



The William Blum Lectures

#34 – Christoph J. Raub - 1993



The 34th William Blum Lecture
Presented at the 80th AESF Annual Convention (SUR/FIN 1993)
in Anaheim, California
June 21, 1993

Hydrogen in Electrodeposits: Of Decisive Importance, but Much Neglected

by
Prof. Dr. Christoph J. Raub
Recipient of the 1992 William Blum
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1992-93 AESF President Richard O. Watson, CEF (L), presents the Scientific Achievement Award to Prof. Dr. Christoph H. Raub at SUR/ FIN 1993.



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Editor's Note: Originally published as *Plating and Surface Finishing*, 80 (9), 30-38 (1993), this article is re-publication of the 34th William Blum Lecture, presented at the 80th AESF Annual Convention (SUR/FIN 1993) in Anaheim, California on June 21, 1993.

ABSTRACT

Because water is the base of most electrolytes the electroplater must handle, hydrogen's influence on the properties of various layers in the electrodeposition process is very important. How and why this is true will be discussed in this lecture, presented by the author at the Opening Session of SUR/FIN 1993.

The element "hydrogen" was first identified in 1766, by English scientist H. Cavendish. Two years later, he also discovered that this newly identified gas, together with oxygen, formed water. The name, in fact, comes from the Greek words for "water" and "forming."



Figure 1 - Cover sheet from T. Graham's textbook published in 1840.

Earlier, Cavendish's fellow countryman J. Priestley had observed that water changes its properties if it comes in contact with electrical current. In 1781, Laurent Lavoisier and Simon LaPlace continued Priestley's work, corroborating in 1782 with A. Volta, who had just invented his famous cell. Their investigations came to a premature end, however, in 1794, when Lavoisier was murdered near the end of the French Revolution -an early case of politics having a negative impact on science!

Among the many names also connected with electrolysis of water, W. Cruikshaw, W. Nicholson and A. Carlisle - all early 19th-century English physicians - are worthy of mention. A German chemist, V. Gruner, and a school teacher, K.W. Böckmann, also became interested in this study. It was Böckmann who coined the expressions "oxygen wire" (anode) and "hydrogen wire" (cathode), on the latter of which metals deposited.¹

The first one to realize that electrodeposited metals may contain fairly high amounts of gases (*i.e.*, hydrogen) was T. Graham, a professor at London University and, later, Director of the Royal Mint, co-founder of the Chemical Society, and author of one of the earliest textbooks on chemistry - a German translation of which had been published by F.J. Otto in 1640.² (Fig. 1.)

The inventor of electroforming, Russian-German M.H. Jacobi, studied the work of Graham, and in 1872 recognized that electrodeposited iron contained "volatile" compounds.³ He had observed, for instance, that electrolytic iron - depending on deposition conditions - has a density of 7.675 g/cm³, which increases in annealing to 7.811, but is lower than the 7.87 of cast, pure iron. He found that annealing reduced hardness and improved brittleness. So he got his friend, R.E. Lenz, to study these effects in greater detail.



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Lenz, a professor from St. Petersburg, found that electrodeposited iron contains appreciable amounts of gases, such as nitrogen, carbon dioxide, and particularly hydrogen, making it hard and brittle.⁴ In annealing, the gases disappeared and the material got softer. He also noted that the side of the deposit that faced the anode contained less hydrogen and was softer than the opposite side. Lenz published an article on his findings, and a year later, Jacobi published one about Lenz's results in the *Annals of the Academy of St. Petersburg*.^{5,6}

There are some very interesting side notes on the observations that came out of St. Petersburg:

- By controlling "gas" concentration and maintaining proper deposition parameters, the Treasury Printing Press in St. Petersburg was able to prepare long-lasting electrotypes of iron or iron composites, as well as objects of art in iron during the last quarter of the 19th century - more than 100 years ago!

An example of the advantageous effect of electroplated iron is that cast electrotypes normally lasted for about 50,000 prints, while a combination of electroformed copper base and hard iron top layer, heat treated, can hold up for as many as seven million impressions.

- What began in the late 1970s continues today: The task of reducing the weight of automobiles to save energy, which increased interest in lighter, aluminum engines. To maintain excellent wear between, cylinders are cast in an Al-Si alloy and later etched to generate protruding silicon particles. Pistons are coated on top with a layer of hard iron, having about the same hardness (more than 800 HV) as hard chromium.⁷
- Hard iron, properly deposited with adjusted "gas and impurity" content, whether heat treated or not, might become an environmentally safe substitute for hard chromium - all the more because the former's properties can be patterned in a wide range, to specific applications.
- The Russian observation of hard iron is a prime example of how accurate observation and explanation of an unexpected effect, which looked purely academic in the beginning, can lead to a tremendous improvement on an existing product, as well as to economic advantages. Iron plating brought the Treasury Printing Press in St. Petersburg such fame that large companies from outside Russia sent their copper electrotypes there because they could not get hard iron coatings of such quality anywhere else.⁸

Theoretical Background

Hydrogen Deposition

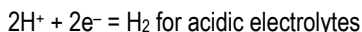
Water is the base of most electrolytes the electroplater must handle, so hydrogen deposition is critical. Some basics will be discussed, before attention is shifted to codeposition of hydrogen and its influence on the properties of various layers. The influence of hydrogen on the base material (*i.e.*, on steel) will not be considered, because this is quite a problem in itself - in many cases arising in such pre-treatment steps as electrolytic cleaning.

In water, the hydrogen ion is present in the hydrated form, with one water molecule bound to it, making it, actually, H_3O^+ . For its discharge, it must be dehydrated in a preliminary step. This takes place in the outer section of the Helmholtz double layer and can occur in several steps. The migration of the hydrated ion to its discharge is determined by at least three processes: The transition of the ion into the outer diffusion range of the Helmholtz layer, where migration is determined to be the concentration gradient, convection and migration in the electric field. Field strength is still rather low and cannot remove the water molecule from the ion, but it is strong enough to generate an orientation of the water dipoles, according to Gerischer.⁹ The hydrogen ion then migrates through the diffusion range of the double layer to its fixed section closest to the cathode where field strength is relatively high (107 V/cm) and H_2O molecules are torn away from the H^+ ion. The hydrogen is then adsorbed at the metallic cathode and discharged. This is, indeed, a simplified explanation, but it describes the essential steps.

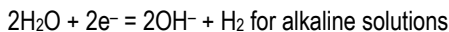
Of the three possible mechanisms that may determine movements of hydrated ions, convection can be virtually eliminated by working at zero gravity, in an outer-space experiment. This was done about 15 years ago, and clearly revealed the differences in

the behavior of hydrogen bubbles, especially in their growth and adhesion to various cathodes (*e.g.*, gold and platinum) (Fig. 2).¹⁰

The overall equation for the discharge of hydrogen at the cathode can be written:



or



In this case, hydrogen is deposited directly from water.

There are, however, quite a number of steps until hydrogen gas finally forms:⁹

1. Transport of the hydrogen ions into the double layer
2. Discharge and change from a solvation bond with water, to an adsorption bond with the cathode metal

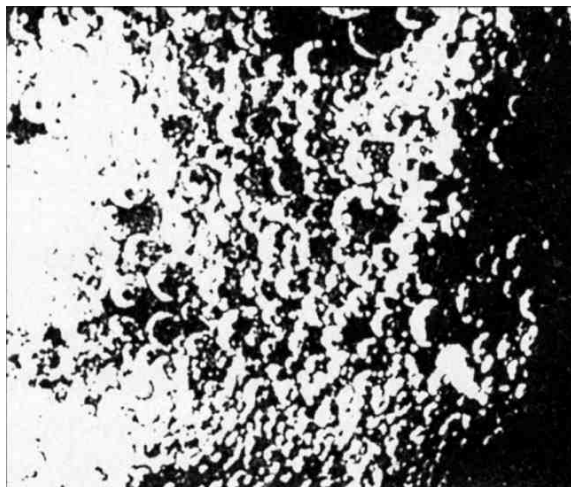
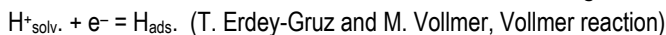
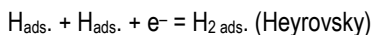
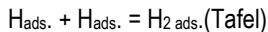


Figure 2 - Hydrogen bubbles at the cathode, at zero gravity.



Here, for the first time, we encounter H_2 atoms adsorbed.

The $\text{H}_{\text{ads.}}$ atoms now will react at the cathodic surface with other $\text{H}_{\text{ads.}}$ or $\text{H}^+_{\text{ads.}}$ atoms and form $\text{H}_2_{\text{ads.}}$



- a) Desorption of the adsorbed H_2 from the cathode and transition into the electrolyte
- b) Removal of H_2 by diffusion and dissolution on the electrolyte or as hydrogen bubbles

Details of steps a and b can be seen nicely in the above-mentioned zero-gravity experiment. At first, hydrogen bubbles grow while sticking to the cathodic surface and pushing each other around as they grow. Another part of the hydrogen dissolves in a zone close to the cathode, while the rest of the electrolyte remains rather poor in dissolved hydrogen, because of the missing convection. Once bubbles reach a certain size, they push each other away from the cathode, into the electrolyte, and after drifting through a hydrogen-gas-enriched zone, they get smaller again, because of the dissolution in the remaining electrolyte, which is low in hydrogen.¹⁰

This adsorption of hydrogen on various metals is technically important in a bubble chamber for studying hydrodynamic flow patterns around profiles. In a chamber filled with electrolytes, a system of cathodically polarized, suspended fine Au or Pt wires is moved through the electrolyte, leaving rows of tiny gas bubbles in solution for a while. A three-dimensional line pattern is formed, through which the profiles to be tested are pulled. If the system is illuminated from the side, the movement of the strings of bubbles around the profiles can be watched. For this system to function properly, a uniform and equally sized generation of the bubbles, along with an appropriate detachment from the cathode, is essential.

The problem of the ad-hydrogen atoms or molecules is a serious one, for nearly every electrochemical process - from fuel cell to battery, and from electroplating of zinc and chromium to the large-scale electrolytic decomposition of water for energy production or storage.

The reversible equilibrium potential of hydrogen deposition is only observed with a special Pt-electrode, covered with Pt-black. In nearly every other case, it is hemmed - or "polarized" - by various effects, summarized by the term "overvoltage." This

hydrogen overvoltage depends on a number of factors, such as temperature, kind of cathodic metal, structure and composition of the cathode's surface, hydrogen pressure and composition of the electrolyte, etc.

In water, with step number one, the concentration polarization is negligible. Of the rate-determining steps, the final one is the slowest, and rate depends on the deposition conditions.

It should be mentioned that the over-voltage ΔE varies with current density " i ," according to the Tafel equation:

$$\Delta E = a - \log i$$

Simultaneous discharge of hydrogen and metals

In two detailed papers, A. Knödler studied the simultaneous discharge of hydrogen with metals and the penetration of hydrogen through electrodeposits.^{11,12}

In electroplating, codeposition of hydrogen with metals is a very important effect, and it can be positive, as well as negative for the electroplater. The positive aspect is the very effective stirring action by gas evolution at an electrode. N. Ibl did calculations showing that this gas stirring is the most active agitation we have in electroplating - most actively reducing thickness of the diffusion layer. At the same time, hydrogen bubbles may shield the cathode, preventing deposition; or also becoming incorporated, creating defects in the layers or even forming alloys, as with palladium. Hydrogen, too, may penetrate the electroplate, especially when it is still porous and defective, and react with the base.^{11,12}

When electroplating from aqueous electrolytes, always keep codeposition of hydrogen in mind, because it can be polarized strongly, but depolarized as well, by constituents of practical electrolytes.

From a theoretical point of view, codeposition of hydrogen can be treated like alloy deposition, considering metal hydrogen systems as alloys, too.

For alloy deposition, imagine three possible cases, illustrated in Fig. 3.⁷

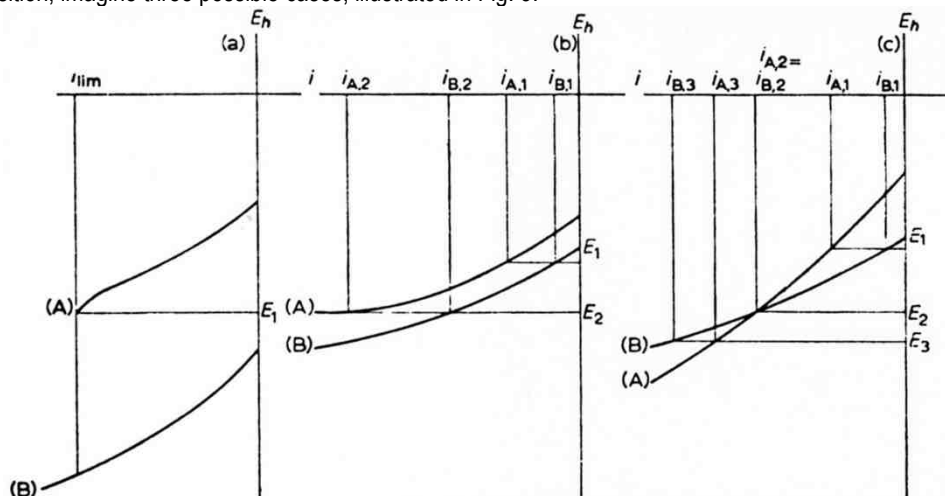


Figure 3 - Cathode potential partial current curves for deposition of two cations A and B.

In case "a," the potential-partial current density curves of both elements to be discharged are set quite apart. At first, the most noble partner, "A," is discharged until, at E_1 , its limiting current density is observed. The potential then becomes less noble and the deposition of the less noble partner "B," starts - this, in many cases, being hydrogen. The deposition of partner "A" will continue the same - absolutely - but diminish, relative to the total amount. In case "b," the two curves are closer. Deposition of the less noble metal begins at potentials that are somewhat close together, with nearly the same partial current densities. Depending on the slope of the potential current density curves, relative deposition of both constituents may differ at low and high



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current densities - as is observed, in reality. If both curves intersect with each other, the two partial current densities are equal. Before and after reaching the intersection - at higher and at lower current densities - the constituents being most strongly discharged may change. This is the often-observed current density effect in alloy deposition, influencing such parameters as current efficiency and composition.

This discussion presumes "ideal conditions," but reality is often different. In most cases, for example, current potential curves of separate metals modify each other during alloy deposition. Another strong influence on the shape of current-potential curves is shown by additives, temperature and chemical changes in the electrolyte caused by ongoing electrolysis.

For hydrogen deposition, in general, concentration polarization is of little direct influence. In a real electrolyte, however, because of concentration or pH changes, it can alter during electrolysis and hydrogen - in the same electrolyte - will be codeposited, more or less. It is even more critical, if we consider the conditions at the various spots of the cathode - especially on a microscopic scale, with the surface of the cathode geometrically, chemically and structurally different, to name a few factors of influence. There may be sites of high and low overpotential for hydrogen discharge; there may be electron tunneling effects through naturally existing oxide layers or through adsorbed monomolecular or even atomic films, all altering deposition conditions for the partners - especially for hydrogen.

Copper from acidic baths and silver from cyanide electrolytes normally are deposited, at the usual current density, with 100% current efficiency. On the other hand, if the limiting current density is exceeded, hydrogen can be enclosed in the layers.

A typical case involves silver flash electrolytes.⁷ The potential current density curves are analogous to Fig. 3b, wherein "B" represents hydrogen. The curve with "A" being hydrogen cannot occur in aqueous electrolytes, because there is no limiting current for hydrogen in aqueous electrolytes, and because there is always ample water available for discharge. Figure 3c, however, represents a very common case. If "A" is the metal, and "B" the hydrogen, the current efficiency for the metal decreases with total current. If "A" is hydrogen and "B" the metal, the current efficiency for metal deposition increases with total current, as in the case of nickel.

E. Raub noted the decisive importance of overvoltage in his book,⁷ and cites the example of zinc deposition: In about one molar (300 g/L) solution of zinc sulfate, the equilibrium potential is near -0.76V. At pH = 3, hydrogen at -0.177V is much nobler, so it should be discharged preferentially. Under these conditions, however, zinc deposits at almost 100% current efficiency, because hydrogen has a tremendous overvoltage on zinc, which shifts its potential to less noble values. On the other hand, zinc cannot be plated on platinum from such an electrolyte because hydrogen overvoltage on platinum is rather low. This overvoltage of hydrogen on certain metals is the explanation as to why some metals can be electroplated, even if they are less noble than hydrogen - far from their equilibrium potentials. D.P. Smith states that hydrogen overvoltage increases from Pd, Pt, Fe, Au, Ag, Ni, Cu, Ta, Sn to Pb and Hg. Metals with the highest hydrogen overvoltage, such as lead and mercury, do not dissolve hydrogen at all.

The influence of hydrogen in practical electrodeposition is often underestimated.¹⁴ Hydrogen not only influences the deposition mechanism and properties directly, by incorporation in the metal and altering mechanical properties, but it has an indirect influence, as well. Hydrogen bubbles formed, for example, can cause a superb stirring action, thereby narrowing down the thickness of the diffusion layer and, by this, increasing partial current density of metal deposition - generally a positive effect - but this, too, may change pH of the cathodic film and facilitate hydrolysis of metal salts that may be adsorbed at the cathode and incorporated into the growing layer. This is seen clearly in transition metal electrolytes, such as those of Pd, Ru and Rh, and Ni. Here, it must be remembered that hydrolysis constants and products are dependent on the kind of anions present: They are different, for instance, for nickel sulfate and chloride.

Another case of indirect hydrogen evolution effects is presented by iron impurities in nickel plating baths, in which iron is only soluble in the divalent state. Oxygen changes it into Fe^{+3} , and at fairly low pH values, ferrihydroxide precipitates, which often exists as a colloid. Because it is positively charged, this colloid is transported to the cathode by cathaphoresis, catches hydrogen molecules or gas bubbles on its way, and the two are incorporated into a growing layer. This may explain, at least in part, why a high hydrogen concentration in a deposit usually goes parallel with other effects (*e.g.*, incorporated constituents of the bath), generating lattice distortions that also favor hydrogen inclusion. Colloidal phenomena may play a role, too, in the



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advantages of using lithium or potassium compounds versus sodium salts. It is wise to quickly oxidize iron in nickel baths, in order to avoid formation of such colloidal iron hydroxide systems.

Adsorbed hydrogen atoms are very reactive and they may reduce other adsorbed molecules or foreign matter included in the substrate. E. Raub discusses the beneficial, though secondary, effect of hydrogen evolution on zinc plating from cyanide baths.^{14,15} Only after passing the limiting current density, do zinc deposits crystallize in a fibrous structure, which is bright and able to be chemically polished. The explanation is that, because of hydrogen evolution, the cathode layer gets a lower pH value, and zinc is discharged favorably via the $Zn(OH)_x$ complex.

The final case of hydrogen is presented by post-deposition reactions of incorporated water molecules - or protons - reacting with the metal matrix, forming hydrogen atoms, which recombine to gaseous hydrogen molecules and exert enough pressure to blow the metal lattice apart. This is discussed further in the section "Hydrogen in Zinc," below.

Under certain circumstances, a similar reaction can be observed in anodized aluminum, where agglomerates of metallic aluminum may react with OH^- or H^+ - after formation of the anodized layer - generating hydrogen bubbles.

Last, but not least, it must be remembered that hydrogen can form stable or metastable hydrides by electrolysis (*e.g.*, NiH, CrH or PdH), which, when present in smaller amounts, determine properties. Some, but unfortunately not all of which can be produced easily on a commercial scale in this manner.

There is only one other alternative method of putting hydrogen into such metallic structures, with similar effects, and that is forcing in hydrogen ions (or protons) by ion implantation. This is the reason the author likes to call the discussed electrochemical hydrogen loading procedure "the poor man's ion implantation method." An electrolysis cell can be made with a spent car battery and a used soft drink cup - costing a few dollars. The cheapest ion implantation unit will be a little more expensive - in the few-million-dollar range!

Now we will look at a few typical cases, most coming from the work of collaborators at the Forschungsinstitut für Edelmetalle und Metallchemie (FEM), but relying on past and ongoing work of other researchers the world over.

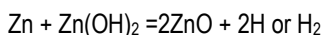
Hydrogen in zinc

Even metals with nearly zero solubility of hydrogen at equilibrium conditions may contain hydrogen, though in smaller amounts, occluded mechanically. It was once believed that this hydrogen was incorporated in molecular form only in these metals,⁷ but Y. Okinaka and H.K. Staschil showed that for electroless copper, hydrogen molecules can form by diffusion of hydrogen atoms and there is no reason why this should be different with other metals.¹⁶ They also demonstrated that molecular hydrogen can remain for quite some time in the layer and not diffuse at room temperature. The story is different for metals with high diffusion rates for hydrogen, such as palladium and other platinum metal group elements (PMGs).

Depending on the plating conditions, zinc and especially bright zinc may contain additives that are adsorbed at the growing cathode and are incorporated. Often, these brighteners are a combination of organics - sometimes polyalcohols - with a fairly high molecular weight and other proprietary chemicals. If, under certain conditions, too much of these additions is incorporated - particularly if they have adsorbed water molecules - water molecules get into the layer. This incorporation may be selective, depending on substrate defects or inclusions and on local current density variations, etc. During storage, especially at elevated temperatures, these water molecules - or zinc hydroxide - can react according to the equations:



or



This hydrogen cannot escape by diffusion through the lattice, but only by diffusion along grain boundaries or along heavily distorted areas. It forms from atoms and molecules that become gas bubbles at sites favored for such a recombination - inclusions, defects, etc., for example. After enough pressure has built up in these bubbles, they can:

- concentrate near the substrate (if they cannot penetrate into it);
- accumulate near a final top coat (wet lacquer or powder coating, because these cannot be penetrated easily by hydrogen molecules, either); or
- just coalesce, statistically, inside the layer.

In every case, a collection of small cavities, or voids, will be seen in a microsection, or depending on length of storage time, a series of smaller-to-larger bubbles (blisters) forms on the deposit's surface. The effect is often very pronounced in powdered-lacquer coatings, because of the sintering step at higher temperatures, promoting the reaction rate of the water. In fact, it is quite common to find the amount of hydrogen in electroplated zinc increasing with time.

Understandably, this reaction and the generation of bubbles and voids in zinc is of great practical and economic importance. It should not be confused with hydrogen embrittlement, even though it may contribute to it, too. According to the author's observations, hydrogen embrittlement is often caused by improper pre-treatment - bad etching, for instance.

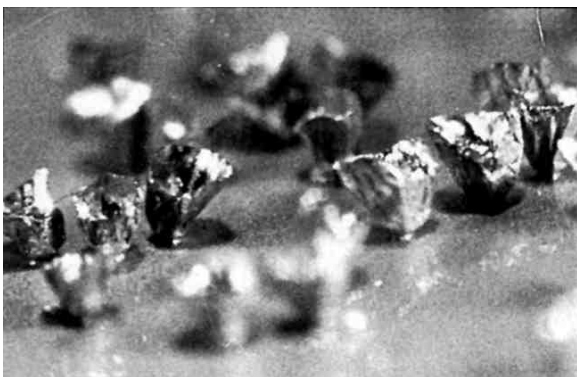


Figure 4 – Cones of zinc, growing at the cathode around hydrogen bubbles.

In addition to this kind of secondary hydrogen formation from water, we definitely have occluded hydrogen present in other forms, as seen in Fig. 4. It is even more interesting, because zinc, if defect-free, can act as a barrier against diffusion of H or H₂.^{14,15} Knödler also observed that the penetration of hydrogen through zinc strongly depends on the deposition parameters - a dense defect-free layer, blocking passage of hydrogen.^{11,12}

Hydrogen in nickel

The codeposition of nickel and hydrogen is one of the most-investigated subjects in electroplating. It is not only of interest to the practical electroplater, but to the theoretical electrochemist and physical chemist specializing in metal hydrides, as well. Because it will be impossible to present even

a semi-qualitative picture on the Ni-H system, the author does not cite any specific literature, but calls the readers' attention to the original papers by B. Baranowski in Warsaw; S. Kaishev and S. Rashkov in Sofia (and their collaborators); work of our American, English and Russian colleagues, along with publications of the FEM. Some of the most recent papers showing how hydrogen charging and discharging can influence mechanical stress in electroplated nickel are by M. Monev,^{17,18,19} (Fig. 5) who also studied the decomposition of NiH by x-ray analysis.^{9,10}

It is sure that hydrogen in electroplated nickel - depending on the deposition conditions - is present in nearly every form possible.

From unpublished results in dehydrogenation experiments of nickel plated at about -15°C, we are fairly sure that hydrogen is present in four to five different states, some being: the solid solution of hydrogen in nickel, the intermetallic phase NiH (most likely HCP, as it is seen by direct x-ray crystallography), and the hydrogen absorbed in different ways (surface, active sites, lattice distortions, etc.). These different bonds of hydrogen-to-nickel showed up in internal stress measurements as well.

It had been thought that hydrogen is present mostly as H, in solid solution in nickel. In addition, it also exists in the form of the metastable phase NiH. Up to now, almost no detailed measurements on the various states of hydrogen in electroplated nickel have existed, so we can only offer preliminary observations.

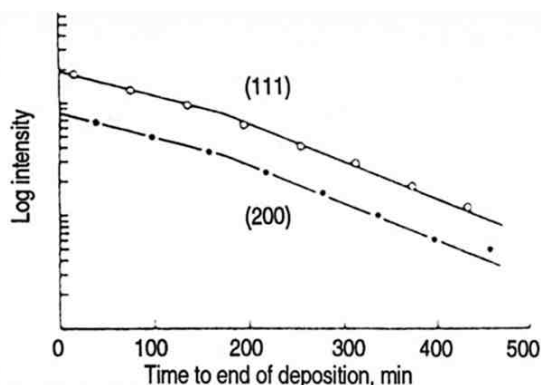


Figure 5 - Stress in nickel layers during electrodeposition and cathodic polarization in sulfuric acid +0.1 g/L thiourea, with and without palladium ions.

As is the case with most electrodeposits, electroplated nickel can exhibit an extremely high supersaturation with hydrogen, under suitable deposition conditions. In the beginning, at least, this hydrogen is present as H, which diffuses to a high extent as hydrogen atom. It may recombine, however, while in the layer or after diffusing out of the layer. This explains the decrease of the hydrogen concentration of nickel in storage, depending on length of time and temperature.

There are very interesting observations on the interaction of incorporated hydrogen and distortions of the nickel-lattice. Normally, the partial current for hydrogen and its relation to the partial current for nickel, determine the uptake of hydrogen in nickel. For nickel chloride electrolytes, however, the partial current for hydrogen is lower than in nickel sulfate baths, under otherwise identical conditions. The amount of hydrogen in deposits from chloride solutions is much higher, however. This may be caused by the same effect, which increases hydrogen values drastically, in layers from chloride electrolytes from pH 5.0, and in sulfate electrolytes from 5.6 on, and must be attributed to the increasing amount of incorporated hydrolysis products (Fig. 6). These generate such high lattice strains and defect areas that, under extreme conditions, x-ray amorphous deposits can be prepared which are tremendously supersaturated with hydrogen, as is the case with palladium.

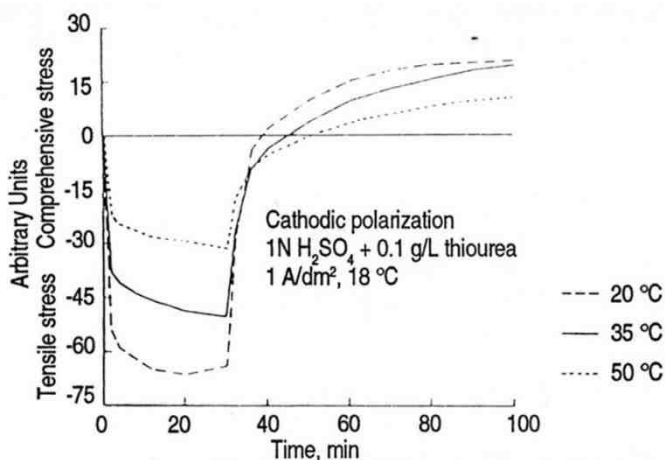


Figure 6 - Internal stress layers from a bright nickel bath, during cathodic polarization and one hour later, in relation to bath temperature.

The uptake of hydrogen by electrodeposited nickel is influenced by every deposition parameter, as we can imagine from the theoretical remarks. It is reduced by higher deposition temperatures and by annealing. Small amounts of certain elements have a pronounced effect on hydrogen in codeposition and in charging nickel with hydrogen, as well. Typical are S⁻², Se⁻², Te⁻² and V group elements/ ions, but small traces of the platinum group and other precious metals, too.

It is not quite clear what is more dominant on the mechanical properties of nickel - the hydrogen in whatever form, or the incorporated, defect generating substances, or a combination of both. The same is true for internal stress, which alters during out-diffusion of hydrogen (Fig. 5).¹⁶⁻¹⁸

In nickel alloys, composition and kind of alloying partner determine the hydrogen uptake, too. This is typically shown by nickel-palladium and nickel-zinc alloys.^{7,18} In the latter, hydrogen concentration increases in proportion to the amount of zinc in solid solution. In alloys richer in zinc, various nickel-zinc alloys form, and the hydrogen content drops very low, in the range of the hexagonal zinc-nickel phase - around 50% zinc. Bright nickel shows a much higher penetration than matte nickel.^{11,12}

Hydrogen in chromium

In a paper on stress and stress relief in chromium, D. Gabe discussed the uptake and release of hydrogen in chromium and its relationship to the properties of the layer.²⁰ In 1963, he summarized: "There has hitherto been no direct experimental evidence of this hydride..." (chromium hydride). He arrived at the conclusion that prompted this statement through discussions on the diffusion of hydrogen through BCC chromium and HCP nickel, promoting decomposition of a possible CrH. He also found a strong effect of arsenic on tensile stress, about which he stated that "the influence of arsenic further supports this idea ..." (of decomposition of an HCP CrH).

At almost the same time, however, A. Knödler, of FEM, was able to synthesize, quantitatively, x-ray clean HCP CrH by electrolysis. He determined its properties and studied the transformation to BCC Cr.^{21,22} This CrH is stable in air; unstable, if powdered and in vacuum (Fig. 7). He supported Gabe's assumptions of the high mobility of hydrogen in CrH experimentally and found that the formation of the hydride is an exothermic process, while the uptake of hydrogen by BCC chromium is endothermic. If HCP CrH transforms into BCC chromium, a volume contraction is found. As earlier guessed, this may explain the crack formation in chromium layers.

Chromium produced by decomposition of CrH is chemically very active and oxidizes at normal room conditions. Solid-state properties were also studied.^{23 24}

Pieces of CrH can easily be set afire with a match and burn with the bluish flame characteristic of hydrogen.

It is now fairly certain that - directly or indirectly - the hydrogen (or CrH) content of hard chromium layers is important to their properties. Because Cr-oxy-hydrates are also incorporated to a high extent, it is again difficult to establish the actual "hydrogen effect." In hard chromium, we do have hydrogen present in solid solution, in the form of BCC Cr, as well as varying amounts of CrH, which is highly dependent on the current wave form.

By low-temperature electrolysis (at -30°C), we were able to synthesize x-ray amorphous Cr-H alloys, highly hydrogen supersaturated (with oxygen impurities, too), which decompose at room temperature, via CrH and β -W-type Cr-O to BCC chromium. The hydrogen released is quite similar in behavior to palladium.²⁵

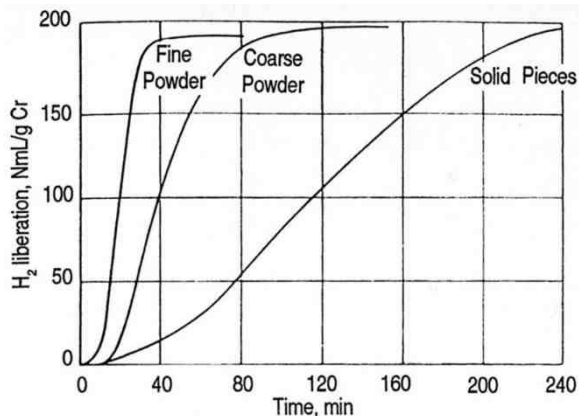


Figure 7 - Decomposition of chromium hydride in different forms (fine and coarse powder and compact chunks) in air at 100°C.

An interesting test - well known to platers - is to drop a hard chromium sample into hot oil and observe the hydrogen development, originating from diffusion of hydrogen and decomposition of CrH - guessing the amount of hydrogen present and using this for production control.

Hydrogen in manganese

Despite the fact that hydrogen in manganese can present problems in industrial electrowinning of manganese because of its ignition, few details are published about the mechanism and the possible existence of an Mn-hydride. Immediately after deposition, there is a value given of 200 ppm hydrogen, which was mostly removed by heat treatment at 500°C.²⁶ Equilibrium solubilities were determined by Sieverts and Moritz in 1938, with electrolytically hydrogen-charged manganese. They stated that, after annealing at 600°C, about 8 ppm is in solution, but during cooling to lower temperatures, some is reabsorbed (to 35 ppm).²⁷

There is evidence that there are tremendous variations in the hydrogen content, depending on the electrolysis conditions, as well as on the determination method. T. Agladze developed a process to replace hard chromium with "hard manganese." He can generate manganese layers with a hardness up to 1000 kg/cm².²⁸ All this shows how little information on electrodeposits of the Mn-H system is published, because the work was aimed almost exclusively in the direction of industrial electrowinning. This prompted a collaboration on manganese electrodeposition among those at FEM and colleagues from Eastern Europe.

Hydrogen in iron

It is most amazing to realize that even if the electrolytically prepared Fe-H alloys are the earliest examples for hydrogen codeposition, detailed information on them is of questionable value. As we have seen by work from Jacobi, Raub and Wullhorst, hydrogen content goes parallel with the inclusion of other constituents, showing the well-known picture of increasing with rising lattice distortion, higher hardness, but superb wear resistance, as well (Fig. 8).

The FEM is again taking up its earlier research on electrolytic iron and iron alloys, largely because iron is one of the safest elements, environmentally speaking.

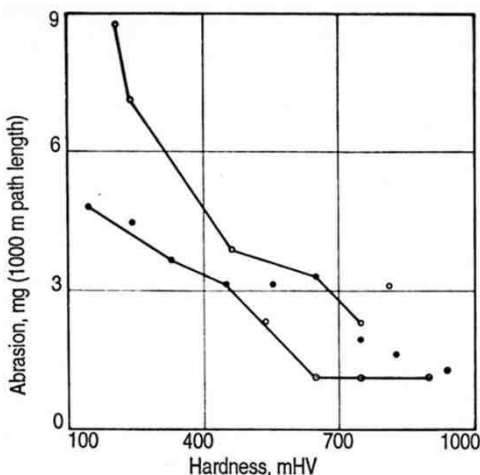


Figure 8 - Wear of iron deposits in dependence on their hardness.

hydrogen, and is used in its pure form, or its alloys, extensively for hydrogen purification in diffusion and fuel cells. Even though the first palladium layers were prepared from chloride electrolytes as early as the late 1800s, little attention was paid to the codeposition of hydrogen.

The main features of electrolytically prepared palladium-hydrogen layers are explained here. Palladium can dissolve fairly large amounts of hydrogen as a solid solution - depending on the deposition conditions - in its FCC-Pd lattice. At normal conditions, the H:Pd weight ratio may go up to about 0.03. At higher hydrogen concentrations, the β -Pd-H phase, tetragonally distorted, forms at an H:Pd ratio of more than 0.57. Its lattice constant is higher by about 3.8%, as compared to the α -Pd-H lattice.

The uptake of hydrogen - as is known from other metals - generates stress, but even more comes from the formation and later disintegration of this β -phase, at room temperature. During storage, hydrogen diffuses out from areas of high H:Pd ratio, and the decomposition of the β -phase and accompanying volume change cause stresses that are released by cracks in the layers, sometimes even days after deposition.

This "hydrogen problem" was well known in the beginning of the electronic use and one effort to cope with it involved heat treating it as deposited palladium, at 500°C. This only shifted the problem from the user back to the plater, however. It was solved through the development of processes that produce practically hydrogen-free deposits. It becomes a bit easier, too, because Pd-alloys, in general, show less tendency to hydrogen uptake than pure hydrogen (Fig. 9).

Today, the "bad names" of nickel and cobalt may force the industry to go back to the laboratory and devise new palladium alloy systems.³¹

Organic additives increase hydrogen concentration and have an influence on the texture of the layer (Fig. 10). The hydrogen-to-palladium ratio may reach 0.8 in the as-deposited state - a high supersaturation. If placed in a liquid at room temperature, the hydrogen bubbles evolving from the layer can be seen. Low temperature deposition experiments from a highly acidic Pd-electrolyte (at about -20°C) are very interesting.²⁵ Under these conditions, extremely distorted and hydrogen supersaturated powders are produced. If these powders, as deposited, are placed in liquid nitrogen, they develop a

Hydrogen in palladium

The electroplating of palladium has attracted much attention, since it showed great potential in the electronic industry. This explains why palladium and its codeposition with hydrogen is thoroughly investigated. In a series of nearly 20 papers, to date, the FEM's team of H.D. Hedrich, M. Butz, F. Friedrich and D. Walz has been studying the influence of hydrogen and electrolytically prepared palladium and palladium alloy layers. Recently M. Monev, from Sofia; M.E. Baumgärtner; M. Kittel and A. Juzikis have joined this group in its efforts. Further work was also done in the UK, the U.S., and in Eastern Europe by such distinguished researchers as Y. Okinaka and J. Abys, both with AT&T Bell Laboratories.

A summary of the work, covering "the great years of palladium," up to 1982 was published by the author that same year.³⁰

Metallic palladium is one of the most "reactive" metals with hydrogen, and is used in its pure form, or its alloys, extensively for hydrogen purification in diffusion and fuel cells. Even though the first palladium layers were prepared from chloride electrolytes as early as the late 1800s, little attention was paid to the codeposition of hydrogen.

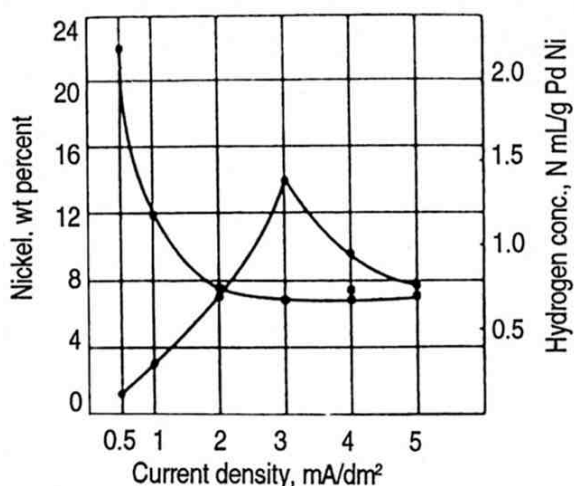


Figure 9 - Dependence of Ni- and H-concentration on current density for Pd-Ni deposition (30°C, pH 8.5).

dense stream of hydrogen bubbles, showing their supersaturation. Layers are x-ray amorphous, and they transform, under heating, to room temperature, to the β -phase, and later to the χ -phase. In these layers, as estimated from dehydrogenation curves, hydrogen must be bound in various forms, first to the amorphous palladium, then to the β -phase, and finally, to the χ -phase. If the purely physically absorbed hydrogen and the H to H₂ recombination are taken into consideration as well, there are at least five states of hydrogen binding involved - some of them even seen in dehydrogenation experiments.

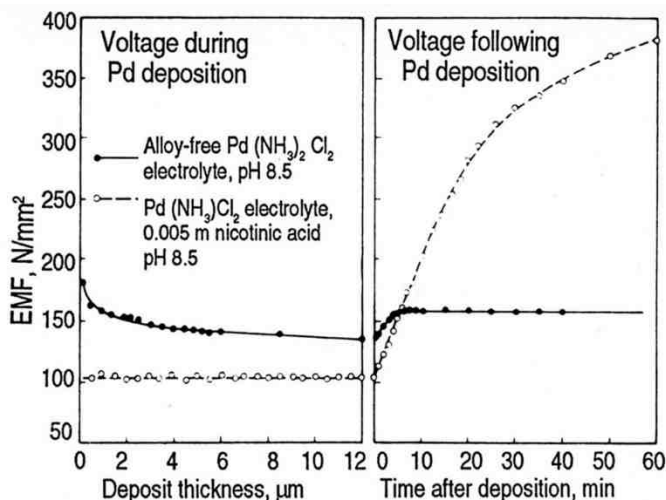


Figure 10 - Stress of Pd layers from a chloride electrolyte, with an addition of nicotinic acid during and after deposition.

This method of producing unstable amorphous Pd-H intermetallics may be considered an example only of the possibilities of electrolytic synthesis methods - not so much a means for generating a "cold fusion material."

M. Monev and collaborators demonstrated interesting effects in nickel-rich palladium-nickel alloys and the influence of trace amounts of palladium and others on the stress of electrodeposited nickel.¹⁷⁻¹⁹

The extensive research in palladium electrodeposition has yielded much insight into the ways of incorporation of hydrogen into electrodeposited metals. This is transferable, at least in part, to other systems, too. It was of decisive importance, in that the hydrogen problem and cracking of layers is no longer a dilemma in modern palladium plating.

Hydrogen in gold

Under equilibrium conditions, gold does not dissolve any hydrogen in its lattice. Electroplated hard gold layers, as they are used for electric connectors, are alloys of gold with iron, cobalt and nickel. They usually contain between 0.3 and a few percent of these, depending on the metal and on the deposition parameters. In addition, alloys can possess organics, with up to more than 1000 ppm C; and hydrogen, which can go up to 1000 ppm.

Inclusion is enhanced ever further by the fact that cyanide helps the recombination of hydrogen atoms to hydrogen molecules, promoting diffusion.

What is too often overlooked, however, in many explanations - most of which refer to the Au-Co system - is that the amount of incorporated foreign matter, including hydrogen, is nearly the same for all three elements of the iron group - a fact, complicating chemical-electrochemical explanations much more. It bears mentioning that cobalt is present in two states in gold: a supersaturated Au-Co solid solution; and an inorganic compound, details of which are unknown, of a K-Au-Co-CN composition, to which hydrogen may be chemically bound. If cobalt is present in the electrolyte as the Co(III) ion, its concentration in the layer and its foreign matter content drop to comparatively low values.

In Au -Fe baths, the incorporation of K-Fe-cyanides and hydrogen is also evident.

This has not yet been proven, experimentally, for nickel, but it is most likely. For Au-Ni and Au-Fe layers, the alloying constituents are, at least in part, in solid solution, which is easier than with cobalt, because gold exhibits a rather high equilibrium solid solubility.

All three systems, in the form of electroplated alloys, exhibit similar properties of hardness and wear resistance, despite their differences in equilibrium chemistry and metallurgy. It is well established, too, that hardness and wear behavior cannot be caused by the metals in solid solution, but must be the result of incorporated foreign matter, including hydrogen.

To a certain extent, this is confirmed by the fact that the so-called "addition-free hard gold" (AFHG) of Y. Okinaka, does not contain metallic elements, but shows up to 1000 ppm C (from inclusions of AuCN) and hydrogen. The same is true for deposits from Au(III) cyanide baths (which may or may not contain cobalt) that reach hardnesses of more than 200 HV on similar grounds.

These hardnesses must be connected with the incorporated foreign matter - be it inorganic cobalt compounds, some organics (tentatively called a "polymer" by G. Munier), or hydrogen. Hydrogen can be removed by heat-treatment or electrolysis at higher temperatures - a fact that is critical to laser plating. On the other hand, all the layers tend to blister and/or crack, or form voids during heating to higher temperatures - another indication of a build-up in gas pressure.

For the Au-Co-H problem, a contributing factor may be that certain cobalt complexes are highly reductive and can even decompose water. But what about the corresponding nickel and iron complexes? Furthermore, up to now, only complex cobalt cyanides are known to adsorb hydrogen atoms. What is identical, however, are the facts that all deposits discussed are lower in density than would theoretically be calculated (remember Jacobi and electrodeposited iron); and all three systems have pores, voids, and are full of defects interfering with slip planes.

These pores were first observed in gold-cobalt by Okinaka and Nakahara, and later shown to exist in gold-nickel as well (Fig. 11), by Reid, Saxer and Flühmann. Okinaka and Nakahara assumed, for the first time, that these voids and pores were full of highly compressed hydrogen gas, formed by recombined hydrogen atoms during electrodeposition - later also found to be true of electroless copper.

The extremely pressurized gas generates a wide distortion area around a void, which results in stresses and high hardness. The incorporated organics add to such a defect area, and facilitate diffusion and recombination of hydrogen in such sites during electrolysis. For metals that do not dissolve hydrogen, such as gold, silver and copper, the effect is especially dramatic, because hydrogen can only disappear rather slowly from those voids.

It is confounding that this model by Okinaka and Nakahara, first developed for gold, was rarely used for other electroplated metals, for which it works every bit as well. This was confirmed for electroless copper in 1986, through an experiment by Okinaka and Straschil.¹⁶

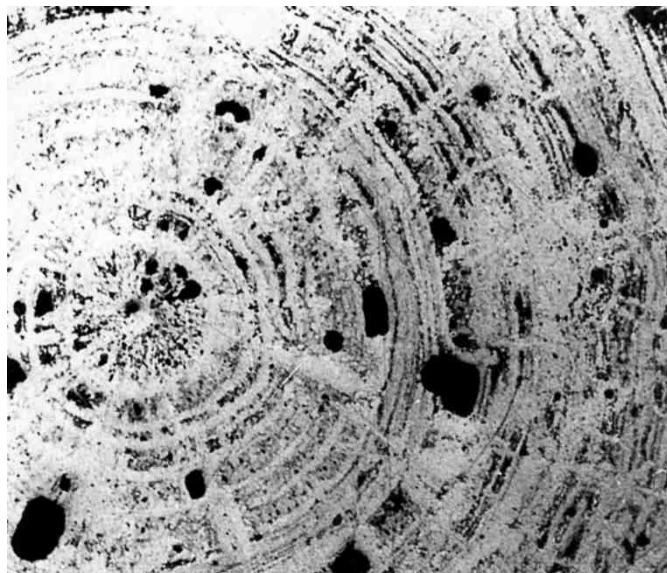


Figure 11 - Porous structure of gold-0.5% Ni deposit, after annealing for two hr at 700°C.

Hydrogen in electroless copper

In the early days of copper electrodeposition, Knödler observed a relatively high development of hydrogen and stated that below 5 μm of thickness, layers can be penetrated by hydrogen - especially if the copper is distorted.^{11,12} This may be important because it is known that not only electrolytic deposits may contain "volatile compounds," but electroless layers may, too.

Y. Okinaka and H.K. Straschil studied this carefully for electroless copper, of special importance to electronic production. The layers contained up to 200 wt ppm hydrogen, and 100 to 800 ppm carbon and other impurities (O, N, Na) (Fig. 12).¹⁶ They suggest that hydrogen gas bubbles are entrapped during electrocrystallization, and hydrogen atoms diffuse through the distorted thin copper layer around them, to recombine and build up pressure inside. This pressure creates large defect areas around voids that hinder the movement of slip dislocation planes during deformation, or hardens the layer. The addition of arsenic - a stabilizer for atomic hydrogen - made it possible to do a reversible recharge of an annealed electroless copper sample, after it had been annealed "empty of hydrogen." Ductility after annealing was 6.6%; after recharging, it came down to only 3.8% (as deposited, 2.1%) - a difference from ion implantation?

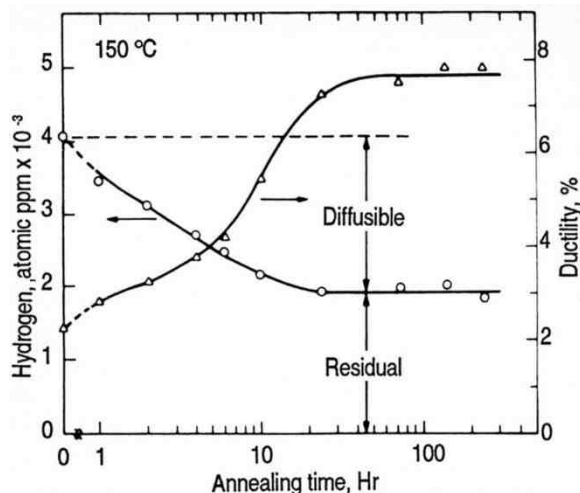


Figure 12 - Variation of hydrogen content and ductility with annealing time at 150°C (deposit plated with 10 mb/L $K_2Ni(CN)_4$ at 70°C).¹⁶

In experiments, Y. Okinaka and a collaborator were able to find clusters of molecular hydrogen, employing a method that uses a calorimetric measurement to determine the slightest amount of heat released during the conversion of ortho-to para-hydrogen, at the temperature of liquid helium.

In the abstract of his paper on the study, Okinaka remarks, "Results show that the hydrogen exists in two different forms: diffusible, which escapes readily on annealing; and residual, which is not removable by annealing. Diffusible hydrogen impairs ductility ... the diffusible hydrogen consists essentially of molecular hydrogen, existing in micro-voids at high pressure ... both the pressure effect of molecular hydrogen and the structural effect of voids influencing the overall ductility. Ductility-promoting additives inhibit both the inclusion of diffusible hydrogen and the formation of voids. Residual hydrogen, together with other elements, constitutes other compounds (*e.g.*, EDTA or H_2O) occluded from the plating solution ... However, when the incorporation of an additive causes an increase in residual hydrogen and carbon contents,

the beneficial effect of the additive can be offset by its influence on grain structure."

This is, in this author's opinion, the perfect explanation of the role of hydrogen in metal deposits formed electrolytically and by electroless methods. It shows, too, how to influence properties of layers by hydrogen incorporation only: look for additives in small amounts that promote building-in of small hydrogen bubbles, promote diffusion of hydrogen (*e.g.*, by adding traces of palladium) (See work by M. Monev, *et al.*), and/or by distortion of the host lattice by an additive concentration in as small a quantity possible. For electrodeposited copper, A. Knödler confirms the use of a matrix through which hydrogen can only diffuse if the metal is thin and highly distorted. It is well known from processes involving steel that such areas may act as "traps" for hydrogen.

In any case, the "poor man's ion implantation" method was already known. It would be interesting to observe real hydrogen ion-implanted copper for similarities - a suggestion to Y. Okinaka.

Acknowledgment

I want to thank the International Branch of the AESF for nominating me for the Society's prestigious Scientific Achievement Award, and the Awards Committee for granting it and inviting me to give this, the William Blum Lecture for 1993.

In a wider sense, I am grateful to my parents for enabling me to study the fascinating field of chemistry, and to my teachers for showing me how exciting it is. I have to thank my wife for giving up a profession she loved in order to move with me to California.

My gratitude to my admired teacher, and later friend, Professor Bernd T. Matthias, who taught me that science, if properly applied, is fun; and my industry colleagues worldwide who showed me that you should test your ideas and results in production; all my collaborators at the FEM, from whatever country they may have come as permanent residents, semi-permanent visitors, or guests, and my friends worldwide, who make life much more colorful. And, especially in connection with precious-metal plating, I thank Dr. Y. Okinaka.

Last but not least, I feel that this award is shared by all who in any way contributed to the change of electroplating from an alchemistic adventure to a modern, economic and quality-ruled process; and by the organizations and people supportive of our work, through funding.

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About the author:

This piece was written at the time Dr. Raub was announced as the recipient of the 1992 Scientific Achievement Award.



This year's Scientific Achievement Award winner, Dr. Christoph J. Raub, has been a member of AESF since 1974. He is currently the head of the Forschungsinstitut für Edelmetalle und Metallchemie, Schwabisch Gmünd, Germany, a post he has held since he succeeded his father, in 1970.

Raub's favorite subjects in school were mathematics, physics and chemistry. In 1951, after successfully finishing his Abitur - a school-leaving examination for university entrance qualification - he was sent by his father to work for W.C. Heraeus Hochvaakuum, in Hanau, to work on high-vacuum equipment production and to see physics in action. There, he did calculations of interference filters by hand, spending weeks writing and adding numbers. "I decided that this may not be the thing to do all my life long," Raub recalls, "so I decided to try something else."

He was accepted at the University of Munster, where he studied under noted professor Wilhelm Klemm and earned his B.S. in chemistry. Raub had wanted to pursue a like degree in physics, but was dissuaded by an assistant at the university, because



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there was more action and excitement to chemistry - precipitates, colors, fires, etc. - than in physics. He would later add an M.S. from the same institution to his credentials, doing his experimental work and thesis on a thermodynamics problem. It was during this time that Raub also acquired an interest in art history and archaeology, often attending lectures in the evening. This remains his favorite leisure pastime today, though he enjoys any activity connected with Nature, from gardening to growing pine trees from seeds.

In 1960, frustrated with the university system in Germany, Raub contacted friends across the Atlantic and was invited by Professor Bernd Theo Matthias to join the Physics Department of the then-newly opened University of California San Diego, in La Jolla, CA. Work included low-temperature properties of various materials; superconductivity of alloys and compounds, especially of oxides and sulfides; crystal structures and phase diagrams.

Raub and his bride, the former Hanna M. Kurz, had been warned that Americans got their food only from cans and that there would be no fresh vegetables there. "I still remember being amazed at the tremendous variety of fresh foods on the supermarket shelves," Raub laughs. The Raubs settled in to their new life - she, as a physician and he, with the university. Their first son was born in 1962, and remains a U.S. citizen today.

It was during this time that Raub was introduced to electrochemistry: The synthesis of the superconducting ternary tungstate bronzes - the forefather of today's high-temperature superconductors by salt-melt electrolysis.

After four years, Raub received an offer from Bell Laboratories to do research, and a call from his former employer, W.C. Heraeus, to head its research and development laboratory. He found the idea of industrial production in one of the bigger companies very appealing, so he accepted and the family returned to Hanau, where two more sons were born.

At Heraeus, Raub did research, development and quality assurance work in industrial production of precious and refractory metals and alloys; industrial precision electroplating for electronics; industrial application of precious metals and production of semi-finished and finished products. He participated in technical metals production, with a concentration on electronics and chemistry. Some of his patented ideas were put into production, he developed new alloys and solved a number of production problems during this stage of his career.

As his father neared retirement from the Institute in Schwabisch Gmund, Raub was approached by its Board about taking over there, and he accepted. Among his goals, he wanted to make the Institute an international center in its field, which he is satisfied he has achieved.

At the Institute, Raub has conducted basic research in precious and refractory metals and in all aspects of surface treatment of metallic and nonmetallic materials, especially pertaining to electroplating. He has done applied research in precious metal technology, refractory metals production and industrial surface treatment; worked on development and quality assurance for various industrial companies; and has done contract research on national and international levels. Raub also teaches at trade school, polytechnics and universities, while pursuing his interest in investigation and restoration of archaeological finds.

Involved

A former member of the AESF Research Board, Raub is a founding member and first vice president of the European Academy of Surface Technology (EAST); a member of the New York Academy of Sciences (U.S.); the Worshipful Company of Goldsmiths (U.K.); a Fellow of that country's Institute of Metal Finishing (IMF), and on that organization's Publication Board; and is a board member of a number of German professional societies. He has been an invited lecturer in virtually all the industrialized countries in the world, many more than once. In 1991 alone, he spoke in the U.S., Bulgaria, Japan, the then-USSR, France, Belgium and the United Kingdom.

Accomplishments

A prolific author, Raub has published more than 300 papers, articles and/or books related to surface finishing. By topic: Superconductivity and solid state physics - 48; metallurgy - 77; surface technology - 188; and general or historical materials - 20.



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He is also editor-in-chief of the *Journal of Alloys and Compounds*, the interdisciplinary journal of materials science and solid-state chemistry and physics.

Raub, who has been granted eight patents, and has others pending, conducted an AESF-funded research project, "Electrolytic and Electroless Preparation of III-V Compounds of Gallium and Indium." Known as AESF Project #72, this investigation of electrodeposition and electroless plating of Ga- and In-based III-V compounds was completed in 1990. The goal was to obtain GaAs or InSb in the Zinblende (B3 type) crystal structure.

Other milestones in Raub's career include the 1964/65 discovery, in cooperation with B.T. Matthias and A.R. Sweedler, of superconductivity of multicomponent oxides; the development, in 1968, of precious metal alloys with high recrystallization temperature (gold bonding wire, Pt-thermocouple wire); and the same year, a method of quality control in palladium contact plating, as supplier to a major computer manufacturer.

From 1970 until now, Raub has also developed today's standard jewelry casting Pt-Co alloy; devised a highly improved electroless nickel-plating process for computers; done basic and applied work on electrolytic and electroless deposition of gold, palladium and their alloys for electrical contacts (with D. Hedrich, D. Walz, M. Kittel and A. Knödler); refined electrolytic deposition of Pt-Co alloys for magnetic storage devices (with M. Baumgärtner and P. Cavalotti); with D. Ott, formulated new gold alloys for jewelry production; worked with H.R. Khan and O. Loebich on the electrochemical formation of amorphous palladium and chromium alloys at low temperatures; corroborated with M. Baumgartner and others on low- and high-temperature electrodeposition of copper; is involved in ongoing research on electrodeposition of refractory metal alloys, with M. Baumgärtner and Dr. Chassaing; and with Ch. Eluere, studied the beginning of gold-coating technology in the Fifth Millennium, B.C.

Awards

The Scientific Achievement Award is not the first time that AESF has acknowledged Raub's contributions to surface finishing, awarding him silver and gold medals for papers the Society has published in *Plating and Surface Finishing*. Other organizations have also honored him: The International Precious Metals Institute awarded him its Henry J. Albert Palladium Medal and Prize. He has all the awards the German Electroplater's Society has to give, was appointed Professor by the State President of Baden-Württemberg in 1988, and in 1990 received the Turkish Electroplating Society's Document of Merit.