II)SO ₄ KSCN H ₂ SO ₄	very low	no	—
Pd-sulfamate Fe(II)SO ₄ NH ₄ S ₃ NH ₄ H ₂ SO ₄ , NH ₄ OH	very low	no	—
Pd-thiourea Fe(II)Cl ₂ or Pd-thiourea Fe(II)SO ₄	very low	no	—
Pd(NH ₃) ₂ Cl ₂ Fe(III)-citrate Na-citrate	low	yes	< 5 %
Pd(NH ₃) ₃ (NO ₂) ₂ Fe(II)-citrate Fe(II)SO ₄ , NaNO ₂ NaNO ₃	low	no	—
Pd(NH ₃) ₄ Cl ₂ Fe(III)-citrate (NH ₄) ₂ SO ₄ (NH ₄) ₂ -citrate	good	yes	80 %
Pd(NH ₃) ₄ Cl ₂ (Fe(III)Cl ₃ K ₃ P ₂ O ₇ (NH ₄) ₂ -citrate NH ₄ Cl	low	yes	< 5 %

*) according to gold-iron electrolyte [187]

Table 10
Behaviour of Different Palladium-Iron Electrolytes during Electrolysis

Therefore, several experiments with iron in the iron(III) state and with different complexing agents at various pH values were carried out. Determination of the possibilities for obtaining palladium-iron coatings, was performed at various electrolyte temperatures, pH and current densities in electrolytes with different compositions and metal ion contents.

The experiments carried out have shown that from an ammoniacal electrolyte in a pH range from pH 7.5 to pH 10.5 electrodeposition in a wide range of composition was possible. The best results were obtained from an electrolyte containing palladium as $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ and iron as Fe(III)-citrate. Ammonium citrate and ammonium sulfate were added as well as ammonia to adjust pH. The palladium source was PdCl_2 . Palladium showed the tendency to form stable complexes with ammonia:



Creation of the ammoniacal palladium-iron electrolyte used for the experiments:

- Dissolution of 20,867 g PdCl_2 (59,9 % Pd) = 12.5 g Pd in 100 ml $\text{NH}_3 \cdot \text{OH}$ (15 %)
- Heating of solution to 60 °C
- If palladium is not dissolved complete, addition of another 100 ml $\text{NH}_3 \cdot \text{OH}$ (15 %)
- Cool of solution to 25 °C, filter of solution, and refill to 250 ml with H_2O
- Solution 1 ml = 0.05 g Pd, = 50 g/l Pd
- Addition of corresponding amount of iron, ammonium sulfate, ammonium citrate, and ammonia to design an electrolyte as following:

0 - 0.3 mol/l	Pd as $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$
0 - 0.3 mol/l	Fe as $\text{Fe}(\text{III})\text{Cl}_3 \cdot 6 \text{H}_2\text{O}$
0 - 0.3 mol/l	$(\text{NH}_4)_2(\text{SO})_4$
0 - 0.3 mol/l	$(\text{NH}_4)_2\text{-Citrate}$
x mol/l	$\text{NH}_4 \cdot \text{OH}$

Electrolyte	Concentration (g/l)					
	Palladium		Iron		Citrate	Sulfate
	PdCl ₂ (59.7 %)		FeCl ₃ ·6 H ₂ O		(NH ₄) ₂ -Citrate	(NH ₄) ₂ SO ₄
	Metal	Solution ^{*)}	Metal	Salt		
1 : 1	10.0	200 ml	5.2	25.4	21.2	12.4
1 : 2	10.0	200 ml	10.4	50.8	42.4	24.8
1 : 4	10.0	200 ml	20.9	101.6	84.8	49.6
1 : 5	10.0	200 ml	26.2	127.0	106.3	62.1
1 : 10	4.0	80 ml	20.9	101.6	84.8	49.6
1 : 20	2.5	50 ml	26.2	127.0	106.3	62.1
1 : 50	1.0	20 ml	26.2	127.0	106.3	62.1
1 : 100	0.5	10 ml	26.2	127.0	106.3	62.1

*) Solution: $\text{PdCl}_2 + 4 \text{NH}_3 \rightarrow [\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$
 100 ml equivalent to 5.0 g Palladium

PdCl ₂ (59.7 % Pd) palladium(II) chloride	SAXONIA, Halsbrücke, Germany
FeCl ₃ ·6 H ₂ O p. a. iron(III) chloride hexahydrate	MERCK, Darmstadt, Germany
(NH ₄) ₂ HC ₆ H ₅ O ₇ p. a. di-ammonium hydrogen citrate	MERCK, Darmstadt, Germany
(NH ₄) ₂ SO ₄ p. a. ammonium sulfate	MERCK, Darmstadt, Germany
NH ₄ ·OH p. a. ammonia solution 25 vol.-%	MERCK, Darmstadt, Germany

Table 11

Chemicals and Composition of Electrolytes used for the Electrodeposition of Palladium-Iron Alloy Deposits

4. RESULTS AND DISCUSSION OF DETAILS

4. 1 Characteristics of Palladium-Iron Electrolytes

The experiments carried out have shown that from an ammoniacal electrolyte in a pH range from pH 7.5 to pH 10.5 electrodeposition in a wide range of composition is possible. Preferred pH range was from pH 8.0 to pH 8.5. Beside the deposition parameters and their effect on the alloy coatings, e.g. composition, hydrogen content, etc., the deposits properties studied were hardness, internal stress, morphology characteristics, wear resistance, contact resistance, corrosion resistance, resistance to copper and gold diffusion and solderability. Bright, semibright and dull layers, with and without cracks up to 25 - 50 μm can be deposited with cathodic current densities of 0.5 - 10.0 A/dm^2 in a temperature range from 25 $^{\circ}\text{C}$ to 75 $^{\circ}\text{C}$. From this electrolyte, therefore, adherent and mechanically stable coatings can be obtained.

The stability of the electrolytes is good, both with a high amount of palladium metal ($\text{Pd} : \text{Fe} = 1 : 1$) and with a very low amount of palladium (metal ratio $\text{Pd} : \text{Fe} = 1 : 100$). The electrolytes are stable enough to use them several times to produce alloy layers with reproducible properties obtained at the same plating parameters. To improve the stability of the process similar layers were deposited every definite interval and compared with samples obtained before (e.g. Pd content, surface morphology, etc.).



Figure 6

Colour of Different Palladium-Iron Solutions for Alloy Electrodeposition

Base Electrolyte: $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{-Citrate}$, NH_4OH

4. 1. 1 Electrochemical Measurements

Various polarisation curves obtained from a rotating platinum electrode in a solution containing 0.3 mol Fe(III)Cl_3 are shown in figure 7. It can be seen, that iron reduction reaction occurs at a noble potential of about 800 mV/NHE (curve 1). This potential is in good correspondence with the theoretical reduction potential for the Fe^{3+} to Fe^{2+} reduction (see table 7, page 33). Current density rose quickly to a limited cathodic current density of 100 mA/cm² (10 A/dm²). Addition of 0.3 mol Na-citrate shifted the reduction potential in the direction of Fe^{3+} and Fe^{2+} reduction (curve 2), but a more distinctive effect is caused by the addition of $(\text{NH}_4)_2$ -citrate (curve 3, 4, and 5). Deposition potential is shifted to values near the hydrogen reduction and closer to iron(II) and palladium deposition.

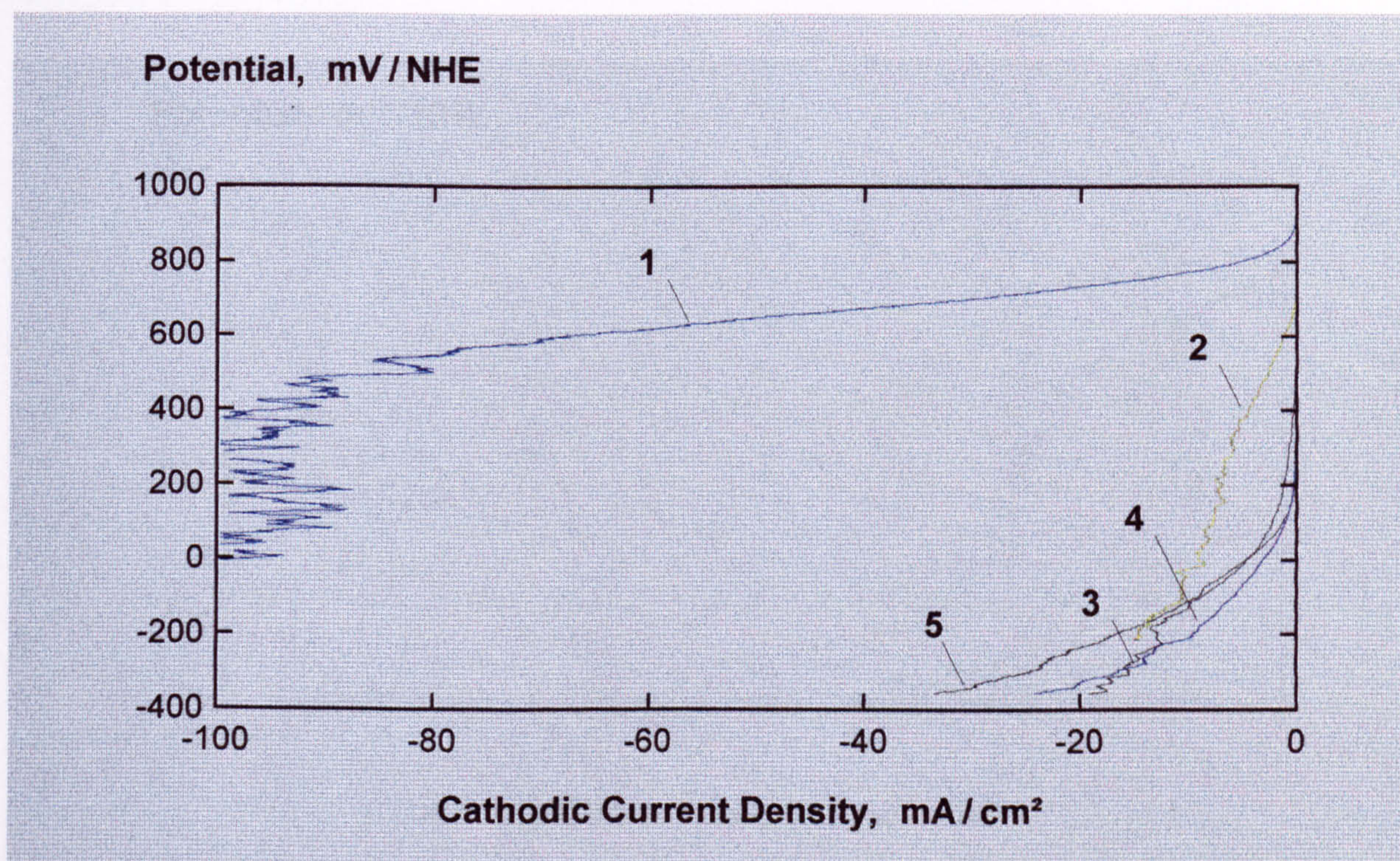


Figure 7

Effect of Na-Citrate and $(\text{NH}_4)_2$ -Citrate on Current Density Potential Curves of Iron Electrodeposition from Electrolytes containing FeCl_3 -Ions, pH = 0.2 - 3.0

Curve 1: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$

Curve 2: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.3 mol Na-citrate

Curve 3: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.3 mol Na-citrate + 0.1 mol $(\text{NH}_4)_2$ -citrate

Curve 4: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.3 mol Na-citrate + 0.2 mol $(\text{NH}_4)_2$ -citrate

Curve 5: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.3 mol Na-citrate + 0.3 mol $(\text{NH}_4)_2$ -citrate

Temperature: 55°C, Substrate: Platinum, Scan rate: 1 mV/s, Rotation: 5000 r/min, Reference-Electrode: Calomel, Counter-Electrode: Glass-Carbon

A similar behaviour was observed, when instead of sodium citrate only $(\text{NH}_4)_2$ -citrate was added to the electrolyte (figure 8). Cathodic current density increased from an noble potential close to the potential obtained without any complexing agents, to a limited current density. The effect of additional $(\text{NH}_4)_2\text{SO}_4$ is comparable to the favourable effect caused by $(\text{NH}_4)_2$ -citrate. The current density/potential curves show that mainly a surplus of (NH_4) -ions shift the deposition potential to negative values. Citrate as the main complexing agent for iron(III) is not sufficient enough. The observed change to a brown colour of the solution after addition of 0.1 mol $(\text{NH}_4)_2\text{SO}_4$ may indicate a partial formation of ammonium iron(III) citrate. Unfortunately this type of compound is not a stoichiometric one, two existing modifications (16,5 wt.-% to 18,5 wt.-% Fe : brown and 14,5 wt.-% to 16.0 wt.-% Fe : green) are known, and solubility is very high. Detection under such conditions was not possible therefore.

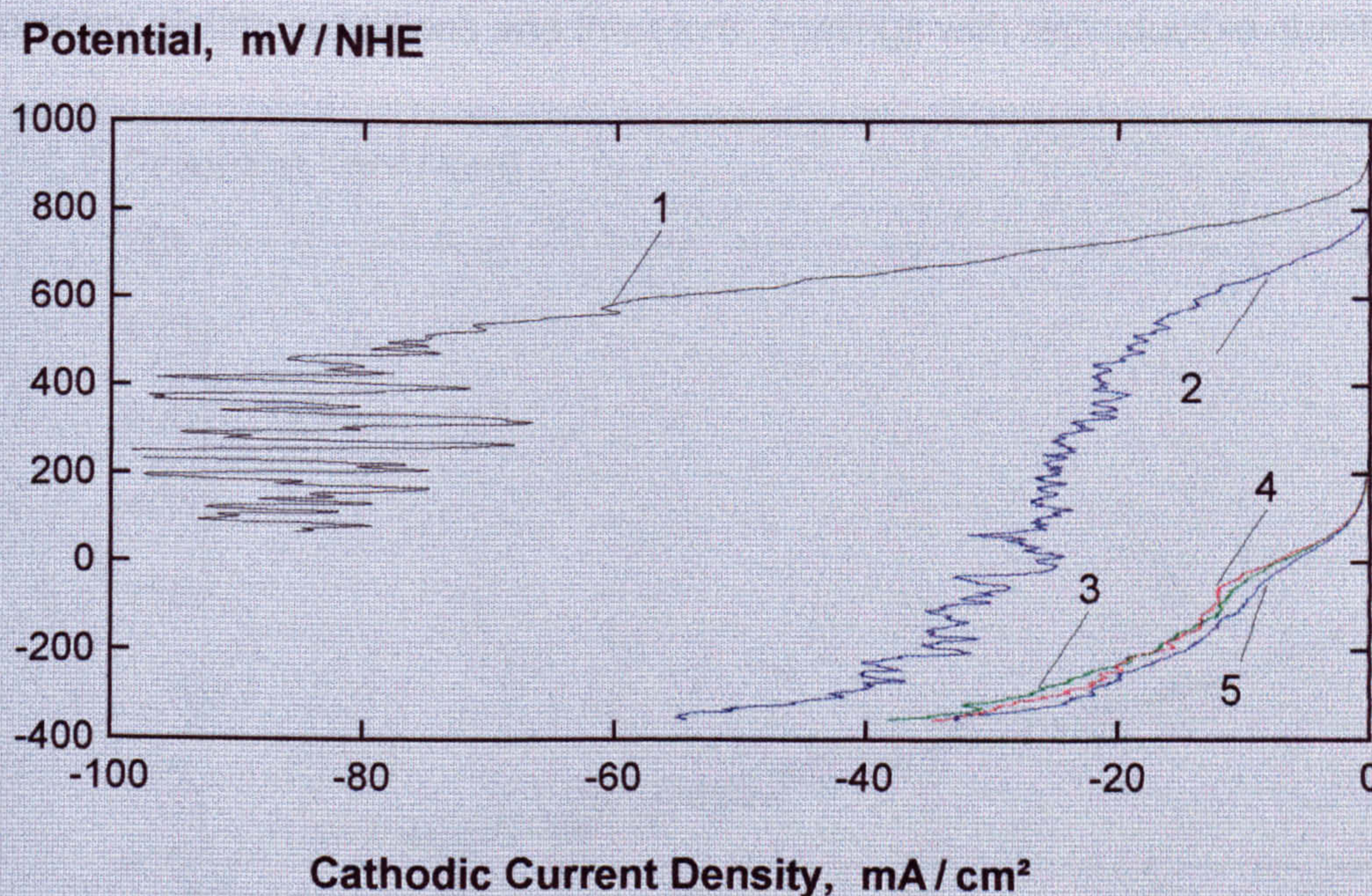


Figure 8

Effect of $(\text{NH}_4)_2$ -Citrate and $(\text{NH}_4)_2\text{SO}_4$ on Current Density Potential Curves of Iron Electrodeposition from Electrolytes containing FeCl_3 -Ions, pH = 0.2 - 3.0

Curve 1: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$

Curve 2: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.3 mol $(\text{NH}_4)_2$ -citrate

Curve 3: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.1 mol $(\text{NH}_4)_2\text{-SO}_4$

Curve 4: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.2 mol $(\text{NH}_4)_2\text{-SO}_4$

Curve 5: 0.3 mol Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.3 mol $(\text{NH}_4)_2\text{-SO}_4$

Temperature: 55°C, Substrate: Platinum, Scan rate: 1 mV/s, Rotation: 5000 r/min, Reference-Electrode: Calomel, Counter-Electrode: Glass-Carbon

Increase of ammonium sulfate from 0.1 mol to 0.3 mol does not change the current density/potential curves. Another disadvantage of this type of electrolyte was, that with the help of current density potential curves reduction of Fe^{3+} to Fe^{2+} could not be observed, because no change in the shape of curves occurred. Considering that the metal deposition could not result from Fe^{3+} and homogenous and partly bright iron coatings were deposited on the samples, reduction of Fe^{3+} to metallic iron via Fe^{2+} reduction must have occurred. Because only the iron electrolyte with ammonium citrate and ammonium sulfate was the appropriate one, in view of both chemical stability and stability during electrodeposition, further experiments were carried out with this type of electrolyte. Figure 9 shows the current density/potential curves versus rotation of the substrate. In the range of 1000 -8000 r/min no change in the shape of the curves appear. Alterations of hydrodynamic conditions is not a compelling reason for a change of the plating conditions. Employment of such an electrolyte for high speed plating should show constant plating conditions and therefore, coatings with reproducible quality.

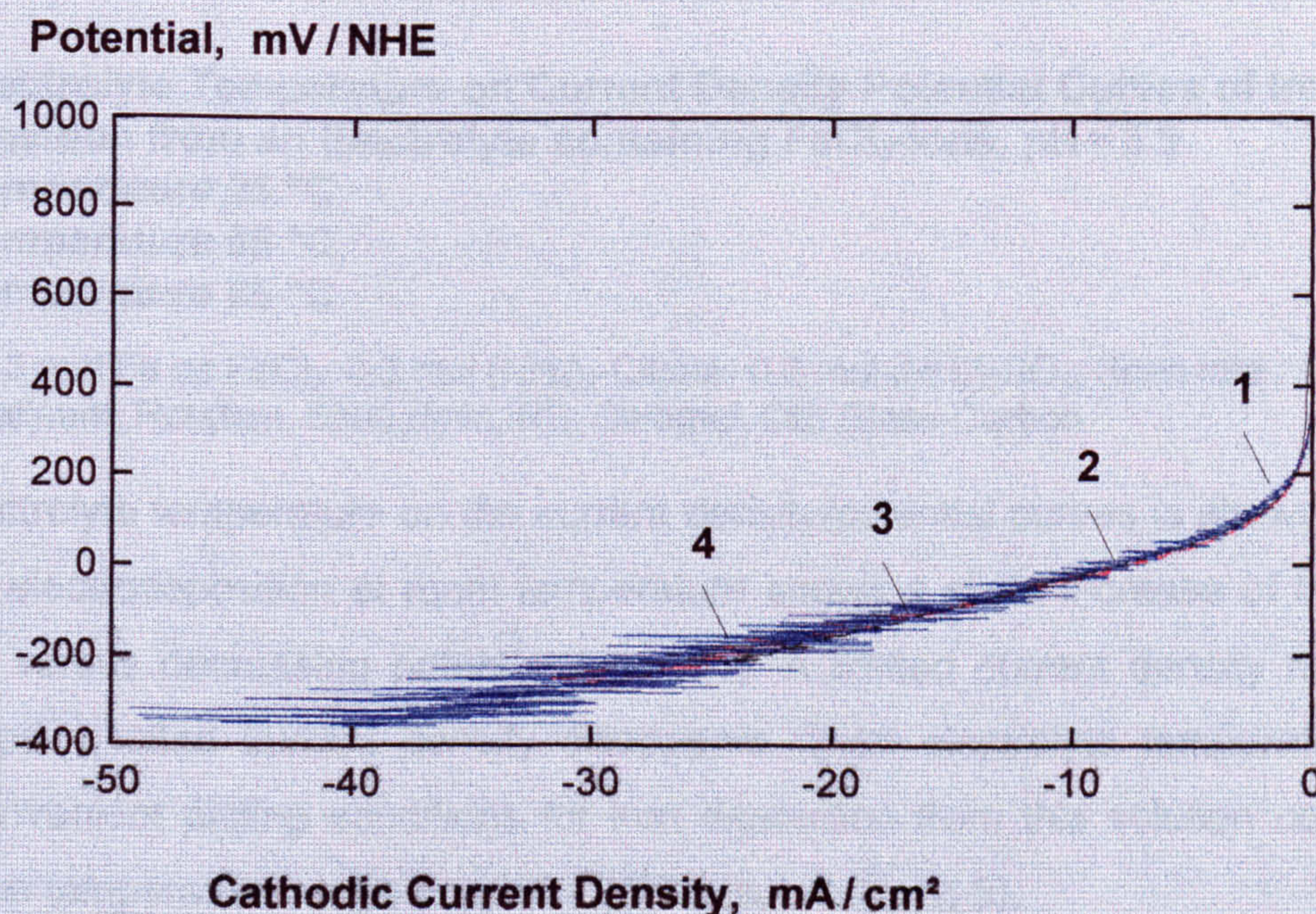


Figure 9

Effect of Electrode Agitation on Current Density Potential Curves of Iron Electrodeposition from an Electrolyte containing FeCl_3 -Ions, pH = 3.5

Curve 1: Rotation 1000 r/min

Curve 2: Rotation 2000 r/min

Curve 3: Rotation 5000 r/min

Curve 4: Rotation 8000 r/min

**Electrolyte: 0.3 mol Fe as FeCl_3 , 0.3 mol $(\text{NH}_4)_2\text{-Citrate}$, 0.3 mol $(\text{NH}_4)_2\text{SO}_4$, Substrate: Platinum
Temperature: 55°C, Scan rate: 1 mV/s, RE: Calomel, CE: Glass-Carbon**

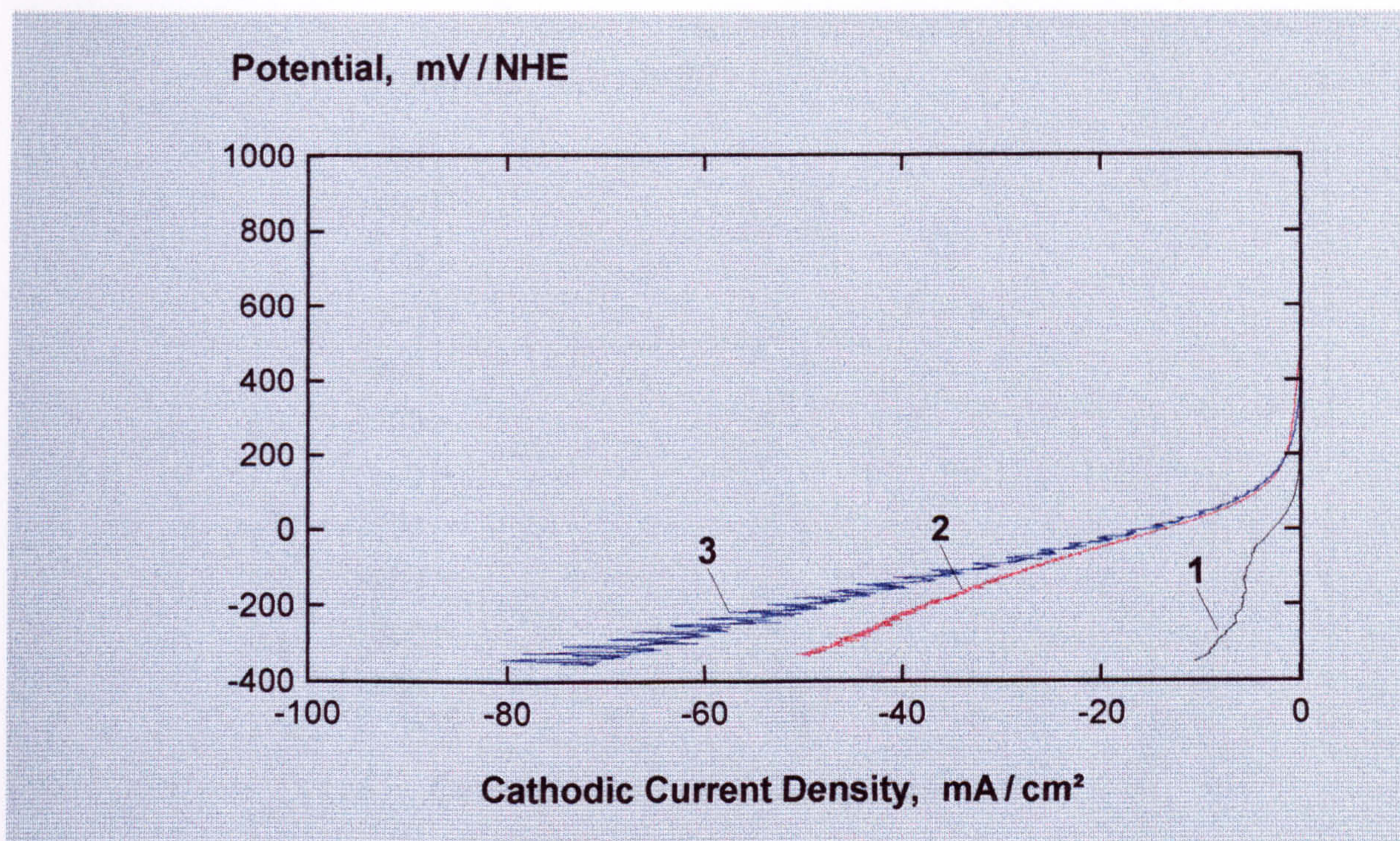


Figure 10

Effect of Electrolyte Temperature on Current Density Potential Curves of Iron Electrodeposition from an Electrolyte containing FeCl_3 -Ions, $\text{pH} = 3.5$

Curve 1: Temperature 25 °C

Curve 2: Temperature 55 °C

Curve 3: Temperature 65 °C

Electrolyte: 0.3 mol Fe as FeCl_3 , 0.3 mol $(\text{NH}_4)_2\text{-Citrate}$, 0.3 mol $(\text{NH}_4)_2\text{SO}_4$, Scan rate : 1 mV/s
Substrate: Platinum, Rotation: 5000 r/min, RE: Calomel, CE: Glass-Carbon

Effect of electrolyte temperature on the current density/potential curves is shown in figure 10. Iron electrodeposition at room temperature shows a slight increase of the current density versus decreasing potential (curve 1). A limited current density range is also observed. Limited current density disappears when electrolyte temperature increases. Convenient plating conditions for iron deposition from this solution could be obtained in an temperature range from 55 - 65 °C (curve 2 and 3).

Current density/potential curves of palladium electrodeposition from different ligands are shown in figure 11. Palladium deposition from PdSO_4 occurs at a noble potential in the range of 600 - 650 mV/NHE. This potential range is in good correspondence to the equilibrium potentials of $[\text{PdCl}_4]^{2-} = + 0.62 \text{ mV/NHE}$ and $[\text{PdCl}_6]^{4-} = + 0.61 \text{ mV/NHE}$ [16]. This potential is typical for simple hydrated anions. If the palladium is present as an ammine complex like diaminodinitrite (curve 2) or palladosamine chloride (curve 3) deposition potentials shift to more cathodic values. The obtained curves come close to

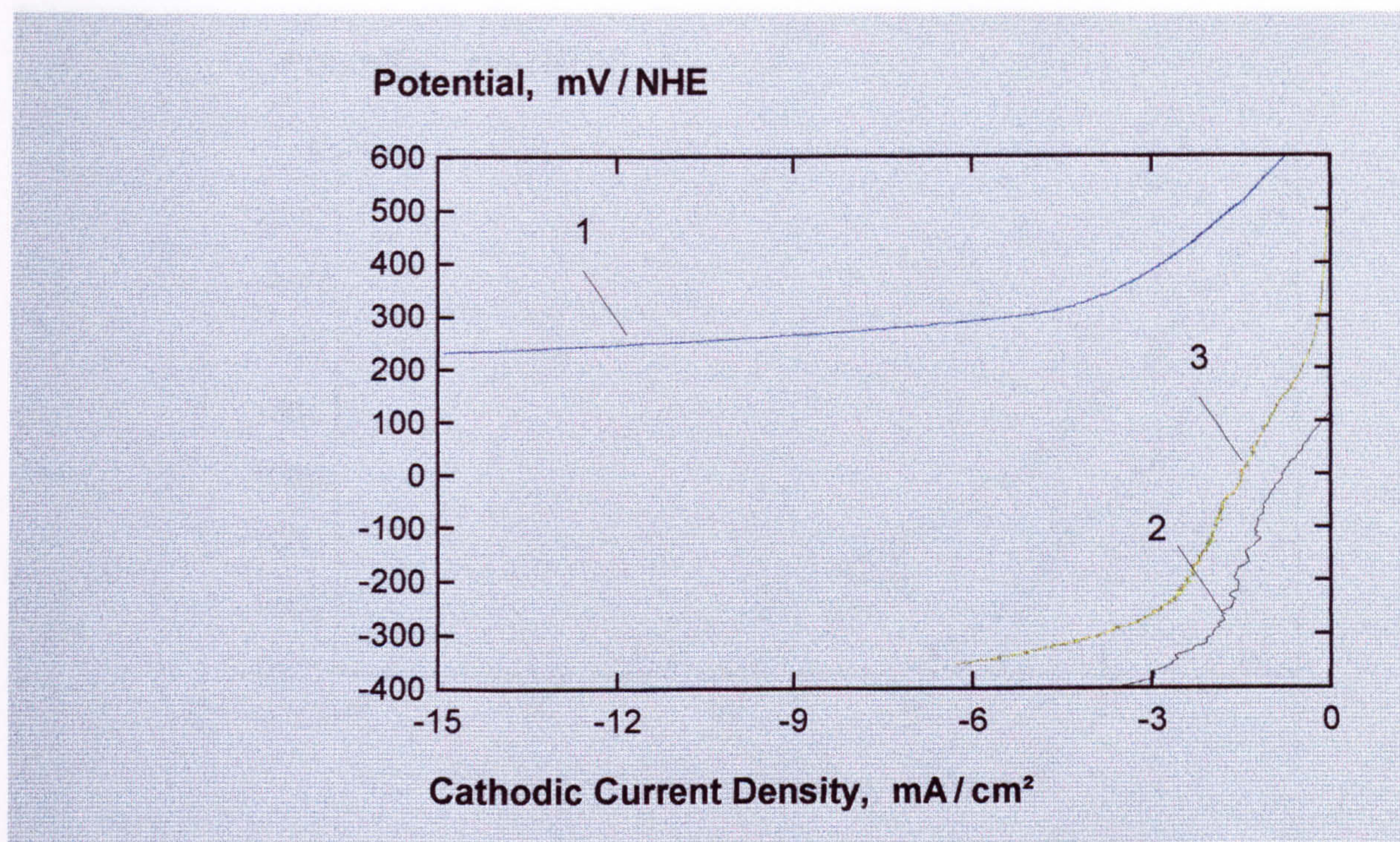


Figure 11

Effect of Palladium Salt on Current Density Potential Curves of Palladium Electrodeposition from Different Solutions

Curve 1: 0.3 mol/l Pd as PdSO₄, pH=5.0

Curve 2: 0.3 mol/l Pd as Pd(NH₃)₄(NO₂)₂, pH=8.5

Curve 3: 0.3 mol/l Pd as [Pd(NH₃)₄]Cl₂, pH=8.2

Temperature: 55°C, Substrate: Platinum, Scan rate: 1 mV/s, Rotation: 5000 r/min, Reference-Electrode: Calomel, Counter-Electrode: Glass-Carbon

the equilibrium electrode potentials ($[\text{Pd}(\text{NO}_2)_4]^{2-} = + 0.340 \text{ mV/NHE}$ and $[\text{Pd}(\text{NH}_3)_4]^{2+} = 0.00 \text{ mV/NHE}$ [16]. Because in most cases good alloy deposition does not occur if the difference between the electrode potential is too large [2], for further experiments an electrolyte containing FeCl₃, [Pd(NH₃)₄]Cl₂, (NH₄)₂-citrate, (NH₄)₂SO₄, and NH₄·OH was selected. The typical current density/potential curves, both curves from electrolytes containing palladium or iron alone and curves for palladium-iron electrolytes with a high or a low amount of palladium are shown in figure 12. The deposition potential of pure palladium (curve 2) in such a solution is more noble than the deposition potential of pure iron electrodeposition (curve 1). As expected, both deposition potentials are close together. The current density/potential curves of the alloy deposition is nearly the same as the curve obtained from iron electrodeposition. Increase or decrease of the palladium content does not change the current density potential curves markedly.

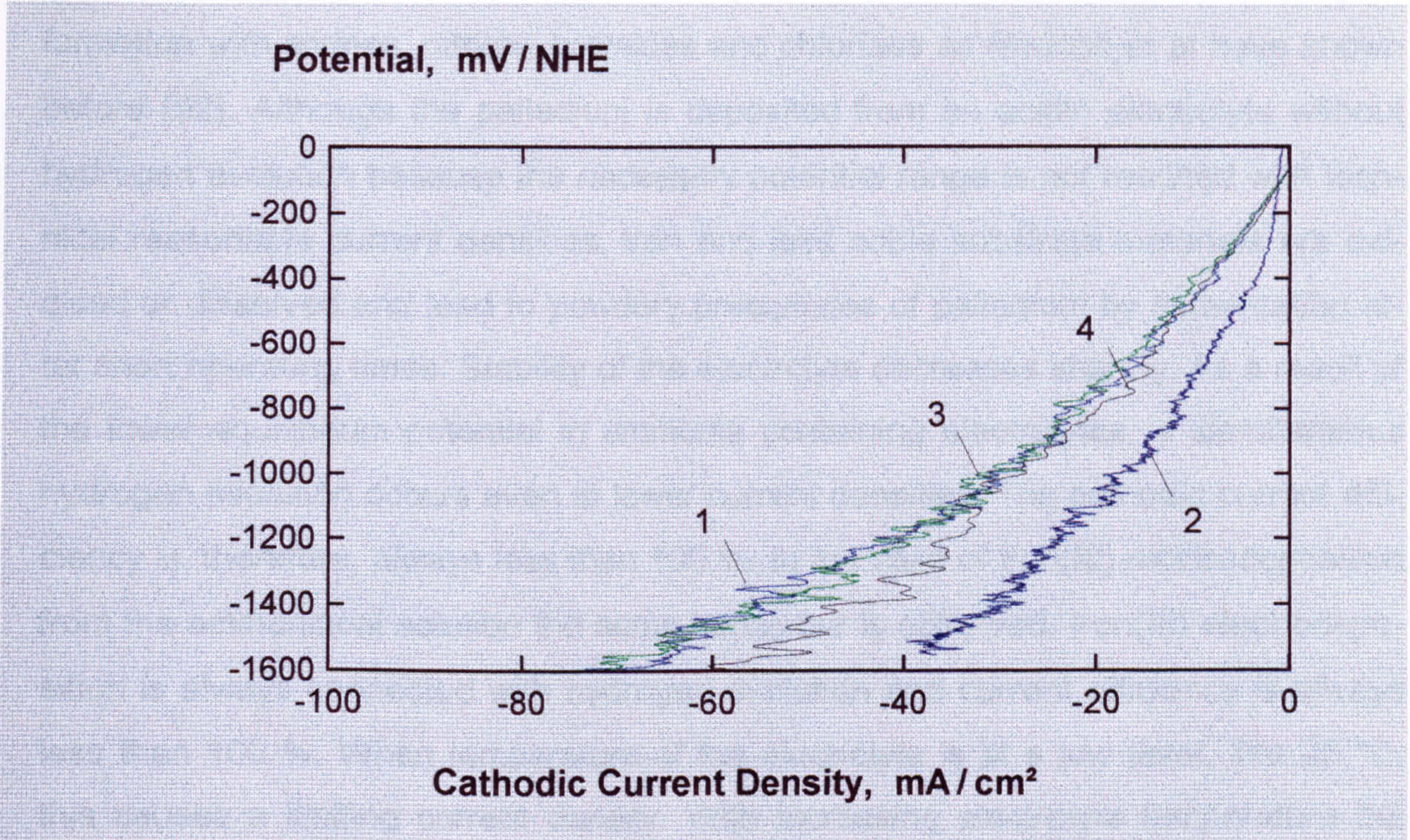


Figure 12
Effect of Electrolyte Composition on Current Density Potential Curves of Palladium-Iron Alloy Electrodeposition from Ammoniacal Solutions
Curve 1: 25 g/l Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$
Curve 2: 10 g/l Pd as $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$
Curve 3: 25 g/l Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 0.5 g/l Pd as $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$
Curve 4: 0.5 g/l Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ + 10 g/l Pd as $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$

Electrolyte: 25 - 110 g/l $(\text{NH}_4)_2\text{-Citrate}$, 15 - 65 g/l $(\text{NH}_4)_2\text{SO}_4$, x ml $\text{NH}_4 \cdot \text{OH}$, pH = 8.2
Temperature: 55°C, Substrate: Platinum, Scan rate: 1 mV/s, Rotation: 5000 r/min,
Reference-Electrode: Calomel, Counter-Electrode: Glass-Carbon

Electrolyte	Iron 0.3 mol Fe	Palladium-Iron Pd : Fe = 1 : 1	Palladium-Iron Pd : Fe = 1 : 100	Palladium 0.3 mol Pd
Substrate				
Iron (5 μm on Gold)	- 125 mV			+ 140 mV
Gold (Bulk)	- 110 mV	- 70 mV	- 70 mV	- 50 mV
PdFe (80/20)		from 0 to - 10 mV	from 0 to - 10 mV	
PdFe (15/85)		from 0 to - 10 mV	from 0 to - 10 mV	
Pd (5 μm on Gold)				+ 130 mV

Table 12
Deposit Potential (mV/NHE) of Palladium, Iron, and Palladium-Iron Electrolytes on Various Metal Surfaces; Measurement Conditions see Figure 12

The cathodic reduction of palladium in aqueous solutions is possible via complex formation with amines, nitrites, bromides and chlorides as *Hedrich* et al have shown before [92]. Although the palladium is deposited from an acidic electrolyte without hydrogen evolution because the necessary potential range is not reached with technical reasonable current densities, iron and less noble substrate materials are oxidised or dissolved and lead to powdery precipitates of palladium by cementation after short operating times. Stability of the electrolyte decreases sharply. As a result of the lower equilibrium potential in ammonia containing electrolytes, a simultaneous hydrogen evolution occurs even at lower current densities. The cathodic current efficiency is, therefore, always less than 100 %. In the case of iron(III) electrodeposition from the ammoniacal solution the same behaviour is observed. Iron(III) electrodeposition is always connected with hydrogen evolution and current efficiency is always less than 100 %. When temperature of the electrolyte is at a low level, like 25 °C; this causes a limiting current density. With increasing electrolyte temperature the limited current density disappears. The experiments with various rotations of the electrode up to 8000 r/min show that iron electrodeposition from ammoniacal solutions is not limited by hydrodynamic effects. There is only a slight decrease in iron electrodeposition or, in the case of palladium-iron alloy deposition, an decrease of the amount of iron co-deposition when plating occur without either substrate agitation or electrolyte agitation. Because palladium in these solution and with these complexing agents is still the more noble one, during electrodeposition palladium reduction is always preferred in the case when the amount of ions for reduction is large enough. If iron rich alloy coatings are desired the amount of noble metal in the electrolyte has to decrease. When the pH of the solution is in the range of 7.5 - 10.5, composition of the deposited alloys therefore, depends mainly on the ratio of the metal ions in the electrolyte. In table 12 the deposition potentials of iron, palladium, and palladium-iron on different substrate are shown. While the difference of deposition potential of iron and palladium on a gold substrate is ca. 50 mV, the difference increases up to more than 250 mV when the substrate is iron. The deposition potential of the palladium-iron alloy electrodeposition depends on the kind of substrate, but it is independent from metal ratio in the electrolyte. In comparison to the deposition potential on gold substrates the deposition potential on palladium-iron substrates (as deposited) is about 60 mV to 70 mV more noble.

4. 1. 2 Electrolyte Characteristics

4. 1. 2. 1 Effect on Alloy Composition of Palladium-Iron Coatings

Composition of the deposited alloys depends mainly on the ratio of the metal ions in the electrolyte as shown in figure 13, while the effect of current density is very slight. From an electrolyte with a metal ratio of Pd : Fe (mol : mol) from 1 : 10 to 1 : 100 iron co-deposition in the alloy coatings is in the range of 80 wt.-% to 85 wt.-%. When the metal ratio of Pd : Fe in the electrolyte is in the range of 10 : 1 or 1 : 2 iron co-deposition is much less in the range of 15 wt.-% to 20 wt.-%.

Metal ratio of Pd : Fe from about 1 : 5 to 1 : 4 enables the electrodeposition of alloys with a metal compound of nearly 50 : 50 wt.-%. Unfortunately such type of deposits are very brittle and no homogeneous coatings could be obtained. The alloy layers peel off from the surface during electrodeposition.

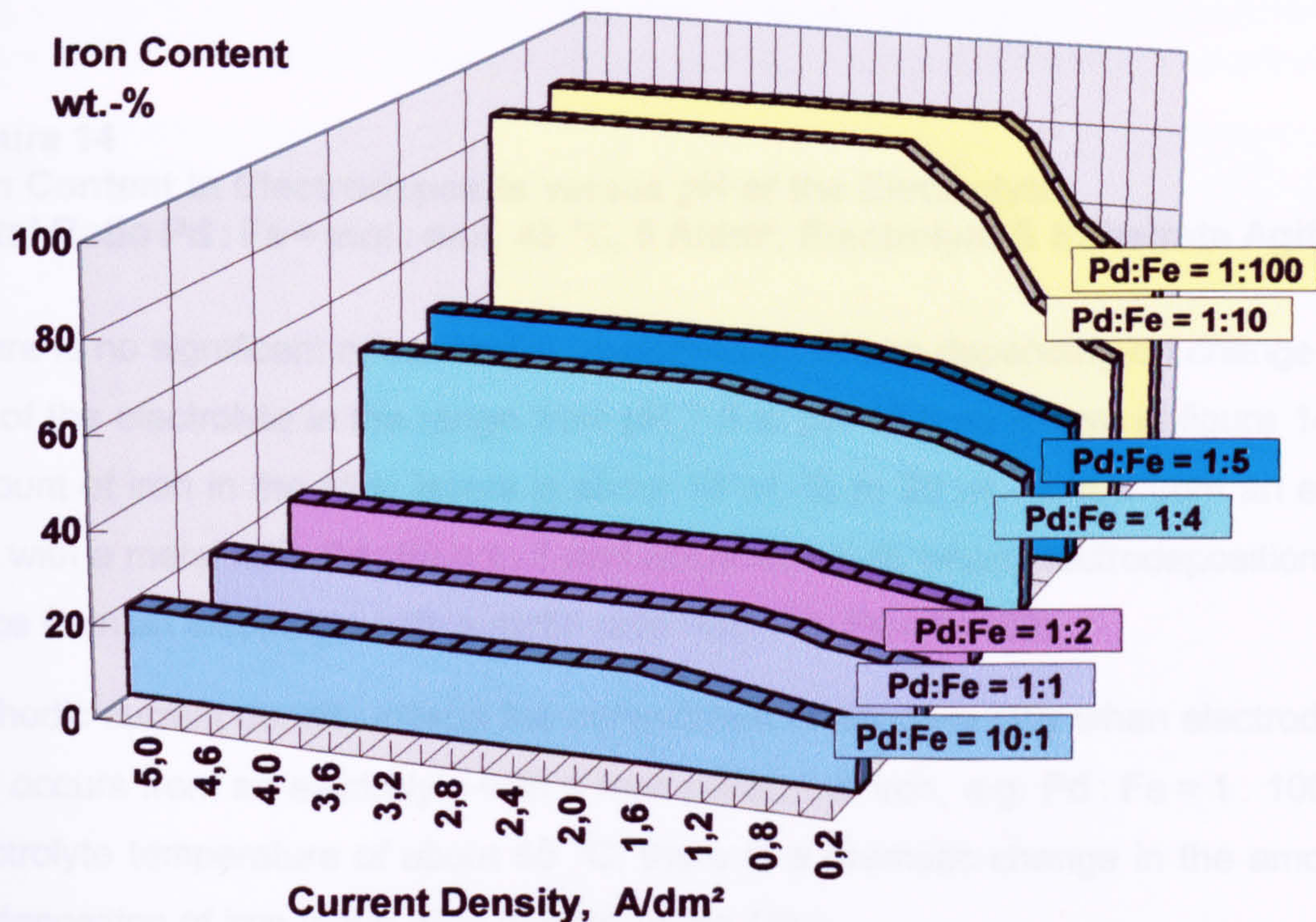


Figure 13

Iron Content in Electrodeposits versus Electrolyte Composition
Metal Ratio: Pd : Fe = mol : mol, 55 °C, 5 A/dm², pH = 8.2, Agitation

Iron Content, wt.-%

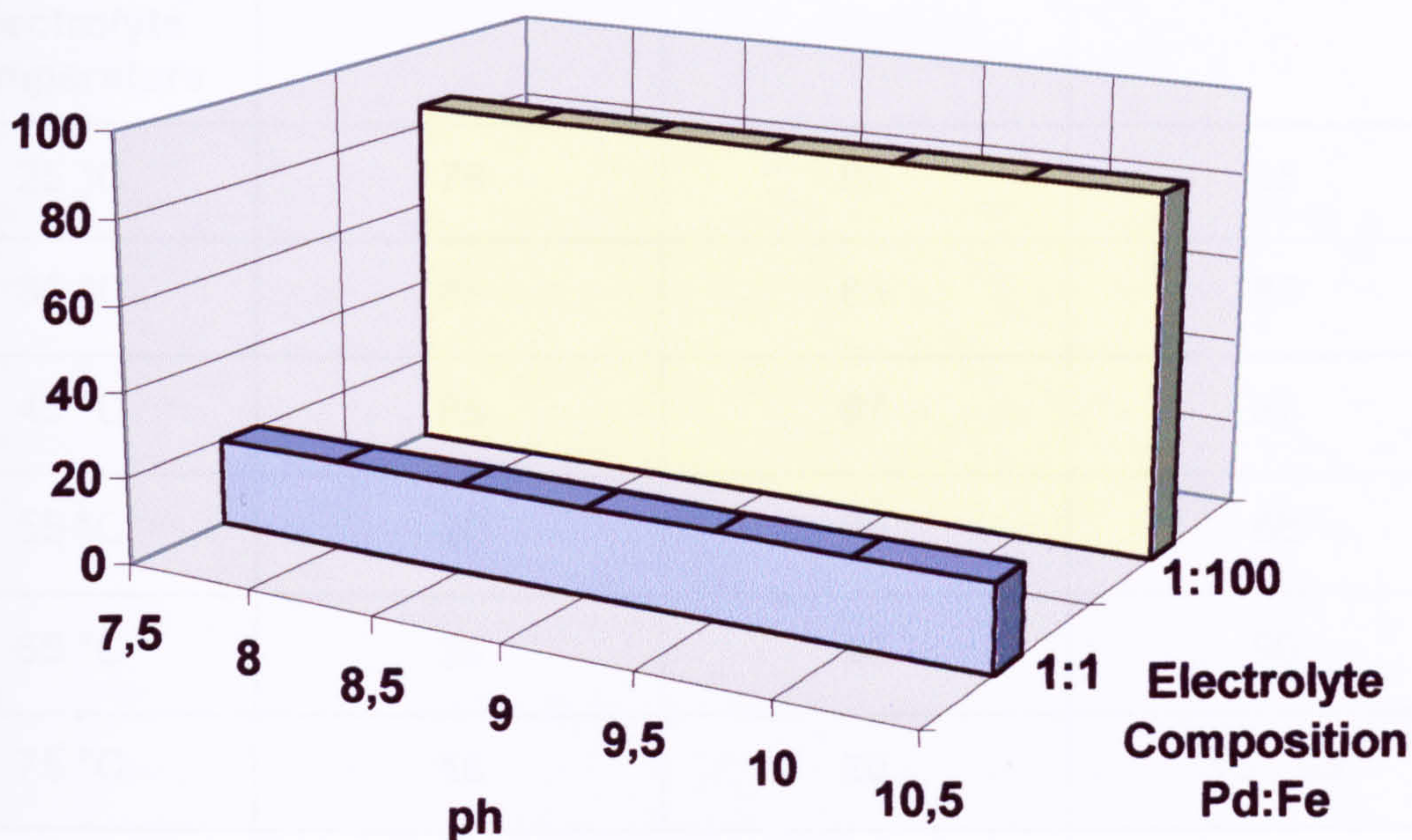


Table 13
Iron Content of Palladium-Iron Deposits versus Electrolyte Temperature and Current Density, Electrolyte Pd : Fe = 100, Substrate & Electrolyte Agitation

Figure 14

Iron Content in Electrodeposits versus pH of the Electrolyte
Metal Ratio Pd : Fe = mol : mol, 45 °C, 5 A/dm², Electrolyte & Substrate Agitation

There is no significant effect on the co-deposition of iron depending on change of the pH of the electrolyte in the range from pH 7.5 to pH 10.5 as shown in figure 14. The amount of iron in the alloy layers is about 18 wt.-% to 20 wt.-% iron from an electrolyte with a metal ratio Pd : Fe = 1 : 1 and about 85 wt.-% when electrodeposition takes place from an electrolyte with a metal ratio from Pd : Fe = 1 : 100.

Cathodic current density affects the composition of deposits only when electrodeposition occurs from an electrolyte with a high content of iron, e.g. Pd : Fe = 1 : 100. At a electrolyte temperature of about 55 °C, there is a dramatic change in the amount of co-deposition of iron in the alloy coating (table 13).

The iron content in the layer drops from 85 wt.-% to a range of 15 wt.-% to 25 wt.-%. Increasing current densities from 3.0 to 5.0 or 8.0 A/dm² reduce this effect at first, but with increasing temperatures up to a range of 65 °C to 75 °C, the co-deposition of iron is only possible in a range of 15 wt.-% to 20 wt.-%.

Iron Content wt.- %	Current Density		
	3 A/dm ²	5 A/dm ²	8 A/dm ²
Electrolyte Temperature			
25 °C	78	85	85
35 °C	85	85	85
45 °C	85	87	87
55 °C	20	88	88
65 °C	20	25	90
75 °C	15	20	15 - 65

Table 13

Iron Content of Palladium-Iron Deposits versus Electrolyte Temperature and Current Density, Electrolyte: Pd : Fe 1 : 100, Substrate & Electrolyte Agitation

Palladium Content wt.- %	Current Density		
	3 A/dm ²	5 A/dm ²	8 A/dm ²
Electrolyte Temperature			
25 °C	80	80	77
35 °C	82	80	80
45 °C	82	80	80
55 °C	80	82	82
65 °C	85	82	82
75 °C	85	85	85

Table 14

Palladium Content of Palladium-Iron Deposits versus Electrolyte Temperature and Current Density, Electrolyte: Pd : Fe 1 : 1, Substrate & Electrolyte Agitation

Deposition at an electrolyte temperature of 75 °C and current density of 8 A/dm² cause two different types of electrodeposition: bright layers with a reduced iron content on the one hand and very brittle layers with a high iron content on the other hand. Palladium electrodeposition is preferred when the electrolyte temperatures are above 55 °C and when high current densities are used (5 - 8 A/dm²). Under such conditions iron co-deposition is inhibited. In contrast electrodeposition from an electrolyte with a high content of palladium, e. g. Pd : Fe = 1 : 1, composition of the palladium-iron deposits is almost constant (table 14).

4. 1. 2. 2 Current Efficiency

Current efficiency of the palladium-iron alloy electrodeposition from ammoniacal electrolyte, pH = 7.5 - 10.5 depends significantly on the ratio of the metal ions in the electrolyte as shown in table 15 and table 16. Current efficiency of an electrolyte with a metal ratio of Pd : Fe = 1 : 1 is typically about 80 % in a temperature range from 45 °C to 65 °C (table 15). Current efficiency decreases with increasing current densities and decreasing electrolyte temperatures to a range of 60 to 70 %.

Current efficiency of an electrolyte with a metal ratio Pd : Fe = 1 : 100 is for temperatures of 45 °C and current densities from 5 to 8 A/dm² in a range of 25 to 30 %. This means 75 % of the energy expenditure are for parallel processes and not for the real electrodeposition of the metals (table 16). If the current densities are in the range of 3 - 5 A/dm² and electrolyte temperatures are above 45 - 50 °C current efficiency of this type of electrolyte drops to a value of about 5 %. Under practical conditions this means that no electrodeposition occurs.

The dramatic decrease in current efficiency takes place in parallel with the decrease of iron content in the alloy coating. Only less than 20 % of the iron is deposited under this conditions compared with electrodeposition from the same electrolyte at 45 °C and 3 - 8 A/dm². On the assumption that the other reactions, like palladium reduction and hydrogen evolution are almost constant under this conditions, the only possible additional reaction is the reduction of iron from the iron(III) state to the iron(II) state. Because the iron ion in the electrolyte is in the iron(III) state and electrodeposition is only possible from the iron(II) state, previous reduction of iron(III) to iron(II) must occur.

Current Efficiency %	Current Density		
	3 A/dm ²	5 A/dm ²	8 A/dm ²
Electrolyte Temperature			
25 °C	70	60	60
35 °C	80	65	65
45 °C	80	75	65
55 °C	85	80	70
65 °C	85	85	70
75 °C	85	85	85

Table 15

Current Efficiency of Palladium-Iron Electrodeposition versus Electrolyte Temperature and Current Density, Electrolyte: Pd : Fe 1 : 1, pH = 8.2, Agitation

Current Efficiency %	Current Density		
	3 A/dm ²	5 A/dm ²	8 A/dm ²
Electrolyte Temperature			
25 °C	5 - 20	25	25
35 °C	15 - 20	20	25
45 °C	17 - 25	25 - 30	25
55 °C	5	30	25
65 °C	5	5	25
75 °C	5	5	5

Table 16

Current Efficiency of Palladium-Iron Electrodeposition versus Electrolyte Temperature and Current Density, Electrolyte: Pd : Fe 1 : 100, pH = 8.2, Agitation

It seems that at higher temperatures and lower current densities conditions are established which prefer the reduction of iron(III) to iron(II) and inhibit the iron electrodeposition to a minimum. Palladium cannot replace the iron, because of the very few amount of palladium in the electrolyte. Palladium electrodeposition occurs very close or at limited current density. Two reactions, which overlap one another, affect mainly the alloy deposition. First the decrease of the reduction of iron(II) to metal electrodeposition and, second, the increase of the amount of iron(III) reduction to iron(II) with increasing temperatures. Only the increase in current density shifts the reduction potential of iron deposition to a range, where iron(II) reduction is preferred.

4. 1. 2. 3 Deposition Rate

The deposition rate of the alloy electrolyte is conducted to the current efficiency of the electrolyte and therefore, mainly depends on the metal ratio in the electrolyte. But current density and temperature of the electrolyte also affect the speed of the alloy deposition. Deposition rate of an electrolyte with a metal ratio of Pd : Fe = 1 : 1 increases with increasing temperature and current densities from 0.5 $\mu\text{m}/\text{min}$ at 25 °C, 3 A/dm² to 1.8 $\mu\text{m}/\text{min}$ at 75 °C, A/dm² (table 17).

Deposition Rate $\mu\text{m}/\text{min}$	Electrolyte Pd : Fe = 1 : 1 Current Density			Electrolyte Pd : Fe = 1 : 100 Current Density		
Temperature	3 A/dm ²	5 A/dm ²	8 A/dm ²	3 A/dm ²	5 A/dm ²	8 A/dm ²
25 °C	0.5	0.8	1.2	0.06	0.2	0.3
35 °C	0.6	0.8	1.3	0.08	0.2	0.3
45 °C	0.6	1.0	1.3	0.1	0.2	0.3
55 °C	0.7	1.0	1.3	0.03	0.2 - 0.3	0.3
65 °C	0.7	1.1	1.4	0.02	0.05	0.3
75 °C	0.7	1.1	1.8	0.02	0.05	0.08

Table 17

Deposition Rate of Palladium-Iron Electrodeposition versus Electrolyte Temperature and Current Density from an Ammoniacal Electrolyte with Agitation

Typical deposition rates for this type of electrolyte are from 0.7 - 1.3 $\mu\text{m}/\text{min}$ at 45 °C to 65 °C (3 - 8 A/dm^2). Deposition rates of electrodeposition from an electrolyte with high iron content are in the range from 0.2 to 0.3 $\mu\text{m}/\text{min}$ at temperatures from 45 °C to 65 °C and current densities from 5 to 8 A/dm^2 . In comparison with an electrolyte with a metal ratio of 1 : 1, this process is slow. If deposition occurs at low current densities and high electrolyte temperatures, the deposition rate is even lower and in a range of 0.02 to 0.05 $\mu\text{m}/\text{min}$. Alloy deposition from this type of electrolyte with a iron content in the range of 20 wt.-% up to a thickness of about 3 - 4 μm means exposition times of about 1.5 to 3 hours. To produce alloy coatings with a layer-thickness more than a few nano-meters, it is important to run the electrolyte at low temperatures therefore. The disadvantage is that only electrodeposits with a high iron content can be (85 wt.-%) obtained under such conditions.

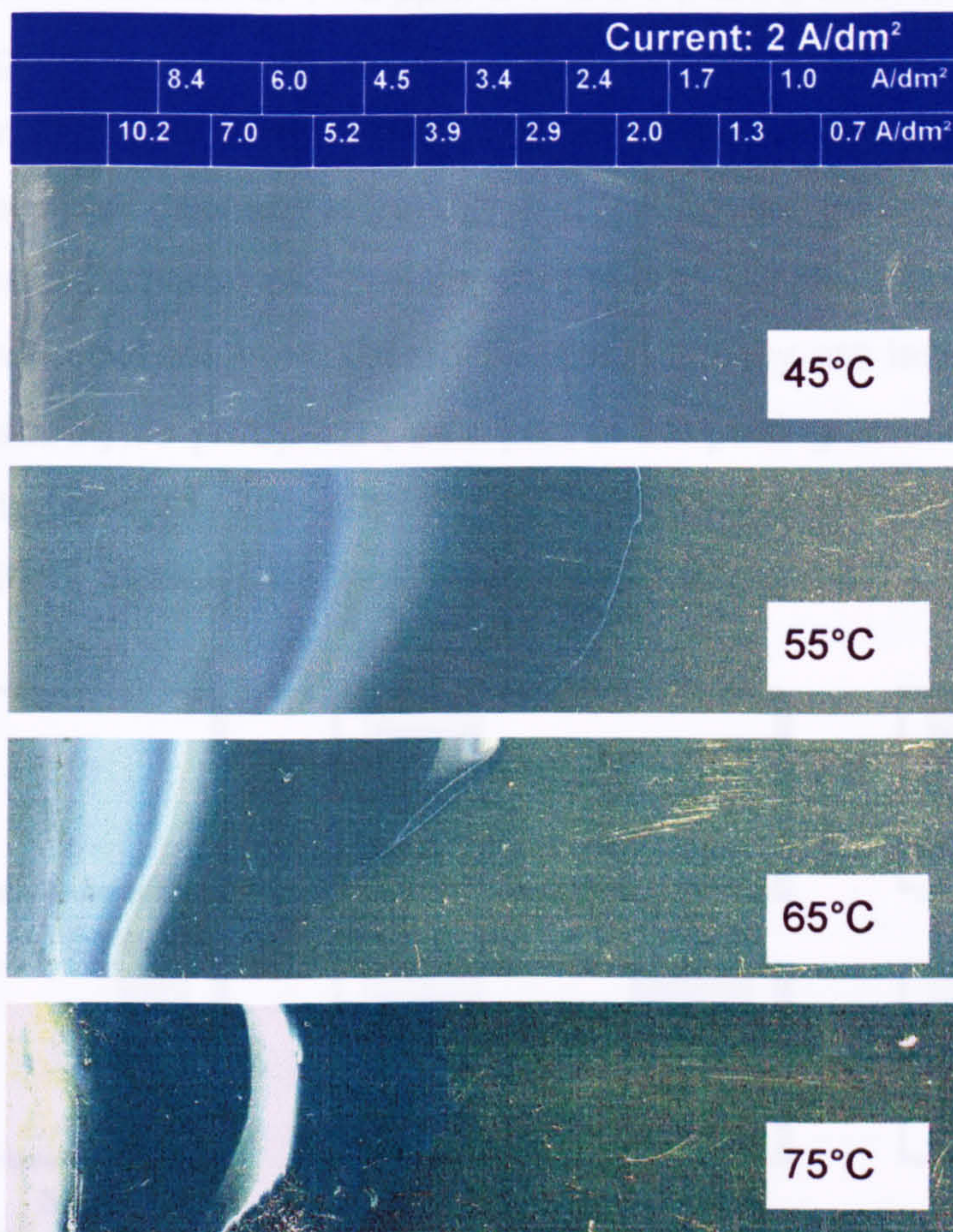


Figure 15

Samples Involving Electrodeposition of a Coating in the *Hull-Cell* According to DIN 50 957 [197], Electrolyte Pd : Fe 1 : 100, Electrolyte Agitation

4. 1. 2. 4 Effect of Impurities on Palladium-Iron Electrodeposition

In palladium and palladium-alloy electrolytes metal impurities (copper, gold and iron) and cyanides cause worsening of the electrodeposition and the properties of the resulting coatings. Especially pure palladium electrolytes are very sensitive to cyanide impurities; cyanide will complex the palladium metal and reduce the amount available for deposition. Palladium-nickel electrolytes are known to be less sensitive. Cyanide impurities come in a plating solution through insufficient rinsing after pre-treatment in cyanide containing solutions and from cyanide impurities as pollution of the air. Therefore, plating shops take care to separate cyanide baths from palladium plating solutions. Cyanide impurities are noticeable in change of the brightness and colour of the coatings deposited with low current densities. In figure 16 the effect on coating properties of an increasing cyanide content in a palladium-iron electrolyte ($E = 1 : 1$) is shown. Addition of 1 - 8 ppm CN^- to the plating solution does not cause any visible change of the layer properties. From 10 - 50 ppm CN^- the brightness of the palladium-ion coatings decreases at the low current density range. 100 ppm CN^- cause dark and dull deposits in the range of low current densities. The results show, that in fact palladium-iron electrolytes are not less sensitive to cyanide impurities in comparison with palladium-nickel electrolytes, but they are less sensitive than pure palladium electrolytes [198]. Iron, as a part of the plating solution was not classified as an impurity. Also it is known from palladium-nickel electrolytes, that iron does not affect deposition, because it simply replaces nickel in the alloy [199].

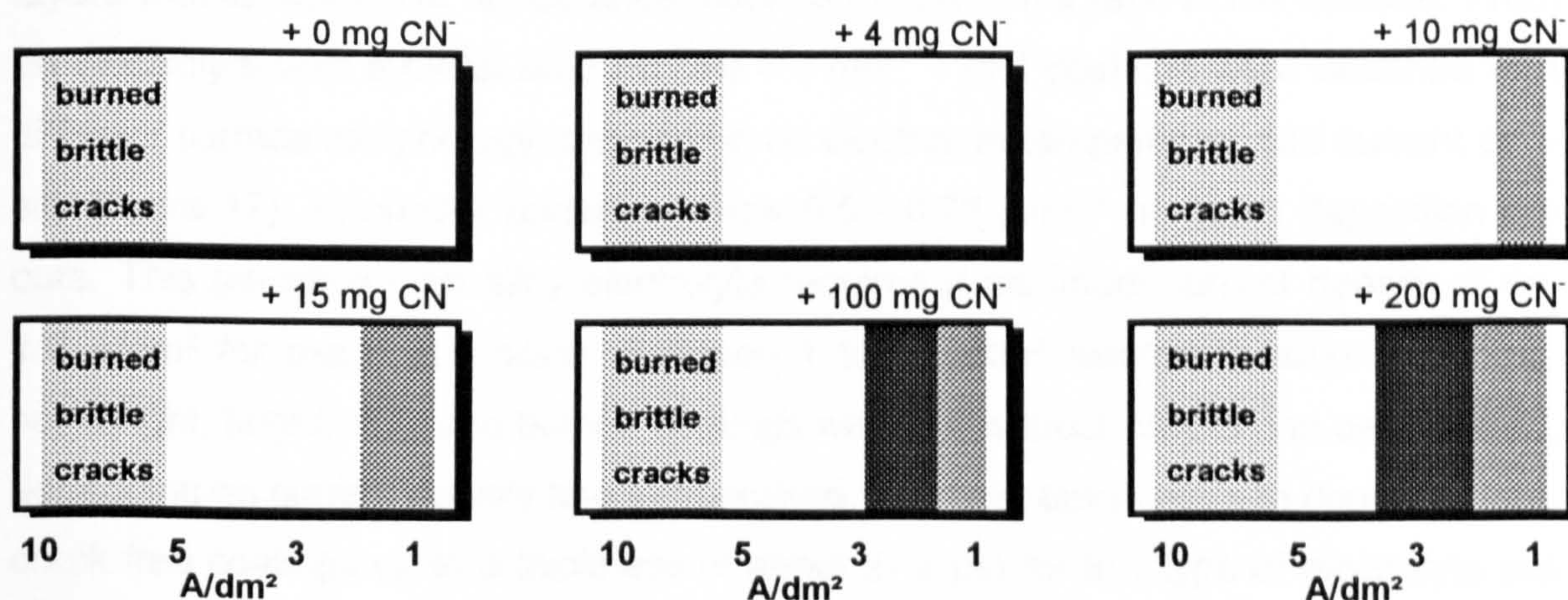


Figure 16

Effect of Cyanide Impurities on Electrodeposition of Palladium-Iron Coatings in the *Hull-Cell* According to DIN 50 957 [197], Current: 2 A, Temperature: 55 °C, pH = 8.2, Exposition Time: 10 min, Electrolyte: 1 : 1, see table 11, page 46

4. 2 Properties of Electroplated Palladium-Iron Alloys

4. 2. 1 Appearance

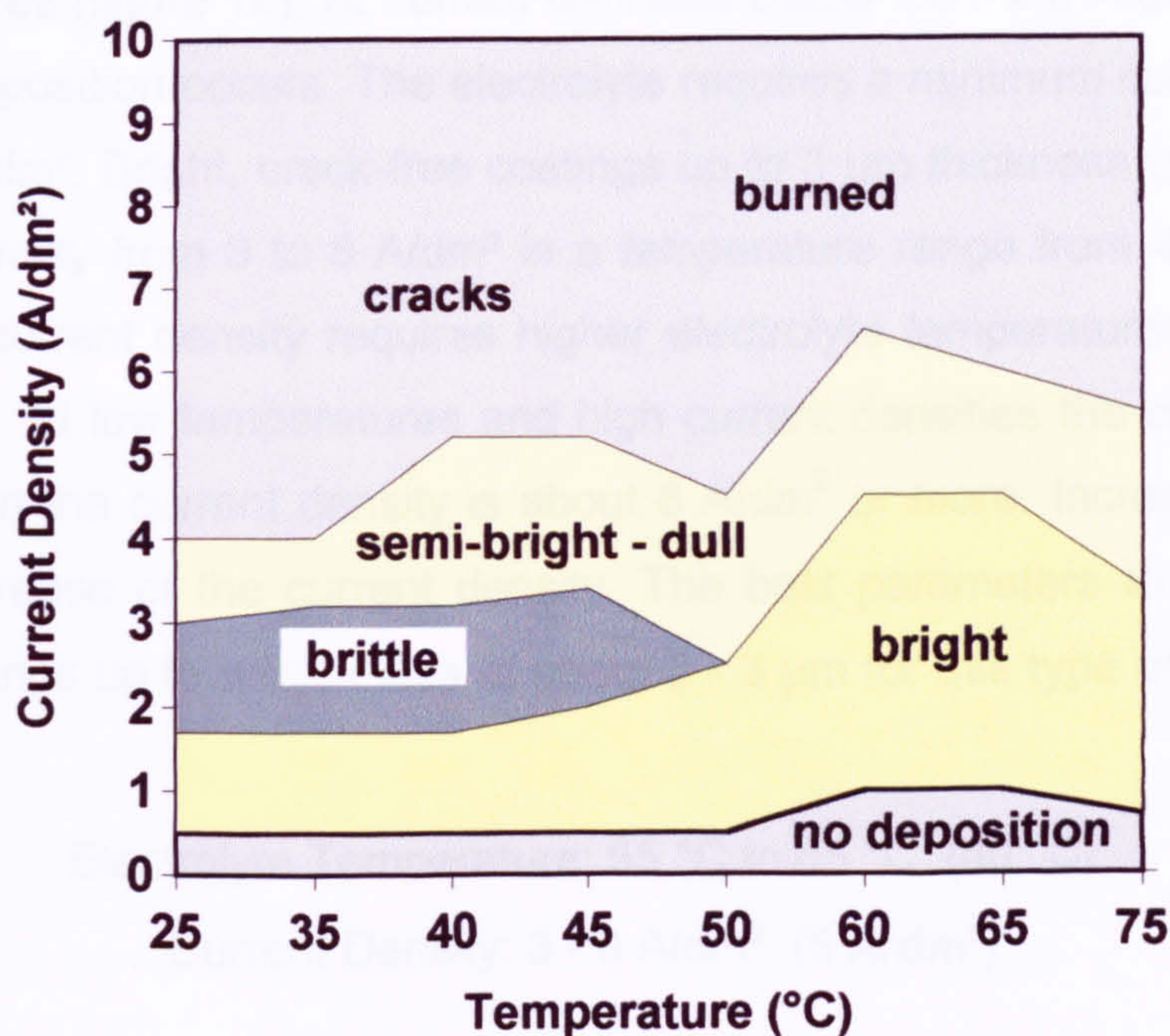


Figure 17

Appearance of Palladium-Iron Alloys versus Electrolyte Temperature and Current Density, Metal Ratio: Pd : Fe = 1 : 1, pH = 8.2, Substrate Agitation: 4 m/s, Electrolyte Agitation: 300 r/min, Coating Thickness: 0.5 - 2.5 μm , Magnification: 200 x

Applicable deposition parameters of this electrolyte, in order to deposit palladium-iron layers with an attractive appearance, depend on the metal ratio in the solution. From an electrolyte with a metal ratio Pd : Fe = 1 mol : 1 mol coatings were obtained with different surface morphology, depending on electrolyte temperature and current density (figure 17). At current densities below 0.5 - 0.75 A/dm² no metal deposition occurs. This palladium-iron alloy electrolyte requires a minimum current density of ca. 1.0 A/dm² for metal deposition. Between 1 to 8 A/dm² electrodeposition of brittle, semibright, bright, dull, and burned coatings with and without cracks can be obtained, depending on current density and temperature. The best parameters to deposit bright, crack-free coatings up to a thickness of about 2- 3 μm for this type of electrolyte are the following:

Electrolyte Temperature: 50 °C to 75 °C (**55° C**)

Current Density: 2 - 4 A/dm² (**3 A/dm²**)

The colour of bright palladium-iron deposits with a high amount of iron tends to appear a little brownish. Especially from electrolytes with a ratio $\text{Pd} : \text{Fe} = 1 : 100$, coatings with a high iron content tend to brownish colours, when current density is low at high temperatures (figure 18). At current densities below $1.5 - 2.0 \text{ A/dm}^2$ no homogeneous metal deposition occurs. The electrolyte requires a minimum current density of ca. $2.5 - 3.0 \text{ A/dm}^2$. Bright, crack-free coatings up to $3 \mu\text{m}$ thickness can be obtained at a current density from 3 to 8 A/dm^2 in a temperature range from 45°C to 75°C . High cathodic current density requires higher electrolyte temperatures in a range of 55°C to 65°C . At low temperatures and high current densities the coatings tend to crack, just when the current density is about 8 A/dm^2 or more. Increase of agitation enables an increase of the current density. The best parameters to deposit bright, crack-free coatings up to a thickness of about $2 - 3 \mu\text{m}$ for this type of electrolyte are the following:

Electrolyte Temperature: 55°C to 65°C (60°C)

Current Density: $3 - 8 \text{ A/dm}^2$ (5 A/dm^2)

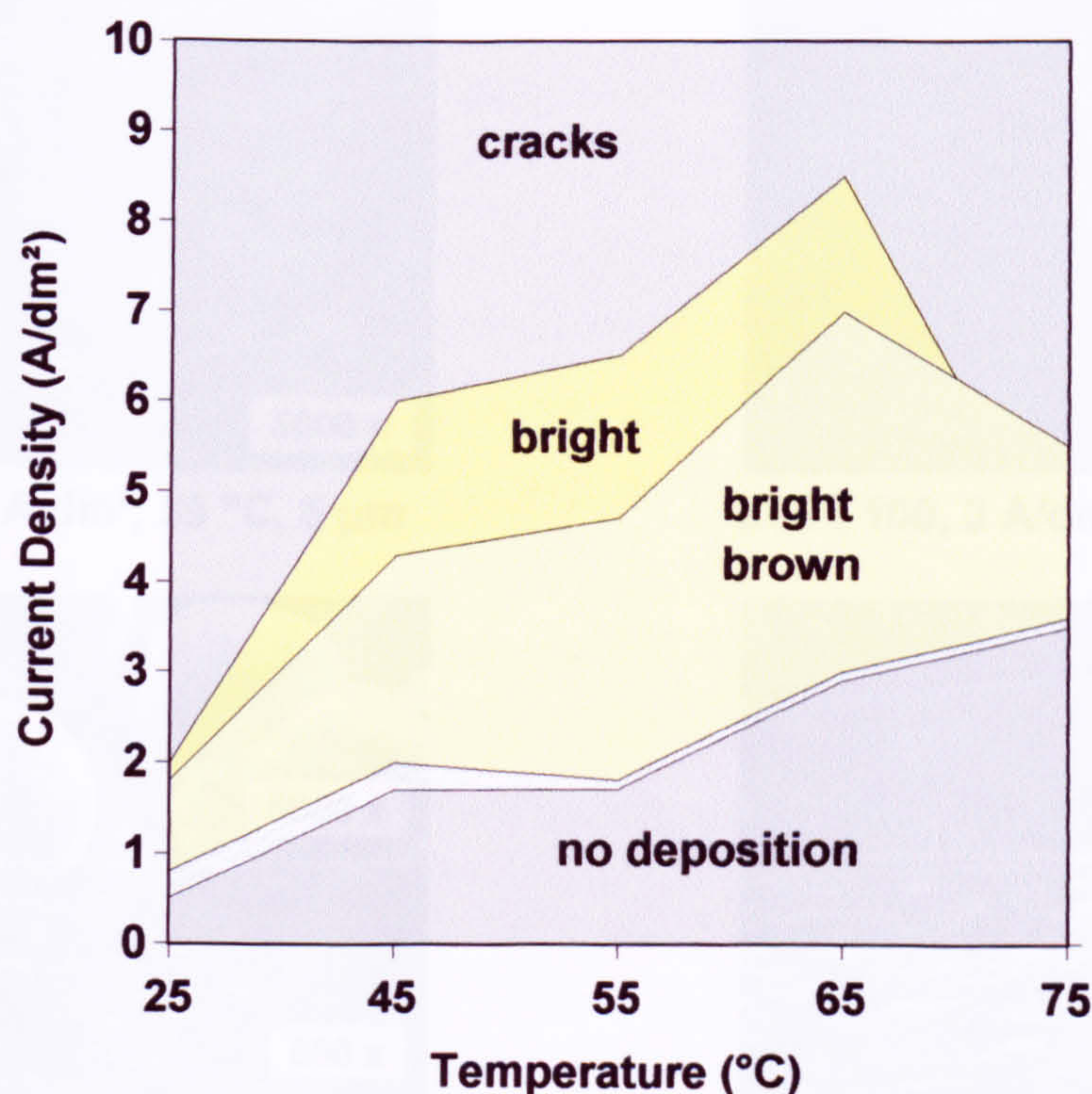
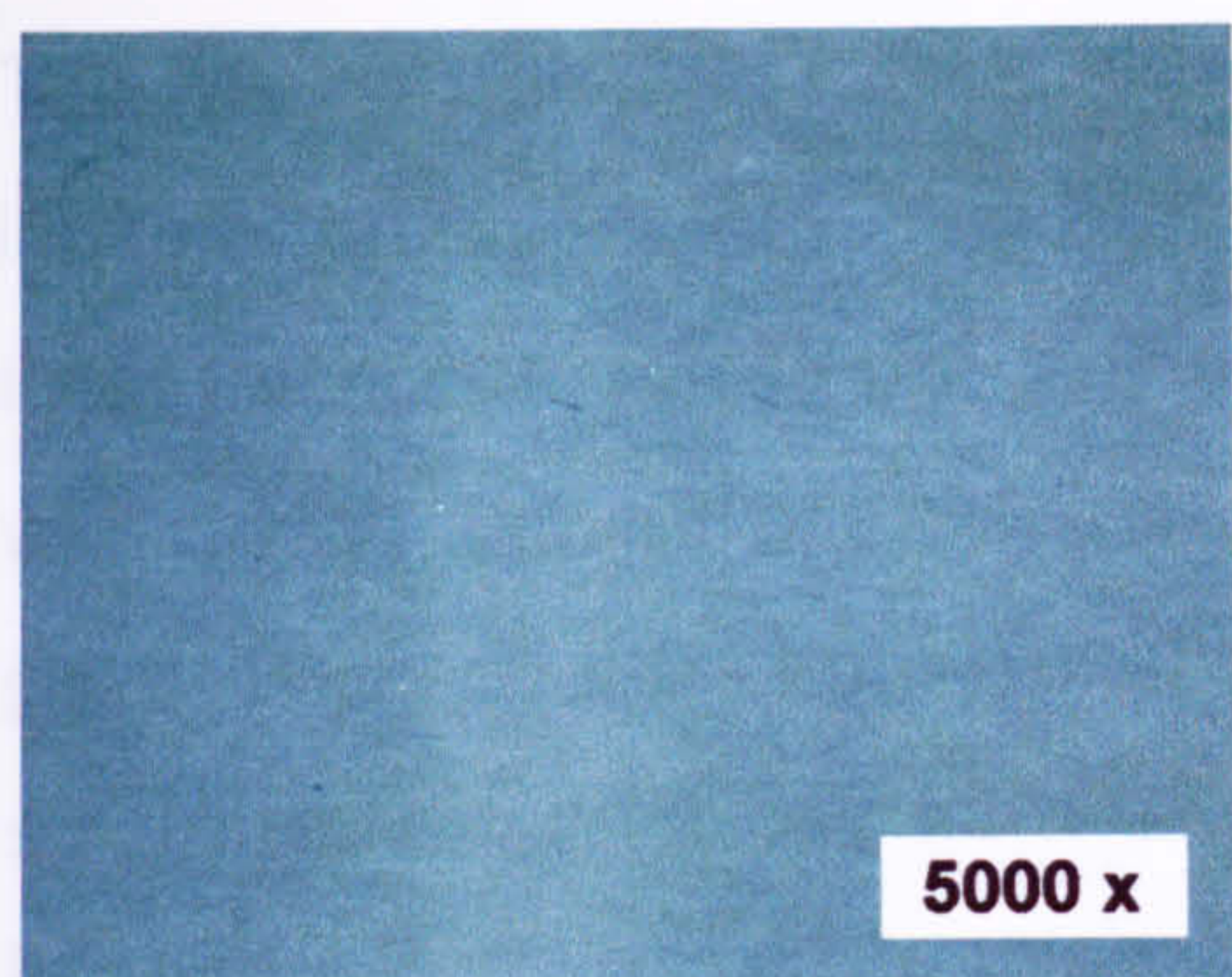


Figure 18

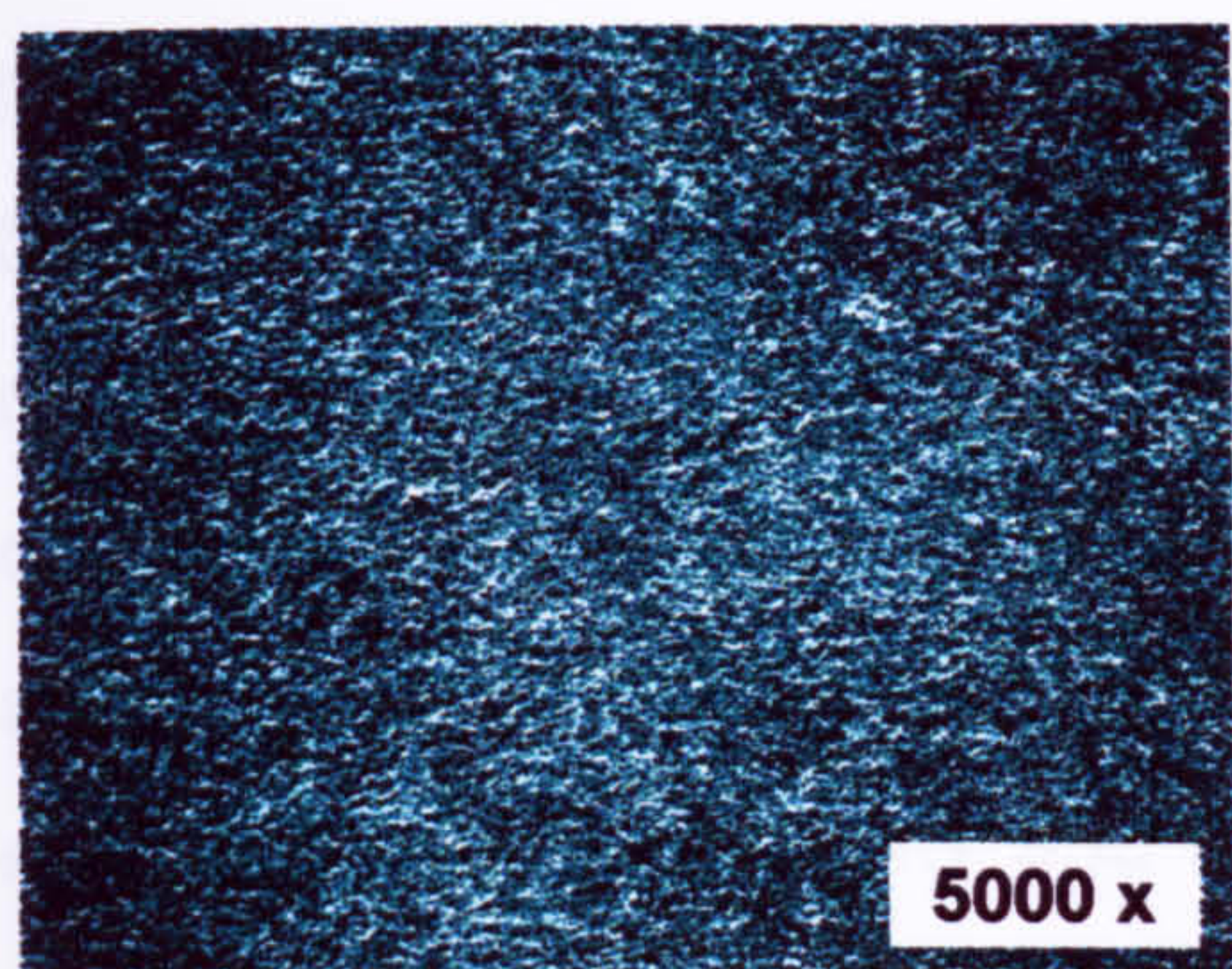
Appearance of Palladium-Iron Alloys versus Electrolyte Temperature and Current Density, Metal Ratio: $\text{Pd} : \text{Fe} = 1 : 100$, $\text{pH} = 8.2$, Substrate Agitation: 4 m/s , Electrolyte Agitation: 300 r/min , Coating Thickness: $0.5 - 2.5 \mu\text{m}$, Magnification: $200 \times$



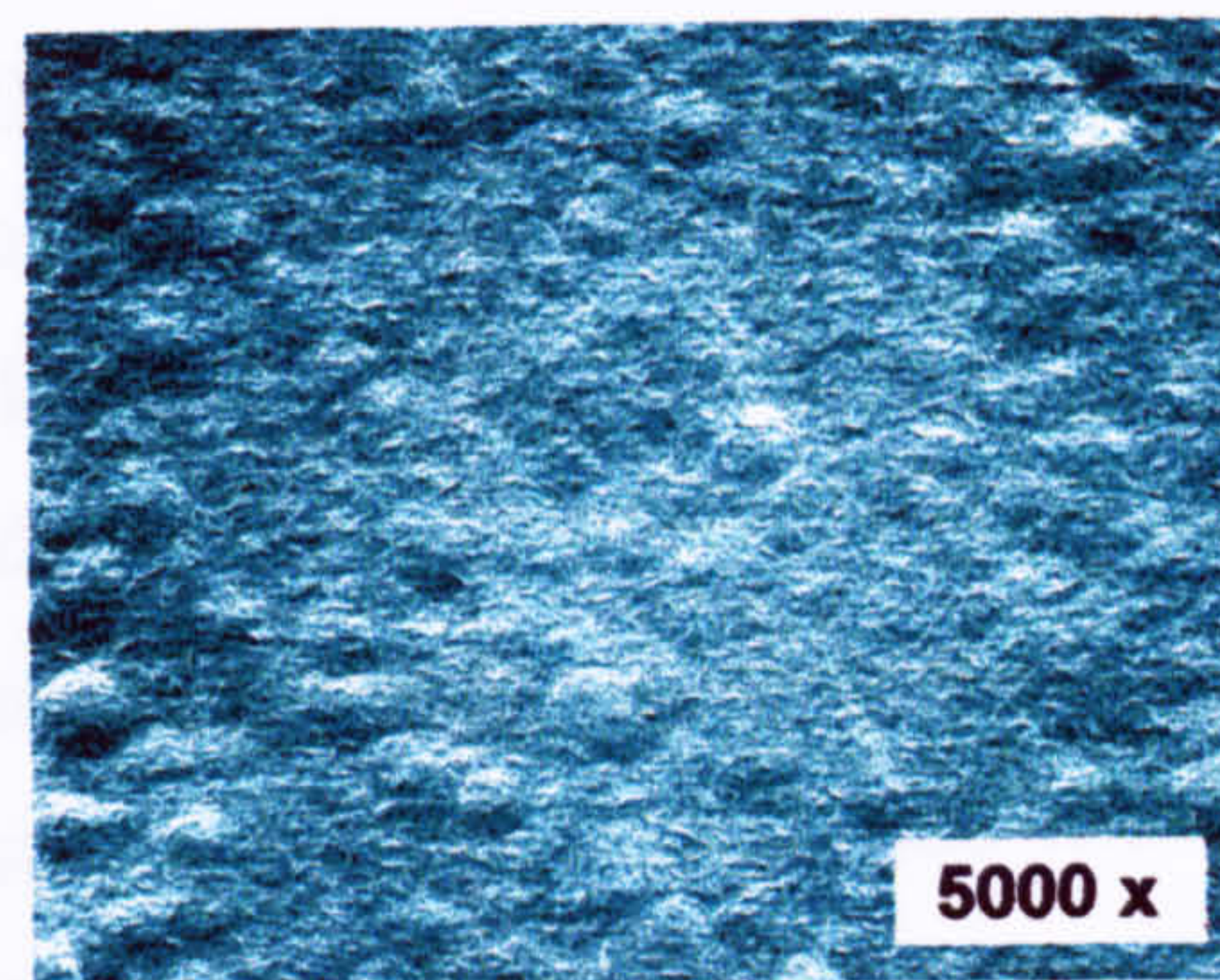
E: 1 : 1, 3 A/dm², 55 °C, 1 µm



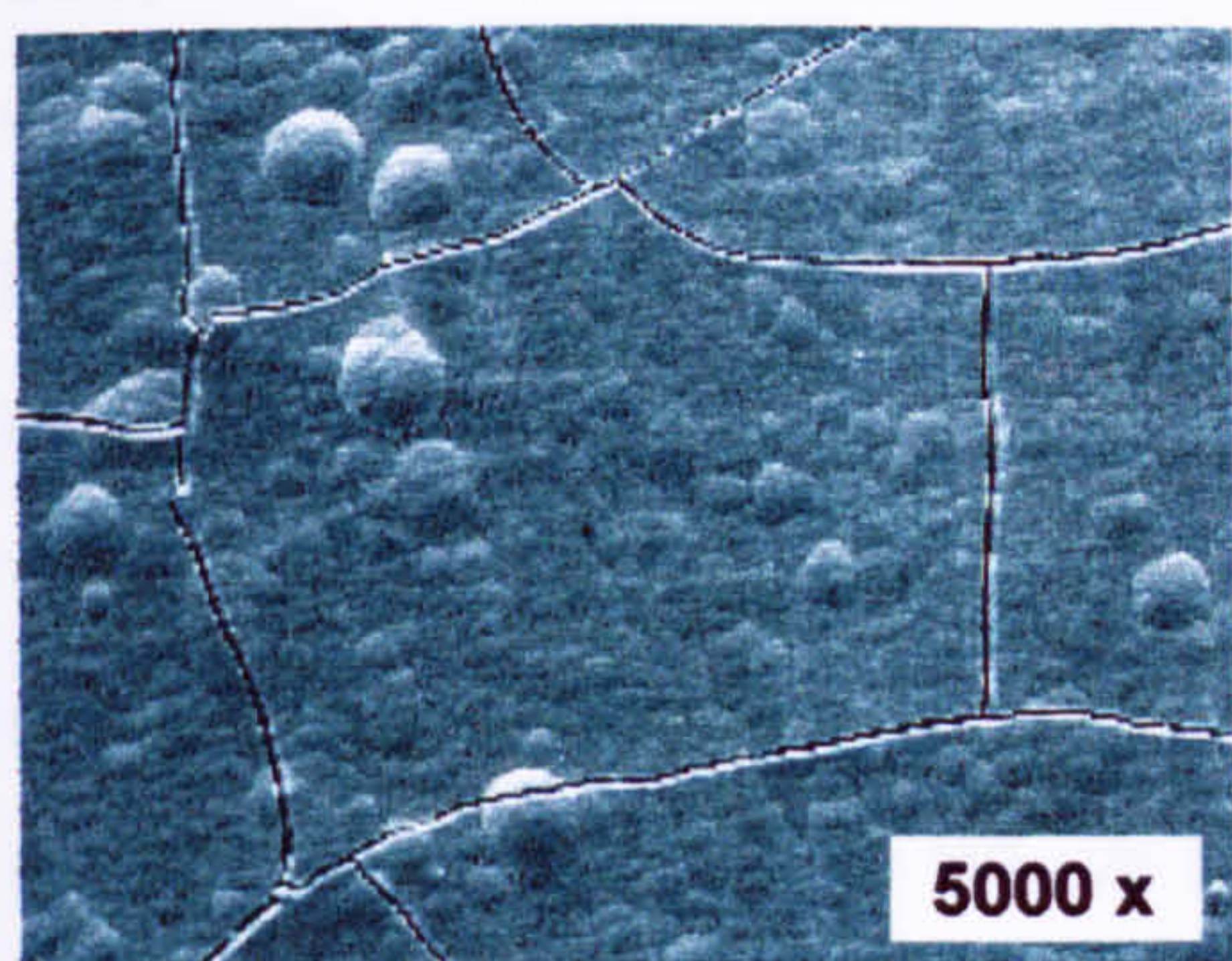
E: 1 : 100, 3 A/dm², 55 °C, 1 µm



E: 1 : 5, 3 A/dm², 55 °C, 1 µm



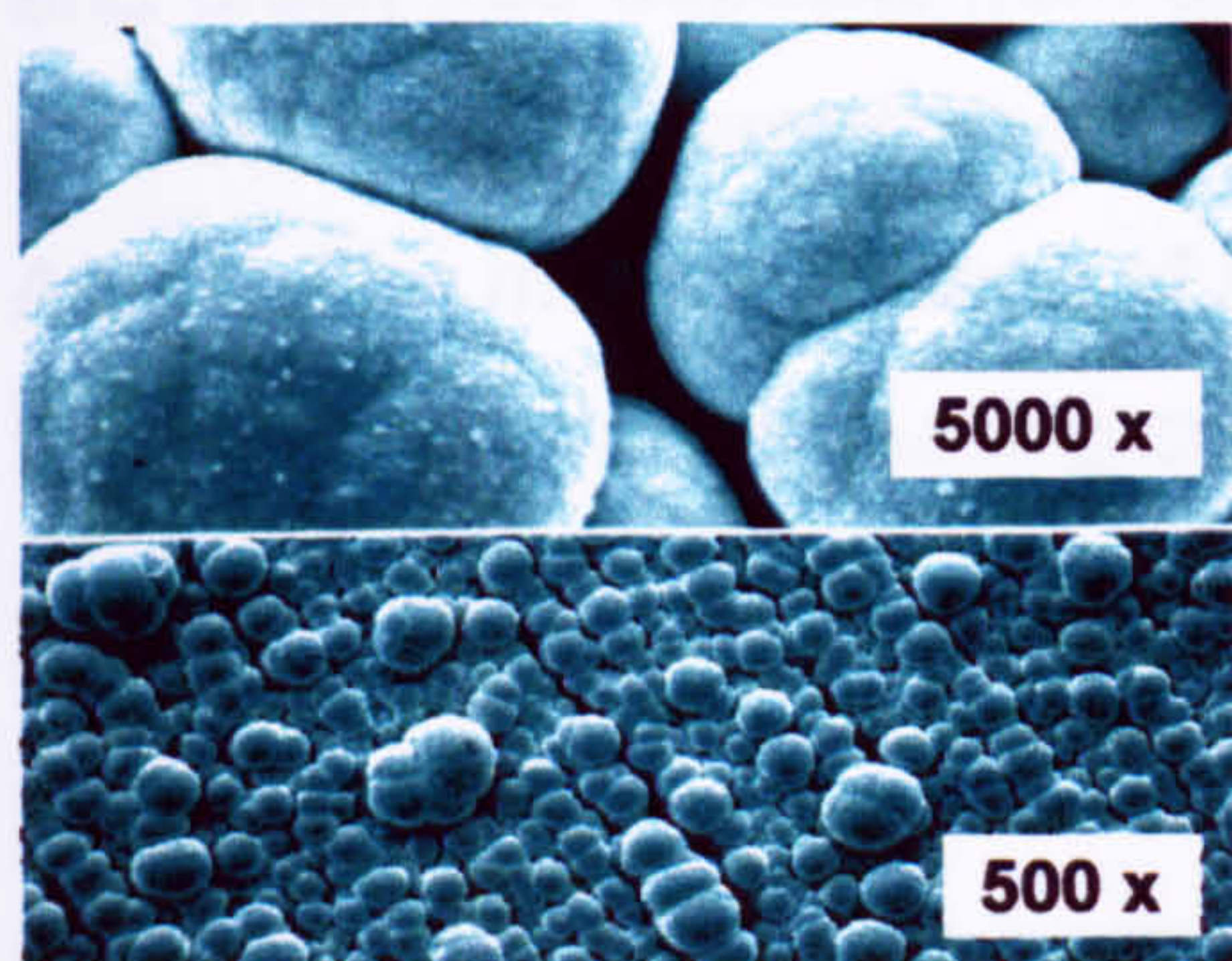
E: 1 : 10, 3 A/dm², 55 °C, 1 µm



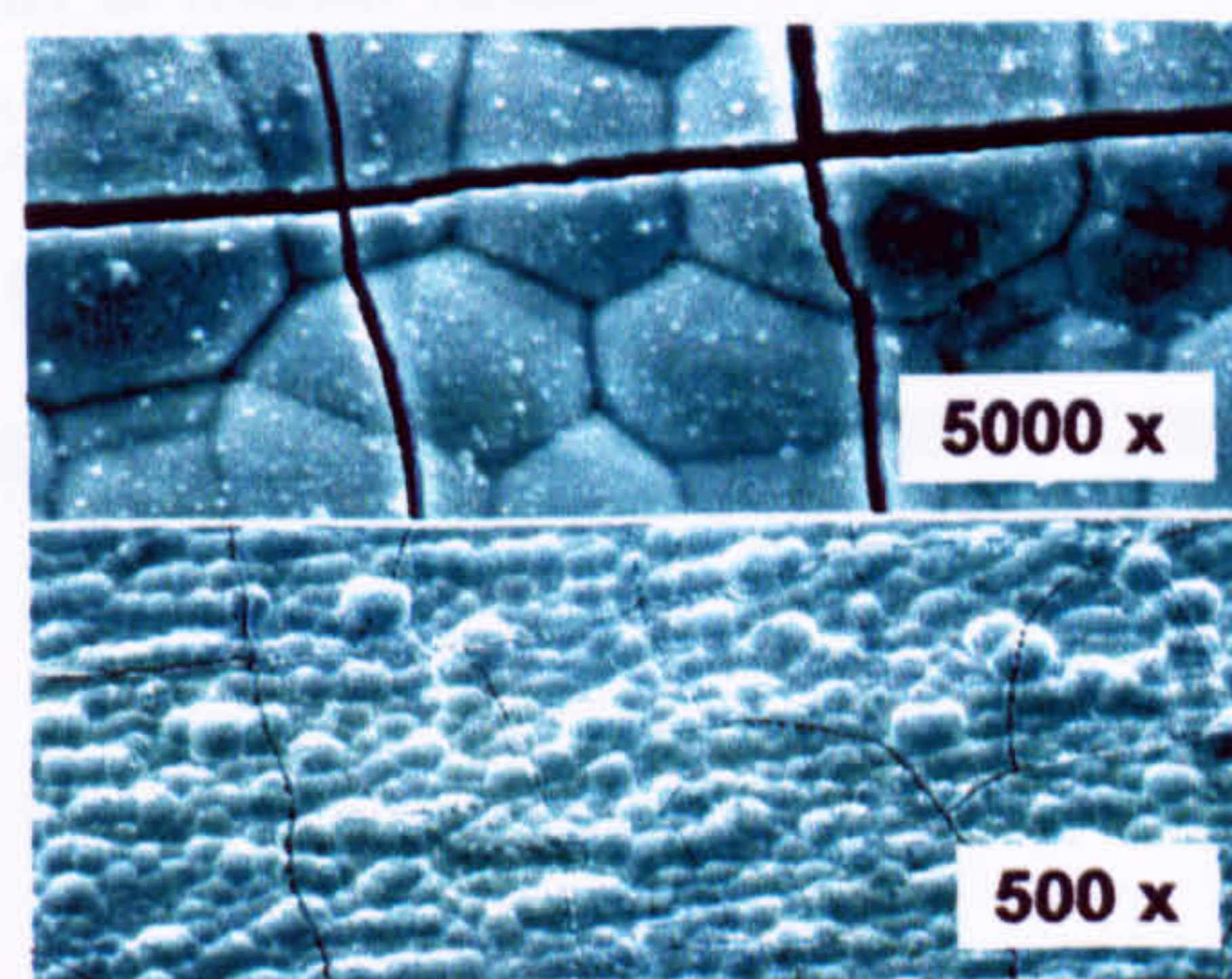
E: 1 : 1, 3 A/dm², 55 °C, 5 µm



E: 1 : 100, 3 A/dm², 55 °C, 5 µm



E: 1 : 1, 8 A/dm², 45 °C, 5 µm

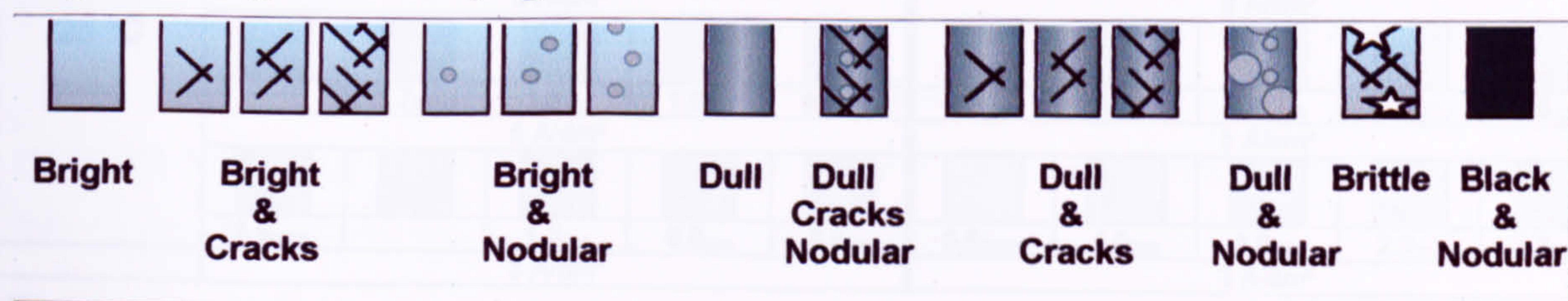


E: 1 : 100, 8 A/dm², 45 °C, 8 µm

Figure 19
Effect of Electrolyte Parameters and Coating Thickness on Surface Morphology of Electrodeposited Palladium-Iron Deposits on Copper and Brass Substrates
 Substrate Agitation: 4 m/s, Electrolyte Agitation: 300 r/min, pH=8.2

The results obtained clearly show the possibility to deposit bright and crack-free palladium-iron layers in a wide range of deposition parameters, admittedly limited by the layer thickness. Alloys with a high amount of iron tend to be slightly darker than alloys with a high amount of palladium. Palladium-iron layers with 80 wt.-% of palladium appear similar to palladium-nickel alloys with 75 - 85 wt.-% nickel. Electrodeposition of single metals or alloys from the platinum group is always considered with cracking beyond a certain coating thickness. Palladium-iron electrodeposition is not an exception to this rule. Typical SEM photographs of palladium-iron alloy deposits produced from various electrolytes and different plating conditions are shown in figure 19. Smooth, bright, and crack-free coatings were obtained from an electrolyte with a metal ratio of Pd : Fe = 1 : 1, an electrolyte temperature of 45 °C - 65 °C, and a cathodic current density of 3 - 5 A/dm². With decreasing amount of palladium in the alloy, surfaces appear more nodular. Decrease of electrolyte temperature and increase of current density and coating thickness cause nodular surfaces with cracks. Palladium-iron layers with a high amount of iron (85 wt.-% Fe) tend to build numerous, fine cracks, while palladium-iron coatings with a high amount of palladium (80 wt.-% Pd) show less, but larger cracks. Figure 20 shows the surface morphology of palladium-iron layers from two types of electrolytes versus electrolyte temperature, current density and coating thicknesses. From an electrolyte with a metal ratio Pd : Fe = 1 : 1, bright, crack-free layers up to 2.5 - 3 µm could be deposited in a temperature range of 45 °C to 75 °C and a current density range of 3 A/dm² to 8 A/dm². Coating composition is 80 - 85 wt.-% palladium, independent from plating parameters (table 14). Electrodeposition at low temperatures (< 45 °C) produces dull deposits. Bright and crack-free deposits from an electrolyte with a metal ratio Pd : Fe = 1 : 100 could be obtained in a temperature range from 45 °C to 75 °C and current densities up to 8 A/dm². The marked change of iron content in the coatings with increasing electrolyte temperature and decreasing current density (table 13) does not influence cracking or brightness of the layers.

Legend to figure 20 on page 67:



Electrolyte	Pd : Fe = 1 : 1					Pd : Fe = 1 : 100				
Temperature										
75 °C										
	4.2 ₆₄₂	2.1 ₅₆₁			0.3 ₅₉₁	0.3 ₁₉₂	1.1 ₁₅₇	1.9 _{180/1}	2.2 ₁₅₉	2.7 _{180/2}
	8 A/dm ²					8 A/dm ²				
		1.2 ₅₆₀		0.4 ₅₉₀		0.5 ₁₉₀	1.0 ₄₀₄		2.2 ₄₀₅	3.1 ₁₉₁
	5 A/dm ²					5 A/dm ²				
65 °C										
	3.4 ₆₄₉	1.8 ₅₅₁	1.6 ₅₅₄	1.1 ₅₅₆	0.4 ₅₈₉	0.6 _{206/2}	0.9 ₅₇₃	1.0 ₅₈₁	2.2 _{201/1}	3.4 _{201/2}
	8 A/dm ²					8 A/dm ²				
	3.1 ₆₆₂	2.0 ₅₄₃	1.3 ₅₅₃	1.1 ₆₂₇		0.4 ₅₇₂	0.8 ₂₀₇	1.8 ₅₇₉	1.9 ₂₀₂	3.5 ₂₀₀
	5 A/dm ²					5 A/dm ²				
55 °C										
	5.5 ₅₄₈	2.1 ₅₄₉	1.0 ₂₅₃	0.7 ₅₄₇	0.4 ₅₈₇	0.5 ₅₇₀	0.8 ₂₀₉	1.4 _{230/3}	2.5 _{230/1}	3.1 ₆₂₆
	3 A/dm ²					3 A/dm ²				
	6.1 ₅₄₄	2.5 ₅₄₅		1.1 ₅₄₂	0.4 ₅₈₇		0.7 ₅₆₉	1.0 ₅₈₄	1.7 ₅₆₂	
	3 A/dm ²					3 A/dm ²				
45 °C										
	4.1 ₆₆₇	1.9 ₅₃₈	1.5 ₆₆₅	1.0 ₅₃₇		0.3 ₅₃₅	0.8 ₅₃₆	1.3 _{169/1}	2.5 ₆₁₈	3.5 ₆₁₉
	8 A/dm ²					8 A/dm ²				
	3.4 ₆₆₄	2.5 ₅₂₈	1.7 ₅₂₇	0.9 ₅₂₅		0.2 ₅₄₁	0.5 ₅₃₉	1.1 ₅₄₀	2.0 _{169/3}	3.2 ₆₂₁
	5 A/dm ²					5 A/dm ²				
35 °C										
	2.8 ₅₂₂	2.6 ₁₇₃	1.7 ₅₁₇	1.0 ₅₁₆	0.5 ₁₄₅	0.2 ₁₂₅	1.2 _{168/2}	2.0 ₅₃₅	2.5 ₆₃₄	3.0 ₁₉₇
	3 A/dm ²					3 A/dm ²				
	3.5 ₅₃₄		1.6 ₅₃₃			0.8 ₅₃₁	1.0 ₅₉₂	1.4 ₅₉₃	2.1 ₅₃₂	4.2 ₂₆₆
	8 A/dm ²					8 A/dm ²				
25 °C										
	2.9 ₅₁₃		1.5 ₅₁₂	0.9 ₅₁₁		0.8 ₅₂₆	0.9 ₅₂₄	1.7 ₅₂₉	2.2 _{184/2}	3.1 _{184/1}
	5 A/dm ²					5 A/dm ²				
	6.3 ₂₆₅	2.5 ₅₀₂	1.6 ₅₀₁	0.8 ₅₀₀		0.8 ₅₁₉	1.5 ₅₂₀	1.7 ₅₂₁	2.3 ₁₈₅	2.6 ₅₂₃
	3 A/dm ²					3 A/dm ²				
25 °C										
	3.2 ₅₁₀	2.2 _{509/2}				0.7 _{594/1}	1.0 ₅₁₄	1.8 ₅₁₅	2.0 _{594/2}	3.2 _{594/3}
	8 A/dm ²					8 A/dm ²				
		2.7 _{507/2}	1.8 ₅₀₄	1.0 ₅₀₃	0.5 _{507/1}	0.7 ₂₉₆	1.2 ₅₈₀	1.6 _{297/1}	2.2 _{297/2}	3.5 _{297/3}
	5 A/dm ²					5 A/dm ²				
25 °C										
	3.5 _{509/1}		1.3 ₂₉₄	0.9 ₂₈₉	0.6 ₂₉₃	0.6 _{231/1}	1.0 ₂₈₈	1.9 ₂₉₁	2.9 ₂₈₂	3.2 _{231/3}
	3 A/dm ²					3 A/dm ²				

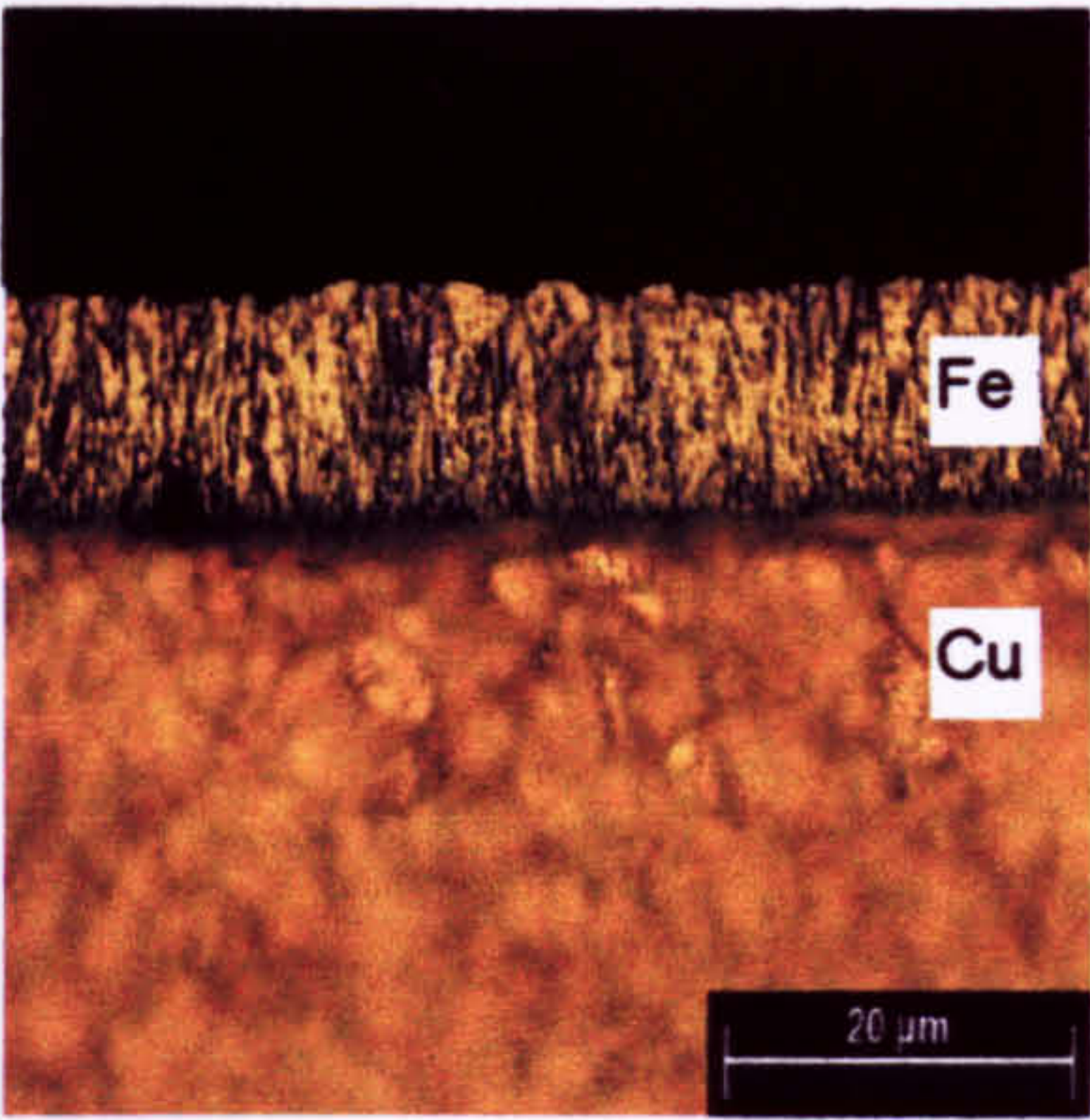
Figure 20

Morphology Characteristics of Electroplated Palladium-Iron Coatings

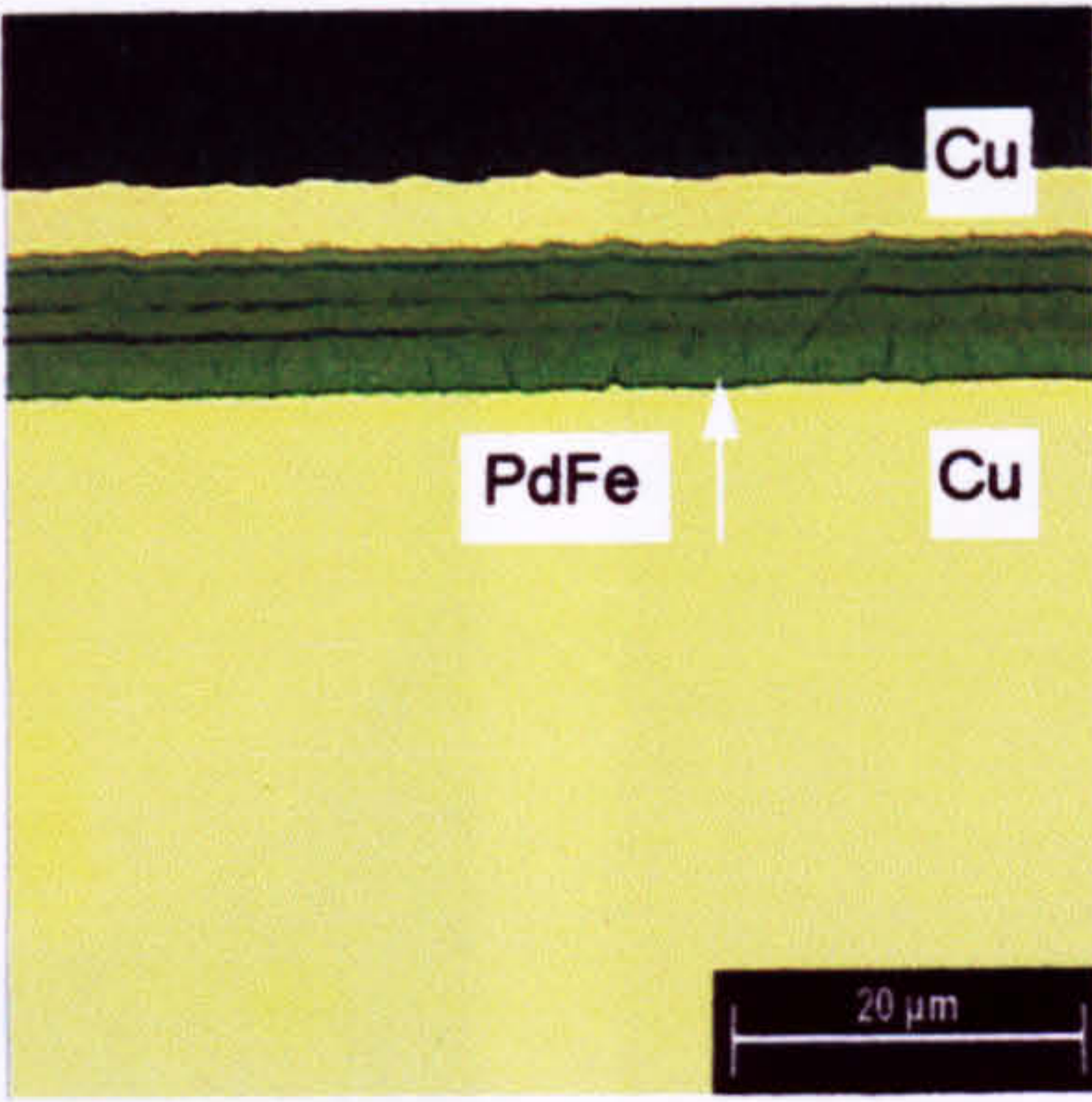
Magnification 200 x

4. 2. 2 Morphology Characteristics of Palladium-Iron Coatings

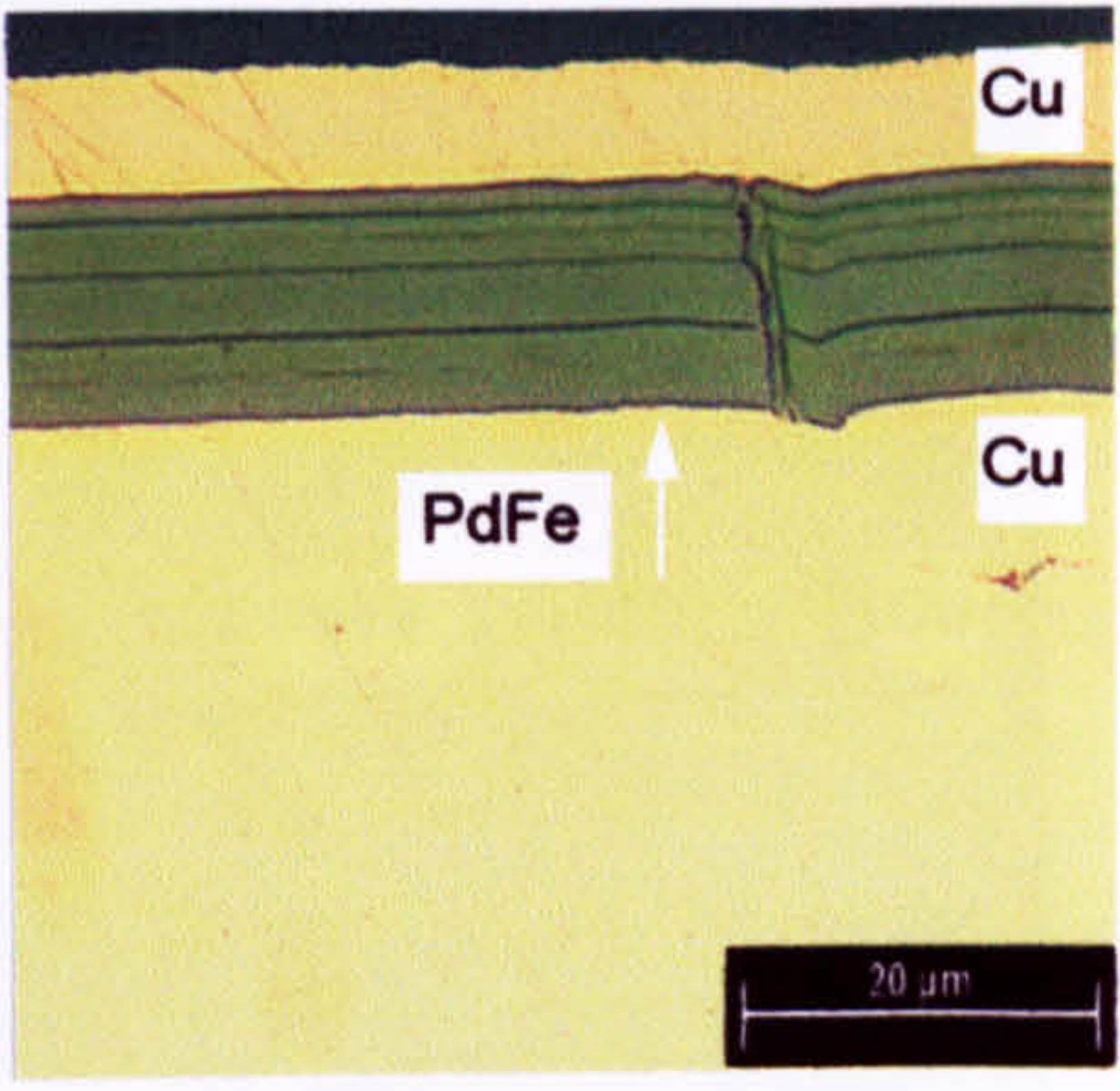
In figure 21 the structure cross sections of iron and palladium-iron coatings, deposited from electrolytes with various amounts of palladium are shown. Iron from this ammoniacal solution is deposited in a columnar (partly fibrous) structure. The morphology of the coatings changes totally when palladium is co-deposited. All palladium-iron alloys show a laminar or banded structure, which runs parallel to the surface of the substrate. The grains within the lamellae are very small. Banded structures are not unique with alloys, as they occur also with coatings of single metals, like nickel deposits. Those deposits are normally bright coatings with a high strength and hardness but low ductility [200]. The banded, or laminar, grain structure observed for the palladium-iron deposits is similar to that found in palladium-nickel coatings [135,143] and palladium-silver coatings [173]. This structure is considered to be useful for high wear resistance and a better corrosion resistance [135, 173]. However, formation of cracks is contrary to good corrosion behaviour. Deposits with high iron content show a homogenous, laminar structure. Palladium-iron layers, deposited from an electrolyte with a metal ratio of $\text{Pd}:\text{Fe} = 1:10$ and $1:6$ were also obtained with a laminar, but very rough and nodular morphology. If the palladium content in the electrolyte is $3:1$, $4:1$ and $10:1$, fine grained lamellae with varying intervals and cracks of various size were obtained. Figure 22 shows structure in cross section of a palladium-iron alloy with 80 wt.-% palladium, deposited in an electrolyte with a metal ratio of $\text{Pd}:\text{Fe} = 1:1$, with an electrolyte temperature of 45°C , and current density of 3 A/dm^2 . As shown in the picture on top-left, the throwing power of this type of electrolyte is good. No increase of coating thickness at the edge of the substrate is observed. Cracks are regular and go through the coating. SEM micrograph of cross section of a palladium-iron alloy with 85 wt.-% iron is shown in figure 23. The throwing power of the electrolyte with a metal ratio of $\text{Pd}:\text{Fe} = 1:100$ is poor compared to the electrolyte with a metal ratio of $\text{Pd}:\text{Fe} = 1:1$. There is an increase (2x) of layer thickness in the range of the edge. Visual appearance of the layers suggest differences in the metal composition of the lamellae (figure 22, magnification 1000x). Unfortunately, a conclusive examination was not possible, because available measurement methods, like Glow Discharge Optical Spectroscopy (GDOS) or Energy Dispersive X-ray Microanalyser (EDX) are not appropriate methods to give satisfactory answers or exclude etching effects at least.



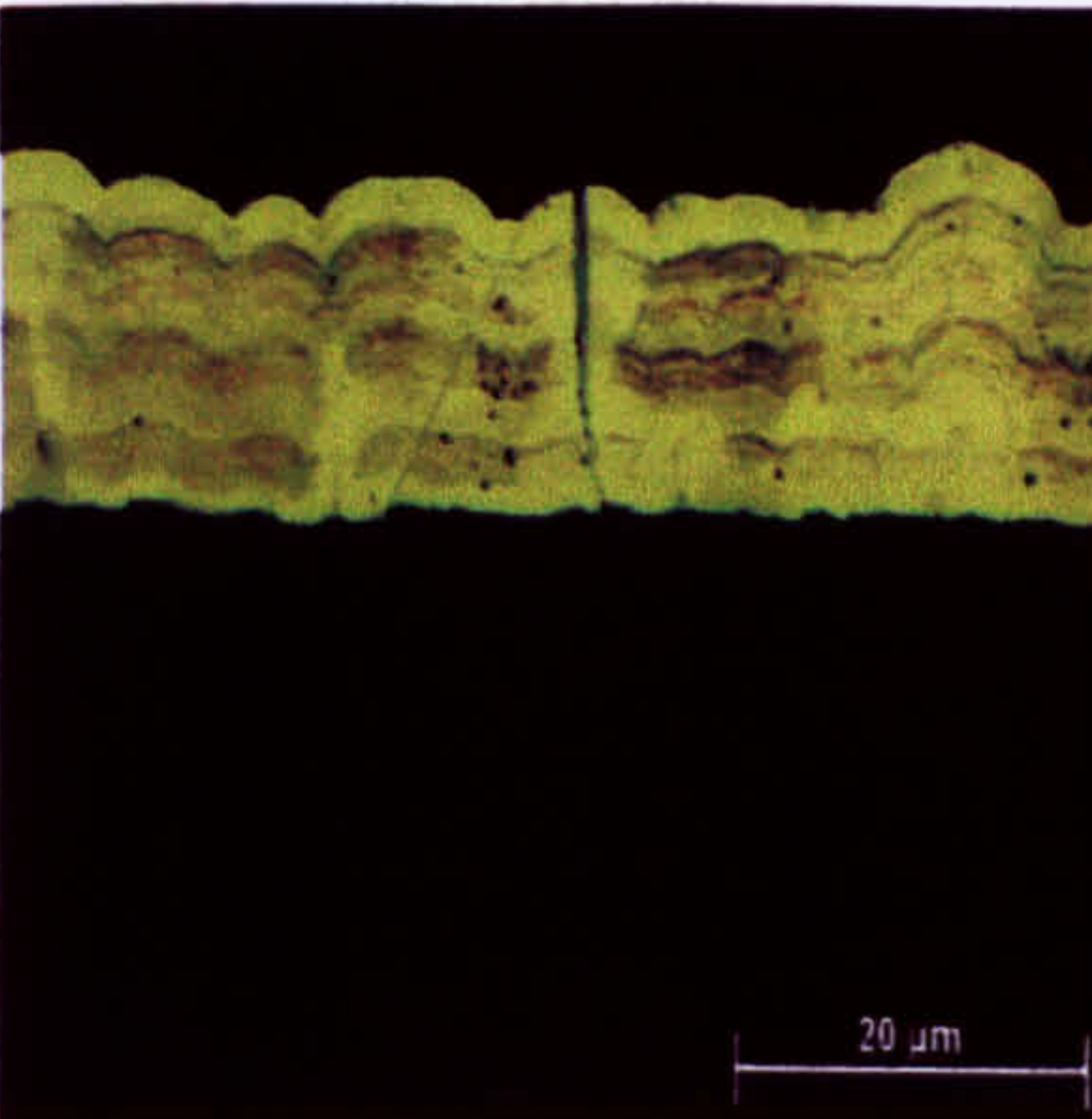
Iron Coating
Electrolyte Fe
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $12\text{ }\mu\text{m}$



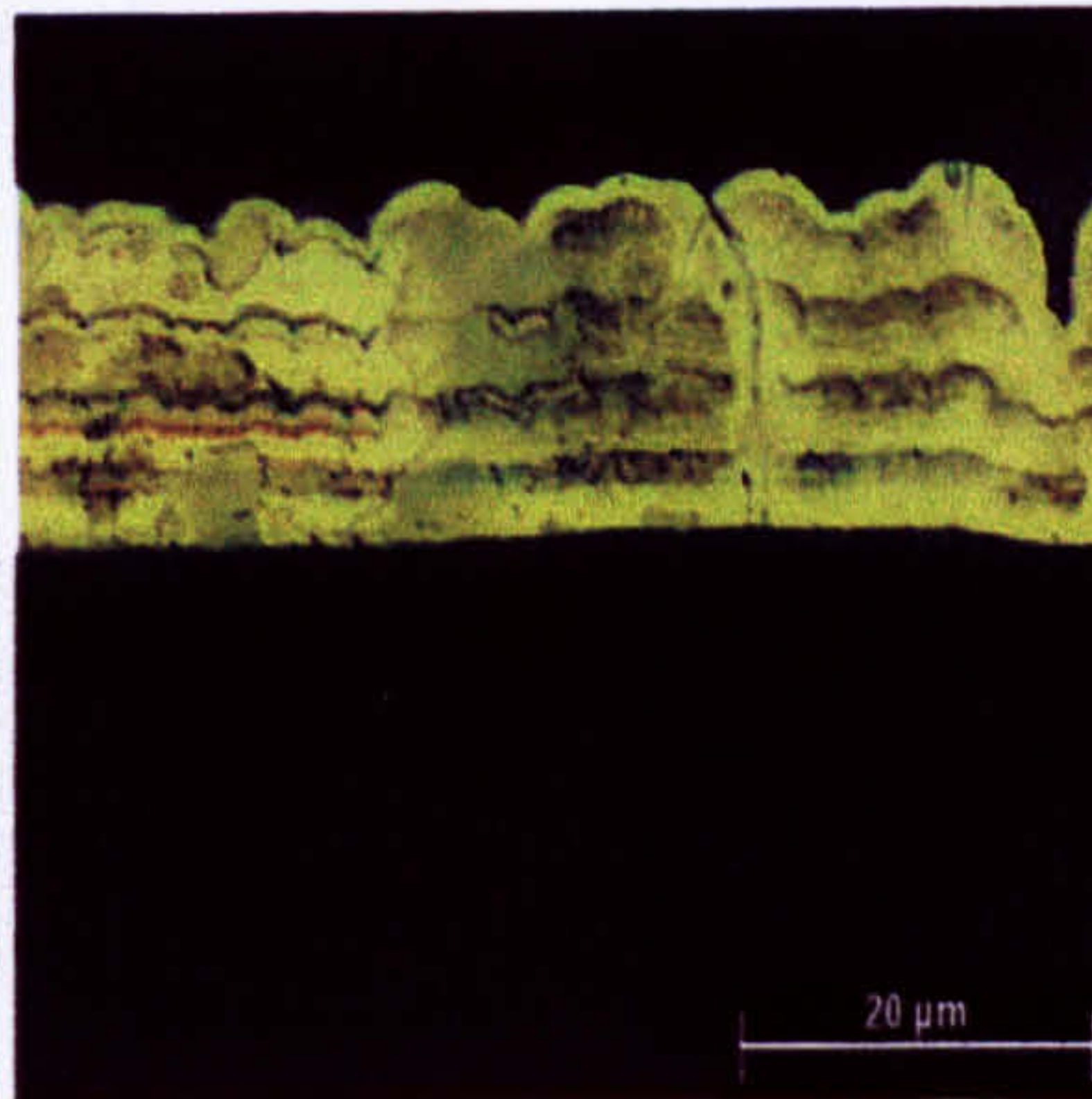
Palladium-Iron Coating
Electrolyte Pd : Fe = 1 : 100
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $10\text{ }\mu\text{m}$



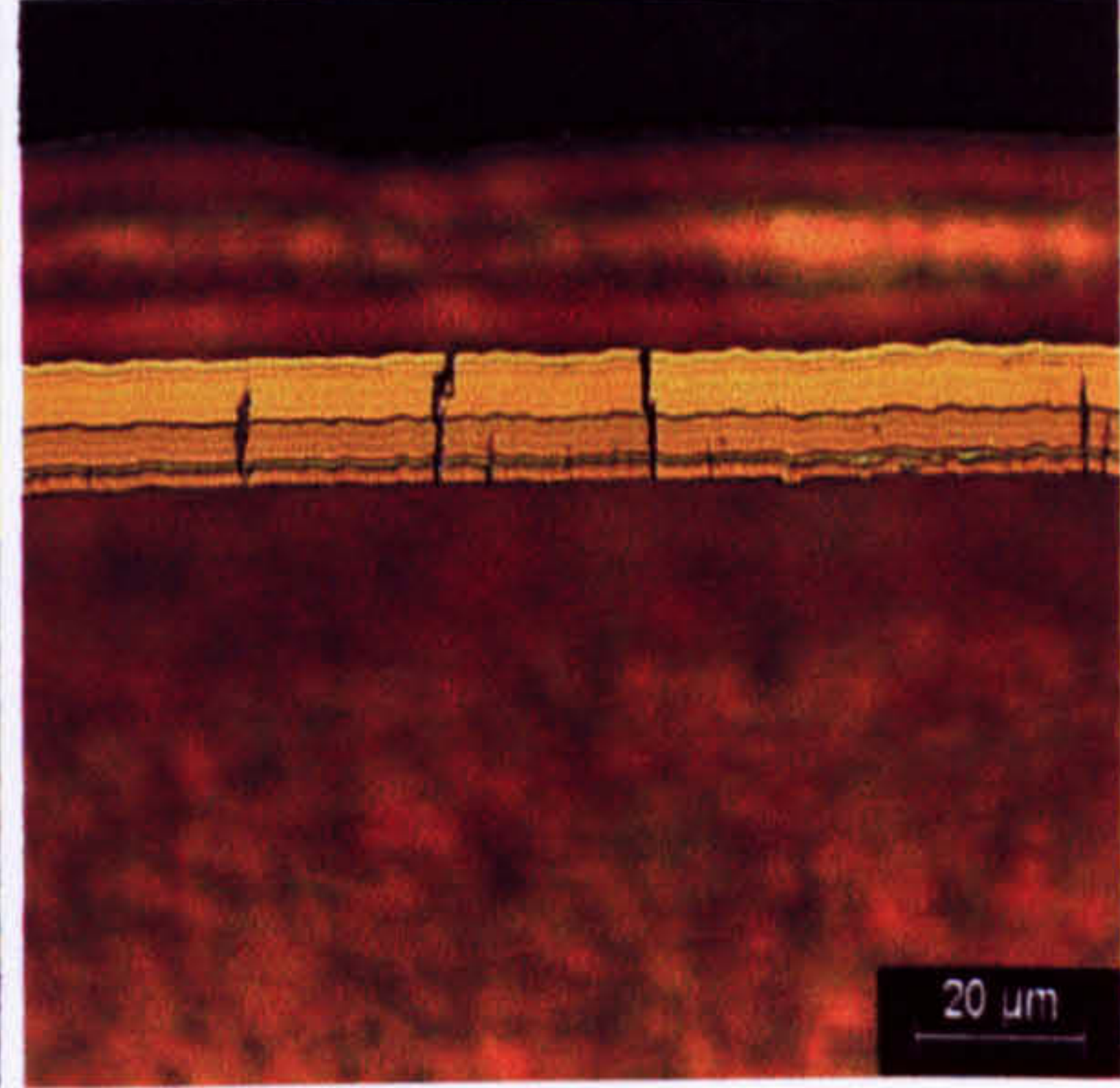
Palladium-Iron Coating
Electrolyte Pd : Fe = 1 : 33
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $12\text{ }\mu\text{m}$



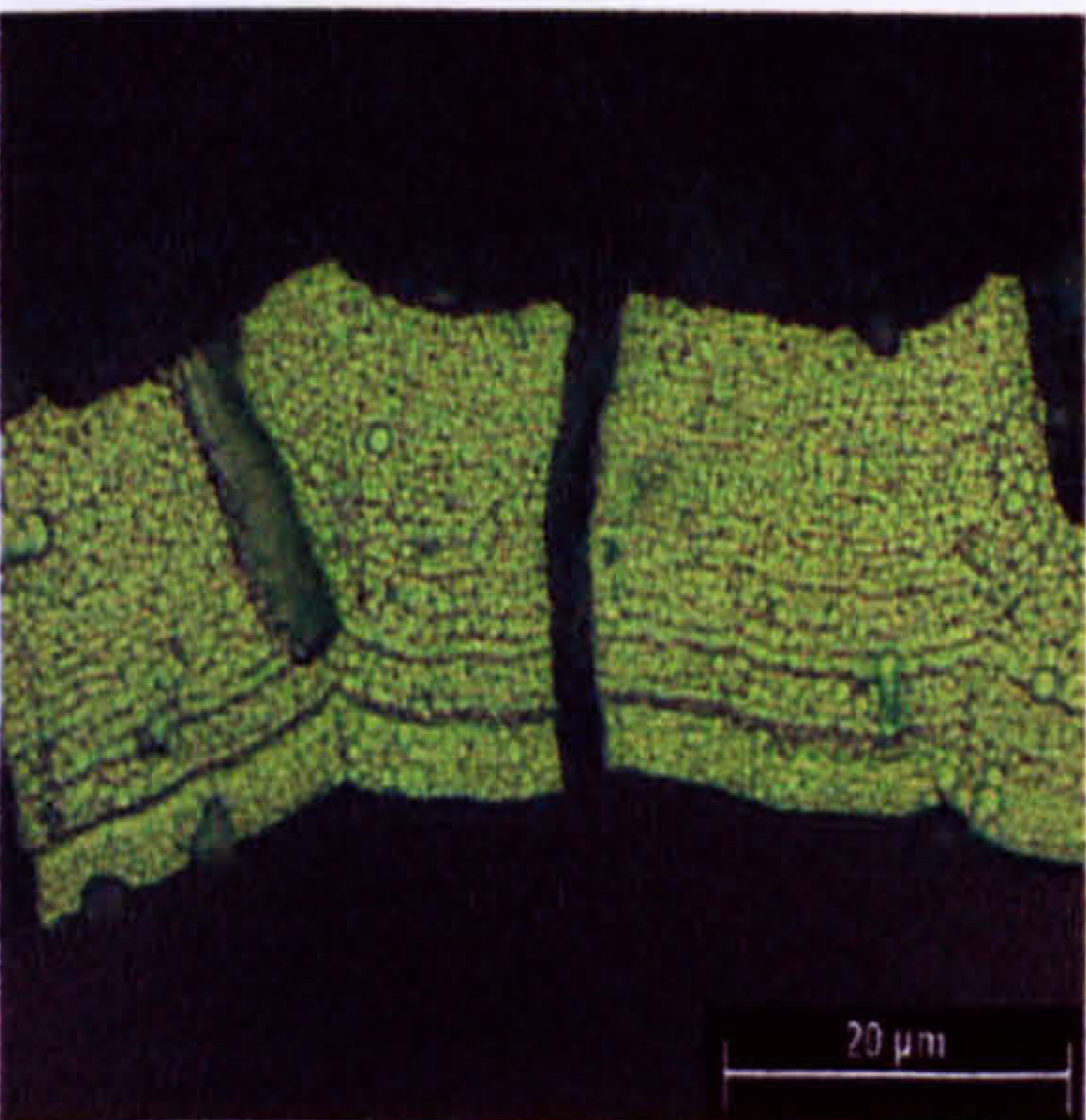
Palladium-Iron Coating
Electrolyte Pd : Fe = 1 : 10
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $15\text{ }\mu\text{m}$



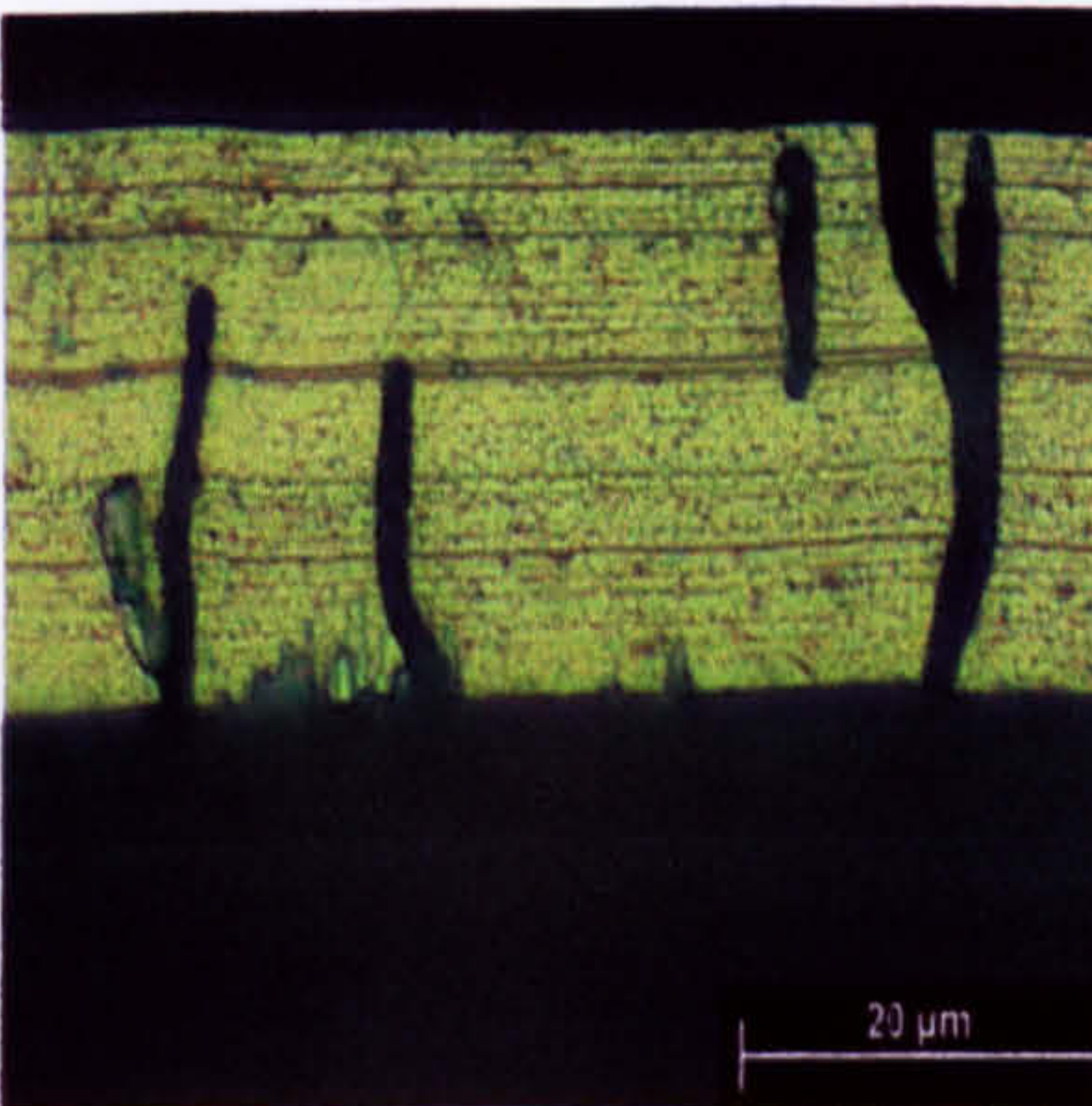
Palladium-Iron Coating
Electrolyte Pd : Fe = 1 : 6
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $15\text{ }\mu\text{m}$



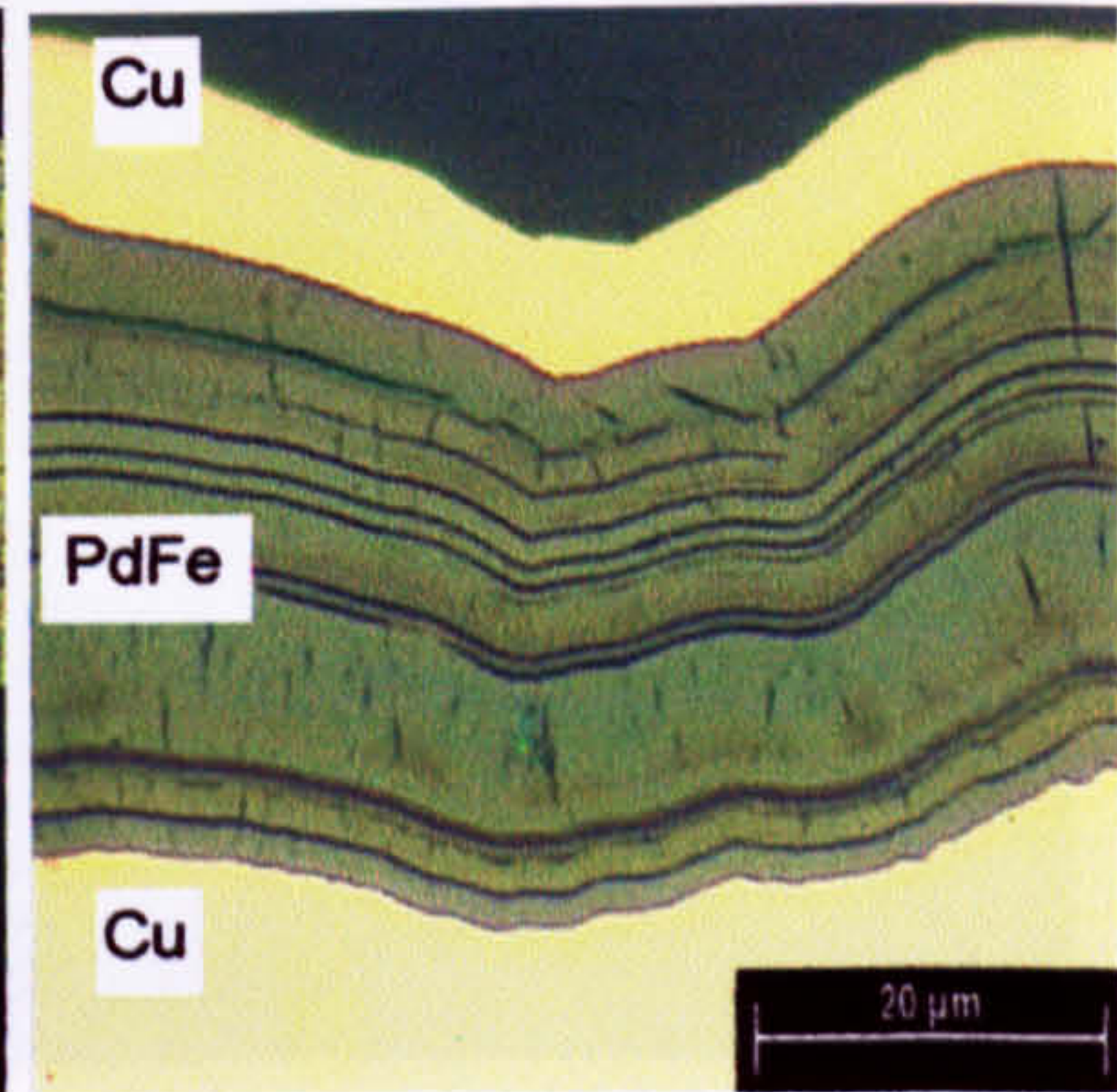
Palladium-Iron Coating
Electrolyte Pd : Fe = 1 : 1
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $10\text{ }\mu\text{m}$



Palladium-Iron Coating
Electrolyte Pd : Fe = 3 : 1
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $22\text{ }\mu\text{m}$

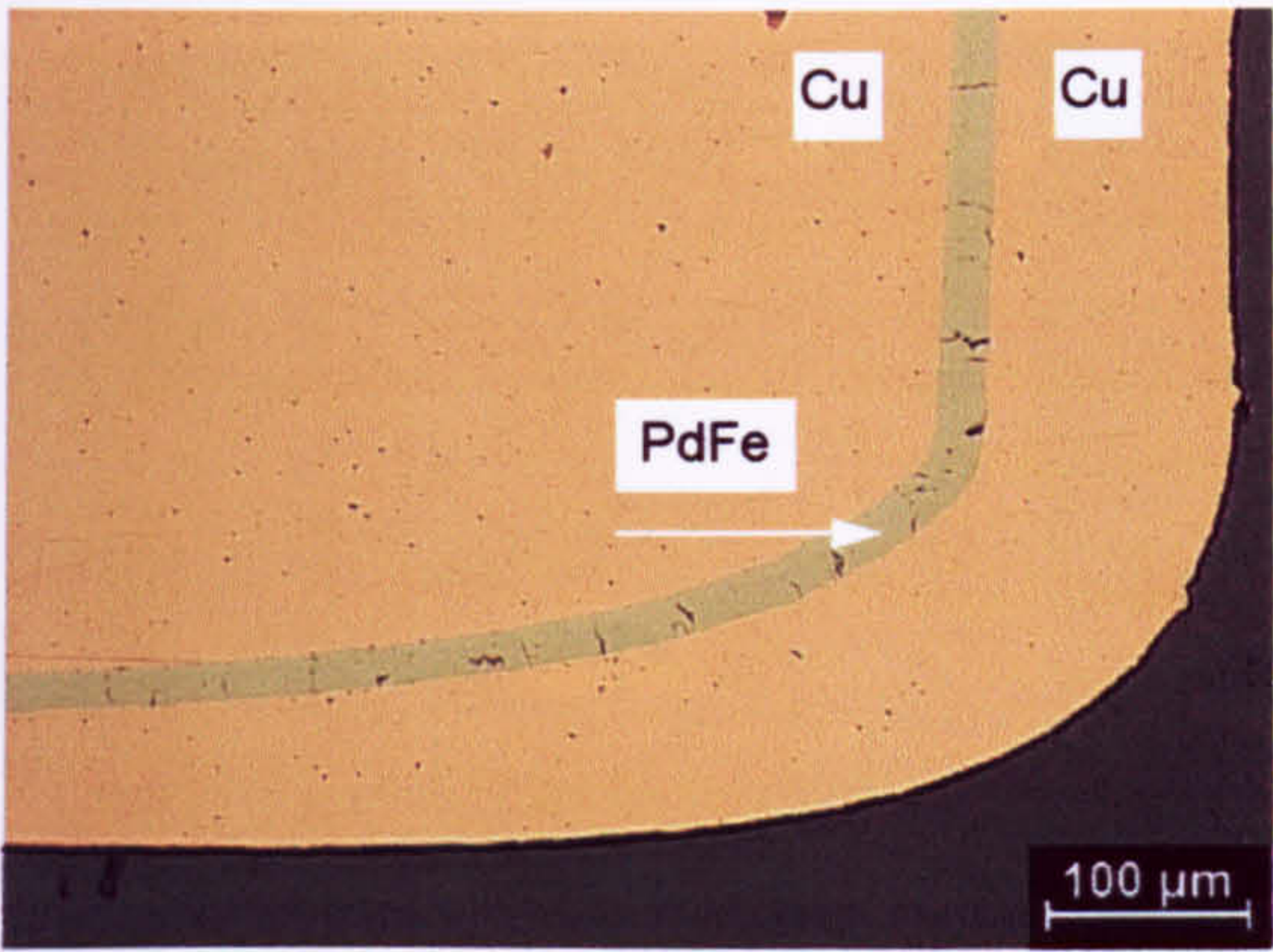


Palladium-Iron Coating
Electrolyte Pd : Fe = 4 : 1
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $30\text{ }\mu\text{m}$

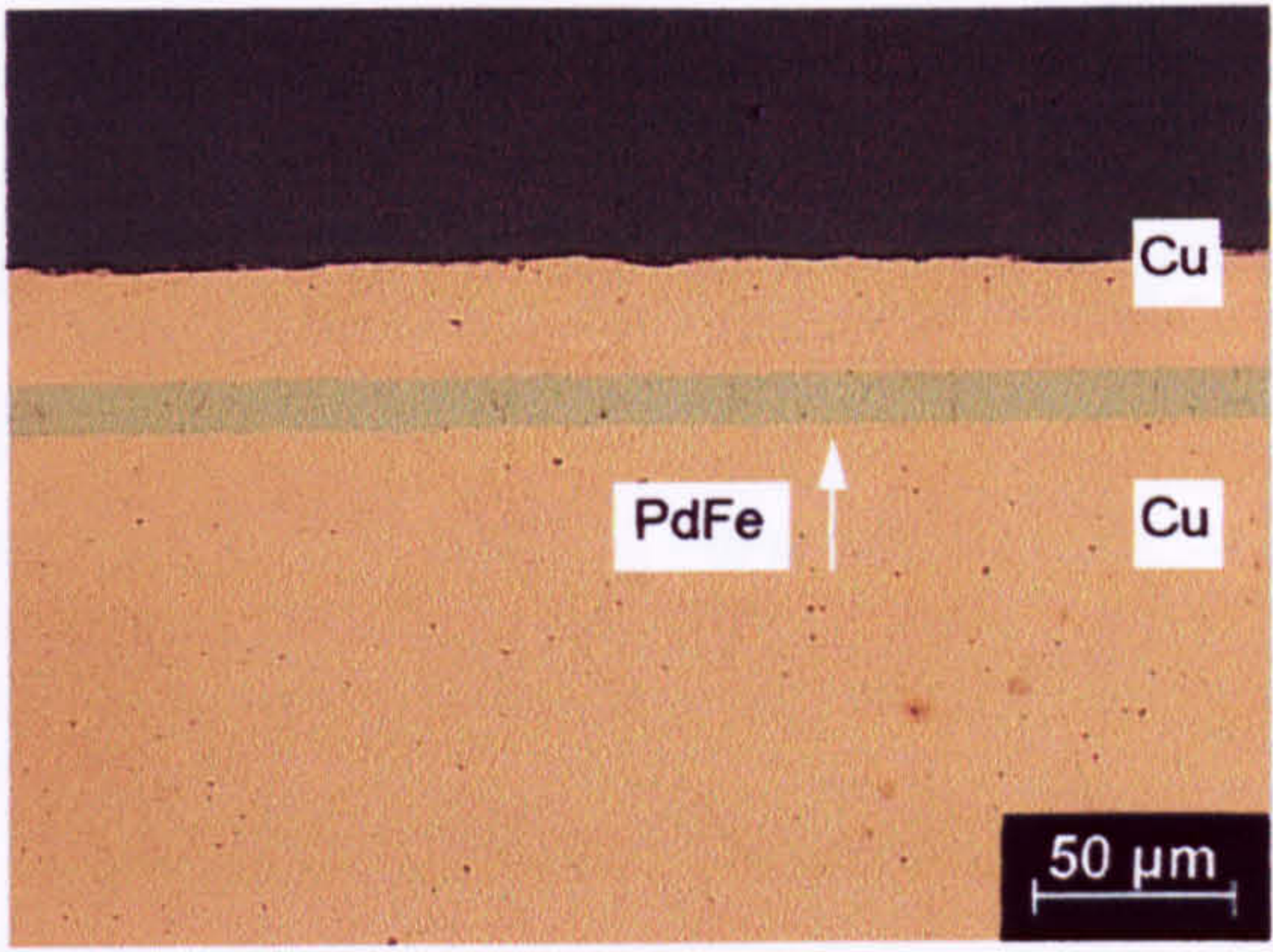


Palladium-Iron Coating
Electrolyte Pd : Fe = 10 : 1
 $T = 45\text{ }^{\circ}\text{C}$, 3 A/dm^2 , $28\text{ }\mu\text{m}$

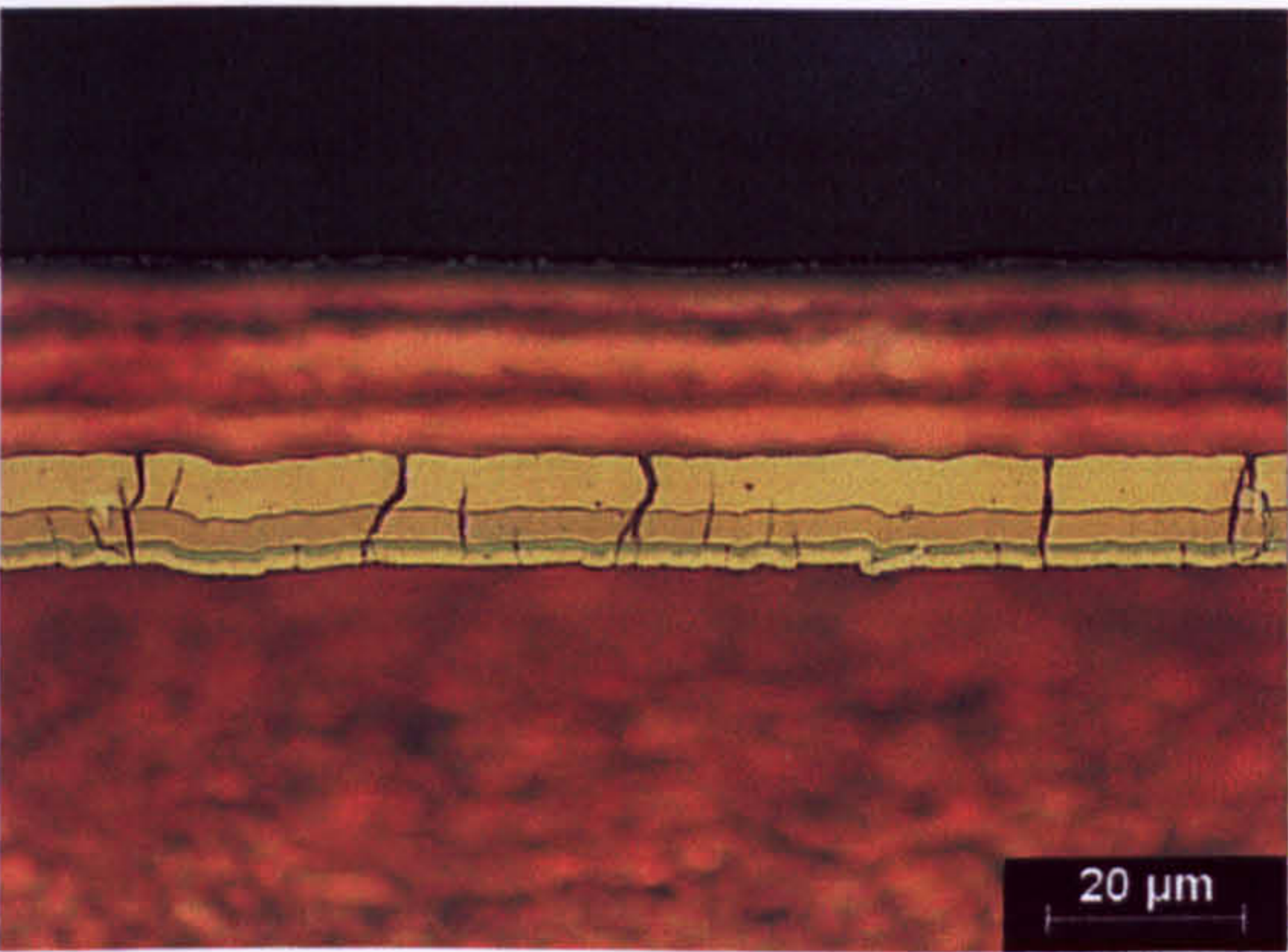
Figure 21
Effect of Electrolyte Composition on Morphology Characteristics of Palladium-Iron Coatings, Pd:Fe = from 1:100 to 10:1, according to table 11, page 46



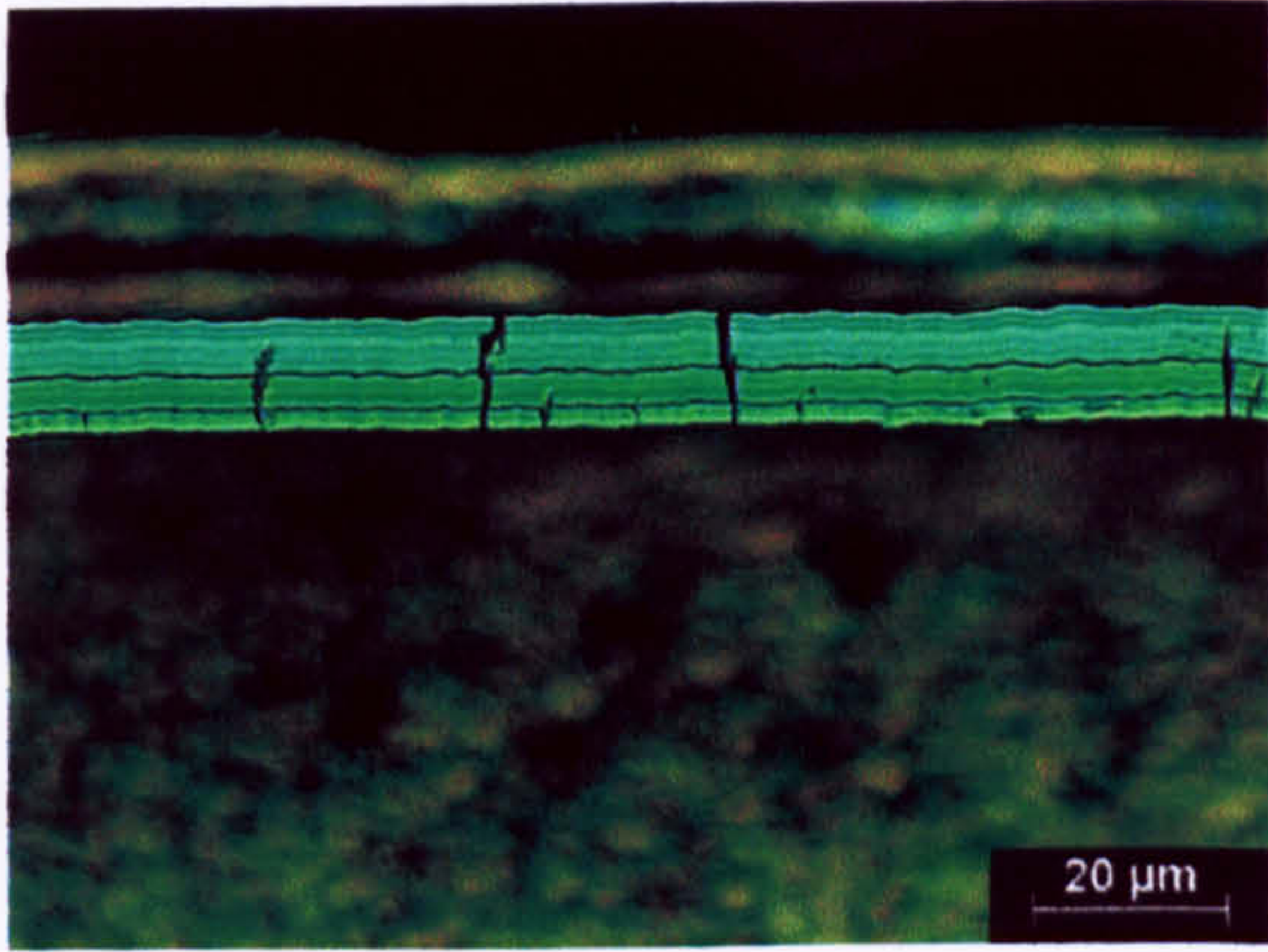
Magnification 100 x



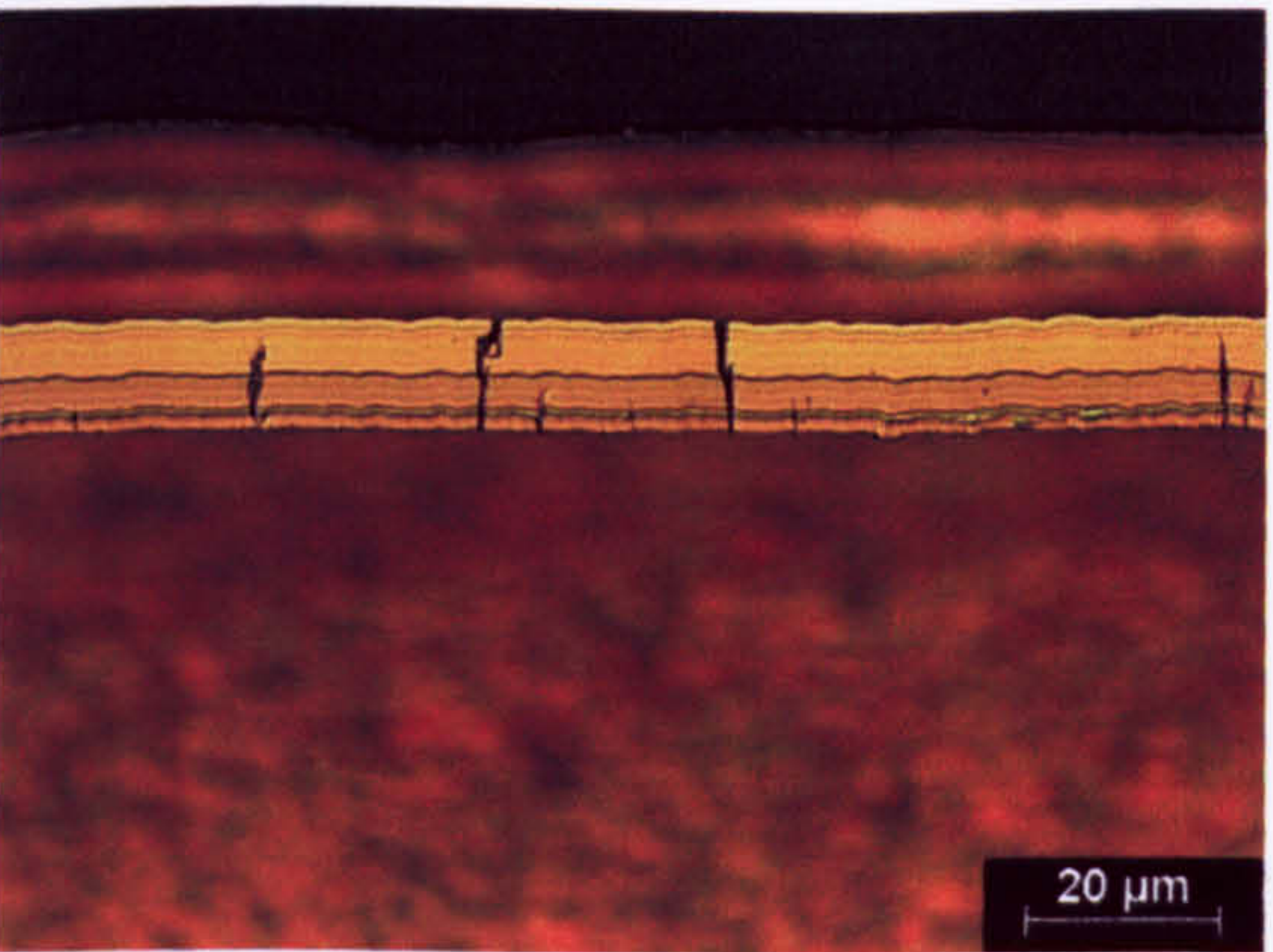
Magnification 200 x



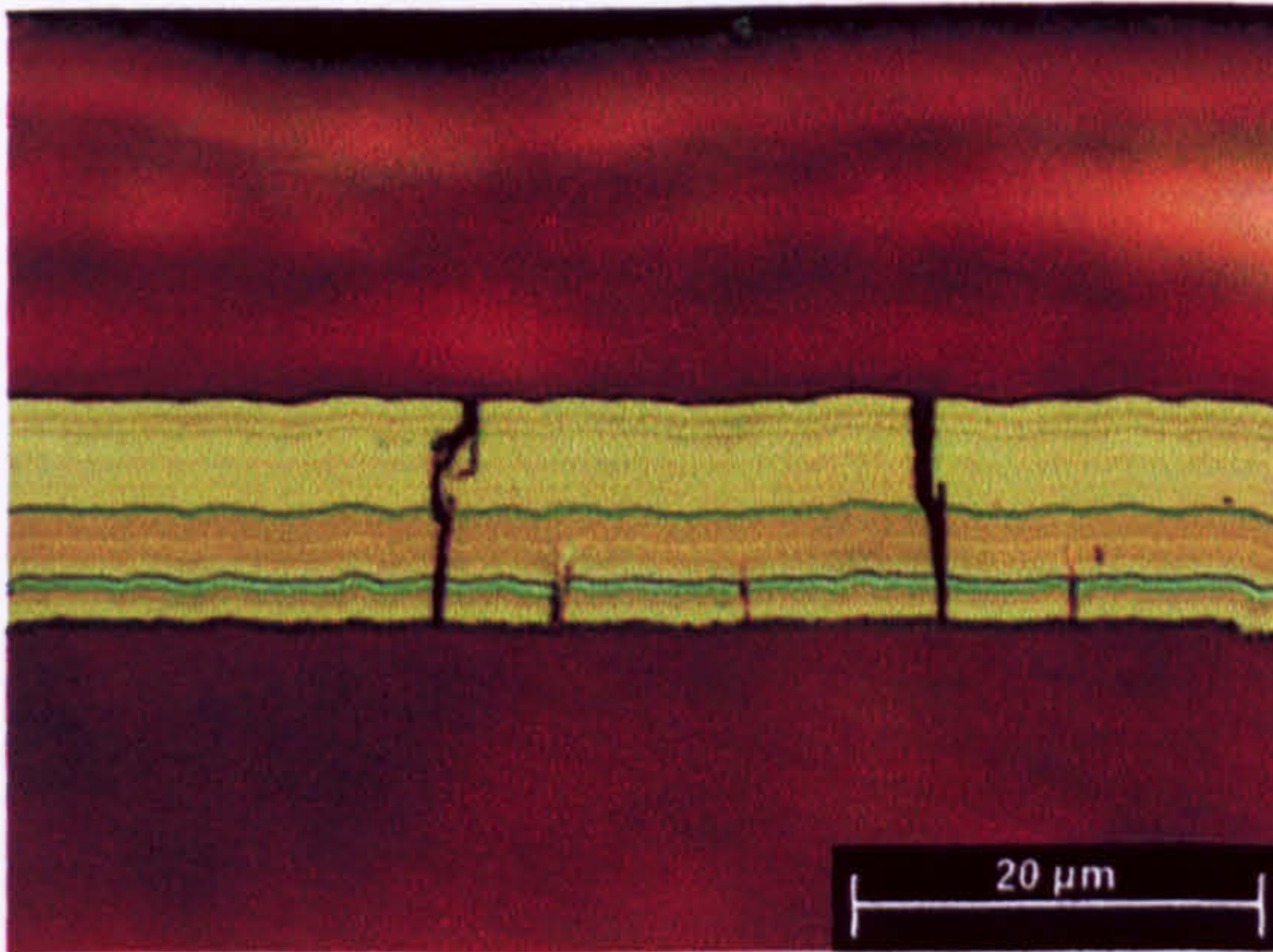
Magnification 500 x



Magnification 500 x

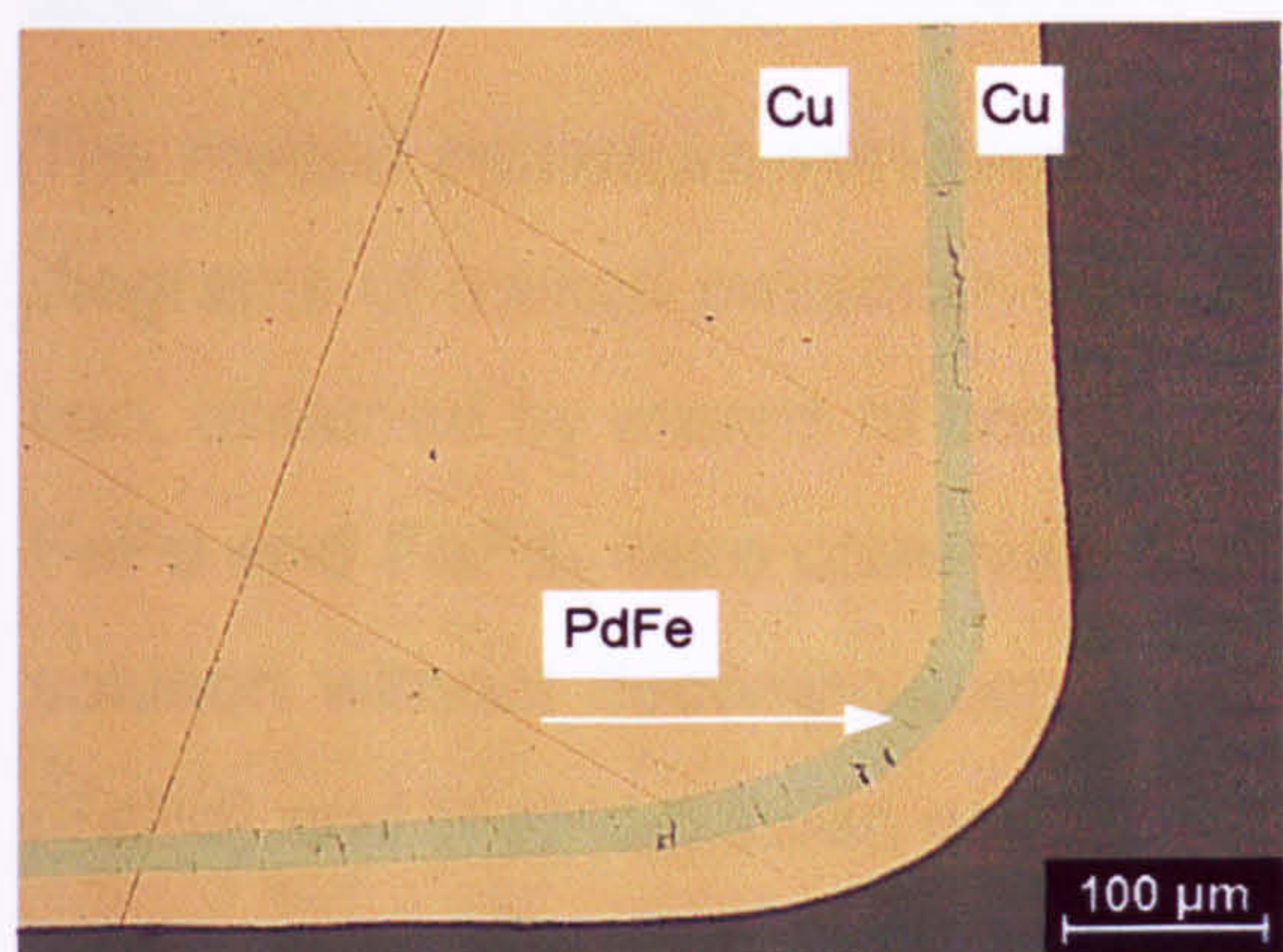


Magnification 500 x



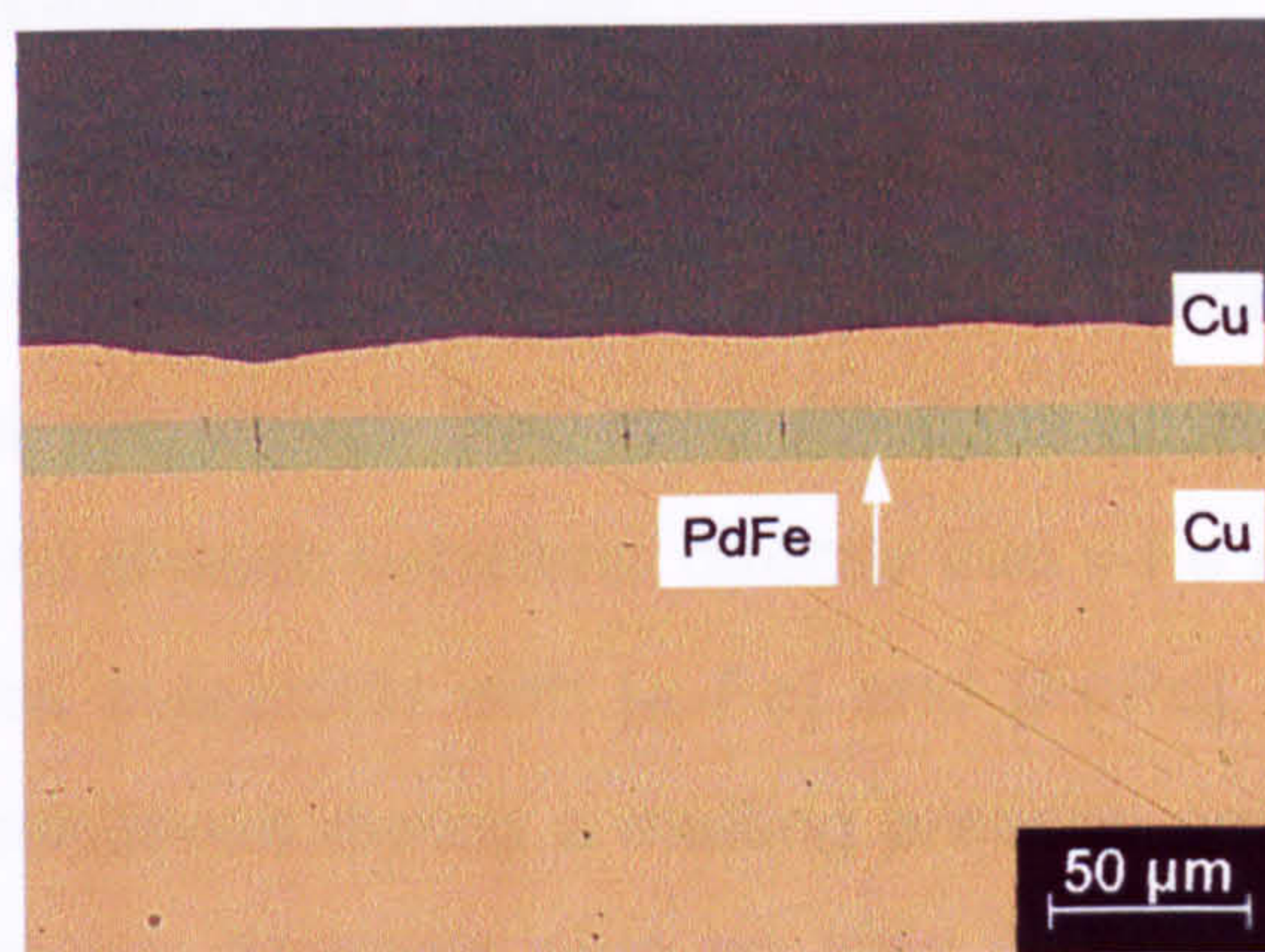
Magnification 1000 x

Figure 22
Morphology of Electrodeposited Palladium-Iron Deposits from an Electrolyte containing Pd : Fe = 1 : 1, T: 45 °C, 3 A/dm², Electrolyte and Substrate Agitation Thickness: 10 μm, Palladium Content of the Coating ca. 80 wt.-%.



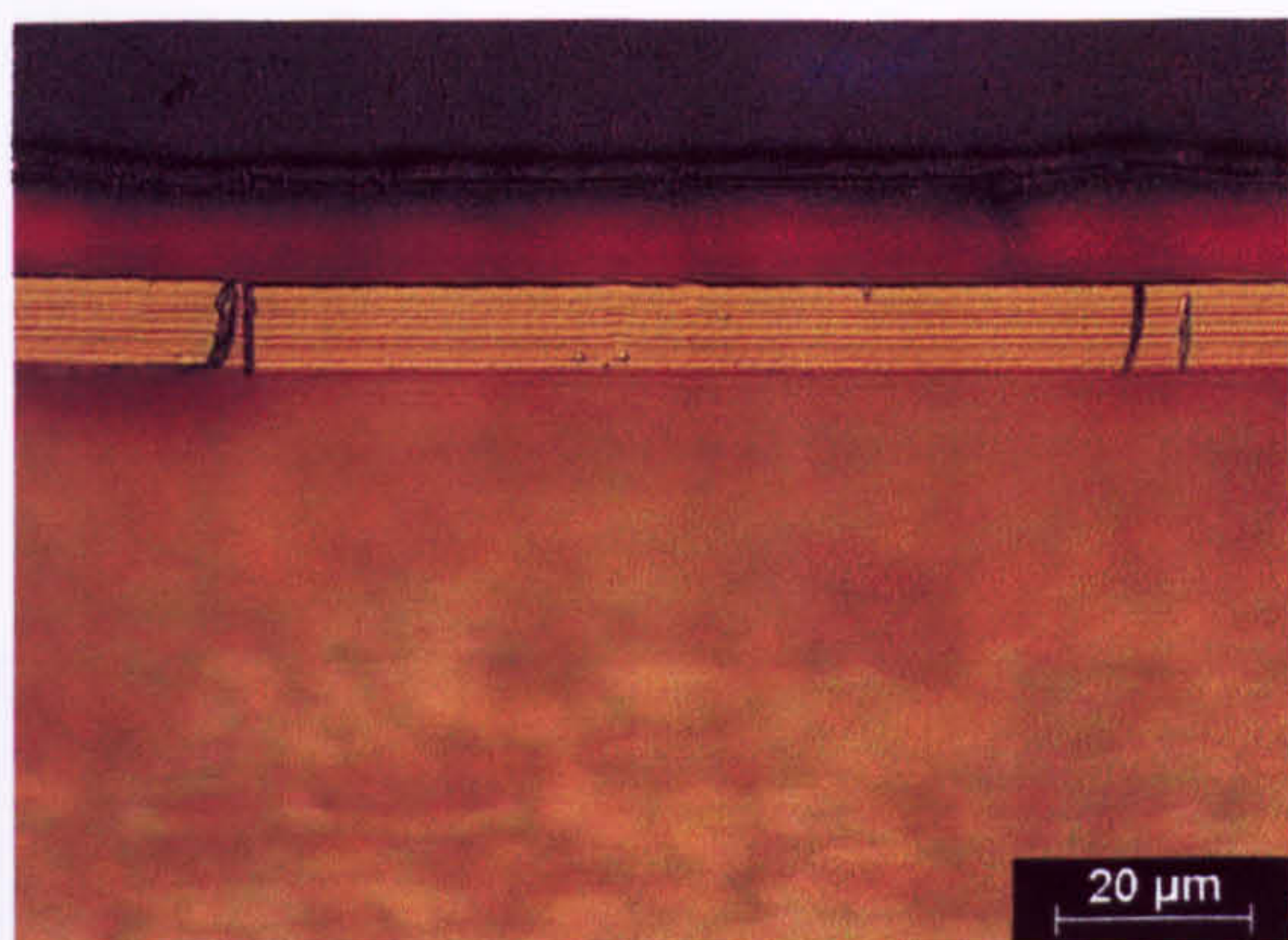
Magnification

100 x



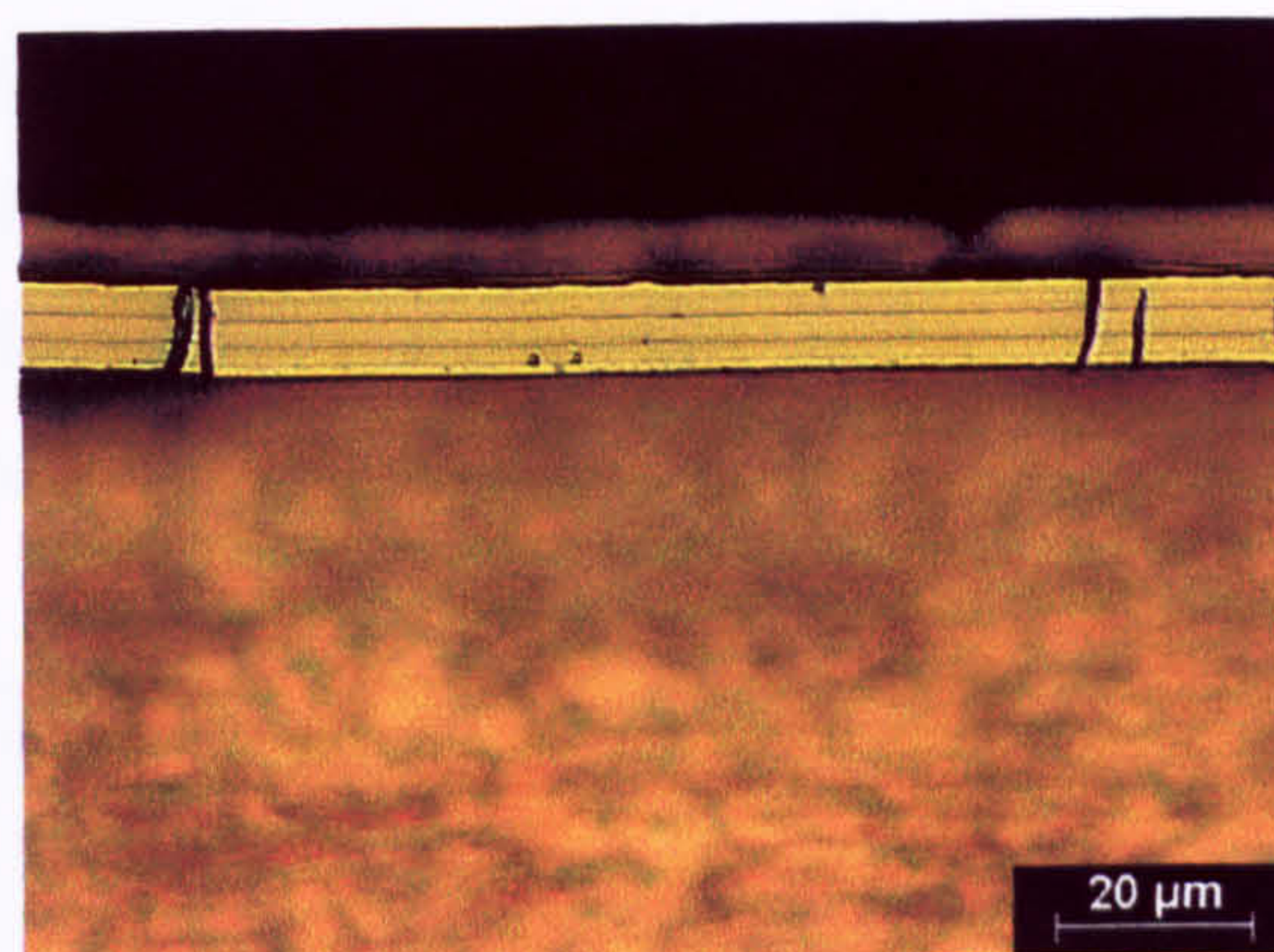
Magnification

200 x



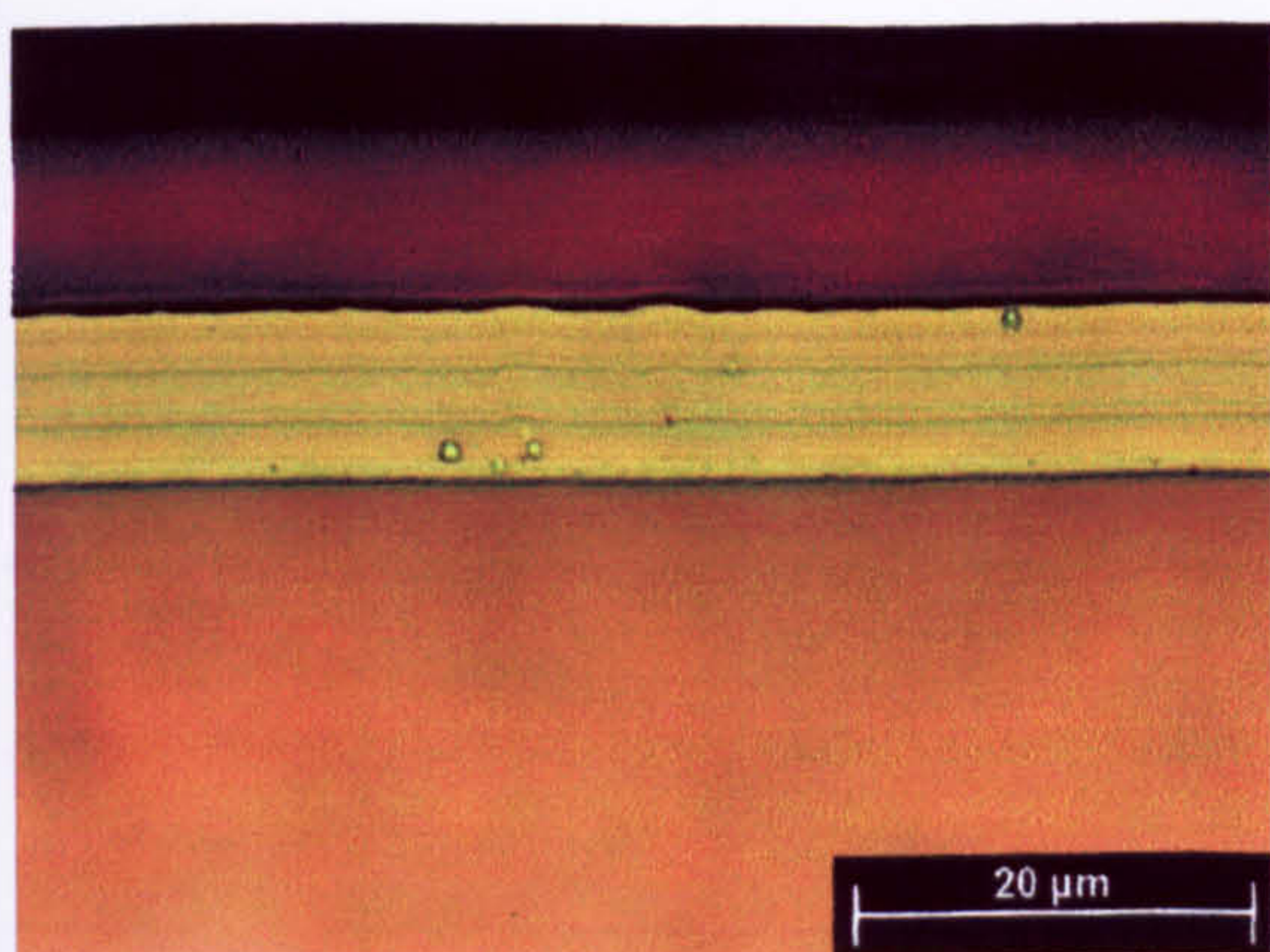
Magnification

500 x



Magnification

500 x



Magnification

1000 x

Figure 23
Morphology of Electrodeposited Palladium-Iron Deposits from an Electrolyte containing Pd : Fe = 1 : 100, T: 45 °C, 3 A/dm², Electrolyte and Substrate Agitation, Thickness: 10 μm, Iron Content of the Coating ca. 85 wt.-%.

4. 2. 3 Crystallographic Structure of Palladium-Iron Alloys

The melted palladium-iron alloy is a solid solution. In figure 24, page 74, the phase diagrams of melted palladium-iron alloys for the beginning and the end of solidification, obtained by means of cooling curves, are shown. Two solid solutions based on FePd and FePd₃ were observed. Both solid phases transform directly into γ -Fe solid solution without decomposition. γ -Fe forms eutectoids with $[\alpha\text{-Fe}]$ and $[\text{FePd}]$, and $[\text{FePd}]$ and $[\text{FePd}_3]$. Even when crystal conditions during a melting process are different to an electrodeposition process, phase diagrams give an idea of the metastable equilibrium obtained by electrodeposits. In many cases this state is equivalent to quenched materials.

While palladium is deposited as a face centered cubic crystal structure, iron deposits show a body centered cubic structure (table 18). X-ray diffraction studies, carried out on several samples with various composition of the palladium-iron alloy, showed the electrodeposits to be a complete solid solution of palladium and iron.

Face centered cubic	Body centered cubic	Hexagonal close pack	Tetragonal
Silver	Chromium	Cadmium	Tin
Gold	Iron	Cobalt	
Copper		Zinc	
Nickel			
Lead			
Palladium			
Platinum			
Rhodium			

Table 18
Lattice Structure of Commonly Electroplated Metals [17]

The addition of iron atoms to the face centered cubic palladium matrix results in a disturbance of the palladium lattice, even at low concentrations. Similar, palladium in electrodeposited iron alloys causes a noticeable disorder of the body centered cubic structure of pure iron coatings (figure 25). The grain size of the palladium-iron alloys decreases with increasing amount of iron to a minimum at alloy composition in the range of 45 At.-% to 50 At.-% iron (curve 9). Up to a palladium content of 35 At.-% to 40 At.-% palladium (ca. 50 wt.-% palladium) the typical body centered cubic structure of α -iron could be observed. Electrodeposited palladium rich alloys show a disorder of the face centered cubic structure when the iron content is increased to a range of 10 At.-% to 15 At.-% iron (curves 14 - 15). Up to an iron content of ca. 40 At.-% iron (curve 11), the typical face centered cubic structure of palladium was measured. Because there is a strong disorder of the structure of the palladium-iron alloy in the range of 40 At.-% to 50 At.-% iron, it could be assumed that at this composition the change from body centered lattice to face centered lattice occurs. *Juzikis et al* [10,11] discovered that between 30 wt.-% and 82 wt.-% palladium an "*unusual broadening of the X-ray lines*" occurred and assumed that "*this may be close to those of an amorphous structure*". X-ray diffraction measurements of palladium-iron coatings, deposited from the ammonium/citrate electrolyte, do not show the tendency of amorphous structure, nevertheless, a broadening of the X-ray lines occurred when the body centered lattice of iron changes to the face centered lattice of palladium. The broadening of the X-ray lines may be also interpreted as an increase of the internal (tensile) stress of the alloy coatings. Electrodeposited palladium-iron alloys with 50 - 60 At.-% iron are extremely brittle and flake of the surface during deposition process. Therefore, reliable X-ray diffraction measurements of an expected FePd-phase or FePd₃-phase in this range of alloy composition was not possible.

Previous heat-treatment with electroplated palladium-iron coatings [9] are in good agreement; with melted palladium-iron alloys. Samples with 20 wt.-%, 35 wt.-% and 70 wt.-% iron were heated at 850 °C for 15 minutes and than water quenched. The results obtained by X-ray fine structure investigations agree with the lattice parameter discovered from melted material. For example, electrodeposited palladium-iron alloys with 70 wt.-% iron disintegrate under such conditions into two α -iron solid solutions with different lattice parameters of 3.66 Å and 3.79 Å (figure 24).

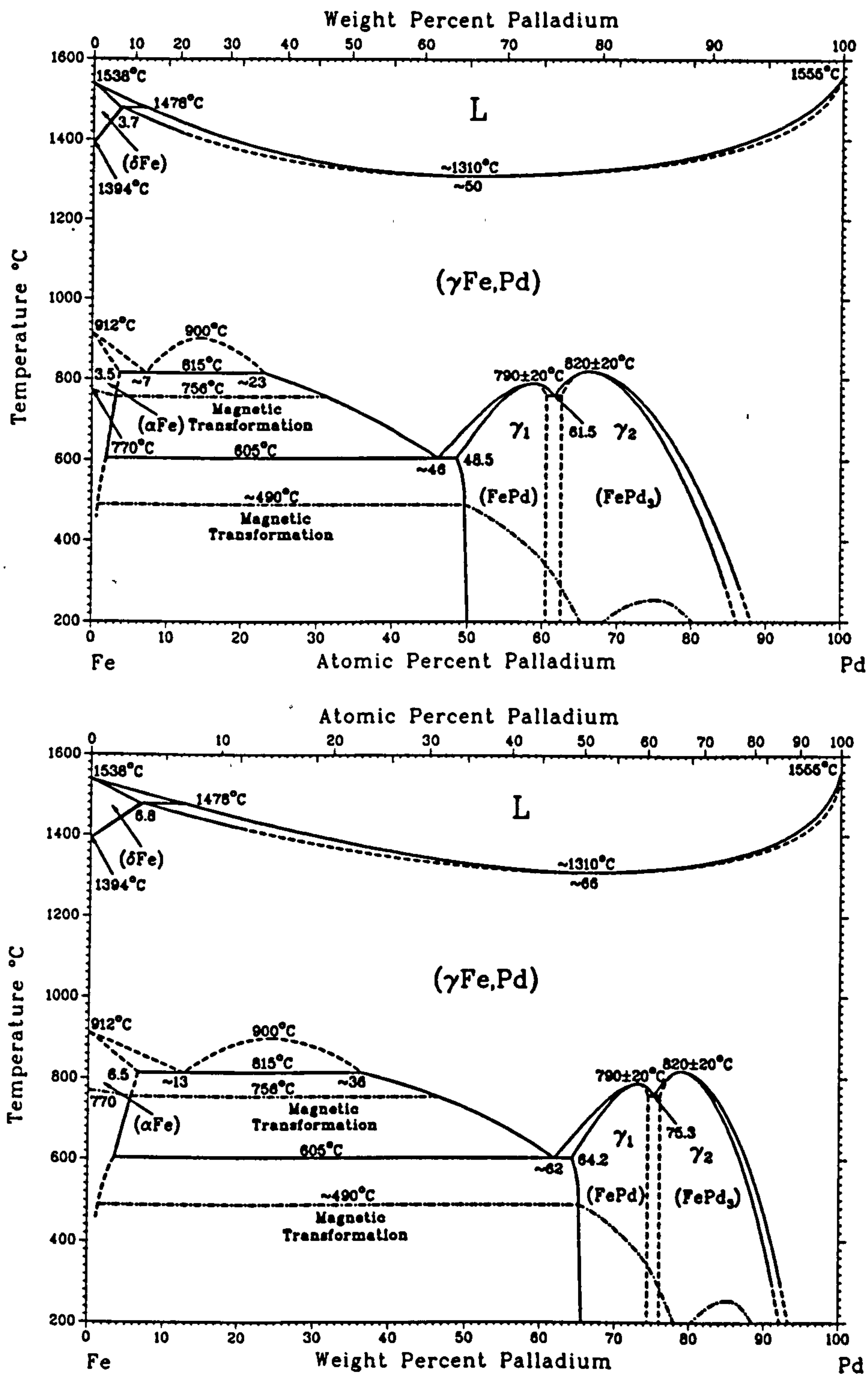
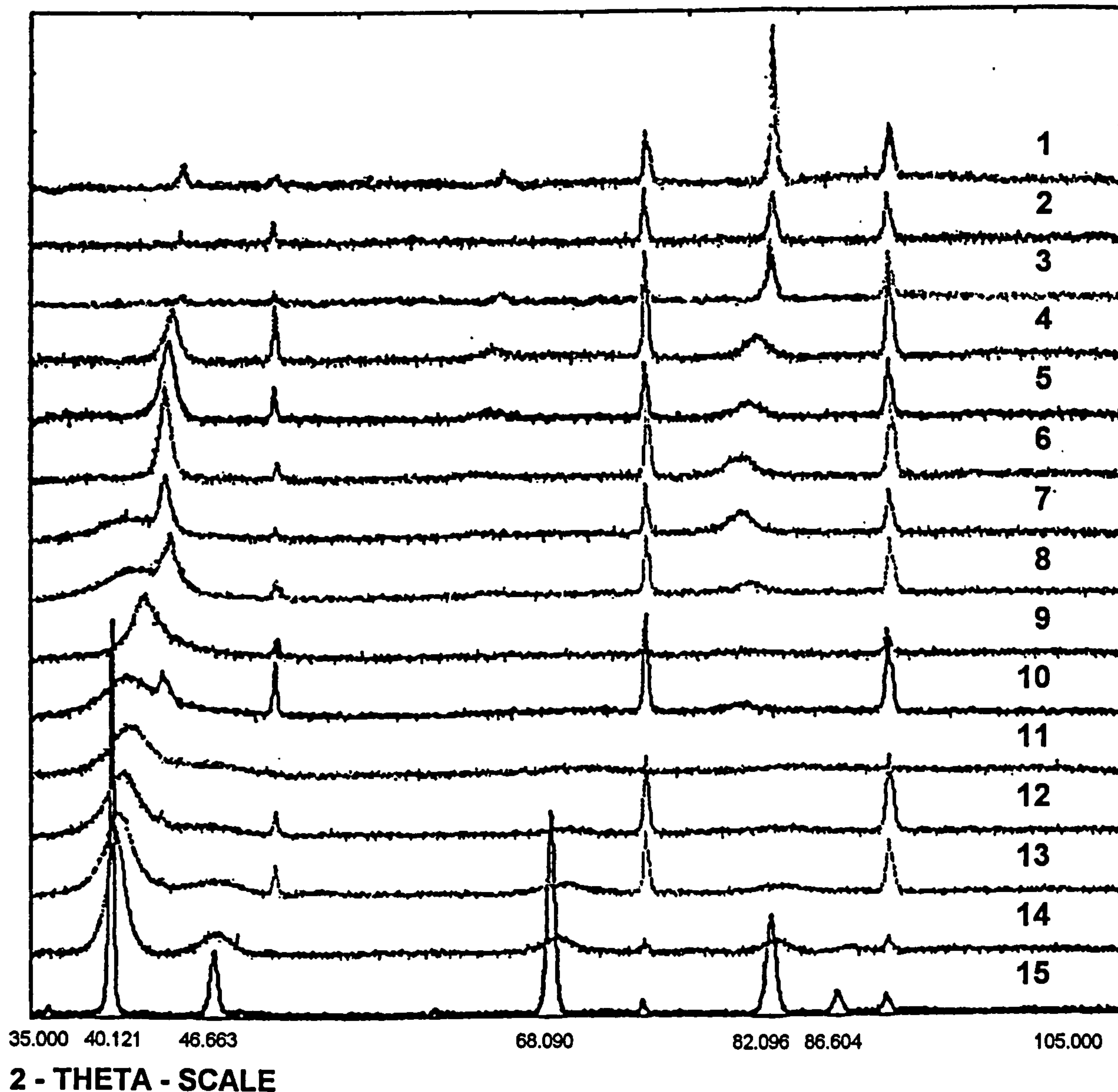


Figure 24
Phase Diagrams of Melted Palladium-Iron Alloys
Massalski, Th. B.: *Binary Alloy Phase Diagrams*; Vol. I, American Society for Metals, Metals Park, Ohio, USA (1986) 1092

INTENSITY (I)



Curve 1: 100 At.-% Fe
 Curve 4: 80 At.-% Fe
 Curve 7: 65 At.-% Fe
 Curve 10: 45 At.-% Fe
 Curve 13: 15 At.-% Fe

Curve 2: 99 At.-% Fe
 Curve 5: 75 At.-% Fe
 Curve 8: 60 At.-% Fe
 Curve 11: 40 At.-% Fe
 Curve 14: 10 At.-% Fe

Curve 3: 97 At.-% Fe
 Curve 6: 70 At.-% Fe
 Curve 9: 50 At.-% Fe
 Curve 12: 25 At.-% Fe
 Curve 15: 100 At.-% Pd

Figure 25

X-ray Diffraction Reference Diagrams of Palladium-Iron Electrodeposits with Various Alloy Composition

4. 2. 4 Hardness

Hardness of the palladium-iron coatings strongly depends on the amount of co-deposited iron in the layer (table 19). Hardness of electrodeposited pure iron is comparatively high, especially when iron is deposited from chloride or citrate electrolytes which allow an incorporation of carbon in the iron coatings.

Typical hardness of those deposits is in the range of about 600 VHN. In contrast to iron, the hardness of palladium is weaker. Electroplated palladium from this type of electrolyte has a hardness in a typical range of 200 to 250 VHN. Increase of the iron content cause an increase of the layer's hardness from 200 VHN up to at least 600 VHN (figure 26). Increase of iron content from some few wt.-% up to 10 wt.-% iron doubles the hardness of the layer from 200 to 420 VHN. From 15 wt.-% iron to 85 wt.-% iron, the increase of hardness is nearly linear with the increase of the iron content in the layer. In the range of 85 to 100 wt.-% iron the change of hardness is about 30 VHN and under a practical employment a constant quality.

The results obtained show that palladium rich alloy coatings, with 80 - 90 wt.-% palladium, have a hardness of 400 - 500 VHN, while a iron rich alloy deposit, with 80 - 85 wt.-% iron, has a hardness of 550 - 580 VHN.

Hardness (VHN_{0.01})	Compound of Iron (wt.-%)
200	0
250	5
370	8
420	10
480	15
490	20
500	40
510	50
530	70
560	80
570	85
580	90
590	95
600	100

Table 19
Hardness of Palladium-Iron Alloy Layers
versus Iron Content of the Coatings

Hardness VHN 0.01

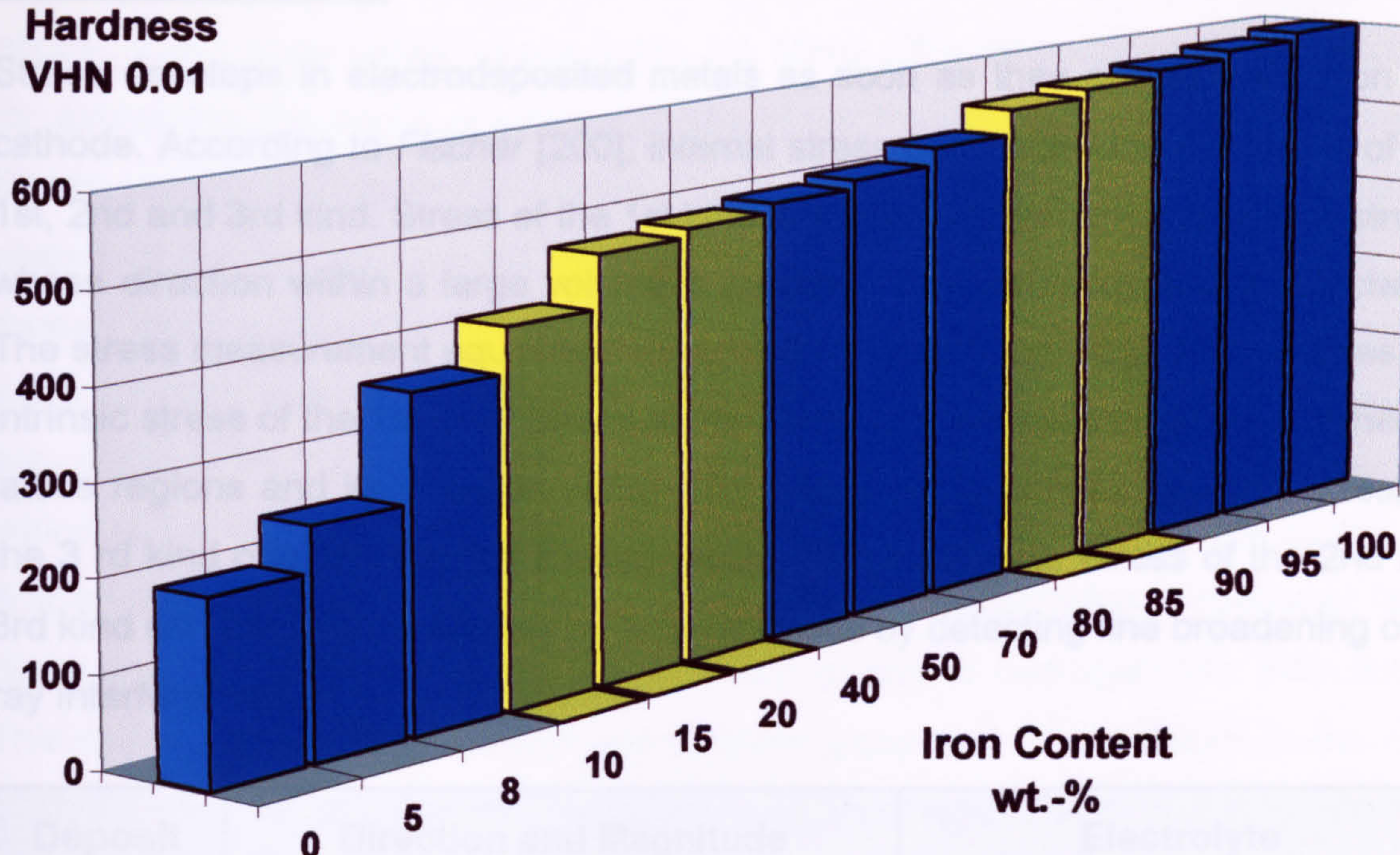


Figure 26

Hardness of Palladium-Iron Alloys versus Iron Content of the Coating

Base Electrolyte: $[\text{Pd}(\text{NH}_3)_4] \text{Cl}_2$, $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{-Citrate}$, NH_4OH

Palladium-iron electrodeposits from ammoniacal electrolytes show a hardness from 400 VHN to nearly 600 VHN. The hardness is nearly the same as the hardness obtained from palladium-nickel deposits (table 20). Palladium-iron layers are harder than palladium-cobalt and palladium-silver coatings, even when the palladium content in the palladium-iron deposits is high. It was not possible to measure a significant change of hardness in the range of 65 wt.-% to 75 wt.-% palladium. In this range the phases change twice, first to γ_1 -phase (FePd) and then to a γ_2 phase (FePd_3). Unfortunately, alloy coatings with this composition are extremely brittle, not coherent, and show a low adhesion. Therefore, no homogeneous deposits for examination could be obtained, even after several experiments were carried out.

Deposit	PdNi 80/20	PdFe 15/85	PdFe 80/20	PdCo 75/25	PdAg 80/20	PdAg 60/40	Pd	AuNi 95/5	AuCo 99/1	AuFe 99/1
Hardness VHN _{0.01}	450 - 600	550 - 600	500 - 550	400 - 500	400 - 450	200 - 250	200 - 250	200 - 250	180 - 220	150 - 180

Table 20

Hardness of Various Electroplated Metals and Metal Alloys

Data from Measurements on Cross Sections; PdAg Literature Data [173,177]

4. 2. 5 Internal Stress

Stress develops in electrodeposited metals as soon as they are deposited on the cathode. According to *Fischer* [200], internal stress can be divided into those of the 1st, 2nd and 3rd kind. Stress of the 1st kind is a large tensile or compressive stress, whose direction within a large volume is constant. It is macroscopically detectable. The stress measurement equipment described in figure 3, on page 38 measures the intrinsic stress of the 1st kind. Stress of the 2nd kind is constant only within coherent lattice regions and its direction varies from one grain to another. Internal stress of the 3rd kind originates within submicroscopic lattice regions. Stress of the 2nd and 3rd kind can be determined only by X-ray methods by detecting line broadening of X-ray interferences.

Deposit	Direction and Magnitude	Electrolyte
Rhodium	Very High Tensile	Sulfate Electrolyte
Chromium	Very High Tensile	Chromium(VI) Electrolyte
Platinum	High Tensile	Acid or Alkaline Electrolyte
Palladium	High Tensile	Ammonium Electrolyte
Nickel	High Tensile	Chloride, Sulfate Electrolyte
Nickel	Slightly Compressive	Appropriate Additives
Cobalt	Moderate Tensile	Sulfate Electrolyte
Iron	Moderate Tensile	Chloride, Sulfate Electrolyte
Silver	Slightly Tensile	Cyanide Electrolyte
Copper	Slightly Tensile/Compressive	Sulfate Electrolyte
Lead	Slightly Compressive	Fluoborate Electrolyte
Zinc	Slightly Compressive	Sulfate Electrolyte

Table 21

Internal Stress of Electrodeposited Metals, their Magnitude and Direction [13]

Internal stress may be either compressive or tensile. Most of the metals and metal alloys usually show tensile stress (table 21). Many different causes can be adducted for explaining the origin of internal stress in electrolytic deposits [13]. Dislocation theory, excess energy theory, hydrate theory and hydrogen theory are the most important of the various theories. Hydrogen theory assumes that the co-deposited hydrogen incorporated into the deposits is responsible for the internal stress by causing a temporary lattice expansion in the deposited metal. With progressive deposition, the hydrogen diffuses either in the substrate material or into the electrolyte. The lattice of the coating then shrinks and tensile stress arises in proportion to this hydrogen diffusion. The theory applies metals in which co-deposition of hydrogen takes place and which are capable of incorporation of atomic hydrogen into their lattice. This occurs for metals of the iron and platinum group and for chromium. In the case of nickel and palladium several experiments with hydrogen charging during and after deposition [124] show that internal stress of these metals is connected with the formation of metal hydride phases ($\alpha + \beta$ phases). Therefore, metal deposition occurs with high internal stress. In the case of nickel various additives were found (saccharin, aromatic disulfonic acids, etc.) which reduce stress or change tensile stress to compressive stress. In the case of palladium the knowledge is slight.

During the first investigations on palladium-iron electrodeposition at the FEM additives, which are useful for reducing the stress in bright nickel deposits, were investigated [9]. Unfortunately, neither saccharin, urea, thiourea, nor boric acid had a significant effect on the stress of electrodeposited palladium or palladium-iron layers. The same behaviour was observed on palladium-nickel deposition from ammoniacal electrolytes [143,144]. *Hedrich* and *Raub* investigated various additives for palladium deposition from $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ salt in an ammoniacal electrolyte [93-95]. The authors discovered that additives like citrate, benzoates, salicylates, nicotinic acid, and nicotinic acid amide shift deposition potential of palladium to negative values (see figure 12, page 53). Therefore, in the range of low current densities the co-deposition of hydrogen increases and hydrogen content in the coating increases too. High internal stress of the deposited layers with cracks is the consequence. Figure 27 shows the internal stress of palladium-iron coatings during electrodeposition with a current density of 3 A/dm^2 from an electrolyte with a metal ratio $\text{Pd}:\text{Fe} = 1:1$. The alloy coatings all have high tensile stress in the range of 350 to 500 N/mm^2 .

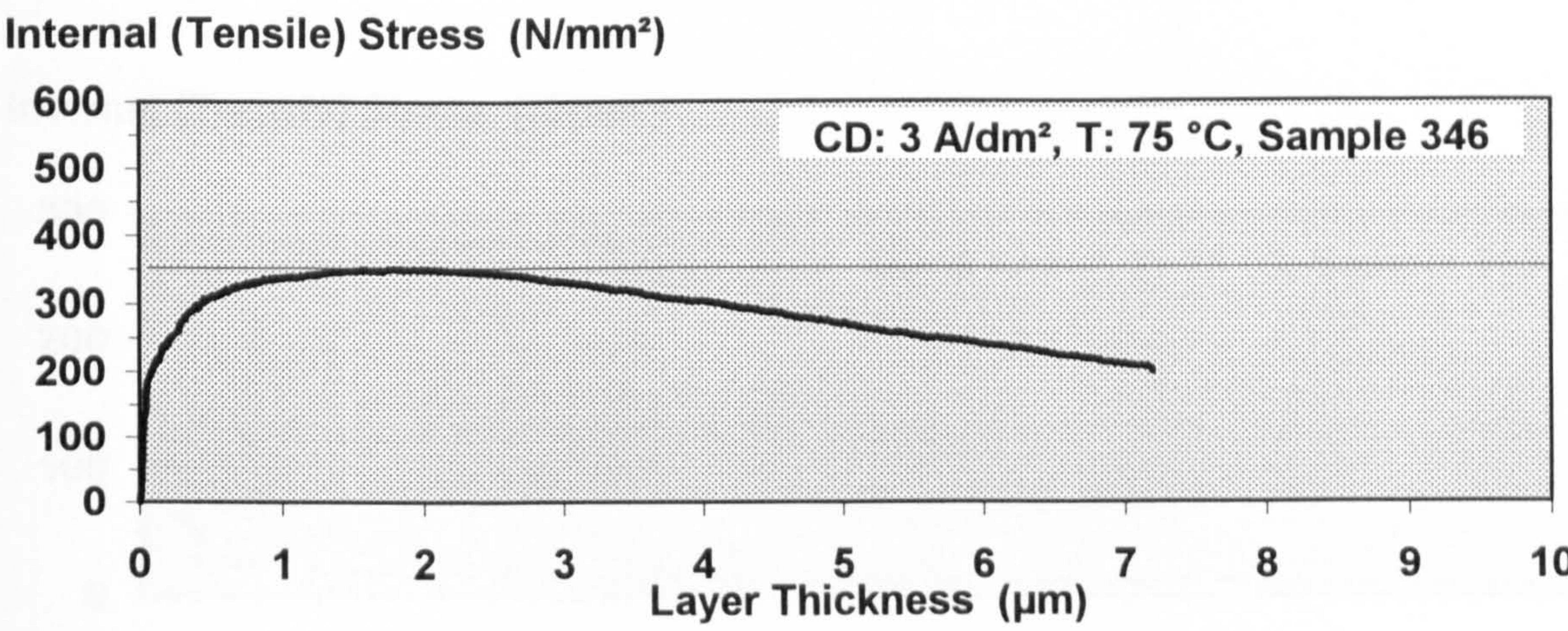
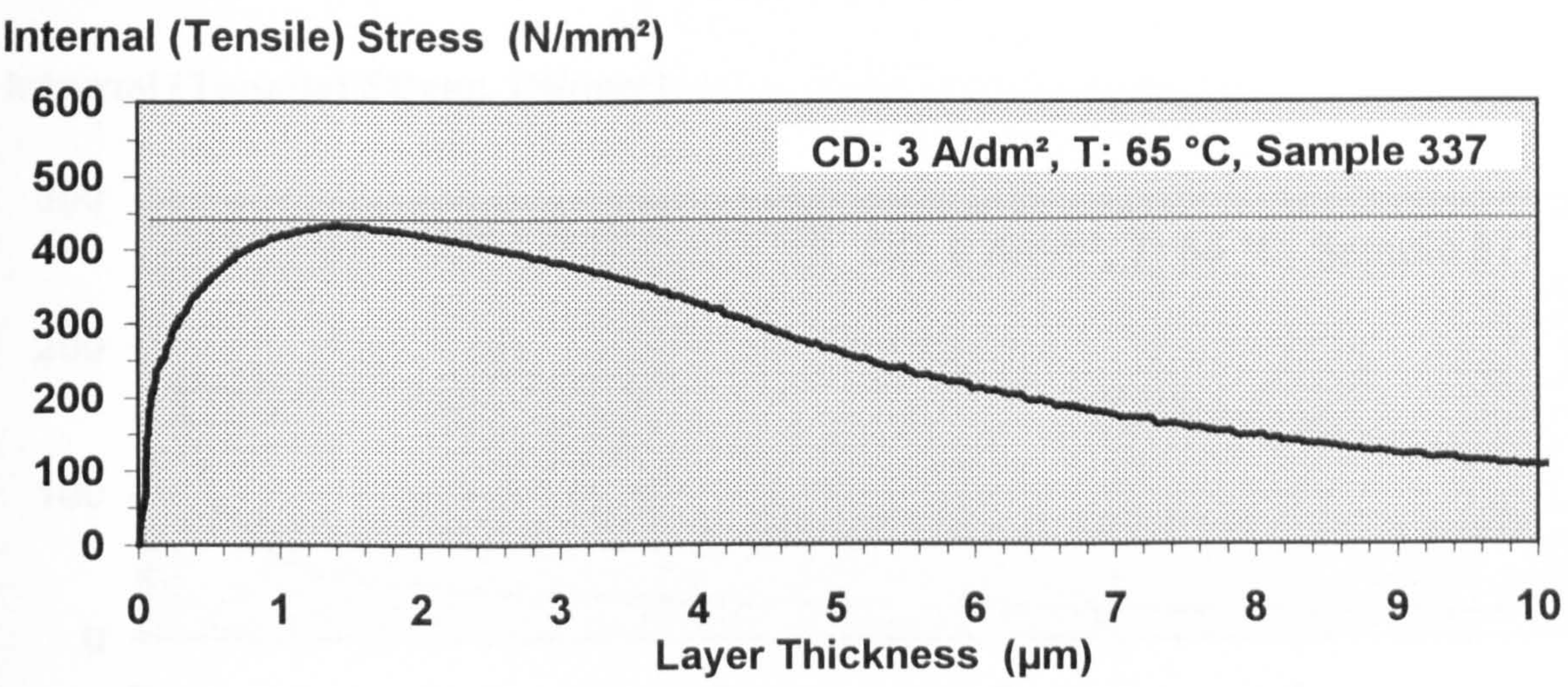
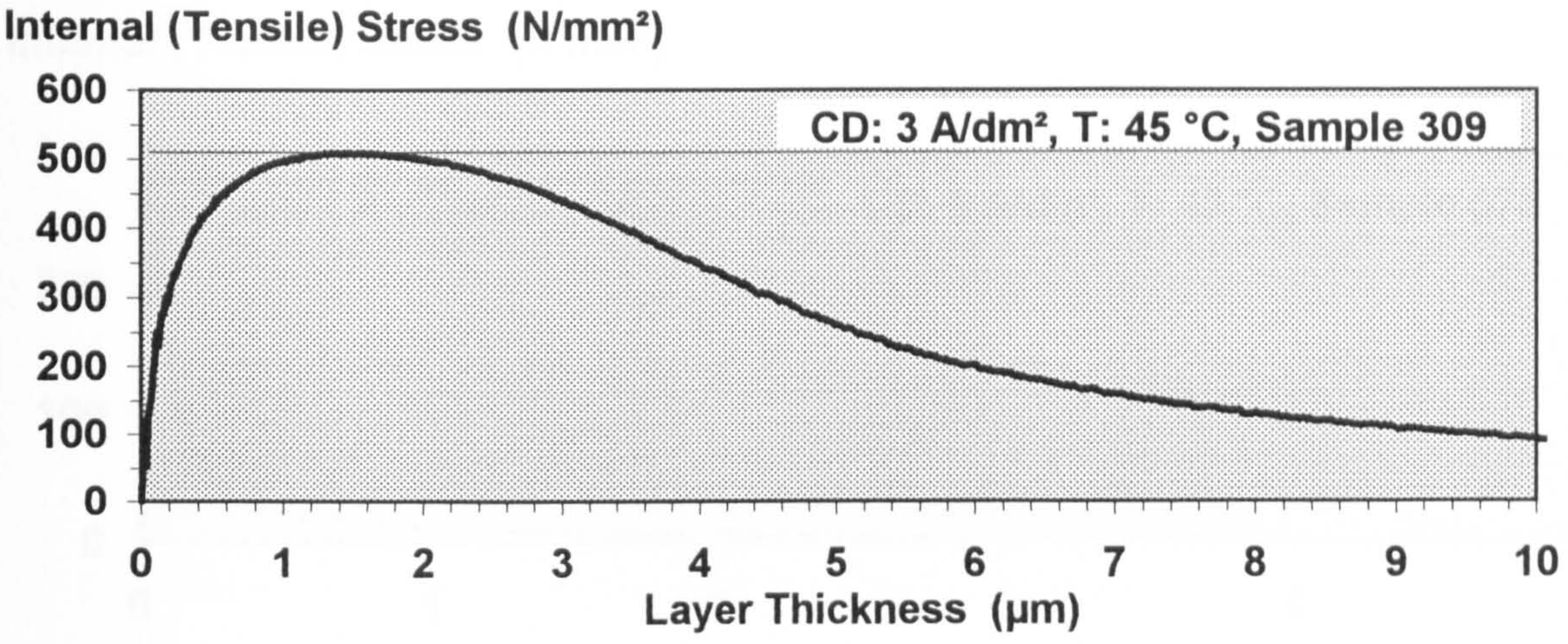
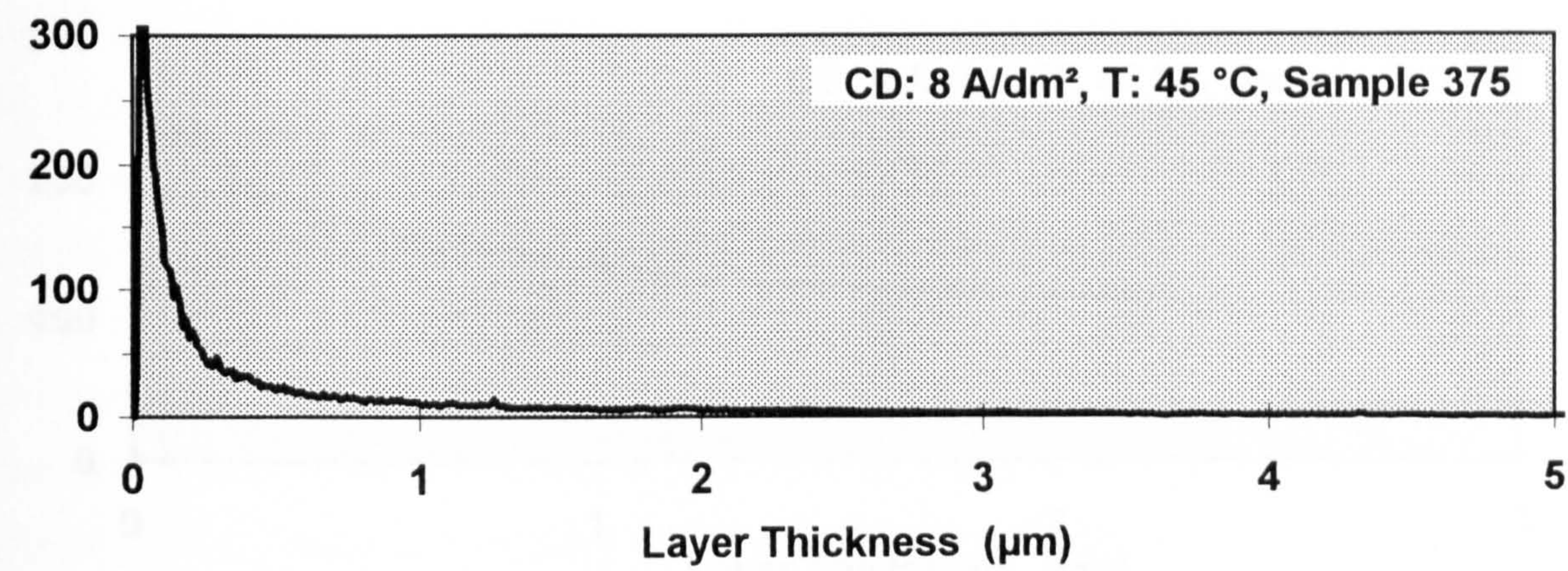
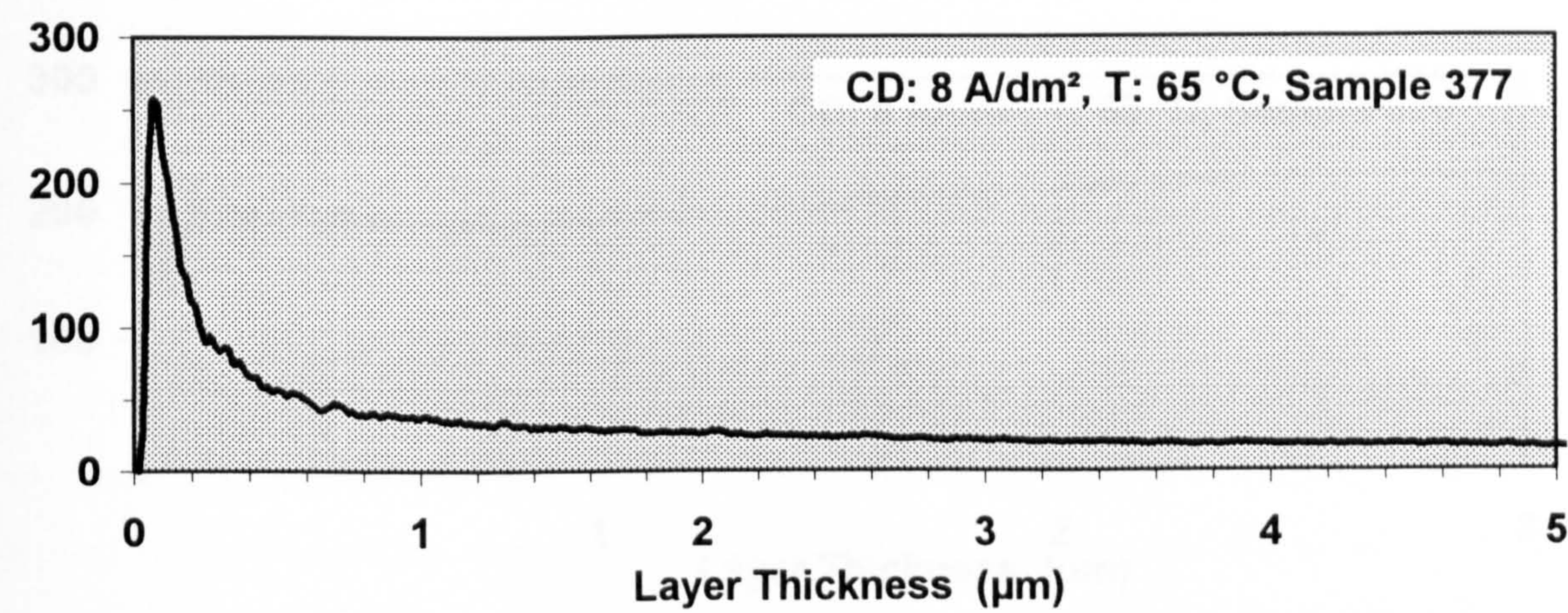


Figure 27
Internal Stress of Palladium-Iron Coatings during Electrodeposition from an Electrolyte with a Metal Ratio Pd : Fe = 1 : 1, CD = 3 A/dm², see table 11, page 46

Internal (Tensile) Stress (N/mm²)



Internal (Tensile) Stress (N/mm²)



Internal (Tensile) Stress (N/mm²)

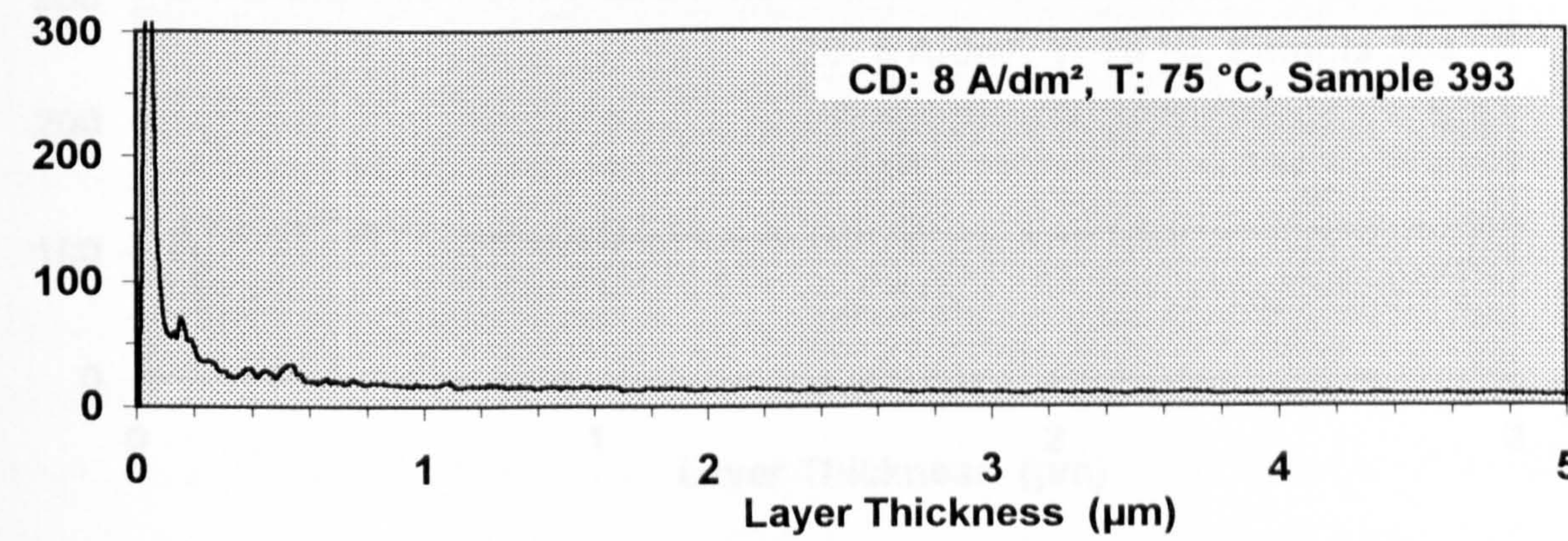
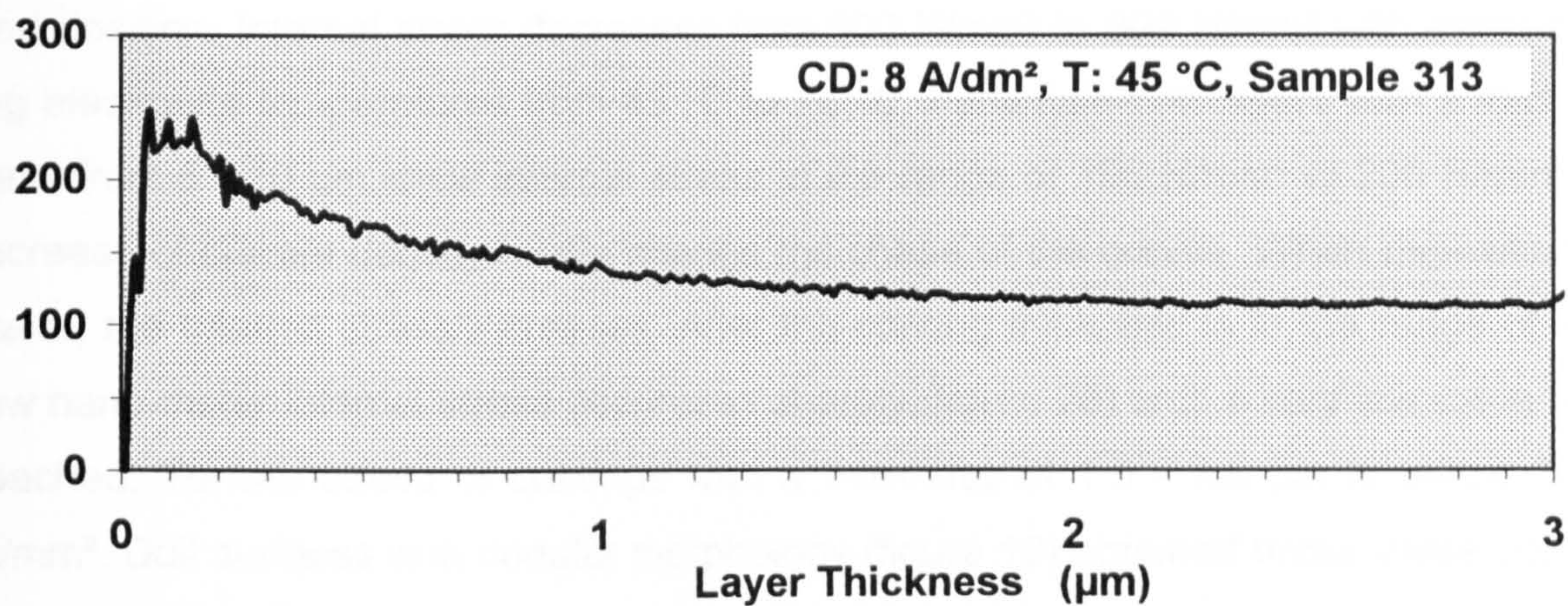
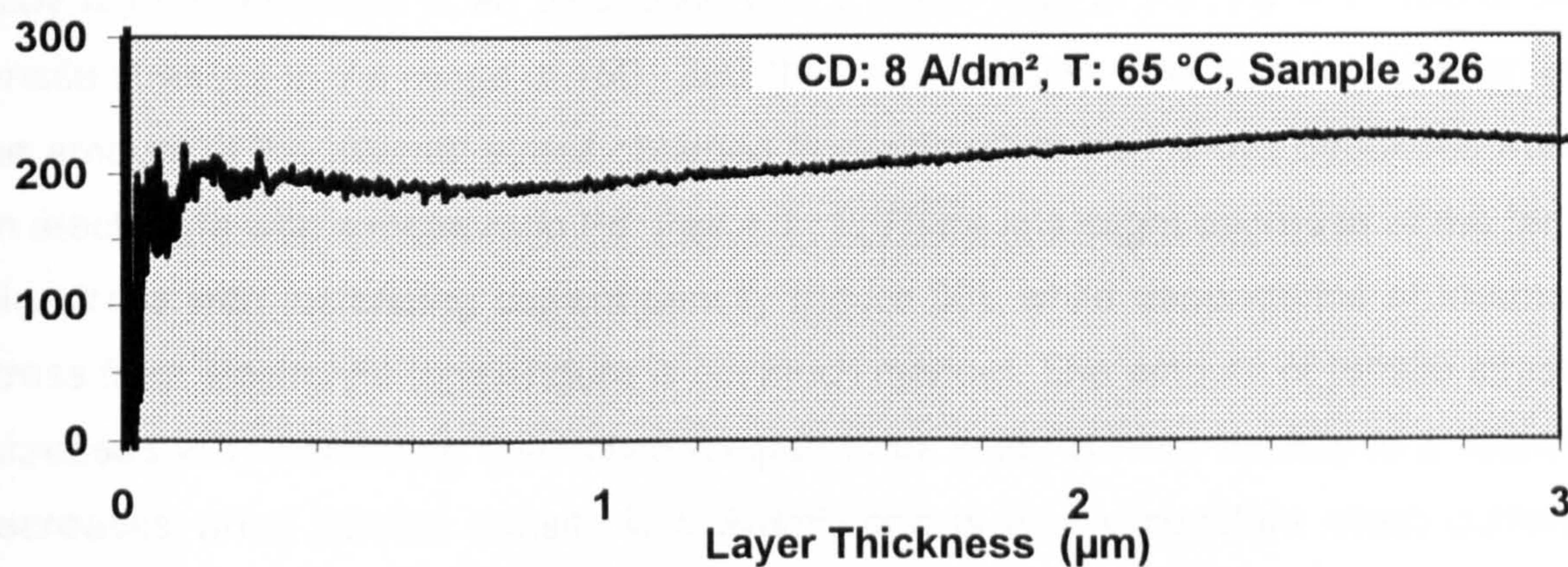


Figure 28
Internal Stress of Palladium-Iron Coatings during Electrodeposition from an Electrolyte with a Metal Ratio Pd : Fe = 1 : 1, CD = 8 A/dm², see table 11, page 46

Internal (Tensile) Stress (N/mm²)



Internal (Tensile) Stress (N/mm²)



Internal (Tensile) Stress (N/mm²)

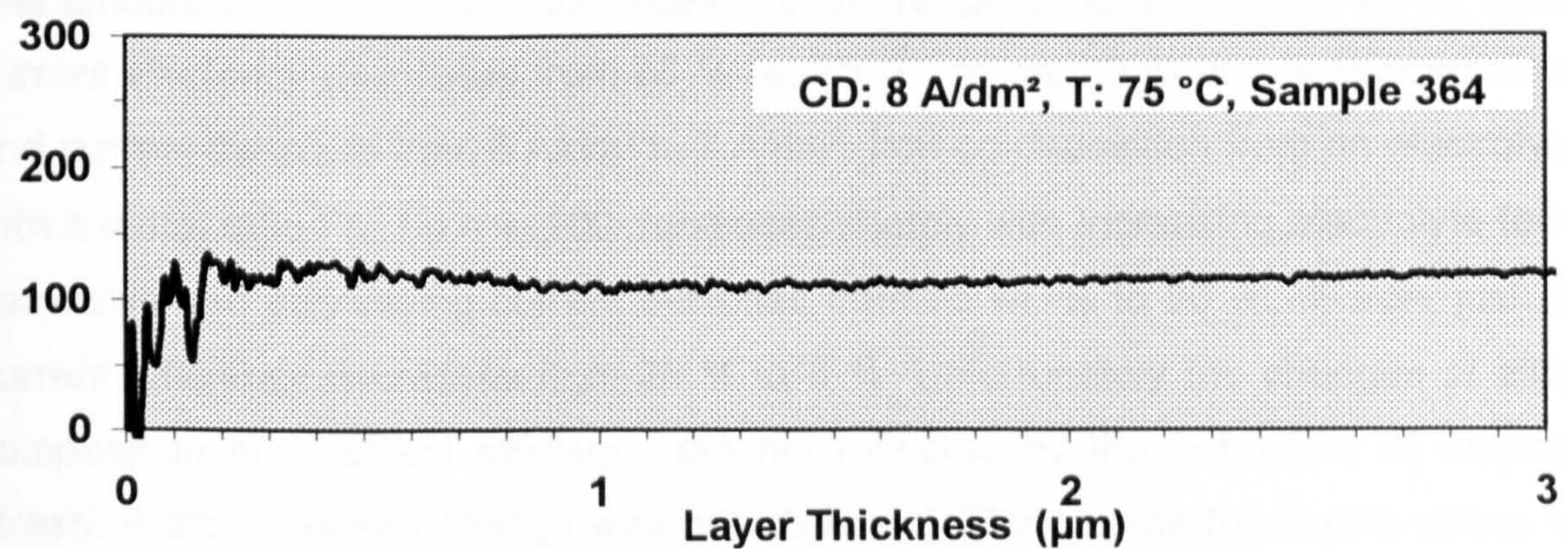


Figure 29

Internal Stress of Palladium-Iron Coatings during Electrodeposition from an Electrolyte with a Metal Ratio Pd : Fe = 1 : 100, see table 11, page 46

From the beginning of deposition the tensile stress of the coatings increases sharply to a maximum. The maximum depends on the electrolyte temperature, both in size and position. Internal stress decreases from 500 N/mm² to 300 N/mm² with increasing electrolyte temperatures from 45 °C to 75 °C. Palladium-iron layers with a thickness from 5 - 10 µm show internal stress in the range of 100 N/mm² to 200 N/mm². Increase of current density totally change the shape of the curves. When deposition starts, the internal stress increases. After the coating thickness is in the range of a few nano-meter internal stress decreases sharply (figure 28) until a very low value is reached. Tensile stress of coatings with a thickness of 1.5 - 2.5 µm is below 20 N/mm². Dull surfaces with nodular morphology (figure 19) obtained under these conditions (figure 20) give an explanation for the very low internal stress of thicker coatings. Alloy layers deposited with 5 A/dm² show a behaviour in between (fig. 30).

Alloy layers deposited in an electrolyte with a metal ratio of Pd : Fe = 1 : 100 show tensile stresses in the range of 150 - 350 N/mm² (figure 29). This is nearly the half of the amount of the internal stress obtained from palladium-iron alloys deposited from an electrolyte with a metal ratio Pd : Fe = 1 : 1. There is a slight decrease of the tensile stress with increasing current density (figure 30), while dependence of internal stress from electrolyte temperature is not much marked. The amount of tensile stress increases with increasing electrolyte temperatures when current density is 3 A/dm², decreases when current density is 5 A/dm², and is nearly constant when current density is 8 A/dm². The results show that palladium-iron coatings from electrolytes with a high content of palladium are deposited with high internal (tensile) stress.

The amount of palladium in such alloys is in the range of 80 wt.-% - 85 wt.-%, while current efficiency decreases from 85 % (at 75 °C) to ca. 70 % at low temperatures and current densities from 5 A/dm² to 7 A/dm². Iron co-deposition from an electrolyte with a metal ratio Pd : Fe = 1 : 100 decreases sharply with increasing electrolyte temperatures and decreasing current densities from 85 wt.-% to 20 wt.-% iron, just as current efficiency decreases from 25 % to 5 %. Unfortunately the changes of alloy composition and current efficiency are not reflected by the behaviour of internal stress. Such a marked change was not observed. The causes for tensile stress of palladium-iron coatings are not directly related to iron concentration and respectively palladium content of the layers, or to hydrogen evolution during electrolysis.

In Appendix A 2-1 to 2-3 all results from internal stress measurement are shown.

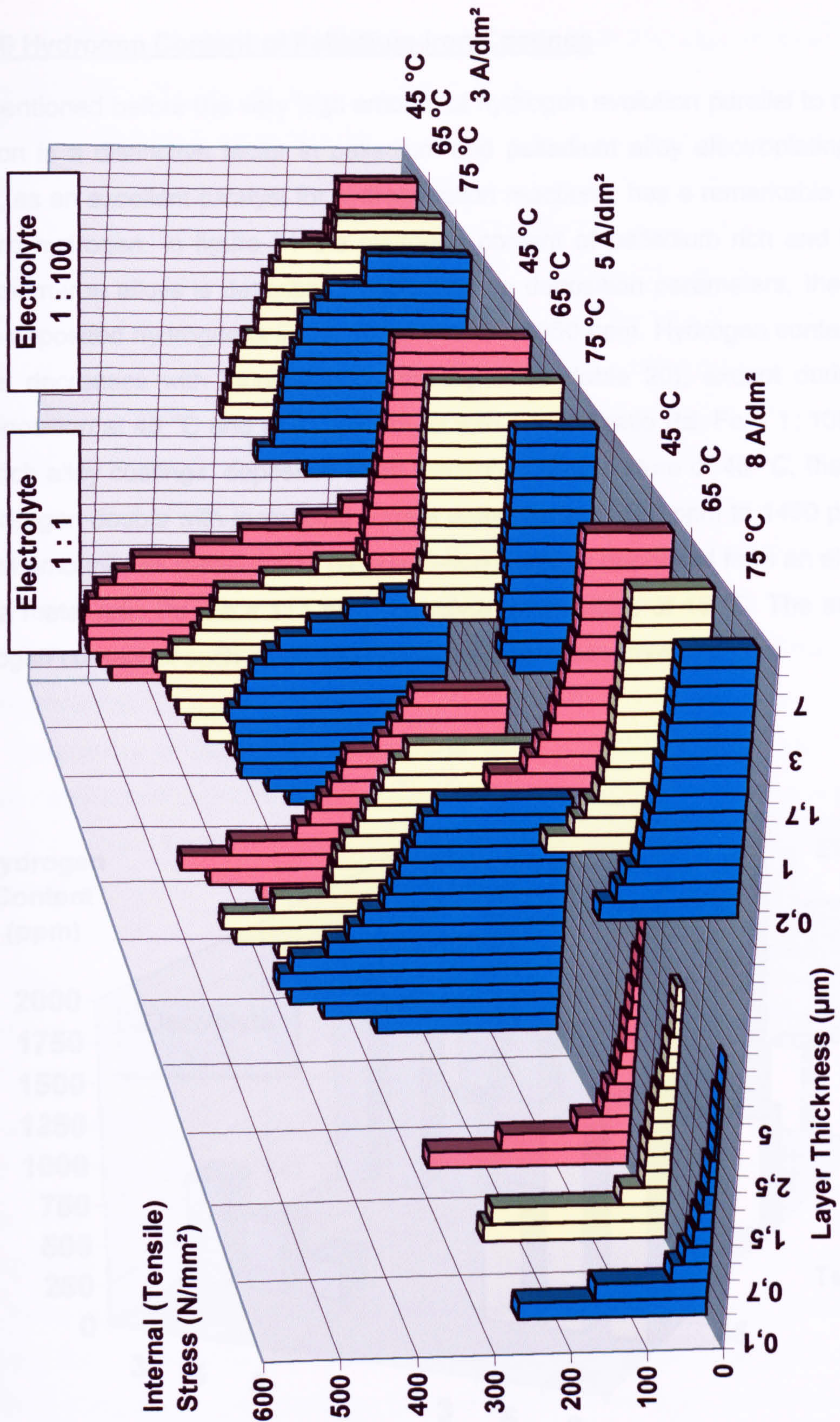


Figure 30
Tensile Stress of Palladium-Iron Coatings during Electrodeposition from two Electrolytes versus Deposition Parameters and Layer Thickness
 Electrolyte Composition: see table 11, page 46

4. 2. 6 Hydrogen Content of Palladium-Iron Coatings

As mentioned before the very high amount of hydrogen evolution parallel to metal reduction is a distinctive factor in palladium and palladium alloy electroplating. Palladium, as an excellent catalyst for hydrogenation reactions, has a remarkable ability to absorb hydrogen. In figure 31 the hydrogen content of palladium rich and iron rich palladium-iron alloys is described. Depending on deposition parameters, the amount of co-deposited hydrogen is in the range of 250 - 2050 ppm. Hydrogen content of the layers decreases with increasing current densities (table 20), except during electrodeposition at 45 °C and in an electrolyte with a metal ratio Pd : Fe = 1 : 100. In this iron rich alloy coatings, deposited at an electrolyte temperature of 45 °C, the amount of hydrogen double with increasing current densities from 750 ppm to 1450 ppm. The lowest amount was measured in palladium-iron coatings deposited from an electrolyte with a metal ratio Pd : Fe = 1 : 1 and electrolyte temperature of 45 °C. The amount of hydrogen content of such palladium rich layers decreases from 670 ppm

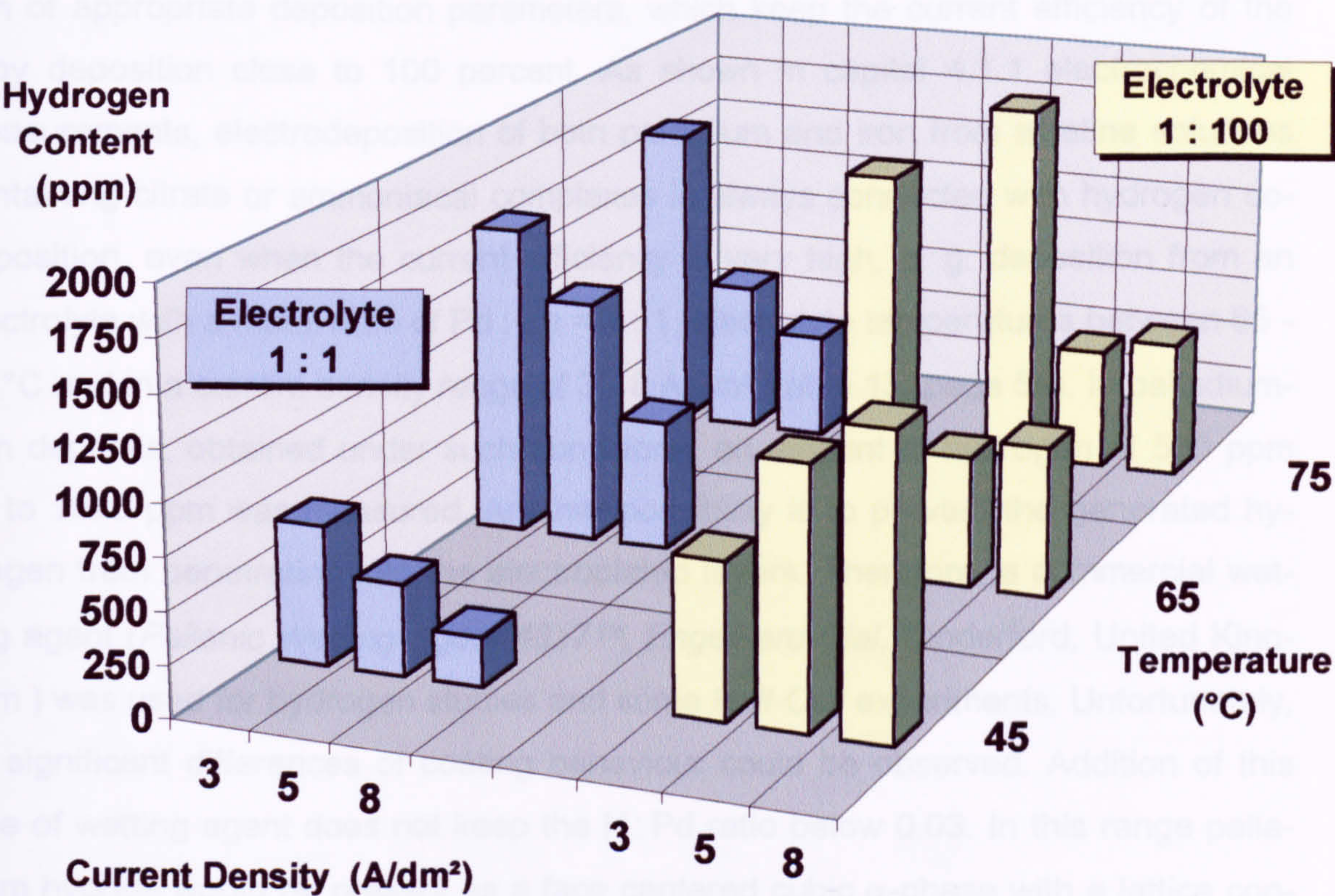


Figure 31
Hydrogen Content (ppm) in Electroplated Palladium-Iron Alloys versus Current Density and Electrolyte Temperature

in coatings deposited with a current density of 3 A/dm² to 250 ppm in alloy coatings deposited with a current density of 8 A/dm². In general the amount of co-deposited hydrogen is higher in palladium-iron coatings with a high amount of iron. This is contrary to the supposed connection between palladium amount and hydrogen amount. In iron rich electrolytes there is a marked decrease of the current efficiency when the electrolyte temperature is above 65 °C (table 16, page 59). Hydrogen content increases when deposition occurs with a current density of 3 A/dm². Unfortunately, at a current density range of 5 - 8 A/dm² this behaviour is no longer observed. But this does not mean that the amount of hydrogen is still low during electrodeposition. For example a main amount of the hydrogen in the deposits could be temporary in the form of the palladium hydrogen β -phase. It could be assumed that this plating conditions are more similar to hydrogen charging conditions than to metal deposition. A large amount of temporary stable β -phase with a life-time below few minutes was already observed during nickel, palladium, and palladium-nickel electrodeposition [124]. To keep the amount of absorbed hydrogen as small as possible the amount of available hydrogen must decrease. One possibility is the selection of appropriate deposition parameters, which keep the current efficiency of the alloy deposition close to 100 percent. As shown in capital 4.1.1 electrochemical measurements, electrodeposition of both palladium and iron from alkaline solutions containing citrate or ammoniacal complexes is always connected with hydrogen co-deposition, even when the current efficiency is very high, e. g. deposition from an electrolyte with a metal ratio of Pd : Fe = 1 : 1, electrolyte temperatures between 65 - 75 °C and in a current density range of 3 - 8 A/dm² (table 15, page 59). In palladium-iron deposits, obtained under such conditions, an amount of hydrogen of 530 ppm up to 1570 ppm was measured. Another possibility is to prevent the generated hydrogen from penetrating into the electroplated layers. Therefore, a commercial wetting agent (*Pallanic Wetting Agent 4317™*, Engelhard-Clal, Cinderford, United Kingdom) was used for hydrogen studies and some *Hull-Cell* experiments. Unfortunately, no significant differences of coating behaviour could be observed. Addition of this type of wetting agent does not keep the H : Pd ratio below 0.03. In this range palladium hydride would be present as a face centered cubic α -phase with a lattice constant close to that of pure palladium, therefore, hydrogen from this structure does not cause significant lattice contraction.

H - Content (ppm)	Current Density			Electrolyte Pd : Fe
	3 A/dm ²	5 A/dm ²	8 A/dm ²	
Temperature (°C)				
45 °C	670	440	250	1 : 1
65 °C	1550	1210	650	1 : 1
75 °C	1570	760	530	1 : 1
45 °C	750	1250	1450	1 : 100
65 °C	2050	660	750	1 : 100
75 °C	1870	610	690	1 : 100

Table 22

Hydrogen Content in Electroplated Palladium-Iron Alloys versus Electrolyte Temperature, Current Density and Metal Ratio of the Electrolyte

H - Content (ppm)		Current Density			Electrolyte Pd : Fe
		3 A/dm ²	5 A/dm ²	8 A/dm ²	
Temperature (°C)					
45 °C	1 st Measurement	632	1029	1364	1 : 100
45 °C	2 nd Measurement	641	1282	1412	1 : 100
45 °C	3 rd Measurement	940	1430	1580	1 : 100
45 °C	Mean Value	750	1250	1450	1 : 100
65 °C	1 st Measurement	1932	461	625	1 : 100
65 °C	2 nd Measurement	2035	654	745	1 : 100
65 °C	3 rd Measurement	2145	858	887	1 : 100
65 °C	Mean Value	2040	660	750	1 : 100

Table 23

Reproducibility of the Determination of Hydrogen Content in Electroplated Palladium-Iron Alloys from Various Electrolytes

4. 2. 7 Sulfur and Carbon Content of Palladium-Iron Coatings

The incorporation of sulfur and carbon in palladium-iron coatings is low in the range of 50 - 100 ppm for carbon and 150 - 200 ppm for sulfur. This amount of non-metallic impurities corresponds to the results obtained from palladium-nickel coatings [138]. There is no significant change of the amount depending on electrolyte composition (metals and ligands concentration) and deposition parameter. This means at a pH range from 8.0 to 9.0 the corresponding components in the alloy electrolytes have an excellent stability, even during electrodeposition. Crack products from sulfate or citrates were not co-deposited. This coincides with the observation that no change in colour or dimming of the electrolyte during electrodeposition or life-time occurred.

4. 2. 8 Wear Resistance

Test procedure according to *Bosch-Weinmann* Wear test [191] indicates good wear resistance by a low amount of weight loss. For example materials with a high wear resistance like chromium coatings have a weight loss after 4 cycles of ca. 0.1 g. Surfaces with a poor wear resistance like gold have a weight loss of ca. 15 mg. The different deposits listed in figure 32 were subjected to 4 x 100 double strokes and the average of weight loss is indicated. All tests were conducted on immersion cleaned, unlubricated surfaces.

The best wear resistance was obtained by using electrodeposited chromium or nickel coatings (figure 32). Good wear resistance is also indicated by using iron, palladium-iron with a high iron content (PdFe15/85) and palladium-nickel (PdNi75/25). Palladium-cobalt (75/25), palladium-iron with a high palladium content (PdFe80/20), copper-tin (CuSn6), pure palladium and pure copper show the same wear behaviour. Surfaces plated with these metals loose ca. 7 - 8.5 mg/9cm² during wear test. Pure gold and gold-cobalt show very poor wear resistance. These results are not totally consistent with results from previous studies [100]. While for many materials, including palladium and palladium alloys, the same wear resistance is measured, independent from the type of test equipment, in the case of gold and hard gold (AuCo) different results could be obtained. The reason is because the cylinder is moved every stroke during *Bosch-Weinmann* test and potential particles from the surface of the test samples are removed in-situ. Abrasive generated gold or hard

particles could, under these conditions, not act like a lubricant. Consequently, gold and gold alloy coatings show poor wear resistance. From practical experience for electronic connectors it is known that flash-gold or flash-hard-gold layers on palladium or palladium alloy coatings are viable gold candidates and approved. However, for better comparison of different materials, and not only for one special application, during this project the *Bosch-Weinmann* test was decided as an appropriate measurement method. As a result, the palladium iron electrodeposits are comparable to palladium-cobalt and palladium-nickel layers. The wear resistance of the alloys decrease with increasing palladium content in the layer. It is in the range between pure iron coatings, deposited from citrate solutions, and pure palladium coatings, deposited from ammoniacal alkaline electrolytes.

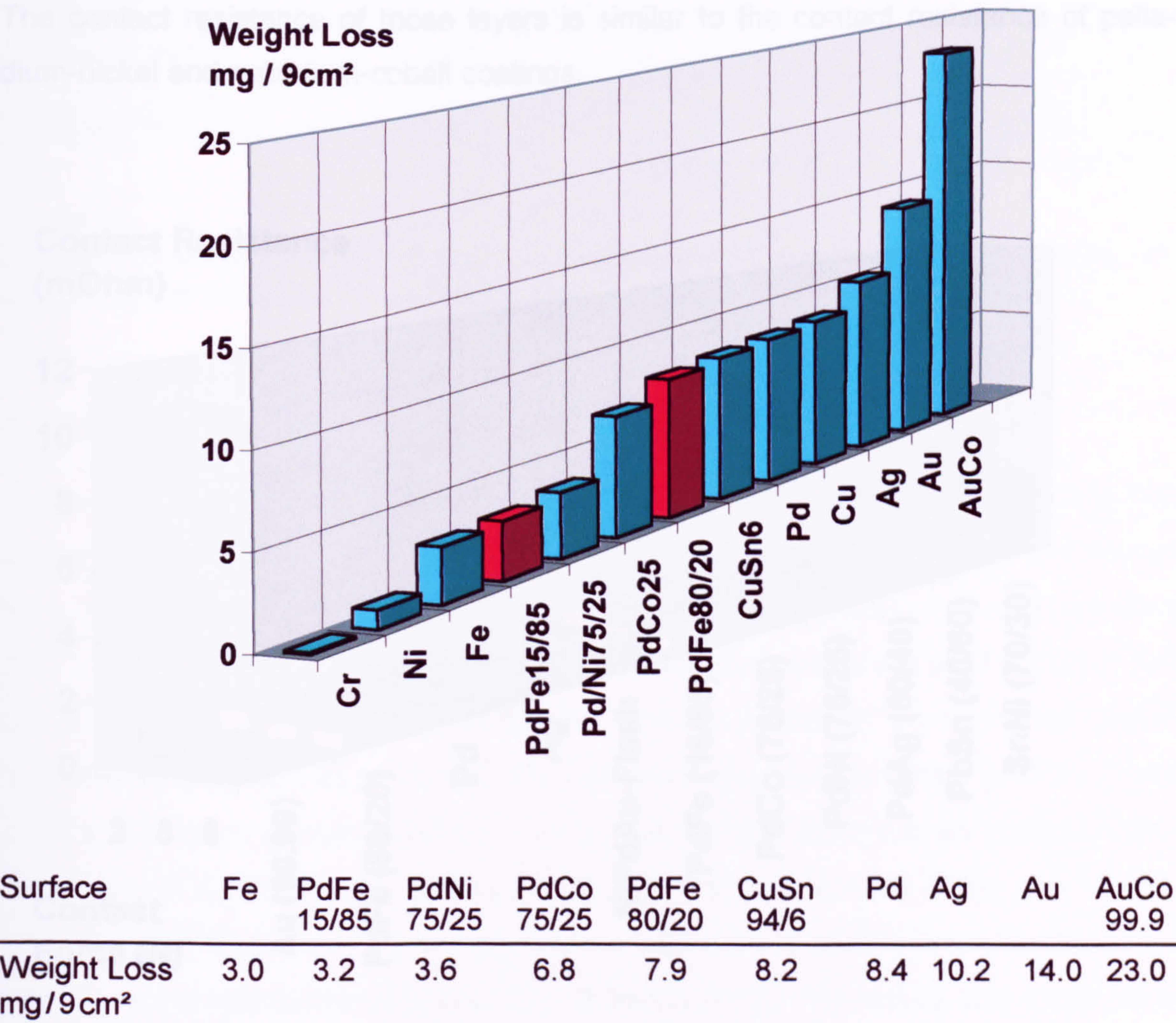


Figure 32
Wear Resistance (Weight Loss) of Electroplated Metals and Metal Alloys
Average of 4 x 100 Double Strokes, Dry Conditions, Abrasive Paper, Grain
Size 1000, Vacuum Blower, *Bosch-Weinmann* Test [191]

4. 2. 9 Contact Resistance

Contact resistance measurements were obtained with three loads between 2 N and 8 N. Table 24 and figure 33 show average values from at least three measurements. Contact resistance of gold surfaces versus gold surfaces being was the lowest, while the contact resistance of tin-nickel versus tin-nickel surfaces was the highest. In general there is a slight decrease in contact resistance with increasing contact force. Formation of oxides on the surface during storage may be the reason for this behaviour. Palladium-iron coatings with a high amount of palladium show an excellent low contact resistance in the range of 0.9 - 0.6 mΩ. Gold surfaces, for comparison show a contact resistance in the range of 0.89 to 0.55 mΩ. An increase of the iron content in the palladium-iron alloy causes an increase of the contact resistance up to 1.3 mΩ. The contact resistance of those layers is similar to the contact resistance of palladium-nickel and palladium-cobalt coatings.

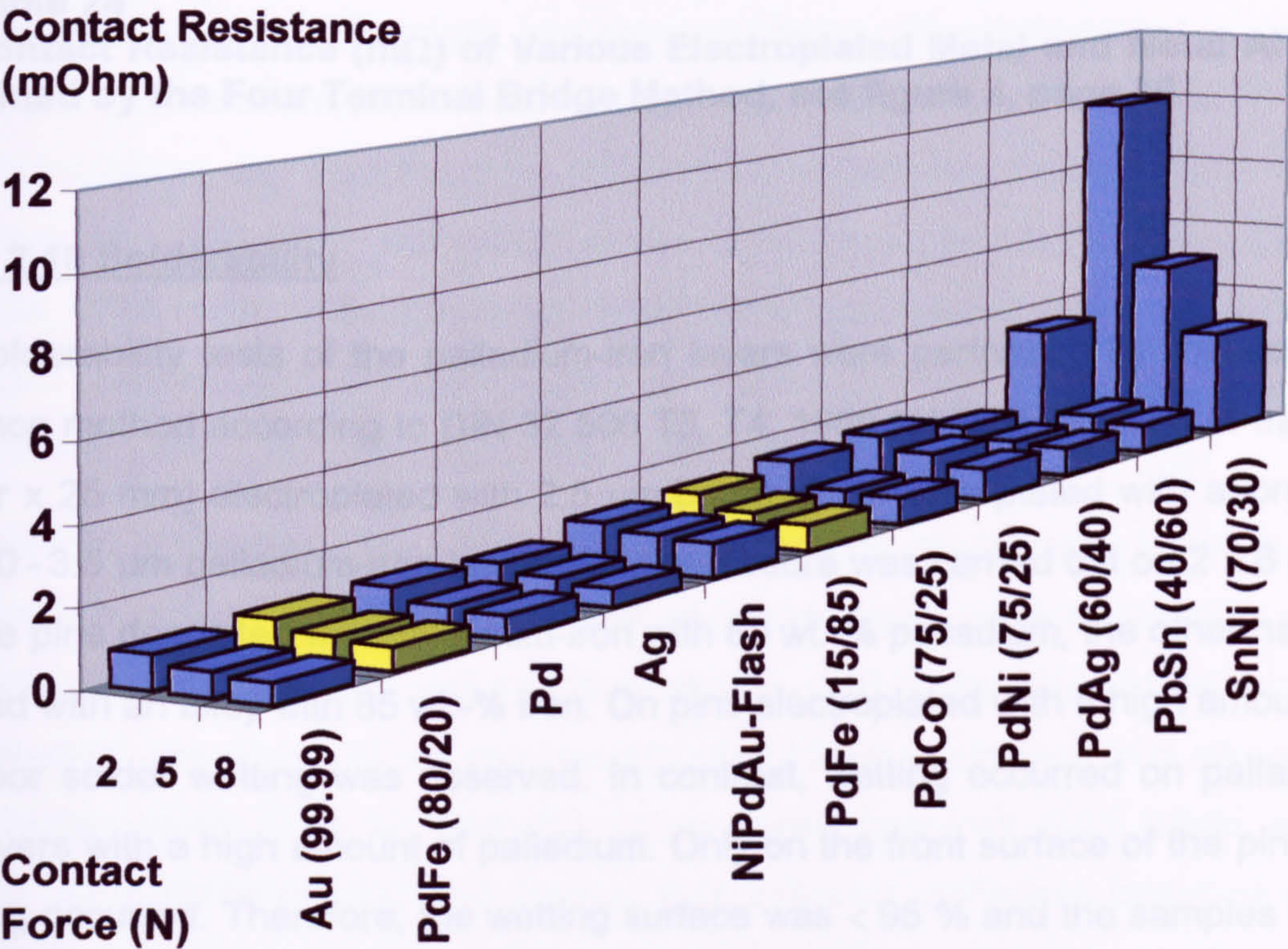


Figure 33
Contact Resistance (mΩ) of Electroplated Metal and Metal Alloys

Sample	Contact Force	2 N	5 N	8 N
Au (99,99)		0.89	0.65	0.55
PdFe (80/20)		0.98	0.70	0.60
Pd		0.95	0.90	0.55
Ag		0.90	0.75	0.60
Ni/Pd/Au-Flash		1.25	1.00	0.95
PdFe (15/85)		1.30	0.90	0.70
PdCo (75/25)		1.50	0.85	0.75
PdNi (80/20)		1.60	1.20	0.90
PdAg (75/25) *)		2.00	1.20	0.90
PbSn (40/60) **)		3.50	1.00	0.80
SnNi (70/30) **)		10.00	5.00	3.00

*) data from [177] **) data from [201]

Table 24

Contact Resistance ($m\Omega$) of Various Electroplated Metal and Metal Alloys, obtained by the Four Terminal Bridge Method, see figure 4, page 39

4. 2.10 Solderability

Solderability tests of the palladium-iron layers were performed by the wetting balance method according to DIN 32 506 T3, T4, 1988 [192]. Brass pins (4 mm diameter x 25 mm) electroplated with 2.5 μm bright silver were plated with approximately 2.0 - 3.5 μm palladium-iron layers. Test procedure was carried out on 2 x 6 pins; half the pins deposited with palladium-iron with 80 wt.-% palladium, the other half deposited with an alloy with 85 wt.-% iron. On pins electroplated with a high amount of iron poor solder wetting was observed. In contrast, wetting occurred on palladium-iron layers with a high amount of palladium. Only on the front surface of the pins no wetting occurred. Therefore, the wetting surface was < 95 % and the samples failed according to the requirements of DIN 32 506 part 3 [192]. The results show that palladium-iron deposits have inferior solderability in comparison with tin-lead coatings. The solderability decreases with increasing iron content of the palladium-iron alloy layers.

4. 2. 11 Palladium-Iron Electrodeposits as a Diffusion Barrier

In general, diffusion is a spontaneous and irreversible reaction in a system to achieve equilibrium. Diffusion can take place, depending on the type of the system, at very high temperatures as well as at RT. Typical systems are copper layer on zinc and gold layer on copper. In gold plated contacts underlying copper can diffuse through a thin gold layer to the surface where it oxidises and increases contact resistance [202]. An effective way to retard diffusion is to use a barrier layer. Certain metals and metal alloys are suitable for barrier layers [190, 203].

For example, nickel and nickel alloys as intermediate layer between copper substrate and gold overplate are well known to inhibit the diffusion of copper into gold. Electroplated palladium, palladium-nickel, palladium-cobalt and iron intermediate layers also act as barrier layers. Therefore, palladium and palladium-nickel coatings are more and more used in electronics applications. In the case of electroplated palladium-iron coatings no experience exists on their suitability as barrier layers against diffusion at temperature ranges reached during employment of e.g. electronic contacts, etc. Therefore, several experiments with electroplated gold layers on copper substrate without and with various intermediate layers were carried out. After electroplating, the samples were subjected to a heat-treatment process on atmosphere. Iron, palladium and palladium-iron were deposited from ammoniacal electrolytes, while nickel and gold were plated from an commercial bright nickel plating solution (Zodiac230™, *Schlötter*, Geislingen, Germany) and an almost additional-free gold electrolyte (Auruna®551, *Degussa*, Schwäbisch Gmünd, Germany).

Table 25 summarises the results of suitability testing of electrodeposited iron, palladium, palladium-iron alloys and nickel as barrier layers against diffusion of copper and gold, obtained after heat-treatment at 120 - 160 °C for 120 and 240 hours. Both palladium rich (PdFe80/20) and iron rich (PdFe15/85) palladium-iron alloys act as a diffusion barrier layer for gold and copper during heat-treatment. While iron layers and bright nickel coating also prevent from diffusion, palladium intermediate layers failed under these conditions. On such samples diffusion of copper and gold already occurs after 120 hours at 120 °C.

Figure 34 shows the metal distribution of gold, palladium, iron, and copper on cross sections after heat-treatment obtained with Energy Dispersive X-ray Microanalyses

(EDX), while figure 35 shows the corresponding investigations on nickel intermediate layers. The figures show that no diffusion of gold or copper occurred during heat-treatment. For comparison in figure 36 a gold-layer on copper substrate without an intermediate layer is presented. After 240 hours at 160 °C copper is detectable. However, less marked, the same behaviour could be obtained from palladium intermediate layers. Disadvantage of this measurement method could be the contamination of impurities during preparation of the cross sections. Therefore, an additional surface analysis by Glow Discharge Optical Spectroscopy (GDOS) was carried out. These examinations confirm the results already obtained (figure 37 - 41). Nickel, iron and palladium-iron alloys, both iron rich and palladium rich turned out to be excellent barrier layers against diffusion of gold and copper.

Sample No	Substrate	Intermediate Layer (µm)					Gold (µm)	Diffusion Gold and Copper		
		Pd/Fe (80/20)	Pd/Fe (15/85)	Pd	Fe	Ni		120 °C 120 h	160 °C 120 h	160 °C 240 h
123	Cu	-	-	-	-	-	1.0	YES	-	-
124	Cu	-	-	-	-	-	2.0	YES	YES	YES
139	Cu	2.4	-	-	-	-	1.2	-	NO	NO
141	Cu	2.7	-	-	-	-	2.7	NO	-	-
119	Cu	-	4.0	-	-	-	3.5	-	NO	No
120	Cu	-	4.4	-	-	-	2.0	-	No	NO
150	Cu	-	-	1.3	-	-	0.9	YES	-	-
154	Cu	-	-	3.6	-	-	1.5	-	YES	YES
153	Cu	-	-	-	3.8	-	2.0	NO	NO	NO
155	Cu	-	-	-	3.0	-	1.2	NO	NO	NO
151	Cu	-	-	-	-	1.0	1.2	-	NO	NO
152	Cu	-	-	-	-	2.5	1.2	NO	NO	NO

Table 25

Suitability of Iron, Palladium, Palladium-Iron Alloys and Nickel as Barrier Layers against Diffusion of Copper and Gold after Heat-Treatment at 120 - 160 °C

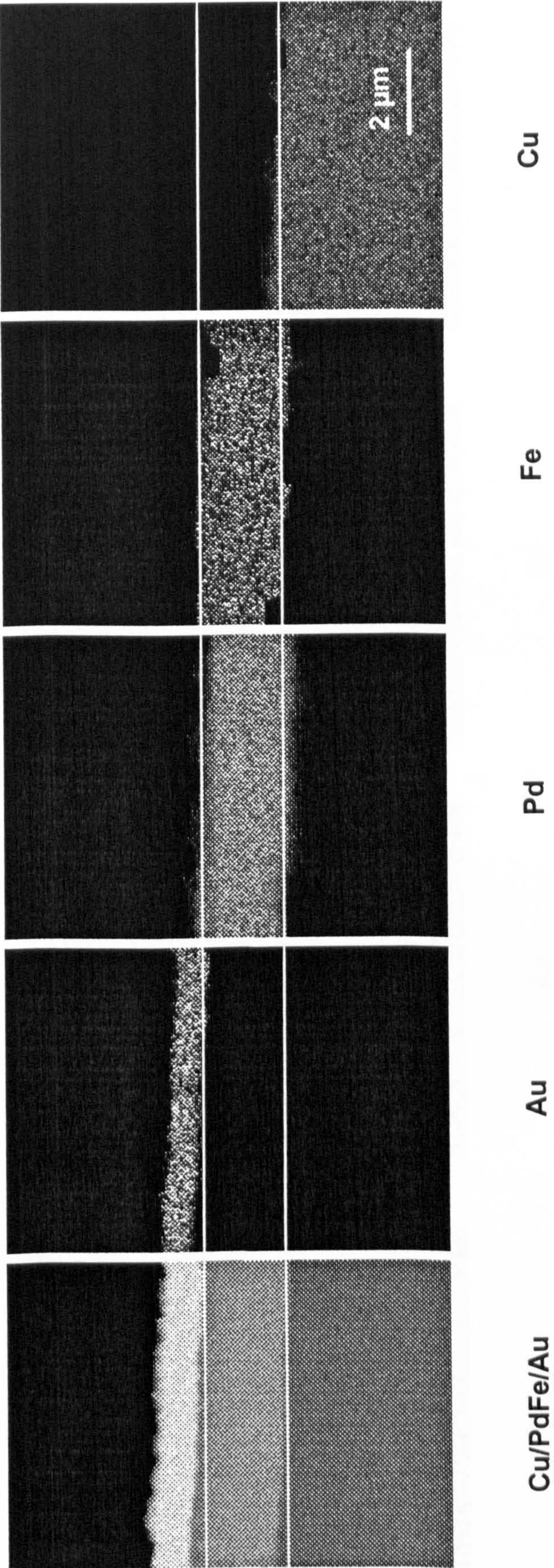
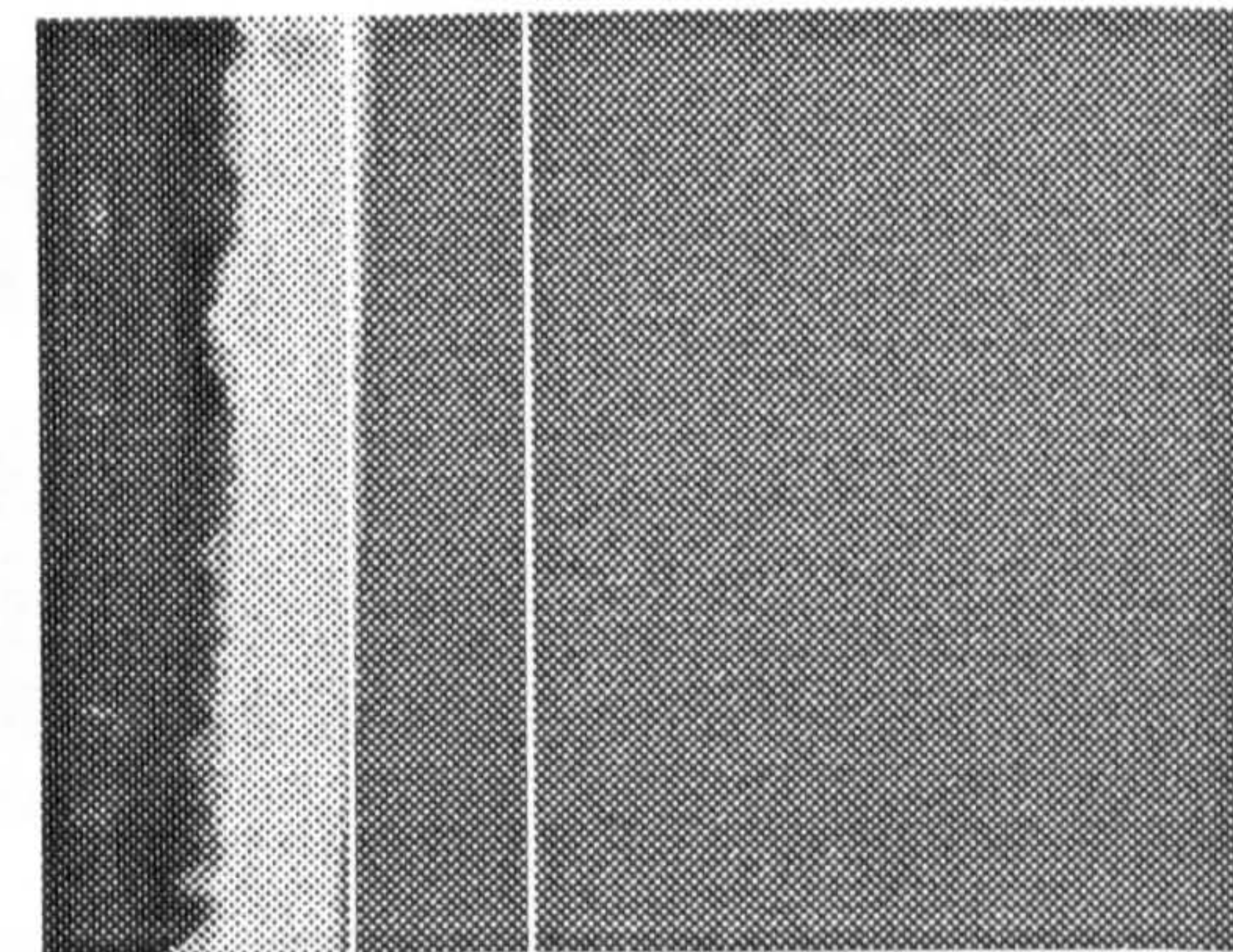
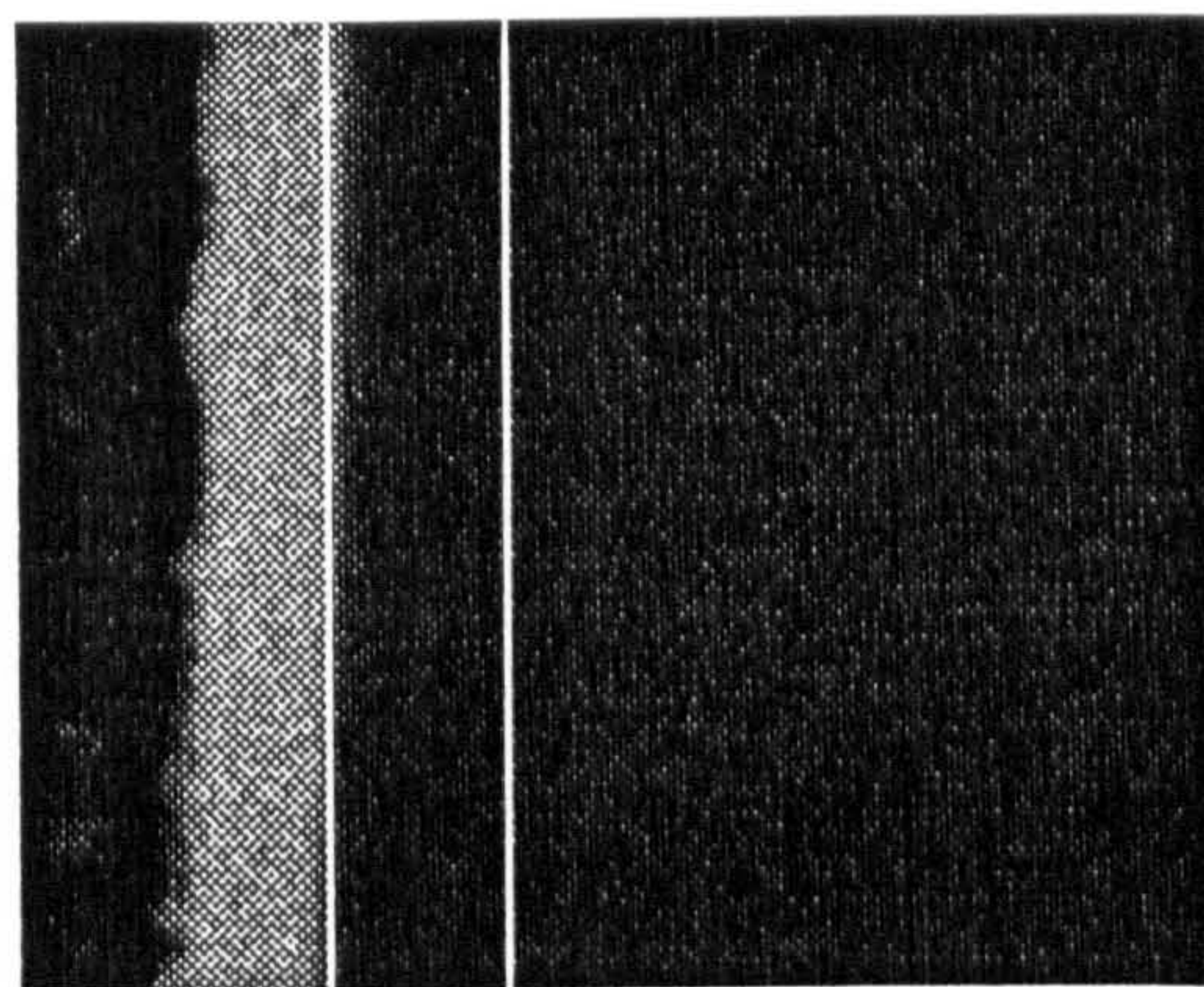


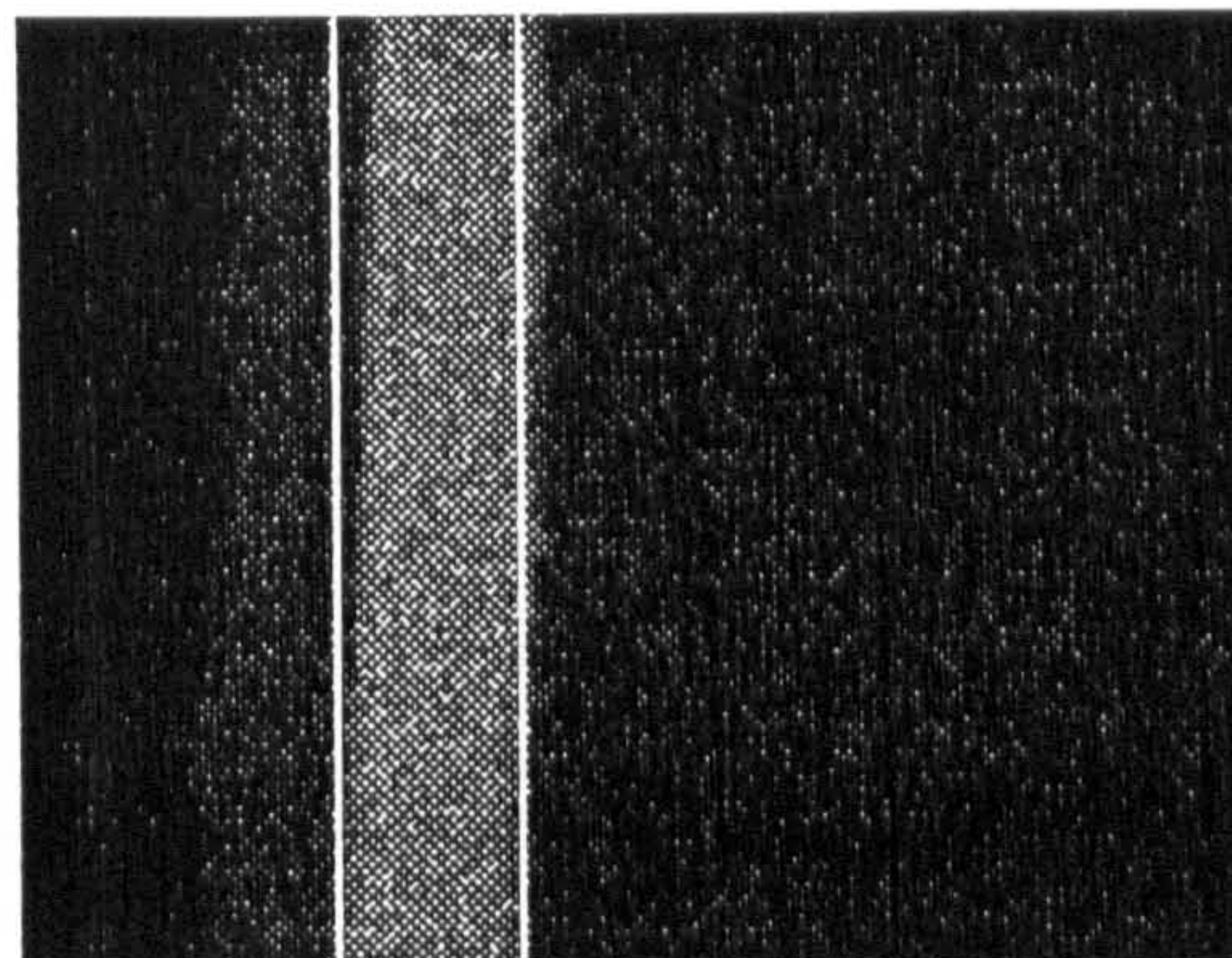
Figure 34
Sample 139: Copper Substrate / Palladium-Iron (PdFe80/20) Intermediate Layer / Gold Layer
after Heat-Treatment 160 °C, 240 h



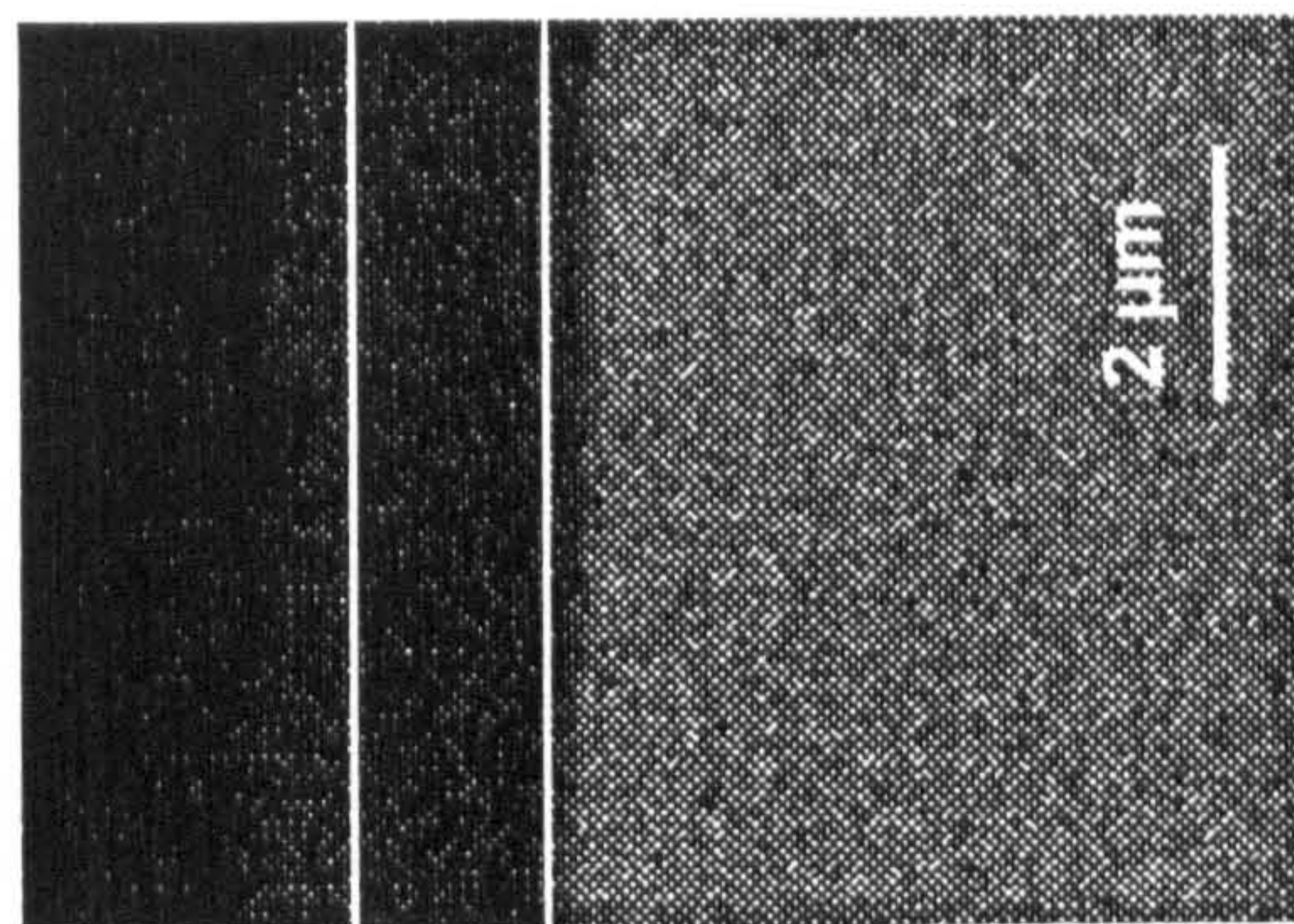
Cu/Ni/Au



Au

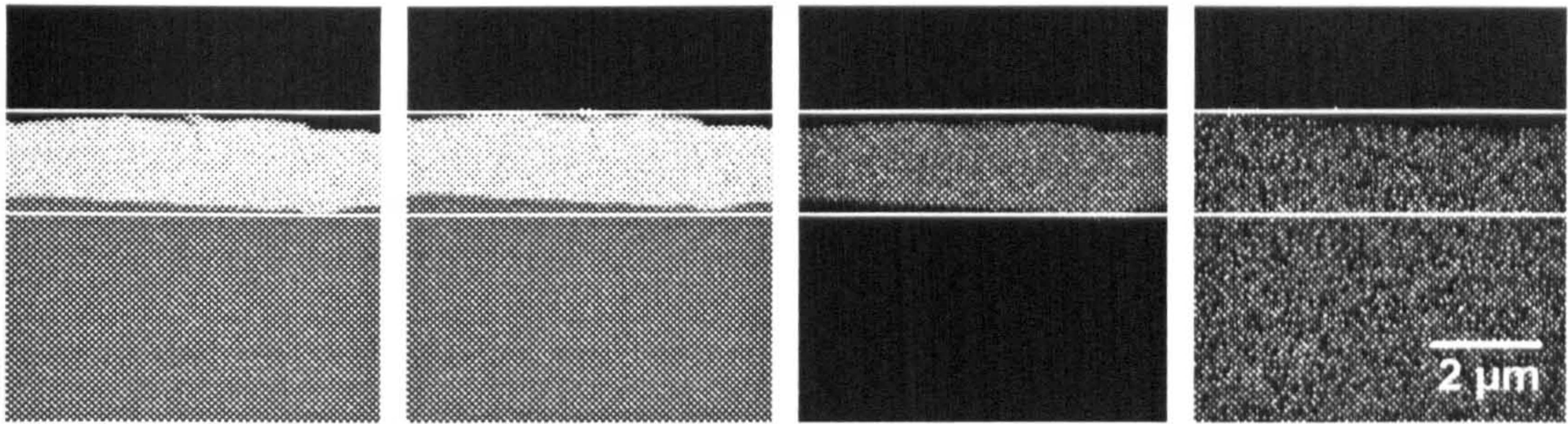


Ni

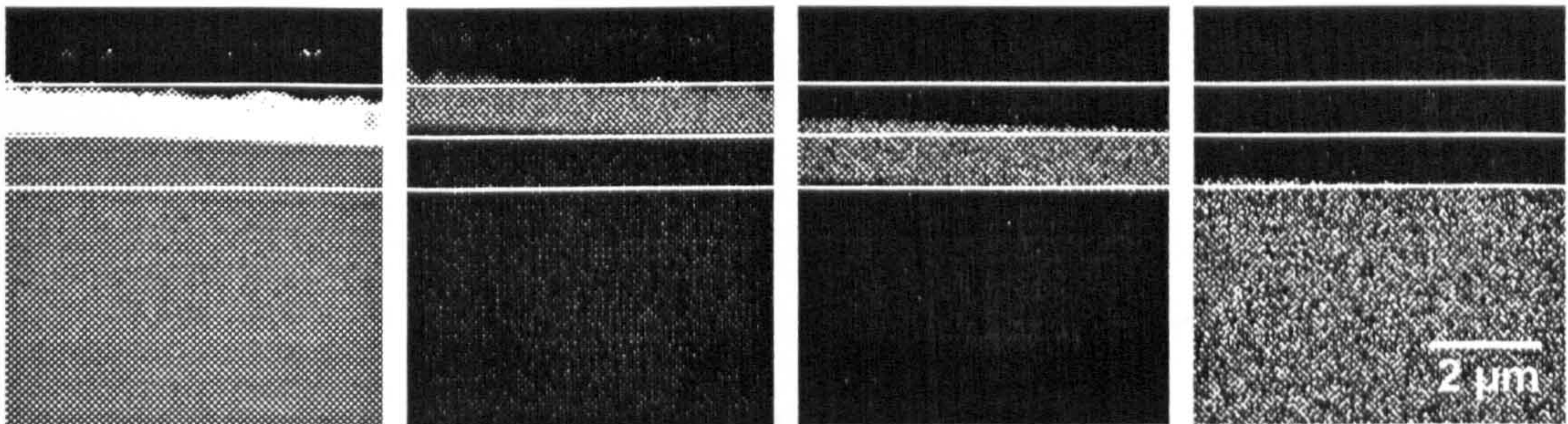


Cu

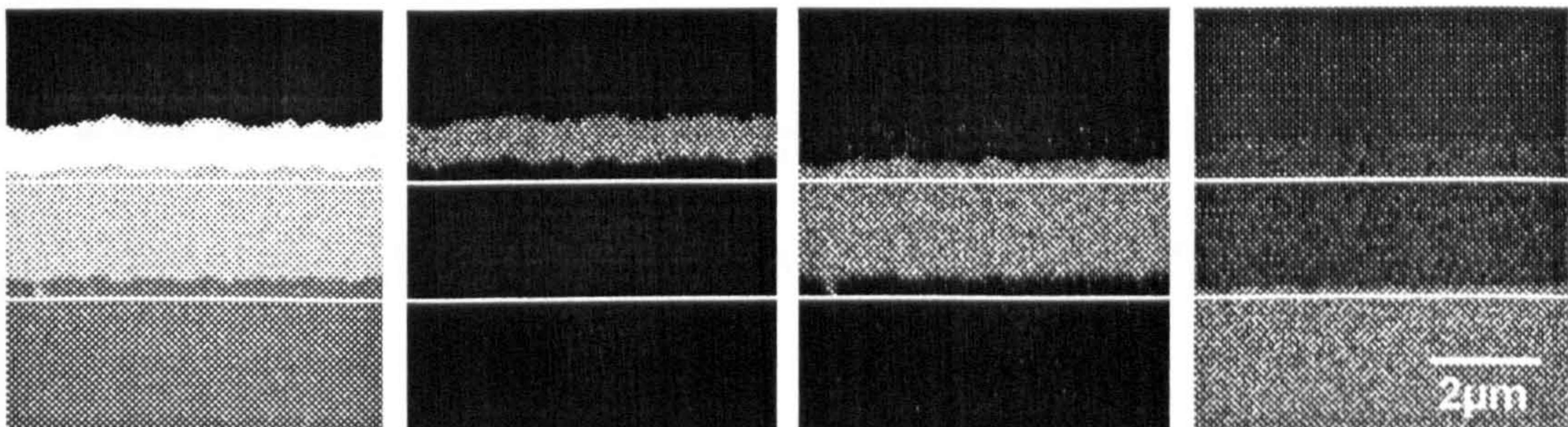
Figure 35
Sample 151: Copper Substrate / Nickel Intermediate Layer / Gold Layer
after Heat-Treatment 160 °C, 240 h



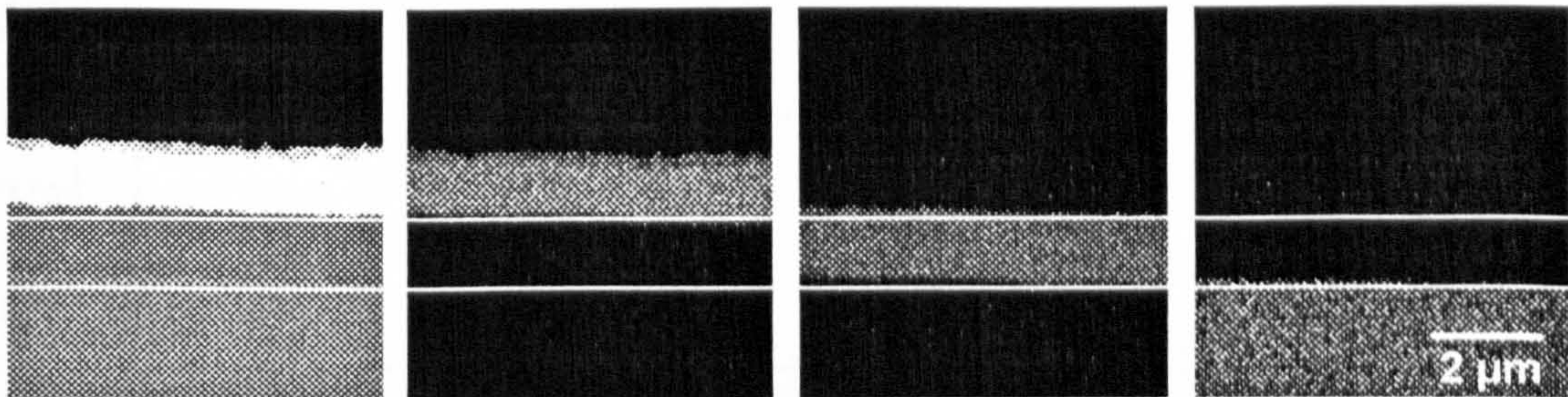
Au/Cu Au/Cu Au Cu
Sample 124: Gold Layer on Copper after Heat-Treatment 160 °C, 240 h



Au/Ni/Cu Au Ni Cu
Sample 151: Gold / Nickel / Copper after Heat-Treatment 160 °C, 240 h

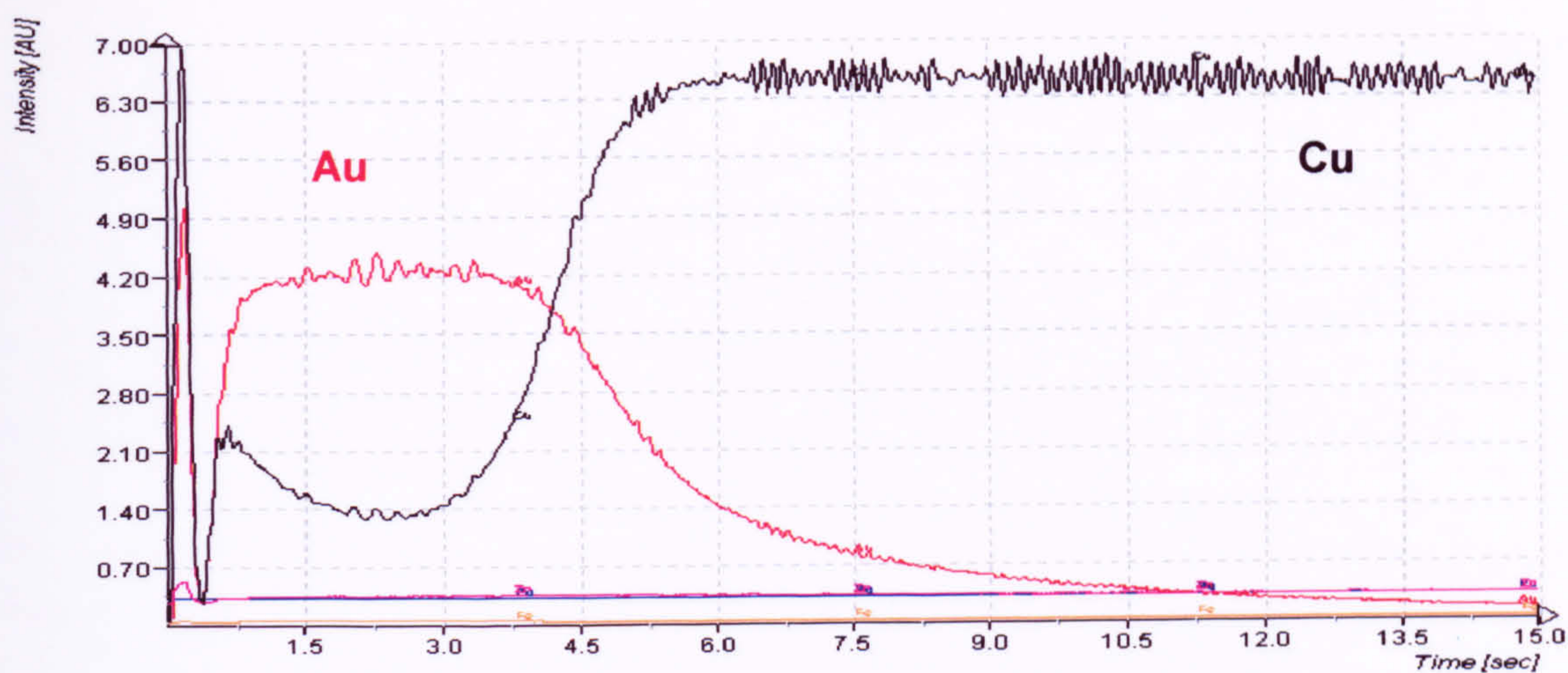


Au/Pd/Cu Au Pd Cu
Sample 154: Gold / Palladium / Copper after Heat-Treatment 160 °C, 240 h

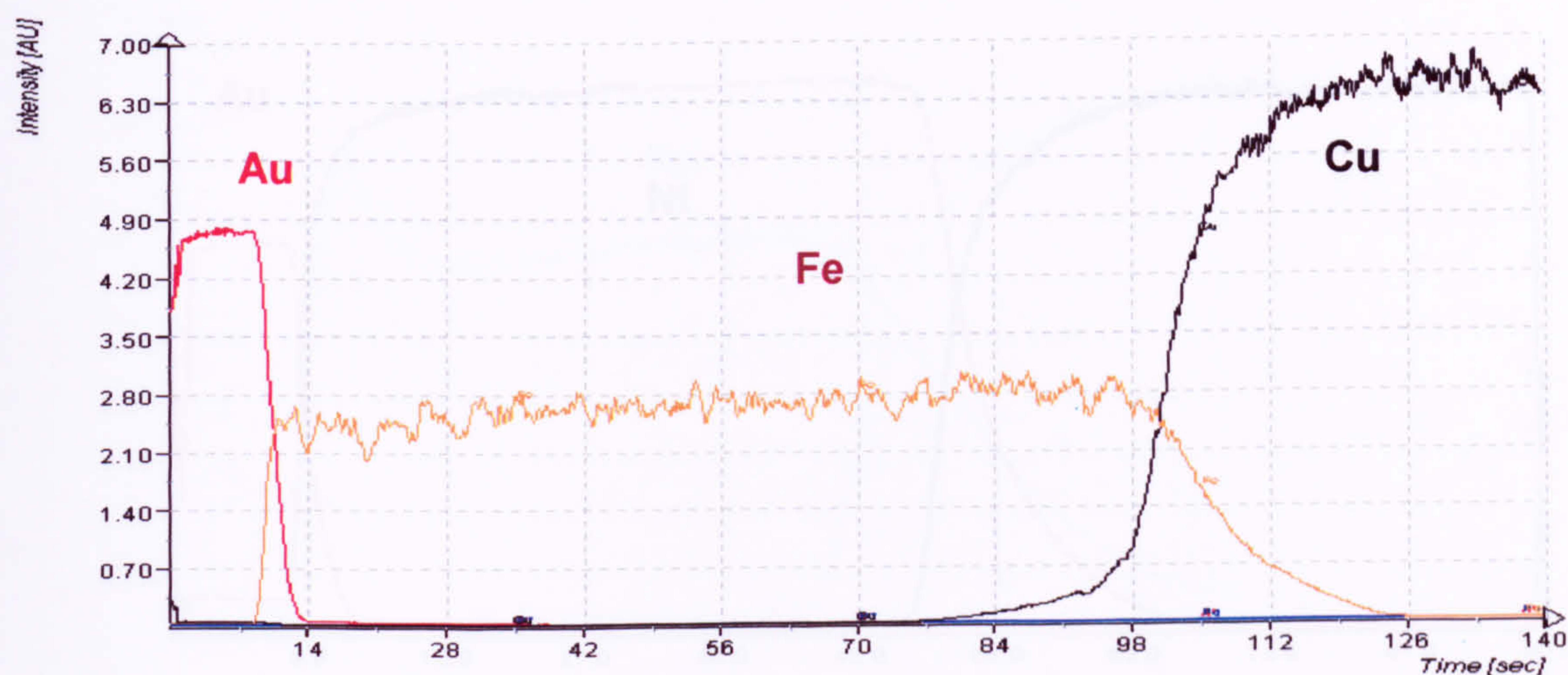


Au/Fe/Cu Au Fe Cu
Sample 155: Gold / Iron / Copper after Heat-Treatment 160 °C, 240 h

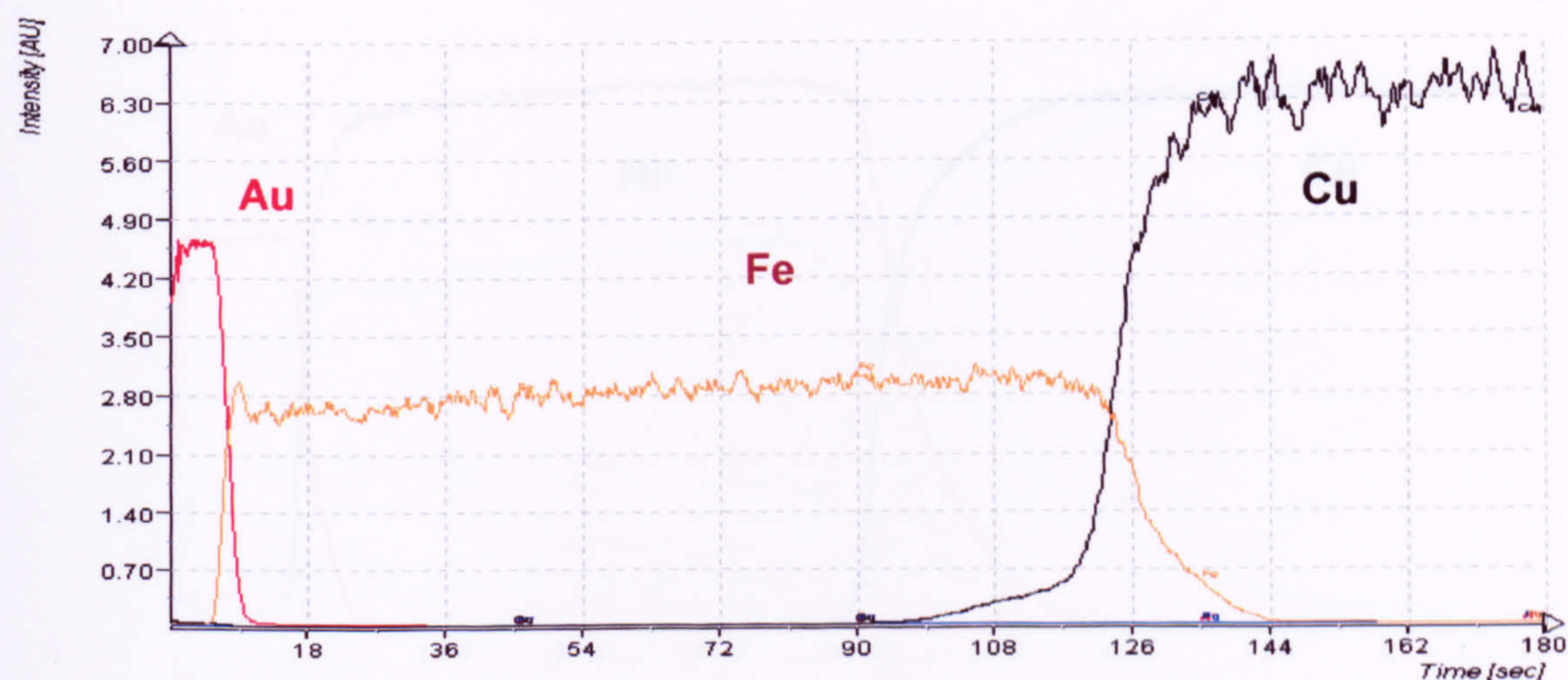
Figure 36
Copper Diffusion in Gold Layers after Heat-Treatment with and without Intermediate Layers



Gold Layer on Copper Substrate after Heat-Treatment 160 °C, 120 h

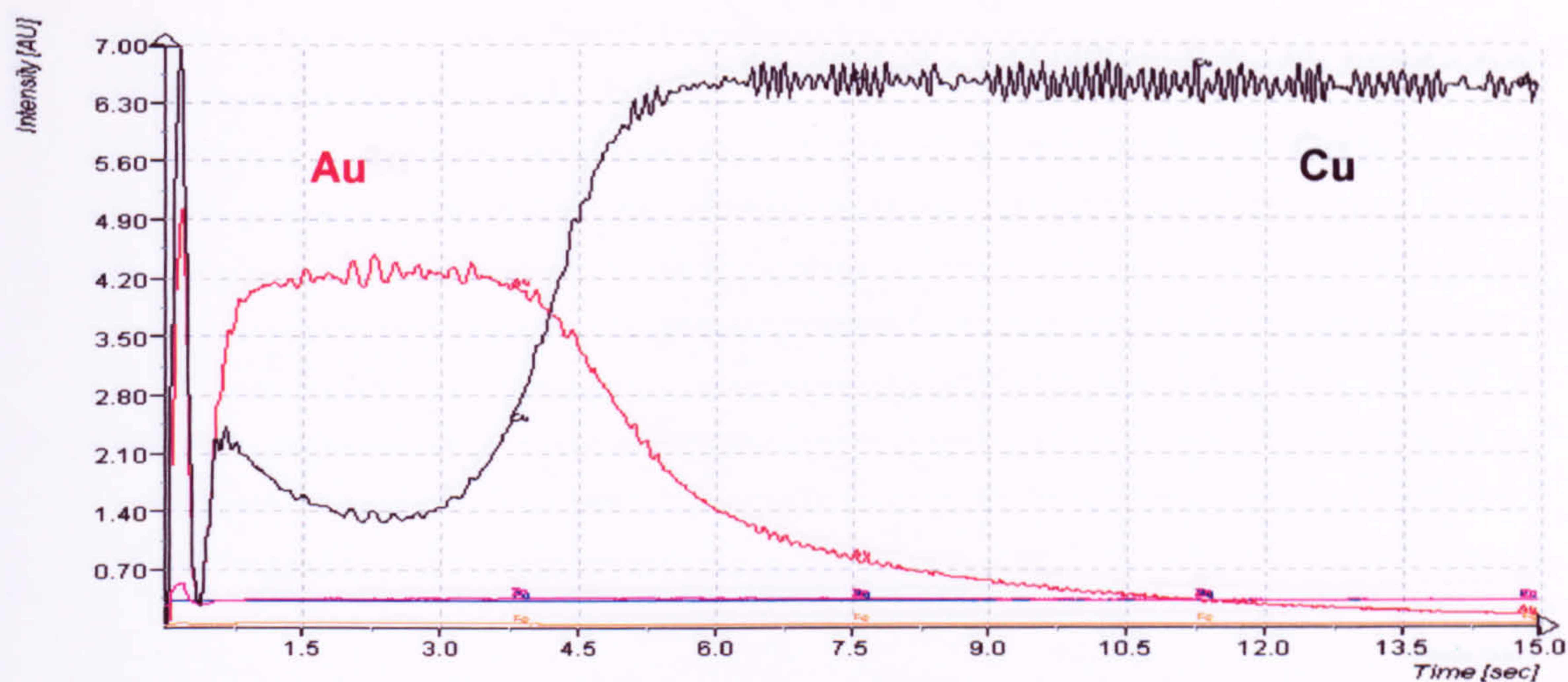


Gold Layer / Iron / Copper Substrate before Heat-Treatment

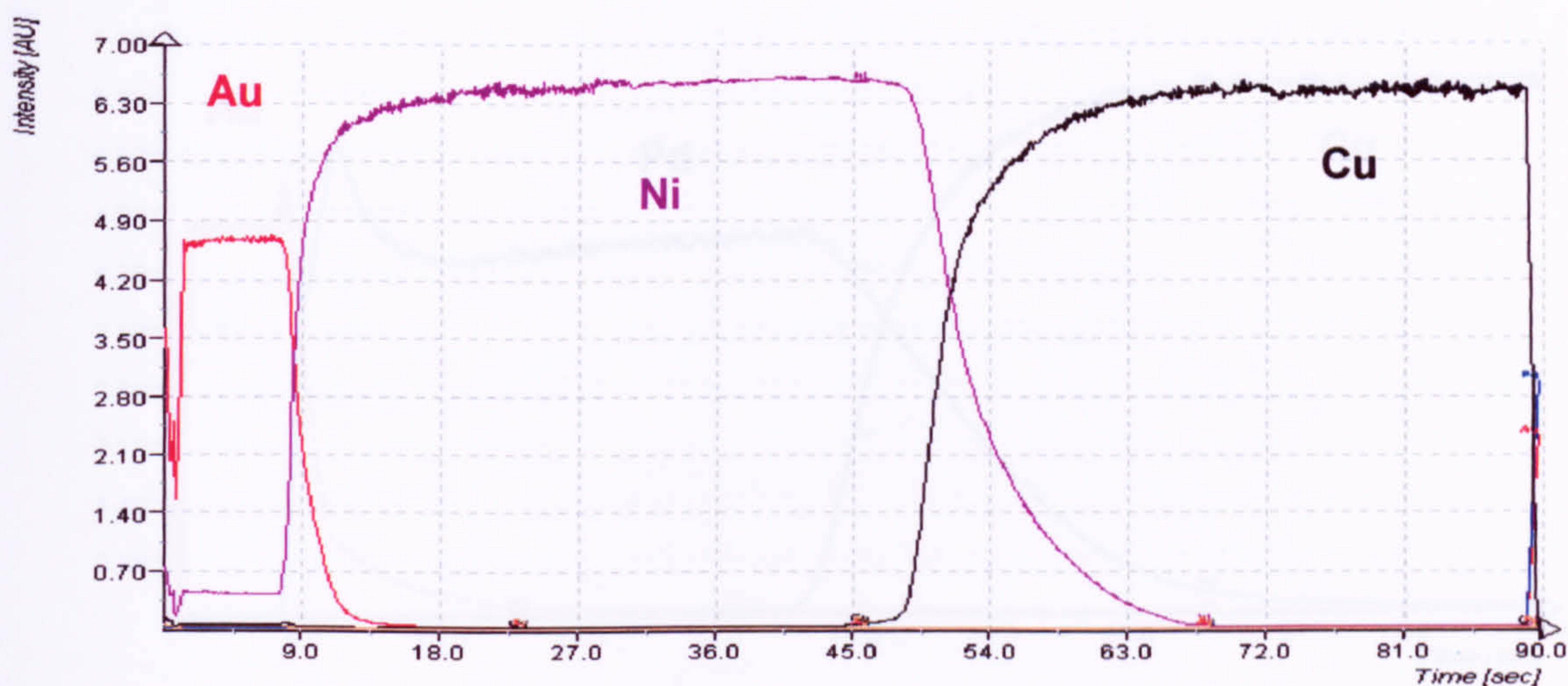


Gold Layer / Iron / Copper after Heat-Treatment 160 °C, 240 h

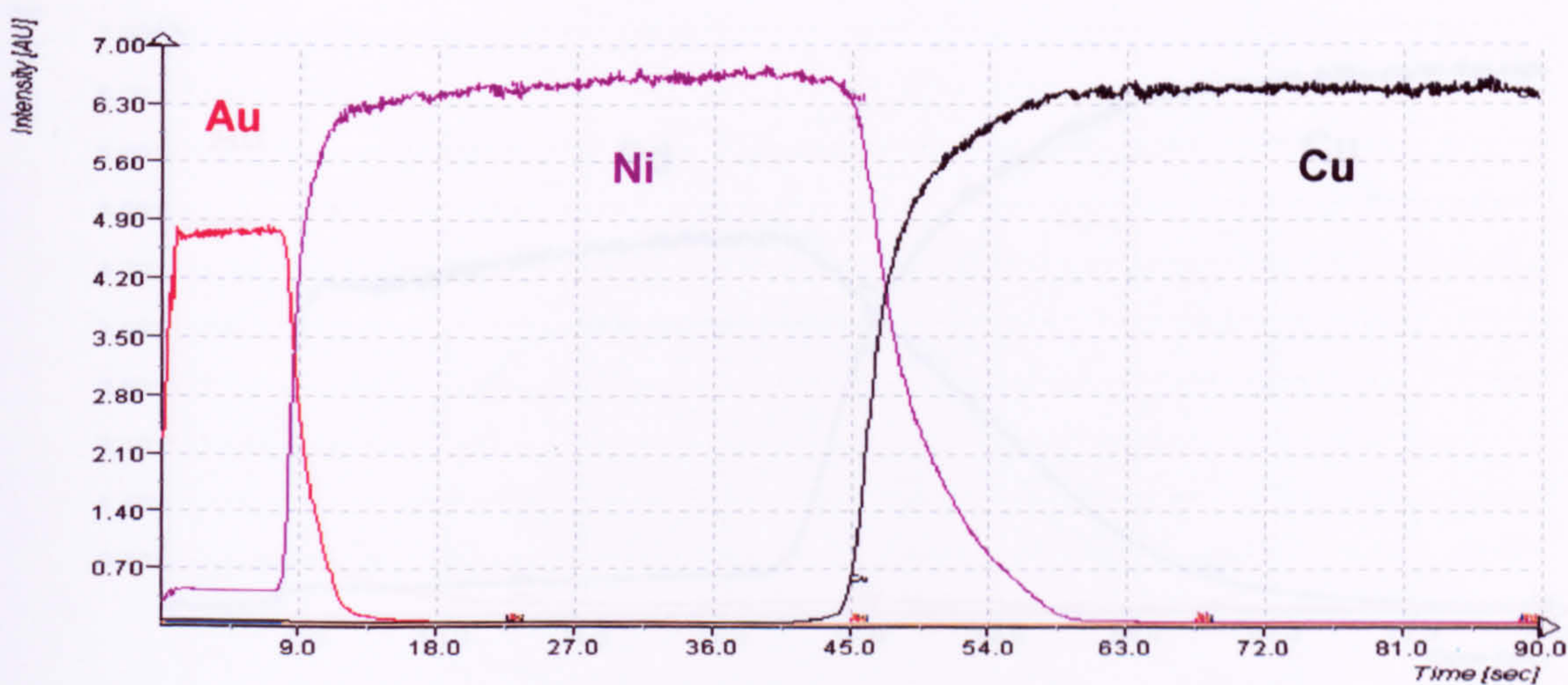
Figure 37
GDOS Analyses of Electroplated Gold Layers on Copper with and without Intermediate Iron Layer before and after Post Plated Heat-Treatment



Gold Layer on Copper Substrate after Heat-Treatment 160 °C, 120 h



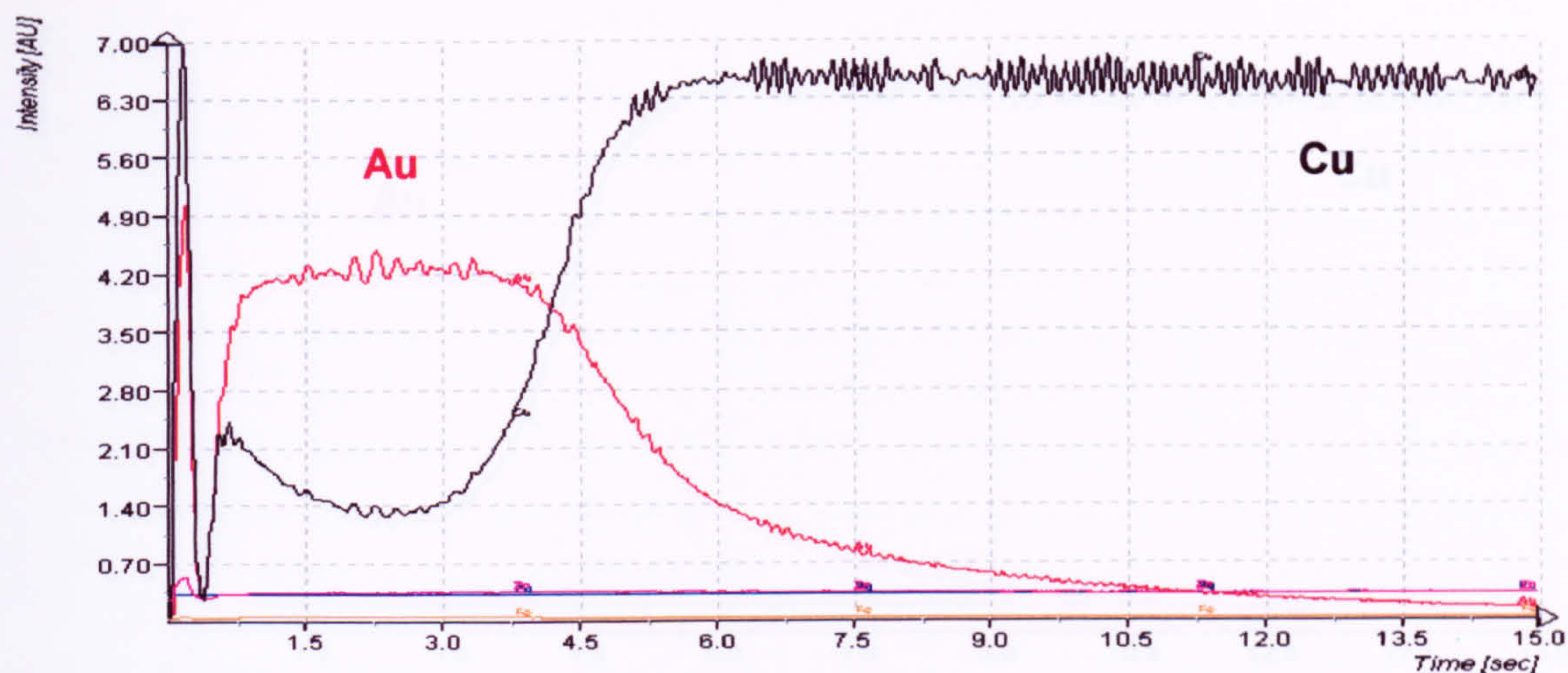
Gold Layer / Nickel / Copper Substrate before Heat-Treatment



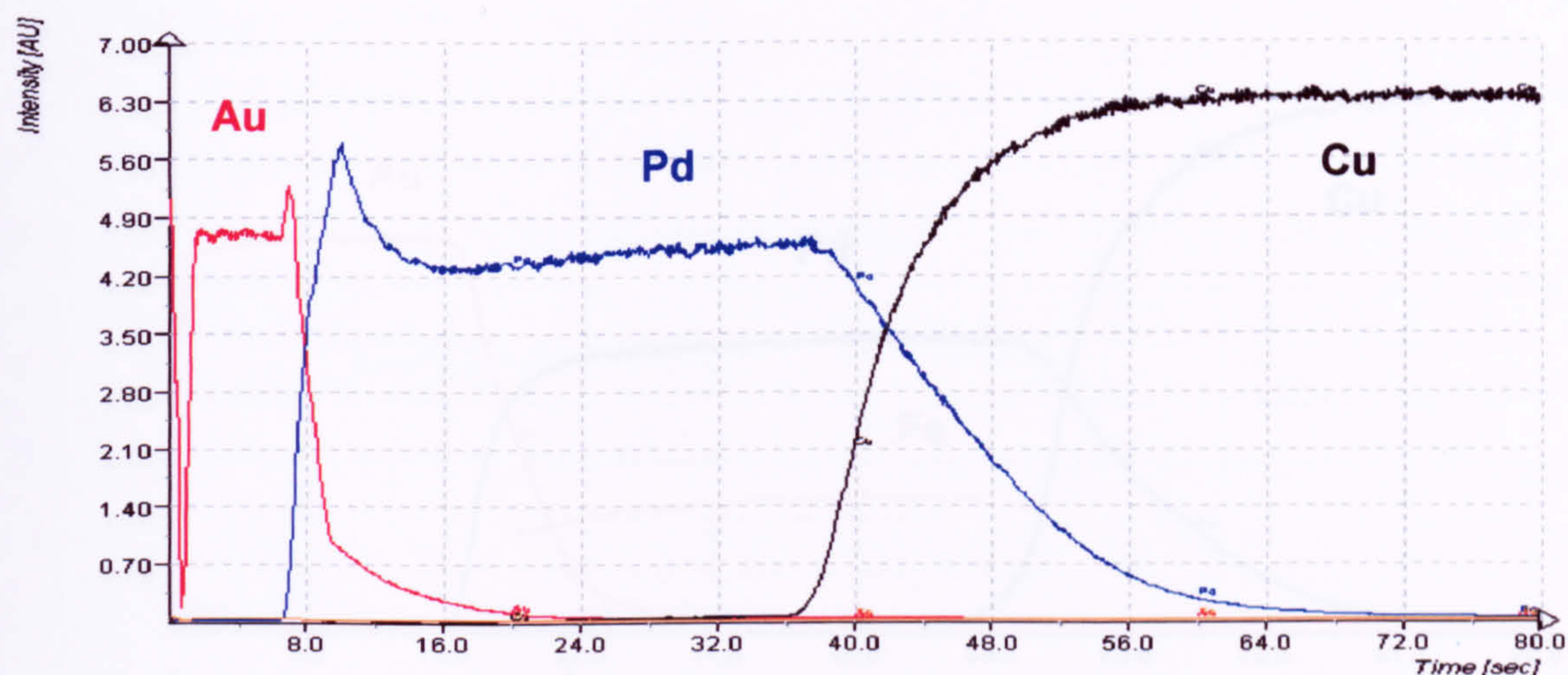
Gold Layer / Nickel / Copper after Heat-Treatment 160 °C, 240 h

Figure 38

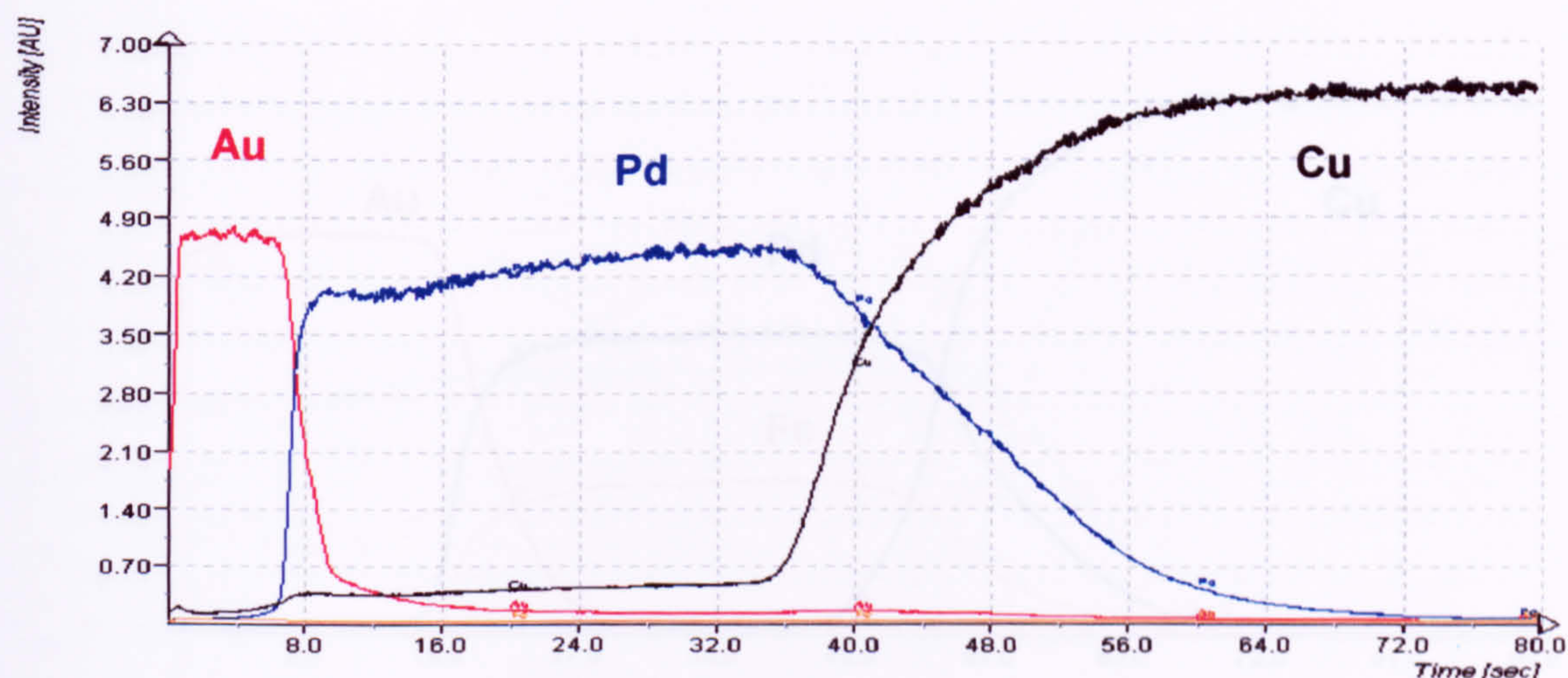
GDOS Analyses of Electroplated Gold Layers on Copper with and without Intermediate Nickel Layers before and after Post Plated Heat-Treatment



Gold Layer on Copper Substrate after Heat-Treatment 160 °C, 120 h

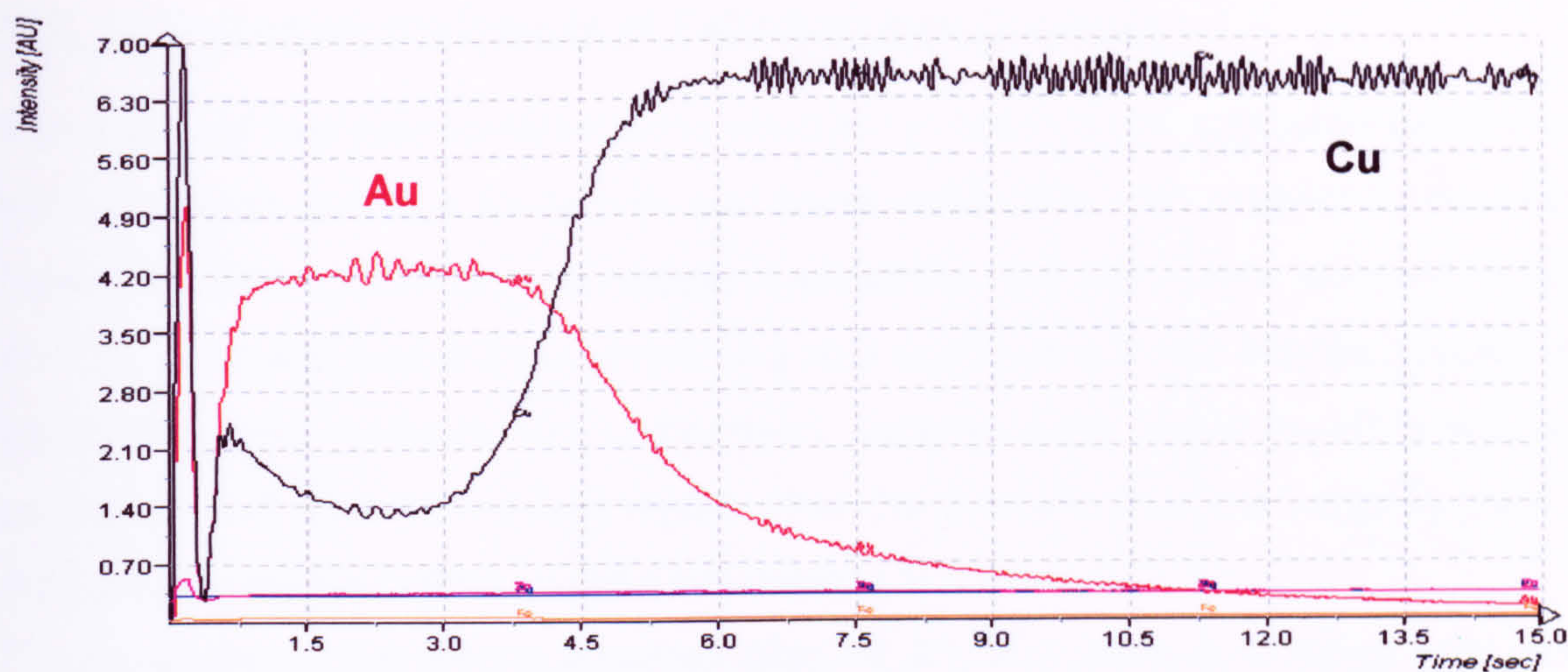


Gold Layer / Palladium / Copper Substrate before Heat-Treatment

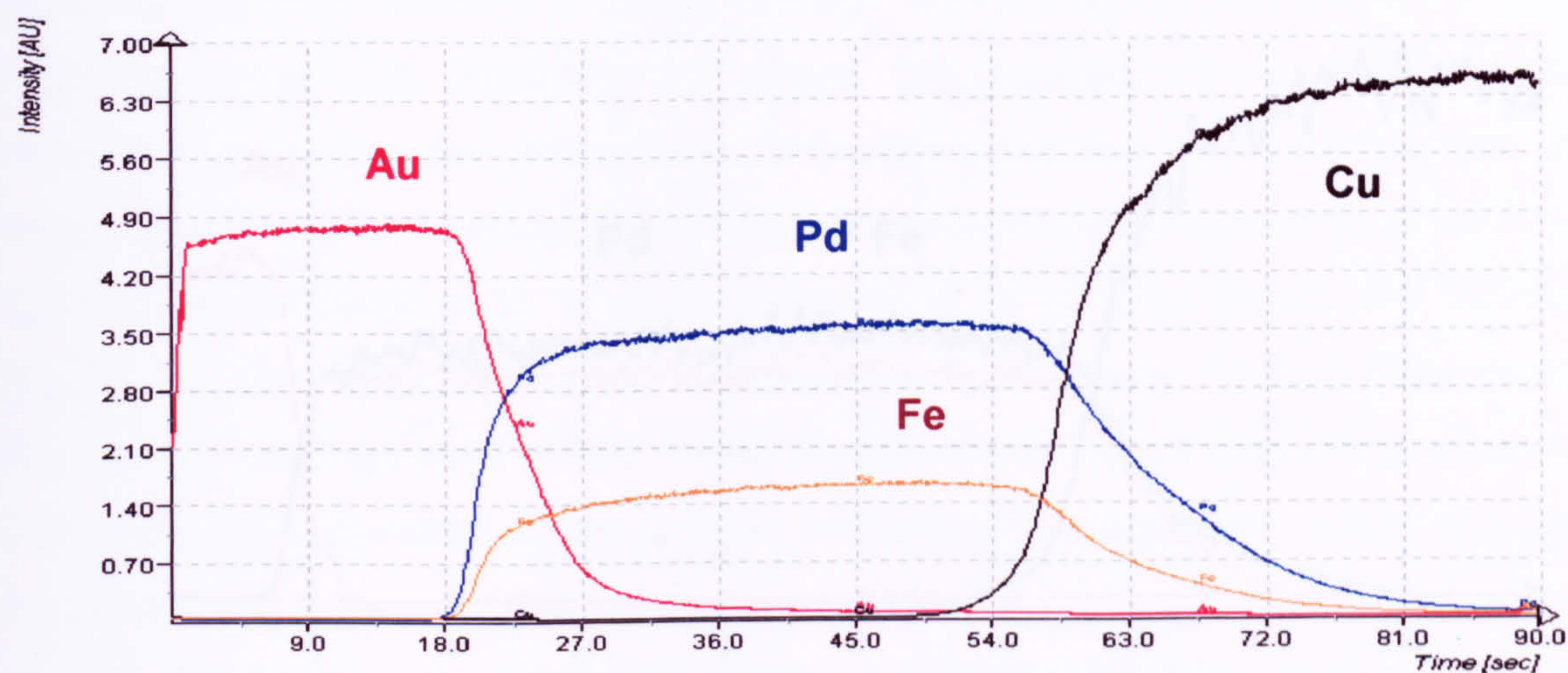


Gold Layer / Palladium / Copper after Heat-Treatment 160 °C, 240 h

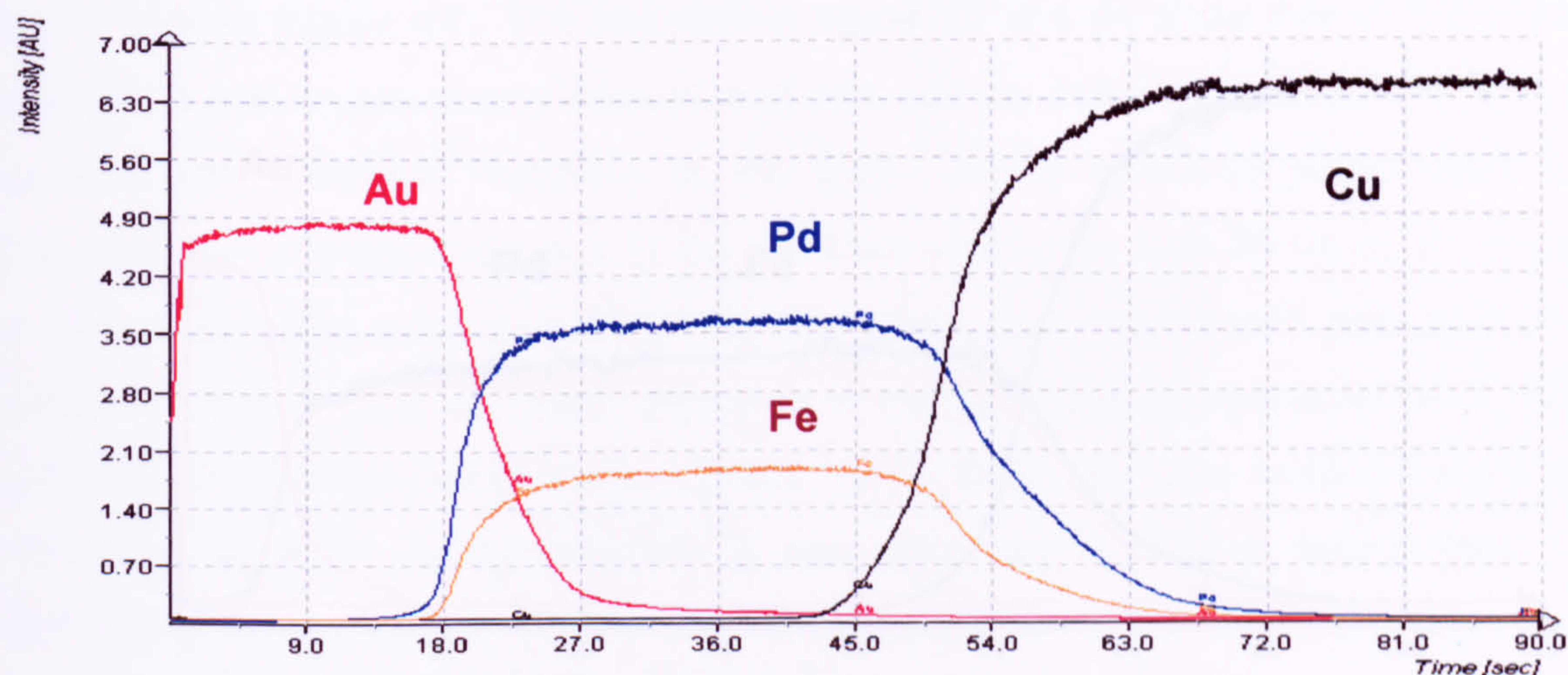
Figure 39
GDOS Analyses of Electroplated Gold Layers on Copper with and without Intermediate Palladium Layers before and after Post Plated Heat-Treatment



Gold Layer on Copper Substrate after Heat-Treatment 160 °C, 120 h

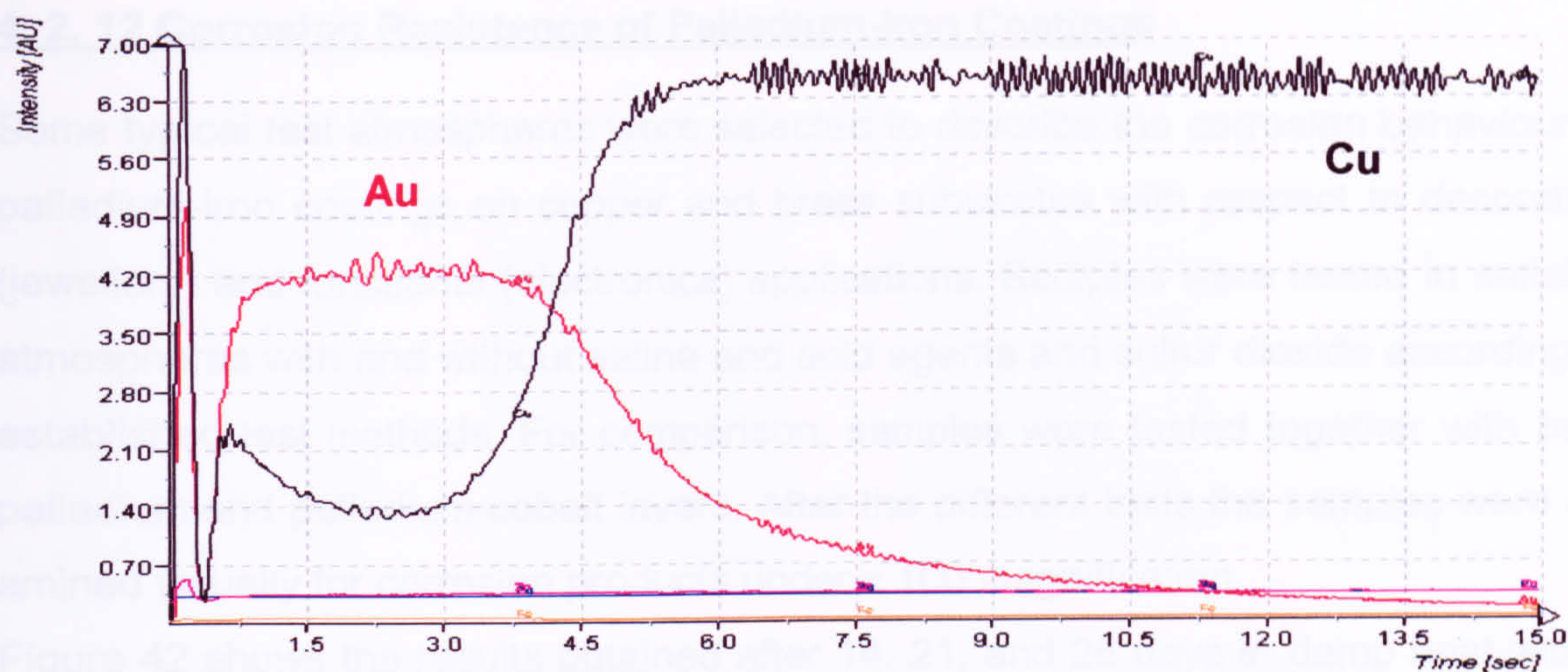


Gold Layer / PdFe (80/20) / Copper Substrate before Heat-Treatment

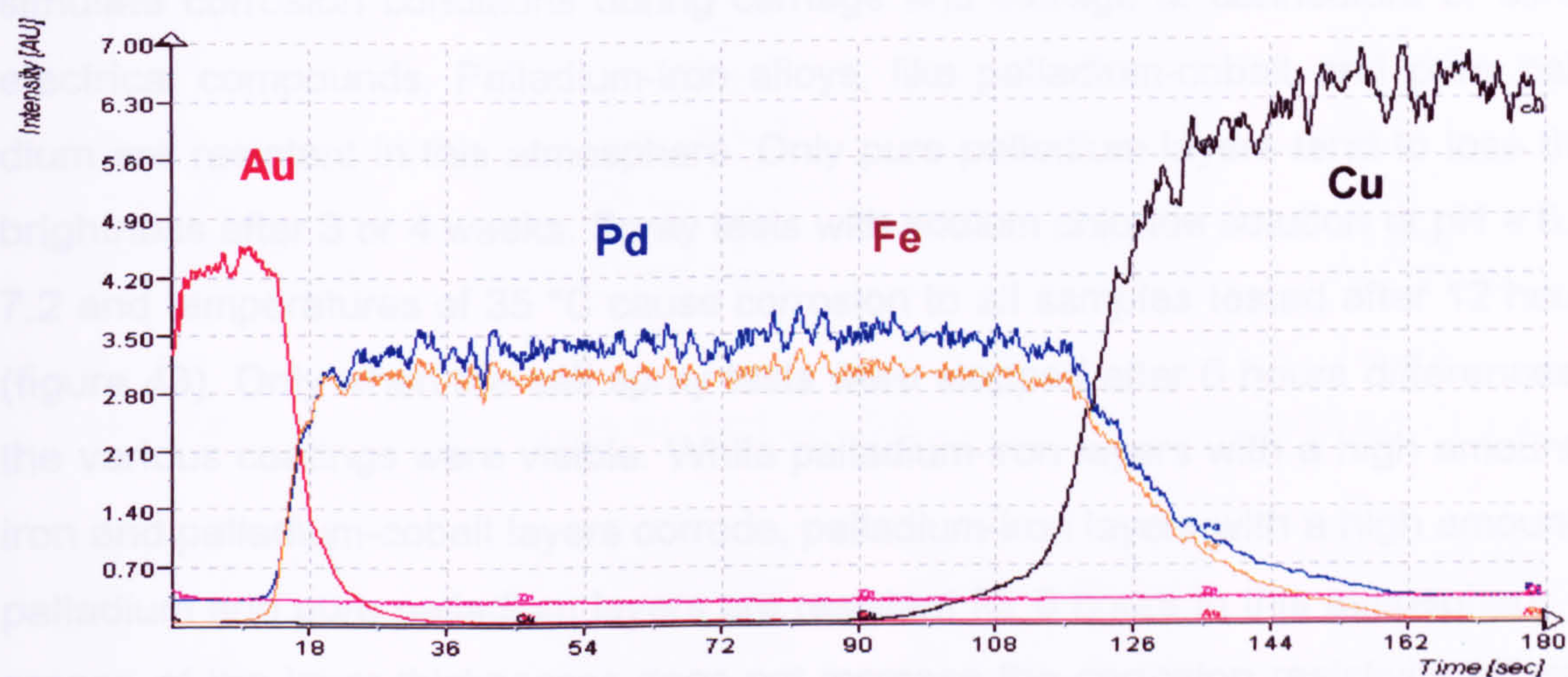


Gold Layer / PdFe (80/20) / Copper after Heat-Treatment 160 °C, 240 h

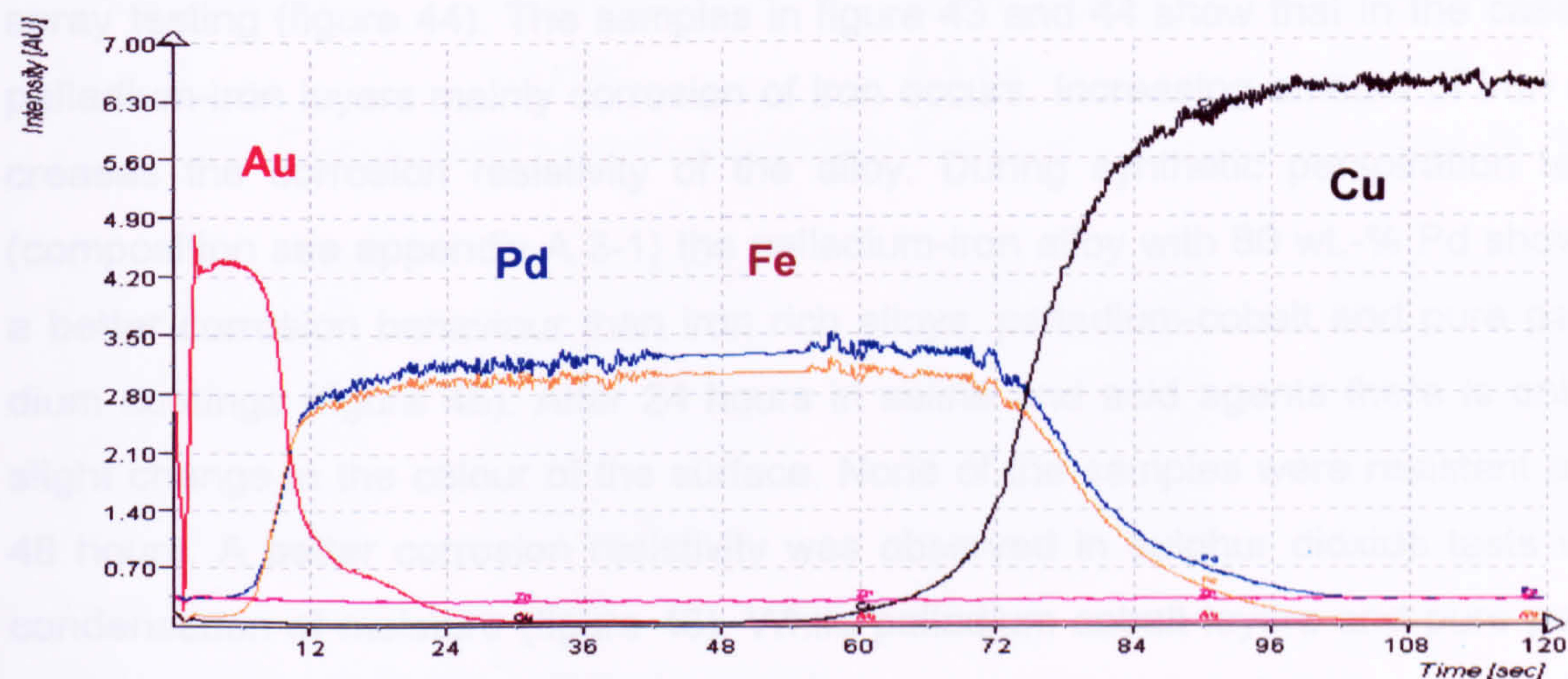
Figure 40
GDOS Analyses of Electroplated Gold Layers on Copper with and without Intermediate PdFe (80/20) Layers before and after Post Plated Heat-Treatment



Gold Layer on Copper Substrate after Heat-Treatment 160 °C, 120 h



Gold Layer / PdFe (15/85) / Copper Substrate before Heat-Treatment



Gold Layer / PdFe (15/85) / Copper after Heat-Treatment 160 °C, 240 h

Figure 41
GDOS Analyses of Electroplated Gold Layers on Copper with and without Intermediate PdFe (15/85) Layers before and after Post Plated Heat-Treatment

4. 2. 12 Corrosion Resistance of Palladium-Iron Coatings

Some typical test atmospheres were selected to describe the corrosion behaviour of palladium-iron coatings on copper and brass substrates with respect to decorative (jewellery) and functional (electronics) applications. Samples were tested in suitable atmospheres with and without saline and acid agents and sulfur dioxide according to established test methods. For comparison, samples were tested together with pure palladium and palladium-cobalt layers. After the different tests the samples were examined visually for corrosion products under x 100 magnification.

Figure 42 shows the results obtained after 14, 21, and 28 days in damp heat with a humidity of 90 % at 60 °C. This test is not a very aggressive one, but often used to simulate corrosion conditions during carriage and storage of connectors or similar electrical compounds. Palladium-iron alloys, like palladium-cobalt and pure palladium are resistant in this atmosphere. Only pure palladium layers tend to lose their brightness after 3 or 4 weeks. Spray tests with sodium chloride solution at pH = 6.5 - 7.2 and temperatures of 35 °C cause corrosion to all samples tested after 12 hours. (figure 43). Only when the salt spray tests were stopped after 6 hours differences of the various coatings were visible. While palladium-iron layers with a high amount of iron and palladium-cobalt layers corrode, palladium-iron layers with a high amount of palladium and pure palladium layers are resistant for 6 hours in this atmosphere. Increase of the layer thicknesses does not increase the corrosion resistivity either of palladium, palladium-iron alloys nor of palladium-cobalt coatings after 24 hours salt spray testing (figure 44). The samples in figure 43 and 44 show that in the case of palladium-iron layers mainly corrosion of iron occurs. Increasing amount of iron decreases the corrosion resistivity of the alloy. During synthetic perspiration tests (composition see appendix A 3-1) the palladium-iron alloy with 80 wt.-% Pd showed a better corrosion behaviour than iron rich alloys, palladium-cobalt and pure palladium coatings (figure 45). After 24 hours in saline and acid agents there is only a slight change in the colour of the surface. None of the samples were resistant after 48 hours. A better corrosion resistivity was observed in sulphur dioxide tests with condensation of moisture (figure 46). While palladium cobalt layers and pure palladium coatings are very sensitive to this test, the palladium-iron layers are resistant after 24 hours, independent from alloy composition. Corrosion for palladium-iron coatings was observed after 48 hours according to two cycles test procedures.

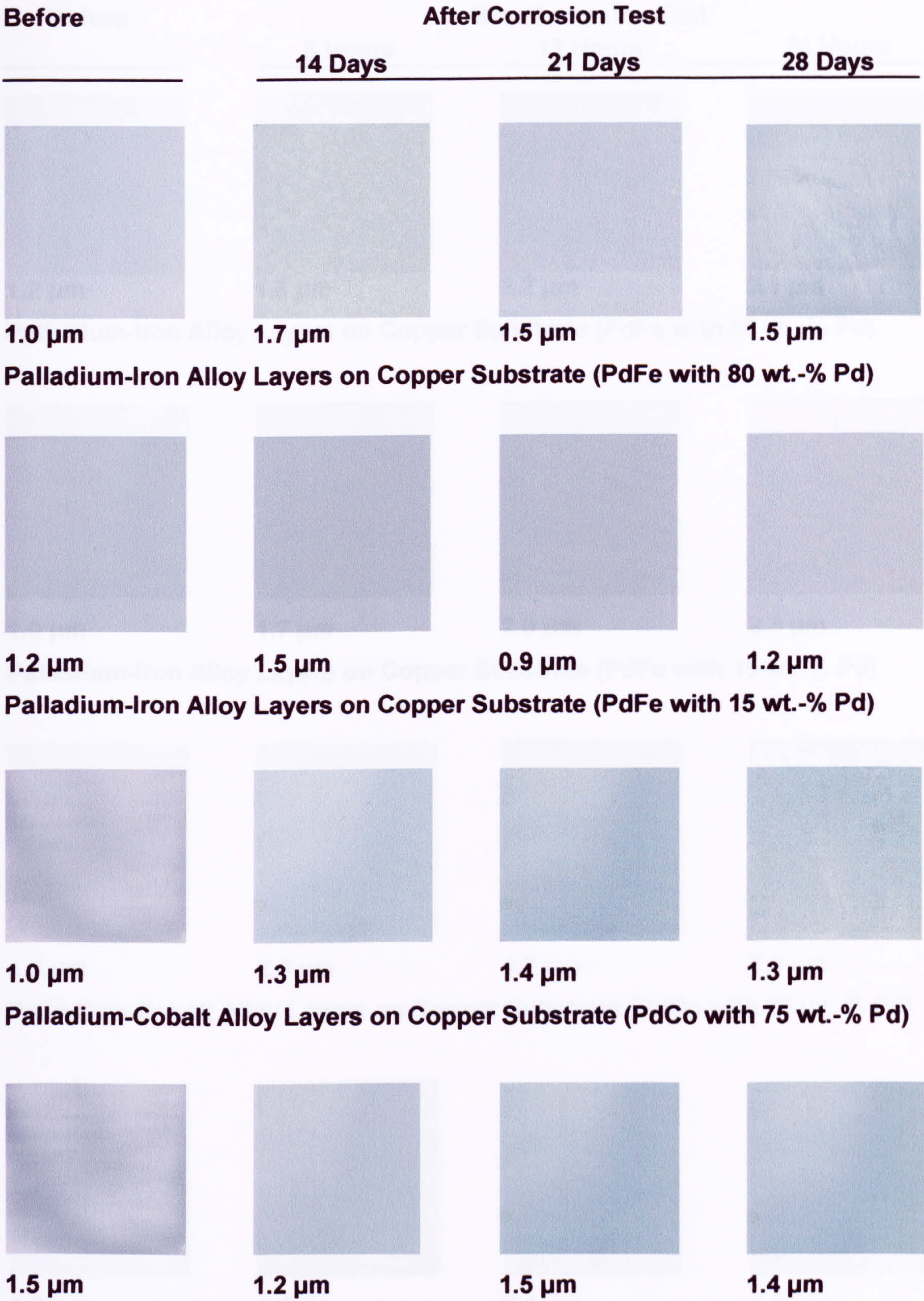
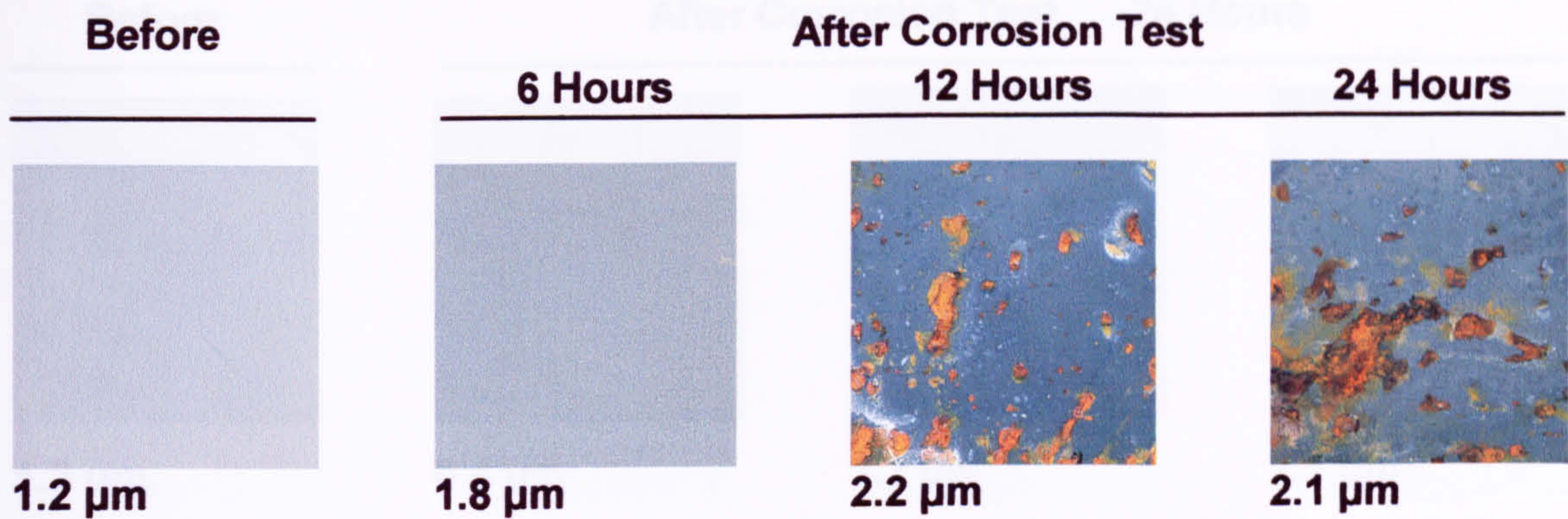
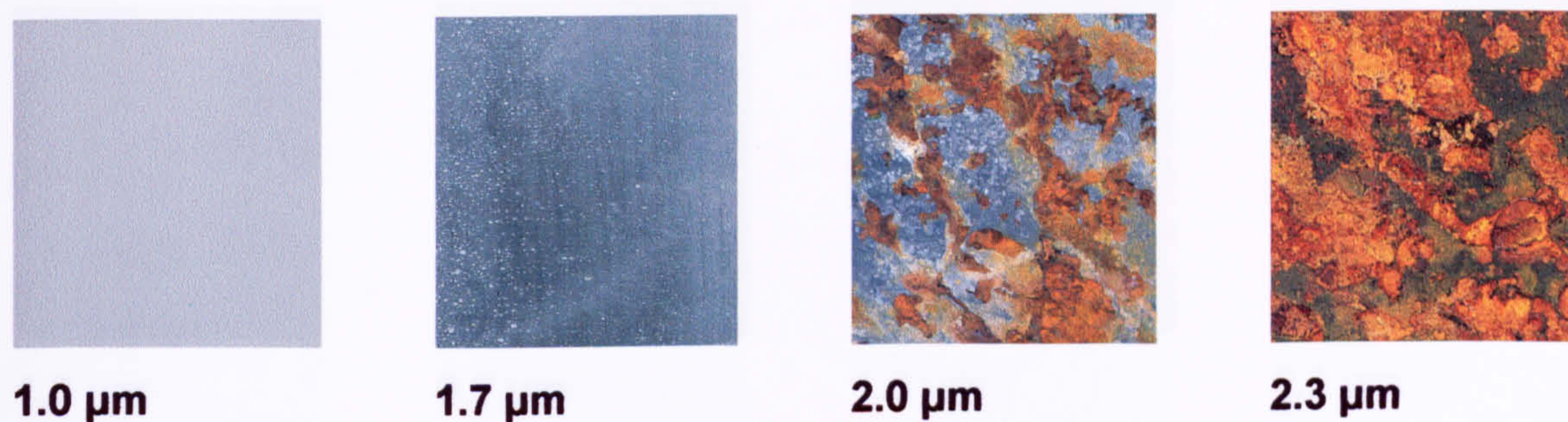


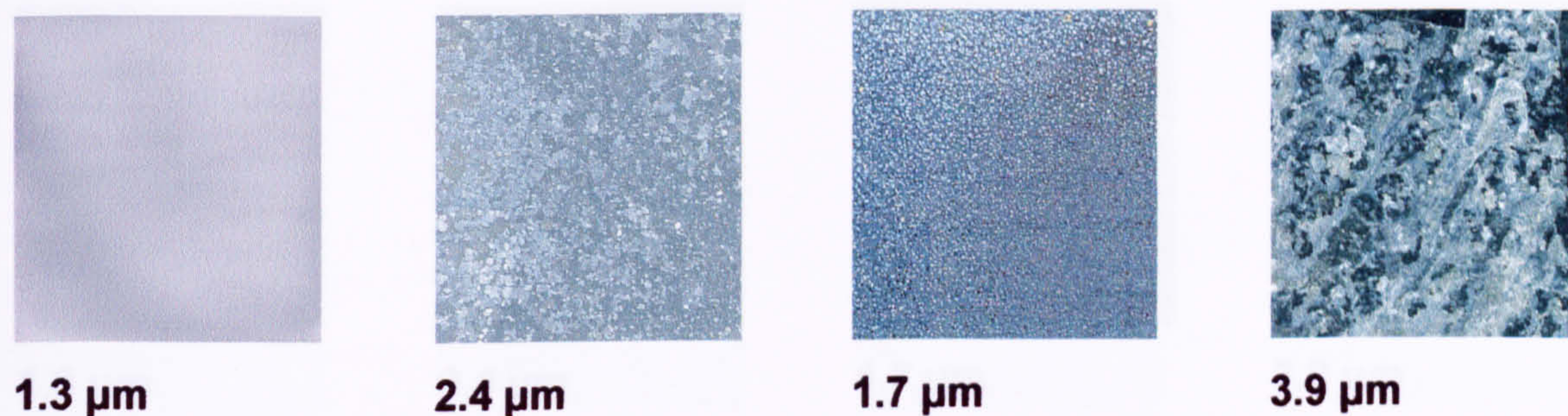
Figure 42
Basic Environmental Testing Procedures, Test Ca: Damp Heat, Steady State Humidity 90 %, 60 °C, 14, 21 and 28 days DIN IEC 68 T 2-3 : 1997



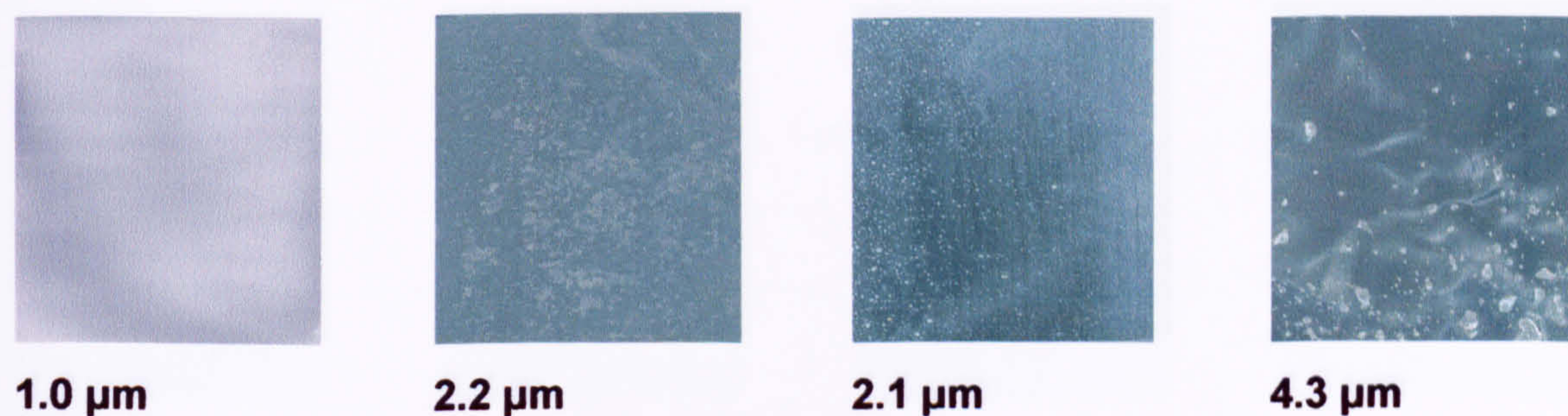
Palladium-Iron Alloy Layers on Copper Substrate (PdFe with 80 wt.-% Pd)



Palladium-Iron Alloy Layers on Copper Substrate (PdFe with 15 wt.-% Pd)



Palladium-Cobalt Alloy Layers on Copper Substrate (PdCo with 75 wt.-% Pd)



Palladium Layers on Copper Substrate

Figure 43
Spray Test with Sodium Chloride Solution DIN 50021 : 1988
NaCl = 50 g/l, pH = 6.5-7.2, 35 °C, 6, 12 and 24 h

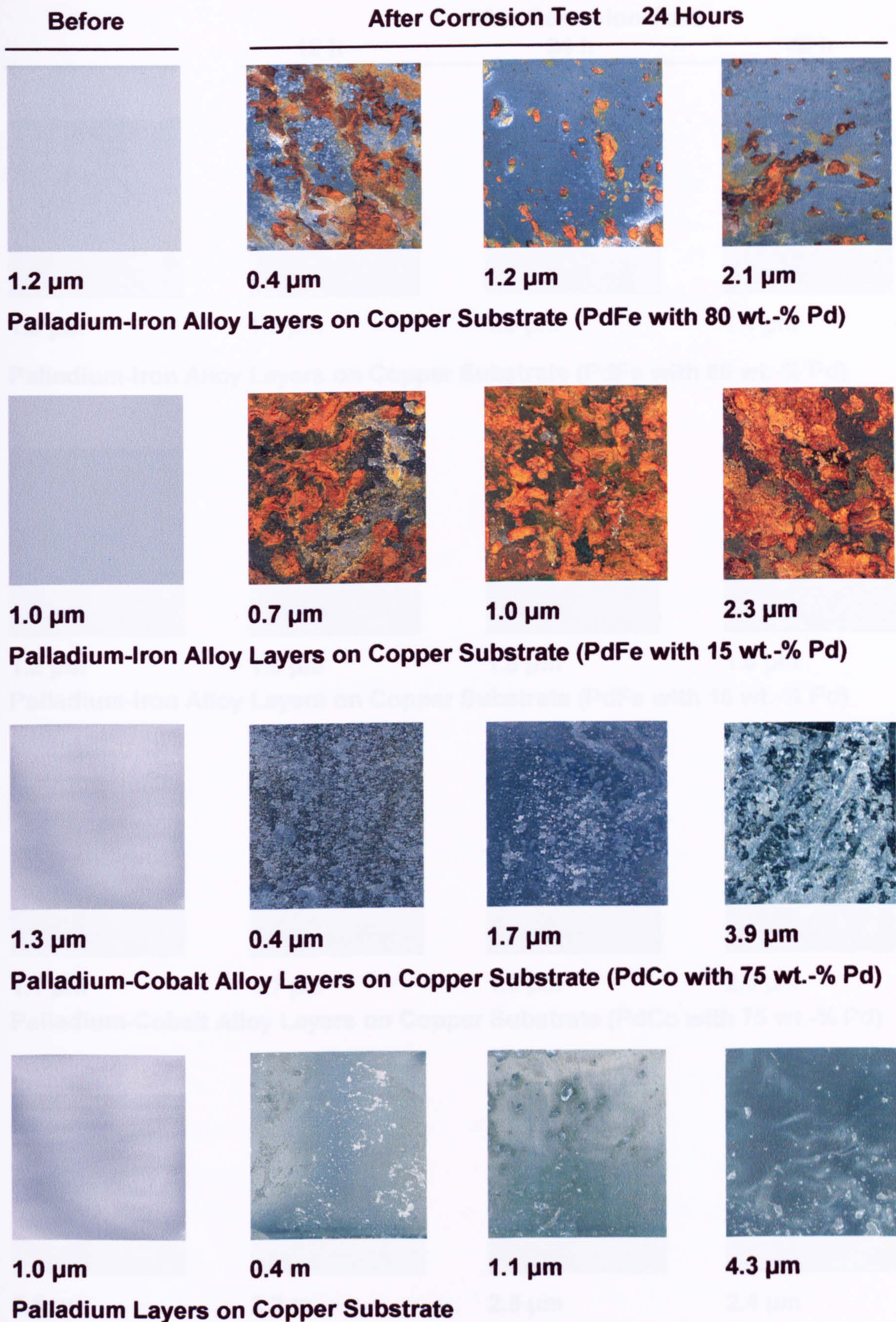


Figure 44
Spray Test with Sodium Chloride Solution DIN 50021 : 1988
NaCl = 50 g/l, pH = 6.5-7.2, 35 °C, 24 h

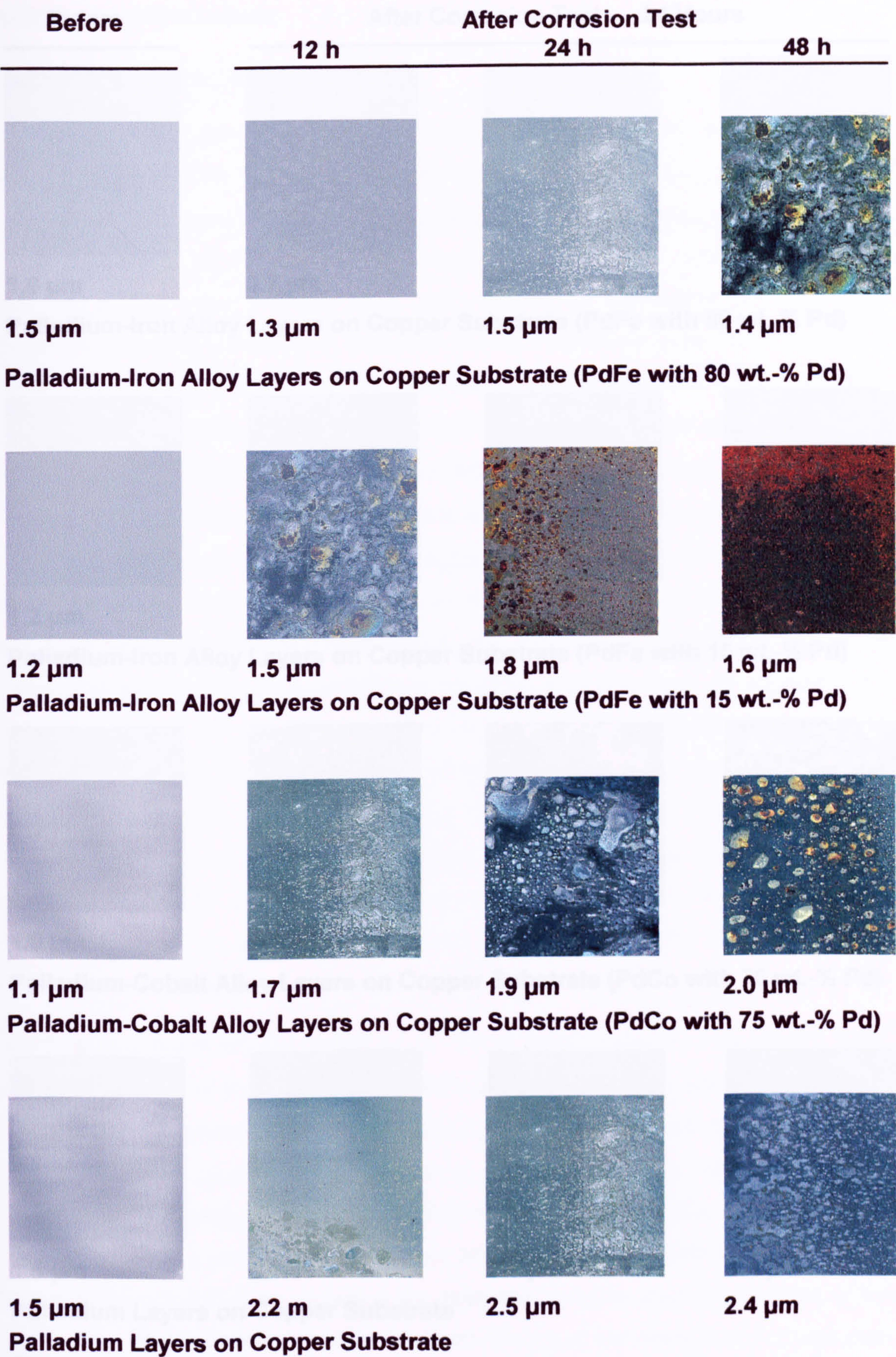
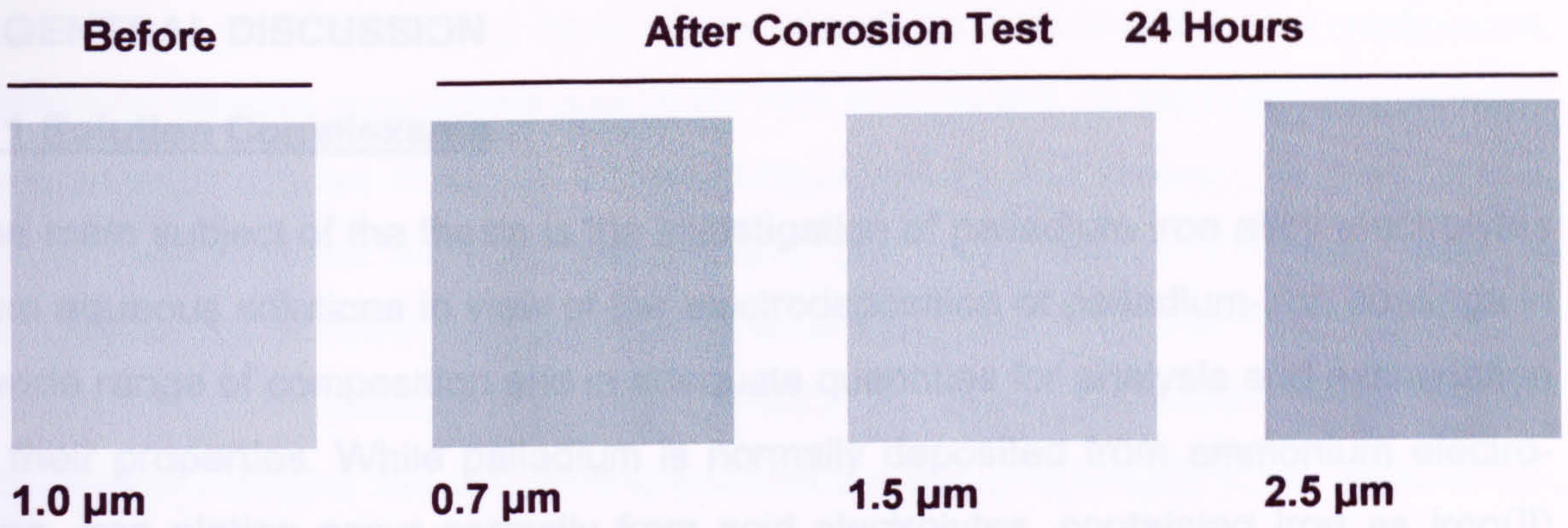
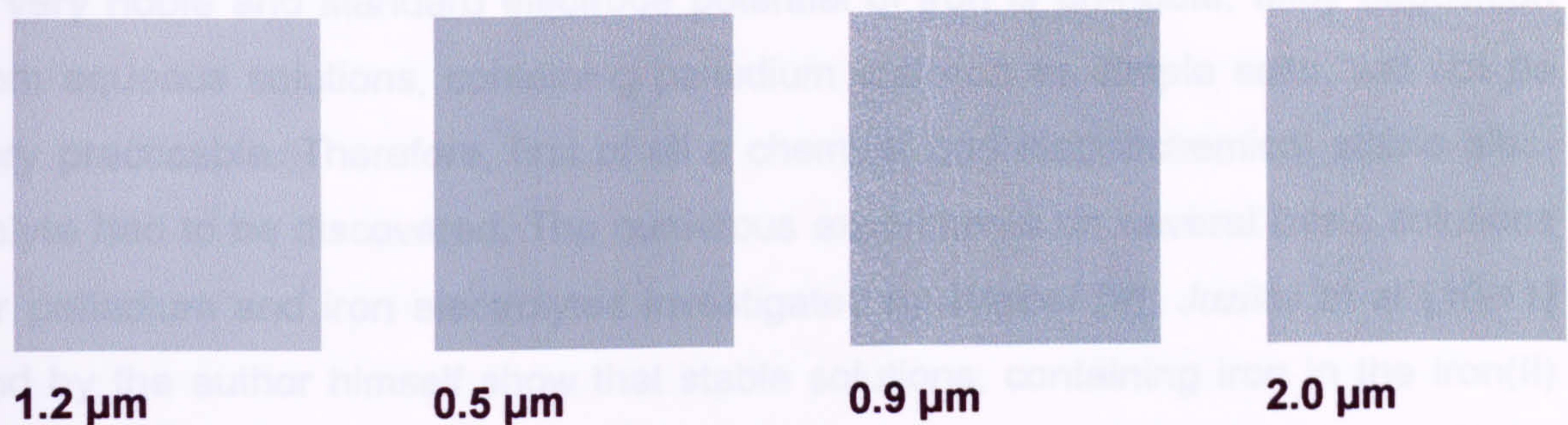


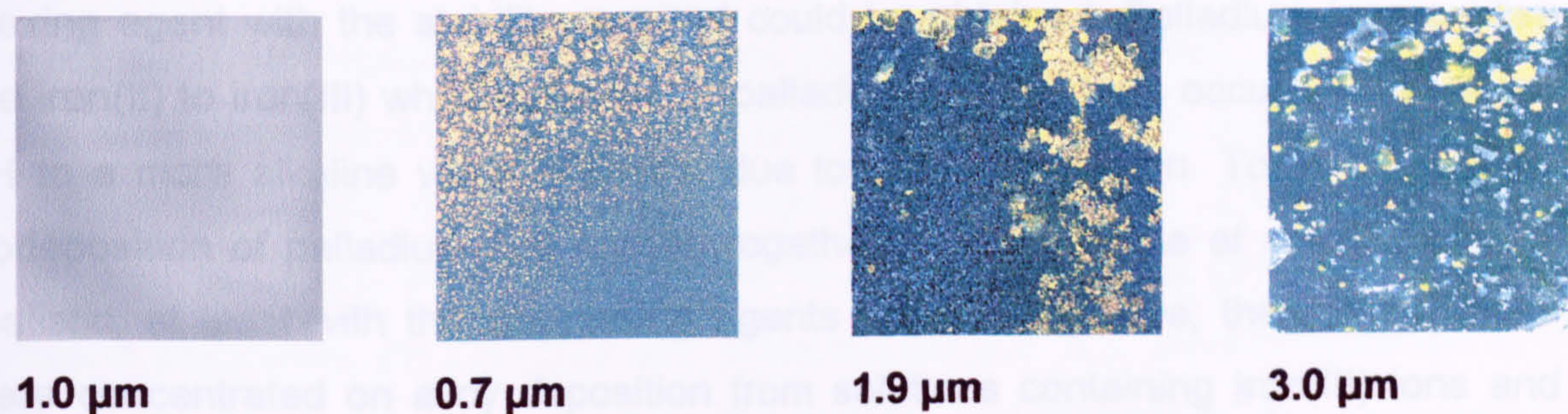
Figure 45
Testing with Saline and Acid Agents (Synthetic Perspiration Test)
ISO 3160-2 : 1992, 40 °C, pH = 4.7, 12, 24 and 48 h



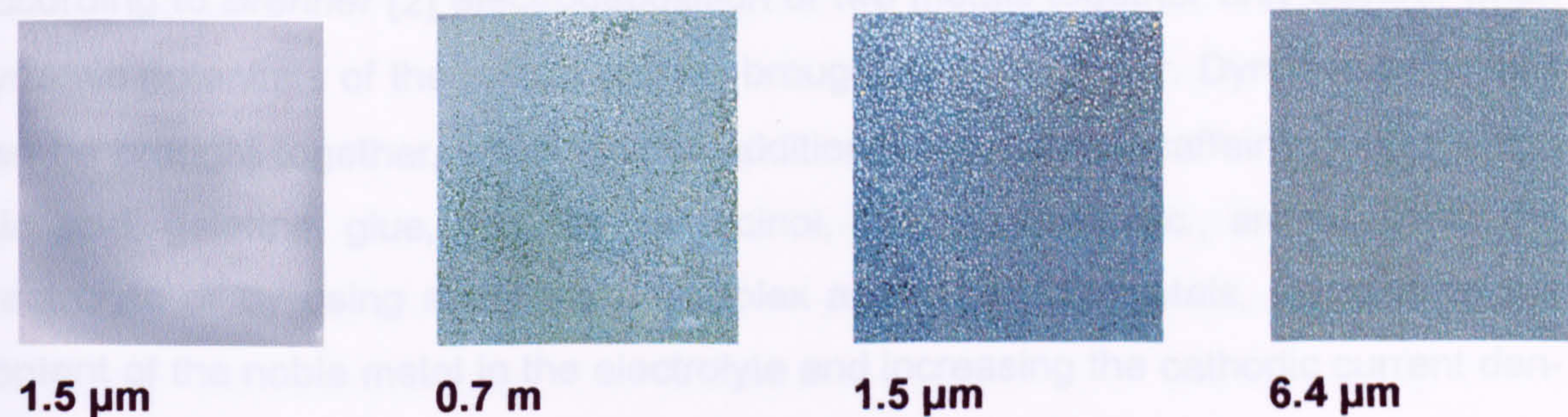
Palladium-Iron Alloy Layers on Copper Substrate (PdFe with 80 wt.-% Pd)



Palladium-Iron Alloy Layers on Copper Substrate (PdFe with 15 wt.-% Pd)



Palladium-Cobalt Alloy Layers on Copper Substrate (PdCo with 75 wt.-% Pd)



Palladium Layers on Copper Substrate

Figure 46
Sulphur Dioxide Test with Condensation of Moisture DIN EN ISO 6988 : 1997
SO₂ = 0.2 Vol.-%, 40 °C, 8 h, 25°C, 16 h

5. GENERAL DISCUSSION

5. 1 Solution Complexants

The main subject of the thesis is the investigation of palladium-iron alloy electrolytes from aqueous solutions in view of the electrodeposition of palladium-iron coatings in a wide range of composition and in adequate quantities for analysis and examination of their properties. While palladium is normally deposited from ammonium electrolytes, iron plating occurs normally from acid electrolytes, containing iron as iron(II) ions as chloride and sulfate salts. Because standard electrode potential of palladium is very noble and standard electrode potential of iron is un-noble, alloy deposition from aqueous solutions, containing palladium and iron as simple salts, will not be very practicable. Therefore, first of all a chemical and electrochemical stable electrolyte had to be discovered. The numerous experiments on several basic solutions for palladium and iron electrolytes investigated by *Waibel* [9], *Juzikis et al* [10,11] and by the author himself show that stable solutions, containing iron in the iron(II) state, from which electroplating of palladium and iron together is possible, could not be simply designed. For an application of iron(II) in acid solutions, no suitable complexing agent with the stability required could be obtained. Palladium ions oxidise the iron(II) to iron(III) while reduction of palladium to solid form occurs. A shift of the pH to a more alkaline value is limited due to iron precipitation. To sum up, electrodeposition of palladium and iron(III) together from such type of solutions is not realistic, at least with the complexing agents tested. Therefore, the investigations were concentrated on alloy deposition from solutions containing iron(III) ions and palladium(II) compounds.

According to *Brenner* [2] electrodeposition of two metals together only occurs, when dynamic potentials of the metals can be brought close together. Dynamic potentials can be brought together, when special additional agents, like caffeine, formate, formic acid, gelatine, glue, thiourea, resorcinol, salicylic acid, etc., are added to the electrolyte or by using appropriate complex agents for the metals. Decreasing the content of the noble metal in the electrolyte and increasing the cathodic current density are further possibilities to favour the deposition of the un-noble partner of the alloy coating. Both change the limited current density of the noble metal. Pulse plating is a similar technique with special parameters.

A disadvantage is the varying local current density on the surface of real workpieces. Therefore, several complexing agents for iron in a neutral or slight alkaline solution were tested. Because citrate as a complexing agent for iron showed the best results, further investigations were carried out with this iron complex. For the palladium electrolytes the ammonia based electrolytes are approved and the most common. In these electrolytes palladium is based mainly on tetrammino-palladous complexes with different anions, like tetrammino-palladous nitrite $[\text{Pd}(\text{NH}_3)_4](\text{NO}_2)_2$, tetrammino-palladous nitrate $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$, tetrammino-palladous sulfate $[\text{Pd}(\text{NH}_3)_4](\text{SO}_4)_2$, tetrammino-palladous chloride $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and tetrammino-palladous carbonate $[\text{Pd}(\text{NH}_3)_4](\text{HCO}_3)_2$ or diaminodinitrite $[\text{Pd}(\text{NH}_3)_2](\text{NO}_2)_2$, which is known as the P-salt. Unexpectedly, the stability of diaminodinitrite with iron(II) solutions was low and no alloy deposition occurred although the deposition potential was close to iron electrodeposition (figure 11). The best results in view of the chemical stability were obtained from an electrolyte consisting of palladium as $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ and iron as iron(III) citrate. According to *Brenner* [2] the next step was to bring the dynamic potentials close together, typically < 300 mV if possible.

Current density/potential curves show that $(\text{NH}_4)_2$ -citrate and $(\text{NH}_4)_2\text{SO}_4$ are appropriate additives. Ammonium citrate ($(\text{NH}_4)_2$ -citrate) turned out to support palladium-iron electrodeposition in a better way than potassium citrate. Therefore, $(\text{NH}_4)_2$ -citrate and $(\text{NH}_4)_2\text{SO}_4$ were added as well as ammonia to adjust pH. From this ammoniacal electrolyte, pH 7.5 - 10.5 with preferred pH 8.2 - 8.5, electrodeposition in a wide range of composition is possible. The stability and life-time of the electrolyte is sufficient enough for electrodeposition of coatings on different samples with reproducible properties. Unfortunately, the addition of citrate shifts the deposition potential of the alloy to a potential range where co-deposition of hydrogen can occur. *Hedrich* et al [94,95] discovered that hydrogen co-deposition is always preferred, especially at low current densities, when citrates, benzoate, salicylates, etc. are present. The same experience was reported by *Juzikis* et al [11] from an electrolyte containing sulfosalicylic acid. The palladium-iron electrolyte shows no significant effect on the co-deposition of hydrogen or alloy composition depending on change of the pH of the electrolyte in the range from pH 7.5 to pH 10.5. This is contrary to the expectation of increasing hydrogen co-deposition with increasing pH of the solution

according to *Nernst* equation $E_{H^+/H_2} = -0.059 \text{ V} \cdot (\text{pH} + \frac{1}{2} \log p_{H_2})$. But, as *Butz et al* assumed [141], from increasing reduction of hydrogen no increasing amount of hydrogen incorporation in palladium-nickel coatings should be expected. The typical behaviour of palladium and hydrogen during electrodeposition of pure palladium deposition [92,93] is not transferable to palladium-alloy deposition. Investigations of the system palladium-nickel-hydrogen with and without hydrogen charging [124] demonstrated that the amount of hydrogen in the coating depends on several parameters, like composition of the alloy, compounds in the electrolyte, stability of α -Pd-H and β -Pd-H phases, etc..

Because palladium in this solution and with these complexing agents is still the more noble metal, during electrodeposition palladium reduction is always preferred when the amount of ions for reduction is large enough. If iron rich alloy coatings are desired the amount of noble metal in the electrolyte has to be decreased. Composition of the deposited alloys depends mainly on the ratio of the metal ions in the electrolyte while the effect of current density is slight. From an electrolyte with a metal ratio of Pd:Fe (mol:mol) 1:1 alloy coatings with a palladium content in the range of 80 - 85 wt.-% were obtained. From an electrolyte with a metal ratio of Pd:Fe = 1:100 alloy coatings were deposited with a palladium content of 15 wt.-% to 20 wt.-% if the current density of the electrolyte is in the range of 5 A/dm² to 8 A/dm² and electrolyte temperature below 55 °C. In the temperature range of 55 °C to 75 °C and with current densities of 3 A/dm² to 5 A/dm² (75 °C, 8 A/dm²) the iron content of the coatings decreases dramatically to an amount of 15 wt.-% to 25 wt.-%.

The dramatic decrease of iron co-deposition takes place in parallel with the decrease of current efficiency of the electrolyte. During electrolysis various reduction reactions are possible. $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$, and $\text{Fe}^{2+} + 2 e^- \rightarrow \text{Fe}$, and $\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$, and $2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2$. In the case, when the iron co-deposition is high and current density is in the range of 25 % to 30 %, the $\text{Fe}^{2+} + 2 e^- \rightarrow \text{Fe}$ (metal deposition) reaction is on an optimum. On the assumption that the other reactions, like palladium reduction and hydrogen evolution, are almost constant, the only possible main reaction in the case of low iron co-deposition is the reduction of iron from the iron(III) state to the iron(II) state. The main amount of current (ca. 95 %) is used for hydrogen evolution, while the amount of palladium ions in the electrolyte is too small to

replace the reduced metal ions. Unfortunately, during electrochemical measurements this important reduction step could not be observed. Because, the iron ion in the electrolyte is in the iron(III) state and electrodeposition is only possible from the iron(II) state, previous reduction of iron(III) to iron(II) must have occurred. Some few experiments were carried out with an iron(III) electrolyte after separating cathodic area from anodic area by a diaphragm showing, at least at a current density of 0.3 A/dm^2 , an increase of iron(II) ions [9]. More information about the ion ratio of $\text{Fe}^{2+} : \text{Fe}^{3+}$ during electrodeposition is clearly desirable.

5. 2 Deposit Characteristics

The appearance of the coatings, concerning dull deposits or the increase of size or amount of cracks, is not affected by a decrease of the amount of co-deposited iron. Cracking of palladium-iron coatings depends mainly on the thickness of the layers. *Morrissey* [109] stated that palladium-nickel alloy electrodeposits are notably less sensitive to hydrogen-induced cracking than are pure palladium deposits. They are however somewhat more susceptible to stress cracking upon deformation than pure palladium. This understanding confirms the experience obtained from production conditions of various parameters influencing the tendency of appearance of cracks [204]. Differences in composition of the layers were not observed, except when the amount of palladium and iron is close to 50 : 50 wt.-%. In this range of composition the palladium-iron coatings are very brittle. During electrodeposition the coatings spall from the surface. For practical employment this type of alloy is consequently unimportant. Therefore, for further investigations two types of palladium-iron electrolyte were selected. One with a metal ratio of $\text{Pd} : \text{Fe} = 1 : 1$ and another one with a metal ratio of $\text{Pd} : \text{Fe} = 1 : 100$. While from the first electrolyte type, alloy coatings with 80 - 85 wt.-% palladium could be obtained, the amount of iron in coatings deposited from the iron rich electrolyte was in the range of 80 - 85 wt.-% iron, except under those conditions discussed before. The advantage of these two electrolytes is the very constant alloy composition over a wide range of electrolyte composition, that could be obtained. Therefore, the reproducibility of the alloy coatings is excellent.

Pure palladium electrolytes are very sensitive to cyanide impurities [62,79,97,198]. Cyanide will complex the palladium metal and reduce the amount available for depo-

sition. Therefore, all attempts to deposit palladium-silver alloys failed, starting in the early thirties by *Grube and Beischer* [166] and repeated later by several authors [154,167,176]. Palladium-nickel electrolytes are known to be less sensitive to cyanide [62,63,198]. The results obtained during this study show, that in fact palladium-iron electrolytes are not less sensitive to cyanide impurities in comparison with palladium-nickel electrolytes, but they are less sensitive than pure palladium electrolytes. Because electrodeposition occurs from an ammonia-based electrolyte pre-plating with gold or palladium-strike on copper or copper alloy substrates are required. In the case of palladium-iron electrodeposition from electrolytes with a high amount of iron, pre-treatment of iron or steel substrates is indispensable, because low hydrogen overvoltage would otherwise only allow hydrogen evolution.

The results obtained show the possibility to deposit bright and crack-free palladium-iron layers in a wide range of deposition parameters, admittedly limited by the layer thickness. Alloys with a high amount of iron tend to be a little bit darker than alloys with a high amount of palladium. Palladium-iron layers with 80 wt.-% of palladium appear similar to palladium-nickel alloys with 75 wt.-% 85 wt.-% nickel. Electrodeposition of single metals or alloys from the platinum group is always considered with cracking beyond a certain coating thickness. Only recently it has been possible to find an electrolyte on the market which allows palladium and palladium alloy deposition over a thickness of 5 μm , although numerous studies on palladium-nickel electrodeposition [127-137,140-155,154,198,204], palladium-cobalt electrodeposition [179-185,205] and palladium-silver electrodeposition [166-174] have been carried out over many years. Even the electrodeposition of pure palladium with constant quality and without cracks is not a trivial challenge for plating shops. Palladium-iron electrodeposition is not an exception to this rule. Several attempts with various chemistries, pulse plating techniques, laser enhanced technology etc. were not successful at last.

Smooth, crack-free palladium-iron coatings up to 2 - 3 μm were obtained from an electrolyte with a metal ratio of $\text{Pd}:\text{Fe} = 1:1$, electrolyte temperature of 45 - 65 °C, and a cathodic current density of 3 - 5 A/dm^2 . With decreasing amount of palladium in the alloy the surfaces appear more nodular. Decrease of electrolyte temperature and increase of current density and coating thickness cause nodular surfaces with

cracks. Palladium-iron layers with a high amount of iron tend to build numerous, fine cracks, while palladium-iron coatings with a high amount of palladium show less, but larger cracks. Electrodeposition at low temperatures cause dull deposits. Bright and crack-free deposits from an electrolyte with a metal ratio $\text{Pd} : \text{Fe} = 1 : 100$ could be obtained in a temperature range from 45 - 75 °C and current densities up to 8 A/dm².

While pure iron from this ammoniacal solution is deposited in a columnar (partly fibrous) structure, the morphology structure of the coatings changes totally when palladium is co-deposited. All palladium-iron alloys show a laminar or banded structure, which runs parallel to the surface of the substrate. The grains within the lamellae are small. Laminar structures are not unique with alloys, as they occur also with coatings of single metals, like nickel deposits. Those deposits are normally bright coatings with a high strength and hardness but low ductility [200]. The banded, or laminar, grain structure observed for the palladium-iron deposits is similar to that found in palladium-nickel coatings [135,143] and palladium-silver coatings [173]. This structure is considered useful for high wear resistance and a better corrosion resistance [135, 173]. However, formation of cracks is contrary to good corrosion behaviour. Deposits with high iron content show a homogenous, laminar structure.

Palladium is deposited as a face centered cubic crystal structure and iron is deposited as a body centered cubic structure. X-ray diffraction studies, carried out on several samples with various composition of the palladium-iron alloy, showed the electrodeposits to be a complete solid solution of palladium and iron. Because there is a strong disorder of the structure of the palladium-iron alloy in the range of 40 At.-% to 50 At.-% iron an broadening of the X-ray lines is measured. *Juzikis et al* [10,11] assumed that this behaviour will be similar to the electrodeposition of an amorphous structure. Recent X-ray diffraction measurements of palladium-iron coatings, deposited from the ammonium/citrate electrolyte, showed that this phenomenon is probably caused by the direct change from body centered lattice to face centered lattice at this composition of the alloy.

In contrast to electrodeposited iron, the hardness of pure palladium coatings is not as high [2]. Most organic impurities, like citrate which in iron electrolytes causes hard and brittle deposits [22,42], cause electroplated palladium from this type of electrolyte to develop a hardness in a typical range of 200 to 250 VHN [62,92,95].

Increasing of iron content from some few wt.-% up to 10 wt.-% iron doubles the hardness of the alloy from 200 to 420 VHN. From 15 wt.-% iron to 85 wt.-% iron, the increase of hardness is nearly linear. In the range of 85 wt.-% to 100 wt.-% the change of hardness is about 30 VHN and, therefore, under a practical employment of constant quality. To sum up, increase of the iron content causes an increase of the hardness of the layer from 200 VHN up to at least more than 600 VHN.

Several electrodeposited metals and metal alloys usually show internal stress [1]. Nickel, chromium and also palladium are well known as metals on which electrodeposition always occur with a high internal (tensile) stress [1,13,14]. Many different causes can be adducted for explaining the origin of internal stress in electrolytic deposits [13]. Dislocation theory, excess energy theory, hydrate theory and hydrogen theory are the most important ones. Hydrogen theory assumes that the co-deposited hydrogen incorporated into the deposits is responsible for the internal stress by causing a temporary lattice expansion in the deposited metal. With progressive deposition, the hydrogen diffuses either into the substrate material or into the electrolyte. The lattice of the coating then shrinks and tensile stress arises in proportion to this hydrogen diffusion. The theory applies metals in which co-deposition of hydrogen takes place and which are capable of incorporating atomic hydrogen into their lattice. This occurs for metals of the iron and platinum group and for chromium. In the case of nickel and palladium several experiments with hydrogen charging during and after deposition [124] show that internal stress of this metals is connected with the formation of metal hydride phases ($\alpha + \beta$ phases). Therefore, metal deposition occurs with high internal stress.

5. 3 Use of Additives

In the case of nickel electrodeposition various additives have been found (saccharin, aromatic disulfonic acids, etc.) which reduce stress or change tensile stress to compressive stress. Additives, which are useful for reducing the stress in bright nickel deposits, were investigated [09]. Unfortunately neither saccharin, urea, thiourea, nor boric acid had a significant effect on the stress of electrodeposited palladium or palladium-iron layers. Similar behaviour was observed on palladium-nickel deposition from ammoniacal electrolytes [143,144]. *Hedrich* and *Raub* investigated various ad-

ditives for palladium deposition from $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ salt in an ammoniacal electrolyte [93-95]. The authors discovered that additives like citrate, benzoates, salicylates, nicotinic acid, and nicotinic acid amide shift the deposition potential of palladium to negative values. Therefore, in the range of low current densities the co-deposition of hydrogen increases and hydrogen content in the coating increases, too. High internal stresses of the deposited layers with cracks is the consequence. Palladium-iron alloy coatings deposited in an electrolyte with a high iron content have tensile stress in the range of 150 - 350 N/mm². This is nearly half of the amount of the internal stress obtained from palladium-iron alloys deposited from an electrolyte with a metal ratio $\text{Pd} : \text{Fe} = 1 : 1$. There is a slight decrease of the tensile stress with increasing current density, whereas dependency of internal stress from electrolyte temperature is not very pronounced. The causes for tensile stress of palladium-iron coatings are not directly related to iron concentration and respectively palladium content of the layers, or to hydrogen evolution during electrolysis.

Depending on deposition parameters, the amount of co-deposited hydrogen is in the range of 250 - 2050 ppm: Hydrogen content of the layers decreased with increasing current densities. The lowest amount was measured in palladium-iron coatings deposited from an electrolyte with a metal ratio $\text{Pd} : \text{Fe} = 1 : 1$ and electrolyte temperature of 45 °C. The measured hydrogen content is in the same range as those obtained from other investigations with palladium [62,69,93,95,105] and palladium alloy electrodeposition [63,122,124,141]. The problem with palladium is that it is a "catalytic" metal and therefore promotes hydrogen generation. But it also has a remarkable affinity for hydrogen in absorbing in large volumes and forming of hydroxide. The problem with iron is that iron is deposited with high cathodic polarisation and relatively low hydrogen overvoltage [22,30,42]. Therefore, during iron electrodeposition hydrogen co-deposition always can occur. To keep the amount of absorbed hydrogen as small as possible the amount of available hydrogen must decrease. One possibility is the selection of appropriate deposition parameters, which keep the current efficiency of the alloy deposition close to 100 percent. Unfortunately, the electrochemical measurements show that electrodeposition of palladium and iron from alkaline solutions containing citrate or ammoniacal complexes is always connected with hydrogen co-deposition. Another possibility is to prevent the generated hydrogen from penetration into the electroplated layers.

Therefore, a commercial wetting agent was used for hydrogen examination and some *Hull-Cell* experiments. Unfortunately, no significant differences of coating behaviour could be observed. Addition of this type of wetting agent does not keep the H: Pd ratio below 0.03. In this range palladium hydride would be present as a face centered cubic α -phase with a lattice constant close to that of pure palladium and, therefore, hydrogen from this structure does not cause significant lattice contraction. The amount of non-metallic impurities like sulfur and carbon correspond to the results obtained from palladium-nickel coatings [138].

5. 4 Properties and Applications

The main application for palladium and palladium-alloys, usually palladium-nickel, is for electrical connectors. Therefore, high wear resistance and low contact resistance are important properties. Unfortunately, there are numerous test methods [90,91,98, 99] with various parameters available [131-134, 138,139,156,162] and comparison of the obtained results is sometimes difficult. To sum up all the results of the investigations carried out, the best properties were obtained from palladium-nickel coatings. The sliding and wear behaviour of palladium-nickel are similar to those of hard gold [77-82,86]. Palladium-nickel coatings may be slightly less porous than gold coatings and they resist tarnish. Only a higher contact resistance is a disadvantage of those alloys. According to the results obtained during this studies, good wear resistance is indicated by using iron, palladium-iron with a high iron content (PdFe15/85) and palladium-nickel (PdNi75/25). Palladium-cobalt (75/25), palladium-iron with a high palladium content (PdFe/80/20), copper-tin (CuSn6), pure palladium and pure copper show the same wear behaviour. Very poor wear resistance under these test conditions show pure gold and gold-cobalt (hard gold) layers. These results are partly different to results from previous studies [100]. An explanation for the bad behaviour of gold and hard gold could be the type of measurement method. Abrasive generated gold or hard gold particles could, under the test conditions, not act like an lubricant. Consequently gold and gold alloy coatings show poor wear resistance. From practical experience for electronic connectors it is known that flash-gold or flash-hard-gold layers on palladium or palladium alloy coatings are viable gold candidates and improved. However, for better comparison of different materials, and not only for one special application, these test procedures were used as appro-

priate measurement methods. As a result the palladium-iron electrodeposits are comparable to palladium-cobalt and palladium-nickel layers. The wear resistance of the alloys decrease with increasing palladium content in the layer. It is in the range between pure iron coatings, deposited from citrate solutions, and pure palladium coatings deposited from ammoniacal alkaline electrolytes.

Contact resistance measurements were obtained with relatively low loads (2 - 8 N) to show influence of oxide layers. As a result, contact resistance of gold surfaces versus gold surfaces is the lowest, while the contact resistance of tin-nickel versus tin-nickel surfaces is the highest. Palladium-iron coatings with a high amount of palladium show an excellent low contact resistance in the range of 0.6 m Ω to 0.9 m Ω . Even an increase of the iron content in the palladium-iron alloy causes only an increase of the contact resistance up to 1.3 m Ω . The contact resistance of those layers is similar to the contact resistance of palladium-nickel and palladium-cobalt coatings.

Solderability tests show that wetting occurs on palladium iron layers with a high amount of palladium, while poor solder wetting was observed on pins electroplated with a high amount of iron. In comparison with tin-lead coatings palladium-iron deposits have inferior solderability.

In gold plated contacts underlying copper can diffuse through a thin gold layer to the surface where it oxidises and increases contact resistance [202]. An effective way to retard diffusion is to use a barrier layer. Certain metals and metal alloys are suitable for barrier layers [190,202,203]. Several experiments with electroplated gold layers on copper substrate without and with various intermediate layers including palladium-iron layers were carried out. After electroplating, the samples were subjected to a heat-treatment process on atmosphere. As a result palladium-iron alloys act as a good diffusion barrier layer for gold and copper during heat-treatment for 240 hours at 160 °C. Investigations with palladium-iron alloy coatings deposited from an electrolyte according to *Juzikis et al* [10,11] show that palladium-iron with 25 wt.-% iron is a more effective diffusion barrier layer than palladium [203]. Copper diffusion through palladium-iron is more noticeable than through nickel for temperatures higher than 300 °C, but the capability for palladium-iron to withstand copper diffusion is comparable to nickel at 300 °C or below [203].

Corrosion testing with palladium-iron coatings were carried out in atmospheres with and without saline and acid agents and sulfur dioxide according to established test methods. Testing with sulfur dioxide is in addition a suitable method for porosity testing. While palladium-iron alloys, as with palladium-cobalt and pure palladium, are resistant in damp heat with a humidity of 90 % at 60 °C, salt spray testing with sodium chloride solution causes corrosion to all samples after twelve hours. After six hours salt spray testing differences of the various coatings were visible. While palladium-iron layers with a high amount of iron and palladium-cobalt layers corrode, palladium-iron layers with a high amount of palladium and pure palladium layers are resistant. The corrosion test shows that in the case of palladium-iron layers mainly corrosion of iron occurs (iron rust). Increasing amounts of iron decreases the corrosion resistivity of the alloy. The same behaviour was observed during tests with synthetic perspiration. Palladium-iron alloy with 80 wt.-% palladium showed a better corrosion behaviour than iron rich alloys, palladium-cobalt and pure palladium coatings. While palladium cobalt layers and pure palladium coatings are very sensitive to sulphur dioxide tests with condensation of moisture, the palladium-iron layers are resistant after 24 hours, independent from alloy composition. This test indicates that palladium-iron layers are deposited with a low amount of porosity. The corrosion measurements show that the corrosion resistivity of palladium-iron coatings is similar to palladium-nickel layers and, therefore, better than those of pure palladium and palladium-cobalt. In the case of iron-rich alloys increase of palladium increases the corrosion resistance notably.

Some few results of pulse plating studies show the possibility of plating attractive multi-layered deposits, which are worth further investigations in more detail. Unfortunately, application of pulse plated techniques, under the applied conditions used, do not result in a decrease of the tendency of cracking with higher thicknesses of deposits .

5. 5 Industrial Usage and Opportunities

The physical, chemical and mechanical properties of the palladium-iron coatings are important criteria for many applications. However, determining these properties for electrodeposits depends very much not only on the method of testing but also on the condition of plating. The summarised properties were collected from samples pro-

duced under laboratory conditions and measured with the equipment described before. Specific concentrations of palladium and iron in the electrolyte and deposition parameters must be selected for each practical application under production conditions depending on particular operating conditions and product requirements.

For several years palladium and palladium-nickel have been recognised as an excellent and established gold substitute in the electronic industry for electrical contacts, especially those operating at low current and voltages [204]. In many respects the properties of palladium and partly of palladium-nickel are closely associated with those of platinum and gold. During the last years several alloys of palladium have been developed to meet specific contact requirements. Palladium provides the required noble metal characteristics while additions of other metals improve hardness, wear resistance or reduce production costs. Primary alloys are palladium with from 30 to 50 percent silver, 15 to 50 per cent cobalt and finally palladium-nickel with 15 to 25 percent nickel. Palladium-nickel is the most common palladium alloy today.

The investigations on palladium-iron electrodeposition show that palladium-iron deposits are true alloys, comparable to palladium-nickel, palladium-silver, and palladium-cobalt alloys. It is possible to create stable palladium-iron electrolytes, which are able to deposit alloy coatings with an excellent reproducibility of properties. From the applicational viewpoint, palladium-iron alloy deposits so far obtained show useful physical properties in a wide range of alloy composition (table 26). From the process viewpoint, the high ammonia content of the electrolyte may constitute a potential disadvantage. Effective ventilation and moderate temperatures of the electrolyte can take remedial action. Advantage of using ammonia are minimised problems in salt concentration of the electrolyte and better inhibition of cyanide pollution from air. Further investigations of the composition of the alloys and properties versus age of the electrolyte as well as investigations on fretting corrosion, contact resistance after heat-treatment, etc. are needed.

From the results of the investigations it can be concluded that palladium-iron coatings could be an alternative to palladium-nickel or palladium-cobalt coatings. Because of their appearance, good contact properties, hardness, high wear resistance and corrosion resistivity to a sufficient extent palladium-iron coatings will find increasing application not only in contact technology.

Electrolyte Composition		Deposition Parameter	
0 - 0.3 mol/l	Pd as $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$	Temperature	45 - 75 °C
0 - 0.3 mol/l	Fe as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$	pH	7.5 - 10.5
0 - 0.3 mol/l	$(\text{NH}_4)_2\text{-Citrate}$	Current Density	3.0 - 8.0 A/dm ²
0 - 0.3 mol/l	$(\text{NH}_4)_2\text{SO}_4$	Current Efficiency	25 - 85 %
x ml	$\text{NH}_4\cdot\text{OH}$	Deposition Rate	1 µm/min
Anode : Cathode Ratio 1 : 1		Anode	platinised Titanium
Electrolyte and Substrate Agitation recommended Strip, Rack or Barrel Plating possible			
Alloy Composition		15 wt.-% and 85 wt.-% Palladium	
Appearance		Bright, Crack Free up to 2 - 3 µm	
Hardness		250 - 600 VHN _{0.01}	
Internal Stress		150 - 500 N/mm ² (Tensile Stress)	
Hydrogen Content		250 - 2050 ppm	
Wear Resistant		High	
Contact Resistant		< 1 mΩ	
Solderability		Poor (without Au flash)	
Barrier Layer Properties		Excellent for Gold and Copper	
Corrosion Resistivity		Good	

Table 26
Palladium-Iron Electrodeposition: Electrolyte Composition, Deposition Parameters, and Layer Properties

6. CONCLUSIONS

Among the main alternatives for gold and hard gold in the electronic industry for electrical contacts, especially those operating at low current and voltages, are palladium and palladium-nickel alloys. Although the price for palladium is extremely high at the moment, the overall cost for a palladium or palladium-nickel plating process is only 35 - 45 percent of that of a corresponding gold or hard gold plating process. In the case of palladium-nickel coatings the ratio is more favourable. Although some companies are considering the renaissance of gold and gold alloys or silver coatings, from the cost stand-point silver would have been an alternative. However, the tendency to form sulfide tarnish films makes it only an alternative as a lower cost finish for semiconductor applications. Therefore, currently palladium and palladium-nickel deposits are still used for electrical contact applications, while decorative applications of palladium and palladium alloys are limited due to the dark colour of the metal.

Economically, substantial cost reduction can be achieved due to the lower price of palladium compared to gold, coupled with its lower density. Technologically important material properties, e. g. hardness, wear resistance, thermal stability, etc. of palladium and palladium alloys are in many instances superior to hard gold. For example, the higher hardness of palladium is beneficial for better wear resistance and it could be supposed from earlier experience with palladium and palladium-alloy surfaces that it can be further enhanced by a thin coating of gold or hard gold.

The results obtained during this project show that palladium-iron electrodeposition from a stable aqueous electrolyte is possible. However, design of a good electrolyte in which iron deposition from iron(II) ions occur, has not been fully realised at last, although composition of the new palladium-iron electrolyte is simple and no special waste treatment is required. Besides the improvement of important properties, induced by the addition of iron, typical palladium disadvantages could not be solved. The addition of iron does not change the co-deposition and incorporation of hydrogen in a positive way, the amount of tensile stress and the tendency to cracking above a distinct coating thickness. But the appearance, hardness, low contact resistance and corrosion resistance of palladium-iron alloy with a palladium content of 80 wt.-% to 85 wt.-%, make this alloy a serious candidate for the replacement of

palladium-nickel or palladium-cobalt. Palladium-iron alloys with a high amount of iron may be less acceptable for a market with the aim to improve iron coatings because of increasing production costs. Technical developments of the last 10 - 15 years have shown for example that at least one platinum metal alloy electrodeposit, palladium-nickel, is an economic alternative to gold and gold-alloy coatings. Palladium-nickel is well-established for electronic connectors. Unfortunately, especially in the jewellery market, palladium-nickel alloys are in controversial discussion and cannot be used any longer: substitution of the nickel is necessary. While much research has been done on palladium-silver and palladium-cobalt alloy electrodeposition only a few researches have been done on palladium-iron electrodeposition.

The chemistry of the designed palladium-iron electrolyte is simple, stable and obviates the use of additives implying facile maintenance in a manufacturing environment, by minimising the number of chemical constituents, i. e. preferential electrolyte without the use of additional organic additives to act as surface modifiers. The palladium-iron electrolyte possesses wide processing windows, poses little environmental concern, is cost effective and requires little capital investment in specialised equipment for it is exchangeable with existing palladium or palladium-nickel facilities. Despite some limitations, palladium-iron electrodeposits are useful alternative materials in certain applications.

Electrodeposited palladium-iron alloy is subject to the same restrictions and is considerably superior to either palladium-nickel or palladium-cobalt, because iron is the most harmless of these three metals. Therefore, increasing investigations to optimise palladium-iron electrolyte for production lines will be more profitable than optimising electrolytes with an uncertain acceptance.

Therefore, the main conclusions may be condensed as follows:

1. Palladium-iron is a feasible deposit with defined properties and could be an alternative to palladium-nickel coatings.
2. Some palladium-iron solutions have been studied and a preferred formulation is given. However, it requires long-term stability testing and adaptation as an industrial process.
3. A number of applications have been identified for which samples need to be assessed.

The described electrolyte was designed to deposit a true alloy of palladium and iron from aqueous solutions. As a result a chemical and electrochemical stable electrolyte was developed, which allows the electrodeposition of palladium-iron alloys with excellent properties, especially the alloy with ca. 85 wt.-% palladium. Although numerous experiments were carried out during the present investigations, future work will be reasonable to commercialise the demonstrated plating solution.

For use as a connector material additional investigations of the slinging wear behaviour under production conditions of palladium-iron coatings with and without a gold flash will be satisfying. Furthermore, more data about the behaviour of the contact resistance after thermal treatments at typical temperatures and atmospheres would be very helpful to improve the suitability as a commercial process.

In addition, further research about the magnetic properties of electroplated palladium-iron coatings would be very interesting. New properties directed to several applications could be expected from the combination of magnetic materials with noble materials. Especially further experiments with palladium-iron multilayers with palladium-poor (15 wt.-%) and palladium rich (85 wt.-%) phases could extend the potential use of such coatings. Finally, pulse-plating techniques which warrant further investigation could decrease the amount of co-deposited hydrogen on palladium-iron alloys. As a result thick palladium-iron coatings without cracks up to 10 or more μm could be possible.

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Appendix A 1-3 : Palladium-Iron Alloy Electrodeposition: Morphology Characteristics

Sample Nr. 70 - 114																		
	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
Thickness (µm)	8.8	11.0	9.6	15.4	12.6	12.7	15.1	8.3	< 0.1	< 0.1	10.4	< 0.1	4.9	3.8	< 0.1	14.0	3.2	
CD (A/dm²)	3.0	3.0	3.0	5.0	5.0	3.0	5.0	3.0	5.0	5.0	4.0	5.0	3.0	3.0	5.0	5.0	3.0	
Temperature (°C)	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	
Electrolyte: Pd:Fe	1:1			1:100			1:33			1:25			1:15			1:50		
	87	88		89	90	91	92	93	96	97	98	99 ^o		100	101	102	103	
Thickness (µm)	8.3	13.8		12.2	3.9	9.4	5.3	9.8	5.8	6.4	7.3	4.6		16.6	1.1	18.1	7.7	
CD (A/dm²)	3.0	5.0		5.0	3.0	5.0	0.5	5.0	0.5	0.5	0.5	2.0		2.0	3.0	3.0	3.0	
Temperature (°C)	50	50		50	50	50	25	50	25	25	25	45		45	45	45	45	
Electrolyte: Pd:Fe	1:25			1:25			Pd	1:10			Pd			1:1			1:100	
	104 ^o	105 ^o		106 ^o		107 ^o	108 ^o		109 ^o	110	111 ^o	112 ^o	113 ^o	114 ^o				
Thickness (µm)	18.7	< 0.1		1.5		18.9	19.5		2.8	3.1	18.0	30.3	13.5	35.9				
CD (A/dm²)	2.0	5.0		3.0		3.0	3.0		3.0	3.0	3.0	5.0	3.0	5.0				
Temperature (°C)	45	45		45		45	45		45	45	45	45	45	45				
Electrolyte: Pd:Fe	1:3.8			1:5		1:2	1:2.4		1:5	1:100	1:2			1:2.4				
<div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div></div>																		
<div>Electrolyte: Na-Citrate pH: 8.2 25 - 50 °C (NH₄)₂SO₄ 0.5 - 5.0 A/dm²</div>																		

Appendix A 1-4 : Palladium-Iron Alloy Electrodeposition: Morphology Characteristics

		Sample Nr. 115 - 166																								
		115 ^o	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135				
Thickness (µm)		1.5	4.8	7.2	<0.1	4.2	4.4	2.0	2.2	1.0	2.0	0.2	0.6	4.7	0.6	0.5	1.6	<0.1	1.5	5.0	3.5	1.3				
CD (A/dm ²)		5.0	5.0	8.0	8.0	8.0	8.0	5.0	5.0	1.0	1.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0				
Temperature (°C)		45	45	45	45	45	45	45	45	50	50	45	45	45	45	45	45	45	45	45	35	75				
Electrolyte: Pd:Fe		1:100										Au										1:100				
		136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155					
Thickness (µm)		6.6	5.7	2.4	2.4	2.4	2.6	1.6	2.6	3.2	0.5	0.9	4.2	9.2	4.8	1.3	2.6	2.6	5.5	3.6	2.9					
CD (A/dm ²)		3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	8.0	8.0	1.0	5.0	5.0	3.0	0.5	5.0					
Temperature (°C)		35	45	45	45	45	45	45	45	45	45	45	75	75	35	45	55	55	45	45	45					
Electrolyte: Pd:Fe		1:1																				Ni	Fe	Pd	Fe	
		156	157	158	159	160	160 _{1/1}	160 _{1/2}	160 _{1/3}	160 _{1/4}	161	161 _{1/3}	162	163	164	165	166	① Electrolyte: (NH ₄) ₂ -Citrate NH ₄ Cl								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100										1:100 (26 g/l Fe ; 0.5 g/l Pd)										Magnification 200 x				
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								
Thickness (µm)		7.0	1.1	14.4	2.2	0.5	0.3	1.6	6.0	3.0	2.4	2.0	1.1	1.7	1.3	1.3	4.0									
CD (A/dm ²)		8.0	8.0	8.0	8.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	3.0									
Temperature (°C)		35	75	25	75	45	45	45	45	45	45	45	45	45	45	45	45									
Electrolyte: Pd:Fe		1:100 (26 g/l Fe ; 0.5 g/l Pd)																								
		1:1																								

Appendix A 1-5 : Palladium-Iron Alloy Electrodeposition: Morphology Characteristics

Sample Nr. 167 - 210																							
	167	168 _{1/1}	168 _{1/2}	168 _{1/3}	168 _{1/4}	168 _{1/4}	169 _{1/1}	169 _{1/2}	169 _{1/3}	170	171	172 _{1/1}	172 _{1/2}	173	174	175	176	177	178				
Thickness (µm)	< 0.1	< 0.1	1.2	1.3	2.0	2.3	1.3	0.7	2.0	1.6	2.4	--	3.0	2.6	--	--	--	--	--				
CD (A/dm²)	3.0	3.0	3.0	3.0	3.0	3.0	8.0	3.0	5.0	3.0	3.0	3.0	3.0	3.0	2.0	2.0	2.0	1.0	1.0				
Temperature (°C)	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45				
Electrolyte: Pd:Fe	1:100																						
Thickness (µm)	1.9	2.7	4.3	4.3	8.9	3.1	2.2	2.3	6.9	1.0	3.6	5.2	0.5	3.1	0.3	6.0	8.0	1.8	2.1	3.2	3.0	7.0	13.0
CD (A/dm²)	8.0	8.0	4.0	3.0	5.0	5.0	5.0	3.0	5.0	3.0	3.0	8.0	5.0	5.0	8.0	8.0	5.0	3.0	8.0	8.0	3.0	8.0	8.0
Temperature (°C)	75	75	75	25	25	35	35	35	45	45	45	45	75	75	75	45	45	45	45	45	45	65	65
Electrolyte: Pd:Fe	1:100																						
Thickness (µm)	3.5	2.2	3.0	1.9	0.8	1.5	2.0	6.3	0.6	0.8	5.1	0.8	1.5										
CD (A/dm²)	5.0	8.0	8.0	5.0	3.0	3.0	8.0	8.0	8.0	5.0	5.0	3.0	4.0										
Temperature (°C)	65	65	65	65	65	65	65	65	65	65	65	65	65										
Electrolyte: Pd:Fe	1:100													Magnification 200 x									
														Electrolyte: (NH ₄) ₂ -Citrate pH: 8.2 25 - 75 °C 1.0 - 8.0 A/dm²									
Bright Bright & Cracks Bright & Nodular Dull Dull & Cracks Dull & Nodular Cracks Nodular Brittle Black & Nodular																							

Appendix A 1-6 : Palladium-Iron Alloy Electrodeposition: Morphology Characteristics

Sample Nr. 211 - 260																						
	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225 _{1/1}	225 _{1/2}	225 _{1/3}	226	227	228	229	
	Hull-cell	Hull-cell																	Hull-cell	Hull-cell	Hull-cell	
Thickness (µm)	--	--	9.0	9.8	11.3	9.7	10.4	5.5	5.2	8.9	9.4	18.2	7.2	10.1	9.1	4.7	3.8	--	--	--	--	
CD (A/dm ²)	2.0	2.0	5.0	3.0	8.0	8.0	8.0	5.0	5.0	8.0	8.0	5.0	4.0	8.0	5.0	5.0	5.0	2.0	2.0	2.0	2.0	
Temperature (°C)	25	35	25	35	35	45	45	75	75	75	25	45	65	65	65	65	65	65	35	45	75	
Electrolyte:Pd:Fe	1:1																		1:1			
	230 _{1/1}	230 _{1/2}	230 _{1/3}	230 _{1/4}	231 _{1/1}	231 _{1/2}	231 _{1/3}	232	233 _{1/1}	233 _{1/2}	233 _{1/3}	233 _{1/4}	235	236	237	238	239	240	241	242	243	244
Thickness (µm)	2.5	0.7	1.4	1.0	0.6	1.0	3.2	5.4	1.0	0.5	2.8	2.0	2.0	2.0	1.0	0.5	0.7	0.9	0.5	0.3	1.1	0.2
CD (A/dm ²)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	5.0	3.0	3.0	3.0	3.0	5.0	5.0	5.0	5.0	3.0
Temperature (°C)	65	65	65	65	25	25	25	75	75	75	75	75	50	50	50	50	50	50	50	50	50	50
Electrolyte:Pd:Fe	1:100										1:100											
	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260						
Thickness (µm)	1.4	2.4	0.4	0.8	0.6	3.0	1.4	<0.1	1.0	2.1	2.1	1.2	0.1	11.5	6.4	5.6						
CD (A/dm ²)	2.5	2.5	2.5	4.0	3.0	3.0	3.0	3.0	3.0	5.0	5.0	5.0	4.0	3.0	5.0	3.0						
Temperature (°C)	40	40	40	40	60	60	60	60	60	60	60	60	60	25	25	25						
Electrolyte:Pd:Fe	1:1										Magnification 200 x											

Appendix A 1-7 : Palladium-Iron Alloy Electrodeposition: Morphology Characteristics

Sample Nr. 261 - 299																
	261	262	263	264	265	266	267	268	269	270	271	272	273	275		
Thickness (µm)	6.6	11,8	11.9	8.7	6.3	4.2	4.8	3.9	10.0	3.6	7.3	11.1	11.4	15.8		
CD (A/dm²)	8.0	3.0	5.0	5.0	3.0	8.0	5.0	5.0	8.0	3.0	8.0	3.0	8.0	5.0		
Temperature (°C)	25	35	35	35	35	35	35	35	35	65	65	45	35	45		
Electrolyte: Pd:Fe	1:100	1:1			1:1	1:100	1:1			1:100		1:1	1:100	1:1		

	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290
Thickness (µm)	7.6	16.4	12.6	6.2	6.1	10.8	8.2	6.1	5.4	0.6	8.6	11.4	1.0	0.9	7.7
CD (A/dm²)	5.0	4.0	4.0	4.0	3.0	3.0	3.0	3.5	3.0	4.0	3.0	3.0	3.0	3.0	5.0
Temperature (°C)	50	50	50	50	60	55	65	65	65	55	25	25	25	25	25
Electrolyte: Pd:Fe	1:100			1:1			1:1			1:100	1:1		1:100	1:1	1:1

	291	292	293	294	295	296	297 _{1/1}	297 _{1/2}	297 _{1/3}	297 _{1/4}	298	299 _{1/1}	299 _{1/2}	299 _{1/3}	299 _{1/4}
Thickness (µm)	1.9	2.9	0.6	1.3	8.0	0.7	1.6	2.2	3.5	1.0	1.5	4.8	2.0	3.5	0.5
CD (A/dm²)	3.0	3.0	3.0	3.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	3.0	3.0	3.0	3.0
Temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Electrolyte: Pd:Fe	1:100			1:1			1:100								
Magnification 200 x															

Bright	Bright & Cracks	Bright & Nodular	Dull	Dull & Cracks	Dull & Nodular	Dull & Cracks	Dull & Nodular	Dull & Cracks	Dull & Nodular	Dull & Cracks	Dull & Nodular	Dull & Cracks	Dull & Nodular
Electrolyte: (NH ₄) ₂ -Citrate pH: 8.2 25 - 65 °C 3.0 - 8.0 A/dm²													

Sample Nr. 300 - 350																														
	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316													
																				Internal Stress Measurement										
Thickness (µm)	2.5	2.5	5.4	5.3	7.7	8.1	18.0	12.0	14.0	15.2	12.2	10.1	12.7	13.0	20.0	22.0	0.8													
CD (A/dm²)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	8.0	3.0	8.0	8.0	8.0	8.0	3.0													
Temperature (°C)	45	45	45	45	45	45	45	45	45	45	75	65	75	45	45	45	25													
Electrolyte: Pd:Fe	1:1										1:100																			
	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334												
Thickness (µm)	1.4	3.4	1.2	1.3	1.4	13.2	12.4	10.0	13.5	17.0	13.0	14.9	12.8	1.5	2.5	2.7	5.5	5.1												
CD (A/dm²)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	5.0	8.0	8.0	5.0	5.0	5.0	3.0	3.0	3.0	3.0												
Temperature (°C)	35	35	35	35	35	45	65	75	65	65	65	65	65	25	25	65	65	65												
Electrolyte: Pd:Fe	1:1										1:100										1:1									
	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350														
Thickness (µm)	8.2	8.0	16.2	16.1	10.8	14.8	6.6	4.4	2.3	4.5	13.2	7.2	3.5	1.9	--	--														
CD (A/dm²)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.0	2.0														
Temperature (°C)	65	65	65	65	65	75	75	75	75	75	75	75	75	75	25	35	Magnification													
Electrolyte: Pd:Fe	1:1										1:1										200 x									
	Bright & Cracks										Bright & Nodular										Dull & Cracks		Dull & Nodular		Brittle		Black & Nodular		Electrolyte: (NH ₄) ₂ -Citrate pH: 8.2 25 - 65 °C 3.0 - 8.0 A/dm² (NH ₄) ₂ SO ₄	

Appendix A 1-10 : Palladium-Iron Alloy Electrodeposition: Morphology Characteristics

Sample Nr. 406 - 455																							
	406	407	408	409	410	411	412	413	414	415	416 _{/1}	416 _{/2}	417	418	419	420	421	422					
Thickness (µm)	9.4	4.8	5.3	2.5	2.8	6.9	5.5	12.9	9.6	5.7	4.4	1.9	5.1	< 0.1	< 0.1	--	--	--					
CD (A/dm²)	3.0	2.0	1.0	1.0	0.5	0.5	0.5	2.5	3.0	4.0	3.0	3.0	5.0	1.0	3.0	2.0	2.0	2.0					
Temperature (°C)	70	75	75	35	35	25	45	60	55	55	55	55	55	55	55	65	65	65					
Electrolyte:Pd:Fe	1:1												1:4		1:50				1:20	1:1			
	423	424	425	426	427	428	429	430	431	432	433	434	435	436 ^①	437 ^①	438 ^①	439 ^①	440 ^①	441 ^①				
	Hull-cell																						
Thickness (µm)	--	1.2	13.9	60.9	1.6	15.3	19.3	18.9	1.2	7.0	6.0	< 0.1	21.9	--	--	2.0	2.0	2.0	2.0				
CD (A/dm²)	3.0	3.0	8.0	8.0	3.0	5.0	5.0	8.0	3.0	3.0	3.0	3.0	3.0	2.0	2.0	2.0	2.0	2.0	2.0				
Temperature (°C)	55	55	55	55	55	55	55	55	55	55	55	55	55	65	65	65	65	65	65				
Electrolyte:Pd:Fe	1:50	1:100													1:20		1:10				1:1 + WA		
	442 ^①	443 ^①	444 ^①	445 ^①	446	447 ^①	448 ^②	449 ^②	450 ^②	451 ^②	452 ^②	453 ^②	454 ^②	455 ^②									
	Hull-cell	Hull-cell	Hull-cell	Hull-cell																			
① Basic Electrolyte 1:1 + Pallanic Wetting Agent 4317™ Engelhard-Clal, Cinderford, UK																							
② Palladure 150™ Lea Ronal, Birkenfeld, Germany																							
Thickness (µm)	--	--	--	--	2.7	5.0	7.4	5.6	5.4	27.6	13.1	6.4	4.6	3.1									
CD (A/dm²)	3.0	2.0	2.0	2.0	3.0	3.0	1.5	1.5	1.5	2.0	2.0	2.0	1.0	1.0									
Temperature (°C)	65	65	65	65	45	45	45	45	45	45	45	45	45	45									
Electrolyte:Pd:Fe	1:10	1:1 + WA			1:1	1:1 + WA	Pd: 8 g/l (Palladure 150™)								Magnification 200 x								
	Bright & Cracks	Bright & Cracks	Bright & Nodular	Dull	Dull & Cracks	Dull & Cracks	Dull & Cracks	Dull & Cracks	Dull & Cracks	Dull Cracks Nodular	Brittle	Black & Nodular	Electrolyte: (NH ₄) ₂ -Citrate pH: 8.2 25 - 75 °C (NH ₄) ₂ SO ₄ 0.5 - 8.0 A/dm²										

Appendix A 1-12 : Palladium-Iron Alloy Electrodeposition: Morphology Characteristics

Sample Nr. 500 - 549																					
	500	501	502	503	504	505	506	507 _{1/1}	507 _{1/2}	508	509 _{1/1}	509 _{1/2}	510	511	512	513	514	515	516	517	518
Thickness (µm)	0.8	1.6	2.5	1.0	1.8	1.7	9.5	0.5	2.7	1.2	3.5	2.2	3.2	0.9	1.5	2.9	1.0	1.8	1.0	1.7	2.8
CD (A/dm²)	3.0	3.0	3.0	5.0	5.0	5.0	8.0	5.0	5.0	8.0	3.0	8.0	8.0	5.0	5.0	5.0	8.0	8.0	3.0	3.0	3.0
Temperature (°C)	35	35	35	25	25	25	25	25	25	25	25	25	25	35	35	35	25	25	45	45	45
Electrolyte: Pd:Fe	1:1																				
	519	520	521	522 _{1/1}	522 _{1/2}	523	524	525	526	527	528	529	530	531	532						
Thickness (µm)	0.8	1.5	1.7	2.8	3.0	2.6	0.9	0.9	0.8	1.7	2.5	1.7	1.3	0.8	2.1						
CD (A/dm²)	3.0	3.0	3.0	3.0	8.0	3.0	5.0	5.0	5.0	5.0	5.0	5.0	8.0	8.0	8.0						
Temperature (°C)	35	35	35	45	45	35	35	45	35	45	45	35	45	35	35						
Electrolyte: Pd:Fe	1:100																				
	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	Magnification 200 x				
																	1:1				
Thickness (µm)	3.5	0.3	0.8	1.0	1.9	0.5	1.1	0.2	1.1	2.0	6.1	2.5	1.3	0.7	5.5	2.1	1:1				
CD (A/dm²)	8.0	8.0	8.0	8.0	8.0	5.0	5.0	3.0	3.0	5.0	3.0	3.0	8.0	3.0	3.0	3.0	1:1				
Temperature (°C)	35	45	45	45	45	45	45	45	55	55	55	55	55	65	65	65	1:1				
Electrolyte: Pd:Fe	1:1																200 x				
																	Electrolyte: (NH ₄) ₂ -Citrate pH: 8.2 25 - 65 °C 3.0 - 8.0 A/dm²				
																	<div> Bright</div> <div> Bright & Cracks</div> <div> Bright & Nodular</div> <div> Dull</div> <div> Dull & Cracks</div> <div> Dull & Nodular</div> <div> Dull Cracks Nodular</div> <div> Brittle</div> <div> Black & Nodular</div>				

Appendix A 1-13 : Palladium-Iron Alloy Electrodeposition: Morphology Characteristics

Sample Nr. 550 - 594

	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569
Thickness (µm)	2.8	1.8	1.9	1.3	1.6	10.7	1.1	2.3	7.0	0.7	1.2	2.1	1.7	0.7	1.0	5.8	3.3	0.4	0.6	0.7
CD (A/dm²)	5.0	8.0	5.0	5.0	8.0	5.0	8.0	8.0	3.0	3.0	5.0	8.0	3.0	3.0	3.0	5.0	8.0	5.0	8.0	3.0
Temperature (°C)	65	65	65	65	65	65	65	65	75	75	75	75	55	55	55	55	55	55	55	55
Electrolyte: Pd:Fe	1:1										1:100									
Thickness (µm)	0.5		0.8		0.4	0.9		0.7	1.1		1.3		2.8	1.8	1.2	1.0	3.4	6.9		
CD (A/dm²)	3.0		3.0		5.0	8.0		3.0	5.0		5.0		5.0	5.0	5.0	8.0	8.0	3.0		
Temperature (°C)	65		60		65	65		65	55		65		55	65	25	65	55	65		
Electrolyte: Pd:Fe	1:100		1:1		1:100		1:1				1:100		1:1		1:100			1:1		
Thickness (µm)	0.3	3.4																		
CD (A/dm²)	3.0	3.0																		
Temperature (°C)	75	75																		
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							
Thickness (µm)	0.3																			
CD (A/dm²)	3.0				3.0	5.0	8.0	5.0	8.0		8.0		8.0	8.0						
Temperature (°C)	75				55	55	55	75	75		35		25	25						
Electrolyte: Pd:Fe	1:100					1:1							1:100							

Appendix A 2-1 : Internal (Tensile) Stress (N/mm²) of Electroplated Palladium-Iron Alloys

Sample Nr	Electrolyte Pd : Fe	CD (A/dm²)	T (°C)	Layer thickness (µm)															
				0.1	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.5	3.0	4.0	5.0	7.0	10.0	
300	1 : 1	3.0	45	200	350	425	435	450	450	445	435	430	430	-	-	-	-	-	
301	1 : 1	3.0	45	210	355	465	470	475	450	445	435	425	425	-	-	-	-	-	
302	1 : 1	3.0	45	255	380	500	520	525	530	535	510	500	475	450	370	270	-	-	
303	1 : 1	3.0	45	280	330	465	480	525	525	500	480	470	460	450	380	290	-	-	
304	1 : 1	3.0	45	240	380	480	500	520	525	530	525	510	480	450	350	270	170	100	
305	1 : 1	3.0	45	280	390	500	520	525	530	530	520	500	490	480	380	300	190	-	
308	1 : 1	3.0	45	245	380	480	495	520	525	530	525	510	475	450	345	265	150	100	
309	1 : 1	3.0	45	250	380	480	500	515	520	530	520	515	480	450	350	265	155	100	
330	1 : 1	5.0	25	300	250	255	245	235	225	225	220	220	220	215	215	215	215	215	
331	1 : 1	3.0	25	280	300	350	380	400	410	405	400	390	340	-	-	-	-	-	
332	1 : 1	3.0	65	300	350	380	400	450	470	450	440	435	430	-	-	-	-	-	
333	1 : 1	3.0	65	290	340	390	420	440	445	440	435	420	400	360	300	290	-	-	
334	1 : 1	3.0	65	300	350	380	410	435	450	450	435	435	430	390	300	280	-	-	
335	1 : 1	3.0	65	280	310	330	380	420	430	405	400	390	375	350	320	29	180	-	
336	1 : 1	3.0	65	300	350	380	400	420	430	440	420	385	370	345	315	270	180	110	
337	1 : 1	3.0	65	310	350	380	400	415	425	440	415	380	370	350	345	270	180	110	
338	1 : 1	3.0	65	300	350	380	400	420	430	440	420	385	370	345	315	270	180	110	
340	1 : 1	3.0	75	250	285	330	335	340	345	355	340	330	320	300	280	230	170	110	
341	1 : 1	3.0	75	250	290	320	330	345	350	345	340	330	320	300	300	-	-	-	
342	1 : 1	3.0	75	245	290	325	330	335	340	350	335	320	310	300	270	230	160	100	
343	1 : 1	3.0	75	245	280	320	330	345	350	345	340	330	310	300	270	230	-	-	
345	1 : 1	3.0	75	250	285	330	335	340	345	355	340	330	320	300	280	230	170	110	

Appendix A 2-3 : Internal (Tensile) Stress (N/mm²) of Electroplated Palladium-Iron Alloys

Sample Nr	Electrolyte Pd : Fe	CD (A/dm ²)	T (°C)	Layer thickness (µm)															
				0.1	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.5	3.0	4.0	5.0	7.0	10.0	
310	1 : 100	8.0	75	170	155	145	140	130	130	120	115	115	110	110	110	105	105		
311	1 : 100	3.0	65	265	355	345	340	330	330	320	305	300	285	275	255	180	180		
312	1 : 100	3.0	75	250	330	305	300	300	295	290	280	270	270	250	230	170	170		
313	1 : 100	8.0	45	225	190	155	145	145	145	140	135	130	125	125	120	120	120		
314	1 : 100	8.0	45	230	180	165	150	145	145	130	125	120	120	115	115	110	110		
315	1 : 100	8.0	45	225	190	165	155	145	145	130	135	130	120	120	120	120	120		
322	1 : 100	3.0	45	180	190	210	205	200	200	195	190	190	180	150	145	140	135		
323	1 : 100	3.0	65	270	335	325	325	320	320	315	310	310	315	275	245	200	200		
324	1 : 100	3.0	75	250	345	325	300	290	285	270	260	260	255	250	245	170	165		
325	1 : 100	5.0	65	180	205	200	195	190	195	210	210	210	210	210	210	210	210		
326	1 : 100	8.0	65	200	165	150	135	130	125	120	120	115	115	115	110	110	110		
327	1 : 100	8.0	65	190	170	150	140	135	130	120	115	110	110	110	110	110	110		
328	1 : 100	5.0	65	175	200	200	200	195	195	190	190	190	190	190	190	190	190		
329	1 : 100	5.0	65	180	200	205	200	200	200	200	200	200	200	200	200	200	200		
361	1 : 100	5.0	45	230	235	240	235	230	230	225	220	220	215	215	215	210	210		
362	1 : 100	5.0	45	245	235	235	225	220	220	215	210	210	205	205	205	200	200		
363	1 : 100	5.0	45	230	235	240	235	230	230	225	215	215	215	215	215	210	210		
364	1 : 100	8.0	75	140	130	125	120	115	115	115	115	115	110	110	110	110	110		
365	1 : 100	3.0	45	200	195	210	205	200	195	190	180	180	170	150	140	135	135		
366	1 : 100	8.0	75	135	130	125	125	125	125	120	120	115	110	105	105	100	100		
403	1 : 100	5.0	75	100	120	115	120	125	115	120	125	120	120	120	120	120	120		
404	1 : 100	5.0	75	110	120	125	120	120	115	110	110	110	110	110	110	110	110		

Appendix A 3-1 : Synthetic Perspiration Test ISO 3160-2 : 1992

ISO 3160 - 2: Watch cases and accessories - gold alloy coverings - Part 2:
Determination of fineness, thickness, corrosion resistance and adhesion

7. 4 Testing with saline and acidic agents (synthetic perspiration test)

The test was carried out in a closed Pyrex glass vessel, which can be heated to 40 °C. The samples were suspended on glass hooks at a distance of at least 30 mm from the liquid and the walls of the vessel. The vessel was filled with the test solution to a depth of about 10 mm. Before the samples were placed in the test atmosphere a fine mist of the test solution was sprayed over the surface of the samples. This procedure was repeated after 24 hours, in this case the duration of test was 48 hours. The temperature during the test was 40 ± 2 °C.

Synthetic Perspiration Test

Test Solution:

sodium chloride : 20.0 g/l

ammonium chloride : 17.5 g/l

urea : 5.0 g/l

acetic acid : 2.5 g/l

lactic acid : 15.0 g/l

sodium hydroxide : pH = 4.7