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The role of hydrogen in metal electrodeposition processes*

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The incidence of codeposition of hydrogen during electrodeposition, described as a cathodic inefficiency in plating processes, is reviewed and the effects of hydrogen on the deposits produced discussed. Characteristic electrode features leading to hydrogen evolution and hydrogen absorption are discussed and the causes of hydrogen embrittlement, which may be regarded as essentially electrochemical in origin, are defined.

1. Introduction

In electrodeposition processes hydrogen is the second element produced at the cathode: in some cases it is ignored, in some cases it cannot be ignored. It is produced electrochemically but its consequences are metallurgical. In his Blum lecture of 1993 Raub [1] discussed some of the effects of hydrogen on the properties of various metal deposits and their substrates and highlighted some of the consequences. Most papers about hydrogen are concerned only with physical effects such as embrittlement [2–4]; this paper will look at the chemical aspects of hydrogen generation beyond the common incidence of hydrogen charging by cathodic evolution in acid solution to other cathodic processes arising during metal processing by cleaning, pickling, etching and electroplating. Codeposition with chromium electroplating is the best documented system [5–9] and, consequently, much of the data to be reported relates to that situation. Few papers have reviewed the practical electrochemical aspects of hydrogen embrittlement during metal finishing [10, 11] and one in particular deserves to be read for data in danger of being forgotten [12].

Although the formation of hydrides is possible for many metals, misleadingly described as passive films in Pourbaix terminology, the kinetics of formation is usually so slow as to preclude their consideration in practical terms. Thus, in a recent consideration of cathode films in electrodeposition [13] they have been entirely disregarded.

2. Competitive cathode reactions

During the cathodic electrodeposition of metals from aqueous solutions, three main types of reaction can occur:

Metal deposition

$$M^{z+} + ze^- \Longrightarrow M^0 \tag{1}$$

Hydrogen evolution

$$2H^+ + 2e^- \Longrightarrow H_2 \text{ or } 2H_2O + 2e^- \Longrightarrow H_2 + 2OH^- \tag{2}$$

Metal ion reduction

$$M^{z+} + e^- \Longrightarrow M^{(z-1)+} \tag{3}$$

Oxygen reduction is, in principle, possible but can be neglected as, even with air agitation replenishment, its contribution is usually very small. Other cathode reactions are in practice also neglectable because either the kinetics or thermodynamics are insufficiently favourable (e.g., hydride formation) or are dependent upon a special combination of chemical and physical conditions (e.g., cathode film formation).

The decision on which reaction actually occurs is, in principle, a thermodynamic one; that is, which reaction occurs at least negative potential. Consequently, it is known as basic knowledge that silver deposition ($E^\ominus = +0.799$) is preferred to hydrogen discharge ($E^\ominus = 0$) and hydrogen discharge to aluminium deposition ($E^\ominus = -1.66$); intermediate relationships give rise to mixed situations as for chromium ($E^\ominus = -0.74$). Reaction 3 only occurs in practice for multivalent transition metals, e.g. copper, cobalt, tin, and represents 2–3% of the total current in most cases; it is generally neglected because the reverse can take place at the anode and if the net effect is small the two reactions are often not noticed!

The fact that electronegative metals can be electrodeposited at all derives from the fact that hydrogen has a large overpotential (up to 1.0 V), that is, it actually deposits at much more negative potentials than the thermodynamic value because of other rate-controlling steps in the discharge process. Such metals include nickel ($E^\ominus = -0.25$), and zinc ($E^\ominus = -0.76$). The value of the hydrogen overpotential (η) depends upon several factors: (i) solution pH, (ii) current density (CD) and Tafel

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parameters a and b, and (iii) the metal concerned defined through its exchange current density i_o.

In practical terms, the hydrogen overpotential can manifest itself through the cathode current efficiency (CCE). Solutions in which Reaction 1 dominates have a CCE which tends towards 100% and the CCE falls as the CD rises. Solutions where Reaction 2 dominates have low CCE or even 0% for very base metals such as Al, Ti ($E^\ominus = -1.63$), but for chromium it is 10–25% and for manganese ($E^\ominus = -1.18$) 20–40%. The presence of complexants radically changes the situation because the discharge potential is markedly lowered while the hydrogen overpotential may be only slightly affected by, for example, the pH. Thus, typical values of efficiency might be as shown in Table 1. For metals such as chromium the CCE tends to increase with CD because hydrogen evolution is the most favoured reaction (i.e., as CD tends to 0%, the CCE tends to 0% as hydrogen is the sole reaction) and chromium is, therefore, the secondary reaction electrochemically.

Discharge of hydrogen takes place in five distinct steps [14] (see Table 2). By comparison, electrodeposition takes place in three, namely, the analogues of steps 1–3. The unique effects of hydrogen can be seen as a consequence of steps 3–5 and can be stated as follows:

(a) Hydrogen absorption occurs in the substrate metal as H atoms not H_2 molecules but may gather as molecule bubbles in voids or vacancies thus leading to hydrogen embrittlement.

(b) Hydrogen bubbles cling to the surface in an adsorbed state; this leads to growth pores as the deposit forms around bubbles before they are released.

(c) Hydrogen bubble evolution can provide a stirring effect and lead to a substantial bubble raft at the solution free surface.

Table 1. Typical cathode current efficiencies during electrodeposition

Solution type	*CCE/%*
Acid copper	98
Alkaline cyanide copper	70–85
Acid zinc	>90
Alkaline zinc	70–90
Chromic acid	10–25
Alkaline tin	65–80
Acid tin	90–98

3. Cathode polarization and efficiency

The generation of hydrogen on cathode metal surfaces is substantially dependent upon the identity and nature of the surface itself; otherwise the overpotential as the driving force for reaction is directly proportional to the logarithm of the rate of generation, expressed as a current density (i.e., the Tafel relationship). The relationship can be shown in tabular data form or graphically (Fig. 1). It is common to compare the polarizability of a metal in this reaction as the overpotential value at a given current density chosen to represent a significant rate of reaction (e.g., 1 A cm^{-2}). Other polarization effects can be cited, for example, the bubble overpotential, but they are less important. In general any parameter which increases the rate of hydrogen evolution also increases the rate of hydrogen absorption in the metal substrate although the exact degree of absorption will vary. Thus the electrochemical factors of importance are: (i) the metal concerned, (ii) the pH of solution, (iii) the current density employed, (iv) the temperature of solution and (v) the cathode current efficiency (CCE). Some typical data are given in Table 3. The general conclusion is that the absorbed hydrogen is

*Table 2. The hydrogen discharge mechanism**

Reaction step	*Rate-controlling process*	*Characteristic*
1	Transport of H_3O^+ ions from the bulk of solution to the diffusion layer	
2	H_3O^+ ions are desolvated and partially discharged at the electrode surface. $H_3O^+ + e^- \Longrightarrow H_{ads} + H_2O$ or $M + H_3O^+ + e^- \Longrightarrow M-H + H_2O$	Volmer rcs where $b = 0.118$ V if $\alpha = 0.5$ and $n = 1$
3	H atoms combine in the adsorbed state to form adsorbed H_2 molecules. Two alternative mechanisms are possible.	
	(a) 'Catalytic desorption' $M-H + M-H \Longrightarrow 2M + H_2(ads)$	Tafel rcs giving $b = 0.03$ V for catalytic behaviour theory.
	(b) 'Electrochemical desorption' $H_3O^+ + M-H + e^- \Longrightarrow M + H_2(ads) + H_2O$	Heyrovsky rcs giving $b = 0.118$ V: electrochemical theory.
4	Desorption of adsorbed hydrogen molecules as bubbles $nH_2 \Longrightarrow (H_2)_n$	Not electrochemical but affected by surface tension.
5	Diffusion of hydrogen bubbles and evolution of gas from the electrode surface.	

* The Tafel equation is of the form: $\eta = a + b \log i$ where η is the overpotential and i is the current density. The Tafel parameters are given as: $b = 2.303RT/\alpha nF$ and $a = b \log i_o$ where i_o is the exchange current density and α is the symmetry coefficient.

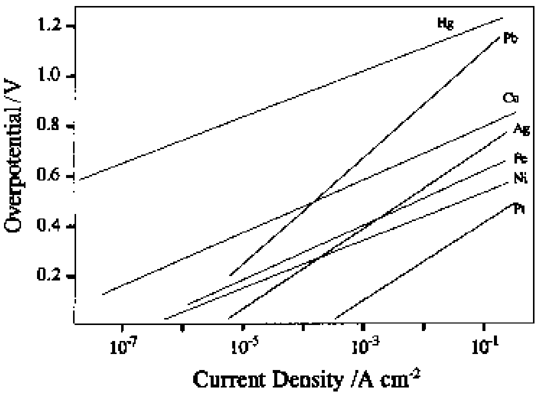

Fig. 1. Hydrogen overpotential data plotted as Tafel plots.

*Table 3. Absorbed/occluded hydrogen in electrodeposits**
Values in cm^{3}g^{-1}

	Current density/A dm^{-2}		
	20	30	40
Chromium	17	18.5	25
Manganese	4.8	5.7	5.4
	Temperature / °C		
	20	40	60
Nickel	0.65	0.4	0.21
Iron	8.8	3.6	2.1
	pH		
	1	2	3
Iron	>5	3.8	2.7
Cobalt	1.0	1.5	0.1

* Data from Vagramyan and Solov'eva [7].

greatest for higher current density, lower temperature and lower pH.

A more complex parameter is the CCE, especially in the case of more base metals where the choice between metal discharge and hydrogen evolution is finely balanced. This is particularly acute for chromium for which substantial data exist and which are represented in Figs 2–6. We can disregard, in the context of this paper, the occurrence of a peak in CCE at critical chromic acid and catalyst con-

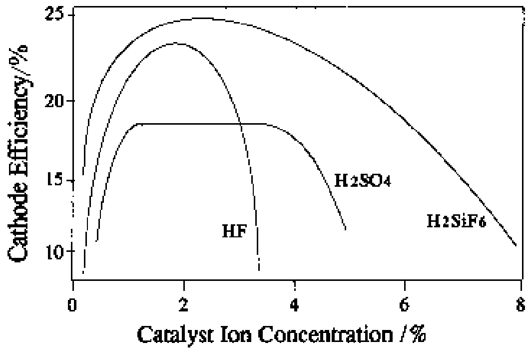

Fig. 3. Current efficiency as a function of the amount of 'catalyst' ion present in chromic acid [6].

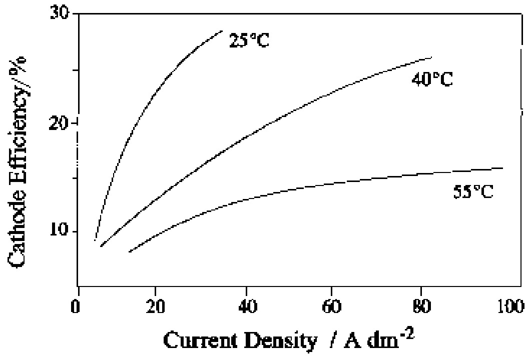

Fig. 4. Current efficiency as a function of current density at various temperatures for 400g/l CrO_3, 4g/l H_2SO_4 [6].

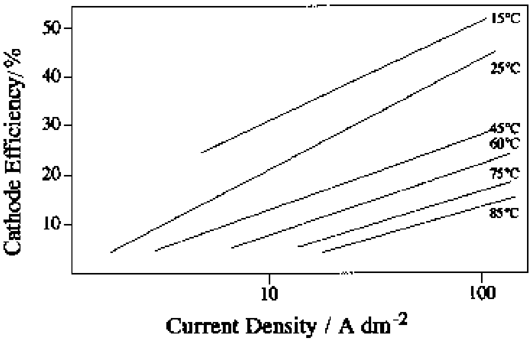

Fig. 5. Cathode efficiency in relation to current density and solution temperature [6].

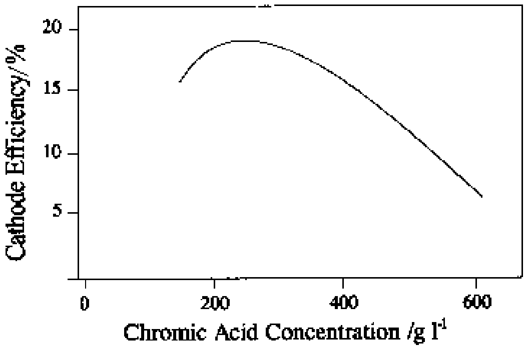

Fig. 2. Relation between cathode current efficiency and chromic acid concentration [8].

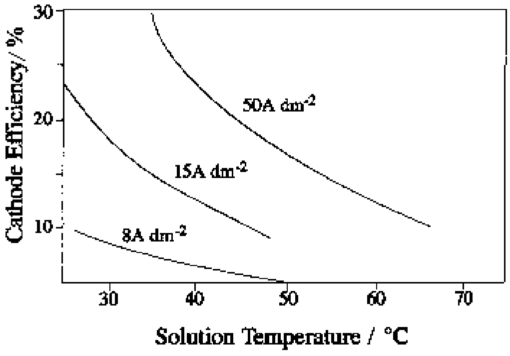

Fig. 6. Current efficiency as a function of solution temperature at various current densities (conditions as for Fig. 4) [8].

centrations because these are related primarily to the necessity of forming a cathode surface film as a transition state whereby the chromate anions CrO_4^{2-} or $HCrO_4^-$ can be cathodically reduced. The other graphs demonstrate a systematic behaviour which is occasionally rationalized in an empirical manner; for example, a Tafel-type relationship is quoted [6] for the relation of CCE and current density (CD):

$$\mathrm{CCE} = a \log \mathrm{CD} + b$$

The CCE, therefore, does not have any fundamental significant meaning and even its effect on total hydrogen absorbed is likely to be small, as most hydrogen produced is evolved as gas bubbles and not absorbed by the substrate.

A number of features may be noted in attempting to determine the significant factors affecting hydrogen absorption:

(a) The discharge mechanism must involve a M–H bond and so acid solutions *per se* are always most vulnerable to absorption tendencies.

$$\text{(acid solution)} \quad H^+ + M + e^- \Longrightarrow M - H$$

$$\text{(alkaline solution)} \quad H_2O + e^- \Longrightarrow H^- + H_{ads}$$

(b) Hydride formation may be possible. Such hydrides could be ionic, covalent or metallic in bonding.

(c) Mechanical occlusion may occur at grain boundaries pores or voids but this could be a physical not chemical mechanism.

(d) Metals like Pd and Re have intrinsically low hydrogen overpotentials and absorb large quantities of hydrogen. Metals like Hg, Pb, Tl have large overpotentials and absorb little hydrogen.

Cr has an intermediate overpotential as does Fe yet absorbs much hydrogen. This could be due to other factors such as hydride formation or its b.c.c. crystal structure.

In the case of freshly electrodeposited nickel, hydrogen bubbles do not easily evolve and they cling to the surface without being markedly occluded or absorbed although gas pores do develop in the deposit. That this is due to surface tension is widely believed [9, 15] largely because additions of a surfactant (e.g., 0.5–1 ml dm^{-3} sodium alkyl sulfate) promote bubble generation without any adverse effect on gas absorption. In this case, rate-controlling step 5 (Table 2) can be assumed to be important.

The solubility of hydrogen in a metal is dependent upon the pressure prevailing and Sievert's law gives:

$$C_o = k\,P^{0.5}$$

where C_o is the dissolved concentration and P the pressure. In the context of electrochemical conditions, P is normally 1 atm, but may be replaced by potential, E, or overpotential, η, as the environmental driving force. Published data suggest that $E/\log C_o$ is linear corresponding with a power law; C_o at $E = 0$ gives a value for C_o similar to that from Sievert's law analysis.

4. Evidence for hydride formation

The evidence for hydride formation as a consequence of cathodic discharge is mainly related to chromium electrodeposition which has been widely regarded as the main metal capable of hydride formation amongst the common electroplated metals. Three hydrides have been suggested:

Hexagonal	CrH
Cubic(?f.c.c)	CrH_2
(Spectroscopic)	CrH_3

The formation of CrH is favoured by low temperature, high current density and high chromic acid concentration.

Hexagonal CrH is thought to decompose to b.c.c. chromium with a 15% volume contraction which is claimed to be a major cause of tensile internal stress development.

Density of electrodeposited chromium : 6.9 – 7.1 g cm^{-2}

Density of cast chromium : 7.138 g cm^{-2}

Shrinkage values are well-documented as shown in Fig. 7.

Decomposition is fastest at 600 °C when recrystallization of the chromium also takes place; both lead to a lowering of the deposit hardness. Below 600 °C hydrogen gas is evolved slowly with relatively little loss of hardness. It should be noted that the hardness of chromium is also attributed to an exceptionally fine grain size of about 10^{-6}cm, internal stresses as high as 200–2000 kg mm^{-2} and oxide (Cr_2O_3) inclusions equivalent to 0.1–0.4% oxygen content. It has been suggested that such hydride decomposition increases deposit porosity, but it is not possible to differentiate in the early literature between micropores and microcracks which clearly would have quite different origins. Furthermore, some coincidences may be discerned. For example, high current densities cause increased hydrogen evolution together with increased hydrogen absorption and increased deposit porosity without necessarily a direct correlation. If hydrogen gas bubbles are occluded brittleness and spalling inevitably occur immediately.

Gas bubbles are known to cause porosity in nickel electrodeposits due to surface tension, but this is

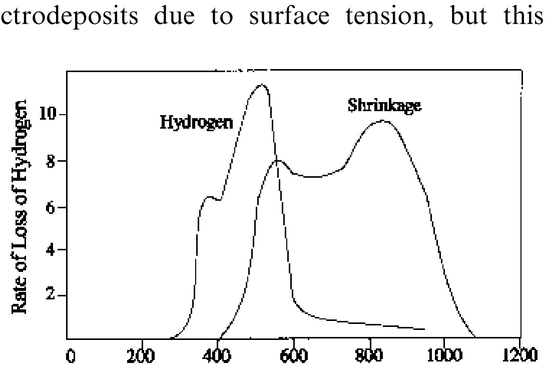

Fig. 7. Rates of gas evolution and shrinkage on annealing electrolytic chromium [14].

normally considered to be distinctively different because they repond to the use of surfactants in the plating solution.

Data reported in the literature for total hydrogen content (the gas is assumed to be wholly hydrogen) of deposits does not always specify solid solution or hydride sources. Typically hard chromium contains 0.01–0.1% hydrogen, average 0.06%. This value depends strongly on the temperature and current density of plating, see Fig. 8. (Note that the oxygen content is 5–10 times greater but it is not usually evolved at the same temperatures).

In the case of nickel, a hydrogen content of 0.01–0.02% w/w is more usual or 13.5 × its own volume. For iron it is 0.1–0.2% w/w or 110 × its own volume. Palladium is an exceptional case as it has long been known to absorb up to 1000 × its own volume of hydrogen, or 5–20 at %. Evidence for hydride formation exists and exploitation of this 'sponge' behaviour has frequently been proposed, especially for hydrogen storage for fuel cell usage.

5. Causes of hydrogen absorption

The mechanism of the Hydrogen Evolution Reaction (HER) has been discussed and individual steps listed in Table 2. The key consideration is at what step is hydrogen actually absorbed in the substrate or electrodeposit. Furthermore, it is necessary to establish why hydrogen gas is not a problem, only hydrogen resulting from cathodic reaction.

The critical stage is the 'nascent' hydrogen step which for acid solutions is

$$H^+ + e^- + M \Longrightarrow M{-}H + H_2O$$

In alkaline solutions it is

$$H_2O + e^- \Longrightarrow H_{ads} + OH^-$$

Such reactions can occur as part of the processes of pickling and cleaning as well as plating.

Herein lies the significant difference: hydrogen is absorbed primarily from reactions in acid solution so the chemisorbed M–H state is vital and the physically adsorbed H_{ads} is of little consequence. The fact that

$$M{-}H + M{-}H \longrightarrow 2M + H_2$$

is a natural succeeding reaction may be unimportant.

This behaviour has an analogy in catalysis where such reactions are integral to reaction. Some of the observations in catalysis theory are

(a) bond strength values are typically:

$$M{-}H : 250\,\mathrm{kJ\,mol^{-1}}\,(\text{i.e., chemisorption})$$

$$H_{ads} : 5\,\mathrm{kJ\,mol^{-1}}\,(\text{i.e., physical adsorption})$$

(b) metals which chemisorb hydrogen well have partially occupied orbitals and are consequently good hydrogenation catalysts. For example,

Cr, Mn, Fe, Co, Ni, Pd, Pt

Furthermore, metals having a high hydrogen absorption capability have two further characteristics:

(c) the metals have non close-packed crystal structures, typically b.c.c. rather than f.c.c or c.p.hex.

Fe, W, Mo, Cr, Ti, Zr

(d) the metals can form hydrides. For example,

Pd, Cr

Thus differences between Cd and Zn on the one hand and Cr and Mn on the other hand are obvious and the ability of steels to absorb hydrogen clear. It is also clear that a low cathode current efficiency *per se* is not a major factor in itself. A further difference is attributable to the relative rates of diffusion of hydrogen in the two metals: in zinc it is high and in cadmium it is low. Consequently, hydrogen trapped below the surface deposit can escape more easily through zinc but less easily through cadmium and this may lead to a recommendation to heat treat steel prior to electroplating if surface oxidation can be minimized.

Zinc is to some extent a test case, because it is electroplated from both acid and alkaline solutions. Furthermore, the alkaline solution is complexed classically with cyanide making the dynamic potential very negative and the hydrogen reaction more competitive. In this case the CCE is typically 70–80% and it decreases with increasing CN:Zn ratio and decreases with increasing current density (Figs 9 and 10). Excessive gas evolution follows, inducing low deposition rates and hydrogen embrittlement can occur. In acid solutions (pH < 2.5) the CCE tends to 100% and hydrogen embrittlement is generally negligible.

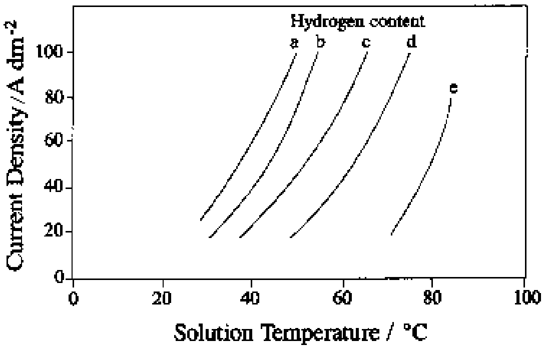

Fig. 8. Hydrogen content of hard chromium as a function of current density and solution temperature: (a) 0.07%; (b) 0.06%; (c) 0.05%; (d) 0.04%; (e) 0.03% [8].

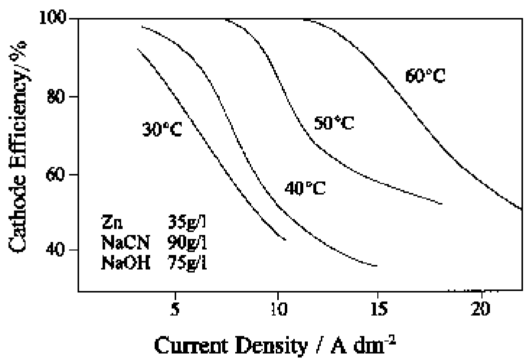

Fig. 9. The effect of temperature on cathode efficiency for cyanide zinc solutions.

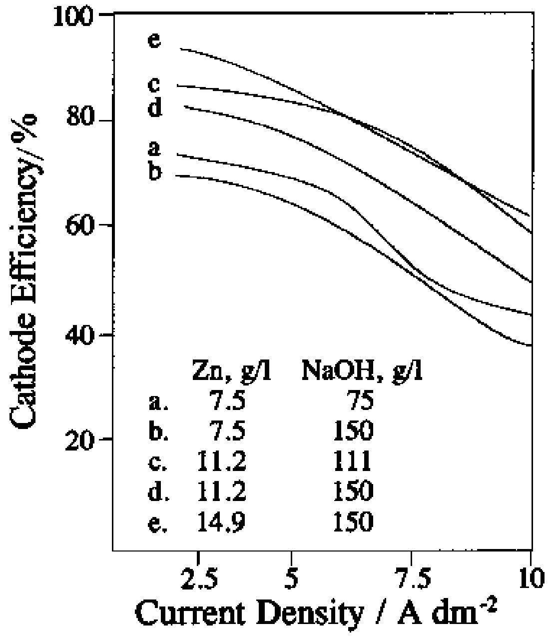

Fig. 10. The effect of zinc and sodium hydroxide concentration on the cathode efficiency of zincate solutions.

For cadmium the alkaline cyanide solution is widely used, CCE is 85–98%, CCE decreases with increasing CN:Cd ratio and increases with increasing cadmium ion concentration, temperature and agitation. Hydrogen embrittlement is a major concern.

The acid fluoborate solution is little used, for which the CCE tends to 100%, but hydrogen embrittlement is essentially absent. The reason for this adverse effect of cyanide is that CN^- is adsorbed strongly on iron surfaces and inhibits combination and oxidation reactions and as a complexant displaces less favourable anions; that is, CN^- increases hydrogen embrittlement by inhibiting the combination reaction

$$M-H + M-H \Rightarrow 2M + H_2$$

and allowing hydrogen ingress to the substrate [17–21]. Yaniv *et al.* [19, 20] have shown that the absorption increases as log[CN] at the usual concentrations of cyanide. Thicker cadmium deposits produced from such a solution slow down the absorption of hydrogen by a steel substrate purely through acting as a thicker diffusion barrier.

The rate of entry of hydrogen is affected by the potential and current density on the metal surface and poisons act by interfering with the catalyst recombination reaction thus allowing increased ingress [21–23]. The effect of poisons can be ranked as follows although not all workers agree on the exact order: P > S > As > Se > Te > Pb > Bi > Hg. While it is often suggested that the nature/identity of the anion has little effect on hydrogen embrittlement, this is not true, although for the common acid radicals, for example, Cl^-, SO_4^{2-}, the effect appears to be negligible. Addition of oxidants, typically nitrates and H_2O_2, reduce hydrogen ingress by providing a cathode depolarization reaction [10], thereby evading difficulties of the combination reaction.

Organic additives are adsorbing agents and, even if their prime role is to provide a brightening action for the growing electrodeposit, they act as catalyst poisoners by virtue of that adsorption so that more hydrogen may become available for absorption and possible eventual embrittlement.

The presence of cathodic second phases may have a marked effect and the use of platinum inserts or studs in iron can provide very efficient sites for hydrogen evolution and thereby avoids gas ingress [24]. The criterion for effectiveness can be expressed in terms of exchange current densities as follows:

$$i_0(\mathrm{Pt}) \gg i_0(\mathrm{Fe})$$

This is analogous to the cathodic protection provided by platinum on titanium anodes which thereby enables platinized titanium to be an effective insoluble anode.

A recent suggestion is that pulse plating techniques may be useful in eliminating hydrogen, either on the surface or in the immediate surface layers, provided that a pulse reverse (i.e., anodic) part cycle is employed. The anodic component is programmed to Faradaically oxidize the hydrogen produced by the cathodic inefficiency [25, 26]. This technique has been applied to chromium from hexavalent solutions (efficiency 20%) and the effect is to increase the nett efficiency from typically 16 to 28% and eliminate stress caused by deposited β-Cr decomposing to α-Cr through hydrogen release. A further effect is the elimination of cracks in the deposit and a lowering of hardness (1000 to 600 VPN) the consequence of which, for product properties and applications, must be fully recognized.

6. Hydrogen embrittlement

Historically, hydrogen embrittlement effects have been known since the middle of the 19th century. The literature is vast but primarily concerned with the mechanical effects and its elimination or avoidance. Recent reviews [2–4] are noticably sketchy on the mechanism of hydrogen formation and its absorption mechanism. High tensile steels are particularly susceptible to hydrogen embrittlement the hydrogen always arising from cathodic/corrosion sources including pretreatment processes such as pickling where, for example, the time of pickling as well as the cross sectional area of the steel and its state of heat treatment are important parameters affecting embrittlement [27]. It is improbable that only high tensile steels are susceptible; however, it is inevitable that these steels will be seen to have the largest effect because of the very substantial number of interface defects or voids which exist at which incipient hydrogen bubbles can gather to have deleterious effects. Body centred cubic (b.c.c.) metals are especially susceptible where stress concentrations exist. This is especially true for surfaces after mechanical working and the 'Beilby layer' remaining after polishing; light etching often reduces this type of susceptibility.

The substantial research information available for steels [28] has drawn attention to a few other aspects of the problem. For example, diffusion studies have long been carried out but with a variety of uncertainties; however, it is clear that hydrogen must primarily exist and diffuse in steel as hydrogen atoms or ions and certainly not a molecular form. Similarly, hydrogen can be considered as an alloying element in steels but, again, as atomic hydrogen. Thus, embrittlement attributed to molecular hydrogen bubbles must be a quite different problem.

Fatigue or tensile properties are affected by slow straining rates; the effect is absent at rapid rates of loading. This is attributed to the ability of hydrogen to diffuse rapidly towards points of stress concentration and adjust its concentration as defects move. A diffusion rate in steel at room temperature of $10\,\mu\mathrm{m\,s^{-1}}$ is often quoted. Although the solid solubility in iron is low (3×10^{-8} at%) it can be high at line and point defects. Such fatigue effects are also found in high tensile aluminium alloys which are f.c.c. in crystal structure but embrittlement is not a significant effect [19].

Theory attributes the embrittling effect of hydrogen to three possible causes: (i) Pressure assistance to crack development at voids. (ii) Reduction of cohesive strength or M–M bonds at crack tips. (iii) Reduced plasticity promoting brittleness which leads to shear-controlled fracture.

De-embrittlement has long been practiced through a heat treatment which allows the hydrogen to disperse to the metal surface and be released to the atmosphere as hydrogen gas. The favoured temperature is 180–220 °C to maximize hydrogen diffusion and minimize deleterious heat treatment (for example, recrystallization) to the steel structure. (It should be noted that at 200 °C the diffusion coefficient is 100× greater than at room temperature.) Formerly relatively short times were cited, for example, 1–3 h, but it is now well-understood that an exponential loss from the steel occurs so that half the hydrogen is lost every 1–3 h and that to achieve >90% removal can require times over 18–24 h. Specifications are usually devised to offset the effects arising from electrodeposition of chromium on high tensile steel bolts where hydrogen embrittlement is clearly most dramatic. A summary of recommended times and temperatures (based on European Aerospace Standard EN2132) are given in Table 4.

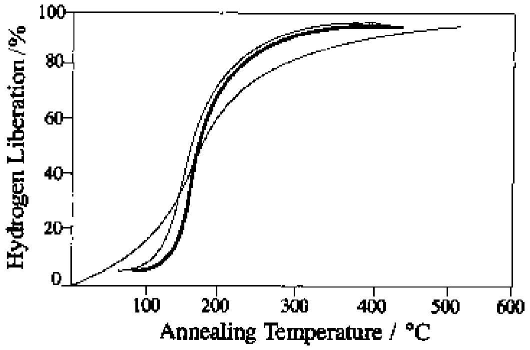

Fig. 11. Hydrogen liberation from hard chromium (annealing for 2–4 hours) [8].

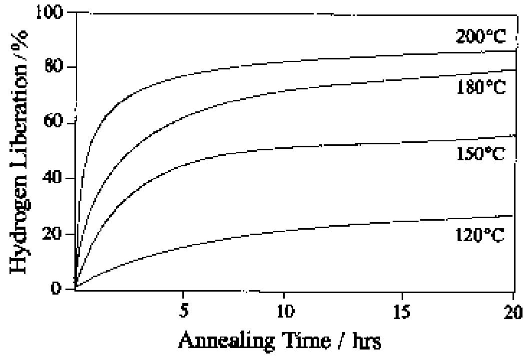

Fig. 12. Hydrogen liberation from hard chromium as a function of time during heating at four temperature [8].

Data for hydrogen liberation during such treatments for chromium deposits has been reported, Figs 11 and 12. The hydrogen is released fast at first and decays exponentially, as already mentioned, indicating diffusion control. For hydrogen in Cr, 0.06% w/w represents almost 2000× its own volume!

7. Conclusions

Hydrogen embrittlement has been shown to depend on a number of factors that can be attributed to process or electrochemical origins. The minimization of the effects can be summarized as follows.

Table 4. Recommended heat treatment times and temperatures for steels being chromium plated

Tensile strength of steel[*] / N mm^{-2}	*Prior to plating*		*After chrome plating*			
	Temp. / °C	*Time* / h	*Temp.* / °C	*Time* / h	*Temp.* / °C	*Time* / h
Up to 1100	–	–	–	–	400–480	1
1100–1450	190–230	1	190–230	2	400–480	1
1450–1800	190–230	18	190–230	16	400–480	1
Over 1800	190–230	24	190–230	18	400–480	1

[*] A value of 1100 N mm^{-2} corresponds to a Brinell hardness of 320 and 1450 N mm^{-2} corresponds to 415.

(i) *Choice of solvent*: Elimination of water from processing will remove the source of hydrogen; in general this is not a practicable proposal.

(ii) *Cathode current efficiency*: If the CCE is nearly 100% the electrochemical source of hydrogen in electroplating is minimized.

(iii) *Physical structure*: A high coating porosity will allow hydrogen to desorb; a low porosity of underlayers will prevent initial adsorption.

(iv) *Solute ions*: Cyanide ions and organic additives tend to poison catalyst effects during hydrogen evolution and, consequently, promote absorption. Nitrates and oxidants depolarize hydrogen evolution thereby removing hydrogen prior to its possible absorption.

(v) *Noble metals*: Platinum and palladium calalyse the hydrogen adatom combination step and therefore promote evolution; this minimizes the tendency to hydrogen absorption in the substrate.

(vi) *Underlayers*: Nickel and copper underlayers act as barriers to hydrogen absorption in steel substrates.

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