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An Investigation of Hydrogen Embrittlement

of

High Strength Steel

due to

Zinc/Nickel Alloy Electroplating

Supervisor:

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Abstract

The work described in this thesis examines the embrittling effect of both cadmium and zinc-nickel electroplating on quenched, tempered and plated and plated and baked tensile specimens of AISI 4340 steel.

Measurements were taken of ultimate tensile strength, reduction in area to obtain an embrittlement index and Vickers hardness. In this way a direct comparison of the extent of embrittlement for the two alternative processes was made, while at the same time, keeping a quality control check on successive batches of specimens. An examination of the microstructure and fracture surfaces was made.

The effect of baking to remove hydrogen dissolved in the electrodeposit and de-embrittle the steel was considered. Being porous to hydrogen, some types of cadmium electrodeposits allow hydrogen gas to exit the substrate during baking. Nickel, however is capable of forming a barrier to hydrogen diffusion and it was found that this could impede the ingress of hydrogen without preventing the degassing of the specimens.

Permeation experiments were conducted, using a cell based on a Devanathan and Stachurski permeation cell, to compare and contrast the amount of hydrogen that entered a steel substrate during zinc-nickel alloy electroplating under various conditions. The amounts of hydrogen that permeated the diffusion membrane were then examined in the light of the results of the tensile tests.

It was found that a close correlation existed between the amount of hydrogen entering the substrate and the extent of embrittlement. This correlation allowed apparently anomalous embrittlement observations to be explained in terms of the pH of the plating solution. The results suggested a modification to the currently accepted hydroxide suppression mechanism for zinc-nickel alloy deposition was possible.

By way of testing predictions made under the modified deposition mechanism, Auger and XPS analyses were used to search for a nickel rich layer predicted to exist adjacent to steel substrate.

Acknowledgements

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Drs Chris Smith and Kevin Baldwin of the D.R.A. deserve a special thanks for their help and suggestions throughout the research.

No work of this nature can be achieved without the dedication and support of an army of technical staff, too numerous to name, assisting with analyses, advising on techniques to obtain better results and machining parts from inexpert drawings. A special mention, however, is deserved by Dr. Sue Impey for the time and trouble taken over Auger and XPS analyses.

My wife, Laura, to whom this work is dedicated, requires a special acknowledgement. Her perseverance in supporting me over the three years of this research made everything possible.

Finally I would like to add an special mention to memory of my father, who died before this thesis was completed.

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1 Introduction

Until recently, cadmium electroplate was successfully used to protect high strength steels and would have been the automatic choice for corrosion protection of fasteners and other items.

Although hydrogen embrittlement has been a potential problem, due to hydrogen absorption during the plating process, subsequent heat treatment can successfully de-embrittle the steel, either by de-gassing the steel and/or by driving the hydrogen into irreversible traps.

Cadmium works by forming a sacrificial coating on steel that does not produce a voluminous corrosion product, as zinc does. The coating itself is commercially attractive in the bright form, and can easily be passivated to produce a longer lasting, yellow coating. In addition to a low volume corrosion product, cadmium is self lubricating, making it ideal for use on fasteners.

Unfortunately, the effluent from the process is environmentally harmful, and removal of electroplating effluent from water supplies is expensive.

The electroplating effluent consists essentially of cadmium cyanide dissolved in a concentrated sodium hydroxide solution. After treatment, the effluent is discharged into the sewer system where it is monitored by the National Rivers Authority and HM Inspectors of Pollution. Cadmium electroplating is carried out only under licence and the plater is expected to follow strict guidelines about amounts discharged as waste.

Treatment involves the oxidation of the cyanide to nitrite and eventually into harmless nitrogen gas. The cadmium remaining has to be removed, since cadmium metal is a bio-accumulating toxic substance, stored in plants and animal fat. Once in the food chain, it is virtually impossible to remove.

Cadmium can be precipitated from water by adjusting the pH to between 9 and 9.5. If necessary, the water may be filtered to remove the suspended cadmium.

Care must be taken not to discharge the effluent into water containing nickel, as this can result in cyano- complexes with nickel that cannot be removed from the water. The effluent must also be isolated from acidic water, such as from peat moorland as this may risk the formation of hydrogen cyanide gas.

In order for water to meet EC surface water drinking standards, the concentration of dissolved cadmium must not be greater than 0.005 mg dm^{-3} .

Because of the environmental problems, less environmentally damaging alternatives to cadmium are being sought. One such possible alternative is zinc-nickel alloy electroplate.

Corrosion studies regarding zinc-nickel alloys are promising, and although coatings are not bright, as are cadmium, they do offer some useful advantages such as not producing a voluminous corrosion product. Such coatings are suitable for fasteners and they accept paint readily, making them interesting to the automotive industry for car body corrosion protection. Furthermore, the rest potential of zinc-nickel alloy is, like cadmium, compatible with that of aluminium alloys used to make aircraft. This makes the use of the alloy for fasteners in aircraft seem possible. Once the corrosion resistance of the zinc-nickel alloy is demonstrated, their suitability or not for high strength steel components rests on the extent, if any, of hydrogen embrittlement due to cathodic hydrogen being co-deposited with the alloy and the ease of de-embrittlement by baking.

This thesis is primarily concerned with the extent of hydrogen embrittlement, the ease of de-embrittlement after plating and how the conditions of plating determine the extent of embrittlement. The deposition mechanism in the initial stages is considered which sheds fresh light on the mechanism itself and also on hydrogen uptake by the substrate.

The current efficiency of zinc-nickel alloy deposition is known to be very high, however, even a small amount of hydrogen, once absorbed by the substrate, is capable of causing severe embrittlement to the high strength steel. De-embrittlement by baking for a short time at 200°C is the usual method of removing the hydrogen. Thermal treatment can, unfortunately have the effect of reducing the UTS of the steel slightly, so the temperature and duration of the baking process must be controlled carefully. It would be advantageous, from both a mechanical and economic viewpoint, if this baking process could be reduced.

It is not the purpose of this work to determine mechanical data about the cracking mechanism, nor is it to determine the mechanism itself, but to monitor the extent of hydrogen embrittlement resulting directly from the electroplating process and to assess the extent of recovery after de-embrittlement.

In order to study the extent of embrittlement, a statistical selection of at least five tensile specimens was taken, each with the same treatment. A Weibull type analysis was performed, in which the Probability of Survival (P_S) was determined and a plot of the $\ln(P_S)$ v "Time to Failure" was made. This gave a series of straight lines that could be used for direct comparison. Further statistical analyses using the Student t-test criteria were used to determine more closely if particular sets of specimens belonged to the same distribution. In other words it was possible to determine if full recovery had occurred or not, or if two sets of results could be considered to be the same or only similar. The same method was also used as a quality control method between specimens that had been heat treated at different times.

Logically, the extent of embrittlement must be related to the ingress of hydrogen, the greater the extent of embrittlement, the greater the amount of hydrogen that would be expected to enter the substrate, and vice versa. If no such correlation is found to, then another explanation must be found to account for the embrittlement.

Nickel is known to be a barrier to hydrogen permeation, since it has a very low diffusion coefficient, of the order of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ or less. However, if mobile hydrogen is stored within the electrodeposit in some way, then hydrogen may slowly diffuse into the substrate, gradually reaching levels that cause embrittlement. A question arises about how soon after plating must a de-embrittling bake be conducted in order to de-embrittle the component. In industry, a delay of one shift (eight hours) is considered sufficient, but this is an empirical value only.

Permeation measurements performed on mild steel membranes during zinc-nickel alloy electrodeposition seek to link the embrittlement measurements of tensile specimens with the quantity of hydrogen produced under specific plating conditions. Experiments were designed to provide fundamental information on the deposition mechanism of the zinc-nickel alloy electrodeposits.

2 Literature Survey

2.1 Hydrogen Embrittlement

Oriani^[1] defines hydrogen embrittlement as ...

"The hydrogen caused reduction of the load-bearing and/or the mechanical energy absorption ability of a metallic alloy."

There are a number of theoretical mechanisms proposed for hydrogen embrittlement. Each theory has been used to explain observed phenomena under specific conditions, but no single theory can explain all cases of hydrogen embrittlement. With increasing understanding of the solute properties of hydrogen, interactions between hydrogen atoms and the metal lattice and the transport properties of hydrogen through a metal, theories have diverged and developed into our present understanding of the problem^[2,3,4]. Irrespective of the differences between proposed models, there is a general consensus on two important matters^[4]...

1. That for any particular metal, it seems likely that more than one mechanism can be in operation within the same specimen. Similarly for any particular metal, under different conditions, the dominant mechanism is not necessarily the same in each case.
2. For all of the mechanisms, the general sequence of events is the same, notably hydrogen must be ...
 - transported to the metal surface,
 - adsorbed,
 - absorbed,
 - transported into the bulk of the metal.

With one form of hydrogen embrittlement, termed the "hydrogen attack" mechanism, an additional requirement is that there be sufficient thermal energy in order to overcome thermodynamic barriers to form chemical bonds.

A discussion of the principal mechanisms and the factors common to each mechanism is given in the following sections.

2.1.1 Internal Pressure

In most metals, dislocation interactions result in stress concentration followed by microvoid formation in the area local to the stress concentration.

Subsequent strain results in the growth and possible coalescence of these microvoids or micro cracks, eventually resulting in fracture of the specimen. In the case of a hydrogen charged specimen, atomic hydrogen may diffuse to these microvoids or microcracks and recombine at the inner surface reforming molecular hydrogen. In so doing, the micro crack is stabilised and their effective number increased.^[5,6]

This has been shown not to be a generally applicable mechanism, since high external pressures of hydrogen are required and crack propagation is known to occur with low (sub-atmospheric) hydrogen pressures.^[7]

A suggestion that hydrogen may be transported along dislocations towards sites of supersaturated hydrogen concentration^[8] was later discounted after supersaturation calculations^[9] and determinations^[10] showed that levels of supersaturation were too low to explain the high pressures necessary.

2.1.2 Surface Energy

For a crack to initiate and propagate within a material, a fresh surface is necessarily produced. This requires that new surface energy be accounted for. Since a crack initiates and propagates due to an applied stress, the surface energy is acquired by the conversion of some of the applied strain energy. Anything that acts to reduce the surface energy will make easier the formation of cracks. Petch and Stables^[11] proposed that hydrogen would adsorb to the crack surface, thereby reducing the surface energy and promoting propagation of the crack at a speed limited by the rate of supply of hydrogen to the crack tip.

A problem with this theory is the apparent contradiction about the adsorption of hydrogen onto the crack surface. Oxygen has a more exothermic heat of adsorption, thereby reducing the surface energy by more than in the case of hydrogen adsorption. However, oxygen not only fails to promote cracking, but also actively reduces the effect of any hydrogen that may also be present.^[7]

Perhaps more serious is the omission of any suggested mechanism as to how the hydrogen facilitates the formation of a new surface so that it can then adsorb to that new surface.

2.1.3 Brittle Hydride Cracking

Westlake^[12] proposed that hydrogen might diffuse ahead of a crack tip to a region of high triaxial stress at which a metal hydride might be stable. The resulting metal hydride, being of lower strength than the metal lattice, would be responsible for brittle failure over the region of hydride formation.

Although some success was had with crack formation in niobium, no convincing evidence has emerged regarding iron and this theory is generally not applied to iron or steel. However, conditions immediately prior to crack formation may allow stability for iron hydride that is lost when the crack opens up.^[13] Subsequent decomposition of the iron hydride would make a determination of the transient hydride difficult to prove.

Although iron hydride has not been found to be stable below 2 GPa^[14] calculations indicate that in the immediate region of the crack tip, hydrogen saturation is at a sufficiently high level to produce behaviour similar to hydride formation.^[15]

More recent work on using statistical thermodynamics to calculate stabilities of some metal hydrides in lattices^[16] seems to indicate that iron hydride, in the fcc structure is only slightly less thermodynamically stable than nickel hydride, also in an fcc lattice. Nickel hydride itself is unstable under normal atmospheric conditions, but does exist long enough to be detected. These statistical thermodynamic calculations give no indication of the kinetic stability of hydrides but it would be reasonable to infer that the less stable iron hydride would decompose faster than does nickel hydride.

These same calculations indicate that iron hydride becomes more stable at lower temperatures, paralleling the calculations of Hirth and Carnahan on hydrogen saturation at crack tips.^[15]

2.1.4 Lattice Decohesion

Originally proposed by Troiano,^[17] hydrogen is capable of diffusing to areas of high triaxial stress, forming more concentrated solutions of hydrogen in iron than would occur without the stress. It was later pointed out that the increase in hydrogen solubility of $3c_0$ (c_0 = concentration of hydrogen in the unstressed bulk material) was insufficient to explain the observed fracture.

In order to reduce the cohesive forces between metal atoms in the crystal lattice, it would be necessary to have a much larger hydrogen concentration than could be obtained using the model suggested by Troiano. However, the idea of decohesion was a good one if the hydrogen concentrations could be justified. Oriani^[18,19,20] and Oriani and Josephic^[21] developed the decohesion theory further by accounting for the extra solubility needed for crack propagation to occur.

There could be two possible types of site at which stress would be high enough to produce a sufficiently high hydrogen concentration, the first would be a few angstroms ahead of a sharp crack subjected to opening forces, the second would be at an interface. The interface could be a surface, inclusion, grain boundary or dislocation.

Hydrogen diffuses to sites of high triaxial stress. Once in these sites, just ahead of the crack tip, the hydrogen interacts with the atoms in the metal lattice such that the cohesive force between the metal atoms is reduced. When the local stress equals the cohesive force between the atoms in the lattice, at the crack tip, then the crack will propagate.

Fig. 2.1 Atomic model of a crack edge.
Straight lines representing linearly stretched bonds, zig-zag lines representing bonds stretched in the non-linear region^[19]

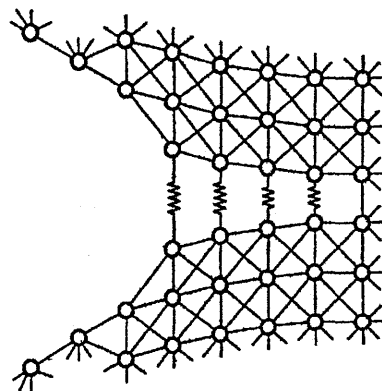


Fig. 2.2a
Relationship
between cohesive
Forces, $F(z)$ and
Strain, ϵ

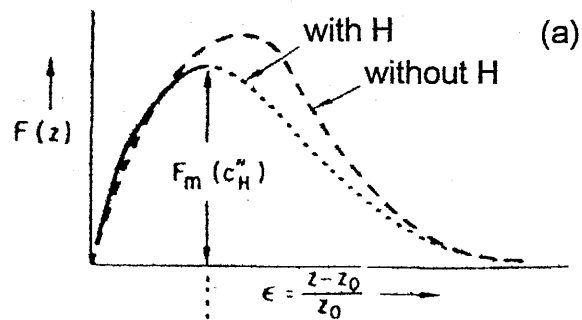


Fig. 2.2b
Relationship
between hydrogen
concentration in
iron and Strain, ϵ

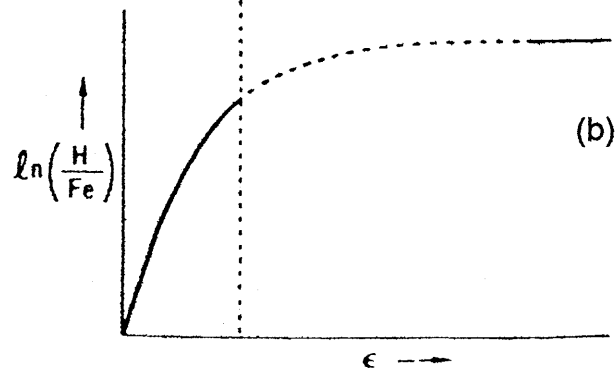


Fig. 2.2^[1] shows the reduction in stress required to produce a given extension, notably lower for the situation involving hydrogen. Fig. 2.2b^[1] indicates the increase in hydrogen concentration corresponding to Fig. 2.2a. As the value of ϵ tends to infinity, the situation described is that of fracture. The area under the curves in Fig. 2.2a represents the work done to cause that fracture, that is, the presence of hydrogen reduces the work necessary for fracture. The hydrogen concentration can be seen to rise quickly with strain before levelling off towards a maximum.

2.1.5 Localised Slip Model

Since a ductile material will extend more than a brittle material before fracture, even when the tensile strengths are the same, the work done in bringing about fracture in a ductile material is greater than that for a brittle material. So it seems unlikely that a material might be embrittled (reduced work to cause failure) by a mechanism that involves plastic deformation. However, as Beachem^[22] proposed, if the plastic deformation is a localised, microscopic effect used to propagate the crack, rather than being an overall macroscopic effect, any apparent contradiction disappears.

The theory as described by Beachem was developed largely by Lynch^[23 - 27] after observing two important features ...

- i) Identical fractographic results can be obtained from stress corrosion cracking (SCC), hydrogen assisted cracking (HAC) and liquid metal embrittlement (LME).
- ii) That very small dimples could be found on cleavage surfaces.

From the first observation, rates of diffusion into the solid metal of liquid metal would be very much smaller than the rate of crack growth. Since crack surfaces due to SCC, HAC and LME are so similar, and if, as Lynch believes, LME occurs at a crack tip on the surface of the solid metal, then by inference, the action of hydrogen in SCC and HAC must also apply to surface crack tips.

The second observation gives evidence of the formation of microvoids in advance of the crack tip.

Lynch considers the embrittlement to be solely a surface effect and gives no plausible explanation about how the hydrogen, or liquid metal, appears ahead of the crack tip. Birnbaum adopts a very similar approach, but in addition to the surface effects, proposes a Hydrogen Enhanced Local Plasticity (HELP) model that considers not only the surface effect, as does Lynch, but also the hydrogen already contained in the bulk of the material.^[28]

In the HELP mechanism Birnbaum suggests that internal hydrogen can associate around discontinuities, such as point defects, inclusions and dislocations, in the metal lattice. Being a light element with high diffusivity, when a dislocation moves, the hydrogen atmosphere is swept along with it, thereby facilitating transport of hydrogen.

Using TEM methods, Birnbaum et al^[29,30] successfully observed failure in thin, hydrogen free specimens, and also in specimens into which hydrogen had been introduced. In this way, ductile processes due to localised hydrogen plasticity have been shown to occur in both cases, but hydrogen was shown to localise the plastic region ahead of the crack tip resulting in embrittlement.

Hirth^[4] gives values of 10 to 50 kJmol⁻¹ for the binding energy of hydrogen. This value indicates a low temperature stability for hydrogen being bound to specific sites in the lattice, but dissociation at high thermal energies. At very low temperatures, hydrogen would be kinetically labile and possibly unable to move with dislocations. In both of these extremes of temperature and for totally different reasons, hydrogen would be unavailable for transport along dislocations. This would suggest that, if dislocation transport of hydrogen is a significant factor in hydrogen embrittlement, then HE would be unlikely at extreme temperatures. This is borne out by the experimental evidence.^[2] illustrated in Fig. 2.3, below...

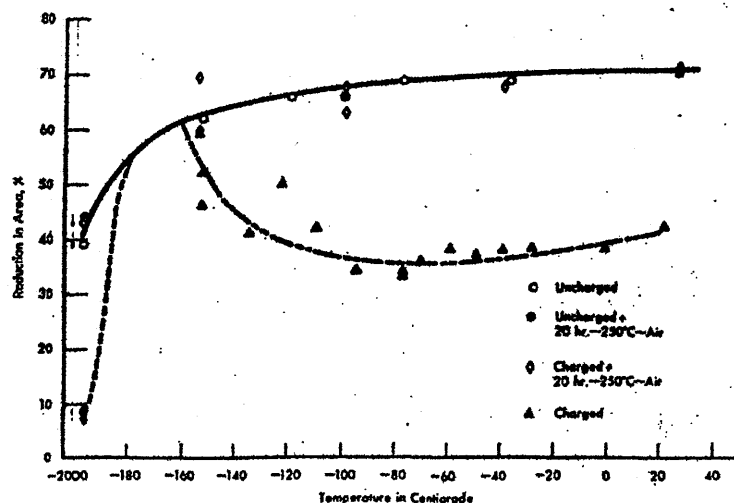


Fig. 2.3 Temperature dependence of HE in steel measured in terms of Reduction in Area (%).^[2]

Zakroczymski,^[31] working with iron, stainless steels and nickel found no increase in bulk diffusion during plastic deformation, which would be expected if dislocation movement was responsible for hydrogen transport. However, experimental evidence did suggest that trapping during plastic deformation increased, reducing the effective diffusivity of the metal. This does not mean that hydrogen is not carried by dislocations, merely that the increase in the trapping of hydrogen during plastic deformation is of greater magnitude.

2.1.6 Hydrogen Attack at High Temperatures

Hydrogen absorbed and diffused into the metal bulk may diffuse towards inclusions or grain boundaries. At these sites, providing sufficient thermal energy is available, corresponding to a temperature of 400 - 500°C, hydrogen may reduce certain compounds, such as carbides and oxide inclusions at grain boundaries to produce methane gas or water. Once combined in this way, the hydrogen is fixed and cannot be removed.^[2]

Subsequent changes in volume at these sites can act as nucleation sites for crack formation. In the case of methane formation, an increase in pressure at the site can also increase local stress and assist in crack formation.

Decarburisation of the steel ensues, leaving the steel with a reduction in strength, but more susceptible to ductile failure rather than brittle failure.

In this need for thermal energy to induce chemical reactions, the hydrogen attack mechanism is different to the other methods discussed^[4] and is irrelevant to this investigation. It is mentioned here only for completion.

2.2 Hydrogen Evolution Reaction

Before hydrogen can cause the embrittlement of any metal, it must first be absorbed by that metal. Hydrogen entry during electrochemical procedures occurs via the reduction of hydrogen ions in acidic solution and of water under alkaline conditions. Since the plating solution used in this work is acidic, only hydrogen ion reduction will be considered.

A mechanistic model, termed the IPZ model, has been proposed^[32-34] which, for the first time, quantitatively accounts for hydrogen surface coverage and concentration, hydrogen discharge, adsorption, absorption and recombination rate constants. Earlier models^[35 - 39] address some, but not all of these kinetic parameters.

The basic chemical steps relating to the hydrogen evolution reaction and entry into a metal substrate are outlined overleaf in Fig. 2.4

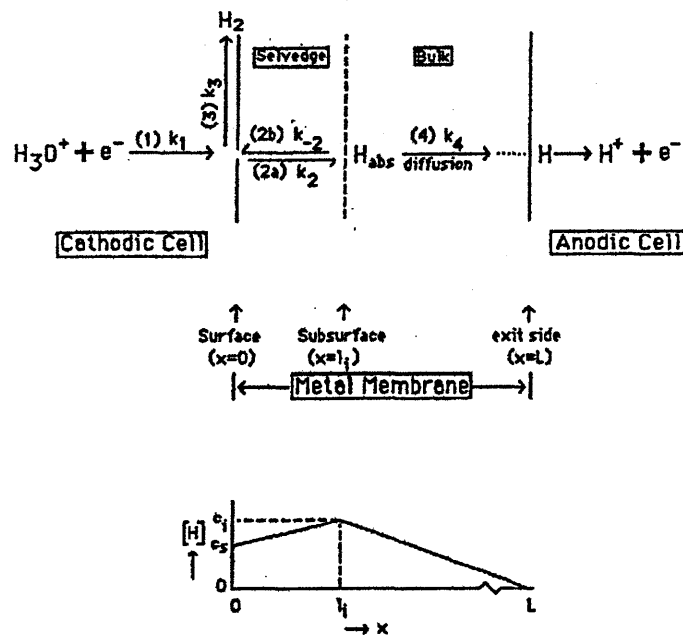
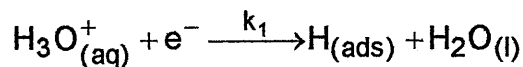


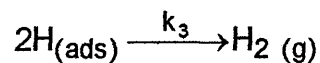
Fig. 2.4 Schematic representation of hydrogen discharge, recombination, permeation and selvedge reactions.

Due to the high overpotential required to produce hydrogen, it is assumed that the oxidation of adsorbed hydrogen is negligible.



This step leaves hydrogen adsorbed onto the metal surface. At this stage, there are two possible successive steps, the recombination of adsorbed hydrogen to form molecular hydrogen by a chemical recombination reaction and the absorption of adsorbed hydrogen into the surface of the metal. Permeation of absorbed hydrogen would then follow.

Once hydrogen atoms are adsorbed onto the surface and coverage is such that adsorbed hydrogen atoms can combine, it is assumed that they do so quickly.



Those metals that can act as hydrogen catalysts, such as palladium and platinum, have a high exchange current density. Consequently these metals rapidly lose their adsorbed hydrogen^[40] and do not have a large surface coverage of hydrogen. For other metals, as hydrogen coverage of the electrode surface increases, there is an increase in the amount of hydrogen absorbed by the metal substrate. Chatterjee, Ateya and Pickering^[35] have shown that thin and even discontinuous coatings of Pt, Cu or Ni on a less noble Fe substrate can delay and reduce the amount of hydrogen entering a steel substrate. They explain this in terms of a catalytic process in which hydrogen is recombined away from the iron surface. This is discussed further in Section 2.4.



In the equation written above, k_2 denotes the rate constant for the forward, absorption reaction, and k_{-2} that for the reverse, desorption reaction. The equilibrium constant between absorption and desorption would be described by the ratio of the two rate constants...

$$k' = \frac{k_{(\text{forward reaction})}}{k_{(\text{reverse reaction})}} = \frac{k_2}{k_{-2}}$$

The effect of surface coverage is significant to the amount of hydrogen that finally enters a metal substrate^[33 - 35] according to...

$$k_2\theta = k_{-2}c_0$$

...where θ and c_0 denote the surface coverage and surface hydrogen concentration respectively.

The region immediately below the surface of the metal and of the order of atomic distances, is termed the selvedge. The selvedge does not necessarily demonstrate the same hydrogen diffusivity as the bulk metal and this can give rise to a discontinuity in the hydrogen concentration gradient close to the surface.

2.3 Hydrogen Diffusion

Diffusion is the process by which matter is transported from one part of a system to another as a result of the random motion of particles. For any single particle, motion is random and chaotic. It is impossible, therefore, to predict a velocity for that particle. However, in the case of solute and solvent particles in which there is a nett excess of solute particles at one extremity of the solvent, there will be a nett diffusion away from the region of high concentration towards the less concentrated region. At a given temperature, because of the large numbers of particles involved in situations of the type in this work, it becomes possible to predict the transport of one substance through another.

Mathematically, the nett diffusion as described above, is equivalent to the conduction of heat through a solid and many analogies can be made. Consequently, there is a wealth of equations and their solutions^[41,42] relating to the conduction of heat that are directly applicable to diffusion. This is useful since the mathematics of diffusion in real situations is not a trivial problem.

The analogy between heat and mass transfer was recognised in 1855 by Fick, who applied the equation of heat conduction previously derived by Fourier.

Fick's First Law of diffusion considers the situation in an isotropic medium in which the flux, J , is directly proportional to the concentration gradient, $\partial c / \partial x$, the diffusion coefficient being assumed to be a constant.

$$J = -D \frac{\partial c}{\partial x} \quad \text{Fick's First Law}$$

$$\text{moles cm}^{-2} \text{ s}^{-1} = -\text{cm}^2 \text{ s}^{-1} \cdot \frac{\text{moles cm}^{-3}}{\text{cm}} \quad \text{Showing Units}$$

The fundamental differential equation of diffusion then becomes...

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{Fick's Second Law}$$

The exact solution of this equation depends on the boundary conditions imposed by the physical conditions. Some of the relevant solutions are discussed in the next section.

2.4 Hydrogen Permeation

Devanathan and Stachurski^[43] described a simple double cell arrangement by which hydrogen that enters and permeates a metal electrode can easily be measured. Fig. 2.5a represents the glass cell described by Devanathan and Stachurski, whereas Fig. 2.5b illustrates the electrochemical principles involved.

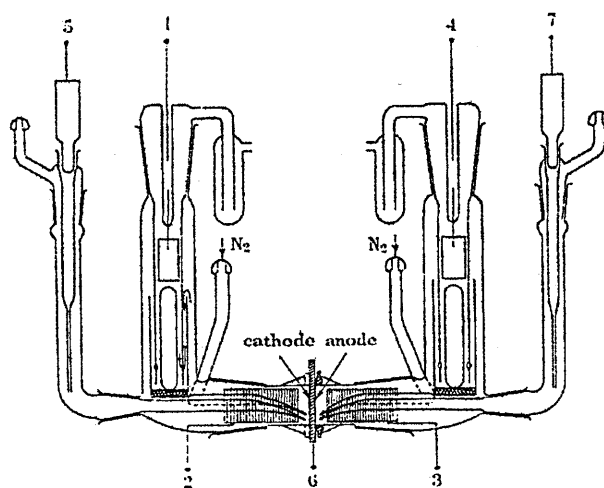


Fig. 2.5a Diagrammatic representation of a permeation cell.^[43]

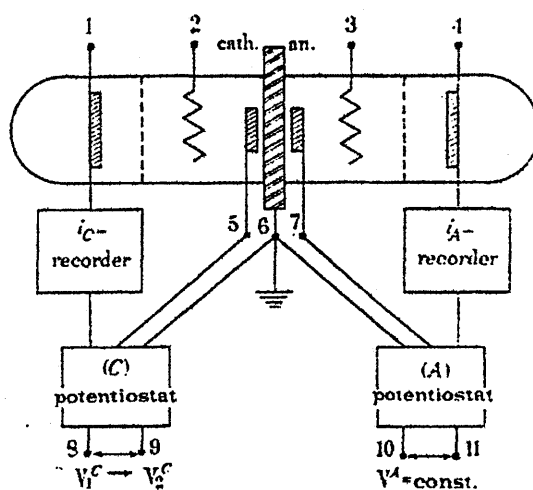


Fig. 2.5b Circuit diagram for a permeation cell.^[43]

A thin membrane electrode, made of the test material, is all that isolates two different electrochemical cells. For one (cathodic) cell, one surface of the membrane acts as a cathode and for the other (anodic) cell, the opposite surface acts as an anode.

Hydrogen ions are reduced from aqueous solution at the surface of the membrane in the cathodic cell. Most hydrogen reduced in this way combines to form hydrogen gas that bubbles away from the electrode surface. A small proportion of the hydrogen is absorbed into the metal surface whereupon it diffuses down a concentration gradient to the opposite surface. Once the hydrogen has diffused to the far side of the membrane it comes under the control of the anodic cell. At this surface, the hydrogen atoms are oxidised back to hydrogen ions and are removed from of the membrane. A zero concentration of hydrogen is, in this way, maintained at that surface. Since the surface hydrogen concentrations at both surfaces are therefore fixed, the hydrogen concentration profile through the membrane gradually approaches a steady state determined by diffusion processes. The current, i , on the exit surface is derived from Fick's First Law by equating each electron of the oxidation current to a hydrogen atom permeating the electrode. If F represents the Faraday constant then the permeation current is given by...

$$i = -DF \frac{\partial C}{\partial x}$$

Derived from Fick's First Law

Devanathan and Stachurski^[43] give an account of how the diffusion coefficient, D , may be determined from a measurement of the breakthrough time (t_b) and/or of the time lag (t_L) from the permeation current transients knowing the thickness, L of the electrode.

$$\text{Breakthrough time} \quad t_b = \frac{L^2}{15.3D}$$

$$\text{Time Lag} \quad t_L = \frac{L^2}{6D}$$

An example of a typical permeation transient, labelled to show t_b and t_L , is given in Fig. 2.6.

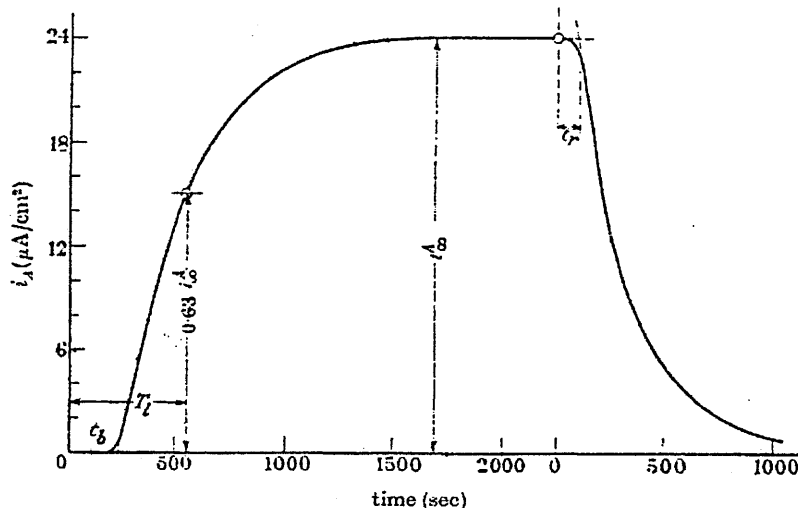


Fig. 2.6 A Typical Permeation Transient.

Boes and Zuchner^[45] considered a number of variations on the basic permeation technique, giving solutions of the diffusion equations for the various boundary conditions defined by the technique. In doing so, they arrived at equations that would predict theoretical permeation transients at the exit side of a permeation membrane and also the hydrogen concentration profiles throughout the membrane for both galvanostatic and potentiostatic charging conditions. The conventional conditions at the entry and exit surfaces being ...

- Galvanostatic (C) conditions maintain a constant flux into the surface, with a variable potential.
- Potentiostatic (P) conditions maintain a constant surface concentration with a variable flux. The exit surface is controlled at zero surface concentration.

Boes and Züchner give the solutions of the partial differential equations and obtain equations that predict the rising permeation transients for these conditions.

Non steady state galvanostatic

$$i_L(t) = i_0 \left(1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left(-\frac{(2n+1)^2 \pi^2 D t}{4L^2} \right) \right)$$

Non steady state potentiostatic

$$i_L(t) = i_\infty \left(1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left(-\frac{n^2 \pi^2 D t}{L^2} \right) \right)$$

Where...

t = Time

i_L = Efflux current density

i_0 = Entrance current density

i_∞ = Efflux current density at
time, $t = \infty$

n = Integer; 0, 1, 2...

L = Electrode thickness

Archer and Grant,^[47] question the widespread assumptions stated in the preceding paragraph relating to boundary conditions at the surface of the membrane undergoing charging. Instead, they suggest that the overall hydrogen entry depends, not only on the electrical method by which hydrogen is introduced to the membrane, but also the rate at which that hydrogen is introduced, taking into account other processes, such as hydrogen recombination and evolution. Although the potentiostatic method is expected to give a constant surface concentration and the galvanostatic method is expected to give a constant flux, it is possible that the transient produced will be intermediate between the two forms.

The I-P-Z model^[32,33,34] considers the effect of hydrogen entry into a metal on the hydrogen evolution reaction. Surface coverage is considered, along with rate constants for discharge, adsorption, absorption and recombination. Comparing this model, which predicts a constant surface coverage, with those for constant surface concentration (potentiostatic control boundary conditions) and constant surface flux (galvanostatic control boundary conditions),^[47] Allcock^[48] has compared theoretically generated permeation transients with experimentally determined transients, as shown in Figure 2.7. Although the experimentally determined transients were obtained under conditions of galvanostatic control, their shape was intermediate between the calculated theoretical surface coverage and constant flux models, but in very close agreement with the theoretical transients for constant surface coverage.

**THEORETICAL RISE TRANSIENTS FOR BSZ25 5mm PLATE FOR DIFFERENT
BOUNDARY CONDITIONS. COMPARISON WITH EXPERIMENTAL.**

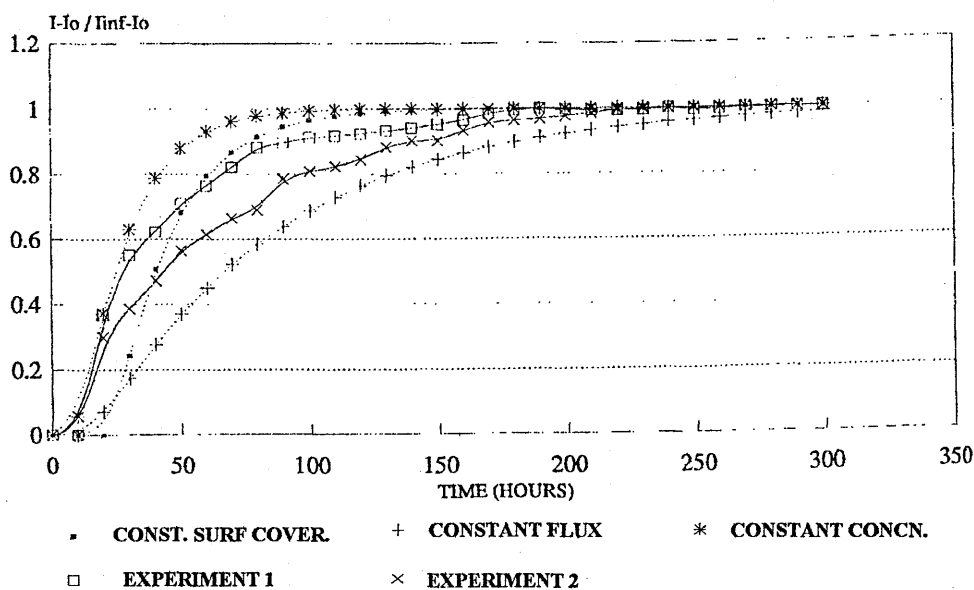


Fig. 2.7 Theoretical and Experimental Transients Compared.^[48]

The methods discussed up to this point in the account refer to permeation across a membrane of constant thickness and, it is assumed, constant composition. Furthermore the diffusion coefficient is generally assumed to be constant also. Unfortunately, the situation that exists during a plating experiment does not fit into this category. As plating continues, fresh deposit of a different material adds to the thickness of the membrane. Consequently, none of the above variables is constant. This complicates the mathematics of diffusion. However, by considering a simplified situation of hydrogen entry at the steel surface, being supplied with hydrogen from the electrodeposit, a diffusion mechanism can be assumed which approximates to a constant surface concentration over short periods of time. Assumptions can then be made about the concentration of hydrogen at the electroplate - steel interface.

Hydrogen permeation through a bilayer comprising a steel substrate with prepared electrodeposited coatings on the entrance side of the electrode have been studied. Chatterjee, Ateya and Pickering^[35] considered the effect on hydrogen permeation of Pt, Cu and Ni electrodeposits at the charging surface. Hydrogen absorption was found to be delayed for a period of time related to the nature and thickness of the electrodeposit.

Chatterjee et al found evidence to support the theory that a physical barrier to hydrogen entrance was, in fact, present. This was indicated by the decrease in the value of J_{∞} for increasing thickness of electrodeposits, as shown in Figs 2.8, 2.9, and 2.10. However, this could not explain all of their findings, since very thin and even discontinuous coatings were found to cause a significant decrease in permeation current density. Figure 2.11 shows that when 20% of an electrode is masked by the electrodeposit, hydrogen permeation is reduced by an amount exceeding the expected 20%. This effect is most evident over short times, with the effectiveness being reduced with aging during charging. In conclusion, they deduced that hydrogen was being produced catalytically at sites corresponding to the more noble metal, reducing the hydrogen overpotential of the composite electrode overall. A more rapid combination reaction for hydrogen resulted in a reduction in hydrogen surface coverage at the electrode surface and a reduction in the amount of hydrogen entering the electrode.

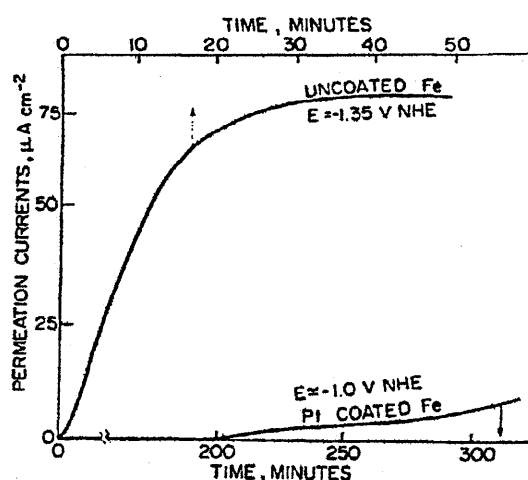


Fig. 2.8 Effect of a Pt coating on hydrogen permeation current.^[35]

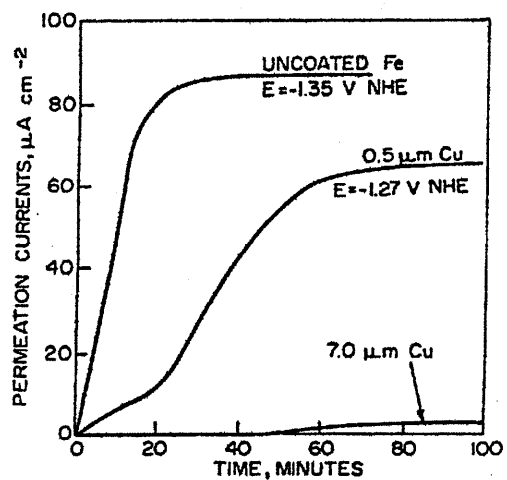


Fig. 2.9 Effect of a Cu coating on hydrogen permeation current.^[35]

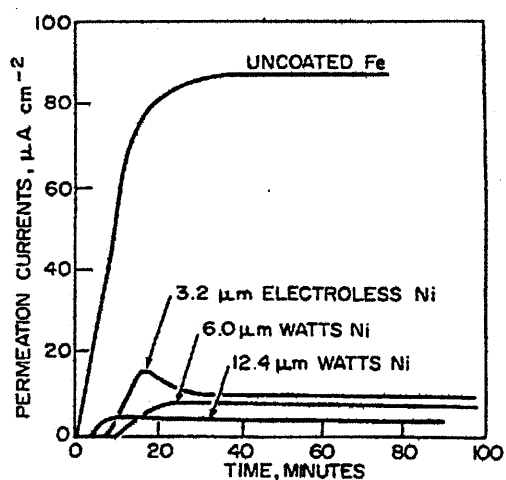


Fig. 2.10 Effect of a Ni coating on hydrogen permeation current.^[35]

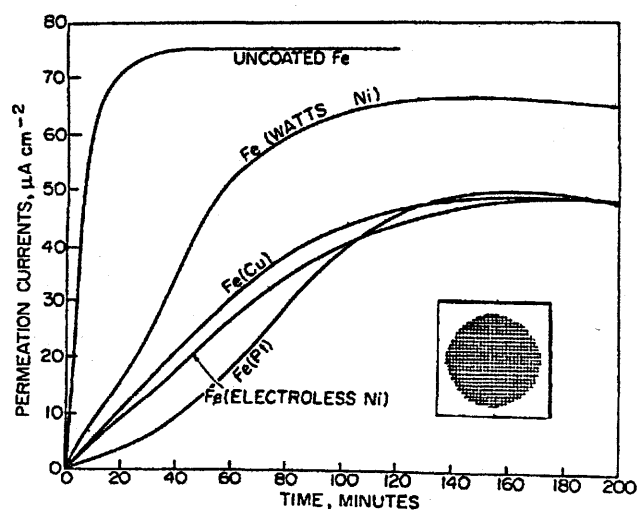
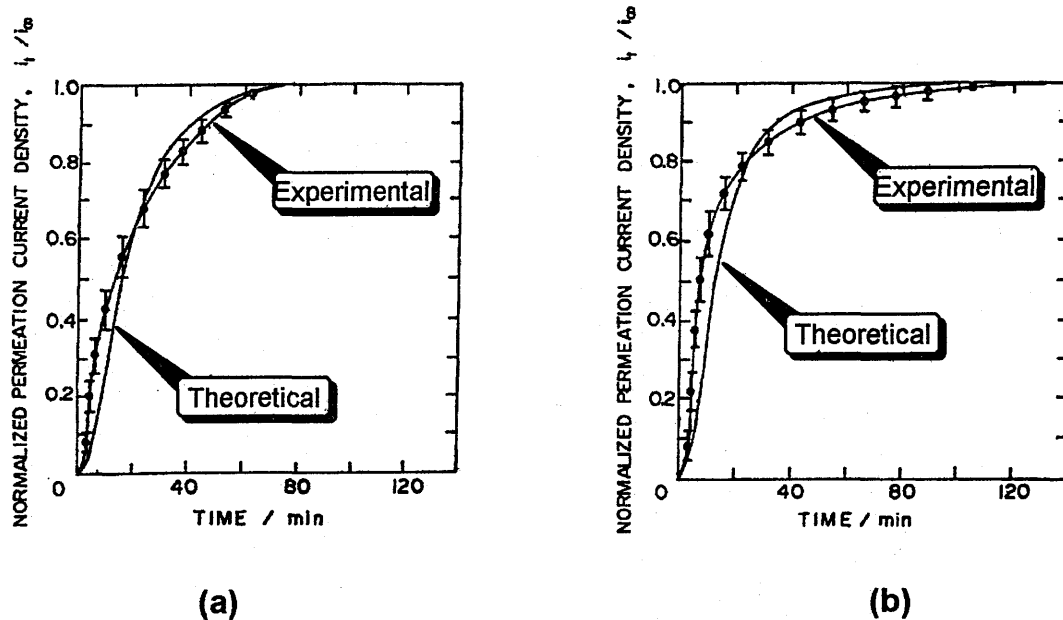


Fig. 2.11 Effect of square grid coating on hydrogen permeation current.^[35]

Song and Pyun^[49] attempted to measure the barrier effect of Ni, and to eliminate any catalytic effects on the entrance surface, they plated the exit surface of the electrode. In order to analyse hydrogen diffusion through the Fe/Ni bilayer, they developed a computer based, numerical solution to the diffusion equations in a bilayer based on the Crank-Nicholson method.^[42] See Fig. 2.12, below



(a) (b)
Fig. 2.12 Hydrogen permeation transients with...
(a) 4.5 μm (b) 6.5 μm nickel coating.^[49]

Song and Pyun^[49] found that no major advantage to a barrier mechanism could be ascertained by using a thicker coating, since the diffusion coefficient itself appeared to increase with increasing thickness (Fig. 2.13) of the electrodeposit. Thus a thin coating of nickel could be virtually as effective as a thick coating in terms of preventing hydrogen absorption by a barrier mechanism.

It is significant that each investigator observes, regardless of their interpretations of the mechanism, that a very thin coating can be almost as effective as a thick coating in terms of reducing hydrogen entry.

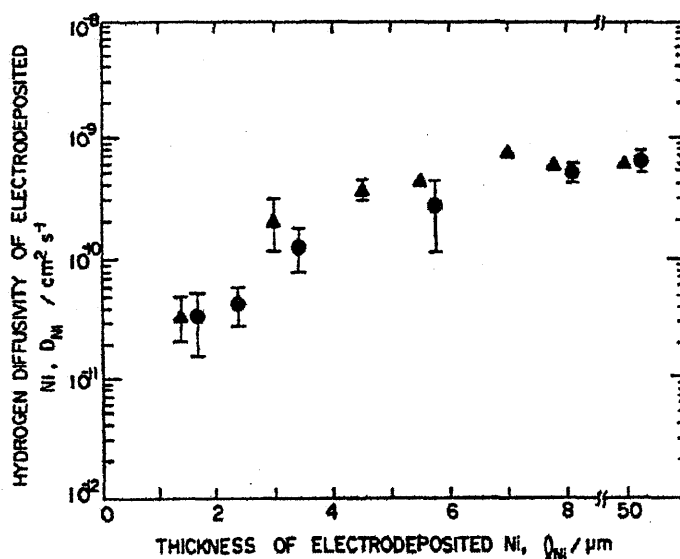


Fig. 2.13 Variation in hydrogen diffusivity with increasing thickness of the deposit.

Hydrogen concentration profiles through the Ni/Fe bilayer are given in Fig. 2.14 below...

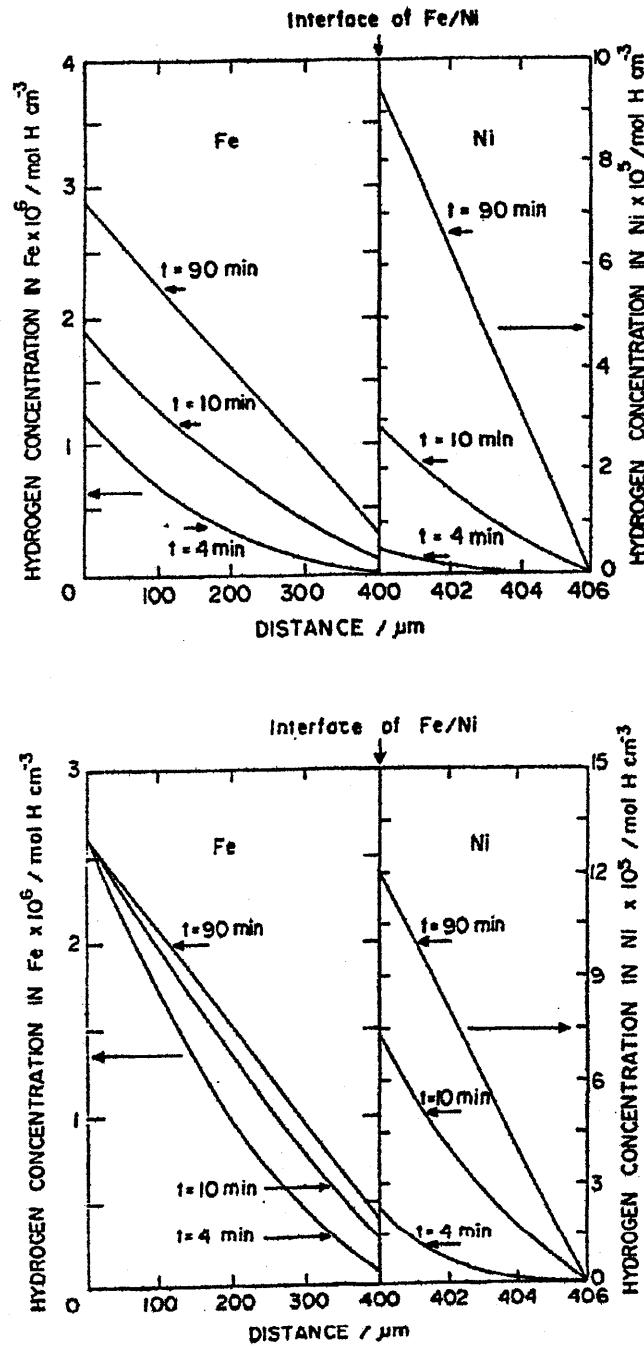


Fig. 2.14 Hydrogen concentration profiles across a bilayer as a function of time, (a) under galvanostatic and (b) potentiostatic boundary conditions.

A further complication to the determination of diffusion parameters is the trapping of hydrogen. It is virtually inevitable that traps will exist, not only within the original membrane and electrodeposited material, but at the interface itself due to stresses imposed by the deposition process itself.^[49]

2.5 Mechanical Testing

Turnbull^[50] describes several methods of measuring environmental assisted cracking, under which hydrogen embrittlement is classified. Two of the most popular methods for measuring the extent of hydrogen embrittlement are the constant load test and the slow strain rate test. Both of these methods generate regions of high triaxial stress around discontinuities, inclusions or other defects. As has been described already, mobile hydrogen dissolved in the steel is then free to diffuse towards these regions of high stress, promoting crack propagation and ultimately inducing fracture. Clearly such a diffusion controlled process requires adequate time for hydrogen to diffuse, and it is the time to failure that is most commonly quoted as the measure of embrittlement in these tests.

Constant load specimens frequently consist of a cylindrical bar, a piece of wire or C-rings supporting a load that is equivalent to a fixed percentage (e.g. between 50% and 90%) of the breaking load of the specimen. In time, any mobile hydrogen present diffuses to crack tips, promotes cracking and fracture follows. This method has been used successfully over a number of years by many investigators, including Johnson et al^[51], who used notched specimens to investigate the delayed failure of high strength AISI 4340 steel after uniform hydrogenation and subsequent de-embrittlement baking. With the 4340 steel, it was found that baking had the effect of de-embrittling the hydrogenated steel, making it possible for a steel to regain its original, non-hydrogenated properties. However, because austenite has a very low diffusion coefficient for hydrogen coupled with a relatively high hydrogen solubility, if the AISI 4340 (or other steel) has an austenitic microstructure, then the austenite can act as a hydrogen reservoir, allowing hydrogen to cause embrittlement long after the baking process is complete.^[52] The importance of microstructural manipulation on structural alloys, with the possibility of increasing hydrogen traps in high strength steels is currently seen to be a possible way forward in avoiding, or reducing hydrogen damage.^[53]

Steigerwald et al^[54], investigated the crack mechanism with respect to applied stress. It was shown that above a threshold stress, the initiation of a hydrogen-induced-crack was principally dependant on the hydrogen concentration. Steigerwald et al predicted that, since the incubation time to failure was an inverse relationship to hydrogen concentration, the rate of diffusion of hydrogen would increase with stress. This prediction was subsequently found not to be the case by Beck et al^[55] and McBreen et al^[56] Although an increase in the permeability of steel (Armco and AISI 4340) was measured due to stress, normalised transients for each stress level were identical. Application of formulae for t_b and t_L ^[43] to the normalised transients shows the constancy of the diffusion coefficient. Independence of the diffusion coefficient to stress and the direct relationship between stress and hydrogen concentration demonstrated that the diffusion coefficient must be independent of hydrogen concentration. Thus permeation data could be used to determine surface hydrogen concentration.

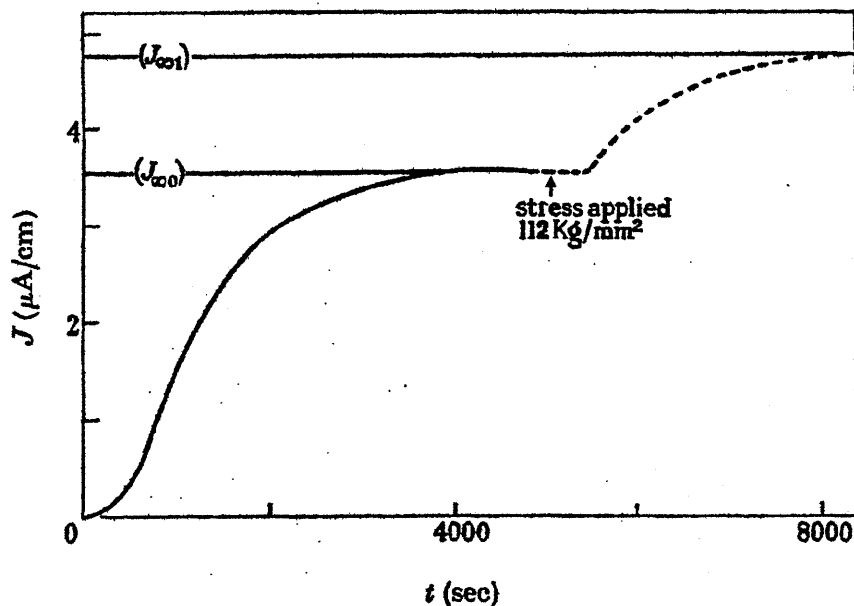


Fig. 2.15 Permeation-Stress Transient for AISI 4340 Steel.

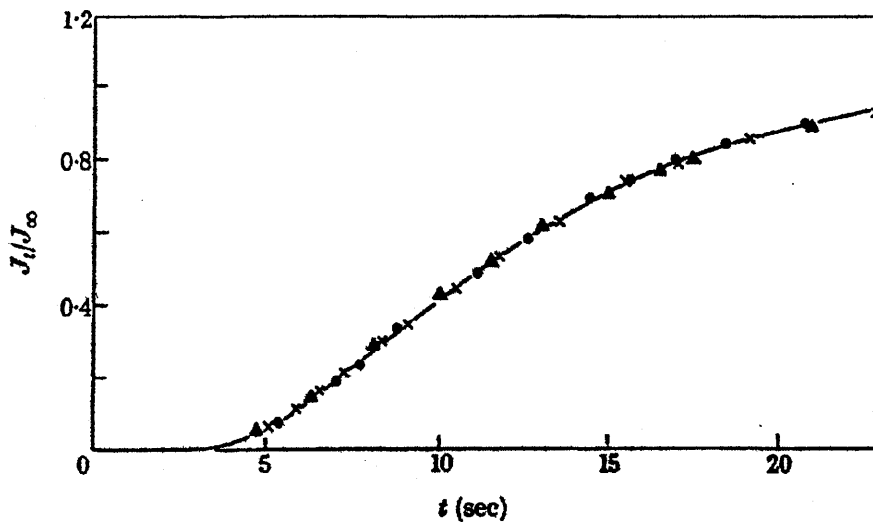


Fig. 2.16 Normalised Permeation-Stress Transients for Armco Iron.

Lucas and Robinson^[57], used a hydrogen probe^[3,59] to determine the mean concentration of the embrittling, mobile lattice hydrogen in BS4360 steel which had been heat treated to simulate the HAZ (Heat Affected Zone) of a weld. Measurements of the threshold stress intensity factor, K_{th} , showed a correlation between the reduction in K_{th} and lattice hydrogen concentration...

$$K_{th} = 91.2e^{-0.49C}$$

...where C denotes the mean lattice hydrogen concentration.

The simplest measurement to take with delayed failure tests is the time to failure. This gives a measure of the extent of embrittlement and a minimum period of time below which failure for a given set of conditions will not occur. However, due to variability in factors such as charging conditions, defect size, and surface imperfections, time to failure measurements are notorious for scatter. This scatter makes quantifying the effects of hydrogen on the strength of steel difficult to determine.

In 1951, Weibull^[60] developed a statistical approach to the scatter observed with the brittle fracture of ceramic materials. Strecker, Ryder and Davies^[61] treated the failure of hydrogenated carbon steel as a stochastic process^[62] in which the state of the system was dependant upon time in the same way as that developed by Weibull. Grundy et al^[63] applied the same principles, with some adaptation, to the failure of embrittled steel, which failed under static load testing. Since then the technique has been successfully applied by other investigators, such as, Robinson and Sharp^[64], who found that baking hydrogenated high carbon steel could, contrary to expectations, increase the susceptibility to embrittlement rather than decrease it. It was postulated that this was due to a release of hydrogen from low energy, innocuous traps during baking, thereby increasing the concentration of mobile hydrogen available for combining with higher energy traps. Under load, these traps then acted as stress concentrators, facilitating a more rapid failure.

The same modified, Weibull analysis was applied by Robinson and Evans^[65] to the investigation of the effect of nickel electroplating on hydrogen absorption and embrittlement of steels. Both a 0.8% C steel and AISI 4340 were used, with the 4340 steel being both cathodically charged and, in separate tests, nickel plated. Comparison of static load tests and permeation studies during nickel plating indicated that hydrogen, which was co-deposited with the nickel, could be held within the nickel deposit. This hydrogen was mobile and slowly diffused into the steel substrate. In this way, only a small amount of hydrogen would enter the steel during plating, but the electrodeposit itself acted as a reservoir for hydrogen, continually supplying the substrate with more hydrogen over long periods of time.

The modified Weibull statistical approach to the scatter in times to failure is discussed in the Appendix.

Slow strain rate testing has also been shown to be highly effective in assessing hydrogen damage. Unlike constant load testing, failure of the test specimen is guaranteed, and a measure of the tensile strength at failure and/or the shape of a stress-strain diagram can be useful in comparing embrittled to non-embrittled specimens.

Problems arise with slow strain rate tests^[66], in that crack progression during testing can result in partial relaxation of the specimen but, more significantly, once necking of the specimen starts, the strain rate can increase locally by up to two orders of magnitude. Since the effect of hydrogen embrittlement is highly dependant on strain rate,^[67-69] such a change in strain rate may result in the specimen being removed from the hydrogen sensitive region. For steel, the effective strain rate for hydrogen embrittlement is typically in the range between 10^{-7} and 10^{-5} s^{-1} . The critical strain rate for the material should be determined before testing, however, either from literature or from experiment^[66]. Technical problems with the stiffness of the frame of the testing machine can also affect the values of time to failure measurements^[66,70] although for a pure ranking purpose, providing the parameters of the testing machine remain constant, this should not be a problem.

Since hydrogen embrittlement is due to the ability of mobile hydrogen to diffuse to crack tips, a significant reduction in temperature would affect the extent of hydrogen embrittlement as shown earlier in Fig. 2.3^[2] with little or no hydrogen embrittlement evident at about -180°C . At liquid nitrogen temperatures, hydrogen should be effectively immobile,^[54] hence hydrogen embrittlement would not be expected at this temperature.

If it is known that a specific steel is susceptible to hydrogen embrittlement,^[71] precautions can be taken to avoid hydrogen ingress during pre-treatments,^[72] such as by avoiding acid pickling and electropolishing. Where the uptake of hydrogen is unavoidable, such as in electrodeposition of protective coatings, appropriate de-embrittlement procedures can be recommended.^[73]

The modified Weibull statistical analysis from slow strain rate data has been applied to times to failure on nickel electroplated specimens by Evans^[3] and on zinc-nickel alloy in this work. Slow strain rate data was collected on AISI 4340 steel by Pollock^[74-77] for cadmium plated specimens, plated baked and exposed to paint stripper. Notched specimens were used and a student t-test statistical analysis was applied to test specimens to compare them with reference populations of embrittled specimens. In this way specimens tested under different conditions could be compared.

2.6 Electrodeposition of Alloys

Electrodeposition of a single metal from a solution containing only one species of metal ion is a relatively simple process. Problems arise with more than one metal ion species present in the same solution. In this case either one species will be deposited but not the other, or a combination of the two, that is an alloy, may be deposited.

It would be expected that the more noble of two or more metals would deposit preferentially, but unexpectedly, anomalous results can be obtained when the more chemically active metal is deposited in preference to the more noble metal.

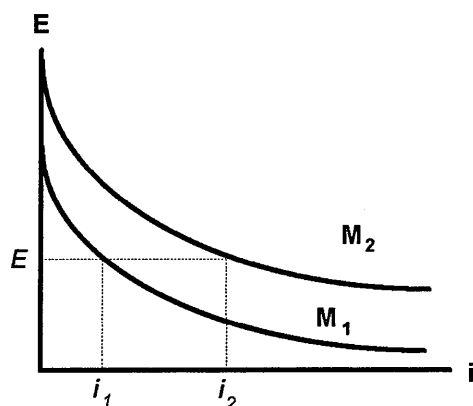
2.6.1 Normal Co-deposition of Alloys

Of two metals in solution, the metal to be deposited will thermodynamically be that one with the more positive electrode potential, since this allows for the reaction with maximum free energy...

$$\Delta G = -zEF$$

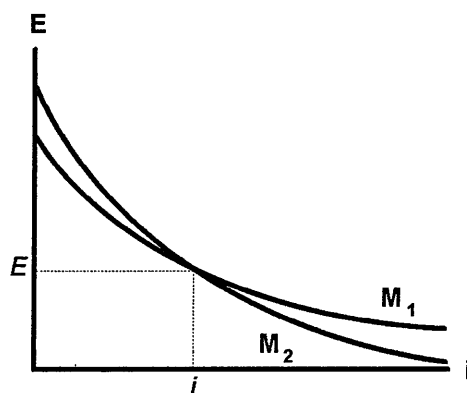
Where ΔG is the Gibbs free energy of a process, z the number of electrons involved in the process, E the electrode potential and F the Faraday constant.

In reality the process is more complicated in that if the two metals have similar values of $E < 0.2V$,^[78] then they may co-deposit from simple salt solutions. This is explained by polarisation bringing the potentials of the two species closer together. This polarisation effect would not close the gap between species with a more significant difference in electrode potentials.



a

M_1 and M_2 with similar polarisation curves.



b

M_1 and M_2 with M_2 being both more noble and polarising.

Fig. 2.17 Conditions of polarisation for co-deposition of metals M_1 and M_2

Two metals with similar polarisation curves, Fig. 2.17a, will each contribute a proportion to the total current and as a result will both be deposited in proportion in the electrodeposit. If z_1 and z_2 are the charges of the ions, i_1 and i_2 are the contributory currents, and A_1 and A_2 are the relative atomic masses respectively, then, assuming 100% plating efficiency...

$$\frac{\text{Mass of } M_1}{\text{Mass of } M_2} = \frac{i_1 A_1 z_2}{i_2 A_2 z_1}$$

In some circumstances, perhaps due to diffusion or concentration differences, one species may be polarised to a greater degree than the other. In Fig. 2.17b M_2 is the more noble metal and should be deposited preferentially. At low polarisation currents, M_2 is deposited preferentially. However, as the current increases, so does the degree of polarisation. At the point of intersection, neither metal is deposited preferentially, but at higher potentials, the less noble metal, M_1 , is deposited preferentially.

In order to control the deposition of a normally deposited alloy, it is generally easier to control the deposition potential of the species in the plating solution.

The Nernst equation provides a convenient way of adjusting the electrode potential of a metal-ion system, simply by adjusting the activity of the ions in solution.

For the electrochemical half reaction, in which M denotes a metallic element and z the number of electrons involved in the charge transfer...



The Nernst equation can be written as...

$$E = E^0 - \frac{RT}{zF} \ln \left(\frac{a_M}{a_{M^{z+}}} \right)$$

Where E denotes electrode potential, E^0 the standard electrode potential, R the gas constant, T the absolute temperature and a the chemical activity of the subscripted species.

In a standard thermodynamic state, $a_M = 1$, so the Nernst equation becomes...

$$E = E^0 + \frac{RT}{zF} \ln(a_{M^{z+}})$$

The concentration of simple salt solutions can be adjusted over two or three orders of magnitude. By using complexing agents to reduce the concentration of the free aqueous ion, many orders of magnitude can be obtained giving greater effect in controlling the electrode potential. The complexed ion then acts as a reservoir for more metal ions, since, as metal ions are removed from solution by deposition, more of the complex will dissociate. As will be seen from an examination of the Nernst equation, removing sufficient of the free metal ions from solution by complexing results in shifting the electrode in the negative direction.

2.6.2 Mechanism of Anomalous Co-deposition of Zinc Alloys

Whereas in normal electrodeposition the less noble metal deposits first, assuming a sufficient difference in the electrode potentials, in anomalous co-deposition, the reverse is true. Although this form of deposition is comparatively rare, it frequently involves zinc and a transition metal. Such alloys are becoming more useful in the automotive trade for corrosion protection of auto body components and aircraft fasteners.

The first investigators of zinc-nickel alloy electrodeposition appear to have been Schoch and Hirsch^[79,80] who investigated the composition of the electrodeposit from sulphate baths for differing temperatures, zinc content of solution and current density. Results indicated that increasing the zinc concentration in the electrolyte not only increased the zinc content in the electrodeposit, but also that the ratio of zinc to nickel in the deposit was up to 14 times greater than that in the plating solution.

Using a similar sulphate bath, Cocks examined the composition of the alloy deposited over a range of current densities, noting a sharp transition between low and high zinc content as the current density was increased.

By measuring the deposition potentials of the alloy, again using sulphate solutions, Glasstone^[81] discovered a large change in potential associated with a critical current density. This potential-current density feature also corresponded to a change from almost pure nickel deposition to one of almost pure zinc. Furthermore, it was discovered that increasing the pH of the electrolyte had the effect of decreasing the critical current density at which the deposition potential and composition of the electrodeposit changed so markedly.

Brenner^[82] attempted to explain the decrease of nickel and increase in zinc by postulating an "addition agent" to nickel resulting in increased polarisation of nickel making zinc deposition more favourable, although he was unable to suggest the nature or origin of the "addition agent".

A year after Brenner made his ideas known, Dahms^[83] investigated anomalous co-deposition using a dropping mercury electrode to eliminate hydrogen formation. In oxygenated electrolyte, Dahms discovered metal hydroxide deposits and a corresponding anomalous co-deposit but using de-oxygenated electrolyte, no hydroxide deposit was observed and normal co-deposition was obtained. Thus by inhibiting hydrogen reduction, anomalous codeposition was also inhibited.

Using a rotating disc electrode Dahms and Croll^[84] demonstrated the suppression of nickel but not of iron in a nickel-iron electrodeposit. The point of suppression of nickel coincided with the deposition of a ferrous hydroxide deposit and a rapid rise in pH at the electrode surface. It was concluded that the formation of the metal hydroxide was a necessary pre-cursor to the anomalous deposition of alloys. This explanation is now referred as the hydroxide suppression mechanism.

Raub^[85] found that even small additions of zinc ions into a Watts nickel plating bath had a pronounced effect on the nickel content of the electrodeposit. Increasing the current density further reduced the nickel content in the electrodeposit. This, Raub postulated, was due initially to the physical barrier of a zinc hydroxide deposit, but also to the same zinc hydroxide being electrochemically reduced to zinc. This, according to Raub occurred via direct reduction of $\text{Zn}(\text{OH})_2$ and also the $\text{Zn}(\text{OH})^+$ species, but not via the reduction of the Zn^{2+} ion.

X-ray analysis on the non metallic deposit indicated zinc hydroxy sulphate hydrate (written as $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$). Evidence of the presence of NiO and /or NiO_2 was also found^[86]

Nicol and Philip^[87] proposed an alternative mechanism to the hydroxide suppression mechanism. During steady state alloy deposition, the component metals continuously deposit onto a surface that is different to both of the component metals. If the work function of the alloy lies between that of the parent metals, then it would be possible for the less noble metal to be deposited at an underpotential. Although this does explain the deposition of some alloys, it does not fully explain anomalous co-deposition. The hydroxide suppression mechanism remains the theory with the most convincing experimental evidence to support it.

The hydroxide suppression mechanism has been used to explain much that happens during anomalous co-deposition. Japanese^[88-92] investigators, in particular, have helped to develop the mechanism in recent years.

By investigating the solubilities of zinc and cobalt hydroxides as a function of pH and the growth of a film on the cathode surface as a function of current density, Higashi et al^[88] provided strong evidence for the deposition of zinc hydroxide at a critical current density by measuring the pH close to the cathode surface and comparing the results to the solubility-pH measurements. According to measurements, zinc hydroxide should be deposited but not cobalt hydroxide, indicating that any cobalt present in the deposit should be metallic. X-Ray Photoelectron Spectroscopy (XPS) analysis of the deposit indicated that this was the case, although because of the nature of the deposit and low content of the cobalt, this determination was not straightforward.

Looking at a range of zinc alloys with iron group metals under various conditions, Fukushima et al^[88-92] obtained similar results indicating a single mechanism, notably the deposition of zinc hydroxide for each alloy. Comparing Figures 2.18a and 2.18b, the connection between the increase in film resistance and growth of the zinc hydroxide can be seen.

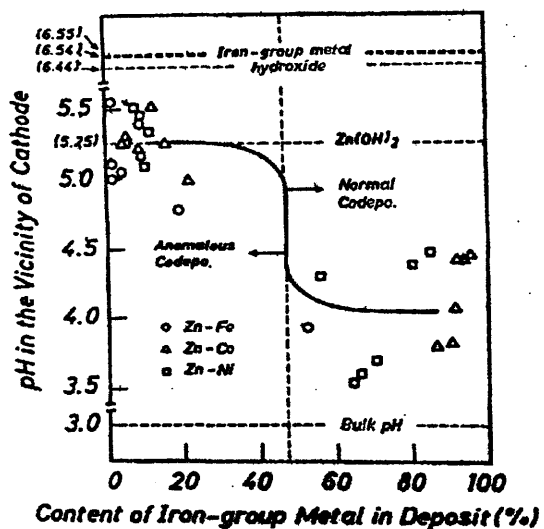


Fig. 2.18a Relationship between alloy content and cathode pH at different current densities.

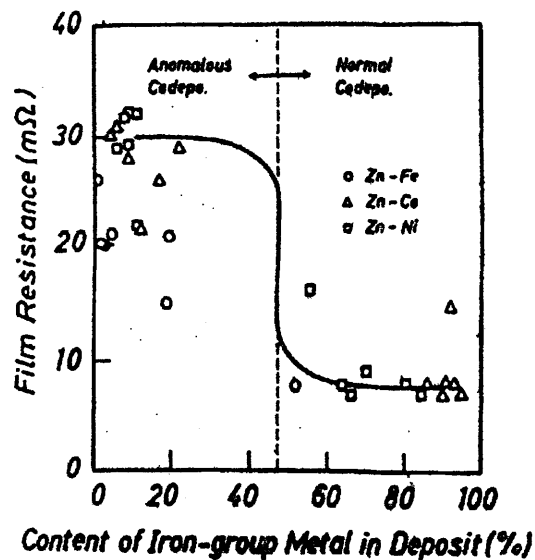


Fig. 2.18b Relationship between alloy content and film resistance at various current densities

From this evidence and the change in pH as a function of current density, as shown in Fig. 2.19, it can be seen that there is a critical current density below which normal deposition occurs. At this critical current density, zinc hydroxide is deposited and a transition is reached between normal and anomalous co-deposition. Above the transition current density, the pH remains constant, being buffered by the deposition of more zinc hydroxide. As long as the pH is maintained, the composition of the alloy electrodeposit remains constant with zinc being the major component.

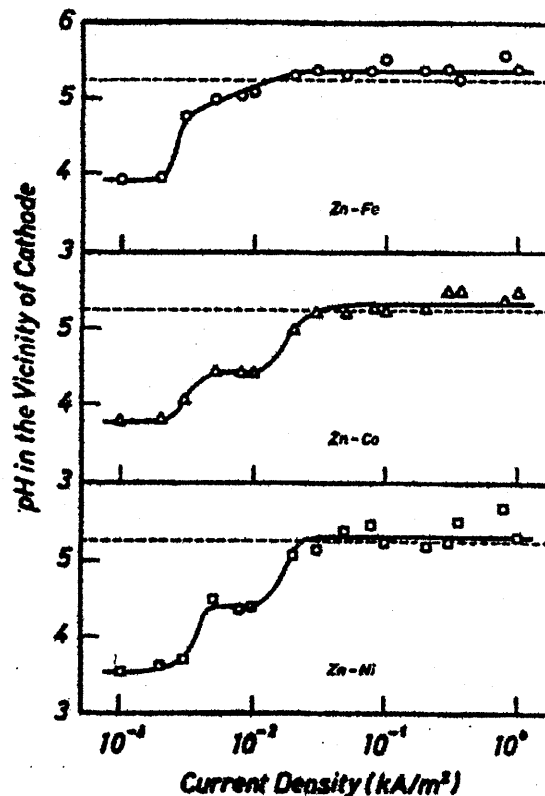


Fig 2.19 Relationship between the pH in the vicinity of the cathode and current density during electrodeposition.

The step at about pH4.4 for the zinc-nickel and zinc-cobalt alloys is probably due to the dissociation of sodium ethanoate (sodium acetate) used as a buffer in the plating solution,^[89,90] although no explanation is given as to why the same step is missing from the zinc-iron diagram.

Continuing their work on the mechanism and factors influencing anomalous co-deposition, Fukushima et al^[91,92] investigated the effect of pH and buffering agent on the content and plating efficiency of zinc-nickel alloy. The plating bath was buffered using sodium ethanoate and varied from pH1 to pH3 in 0.5pH units.

The hydroxide suppression mechanism would predict that a decrease in the pH of the plating bath would make the deposition of zinc hydroxide more difficult resulting in a higher transition current density. As can be seen in Fig. 2.20, this was found to be the case. Current efficiency measurements over the pH range measured increased with increasing pH. This is also predicted by the hydroxide suppression mechanism

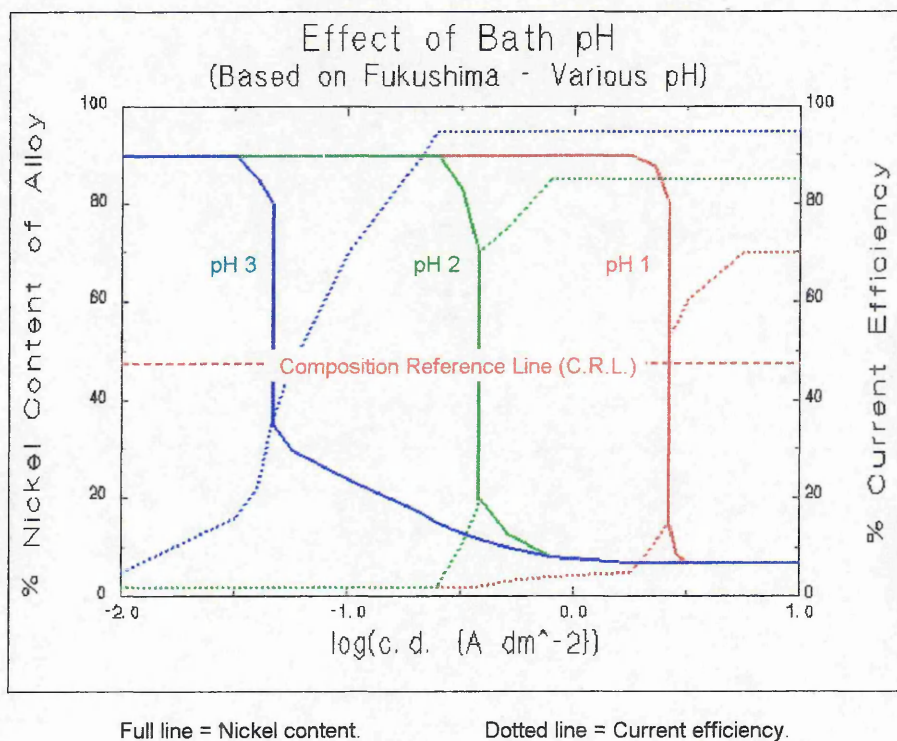


Fig. 2.20 Effect of pH on Transition Current Density

The theory proposed by Higashi and co-workers concerning the hydroxide suppression mechanism can best be summarised with the aid of Figure 2.21. The diagram is divided into three sections...

- **Section I** : In which normal deposition occurs at low current density and low current efficiency.
- **Section II** : In which anomalous co-deposition occurs at higher current densities and very high current efficiency. The composition of the deposit shows little variation with current density.
- **Section III** : In which the more noble metal content of the deposit increases with increasing current density but decreasing current efficiency.

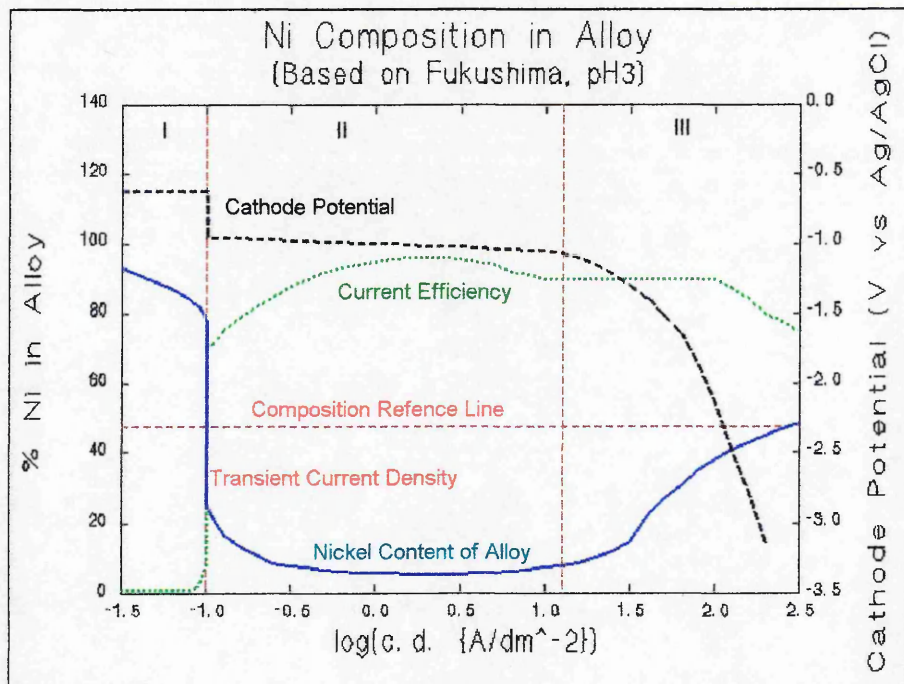


Fig. 2.21 Effect of current density on alloy composition and current efficiency.

The onset of anomalous co-deposition is marked by a sharp decrease in the cathode potential due to resistance from the zinc hydroxide layer. This layer is maintained at a constant thickness by the equilibrium between the rate of reduction and the rate of deposition. Inhibition of both nickel and hydrogen ions at the cathode surface results in the failure of these ions to achieve reduction. Consequently nickel content in the alloy is reduced and current efficiency is increased.

At extreme current densities, the rate of reduction of the zinc hydroxide exceeds the rate at which the deposit can be formed. Consequently the zinc hydroxide film thins, becoming less of a barrier to both nickel and hydrogen ions. This results in the increase of nickel content in the alloy and a reduction in current efficiency corresponding to the increase in hydrogen gas production.

Baldwin^[93] measured the pH at the cathode surface during plating for a wider range of current densities than other investigators. At a current density of about 10 A dm^{-2} the pH increased beyond the value of pH 5.25 which had been buffered by zinc hydroxide deposition. These changes coincide with the onset of region III in the anomalous co-deposition diagram. Baldwin uses this evidence to support the hypothesis of Fukushima et al that in region III, consumption of zinc hydroxide supersedes its deposition. Whereas this may be part of the explanation, it does not explain the situation fully. The increase in pH at the electrode surface is taken simply as a consequence of increased hydrogen production and the reduction in current density. In fact zinc hydroxide is an amphoteric compound and will dissolve at the higher pH. This is indicated by the relative increase in nickel content of the alloy and a decrease in current efficiency. It would seem likely that, at such high current densities, the buffering capacity of the zinc hydroxide is exceeded, leading to a further increase in pH. Sufficient increase in pH would result, not in the formation of insoluble zinc hydroxide, but the soluble hydrogen zincate (bizincate) anion. This will be discussed later in Section 6.

Baldwin also investigated the morphology of the cathode surface in relation to the plating potential during a potential sweep of the surface. SEM micrographs of the surfaces show a progression in both coverage and size of zinc hydroxide whiskers throughout what corresponds to region II in Fig. 2.21. In region III, the amount of zinc hydroxide observed on the surface decreased as would be expected from the current theory.

In sharp contrast, however, Fratesi and Roventi,^[94] after a thorough investigation of zinc-nickel alloy deposition using a plating solution containing NH_4Cl , were unable to confirm the hydroxide suppression theory, since the presence of NH_4Cl suppresses the formation of zinc hydroxide by complex formation, and yet they were obtaining anomalous co-deposits, comparable to those of other investigators. pH titrations indicated that, in the presence of NH_4Cl , zinc hydroxide did not precipitate from their plating solution until about pH8, and even then there was no sudden change in pH as happened in a solution containing uncomplexed zinc and nickel salts. The fact that the pH did not dramatically increase with the first addition of NaOH is an indication of a buffering effect from the solution. The effect of complexing with NH_4Cl is to reduce the concentration of zinc ions in solution, but not to eliminate them. It seems likely that although the hydroxide formation is suppressed, it is not eliminated as Fratesi and Roventi seem to be suggesting. An examination of SEM photographs of their electrodeposits indicates further a slight surface charging which can be due to the effect of a surface hydroxide deposit. In conclusion, then, the work of Fratesi and Roventi does not disprove the hydroxide suppression mechanism.

Some indirect evidence to support the hydroxide suppression mechanism comes from work on the effect of additives to zinc-nickel alloy plating solutions by Shukla^[116] et al, who found that the nickel content of an electrodeposit increased with increasing concentration of glycine. Glycine can be used to remove zinc corrosion products without affecting the zinc substrate, so increasing the glycine concentration of the plating bath would make the formation of zinc hydroxide increasingly more difficult, consequently reducing the zinc hydroxide deposit and allowing more nickel to be reduced.

2.6.3 Kinetic Modelling of Anomalous Co-deposition

Some recent investigations have been undertaken which examine the deposition of zinc alloys from the standpoint of chemical kinetics using the rotating disc electrode. These methods monitor how fast a reaction proceeds, which steps are rate determining and can also suggest the existence of intermediates in a reaction path.

Mathias and Chapman^[95] used chloride based electrolytes, Roehl ($\text{ZnCl}_2 = 0.92\text{M}$; $\text{NiCl}_2 = 0.57\text{M}$; Ethanoic acid = 0.366M) and modified Roehl ($\text{ZnCl}_2 = 0.57\text{M}$; $\text{NiCl}_2 = 0.92\text{M}$; Ethanoic acid = 0.366M) plating solutions, to develop a model to predict the composition of a zinc-nickel alloy electrodeposit. Partial current densities for zinc and nickel were determined experimentally by dissolving the electrodeposit and analysing the solution produced. Hydrogen current efficiency was estimated from the metal partial current densities and a knowledge of the total current. It was assumed that this hydrogen partial current was solely responsible for pH changes at the cathode surface, and in using this hydrogen partial current, it was then calculated that the pH change would be insufficient to precipitate zinc hydroxide. Mathias and Chapman concluded that zinc hydroxide could not be responsible for the anomalous co-deposition observed in their experiments.

Working with iron-nickel alloys, Dahms and Croll^[84] had deduced that a pH increase at the cathode surface was responsible for a deposit of ferrous hydroxide, which, like that of zinc hydroxide, suppressed the deposition of nickel. This work, on iron-nickel anomalous co-deposition, was investigated by Gangasingh and Talbot^[96] who derived a mathematical model capable of calculating the pH at the cathode surface in the presence of a pH buffer. In this equation, it is once again assumed that the pH change at the surface of the cathode is solely due to the hydrogen reduction reaction in which molecular hydrogen is produced. If the pH is increased at the cathode surface by means other than the reduction of hydrogen ions to molecular hydrogen, then the model fails.

$$\begin{aligned}
\frac{i_H \delta}{F} = & D_H (C_H - C_H^0) + D_{OH} K_W \left[\frac{(C_H - C_H^0)}{C_H C_H^0} \right] \\
& + 2K_W^2 \sum_i D_{M_i(OH)_2} K_{M_i(OH)_2} C_{M_i}^0 \left[\frac{(C_H^2 - C_H^0)}{C_H^2 (C_H^0)^2} \right] \\
& + \sum_j D_{HA_j} K_{HA_j} \bar{C}_{HA_j} \left[\frac{(C_H - C_H^0)}{(C_H + K_{HA_j})(C_H^0 + K_{HA_j})} \right]
\end{aligned}$$

...where i_H denotes the hydrogen reduction partial current across a diffusion boundary layer of thickness δ , separating surface and bulk hydrogen concentrations C_H and C_H^0 respectively. Subscripts i and j denote metallic and buffer species in turn. The Faraday constant and ionic product of water are denoted by the usual symbols, F and K_W .

In the case of high current efficiency, characteristic of anomalous co-deposition, the value of i_H is very small. In such a situation, as i_H tends to zero, the hydrogen ion concentration change across the diffusion boundary layer thickness, δ , also tends to zero. Therefore, according to the model, the pH cannot change sufficiently to cause the precipitation of iron hydroxide as postulated by Dahms and Croll.^[84] This principle should also be applicable to situations involving zinc-nickel alloy, thereby apparently confirming the conclusions of Mathias and Chapman.^[95] However, as has been demonstrated in this work, and will be discussed in Section 6, zinc hydroxide whiskers can be found on iron surfaces even in the absence of a plating current. In this situation, as the steel corrodes, hydrogen is reduced in sufficient quantities to raise the surface pH and cause zinc hydroxide to precipitate onto the steel. Baldwin^[93] has also shown zinc hydroxide whiskers to be present at low current densities.

Polarisation curves for the partial zinc and nickel currents have been investigated by Chassaing and Wiart,^[97] the results of which are displayed in Fig. 2.22, showing the effect of increasing nickel content of the plating solution and in Fig. 2.23 which illustrates the effect of pH. Neither of these figures are in complete agreement with the effects predicted by the classical hydroxide suppression mechanism.

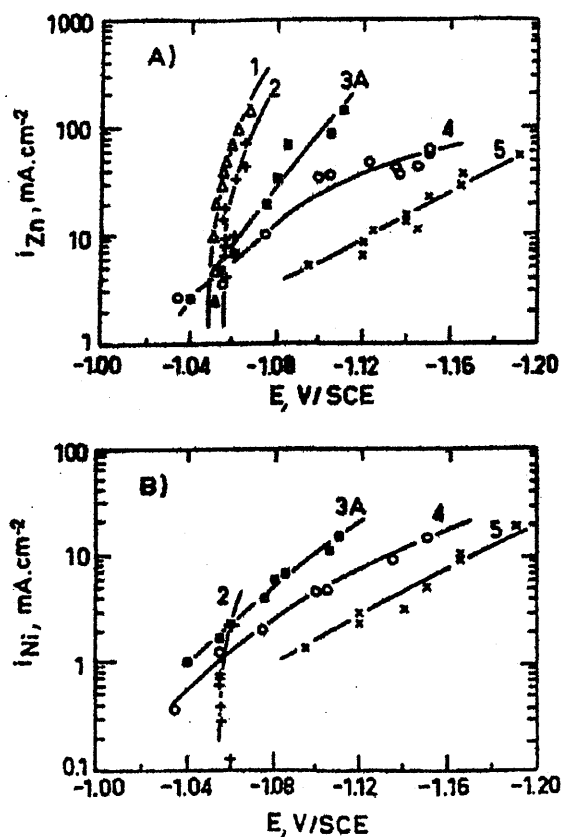


Fig. 2.22 Partial Polarisation curves for zinc, (a), and nickel, (b), discharge.

Curve 1 in (a) represents the situation with no nickel in the plating solution. Curves 2 to 5 represent increasing nickel to zinc ratios. This shows that small amounts of added nickel ions will slightly impede the deposition of zinc. At higher nickel content, the polarisation slopes are less steep showing that zinc deposition is impeded by nickel and not, as implied by the classical hydroxide suppression mechanism, only the nickel. It should be noted that at very low polarisations, zinc discharge appears to be de-polarised as compared to zinc only deposition. Similar results are observed for nickel, although current densities are in the region of one order of magnitude lower.

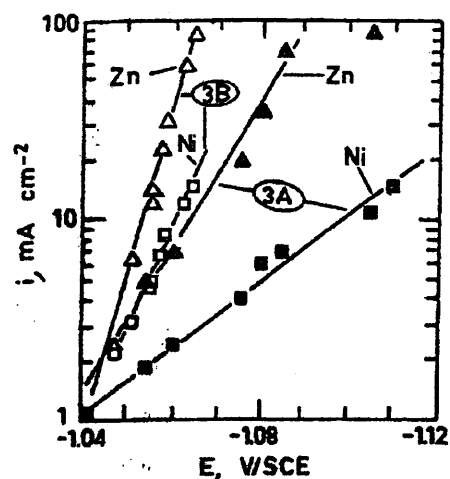
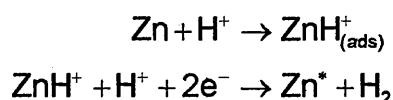


**Fig. 2.23 The effect of pH on zinc and nickel partial polarisation.
(3A=pH2, 3B=pH4.4)**

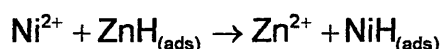
The effect of pH on the partial polarisation of zinc and nickel also seems to disagree with the classical hydroxide suppression mechanism. It would be expected that increasing the pH of the plating solution would favour the deposition of zinc over nickel, resulting in a higher zinc content of the alloy. Evidence of this might be a reduction in the polarisation slope for nickel, with the slope for zinc polarisation either remaining the same or increasing slightly with increasing pH. Fig. 2.23 clearly shows that for increasing pH, at a given potential, both the zinc and nickel partial currents are found to increase significantly.

Chassaing and Wiar^[97] conclude that the deposition process proceeds via a two step discharge mechanism for zinc, and nickel deposition proceeds via an intermediate $(\text{NiZn})^+_{(\text{ads})}$ surface compound.

Polarisation of the surface by an adsorbed species, thought to be ZnH^+ impedes both zinc and nickel discharge. Furthermore, renewal of the hydrogenated blocking adsorbate is accounted for by...

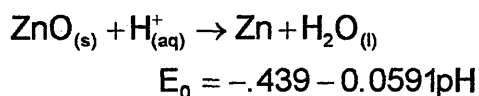


This latter model poses some attractive features, yet there is no explanation of the presence of, let alone the role played by, zinc hydroxide which is known to be present on the cathode surface. Cachet and Wiar^[117] acknowledge that nickel co-deposition proceeds via a heterogeneous process coupled to zinc deposition, probably either the $\text{Ni}^+_{(\text{ads})}$ or $(\text{NiZn})^+_{(\text{ads})}$ complex, but for simplicity they explain the presence of nickel using the following reaction...



In each of the models described above, it is assumed that the pH increase at the cathode surface is insufficient to give rise to significant, if any, zinc hydroxide precipitation. If the pH change was due solely to the formation of molecular hydrogen from hydrogen ions, whether directly or via a hydrogenated intermediate, this would be correct, however an alternative mechanism will be discussed later which allows for zinc hydroxide to be deposited at this low hydrogen partial current and which allows for the presence of both zinc and nickel in the final deposit.

Pourbaix has considered the equilibria of several reactions involving zinc ions in both acidic and alkaline conditions. It is clear from his work that zinc hydroxide can be reduced by hydrogen ions under conditions existing in the plating bath. Hydrogen ions involved in reducing zinc hydroxide would produce water, not hydrogen gas, thus, since the oxidation state of the hydrogen remains unchanged and only the zinc is reduced, the process maintains a high current efficiency, simultaneously increasing the local pH at the cathode surface. The principal reaction is as follows...



During anomalous co-deposition from a 0.92M solution of Zn^{2+} ions, the pH at the cathode surface rises to 5.5.^[93] Using the above formula at this pH, a value of 0.764V is obtained for the deposition potential of zinc, which compares favourably with the calculated value of 0.762V for the direct reduction of Zn^{2+} ions from a similar solution.

2.6.4 Hydrogen embrittlement from zinc-nickel alloy electroplate.

Any cathodic process in aqueous acidic media will produce hydrogen. Cadmium electroplating processes are inefficient, producing relatively large amounts of hydrogen which needs to be baked out of the steel and electrodeposit,^[100] albeit at a financial cost.^[17,51,107]

One of the major reasons for interest in zinc-nickel alloy electroplate is the fact that the process is relatively benign with respect to hydrogen embrittlement. Hsu^[101] reports zinc-nickel electrodeposits to be low hydrogen embrittling coatings suitable for use by the Boeing company with high strength and low strength steels. However, not all plating processes have equally low embrittling characteristics.^[102] Kamitani^[103] et al go as far as to suggest that zinc-nickel plating may, subject to type of pre-treatment, not need any post plating heat treatment. The low hydrogen uptake has been credited to low diffusivity of hydrogen in zinc,^[103] but apparently without any detailed experimental work or reasoning. Davis and Gray,^[104] however performed their own investigations on hydrogen permeation through bare steel and pre-deposited coatings including nickel, cadmium and zinc-nickel alloy. Cadmium offered the best barrier to hydrogen, with zinc-nickel almost as efficient. Pure nickel reduced hydrogen uptake compared to the bare steel, but when alloyed had a tendency to allow higher permeation due to an increased solubility of hydrogen in the electrodeposit. Earlier work by Beck and Jankowsky^[105] indicated that an electrodeposited undercoat in the region of $1\mu\text{m}$ of either copper or Watts nickel ($\text{NiSO}_4 = 270\text{gdm}^{-3}$; $\text{NiCl}_2 = 40\text{gdm}^{-3}$; $\text{H}_3\text{BO}_4 = 27\text{-}33\text{gdm}^{-3}$)^[78] would reduce embrittlement which resulted from cadmium plating. The reduction in embrittlement was assumed to be due to nickel being impermeable to either atomic hydrogen or to protons, hence acting as a diffusion barrier.

3 Mechanical Testing

3.1 The Test Material - AISI 4340

AISI 4340 is a deep hardening, ultrahigh tensile strength steel. Usually, the alloy is quenched to achieve a maximum hardness, although it is also capable of air hardening in thin sections.

Hydrogen embrittlement is a problem when the strength exceeds 1400 MPa if the steel is exposed to gaseous or electrolytic hydrogen. De-embrittling by baking is recommended between 190° and 230°C for a minimum of 18 hours for steels in the category 1451-1800MPa and 24 hours for 1801MPa and above.^[73]

To harden the steel, it is recommended that the steel is heated to between 800° and 845°C for 15 minutes minimum followed by an oil quench. Tempering to relieve internal stresses and allow further hardening by precipitation processes can be between 200° and 650°C for a minimum of 30 minutes followed by air cooling. Tempering times and temperatures are at the discretion of the operator who can adjust them to control the final hardness of the steel.^[106]

Tempering temperatures can produce a pronounced reduction of tensile strength^[107] as shown in Fig. 3.1 and so it is important to minimise the time taken in tempering.

Steel which contains hydrogen either from a deliberate pre-charging, or from an industrial process, is known to benefit from a post treatment baking. Baking temperatures are kept as low as possible to avoid unnecessary loss of strength, but high enough to facilitate the diffusion of hydrogen. Hydrogen may either be lost to the atmosphere and/or absorbed by traps. The duration of baking and the effect on hydrogen damage is illustrated in Fig. 3.2.^[51] Although baking is a reliable method of removing hydrogen from steel, it must be remembered that the process is costly both in time and fuel.

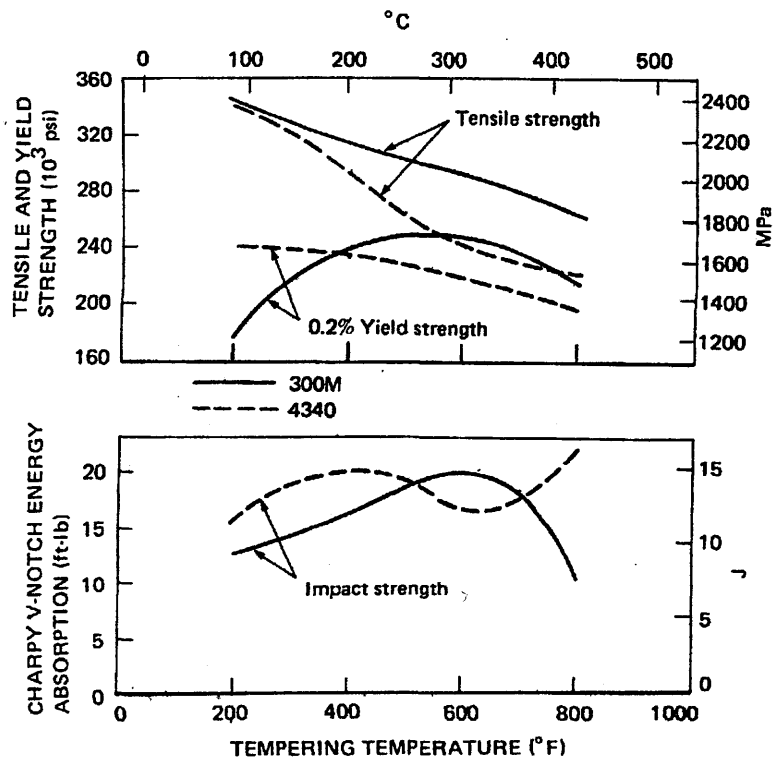


Fig. 3.1 Effects of tempering tensile properties of 4340 and 300M steels^[51].

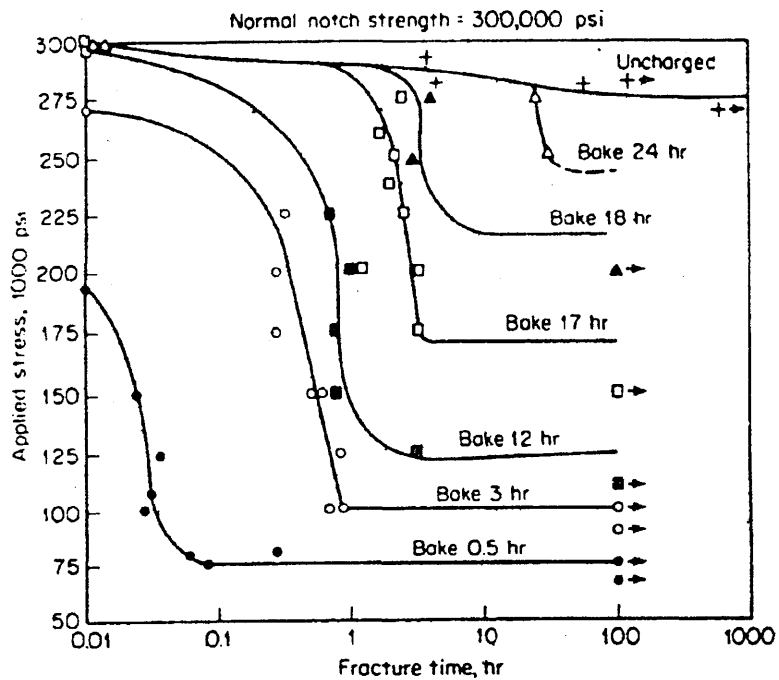


Fig. 3.2 Static fatigue tests on AISI 4340 steel previously charged with hydrogen, after different baking times.^[51]

3.2 A Metallographical Examination of the Test Material

Hydrogen in steel may be either mobile and free to diffuse to sites of high triaxial stress, or trapped and immobile within the structure. Mobile hydrogen is embrittling but irreversibly trapped hydrogen is not, hence a fine dispersal of trapping sites throughout the structure of the steel could be beneficial if it is to be exposed to embrittling environments. This is even more important in the case of electroplating, since electroplated layers can act as a barrier, preventing absorbed hydrogen from effusing the surface. Baking such steel serves to remove most of the hydrogen from the electrodeposited layer, and diffuse some further into the steel, simultaneously reducing hydrogen concentration near to the surface and driving hydrogen into irreversible traps.

Photo. 3.1 shows photographs of the surface of a QT (see Sect 3.5.8) test piece clearly showing inclusions striated in the rolling direction of the material. Elongated inclusions are thought to consist of manganese sulphide which is relatively plastic whereas the circular features are more likely to be oxides.

Microstructures of the as received and heat treated specimens can be seen in Photos 3.2 to 3.4. The as received microstructure shows the normalised steel with pearlite in a ferrite matrix. After quenching and tempering, a martensite and troostite structure is obtained, while baking has essentially maintained the troostite structure.

Photos 3.5 and 3.6 show the fracture surface of a QT specimen, but which is also representative of QTPB (see Sect 3.5.8) specimens. The features show the classic dimpled effect due to microvoid coalescence. Some cavities can also be seen, which are likely to have been the sites of oxide inclusions.^[63]

Photo. 3.7 indicates a brittle failure close to the corner of a cadmium QTP (see Sect 3.5.8) tensile specimen. Under tensile stress, corners will act as stress concentrators, increasing the likelihood of a corner being the site of crack initiation. This would only be a problem if the purpose of the study was to study the fracture mechanics. Furthermore, Hydrogen concentrations are higher close to corners than at a flat face due to hydrogen diffusing from two perpendicular directions. Higher hydrogen concentrations increase the incidence of hydrogen embrittlement, hence cracks are more likely to initiate at or close to a corner. A brief mathematical representation of diffusion at a right angled corner is given in section A.2.

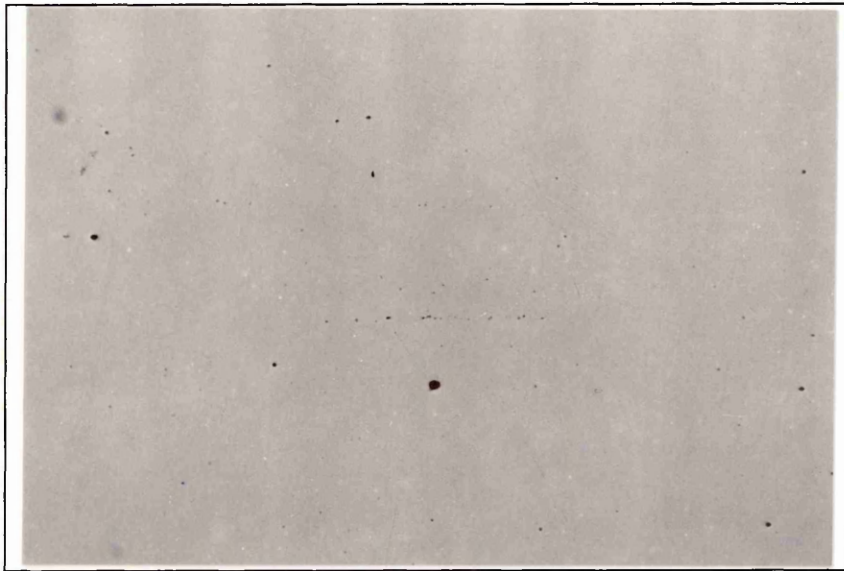


Photo. 3.1 Surface of as received AISI 4340 not etched, x45

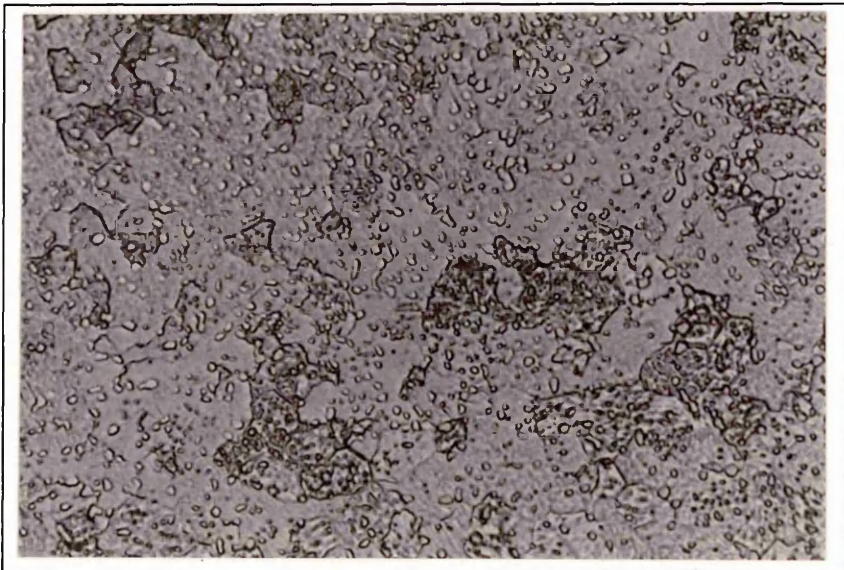


Photo. 3.2 Surface of as received AISI 4340 steel etched in 2% nital x1000.

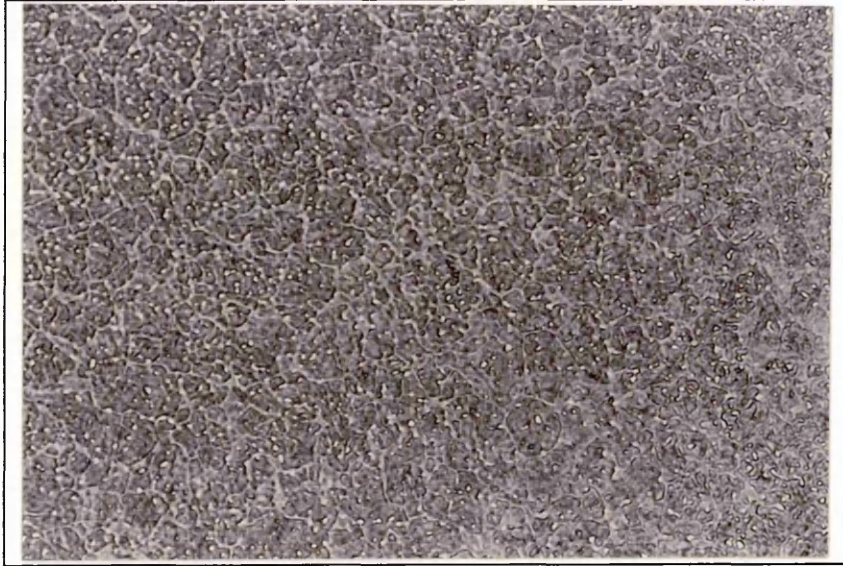


Photo 3.3 Surface of quenched and tempered AISI 4340 steel etched in 2% nital x1000.

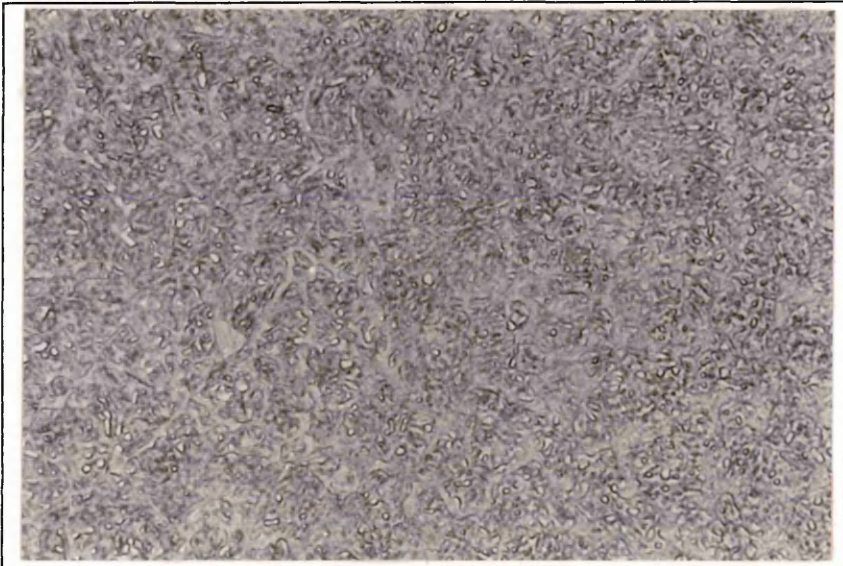


Photo 3.4 Surface of quenched, tempered and baked AISI 4340 steel etched in 2% nital x1000.

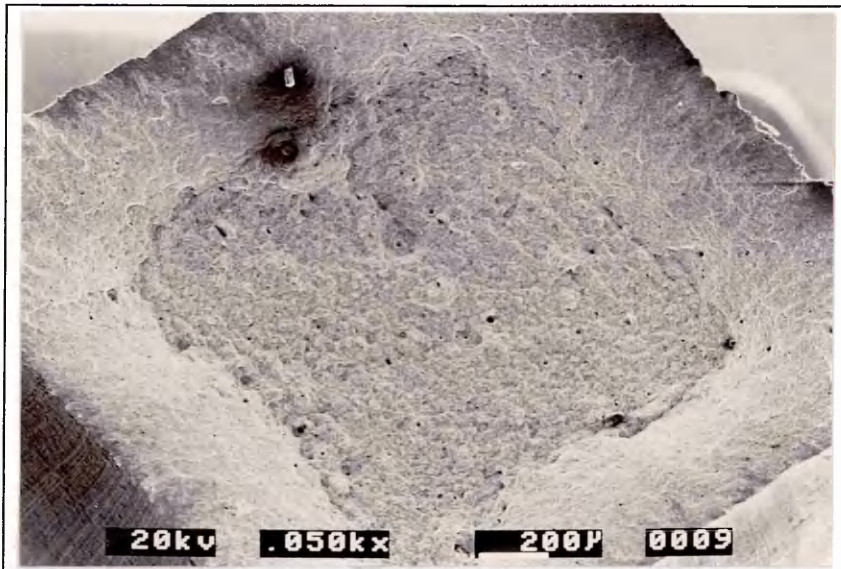


Photo 3.5

**Fracture surface
of a a QT tensile
specimen.**

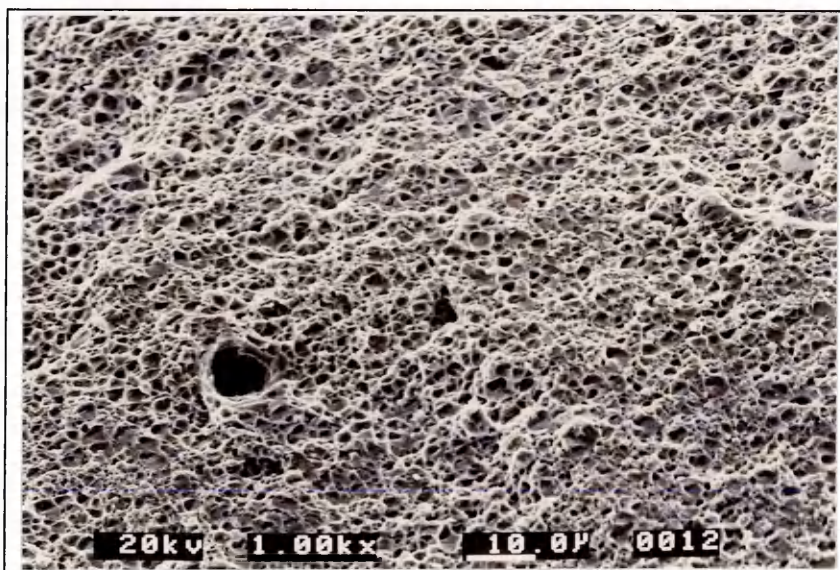


Photo 3.6

**Fracture surface
of a a QTPB
tensile specimen
in close up
showing dimpled
structure of
microvoid
coalescence.**

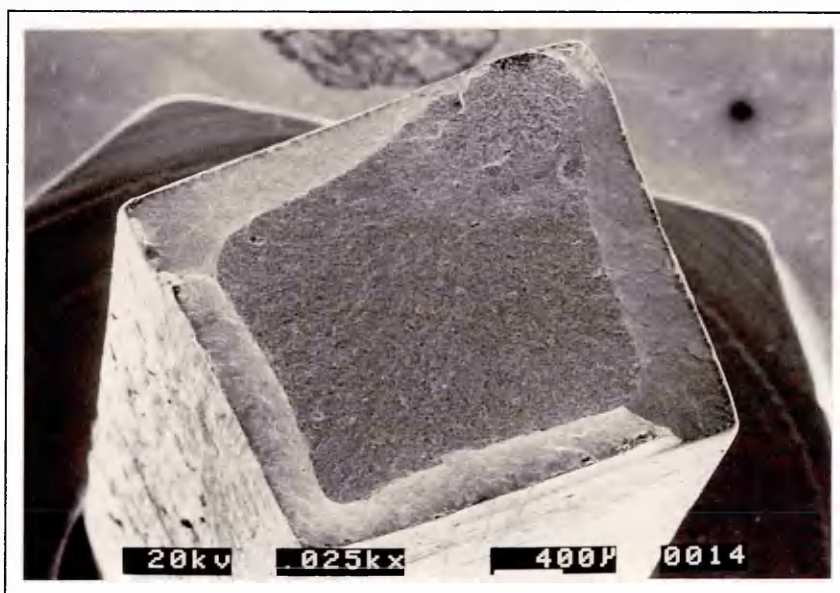


Photo 3.7

**Fracture surface
of a Cadmium
QTP tensile
specimen
showing crack
initiation at a
corner.**

3.3 Background to the Experimental Method

The slow strain rate (SSR) method of testing has been used extensively over the past 15 years to examine the effect of stress corrosion cracking and the closely related phenomenon of hydrogen embrittlement of high strength steels as compared to unaffected samples of the same steels. Initially the technique was intended simply as a quick comparative test based on a simple measurement of time to failure, but is now increasingly being used quantitatively as a measure of the extent of embrittlement.

When a metal is subjected to strain, mobile hydrogen will diffuse to high stress fields within the structure. This may result in, for example, the pinning of dislocations. The resulting increase in the stress field at these points may be sufficient to produce cracking due to localised hydrogen induced plasticity and failure at lower applied stress than would be expected in the absence of hydrogen. If the strain rate is too high to allow hydrogen to diffuse to these high stress fields before failure occurs, then no hydrogen embrittlement is observed. This principle is employed in estimating the ultimate tensile strength of tensile specimens using the Vickers hardness test. Since, during hardness testing, the strain rate resulting from the indentation is large, no embrittlement is observed and the yield strength, which determines the size of the indentation, can be related to the ultimate tensile strength of the non-embrittled specimen^[98]. Conversely, a slow strain rate that does allow time for the hydrogen to diffuse will detect the effect of embrittling hydrogen present in the structure. Ideal strain rates^[68] for observing the effects of hydrogen embrittlement are in the range of 10^{-6} to 10^{-5} s^{-1} . For the purpose of this work, a strain rate value of 1.1×10^{-6} has been used.

Hydrogen embrittlement is a particular problem in high strength steels with a tensile strength in the region of 1800 MPa or above, such as AISI 4340 steel used in fasteners in the aircraft and automotive industries. It is necessary, therefore to commence this work with the heat treatment necessary to give the as received steel sufficient strength for the embrittlement tests.

3.4 Heat Treatment of Tensile Specimens

The purpose of this initial investigation was to determine the conditions of heat treatment most suitable for tensile specimens of AISI 4340 steel to provide UTS values in the region of 1800 MPa.

Specimens were cleaned using 1200 grit carborundum paper before being degreased in iso-propanol and suspended on a frame. The whole arrangement was then inserted into a pre-heated, water cooled vertical furnace containing an argon atmosphere as indicated in Fig. 3.3, below.

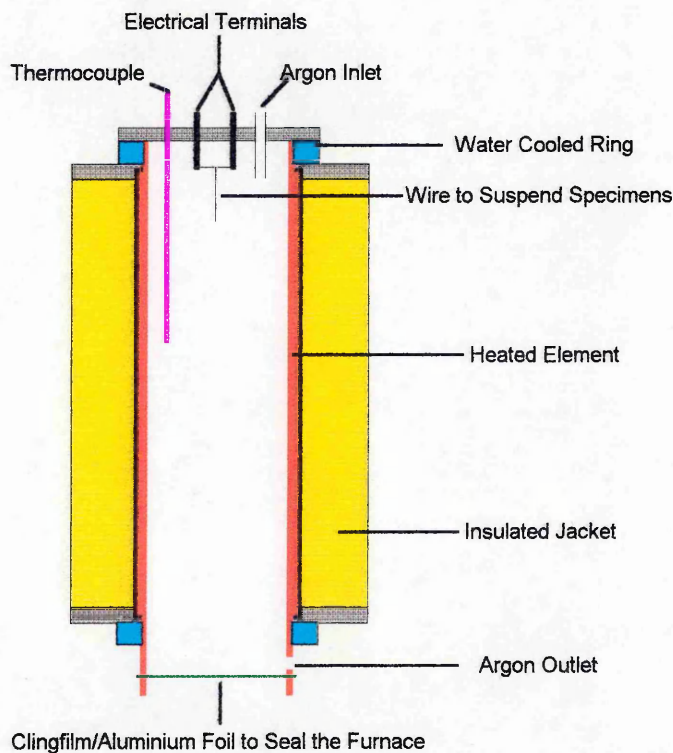


Fig. 3.3 Vertical, cylindrical furnace arrangement.

Specimens were held at temperature for a period of 15 minutes before quenching directly into oil after falling through the plastic/metal foil seal..

In order to determine an optimum tempering regime, some specimens were tested to failure using an Instron tensile testing machine at a strain rate of 2.7×10^{-3} (cross-head speed of 4 mm min^{-1}) without tempering. Other specimens were tempered in a range of temperatures between 200°C and 300°C for various times between 30 minutes and 24 hours.

From these tests, an initial heat treatment was decided upon consisting of raising the temperature of the specimens to 850°C and holding for 15 minutes before quenching into oil at room temperature. A subsequent temper of 250°C for 30 minutes was applied.

In obtaining these results, it was realised that for long term reproducibility of large numbers of tensile specimens, the cylindrical furnace was unsuitable. Consequently, having determined the desired heat treatment, it was decided to contract out the heat treatment to a commercial heat treatment company (Holt Brothers, Halifax, Ltd.). In this case, the tensile specimens were immersed in a neutral salt bath, pre-heated to 850°C for 15 minutes before being quenched into oil at room temperature. Tempering was maintained at 250°C for 30 minutes. In this way, a high standard of reproducibility was obtained for these specimens.

In addition to determining an initial heat treatment for the tensile specimens, tests were conducted to determine a suitable temperature for a post plating de-embrittlement baking. It was found that baking at 200°C for 24 hours, subsequent to tempering, had a minimal effect on the UTS of the specimen. This treatment was conducted on campus using a fan assisted oven.

Typical values obtained during these tests for AISI 4340 are given in the table below. Results from the preliminary experiments are also compared to values obtained in slow strain rate tests using tensile specimens heat treated at Holt Brothers, Halifax Ltd. The spread of results for QT and QTB of less than 2% falls within experimental error.

Heat Treatment	Typical UTS /MPa
Quenched only - Q	2098
Quenched and tempered - QT. (Preliminary)	1768
Quenched, tempered and baked - QTB. (Preliminary)	1736
Quenched and tempered - QT. (Holt Bros.)	1741
Quenched, tempered and baked - QTB. (Holt Bros.)	1769

Table 3.1 Summary of UTS Obtained from Heat Treatments

3.5 Slow Strain Rate Tests

3.5.1 Tensile Specimens

AISI 4340 steel as used in these slow strain rate (SSR) tests was supplied in cold-rolled sheet form. Tensile specimens were manufactured to the dimensions specified in Fig. 3.4 from 2mm thick sheet using a CNC vertical mill. Dimensions were such that the tensile load would be applied in the rolling direction of the sheet and that the load would be applied to a rectangular cross sectional area of approximately 4mm² cross section.

Material specification for the alloy is given in Table 3.2, below.

Element	AISI 4340	Shim
C	0.380	0.040
Si	0.260	<0.020
Mn	0.510	0.240
P	0.015	0.008
S	0.018	0.012
Cr	0.050	<0.010
Mo	0.030	<0.030
Ni	0.020	0.020
Al	<0.010	0.050
Cu	0.040	0.040

Table 3.2 Analysis of AISI 4340 and mild steel shim used in this work

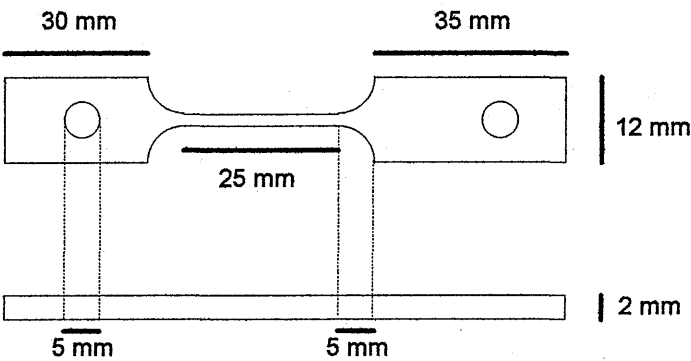


Fig. 3.4 Tensile specimen, schematic.

3.5.2 Slow Strain Rate Apparatus

The apparatus made use of a Hounsfield Tensometer, type W, driven by an electric motor via a step-down gear box and toothed belt. The motor was fitted with a variable speed control by which the cross-head speed could be set. The strain rate was adjusted and checked periodically to ensure a constant strain rate in the test specimens of $1.1 \times 10^{-6} \text{ s}^{-1}$.

3.5.3 Cross-Sectional Area of Tensile Specimens

Each specimen was carefully measured individually using a profile projector before plating in order to measure the thickness and width of the tensile section. This was necessary to determine both the cross sectional area of the specimen, and the surface area to be plated, where applicable. After fracture in SSR experiments, the cross sectional area was again measured in order to determine the reduction in area over the fracture surface. Hence a value for the embrittlement index was obtained (see section 3.5.6). Electroplated layers were included in this final measurement, since to remove them may have damaged the fracture surface or have led to a greater error by removing steel. As the plated layer was thin compared with the overall thickness, and would be reduced further by straining, it was decided that the error was acceptable at about 2% or less.

3.5.4 Cadmium Electroplating Process

Cadmium plating was initially performed at the plating shop on the Cranfield campus. Tensile specimens were initially cleaned by abrasion followed by degreasing in propan-2-ol. No pickling, anodic or caustic cleaning was used to avoid hydrogen uptake by any means other than plating. The plating process itself used a barrel method of plating from an alkaline cadmium cyanide bath and gave a bright finish 4µm thick when measured on the flat end of the specimen. No passivation treatment was given to the specimens after plating. Those specimens that were plated in this way include all of the cadmium specimens referred to as Series E and Series G. Due to the subsequent closure of the plating shop on campus, cadmium plating was kindly performed by Stotfold Plating Co. Ltd., Hitchin, Herts. The essential differences between the processes involved a change from a barrel to rack plating process, and approximately a doubling of the thickness of the cadmium plate. Specimens plated in this alternative fashion were identified as belonging to Series H.

Due to the fact that several specimens were necessarily plated together, liquid nitrogen was used to cool specimens until they were required. In this way, mobile hydrogen was effectively immobilised until reheated to room temperature before continuing with the tests.

3.5.5 Alloy Electroplating Process

Preparation of tensile specimens for alloy plating was identical to that for cadmium plating, with an abrasive used to remove surface oxides from the heat treatment, followed by degreasing in an organic solvent, propan-2-ol.

However, it was unnecessary to plate the whole specimen and a flat end of the tensile specimens was masked off by PVC insulating tape. This end protruded from the plating solution and was connected by a crocodile clip to a galvanostat as shown in Fig. 3.5, below.

Plating was initially conducted in a beaker, using a platinum counter electrode, at a current density of 20 mA cm^{-2} for 15 minutes. For reasons described later in Section 4.1.2, this was later changed to a two chamber process, similar in principle to that incorporated in the permeation cell.

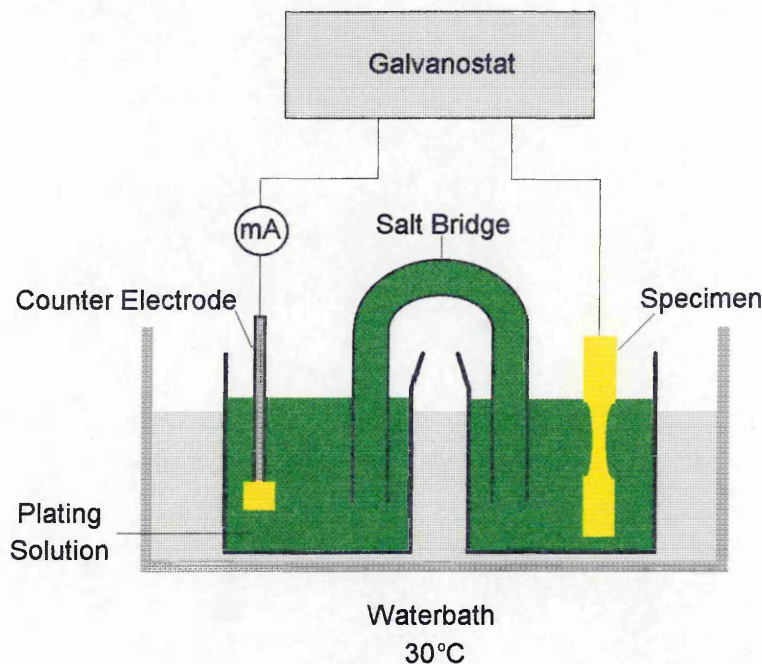


Fig. 3.5 Plating Arrangement for Tensile Specimens

After plating, specimens were rinsed in distilled water to remove any plating salts, followed by propan-2-ol to assist with drying.

Tensile specimens were immediately strained in the tensometer unless they were scheduled for baking. In this latter case, specimens were stored in liquid nitrogen to immobilise any free hydrogen until five or six specimens had been prepared and the oven had been preheated to 200°C . In this way, all of the specimens were given identical baking conditions

3.5.6 Embrittlement Index (M)

There are various ways for the investigator to represent the degree of embrittlement in a tensile specimen. In the absence of any generally accepted standards on embrittlement, it is left, therefore, to the investigator to define a relationship that can readily be applied to the methods employed.

For the purpose of this investigation, it was necessary to obtain a simple measure of embrittlement that would give a rank order when compared to a reference, non-embrittled test piece. For convenience, it was decided that an embrittled value should be greater than a non-embrittled one. Reduction in cross sectional area of the tensile section of the test specimens was chosen as being the most suitable quantity to measure. The standard reference value was taken to be the mean percentage value of the reduction in area of all Quenched and Tempered, i.e. non-embrittled, specimens. In this work, the embrittlement index, M, was defined as...

$$M = \left(1 - \frac{A_f}{A_0}\right) \quad 3.1$$

Where A_0 and A_f are the percentage area reductions of the mean value of the cross sectional areas of all of the quenched and tempered (reference) specimens and the individual test specimen, respectively.

3.5.7 Stress-Strain Diagrams

Load versus time measurements were recorded manually. Using the known values for the cross sectional area and strain rate, these values were then converted into true stress - true strain diagrams.

3.5.8 Times to Failure

An initial load of 0.05 tons, equivalent to 498 Newtons, was applied to the test specimen in order to ensure a consistent starting point for all specimens. Since time to failure was the principal purpose of these experiments, a consistent starting point was of prime concern. However, in determining extension for the calculation of strain, the initial extension had to be determined by extrapolating the stress - strain diagram to obtain initial extension.

It was found that, since times to failure for any given set of measurements were generally very consistent, a satisfactory population of times to failure required only five or six specimens.

The following statistical analyses were applied to sets of test data...

- a. **Student t-test** was used to determine whether or not two populations, which appeared to be identical, did in fact fall within the same distribution with an acceptable probability, usually 95%. This was a valuable tool for quality control between batches of samples that were heat treated or plated on different occasions. Also, it was useful to establish whether or not baking had resulted in the complete recovery of embrittled samples.
- b. **Weibull Analysis** was used as a statistical tool that allowed for certain random factors within a given distribution, such as size, shape and position of inclusions and defects between tensile specimens. This technique allowed an accurate assessment of incubation time for embrittlement and mean time to failure during SSR tests. In addition, since the value of the Weibull slope is sensitive to the mechanism of failure, the method also allowed failure by more than one mechanism to be identified, simply by an examination of the Weibull slope.

SSR tests were conducted on tensile specimens that had been treated in four main ways in order to determine the relative extent of embrittlement caused by plating and the effect of heat treatment subsequent to that treatment. Those methods are briefly described below.

- **QT Quenched and Tempered** These samples were used to check the consistency of heat treatments provided by Holt Brothers Ltd. In addition, failure times and reduction in area provided useful standards against which plated specimens could be compared.
- **QTP Quenched, Tempered and Plated.** These samples represented the "as plated" situation, and were a measure of the extreme case of embrittlement due to the plating process only. The electroplated layers under investigation included both cadmium and zinc/nickel alloy. In order to simulate the effect of leaving industrially plated components for one or more shifts, separate batches were plated and either strained immediately, after a delay of 8 hrs or after a delay of 24 hrs. Samples that were plated at the same time, but then individually tested at a later date were stored in liquid nitrogen until required. In this way, any hydrogen absorbed by the steel was effectively immobilised until the specimen could be strained at room temperature.
- **QTPB Quenched, Tempered, Plated and Baked.** The method for these specimens was the same as for the QTP specimens above, but also including the extra step of baking samples in order to de-embrittle prior to straining.
- **QTB Quenched, Plated and Baked.** These specimens were given the same heat treatments as the QTPB specimens, but had not been plated. It was important to know if the post plating heat treatment would have a significant effect, if any, on the mechanical behaviour of the specimens.

3.5.9 Cadmium Plate Tests

The effect of delaying the testing of cadmium plated specimens for 0, 8 and 24 hours has important implications for industry, in that, after cadmium plating it is required that a de-embrittling bake is performed as soon as possible and not later than 8 hours, or a full working shift, after plating. Little work has been performed to test this standard. In an attempt to test the validity of this practice, Weibull analysis and Student's t-test have been applied to cadmium plated tensile specimens. The additional considerations of doubling the cadmium thickness and of reducing the baking time to 2 hours were also included.

3.5.10 Alloy Plate Tests

Tensile specimens were electroplated in the manner described in Section 3.5.5 at different pH values. Initially, the significance of plating technique and pH control was not understood, but Weibull analyses of TTF results ties in closely with, and complements the results obtained from permeation experiments indicating that the deposition of an initial pH related deposit can affect significantly the amount of hydrogen that enters the steel.

All tensile specimens were plated after a contact time of 1 minute. The term "contact time" refers to the time that the specimen was in contact with the plating solution before the plating current was switched on. The significance of the contact time is discussed later in Section 4.3.2.

3.5.11 Ultimate Tensile Strength

Ultimate tensile strengths of each specimen were recorded both directly from slow strain rate tests and indirectly from Vickers indentation tests. Vickers pyramid numbers were calibrated to give values of approximate UTS. This was used as another quality control check and since the indentation was made at a high strain rate the value obtained was free of hydrogen embrittlement effects. Consequently, this test provided a check on any individual specimens that appeared to give anomalous results, since it was possible to back-check to determine if the original heat treatment was consistent with the other specimens.

3.6 Mechanical Results

3.6.1 Quality Control

The Student t-test was applied to as-received Quenched and Tempered specimens in order to verify quality control between separate heat treatments. Student's t-test was used to lend support to the assertion that plated and baked specimens were fully recovered from their embrittling electroplating treatments, or, if appropriate, to demonstrate that a particular plating experiment had proved not to be embrittling. This t-test was usually applied to Times To Failure (TTF) resulting from SSR Testing, since this was the parameter used in the Weibull analyses to compare the effects of hydrogen embrittlement.

Tensile test specimens were heat treated to a very high degree of reproducibility at Holt Brothers Ltd., Halifax over the duration of this project. However, the latest samples (referred to as the H Series) gave rise to some concern when SSR Test values for the TTF and UTS of the steel based on QT control specimens, did not appear to match the expected values of earlier specimens. According to the Student's t-test, as applied to the most recent heat treatment, values of the TTF and UTS could not be considered to belong to the same distribution as the earlier two heat treatments. Applying Student's t-test to UTS values deduced from values of the Vicker's Pyramid Number, there was, by contrast, good correlation between the three separate heat treatments. This latter test must be taken as direct evidence that the heat treatments themselves were fully consistent and that some other factor was responsible for the deviations in parameters obtained from SSR tests.

Since the heat treatments were consistent, the deviation in TTF values, mentioned above, was deduced to result from the nature of the method of testing employed. The H Series QT values were, therefore, subsumed into the control set of results, together with the D and E Series.

It is now believed that room temperature is a more significant parameter than was at first believed, and that the SSR is more sensitive to hydrogen embrittlement than was originally supposed, since an examination of data indicates that slightly longer TTF values were obtained over winter months, when temperatures, and consequently hydrogen diffusion, were reduced. Although this observation comes too late to be eliminated from this investigation, future investigators would be well advised to take room temperature into account. For now, this variable must be accepted as an increase in experimental error,

A summary of relevant t-test values are given in Table 3.3, below.

Samples Compared	Parameter Chosen	Degree of Freedom	Limiting value	t Value	Accept Reject
{DQT + EQT} : HQT	TTF	21	2.08	4.19	Reject
	UTS/SSRT	21	2.08	5.22	Reject
	UTS/VPN	21	2.08	0.73	Accept

Table 3.3 Student t-values of various parameters for the same specimens

3.6.2 Stress-Strain Results

Fig. 3.6 shows the stress strain diagram for AISI 4340 steel, cadmium plated to a depth of 8 μm . Of the specimens illustrated, all behave in a virtually identical manner until a stress slightly greater than 1400 MPa is reached. At this stress, the QTP specimens failed very rapidly, indicating a brittle failure. This would explain the appearance of the test specimen after failure with very little reduction in area while the fracture surface exhibits predominantly the dimpled structure indicative of ductile failure, see Section 5, Surface Analysis. Thus the effect is of brittle failure in spite of the surface appearance of a ductile mode of fracture. Those QTPB specimens that had been baked subsequent to plating, exhibited a greater tensile stress at failure, but more importantly, they also show the ductile flow that corresponds to the reduction in area resulting in the lower embrittlement index.

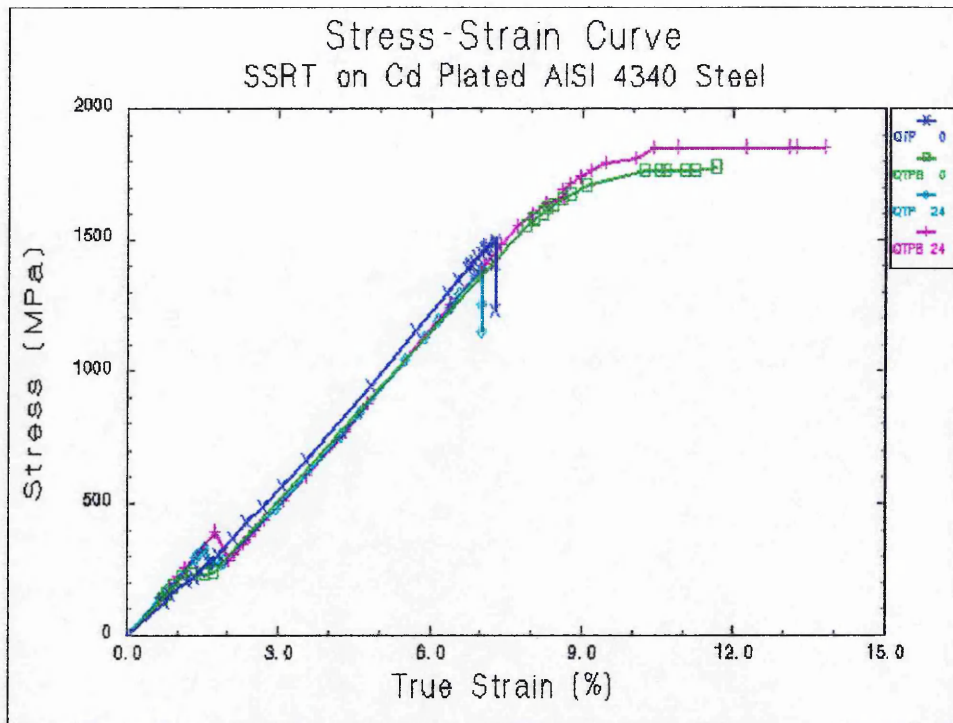


Fig. 3.6 Stress-strain diagram for cadmium plated specimens in both the as plated and baked conditions.

The anomaly in the lower region of the lines has been attributed to the tensometer itself rather than to the specimens.

3.6.3 Cadmium Plate Results

Fig. 3.7a shows the effect of 0 to 2, 8 and 24 hour delays on cadmium plated tensile specimens. Fig. 3.7b shows the corresponding analysis of baked specimens, taken from the same heat treatment batch. Fig. 3.8 represents the effect of baking plated specimens for 2 and 24 hours respectively. In the legends of the graphs, numbers *before* letters denote the delay time in hours, whereas numbers *after* the letters denote the duration of baking at 200°C in hours.

No difference can be discerned between the delay times in Fig. 3.7a with respect to Weibull data. Values for the Student's t-test in Table 3.4 further illustrate the similarity between the data, indicating a better than 95% probability correlation. However, an examination of the embrittlement indices of the 2 and 24 hour delayed specimens indicates that, contrary to expectations, the 24 hour specimen has started to de-embrittle. This is indicated by the decrease in the mean embrittlement index together with a corresponding increase in the standard deviation of the 24 hour delay specimens.

Similarity between these values seems to indicate that embrittlement is not worsened by the delays. However, the shorter delay times may be misleading, due to the duration of the test itself lasting in excess of 14 hours. It seems more likely that, in the absence of strain, no change is experienced in embrittlement until much longer delay times, if then.

Baking specimens after plating for 24 hours had the effect of de-embrittling the specimens fully, as evidenced not only by Weibull and t-test data, but also by the embrittlement index, even in the case of the 24 hour delay. It was feared that, based on diffusion calculations described in the Appendix, the extra delay in baking may allow hydrogen to diffuse deep into the substrate. Once in the steel, there would be a greater chance of causing irreversible damage. This was not found to be the case under the conditions of these experiments.

Fig. 3.8 illustrates the effect of baking cadmium plated specimens for 2 and 24 hours. As can clearly be seen from the diagram, the 2 hour bake coincides closely with the line QT reference line, seemingly indicating full recovery. The 24 hour baked specimens appear to exceed, slightly, the values of the reference. This was considered earlier, in Section 3.5.1, as being due to a drop in testing temperature. Applying Student's t-test to these figures still places them within the 95% probability of belonging to the same distribution. It is in the nature of these Weibull plots that the position of points along the $\log(P_s)$ axis is determined by the number of data points. It is important to note that, although the lines for the QT and QTPB(24) are not as close as might be hoped, the values of the latter do lie within the limits of the former.

The specimens forming the subject matter of Fig. 3.8 belong to the H Series of specimens plated by Stotfold Plating, Hitchin. These specimens were plated to a depth of approximately 8µm, approximately double the thickness of the other cadmium specimens. Regardless of this fact, the QTP line in Fig. 3.8 closely resembles its counterpart in Fig. 3.7a. Student's t-test of the two data sets gives a close correlation between both QTP data sets. Although the embrittlement index of the double thickness, H Series QTP specimens is slightly greater than the corresponding G Series QTP, the standard deviation is also slightly higher, making the difference between the two values insignificant.

Permeation experiments based on alloy deposition indicated that most hydrogen entered the steel from the electroplated layer in the first 8 hours. Assuming that similar processes and rates are involved, it is probable that sufficient hydrogen to cause embrittlement would have been absorbed by the steel before the SSR method can achieve the relevant UTS. One possible way to obtain a positive result from this method may be to pre-load the specimens to 80% or 90% of their embrittled UTS before commencing SSR tests. This should reduce TTF by about 10 hours bringing the TTF well within the time limit for diffusion into the bulk material.

In order to obtain a more complete picture of the embrittlement and de-embrittlement, it was necessary to consider the embrittlement index for each specimen.

Samples Compared		Deg. Freedom	t Statistic
Sample	Compared to	v	t
G 0 QTP	H 0 QTP	11	1.370
"	E 8 QTP	10	0.602
"	G 24 QTP	10	0.871
Ref. QT	G 0 QTPB	26	0.341
"	E 8 QTPB	27	0.214
"	G 24 QTPB	26	1.215
"	H QTPB 2	27	0.177
"	H QTPB 24	27	1.228

Table 3.4 Student t-test results for cadmium plated specimens.

Table 3.5, below, summarises data relating to cadmium plating.

In examining Table 3.5, it must be borne in mind that the H Series values refer to approximately double the thickness of cadmium electroplate and therefore these are in a potentially more embrittling situation than in either Series E or G. In Fig. 3.8 the QTPB samples baked for 2 hours indicated a full recovery based on Weibull data, Student's t-test and mean time to failure. However an examination of the embrittlement index and respective standard deviation for these specimens revealed that while some specimens did exhibit complete recovery, others in the same batch remain embrittled. This gives rise to a deceptively reduced mean embrittlement index, but a very much increased standard deviation for the index. Thus, the embrittlement index and its standard deviation together provide valuable information on the state of recovery of the specimens.

Series	Delay	Bake Time	Weibull Slope	Incub'n Time	Mean TTF	Emb. Index	Std. Dev'n
G QTP	0 - 2	N/A	-0.35	14.6	17.5	0.90	0.03
G QTPB	0 - 2	24	-1.30	29.5	30.2	0.02	0.08
E QTP	8	24	-0.65	14.9	16.4	0.93	0.08
E QTPB	8	24	-0.87	28.9	30.0	-0.04	0.05
G QTP	24	N/A	-0.32	15.3	18.4	0.79	0.24
G QTPB	24	24	-0.41	28.5	31.0	0.03	0.02
H QT	N/A	N/A	-1.25	30.2	31.0	0.10	0.00
H QTP	N/A	N/A	-0.35	13.3	16.2	0.95	0.07
H QTPB	N/A	2	-0.69	28.8	30.3	0.25	0.34
H QTPB	N/A	24	-0.57	29.0	30.8	0.08	0.04
D&E (Ref.)	N/A	N/A	-0.92	28.6	29.6	0.00	0.10

Table 3.5 Summary of Weibull Data all cadmium tests. Times measured in hours.

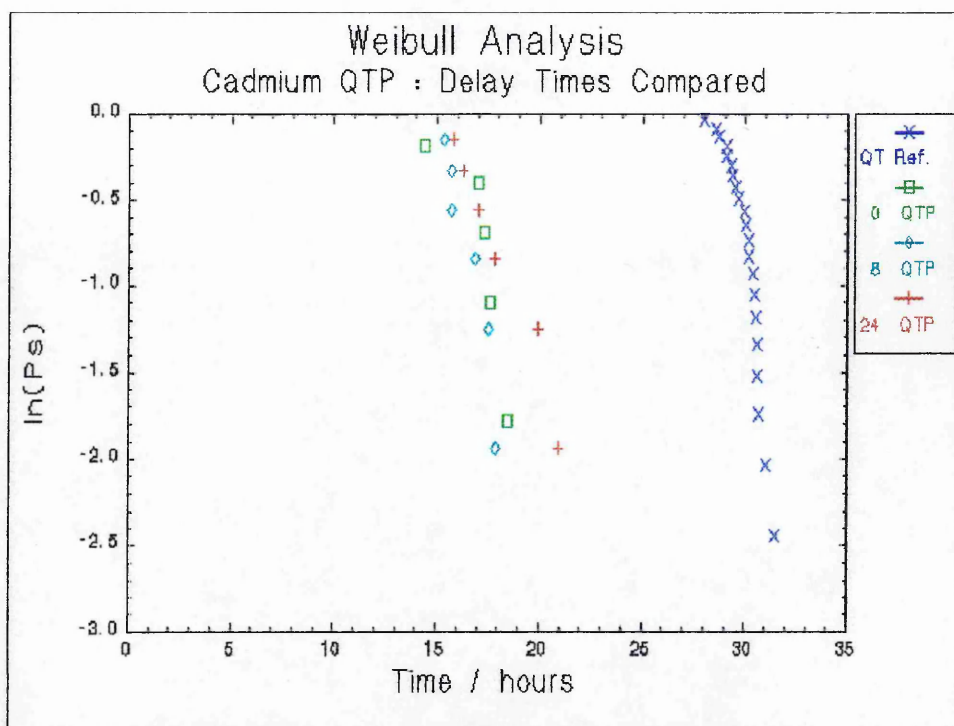


Fig. 3.7a Weibull Analysis - Cd QTP : Delay times compared

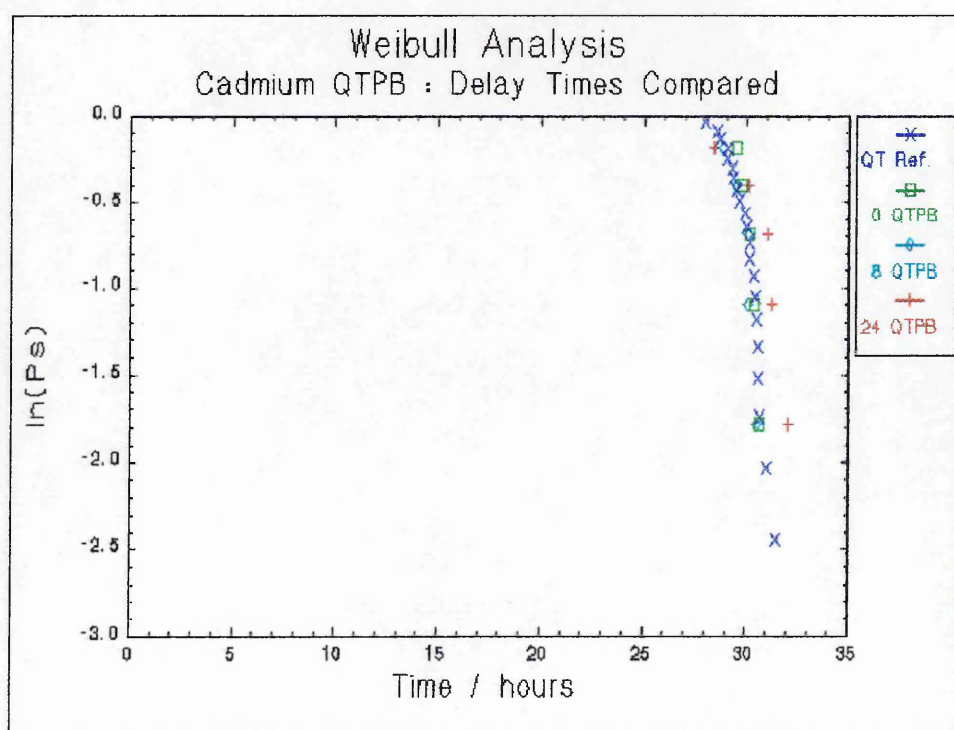


Fig. 3.7b Weibull Analysis - Cd QTPB : Delay times compared

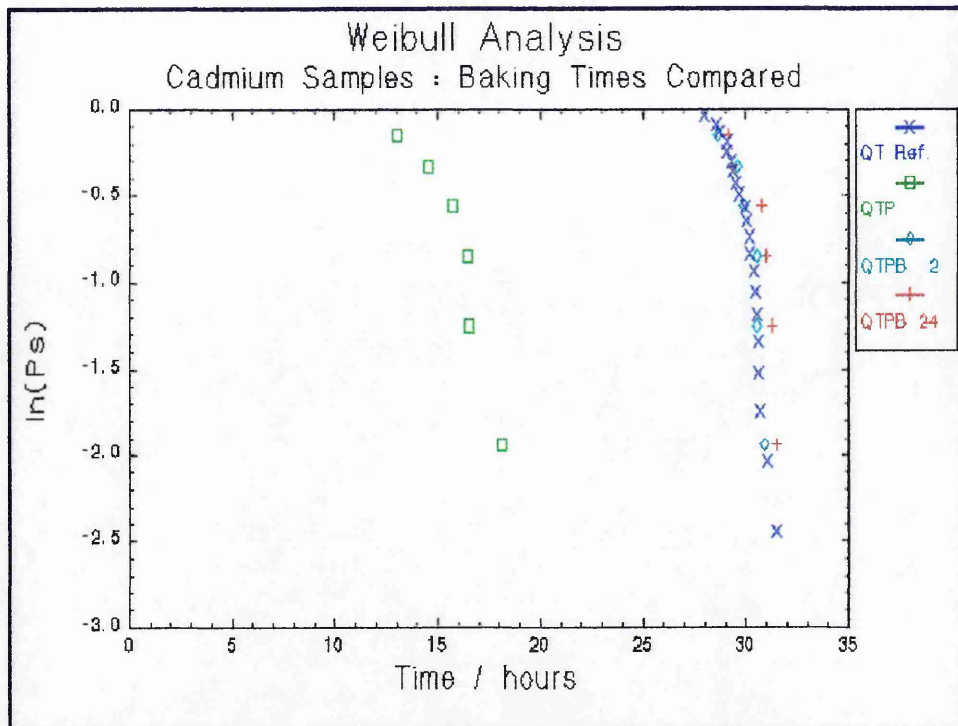


Fig. 3.8 Weibull Analysis - Cd : Baking times compared.

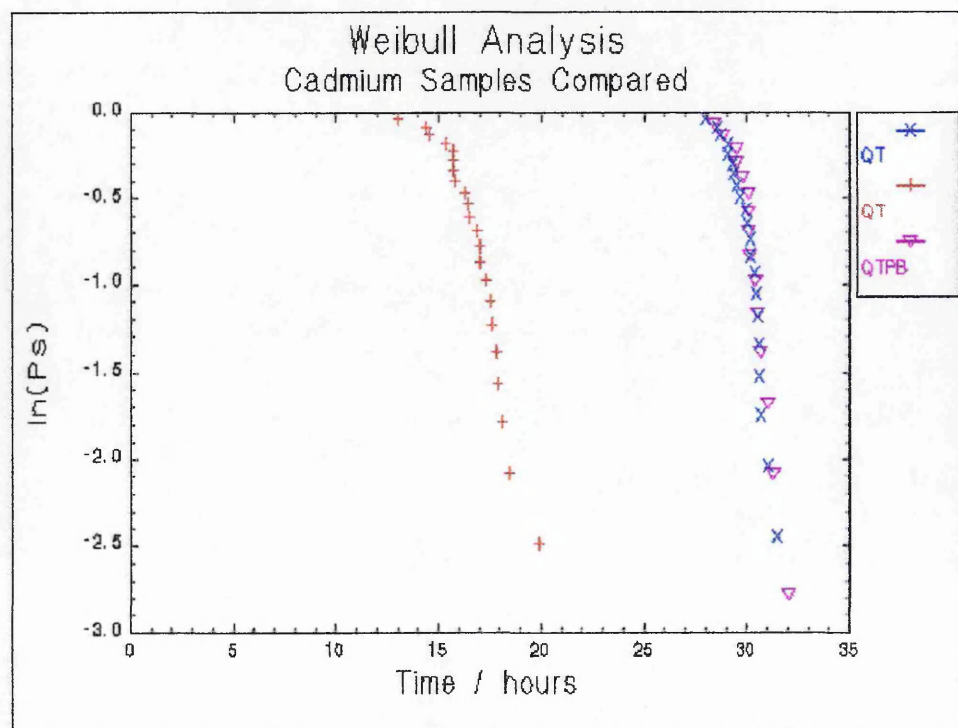


Fig. 3.9 Weibull Analysis - Cd : All samples compared.

3.6.4 Alloy Plate Results

Preparation and plating procedures were described in Section 3.5.5

As with cadmium plated specimens, it was found that baking plated specimens for 24 hours at 200°C resulted in full de-embrittlement.

Fig. 3.10 shows the Weibull plot of all relevant alloy plated tensile specimens as either QTP or QTPB data sets compared to the unembrittled QT specimens. As can be clearly seen, the lines corresponding to the baked and de-embrittled specimens is in close agreement with the unembrittled QT specimens. QTP data points, however, appear to form two distinct lines, unlike those of the cadmium plated QTP specimens. Whereas cadmium electroplate was always severely embrittling, Fig. 3.10 indicates that this is not always the case with alloy plating. As the data is presented, it is impossible to tell if the lower, steeper branch of the alloy QTP line is demonstrating no embrittlement at all, or if a less severe embrittlement is evident.

To determine the nature of these two sections, Fig. 3.11 represents the same data points, but with the QTP points split into separate groups. In this case it is clear that although one group is severely embrittled, the extent of embrittlement is not as severe as in the case of cadmium plating. The second QTP line exhibits no indication of severe embrittlement, coinciding well with the QT Reference line.

It will be noted, in Fig. 3.10, that there is no discontinuity in values for times to failure between the embrittled and non-embrittled specimens. This seems to indicate that embrittlement may be related to some continuous variable related to the plating process, not identified in this diagram

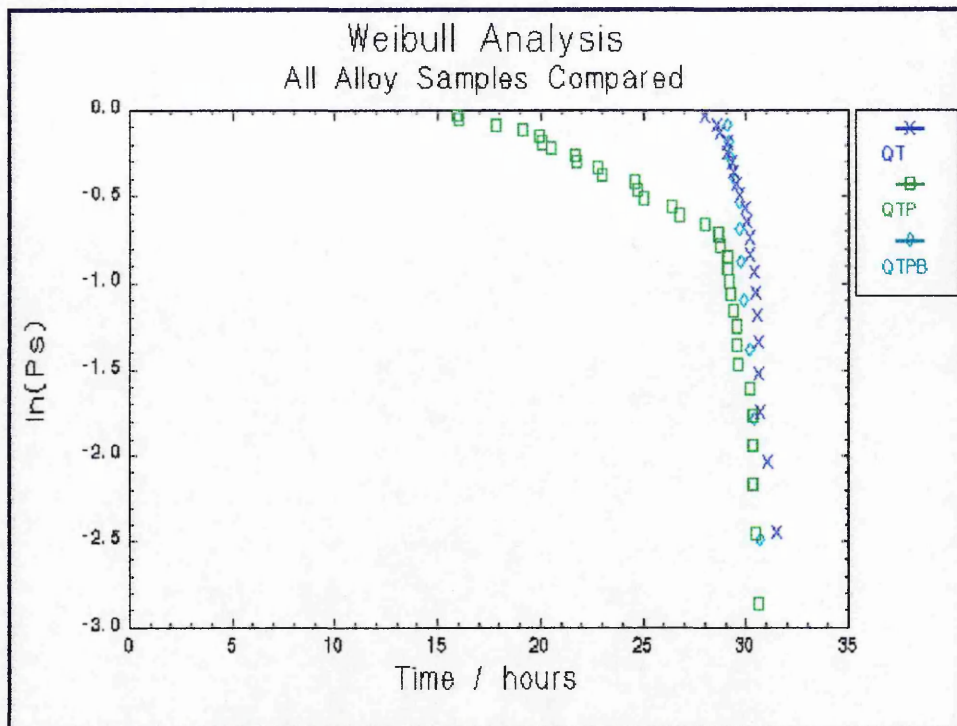


Fig. 3.10 Weibull Analysis - Alloy : All samples compared.

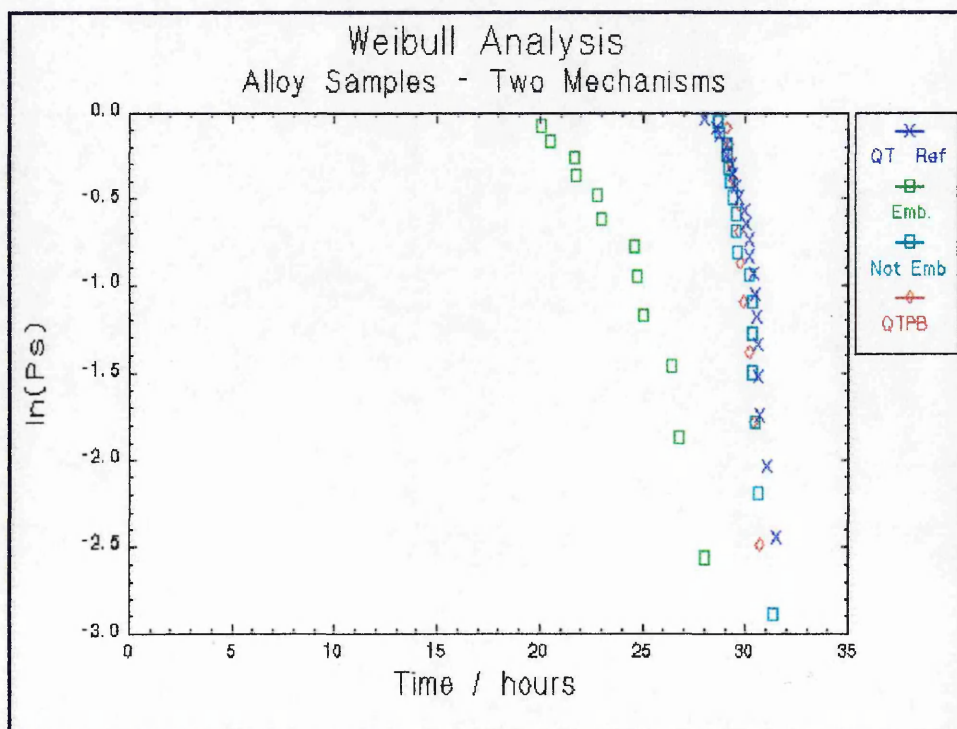


Fig. 3.11 Weibull Analysis - Alloy : Showing two mechanisms.

The most logical way to divide QTP data points was according to pH of the plating solution at the start of the plating process. Because the actual pH was difficult to adjust to a precise, repeatable value in consecutive experiments, these data points have been banded according to pH values used in the permeation experiments. These ranges are narrow, being typically, approximately 0.3pH units wide, but do introduce variability to the tests.

Initially, it was expected that low pH values would be more embrittling than high pH values, simply because the more acidic solution contains the greater hydrogen activity and the alloy deposition was accompanied by bubbles of hydrogen gas at the cathode. Electrodeposition from higher pH solutions, with lower hydrogen activity, producing little or no visible hydrogen evolution was, therefore, expected to result in less hydrogen embrittlement. The results depicted in Fig. 3.12 contradict these initial expectations. Furthermore, a gradation was expected from the more embrittling at one end of the pH scale, to the least embrittling at the other. This expectation was also seen to be erroneous.

Logical sense of the results can, however, be extracted by interpreting them in the light of the permeation experiments discussed in Section 4. Permeation experiments indicate that a chemical deposit is left on the surface of steel left in contact with the plating bath. As will be discussed later in Section 5, two different deposits are possible, the natures of which are pH dependent. These deposits influence the uptake of hydrogen in different ways. Zinc hydroxide, formed at approximately $\text{pH} \geq 4$ appears to produce a thickness related barrier to hydrogen, whereas the deposition of metallic nickel, formed at approximately $\text{pH} \leq 4$, forms a much more efficient barrier to hydrogen ingress, possibly by forming a thin, but effective, surface layer of nickel hydride. Such is the effect of this nickel layer that, together with solutions containing in the order of 1000 times the hydrogen ion concentration, only 0.1 times the amount of hydrogen enters the steel. Thus, pH5 provides the most embrittling environment, with pH3 the least embrittling. pH2 is slightly more embrittling than pH 3. Fig. 3.12 suggests that pH4 spans the changeover in the nature of the chemical deposit, whereas permeation experiments seem to indicate a slightly lower pH. These differences may be attributed to the composition of the substrate steels.

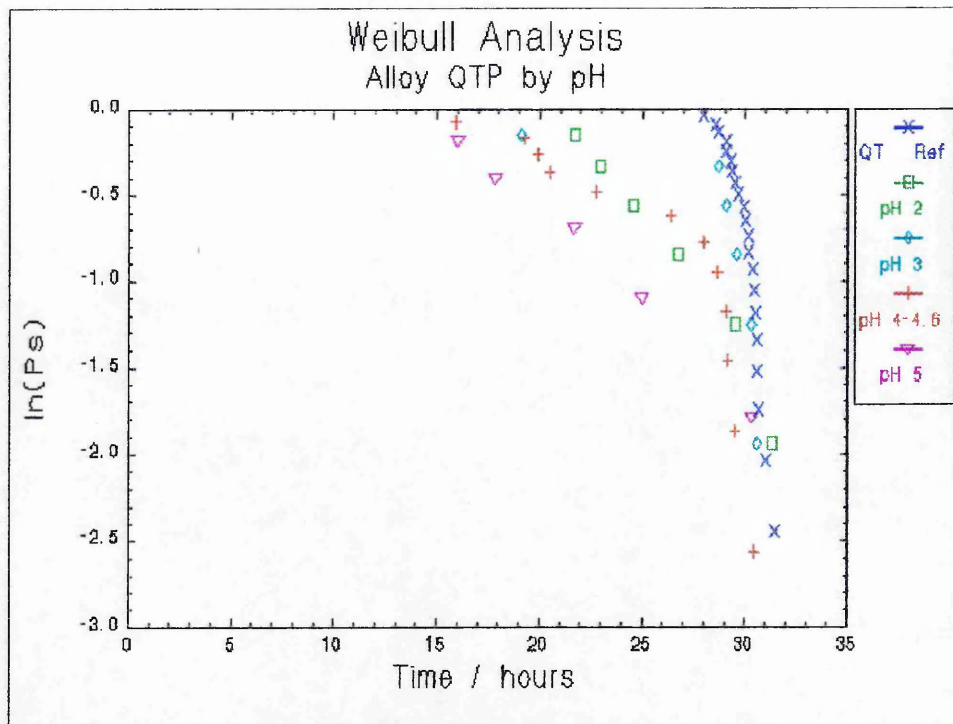


Fig. 3.12 Weibull Analysis - Alloy : QTP specimens wrt pH.

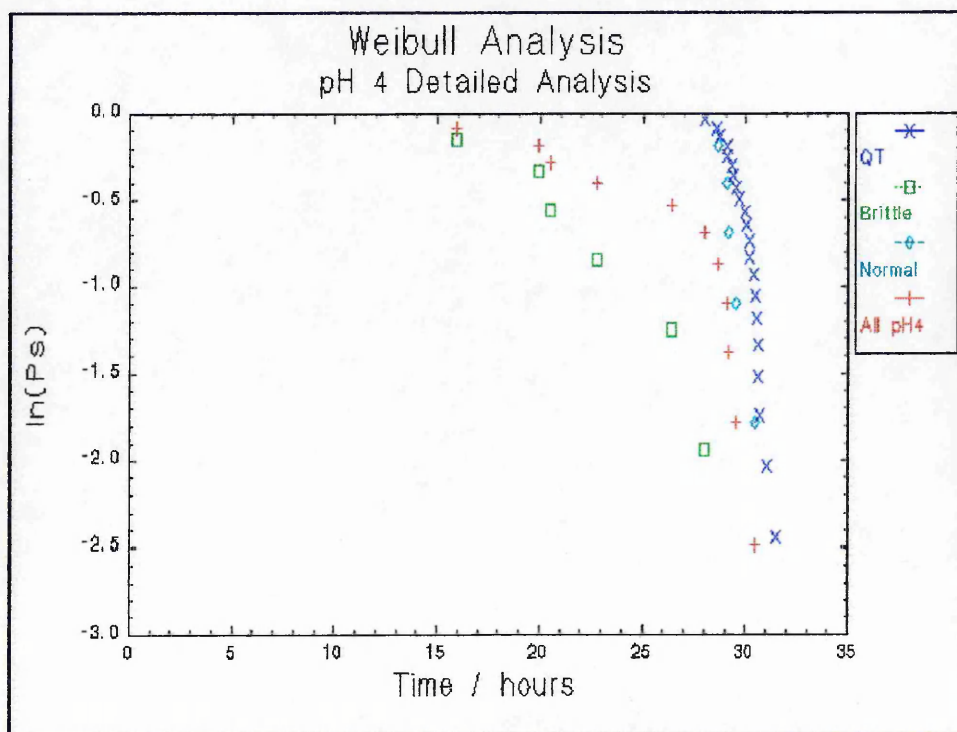


Fig. 3.13 Weibull Analysis - Alloy : pH4 detailed analysis.

By splitting up the two branches of the QTP line for the pH 4 solution into two separate lines, it can be seen that there exist two distinct fracture mechanisms within the data set. Examination, where possible, of the pH values reveals that the embrittled specimens were plated at, or above pH4.2, whereas the unembrittled specimens were plated at pH4.0 to 4.2. Some small indication of embrittlement may be evident for the least embrittled specimens (labelled "normal") in Fig. 3.13, but this is not conclusive.

From an examination of embrittlement indices, as summarised in Table 3.6 below, it can be seen that, unlike cadmium plating, which gives a consistently high degree of embrittlement resulting in low standard deviations, the alloy plate tends to produce high standard deviations. This arises from the wide range of embrittlement indices, relative to cadmium, associated with all pH values. Thus, embrittlement indices must be considered together with Weibull data.

pH	Emb. Index	St'd. Dev'n
2	0.51	0.42
3	0.25	0.32
4 (all)	0.31	0.43
5 (small sample)	0.48	0.52

Table 3.6 Embrittlement Indices for Alloy Plated Specimens.

3.7 Summary of Plating Experiments

3.7.1 Cadmium Summary

- a. Cadmium electroplating is relatively more embrittling than zinc/nickel alloy electroplating.
- b. There appears to be little difference between results obtained after delays of 0 to 2, 8 or 24 hours before the baking treatment. This may be due to the duration of the SSR tests themselves rendering them too insensitive for this kind of determination, although hydrogen appears to start outgassing by 24 hours delay at room temperature.
- c. From incubation times and embrittlement indices for QTPB specimens for Series E and G there appears to be no significant benefit detected in baking as soon as possible after plating, providing that baking is for 24 hours.
- d. The incubation time for Series H, QTP indicates more severe embrittlement due to the thicker cadmium plate. However the embrittlement index is not significantly greater than that of the Series G, QTP specimens.
- e. Complete recovery of mechanical properties is possible with 24 hour baking at 200°C.
- f. By comparing the 2 and 24 hour baked samples of Series H with the QT values from Series H, it appears that there is little difference between the two baking times. However, the Embrittlement Index clearly indicates that the 2 hour baking is insufficient for full recovery.
- g. TTF measurements from SSR tests on AISI 4340 seemed to be significantly affected (approximately 3%) by temperature variations between about 5° and 20°C. This would appear to be related to the rate of hydrogen diffusion which is known to be temperature dependent.
- h. Future SSR tests may benefit from being conducted at constant temperatures with an initial load related to the expected UTS of the embrittled specimen, as with constant load tests. This would shorten the test times making the tests more sensitive to delay times. Hence the principal advantages of SSR and constant load tests could be combined.

3.7.2 Alloy Summary

- a. Zinc-nickel alloy is less embrittling than cadmium plating.
- b. Complete recovery is possible with baking.
- c. pH dependant chemical deposits are more important in affecting hydrogen entry than the pH of the plating solution itself.
- d. Commercial plating solutions operating in the pH6 region may well be more embrittling than more acidic solutions at $\text{pH} \leq 4$, contrary to expectations.
- e. A minimum of hydrogen entry appears to occur in the pH range 3 to 4.
- f. It may be possible to deposit zinc-nickel alloy within the above pH range without the need for de-embrittlement.

4 Electrochemical Testing

4.1 Background

4.1.1 Plating Solution

The compositions of industrial plating solutions are complex, and in many cases secret. Additives may be used to enhance the throwing power, influence the proportions of zinc and nickel, or alter the surface finish and control the pH of the bulk solution. Any or all of these may influence the uptake of hydrogen by the electroplated layer and/or steel. In the face of so many variables it would be impractical to use a commercial plating solution for a fundamental study of this nature. Consequently, a simplified plating solution was adopted in order to complement work on the corrosion protection offered by zinc-nickel alloy, elsewhere. This plating solution comprised 0.92M zinc sulphate and 0.52M nickel sulphate with $0.4 \text{ cm}^3 \text{ dm}^{-3}$ teepol to act as a surfactant. This solution, once made, had a pH in the region of 4 to 4.5 due to hydrolysis of dissolved metal ions. In appearance, the slightly acidic solution adopted the strong dark green colour of the aqua nickel(II) ions.

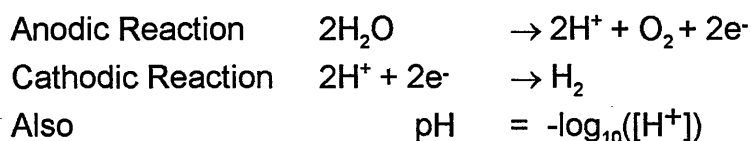
4.1.2 Permeation Cell

Permeation data is presented which is based on an experimental arrangement developed by Dévanathan and Stachurski^[43] and used by many others. The cell is divided into two sections separated by an electrode made of a thin membrane of the test material. One side, the charging side, contains an electrolyte which allows the reduction of hydrogen ions at the metal cathode surface. Some hydrogen is absorbed by the cathode and diffuses through the metal, down a hydrogen concentration gradient, to the far side of the electrode. The far side of the electrode is also the surface of the anode of the depletion cell. This surface is maintained at a potential of +150 mV (NHE) in order to oxidise the hydrogen as it reaches the surface. The electrolyte used is 0.2M NaOH solution which removes the hydrogen ions as they are formed. In this way, the anode surface is maintained at effectively zero hydrogen concentration, thereby giving a fixed point for diffusion rate calculations.

The depletion cell is much as was used by Devanathan and Stachurski. The charging side of the standard permeation cell was deliberately intended to provide a high surface concentration of hydrogen in order to promote permeation. To this end solutions of 10% sulphuric acid containing cathodic poisons such as arsenic or tin(II) chloride have been used. In this there is a significant difference in approach to the present investigation.

It is not the purpose of these permeation experiments to encourage hydrogen entry and permeation, but to establish the quantity of hydrogen which is absorbed as a result of electroplating a steel surface with a zinc/nickel alloy. Consequently, all variables which affect the absorption of hydrogen at a metal surface must be controlled.

In a typical Devanathan and Stachurski charging cell, the anode is present in the same compartment of the permeation cell as the steel membrane. During charging, water is oxidised to produce hydrogen ions. During the course of a simple permeation experiment, the pH of the charging solution remains constant, since the anodic production of hydrogen ions is balanced by the cathodic reduction of an equal quantity of hydrogen ions, as indicated in the equations below. Also, due to the logarithmic nature of pH, a small change in hydrogen ion concentration at a low pH will be negligible compared to the total hydrogen ion concentration, giving rise to a negligible change in pH.



The pH of the plating solution in the zinc-nickel alloy plating experiments is high (pH5) compared to the charging solutions of many other investigators using acidic electrolytes and so even relatively small changes in hydrogen ion concentration will have a significant effect on the pH of the plating solution. Moreover, unlike the traditional permeation method, metal ions, rather than hydrogen are discharged at the cathode. This means that the production of hydrogen ions at the anode does not balance the reduction of hydrogen ions at the cathode. Consequently, a significant increase in hydrogen ion concentration (drop in pH) occurs with time, which is directly dependant on the amount of reduced metal...



Industrial zinc-nickel plating baths use separate electrodes of zinc and nickel with the different anodes dissolving at rates determined by electronically controlled impressed currents. In this way, the pH variations in the solution are largely eliminated, with regularly adjusted buffers ensuring a constant process pH. In this work, early permeation experiments attempted to partially reproduce this feature by using a zinc anode. Unfortunately, displacement of nickel from solution by the more reactive zinc metal left a black deposit on the anode and could have adversely affected the nickel ion concentration. This would have caused additional problems with the composition of the plating solution. Some of these deposits would then break away as the anode dissolved leaving particles suspended in the plating solution.

Using a platinum anode alleviated these effects, but it was found that the pH of the solution could fall by as much as 2 pH units during the course of a single experiment. This explains why, in these early permeation experiments, the expected plateau for a permeation experiment was not observed, since the decrease in pH with time corresponded to an increasing surface hydrogen concentration on the steel membrane. A form of pH control was needed together with a different approach to permeation work which would also reduce the plating time.

To avoid the addition of chemicals to act as a buffer, the anode had to be removed from the plating cell. This was achieved by placing the anode in a separate chamber and connecting this to the plating bath via a salt bridge filled with plating solution. Hydrogen ions produced in the anode compartment were, for the period of plating, unable to diffuse to the cathode chamber, or plating bath, in sufficient quantities to affect pH measurements there. This not only avoided the very large pH drop of the bulk plating solution, but also made possible the measurement of the small pH change in the bulk solution resulting from hydrogen ion reduction. Thus, measuring the pH of a known volume of bulk solution gave a quick and simple means of determining hydrogen ion reduction and hence current efficiency. An alternative method would involve weighing very small amounts of electrodeposit, baking to dehydrate the zinc hydroxide, re-weighing and then calculating the amount of zinc hydroxide in the deposit before being able to determine the mass of alloy deposited. This latter method would involve a large error due to errors in weighing and re-weighing small quantities.

A diagram of the plating cell is given below in Fig 4.1.

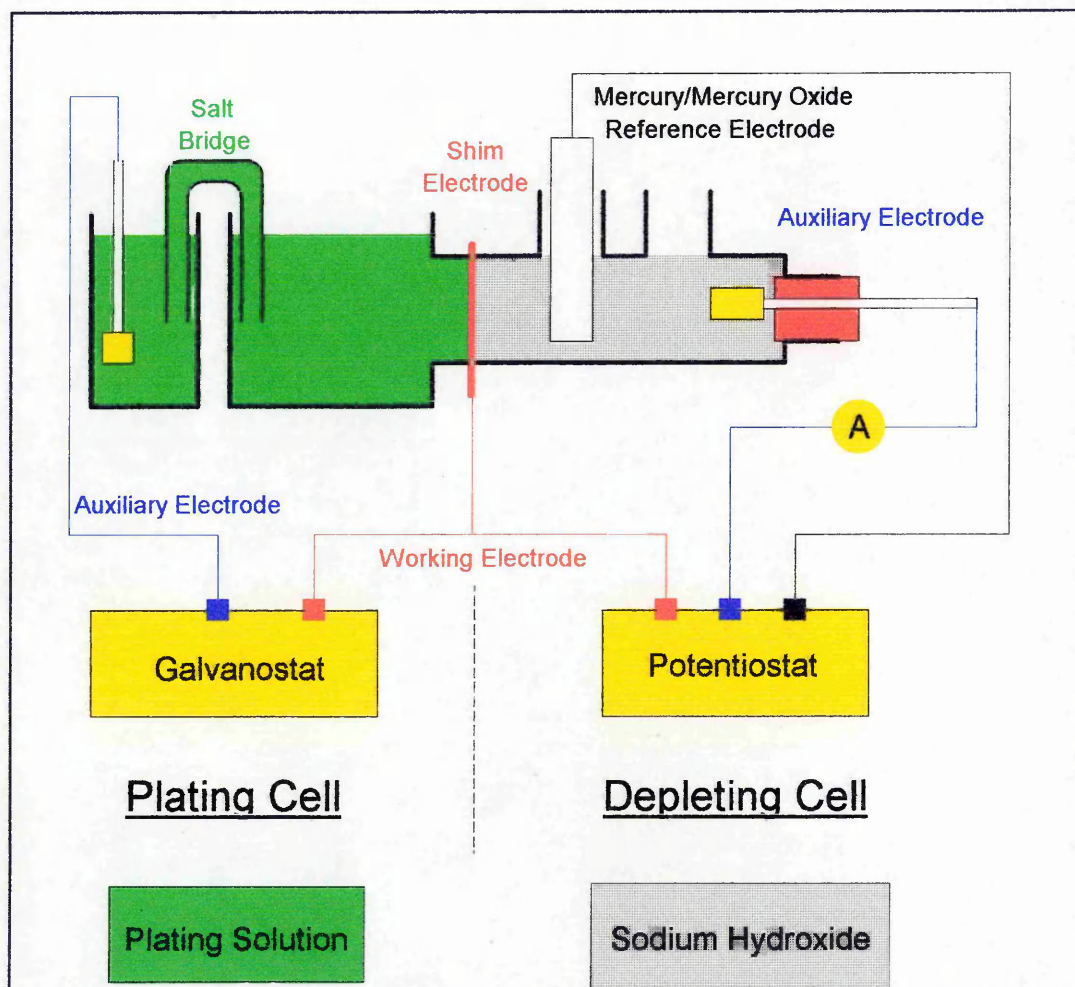


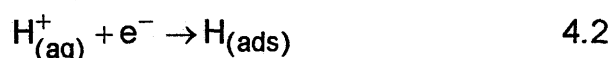
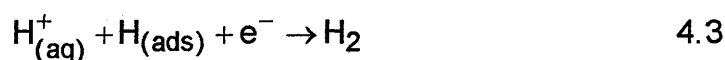
Fig. 4.1 Permeation Cell, Schematic.

The anodic, or efflux, side of the cell was held potentiostatically at +150mV (NHE) to deplete the electrode and while plating. Plating, and assuming a constant current efficiency, hydrogen charging was controlled galvanostatically. Current measurements were recorded by a chart recorder which had been modified by a buffer amplifier to have a high input impedance. The voltage drop across a 0.1M Ω resistor was measured to obtain a value for the total anodic current. Due to considerable electronic noise, it proved necessary to shield all external leads and insert an ac filter in series with the signal from the resistor to the chart recorder.

4.1.3 Electrochemical Method for Determining Current Efficiency

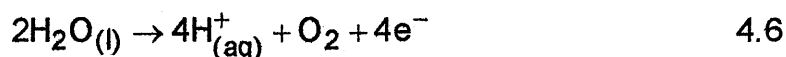
If, as a result of removing the anode, pH changes in the cathode compartment were unaffected by anodic pH changes, then any pH change in the cathodic chamber must be due to a cathodic process. Now, if the cathodic process for metal deposition was 100% efficient, then no pH change would be expected. Conversely, if hydrogen is produced cathodically, then the cathodic reaction is less than 100% efficient and there would be a corresponding pH increase in the solution. It is, therefore, possible to monitor current efficiency in the absence of any buffering process by monitoring pH changes in the bulk solution. The general reactions taking place at the electrodes can be represented as:-

- **Cathodic Reactions** These are the reduction primarily of metal ions to produce a metallic phase but also of hydrogen ions to form hydrogen at the cathode surface involving an exchange of electrons. This hydrogen will subsequently either form molecular hydrogen, or be absorbed into the metal surface where it will then be free to diffuse and potentially result in embrittlement of the metal.



The removal of hydrogen ions, by any mechanism, results in an increase in pH. If it is assumed that the loss of hydrogen ions is the sole cause of plating current inefficiency, then, by measuring the resulting increase in pH, the amount of hydrogen reduced at the cathode surface and the plating current efficiency can be determined.

Anodic Reaction. In the acidic medium of the plating solution the most favourable anodic reaction is the oxidation of water, represented by the following reaction..



As can be seen, two moles of H^+ are produced for each mole of metal ions reduced. In the relatively small volume of the permeation cell, or the even smaller container in which tensile specimens are plated, this results in very significant changes in pH and surface concentration of hydrogen.

If both of the outlined processes occur within the same cell, then the pH changes due to the cathodic process will be negligible compared to those from the anodic process. By separating the two processes and completing the circuit with a salt bridge containing more plating solution, then the cathodic pH changes can be studied independently.

4.2 Experimental Procedures

4.2.1 pH Determined Current Efficiency

As stated above, if 100% of the plating current is used to deposit metal on a steel surface, then no pH change will take place. If, however, hydrogen is also produced then the current will be less than 100% efficient and the pH will rise as a consequence.

pH changes during the plating of some tensile specimens were monitored so that the effect of plating solution pH and current efficiency could be compared with times to failure. In the early tests, tensile specimens were plated in a beaker containing both anode and cathode. As is discussed in Sections 3.5.5 and 4.1.2, this is no longer acceptable due to the possibility of relatively large changes in pH affecting the uptake of hydrogen.

Two beakers, joined by a salt bridge and containing plating solution throughout were set up as shown in Fig. 3.5 One beaker contained the tensile specimen to be plated, the other the counter electrode, thus isolating the tensile specimen from pH changes resulting from the anodic reaction. This arrangement allowed pH changes due to plating to be measured and for the current efficiency to be deduced over a single plating period of 15 minutes. These data were used to complement tensile test results obtained. More importantly, these tests allowed the investigation of the effect of both pH and current efficiency on times to failure of a tensile specimen. Results of these investigations are dealt with in Section 3.6.4.

After plating, it was sometimes necessary to adjust the pH of the plating solution back to a suitable starting point. This was achieved by adding small amounts of 10% sulphuric acid to reduce the pH and either dilute sodium hydrogen carbonate solution, or solid sodium hydrogen carbonate powder to raise the pH. Sodium hydrogen carbonate was preferred over sodium hydroxide since the latter was found to be more likely to result in the localised precipitation of zinc and nickel hydroxides from solution. Once formed, these precipitates could take a long time to re-dissolve, even at bulk pH below which they should dissolve. It is suggested that the precipitate may have been stabilised by the presence of the Teepol used as surfactant.

4.2.2 Permeation Methods

The purpose of this work was not to determine diffusion parameters for the hydrogen ingress into steel which had been electroplated with zinc-nickel alloy, but to determine the extent of hydrogen embrittlement resulting from the electroplating process. With this object in mind, permeation experiments were conducted in such a way as to determine a rank ordering of the amount of hydrogen permeating a shim electrode as a result of the deposition of approximately 8 μ m of alloy onto a shim electrode.

4.2.2.1 pH - Current Efficiency

pH measurements, using a pH electrode accurately calibrated using pH 4 and pH 7 buffers, were made of the plating solution both before and after plating. Knowing the total plating current and the volume of solution it was possible to calculate the plating current efficiency using the method outlined in Section A3.

Difficulties due zinc(II) species adsorbing onto the bulb of the glass electrode made it necessary to wait several minutes in order to obtain steady pH measurements. These zinc(II) species resulted in a precipitate from solution of pH 7 buffer material. To avoid cross contamination between plating solution and the pH 7 buffer, the glass electrode was rinsed well first in distilled water and then in pH 4 buffer to remove any adsorbed zinc(II) species. Adsorbed zinc(II) species appeared to have no effect on the efficiency of the pH 4 buffer.

Current efficiency measurements were made during experiments in which the measurement of pH changes was the sole purpose, but also during permeation and tensile specimen plating experiments.

4.2.2.2 Preparation of the Shim Electrode

Shim mild steel, supplied by Knight Strip Metals, Potters Bar, was cut to shape and abraded with 1200 grit carborundum paper on both sides before being degreased using propan-2-ol. The final thickness of the shim was of the order of 50 μ m.

The electrode was held in place between the rubber washers of the depletion cell and plating cell adapter by metal bulldog clips. Vacuum grease was applied between surfaces to ensure a water tight seal.

0.2M sodium hydroxide solution was poured into the depletion cell and the apparatus was wired to both the galvanostat and potentiostat.

The potential of the exit side of the electrode was held at +150mV (NHE) by a mercury oxide reference cell, recently calibrated against a saturated calomel electrode at the operating temperature of 30°C.

A current, in the region of $50\mu\text{A cm}^{-2}$ or greater, flowed from the exit side immediately on applying the potential, but decayed rapidly. However, once the current decayed to below about $1\mu\text{A cm}^{-2}$, further current decay was very slow. In order to achieve a desired background current density of below $0.05\mu\text{A cm}^{-2}$, it was necessary to leave the electrode to deplete for 48 hours or longer.

Once a constant, minimum background had been achieved, the plating cell could be prepared. It was necessary to measure the time elapsed between wetting the shim-cathode and switching on the plating current. This "contact time" is discussed later in Section 4.3.2. A temperature of 30°C was aimed for, and achieved to within $\pm 1^\circ\text{C}$.

The plating current was switched on at a current density of 20mA cm^{-2} for 15mins. This had the effect of depositing a layer of alloy of 8 to $10\mu\text{m}$ average thickness, which is comparable to that used in cadmium plating of high strength steels and that usually used with zinc-nickel alloy coatings.

A chart recorder maintained continuous recording of permeation currents. After plating for 15mins, the plating current was switched off and the plating cell was drained. Distilled water was used to rinse the fresh alloy deposit, an action which invariably disturbed the output for one or two minutes.

Once the rate of change of permeation current reduced, the speed of the chart recorder was reduced. Recording was maintained until the final background current matched the initial background current. This usually took between two and five days.

The total permeation current measured was read directly from the chart recorder and entered into a spreadsheet which calculated the true permeation current density and converted this value into the amount of hydrogen atoms to completely permeate the shim-electrode, measured in moles.

Data were correlated according to solution pH at the start of the experiment, contact time, the calculated permeation current density and quantity of permeated hydrogen as a function of time.

4.3 Experimental Results

4.3.1 Current Efficiency

Results of the current efficiency experiments are summarised in Fig. 4.2, below.

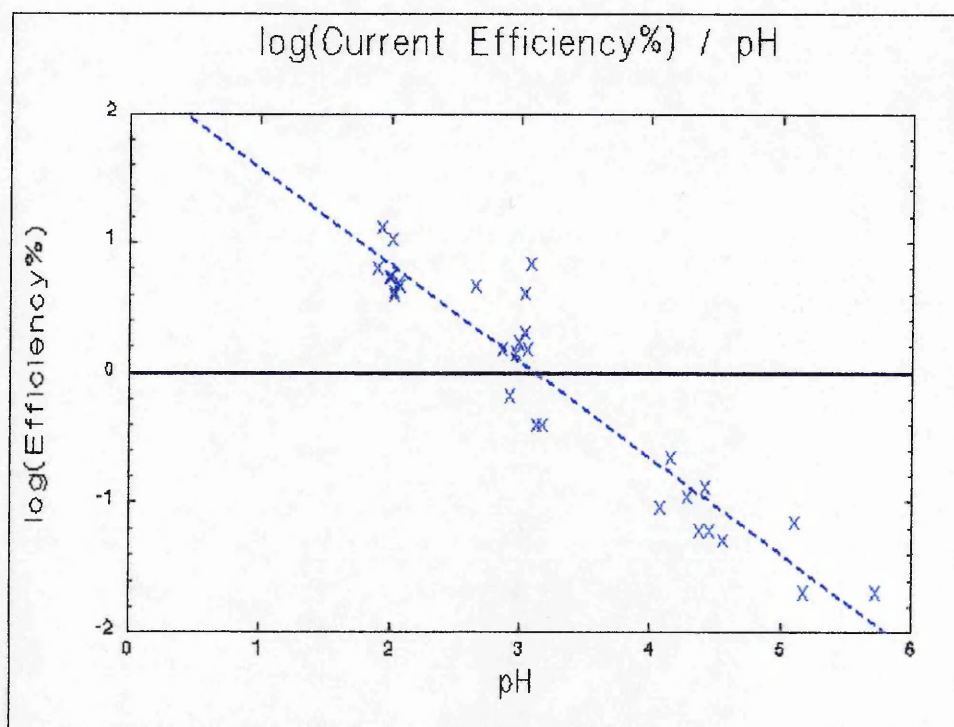


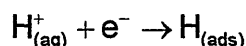
Fig. 4.2 Relationship Between pH and Hydrogen Current Efficiency

As can be seen from Fig. 4.2, there appears to be a linear relationship between pH and $\log(\text{current efficiency \%})$ over the range of the investigation. The line suggests that a linear relationship between hydrogen concentration and the efficiency of the current producing hydrogen gas. Clearly it is not possible to extrapolate this line beyond a current efficiency of 100%, but it suggests that 100% of the current may be used to produce hydrogen (and consequently no alloy deposition) at a pH value of about 0.4.

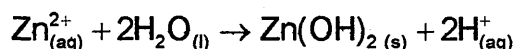
This relationship would be expected to change under conditions of forced convection, since the hydrogen current efficiency is diffusion controlled, but for a specific system, such as this one, the relationship should be a valid one.

This last statement is explained by considering the mechanism of anomalous co-deposition.

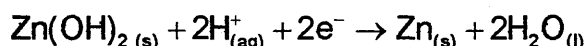
Initiation. Sufficient H^+ is reduced to locally depress pH.



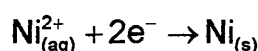
H^+ and $Zn(OH)_2$ are both produced at the cathode surface.



H^+ and $Zn(OH)_2$ are both removed as Zn is discharged.



Nickel is discharged directly



From these equations, the hydrogen ion appears to behave as a catalyst to the deposition of zinc from the aqueous zinc ion in the acidic plating bath.

Provided that a small quantity of hydrogen ions are reduced in order to initiate zinc hydroxide precipitation, the process of reducing the zinc hydroxide under electrochemical conditions is self buffering. More hydrogen reduction is only required to make up for the inward diffusion of hydrogen ions from the bulk solution. Hydrogen ion reduction would be minimised by holding the bulk pH as close to pH 5.5 as possible and limiting convection, resulting in higher plating current efficiency.

Deposition of zinc alloy, therefore, is possible only because zinc hydroxide is initially deposited at pH values of about 5.5 and this is below the critical pH for nickel hydroxide. In acidic solutions, this would not be possible but for a localised, relatively high pH region adjacent to the electrode resulting from the reduction of hydrogen ions. By affecting this diffusion layer, the rate at which hydrogen ions must be removed from solution is necessarily increased. That is by increasing the pH of the bulk solution, or by stirring, hydrogen ion diffusion toward the electrode is assisted and the plating current efficiency is decreased.

A more detailed discussion of the mechanism of anomalous co-deposition is given later in Section 6.4.

SEM analysis of the electrodeposit gave a typical nickel composition in the region of 4% which was low compared with the 8% obtained by Baldwin under similar conditions^[93].

4.3.2 Contact Time

Initially, permeation transients were not consistent. Temperature and electronic control were each suspected, correctly, of being at least part of the problem and methods and equipment were modified and improved. However anomalies still occurred. In considering the reason for this difficulty, a number of printouts from permeation experiments were re-examined to see if any common factor could be identified as being a cause of the lack of reproducibility. Just such a factor was found to be the delay in time between introducing the solution into the plating cell and beginning plating. Since standardising this "contact time" between the solution and the shim-cathode, experiments have had a high degree of reproducibility.

A conclusion from the above observation is that a chemical deposit, resulting from chemical processes not necessarily related to plating, was formed on the cathode surface. This deposit was capable of forming a barrier to hydrogen entry of the steel from the subsequent alloy deposit.

Since nickel is chemically less active than iron, it seemed reasonable to assume that nickel was being displaced from solution by the iron. It is known that nickel surfaces present a substantial barrier to hydrogen influx^[104], readily forming a non-stoichiometric hydride with the adsorbed hydrogen^[16,28]. The surface is soon saturated to a relatively high hydrogen concentration, inhibiting further adsorption. Diffusion through the bulk of the alloy is slow, and so the rate of removal of surface hydrogen is slow, leading to a slow uptake of hydrogen by the steel. Nickel can, however, dissolve relatively large amounts of hydrogen, compared with steel, acting as a reservoir which allows hydrogen to continue to enter the steel over a long period of time.

Further analysis of this chemically deposited layer is considered later, in Section 5. For now, it will suffice to state that this deduction was only part of the explanation.

4.3.3 Permeation data

a. A typical permeation curve

Plating of the cathode lasted for 15 minutes only, and the breakthrough time which lay between 0.5 and 3 minutes, depended on the plating conditions. During plating, only a small amount of hydrogen permeated the shim, but after plating, unlike the hydrogen charging experiments of other investigators, the hydrogen permeation current continued to rise rapidly for a considerable time before slowly reaching a maximum and slowly beginning to decay. Several days (up to 8000 minutes) elapsed before all of the hydrogen had been removed from the cathode and its electrodeposit. The complete shape of a typical permeation curve is given in Fig. 4.3, while Fig. 4.4 gives a detail of the same curve. It is useful to note the amount of hydrogen permeating the electrode at the time at which plating stops and compare this with the total amount of hydrogen as represented by the area under the curve.

The shape of the curve is indicative of the way in which hydrogen enters the steel from the electroplate. First of all, since the hydrogen permeation current continued to rise long after plating had ceased, the electrodeposit itself must have acted as a source of hydrogen for entry into the steel once plating had ceased. Secondly, since the permeation current is slow to reach a maximum (about 35 minutes as compared with less than 10 minutes in the case of a simple charging experiment on the same thickness of electrode), and much slower to deplete, it can be inferred that diffusion across the electroplate-steel interface is a slow process.

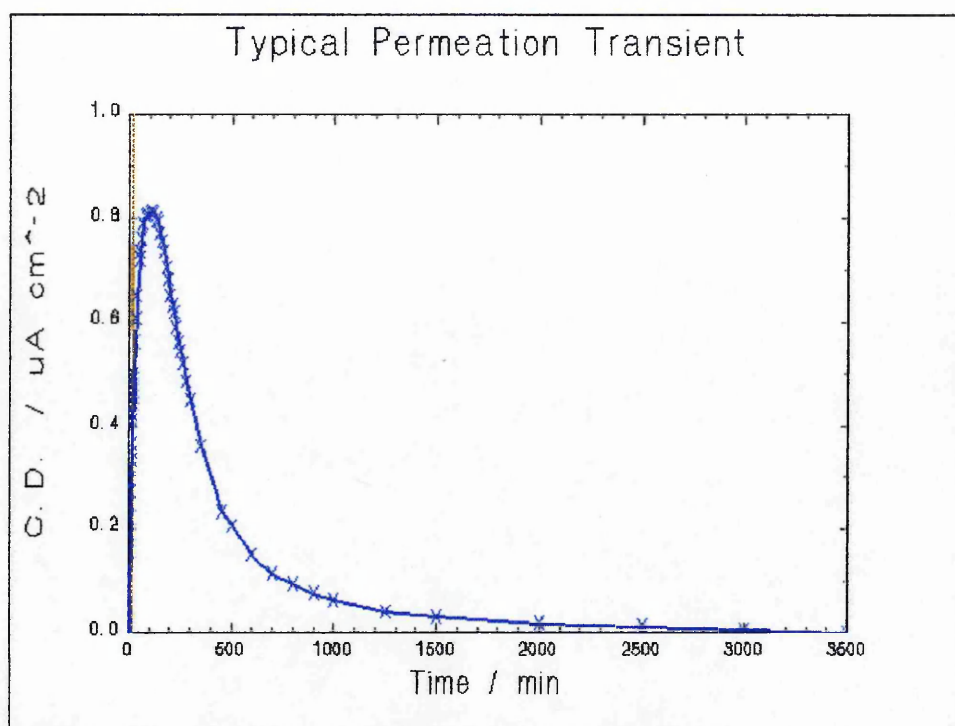


Fig. 4.3 A typical permeation transient.

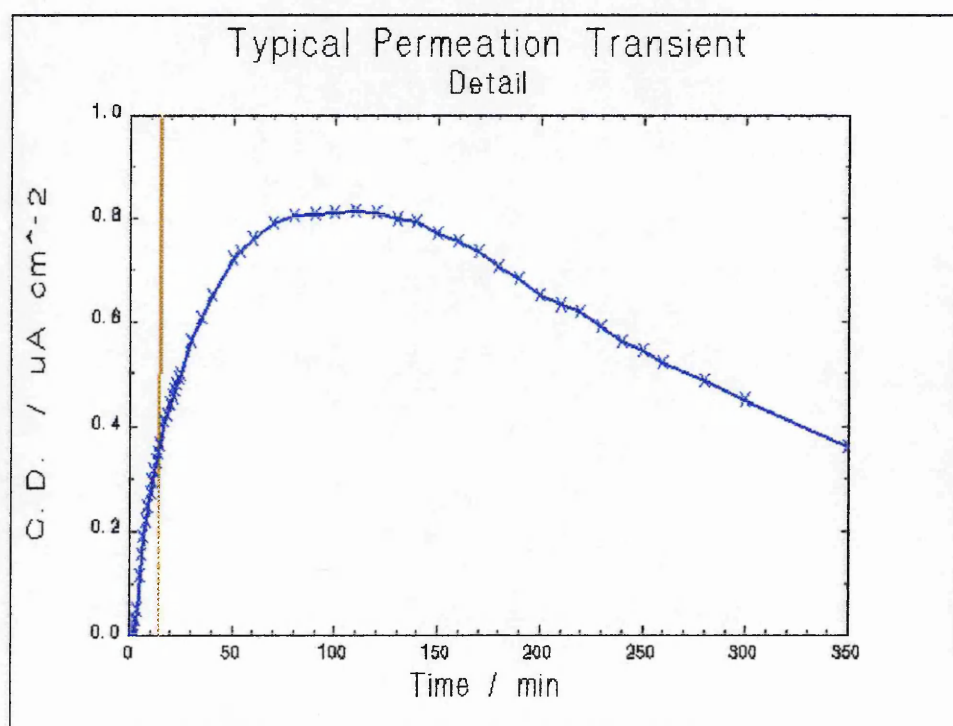


Fig. 4.4 A detail of a typical permeation transient

b. Permeation at various pH values

It has been stated that at long contact times using a plating solution at pH 5, less hydrogen was observed to permeate the shim electrode than at short contact times. In conclusion, it was inferred that a deposit was left on the surface of the steel cathode which presented a barrier to hydrogen entry. The purpose of this set of experiments was to determine to what extent, if any, the pH of the plating solution was likely to affect this deposit and its effect on the total amount of hydrogen entering the steel substrate. Initial expectations were that as pH decreases, the amount of hydrogen entering the steel would increase, so that high pH with high plating current efficiency would result in low hydrogen permeation and would consequently represent a less embrittling situation. This was found not to be the case as the evidence shows.

Figures 4.5 to 4.8 show the results of permeation experiments in which the two variables of contact time and solution pH were varied at a constant temperature of 30°C. The upper graphs of each figure show the permeation transient as measured as a result of plating one side of a shim electrode for 15 minutes only, while the lower graphs show the total amount of permeated hydrogen atoms, in moles, as obtained from the area under the corresponding transient. The area under the permeation transient was calculated using a method similar to Simpson's rule.

Fig. 4.5 shows clearly that increasing the contact time reduces both the maximum value of the permeation current density and the total amount of hydrogen permeated. In this way the existence of a chemically deposited film offering some resistance to hydrogen permeation is demonstrated.

It should be explained that the permeation current for the 0.5 minute contact time was inadvertently allowed to experience a temperature drop of a few °C resulting in the irregular shape of the transient as seen in Fig 4.5a. However, this change in temperature only reduces the diffusion coefficient and hence the time taken for the hydrogen to permeate, not the total amount of hydrogen measured, hence the experiment is still a valid one.

Fig. 4.6 shows the effect of reducing the solution pH to a value of approximately pH4. It can be seen by comparing Fig. 4.5 with Fig. 4.6 that the trend continues in that a longer contact time results in reduced hydrogen permeation. As might be expected, the more acidic solution does result in an increase in hydrogen permeation for each given contact time, although the difference becomes less noticeable with increased contact time as the effect of the chemical deposit becomes more significant. Thus it can be assumed that any chemically deposited layer at pH4 is consistent with that layer deposited at pH5.

Fig. 4.7 Shows a radically different situation. First of all, the contact time appears to bear a relationship to neither the maximum of the transient nor to the amount of hydrogen permeated. Also, and perhaps more interesting, is the fact that magnitudes of permeation maxima and the total amount of permeated hydrogen are an order of magnitude less than in the case of less acidic experiments. This point will be returned to after comments on the experiments at pH 2.

Fig. 4.8 represents the most acidic case in this set of results. Again the permeation transients and amount of hydrogen permeated are increasing from those of Fig. 4.7, although not to such high values as at pH 4 and 5. A close examination reveals another surprising feature, in that the sequence of the lines is reversed compared with corresponding values at pH 4 and 5. That is longer contact time results in more hydrogen being permeated. This seems to indicate that the chemical deposit at this pH, if any, is of a different nature to that at pH 4 and above. In fact, the nature of the surface at this point appears to be such that any barrier to hydrogen which may be present is not improved by increasing the contact time. Here, the measured increase in hydrogen uptake could be explained as being due entirely to the more extensive corrosive reaction. Thus, in the region of, pH 3 there appears to be a change in mechanism and this changeover corresponds to a minimum in hydrogen permeation.

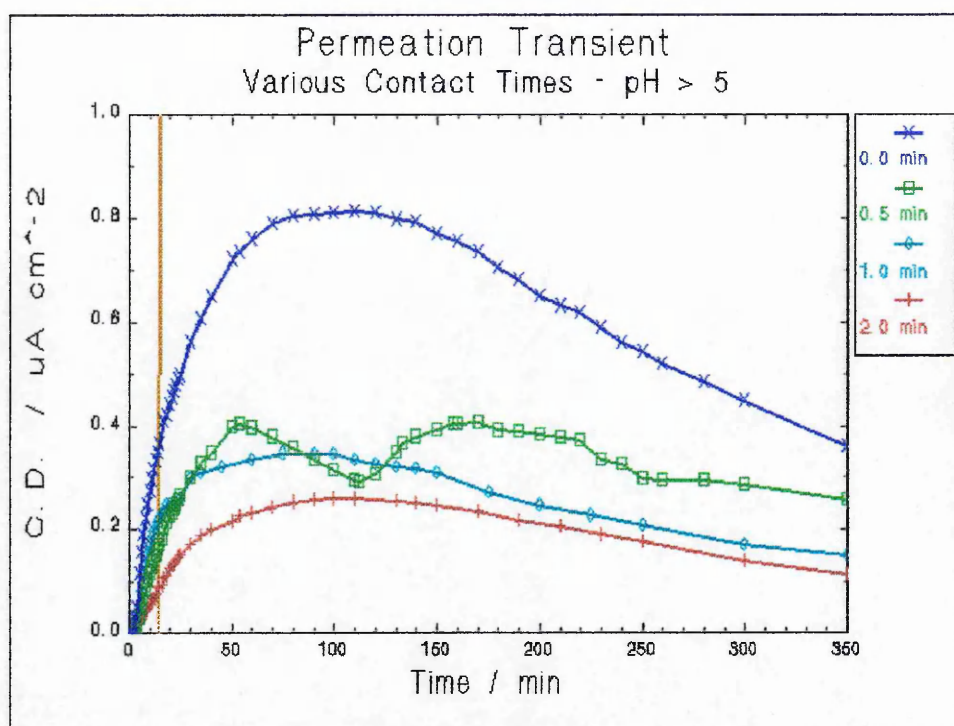


Fig. 4.5a Transients at pH>5, various contact times.

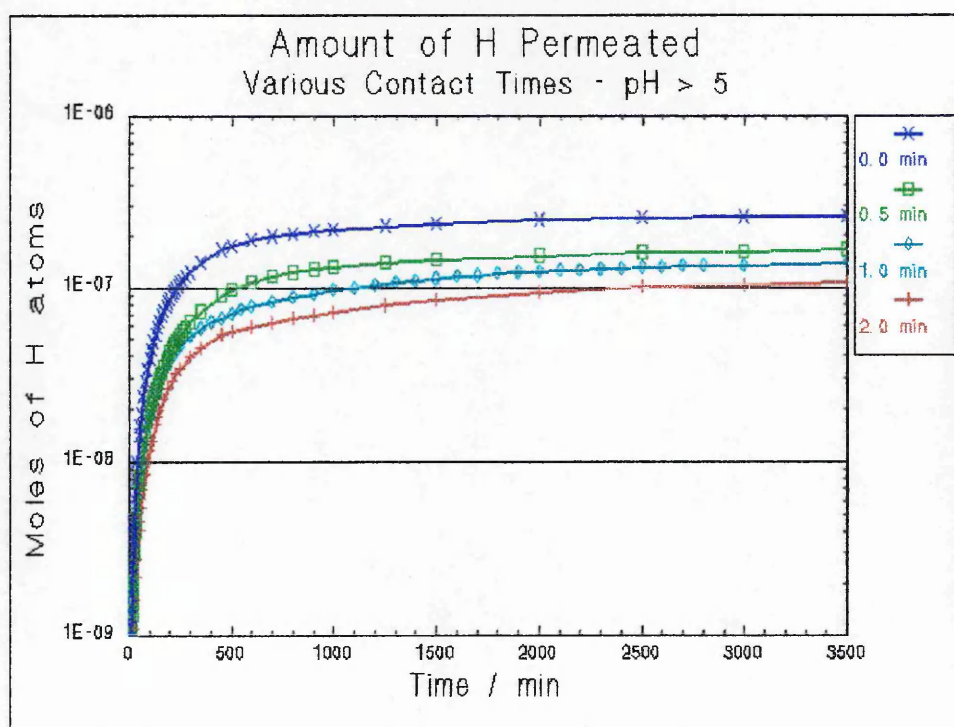


Fig. 4.5b Total permeated hydrogen at pH>5, various contact times.

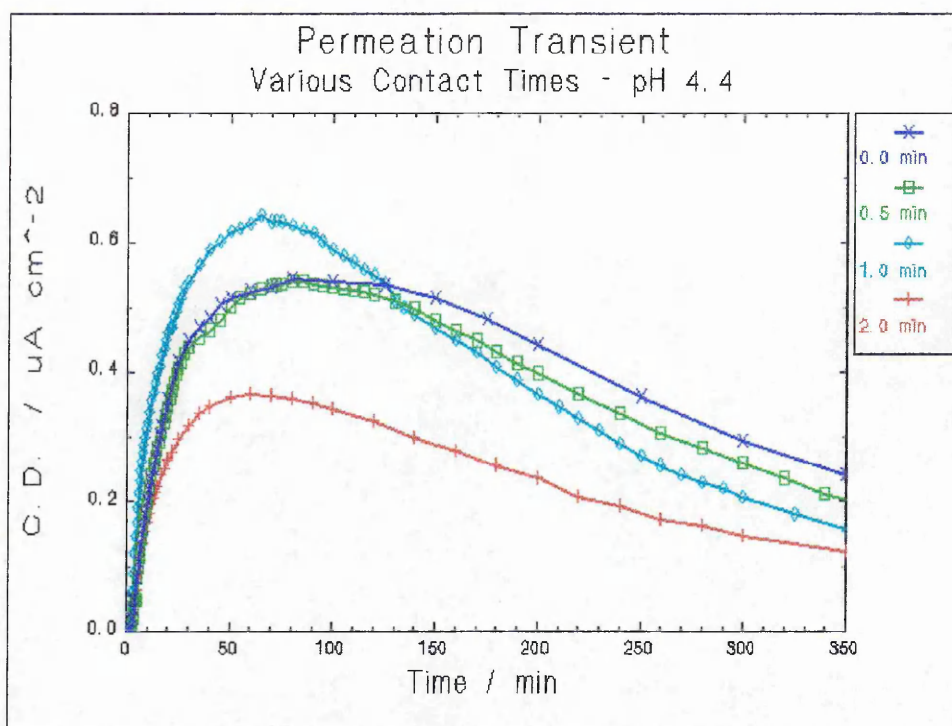


Fig. 4.6a Transients at pH4.4, various contact times.

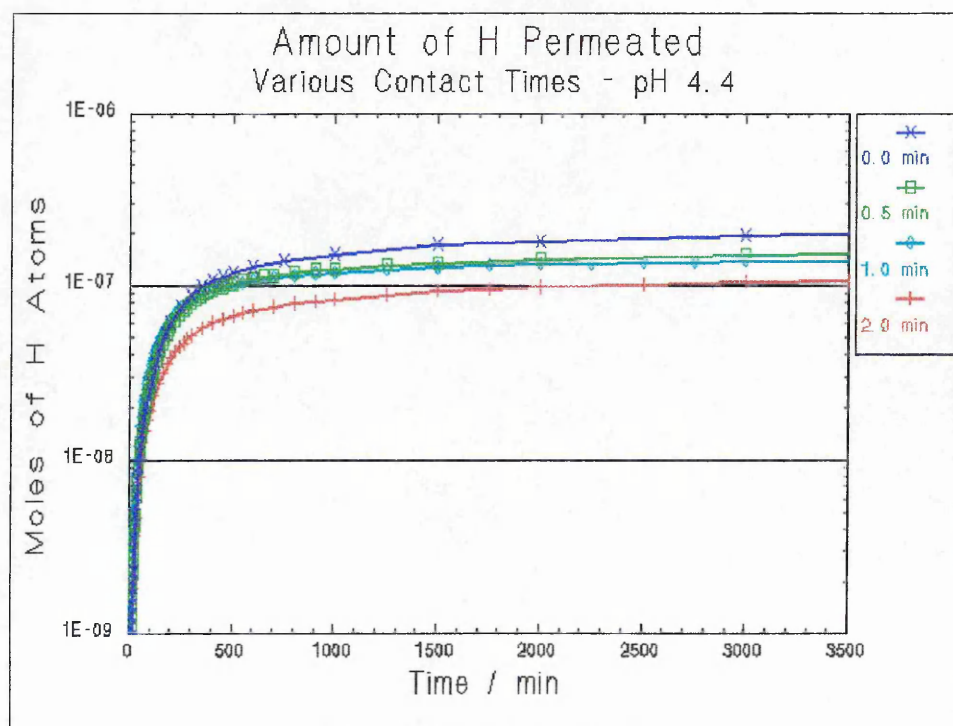


Fig. 4.6b Total permeated hydrogen at pH4.4, various contact times.

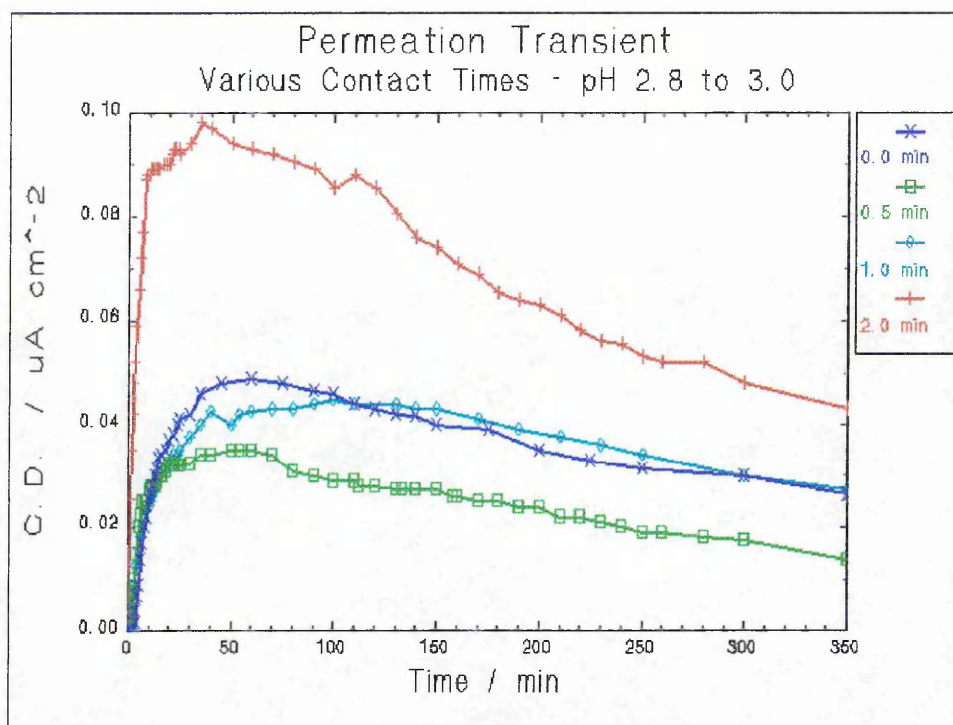


Fig. 4.7a Transients at pH2.8 - 3.0, various contact times.

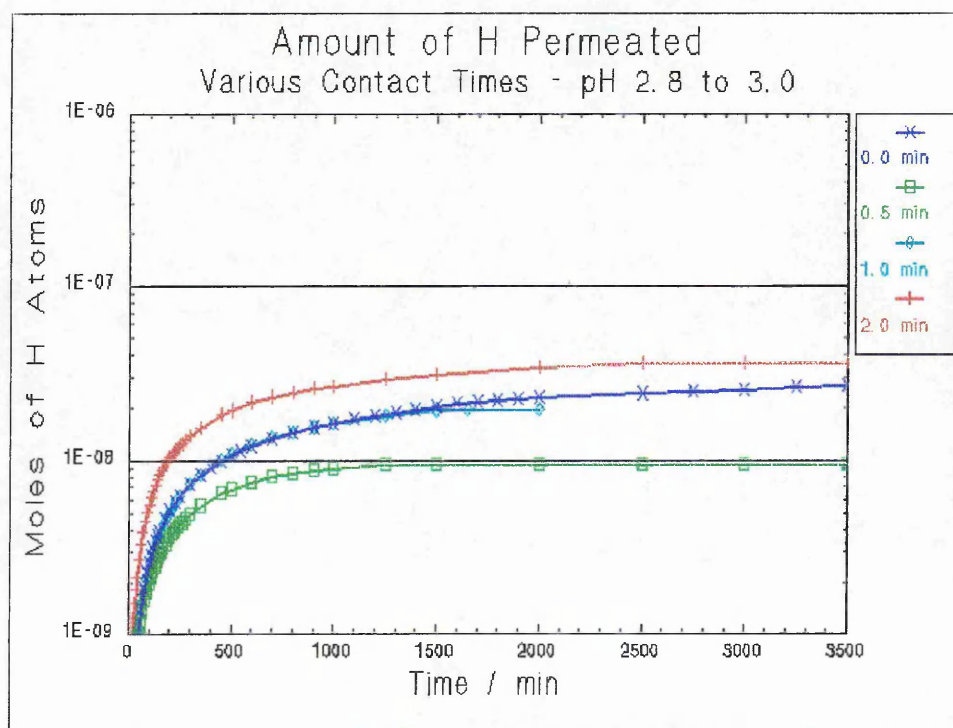


Fig. 4.7b Total permeated hydrogen at pH2.8 - 3.0, various contact times.

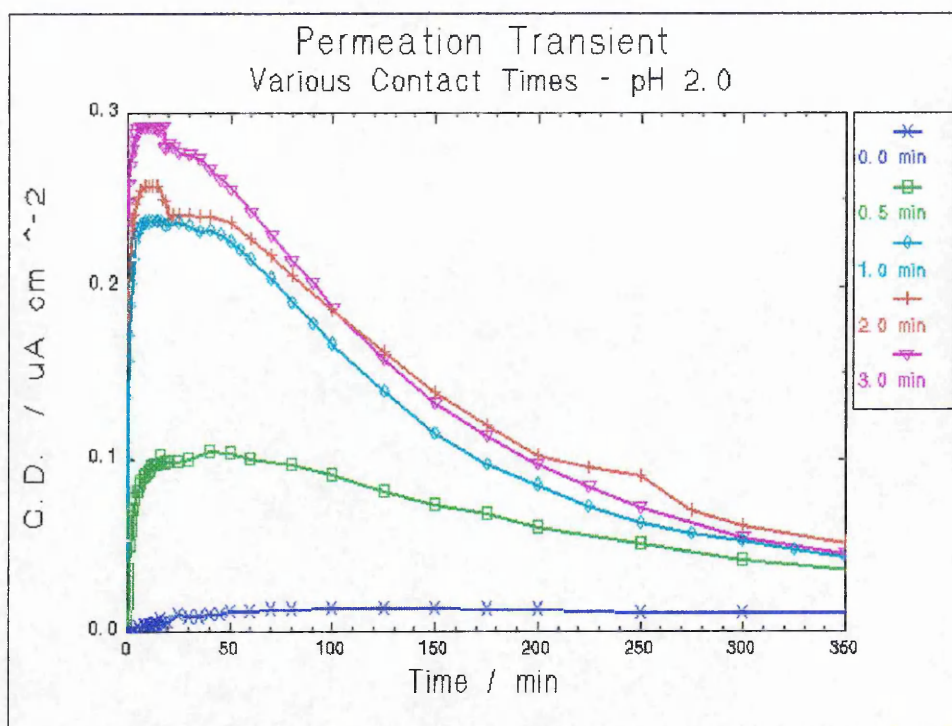


Fig. 4.8a Transients at pH2.0, various contact times.

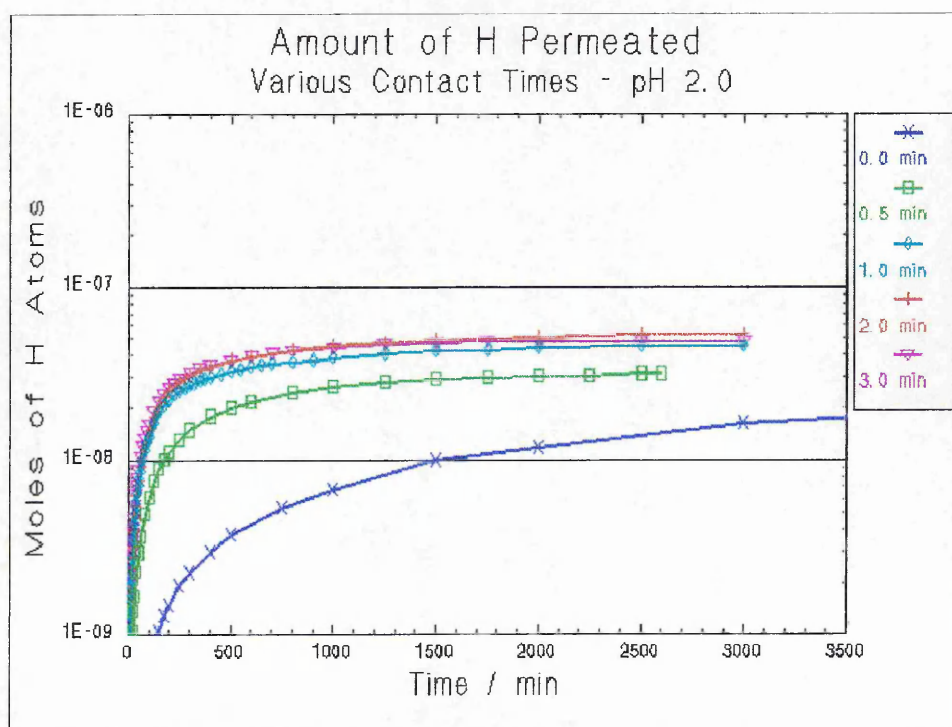


Fig. 4.8b Total permeated hydrogen at pH2.0, various contact times.

4.3.4 Effect of Contact Time

More information is available from the data presented in the previous section than is initially apparent. In order to highlight this information, the data have been re-grouped and are presented in a slightly different way.

Data are now presented according to various pH values with the same contact time. In this way it is possible to examine more closely the effect of pH on hydrogen permeation.

It has been stated that two mechanisms, resulting from different solution pH, influence hydrogen entry and permeation of the steel. This is most clearly seen in Figures 4.9a and 4.9b, in which hydrogen permeation curves and moles of permeated hydrogen respectively show a marked difference between the pH4 and pH5 data and the pH2 and pH3 data.

A number of observations give rise to deductions relating to the nature of the pre-plating chemical deposit, conditions at the onset of plating and the initiation of anomalous co-deposition.

- **Two distinct sets of curves exist at zero contact time.**

Since this represents the zero contact situation, it must be assumed that, apart from an inevitable oxide film on the surface of the cathode, no chemical deposit will be present to influence hydrogen entry. Differences must, therefore, be due to the initial conditions of plating, assuming that anomalous co-deposition occurs in both experiments.

It is significant that at pH 2 and 3, when both the plating current is much less efficient (Fig. 4.2) due to increased hydrogen evolution and the solution contains a much larger hydrogen ion concentration, that hydrogen permeation is a full order of magnitude less than that at either pH 4 or 5. This can be explained by referring to the hydroxide suppression mechanism.

Equations in Section 4.3.1 denote the process by which zinc is deposited anomalously. It is necessary to remove hydrogen from the immediate vicinity of the cathode in order to produce zinc hydroxide. The lower the pH, the more hydrogen must be removed before the anomalous co-deposition can begin and also the more hydrogen must continue to be removed in order to maintain the pH at a value of 5.5 against the inward diffusion of hydrogen ions. This explains the decrease in plating current efficiency with decreasing pH, but also indicates that more *time* is required to increase the pH to the critical value. During this, albeit short, time period, nickel metal is deposited under normal, or near normal, plating conditions. Thus a thin, nickel rich zone adjacent to the steel substrate would be expected. Under these conditions a very effective barrier to hydrogen ingress would be expected as a consequence. Plating at pH 4 and 5, while following the same deposition mechanism, attains the critical pH of 5.5 so much more quickly that only very small amounts of nickel may be deposited. Thus any barrier to hydrogen influx is less complete. The separation of curves in Figures 4.9a and 4.9b gives evidence to support this assumption.

Further evidence for this hypothesis lies in the sequence of both transient and total hydrogen curves, with the order of permeation being...

$$\text{pH } 5 > \text{pH } 4 \gg \text{pH } 3 > \text{pH } 2$$

...that is the least acidic member of each set allowing the greatest permeation, because it produces either the least complete, or thinnest nickel-rich initial deposit.

- **The contact time changes the sequence of curves.**

Given the division of the curves into separate sets, we see the expected sequence of lines, with the more acidic solution in each set producing the greater amount of hydrogen permeation for a contact time, $t \geq 0.5\text{min}$...

$$\text{pH } 4 \approx \text{pH } 5 \gg \text{pH } 2 > \text{pH } 3$$

...since some hydrogen enters the shim cathode before plating and hence before the initial nickel-rich layer. Differences in amounts of permeated hydrogen at pH 4 and 5 differ by smaller amounts than at pH 2 and 3, due to the logarithmic nature of pH, that is, the hydrogen ion concentration at pH 3 is 100 times that at pH 5.

- **Increasing contact time reduces hydrogen permeation at pH 4 and 5**

It would be expected that from an acidic medium, such as the plating solutions, longer contact times would result in greater amounts of hydrogen permeating the shim cathode. The converse is, in fact, found to be the case at pH 4 and 5. It is deduced that this is due to the precipitation of zinc hydroxide (see Sections 2.7 and 5.3) forming a physical barrier which thickens with time and exposure of the cathode to the plating solution.

- **Increasing contact time increases hydrogen permeation at pH 2 and 3**

Hydrogen rapidly permeates the shim cathode with a breakthrough time of about 30 seconds at low pH, with the amount of hydrogen permeation increasing with exposure, as would be expected if no permeation barrier was present. Clearly, at such low pH, zinc hydroxide cannot form on the cathode surface. There is some evidence, however, that a chemical deposit of nickel is laid down before plating. This suggests that a thin, chemically deposited layer lies beneath a second thin, but electrochemically deposited nickel (or nickel-rich) layer. It would be very difficult to differentiate between these layers, and so prove that both exist.

- **Curves of both sets converge with increasing contact time.**

The effect of the points just raised is that the curves for both the transients and the total amount of permeated hydrogen tend to approach each other with increasing contact time. This trend is illustrated in Fig. 4.13.

- **Shape of curves with contact time.**

In the case of pH 4 and 5, apart from the height of the curves, the general shape remains consistent throughout the range of permeation transient curves for different contact times, including the approximate positions of peaks. However, this is not the case for pH 2 and 3.

A slow rise in the total hydrogen permeated is observed at zero contact time, whereas at positive contact times, the curves rise more sharply. This is due, not to hydrogen entering the steel as a result of electrochemical processes, but to that hydrogen entering the shim cathode before plating commenced.

4.3.5 Total Hydrogen Permeated

From Figures 4.13a and 4.13b, the total amount of hydrogen permeating a shim cathode can be seen to vary with both pH and contact time.

Fig. 4.13a shows the apparent convergence to a value of hydrogen atoms of the order of 10^{-7} Moles. The difference between $\text{pH} \geq 4$ and $\text{pH} < 4$ is quite clear. With increasing time, $\text{pH} \geq 4$ produces an increasingly more effective barrier to hydrogen which appears to be absent at $\text{pH} < 4$.

The pH dependence of total permeated hydrogen is evident in Fig. 4.13b, which indicates a minimum of hydrogen entry between pH 3 and pH 4.4. Further evidence, from mechanical tests indicates a transition at, or about a pH value of 4.0 or less. Between pH 3 and 4, insufficient hydrogen entered the steel tensile specimens to cause embrittlement. This is further discussed in Sections 3.6.4 and 4.3.3.

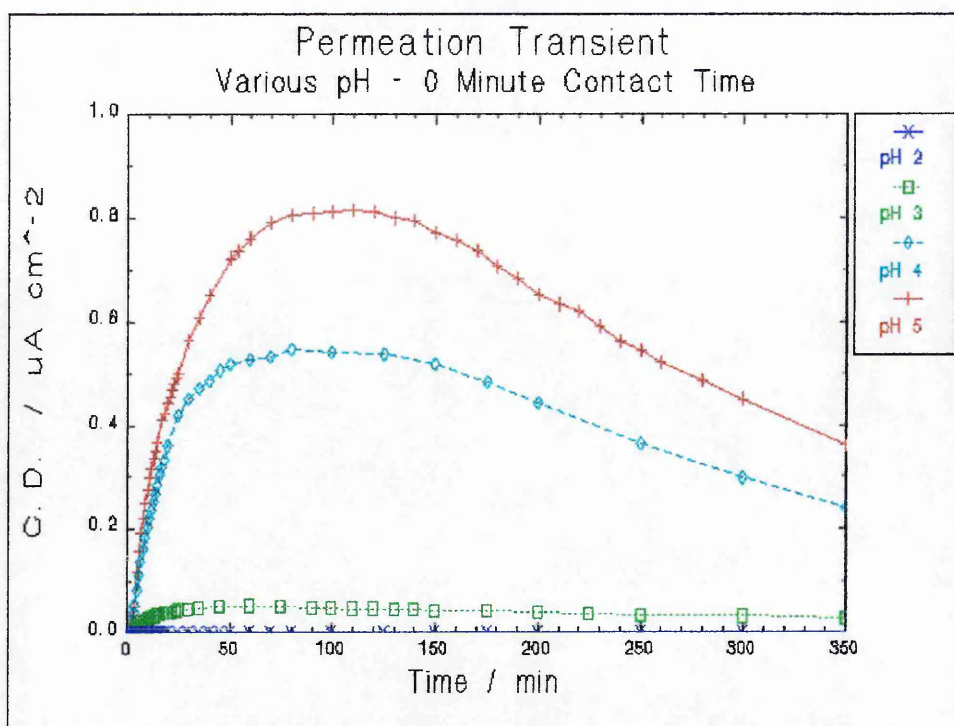


Fig. 4.9a Permeation transient, contact time = 0 min, various pH.

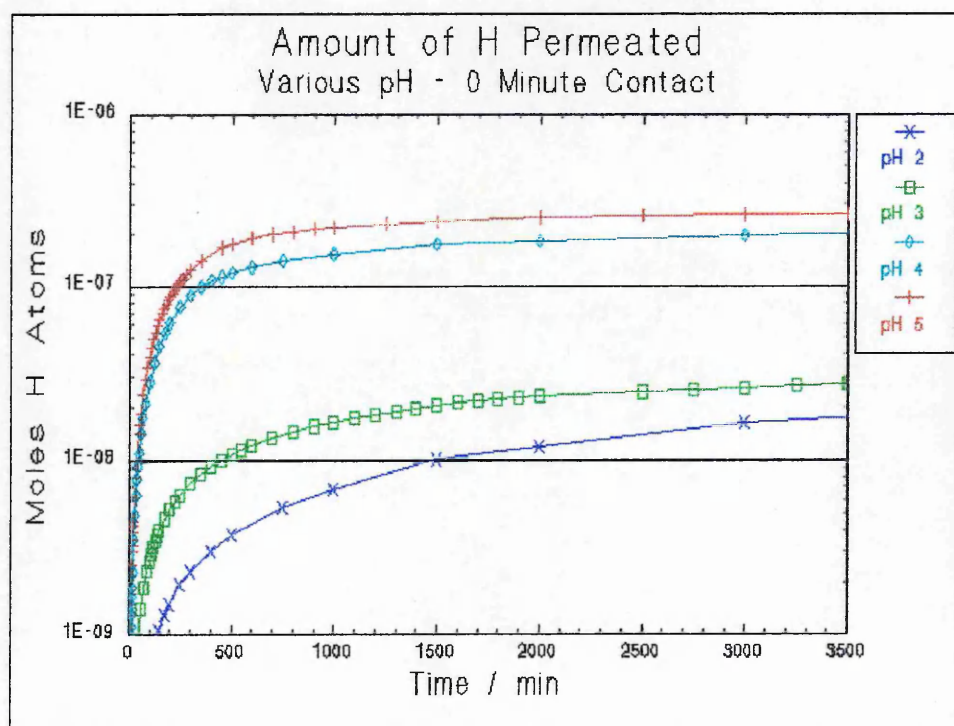


Fig. 4.9b Total permeated hydrogen, contact time = 0 min, various pH.

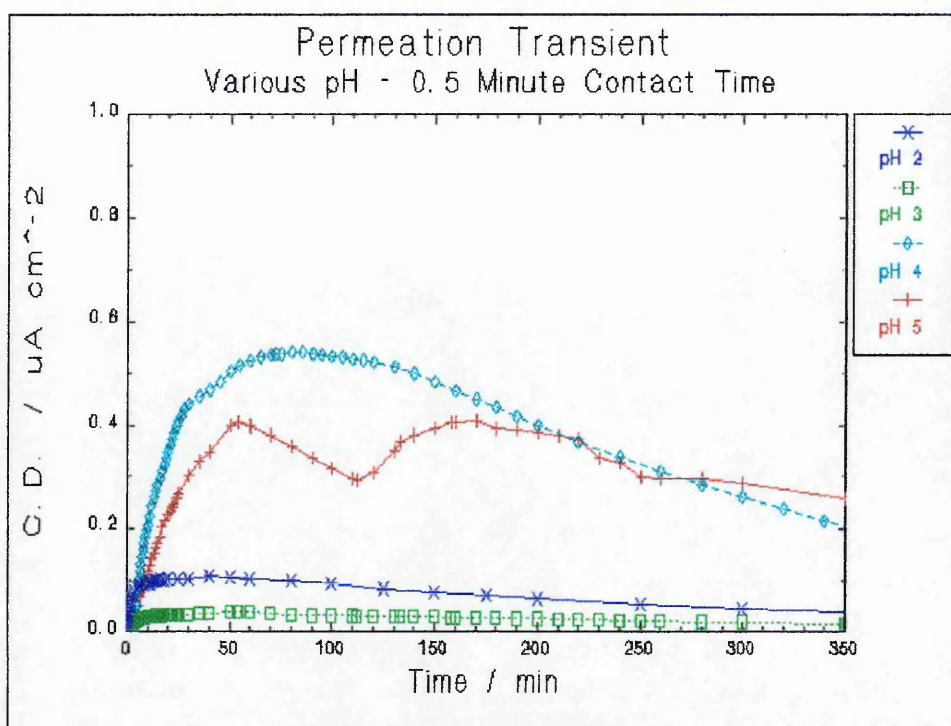


Fig. 4.10a Permeation transient, contact time = 0.5 min, various pH.

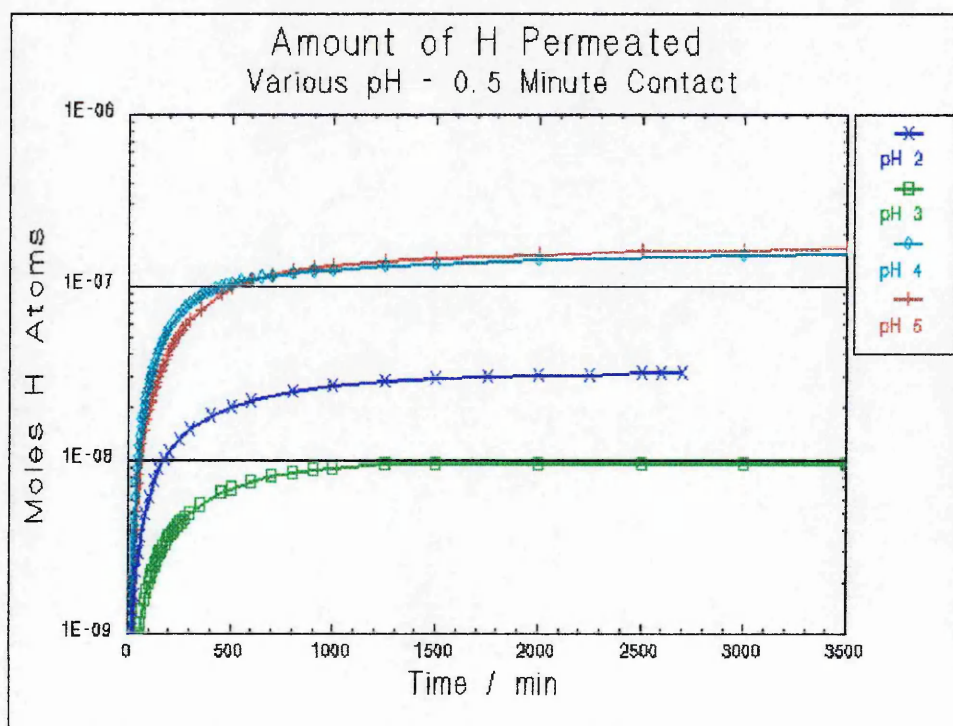


Fig. 4.10b Total permeated hydrogen, contact time = 0.5 min, various pH.

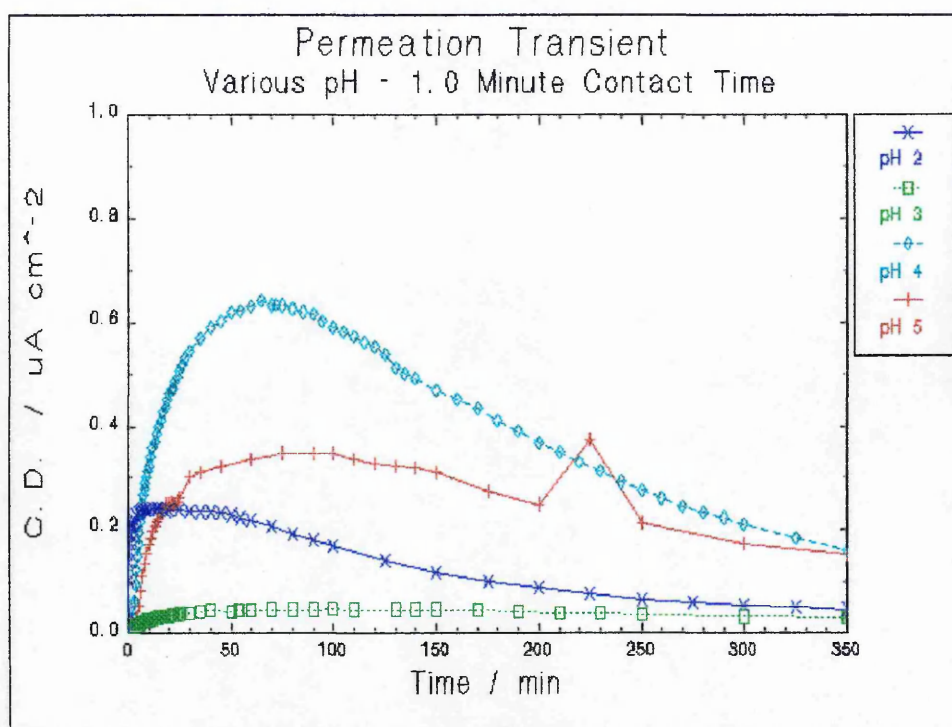


Fig. 4.11 Permeation transient, contact time = 1 min, various pH.

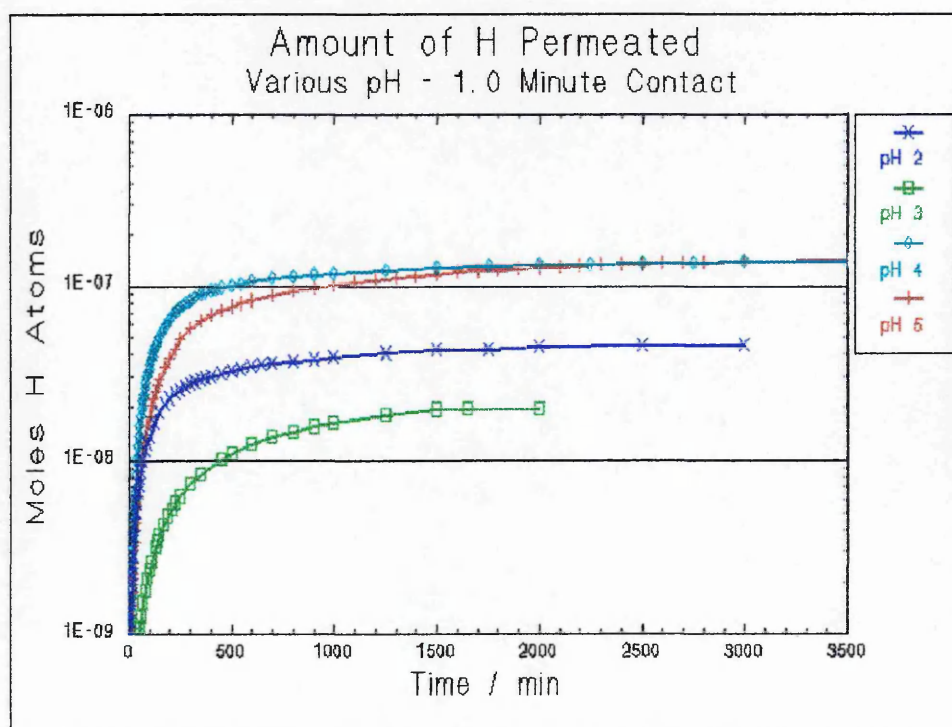


Fig. 4.11b Total permeated hydrogen, contact time = 1 min, various pH.

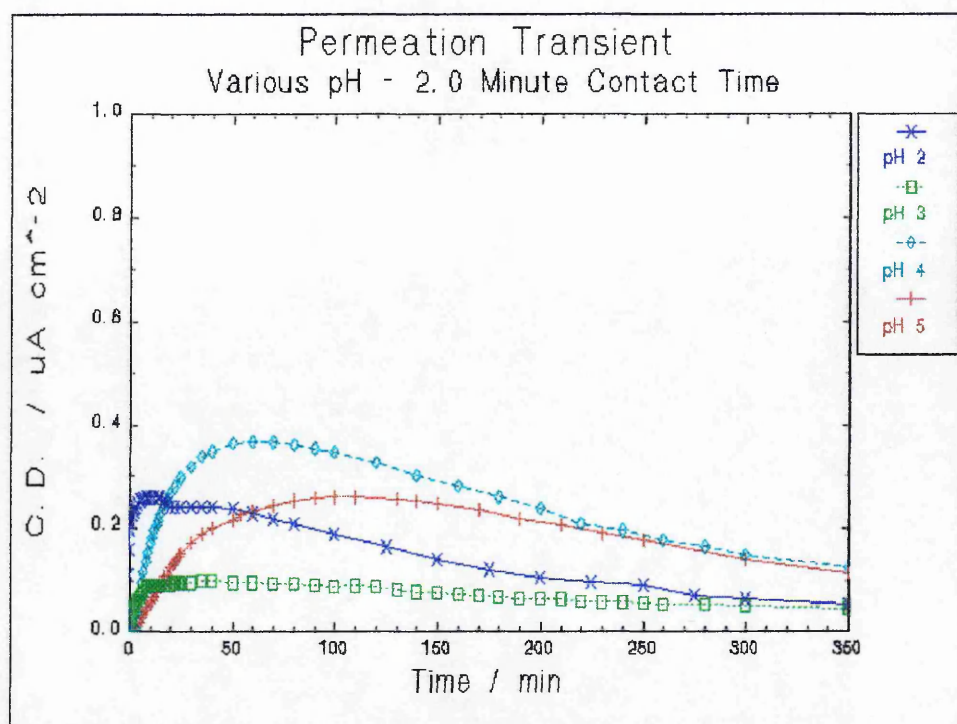


Fig. 4.12a Permeation transient, contact time = 2 min, various pH.

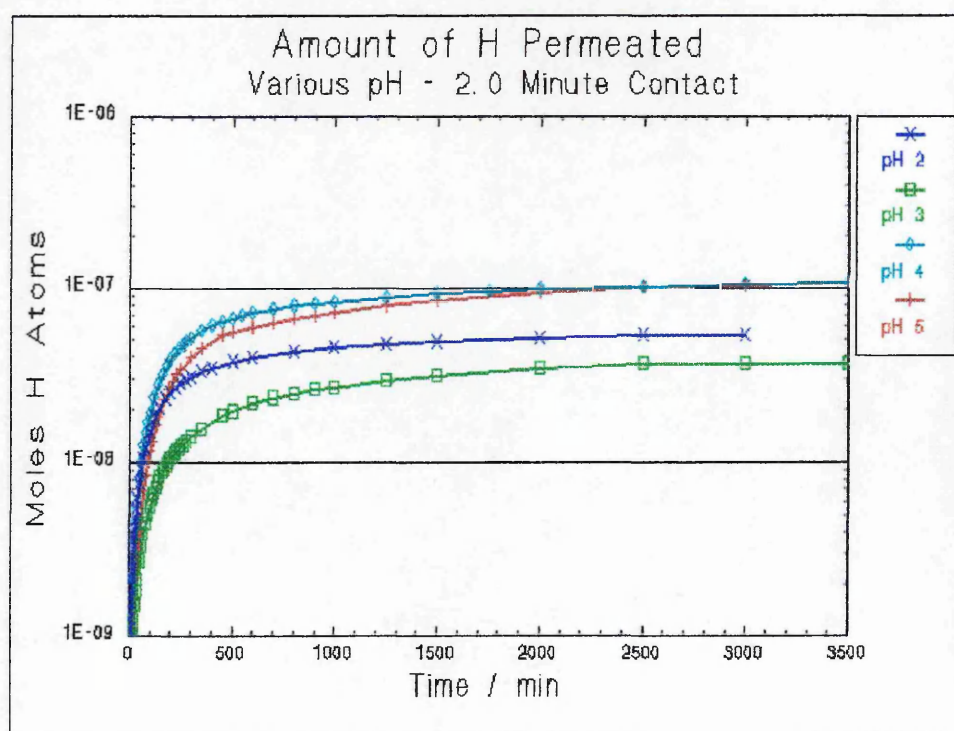


Fig. 12b Total permeated hydrogen, contact time = 2 min, various pH.

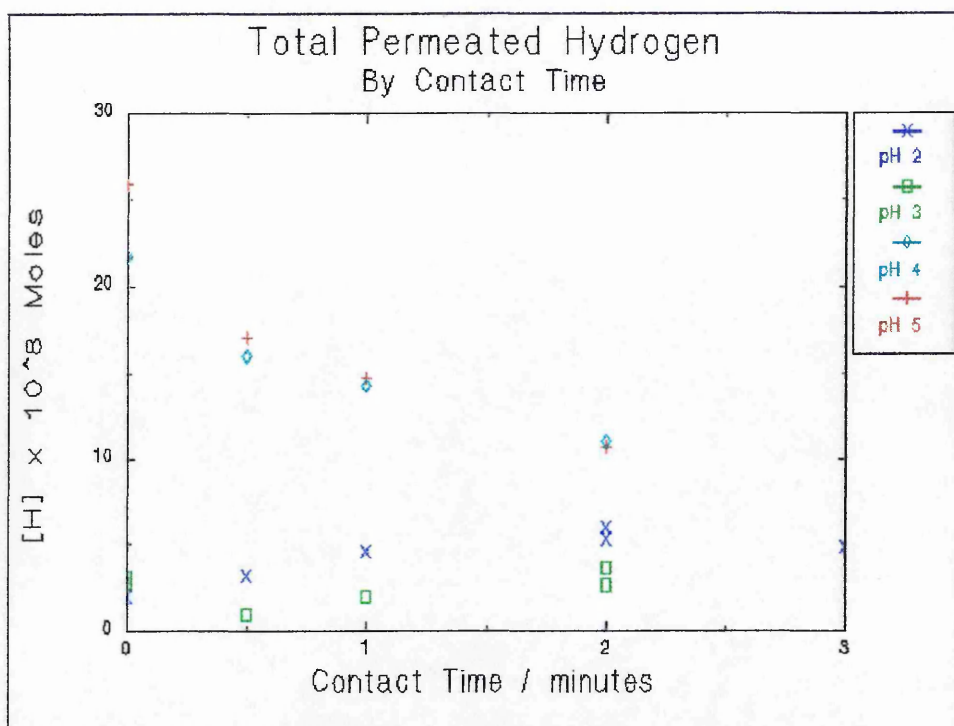


Fig. 4.13a Total hydrogen permeated v contact time

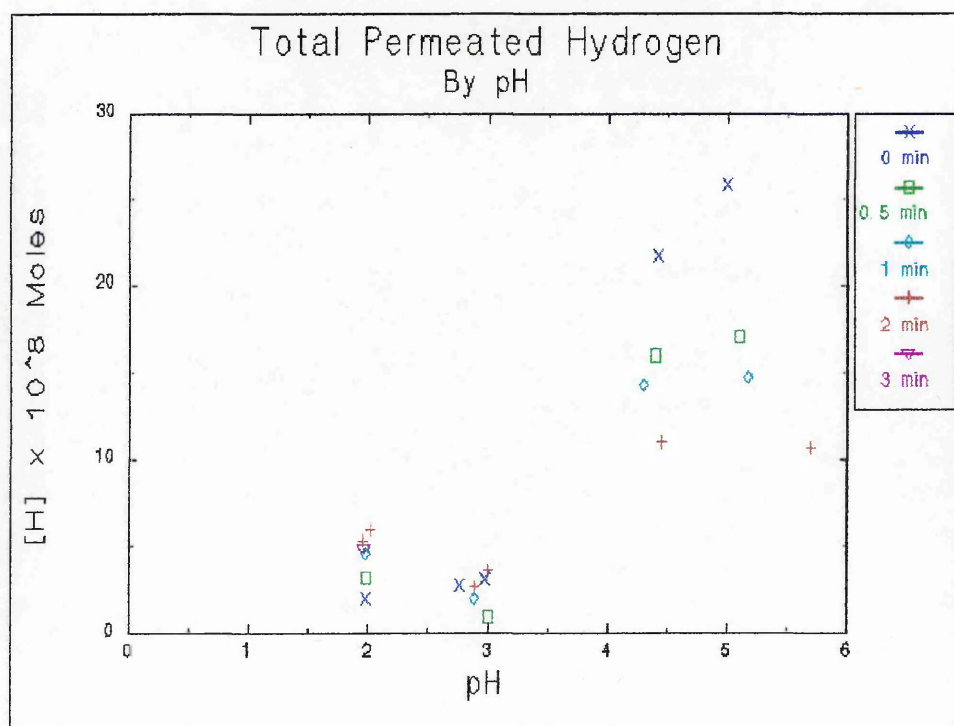


Fig. 4.13b Total hydrogen permeated v pH

5 Surface Analysis

5.1 Background

5.1.1 Choice of Experimental Parameters

The nature of the chemical deposit that has been shown by both permeation and mechanical experiments to have such a marked effect on hydrogen permeation was initially thought to be nickel. Since the plating solution contained only zinc and nickel ions at approximately pH4, it seemed that the simplest explanation of the facts was that metallic nickel formed on the surface by a simple chemical displacement by metallic iron. Nickel metal is known to present a barrier to hydrogen diffusion due to its low hydrogen diffusion coefficient. Analyses of contact and electrodeposits were, then, primarily looking for nickel enrichment and possibly nickel metal in the region of the steel substrate.

In spite of its significant effect on hydrogen permeation, the contact layer was found to be very thin, requiring XPS (X-Ray Photoelectron Spectroscopy) analysis of the surface atoms. This revealed that the predominant species present in the deposit was zinc hydroxide. Nickel could also be detected at long exposures to the plating solution but this appeared only as a minor component in the deposit.

The barrier effect in permeation experiments was most noticeable in the pH3 region, as indicated in Figs 4.9-4.12, hence the first contact deposits were analysed for nickel and were prepared at this pH. Subsequent examinations were made from pH values both above and below this value.

Since the contact deposit was produced from a double salt solution, it was also considered useful to examine the contribution made by each of the components separately. To achieve a maximum effect a long exposure time of 200 minutes was used in order to maximise any contact deposit. Single salt solutions produced relatively thick contact deposits. The combined salt solution produced what appeared to be a much thinner layer, but with characteristics identifiable to each of the separate salts. By precipitating hydroxides from the above mentioned solutions, using sodium hydroxide solution, further information about the nature of these deposits was obtained.

Depth analyses of the interface between the steel substrate and initial electrodeposit using argon ion beam etching and elemental analysis were also performed. It was anticipated that nickel metal may have been deposited, in the first instants of plating, prior to an increase in pH to a value of 5.4. Depth profiling of a very thin electrodeposited layer (approximately 0.2 μ m thick) to determine concentration profiles within the electrodeposit itself proved to be difficult. A number of techniques were attempted but the efforts made were eventually rewarded. Fig. 5.1 shows a schematic representation of the surface analysis performed.

5.1.2 Auger and XPS Spectra - Basic Principles

Bombarding a surface with X-rays can result in inner K shell electrons being emitted from an atom (Auger electrons). This leaves empty orbitals within the atom that are filled by higher energy electrons cascading downwards. In turn, this can lead to further, but lower energy electrons being emitted, this time from an outer shell. These latter electrons are of lower energy, but result in sharp signals. Also, as the electrons originate from the outer, bonding shell, it is often possible to detect shifts in a signal that can indicate whether an atom is bonded or not.

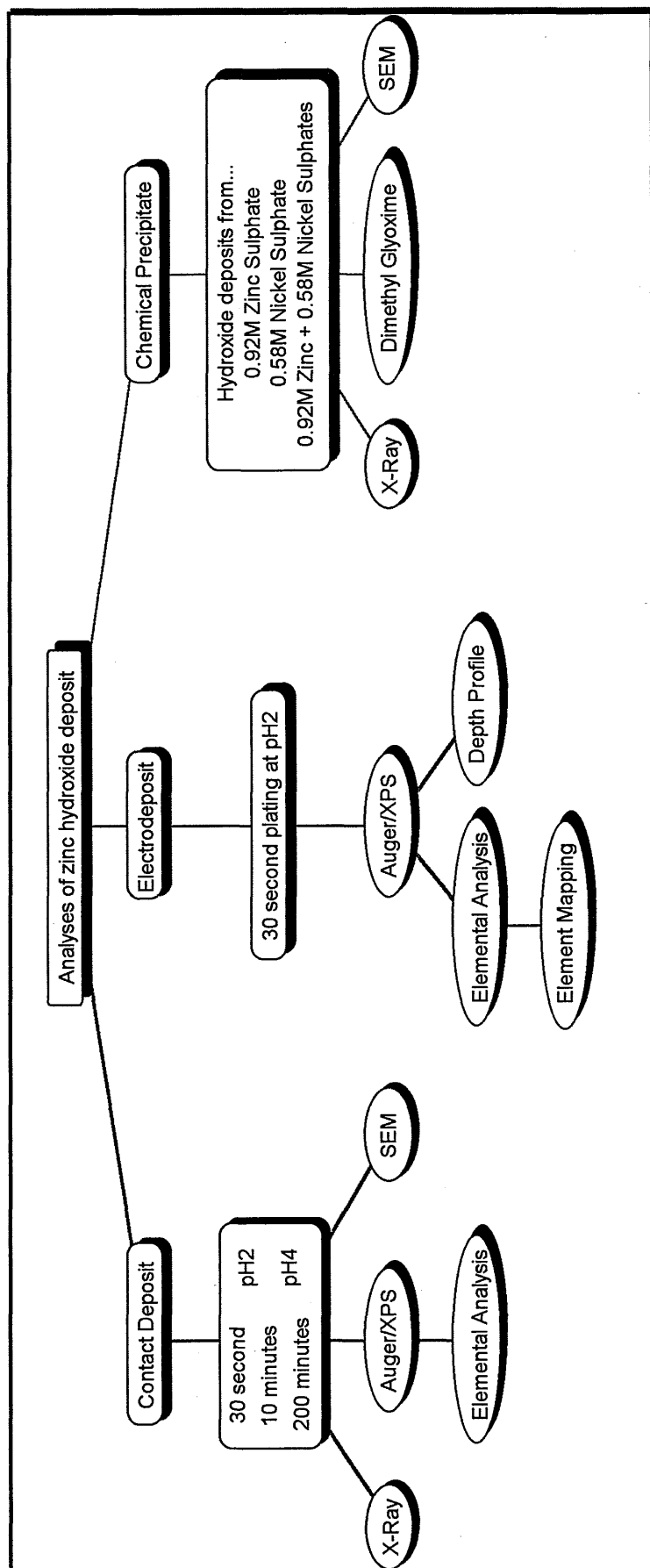


Fig. 5.1 Schematic representation of surface analysis tests performed on the zinc hydroxide and early electrodeposited layer.

5.2 Experimental Methods

5.2.1 Growth and Nature of the Contact Deposit

Pieces of steel shim were cleaned by abrading with a 1200 grit abrasive paper, followed by degreasing in propanol in the same manner as the shim electrodes for permeation experiments. The cleaned steel was then exposed to the plating solution at pH 3 for 0.5, 3 and 10 minutes. A solution at pH 3 was chosen, since from permeation experiments, this pH had provided the greatest barrier to hydrogen influx.

After exposure, the steel strips were rinsed with distilled water and dried using propanol. A preliminary X-ray analysis using a SEM (Scanning Electron Microscope) failed to detect any deposit, even though a change in the appearance of the surface could be seen with the unaided eye. It was deduced that the deposit formed a layer too thin to be measured by this method.

When repeated with the specimen exposed for 200 minutes, a small amount of zinc was found to be present at pH4.4, but not at pH2. The opposite was noted for nickel, not being measured at pH4.4, but being present at pH2. Similar specimens washed in dilute hydrochloric acid showed that the zinc was removed, as would be expected if the zinc were present as the hydroxide, but that some nickel remained as might be expected if the nickel was present in the metallic form. These results prompted more detailed surface analysis as described below.

Further analyses were performed on the 0.5 and 10 minute exposed samples using the XPS technique, which is capable of analysing deposits in the region of a few nanometres thick, effectively giving a true surface analysis. Oxygen and zinc were found to be present in all of the contact deposits. Initially, inconclusive results were obtained with respect to nickel. In order to increase any existing signal from nickel, a fresh specimen was prepared with a 200 minute contact time. This time a strong nickel signal was evident. The results of these analyses are discussed in full in the section 5.3.2.

Photomicrographs of the surfaces of these specimens were taken, and are shown in Photographs 5.1 to 5.5.

Successive surface layers of the order of atoms thick were etched away using an argon ion beam in order to obtain depth profiles of elements in the deposit. This was used essentially to answer two questions..

- Was the detected oxygen a surface feature only, indicating atmospheric oxidation, or was the oxygen concentration constant throughout?
- Could nickel have formed a substratum to the zinc hydroxide?

No conclusive results were obtained from these initial depth profile analyses, possibly due to the absence of a nickel rich layer, but also possibly due to insensitivity of the procedure failing to detect a layer no more than a few atoms thick.

In view of the developing ideas based on permeation, mechanical results and recent developments with surface analysis, it became clear that two distinct barrier mechanisms regarding the deposition were in operation. These appeared to be pH dependent. Consequently it was decided to examine separate samples obtained, not from the pH of minimum hydrogen permeation, but from regions clearly belonging to the different mechanisms. pH values of 2 and 4.4 were used for this purpose. Of the two regions, pH2 was thought to be the more likely to produce a strong nickel signal with XPS analysis, due to the low pH inhibiting the formation of zinc hydroxide. Deposits were therefore obtained from separate plating solutions of pH4.4, which was the normal pH of a freshly made solution, and pH2 obtained by adjusting a freshly prepared solution using sulphuric acid.

Specimens were prepared in the usual way before being exposed to different plating solutions at pH2 and pH4.4 for 200 minutes. XPS analyses of the surfaces compared with a reference blank surface are shown in Fig. 5.5. Detailed comments on this figure are given in the next section.

5.2.2 Contact Deposits from Separate Zinc and Nickel Sulphates

Samples of steel were prepared as before, but were exposed to different solutions for 200 minutes in order to deposit a thick layer. Solutions used included single salt solutions of 0.58M NiSO₄, and 0.92M ZnSO₄ and a reference plating solution containing both 0.58M NiSO₄, and 0.92M ZnSO₄. The aim of this test was to determine if the plating solution produced a contact deposit that resulted from either a simple combination of the nickel and zinc sulphates, or if the deposit resulted predominantly from one salt or the other. Although similarities were evident with both single salt deposits, the composite contact deposit was significantly thinner than either of the separate, single salt deposits indicating an interaction between the zinc and nickel species to produce a less permeable deposit.

SEM photographs were taken of the respective surfaces.

SEM analysis of the specimen exposed to plating solution for 200 minutes indicated a ratio of zinc : nickel of between 1.5 : 1 and 2 : 1.

5.2.3 Chemical Precipitation from Solution Using Sodium Hydroxide

For this test it was assumed that the contact deposit grew on the steel surface as a result of a local increase of hydroxyl ion concentration due to either a plating current or simply the corrosion of steel. It was further assumed that this change in local hydroxyl ion concentration could be duplicated by the slow addition of hydroxyl ions using a sodium hydroxide solution.

Since the nature of the deposit was difficult to determine as a thin film, samples of precipitate were prepared from single salt solutions of 0.58M nickel(II) sulphate, 0.92M zinc sulphate and the normal plating solution, by the slow, dropwise addition of sodium hydroxide. The very fine, powdery precipitates obtained were collected by vacuum filtration and washed three times in boiling, distilled water to ensure that no soluble species remained adsorbed onto the surface of the precipitate. Care was taken not to deplete significantly the salt solutions of their respective metal ions, since the deposition process is determined by equilibria involving not only hydroxyl ions, but also the metal ions in solution.

Samples of each precipitate were split for ..

- a. X-ray analysis, using copper K_{α} radiation.
- b. A chemical test, using dimethyl glyoxime, to detect the presence of nickel and...
- c. A small amount for future reference if necessary.

The chemical test involved adding a small amount of each precipitate to an alcoholic solution of dimethyl glyoxime. (Dimethyl glyoxime forms a bright red complex with nickel(II) compounds and is used both as an indicator for the presence of nickel(II), as here, and in gravimetric analysis of nickel.) By comparison of the observations and the results of the X-ray analysis, it was demonstrated that the precipitate from the plating solution contained a small amount of amorphous nickel(II) ions that appeared to be uniformly distributed throughout the precipitate.

A detailed summary of these results is given in Table 5.2 in the next section.

5.2.4 Examination of the Interlayer of Electroplated Specimens.

Increasing the contact time has been demonstrated to influence the uptake of hydrogen at pH 5.5. However, this does not explain the remarkable decrease in hydrogen uptake at pH values below about 3.5.

It is postulated that, within the diffusion boundary layer, the pH falls as time passes. Before the critical pH for the precipitation of zinc hydroxide has been achieved, nickel metal, or at least a nickel rich deposit forms. A layer rich in nickel, even of only one or two atom thicknesses and not continuous,^[49] could dramatically reduce hydrogen entry. If this postulation is correct, a very thin layer, rich in nickel, should be found immediately adjacent to the steel substrate and this should be easier to detect for lower pH situations.

In searching for this nickel-rich layer, XPS surface analyses were made of very thin electrodeposited layers. These electrodeposits were obtained by plating for 30 seconds without a contact deposit, giving an estimated electrodeposit thickness of about 0.2 μ m. Argon ion beams were used to etch away the surface atoms, stopping at intervals to perform elemental analyses. Gradually, concentration profiles were built up for iron, oxygen, zinc and nickel throughout the electrodeposit. It was observed that the etching produced a very shallow sided pit through the layer, in itself forming a profile of the deposit on its surface. An examination of this new surface provided a means of allowing elemental mapping for the elements under investigation, albeit not at an accurately known or constant angle. However, it did facilitate a qualitative analysis of the distribution of the elements adjacent to substrate.

SEM photomicrographs and element maps of the relevant areas were taken. These are shown and discussed in detail in section 5.3.4.

5.3 Experimental Results

5.3.1 Growth and Nature of the Contact Deposit

XPS analyses of the initial contact deposits at different exposure times, 30 seconds and 10 minutes, at pH3, were inconclusive. Little or no nickel could be detected on the metal surface in the early stages of deposition. With increased exposure to the plating solution of 200 minutes, however, the nickel signal increased in strength. A closer examination revealed that a very small signal from nickel could, in fact, be discerned even at the shorter, 30 seconds exposure. The strength of the nickel signal clearly increased with increasing contact time. These results are shown in Figs 5.2 to 5.4

Each spectrum displayed is identified by the colour code on the graph matched to the colour coded key below each abscissa. For Figs 5.2 to 5.4 the data files used to identify the spectra are as defined in Table 5.1 overleaf. Spectra of deposits differing only in contact time are overlaid for the purposes of comparison.

File name	Description of Spectrum
mcblank.dat	Fresh, cleaned steel surface used as a reference.
mc030.dat	Surface after 30 second exposure.
mc10.dat	Surface after 10 minute exposure.
mc200.dat	Surface after 200 minute exposure.
mcph2.dat	Surface after 200 minutes exposure at pH2
mcph4.dat	Surface after 200 minutes exposure at pH4.4

Table 5.1 Index to Data Files and XPS/Auger Spectra

Fig. 5.2 clearly shows the inevitable contamination of oxygen from atmospheric oxidation and carbon, largely from residues remaining after cleaning with iso-propanol but also possibly from carbonate deposits arising from aerial carbon dioxide. These peaks are present on all XPS spectra at the positions indicated, except where the surface has been etched by an argon ion beam.

Signals identified as resulting from iron are strong and present in all spectra. However, with increasing exposure, the iron signal does diminish as the contact deposit more efficiently covers the steel surface.

Peaks identifying zinc are clearly visible on the 30 second and 10 minute exposed specimens, but, as expected are totally absent from the reference, blank, specimen. It is important to note that the magnitude of the signal for zinc is stronger on the 10 minute specimen than on the 30 second specimen.

No clear signal can be discerned above background noise, in this figure, to indicate the presence of nickel.

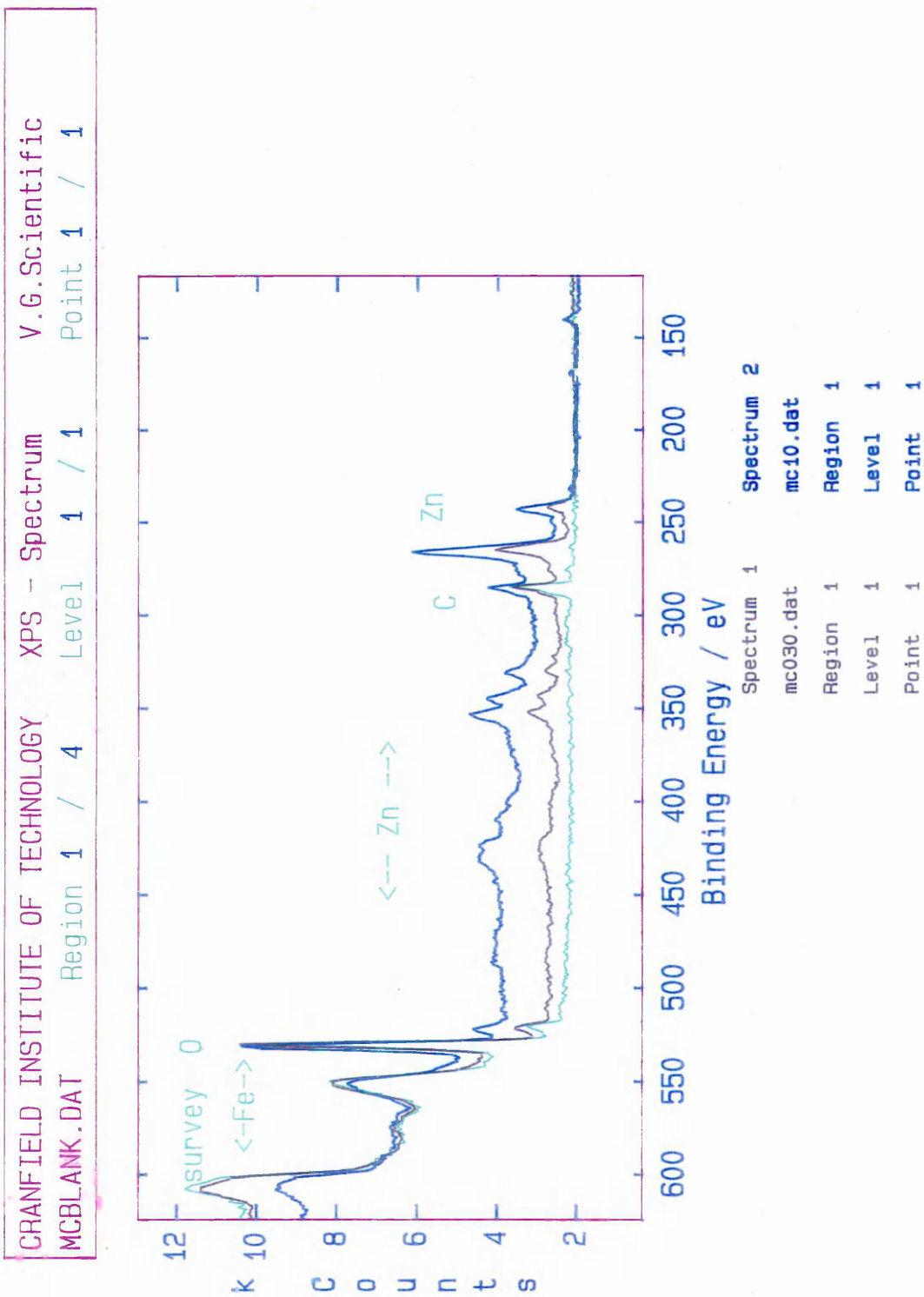


Fig. 5.2 XPS spectra for contact deposits of different exposures.

Fig. 5.3 shows a different region of the XPS spectra for the specimens indicated in Fig. 5.2, together with the spectrum for the 200 minute specimen. This region avoids signals from oxygen and carbon contaminants, whilst giving clear indications of the presence of zinc and nickel in the deposits.

These spectra clearly show strong zinc signals for all deposits, and a decreasing intensity of the iron signal as the deposit thickens with increasing exposure time. However, of major importance is the clear signal from nickel in the two doublet peaks at a binding energy of about 880 and 860 eV. Closer examination of the other spectra in this region indicates a possibility of a faint nickel signal in the 10 minute spectrum and changes in the background count of even the 30 second spectrum as compared with the overall background of the blank specimen. This did not prove the presence of nickel in all of the deposits but a closer look at the region bracketing the nickel peaks at 860 and 880 eV was desirable. Fig. 5.4 shows the result of enlarging the scale in the vicinity of the signals in question and reducing the background noise.

The two nickel doublets between 855-865 eV and 870-885 eV can clearly be seen in the 200 minute specimen. In the 10 minute specimen, the signals are not as clear, although the shape of the doublet between 855-865 can be identified. The second doublet is a weaker signal and cannot clearly be separated from the background.

Within the spectrum for the 30 second exposure time, no clear signal within the range under examination can be obtained for identification. However, a small inflexion at about 868 eV may indicate the existence of a small signal being overlaid by a larger background noise. In view of the apparent time dependence for the deposition of nickel species in the deposits, a clear signal after 30 seconds would not be expected. Thus a failure to detect the presence of nickel neither proves nor disproves the presence of nickel in this deposit.

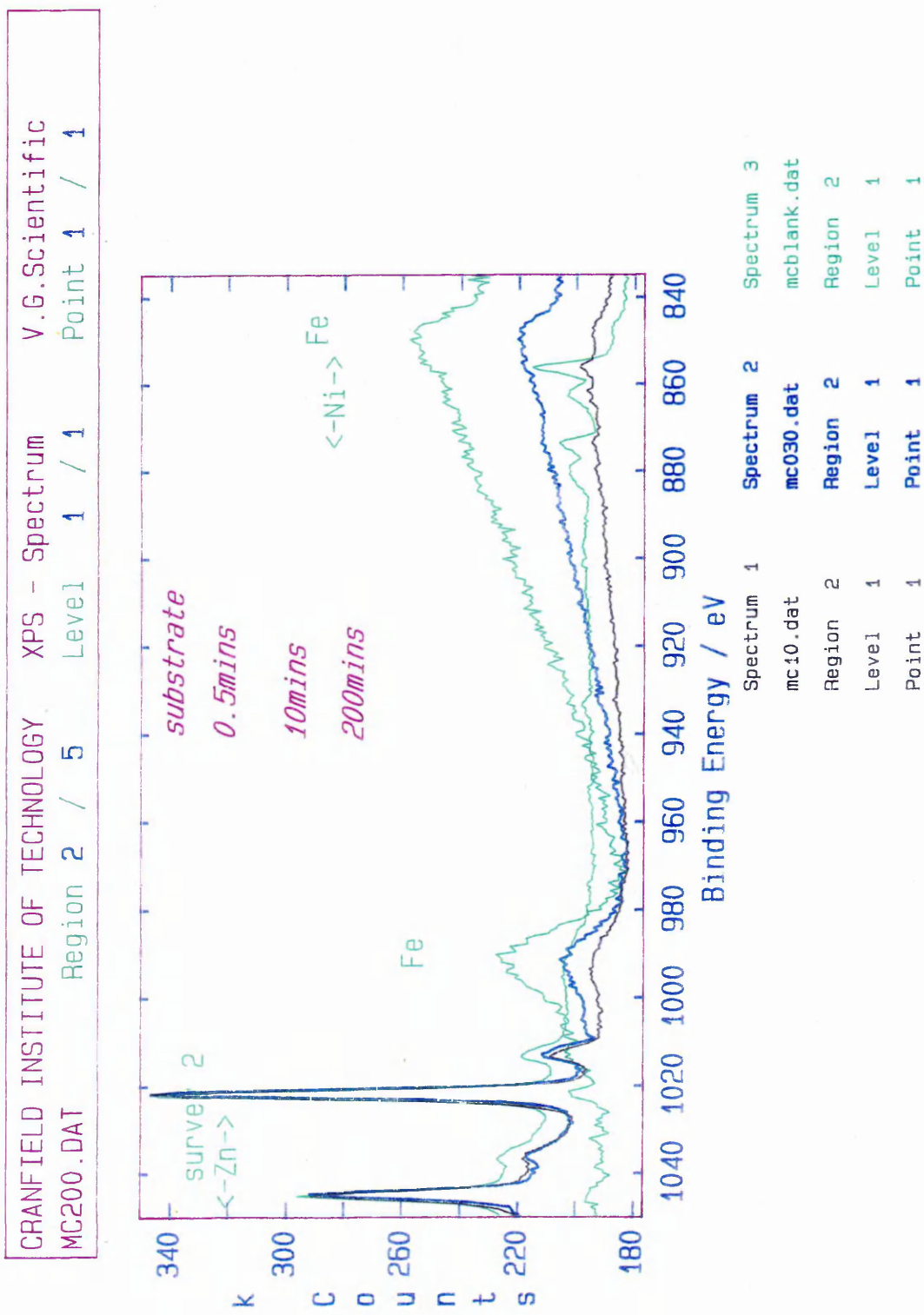


Fig. 5.3 XPS Spectra showing zinc and nickel peaks with increasing contact time.

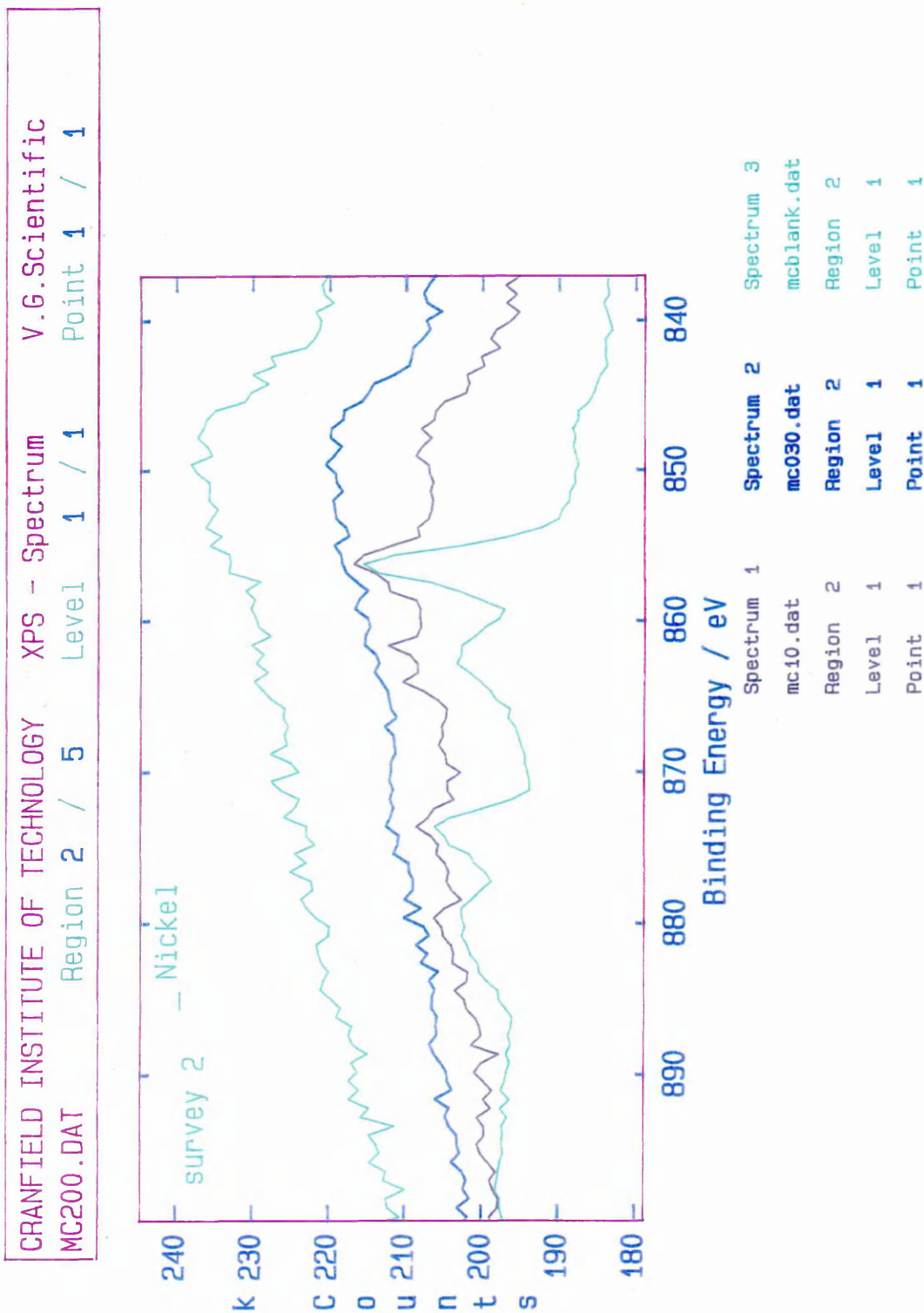


Fig. 5.4 XPS spectra - close up of the region indicating nickel presence.

Results of XPS analyses of the surfaces for the contact deposits obtained at pH2 and pH 4.4 are given in Fig. 5.5.

All samples, including the blank, indicate surface presence of oxygen and carbon. As has already been explained, these were the expected atmospheric contaminants for this type of analysis.

The blank specimen clearly shows no signals indicating a presence of either zinc or nickel.

The surface for the pH2 and pH4.4 are significantly different in composition. As would be expected, the pH 4.4 indicated that little or no nickel could be detected, but significantly strong signals identifying zinc species were evident. In this way, the pH4.4 was very similar to spectra obtained earlier. By contrast, although zinc was indicated as being present on the surface at pH2, these signals were small compared to the stronger signals from nickel.

At different pH values, therefore, deposits of different nickel composition are found on the surface of the steel. At high pH, the nickel content appears to increase with contact time, explaining why hydrogen permeation is decreased at these values with increasing contact time. Low pH of the plating solution results in a deposit richer in nickel and therefore much more efficient at preventing hydrogen entry, compared to the same contact time at a higher pH. It is evident from permeation data at low pH that, in spite of a greatly increased hydrogen ion activity, in excess of two orders of magnitude, this nickel barrier is much more efficient, resulting in less, rather than more, hydrogen permeating the steel. This decrease in permeation is contrary to all initial expectations.

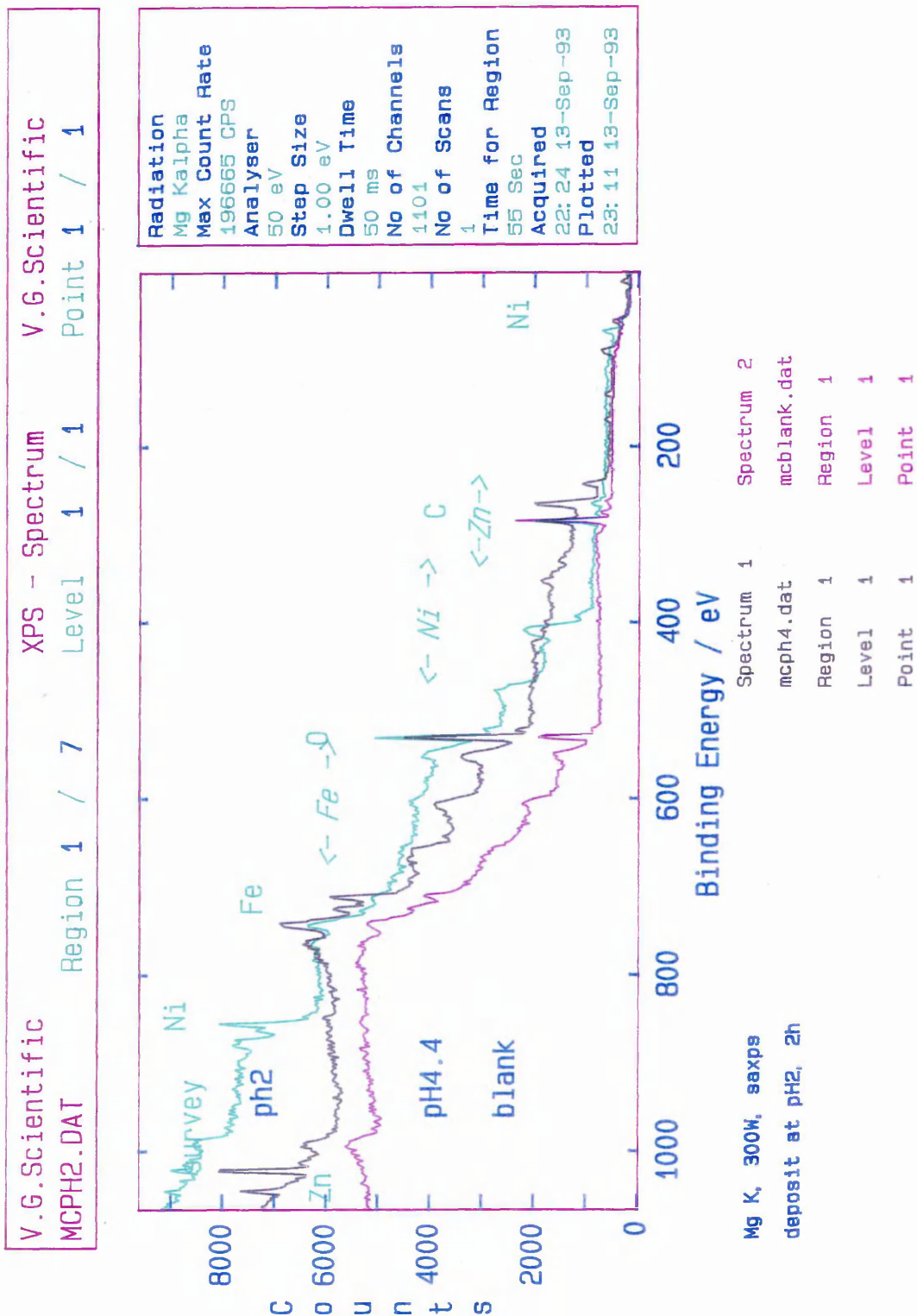


Fig. 5.5 XPS spectra showing differences in composition of the contact deposit due to the pH of plating solution.

Electron micrographs of a bare steel surface and surfaces exposed to plating solution for 0.5, 3 and 10 minutes are shown in Photographs 5.1 to 5.4.

On the specimen exposed to the plating solution for 10 minutes, light and dark areas can be seen, a feature that is only just apparent on the 3 minute exposed sample and is not noticeable on the 30 second photograph. Furthermore, in using the SEM to obtain these images, it was noticed that contrast and focusing were progressively more difficult to achieve with exposure time than on the blank sample, shown in Photo. 5.1. This appeared to be due to the growth of a thin layer of zinc hydroxide on the surface of the steel from which the zinc hydroxide whiskers grew. As an insulator, the zinc hydroxide collects charge and appears brighter on the screen. Light and dark areas may, in this case, be interpreted as regions of varying thickness of zinc hydroxide, lighter areas having the thicker deposit. This assumption is supported by the observation that the whiskers are more common in the lighter regions and is illustrated in Photo's 5.2 to 5.4. The uneven build up over the steel surface helps to explain why XPS spectra continue to show strong signals from the iron atoms at the surface of the steel after the deposit has started to build up. In addition, as will be shown later, the steel surface in contact with plating solution corrodes, thus some iron(II) ions are likely to be present at the surface of the deposit, regardless of the thickness of any contact deposit.

Photo. 5.5 shows what appears to be the site of a hydrogen bubble formed by the reduction of hydrogen ions at the surface of the steel. This forms part of the process of the corrosion of iron. By reducing the hydrogen ion concentration adjacent to the steel surface, the pH is raised. At a pH of 5.4 for 0.92M zinc sulphate solution, zinc hydroxide precipitate is formed. This explains the localised formation of zinc hydroxide whiskers around the site of what is probably a hydrogen bubble.

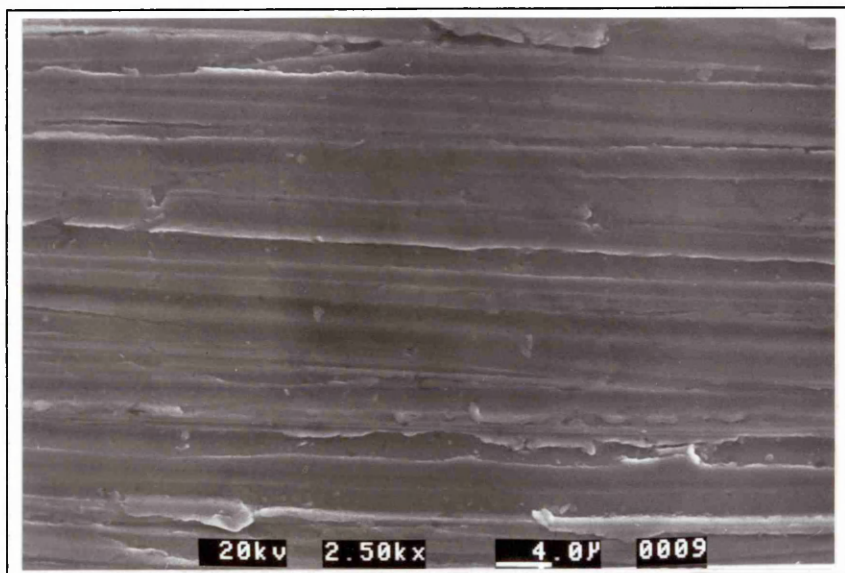


Photo. 5.1 Bare metal surface.

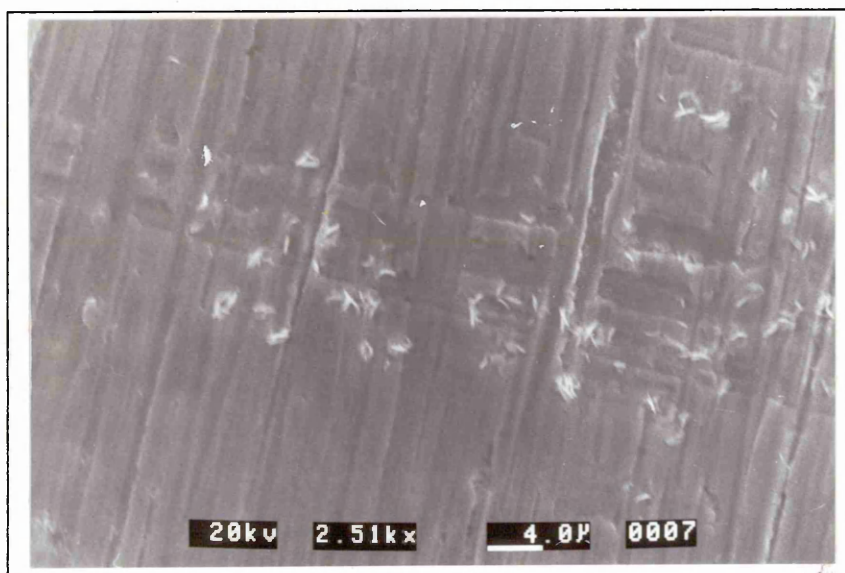


Photo. 5.2 Surface after 30 sec contact exposure

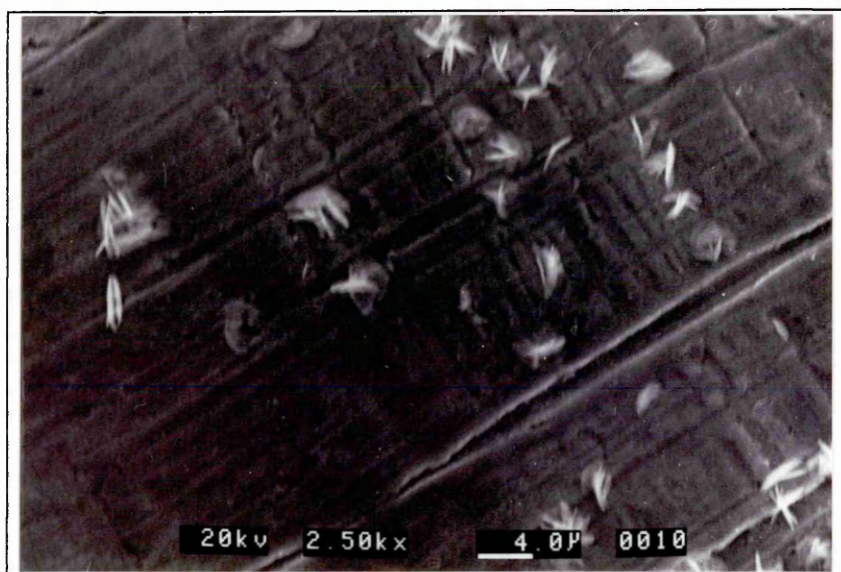


Photo. 5.3 Surface after 3 min contact exposure.

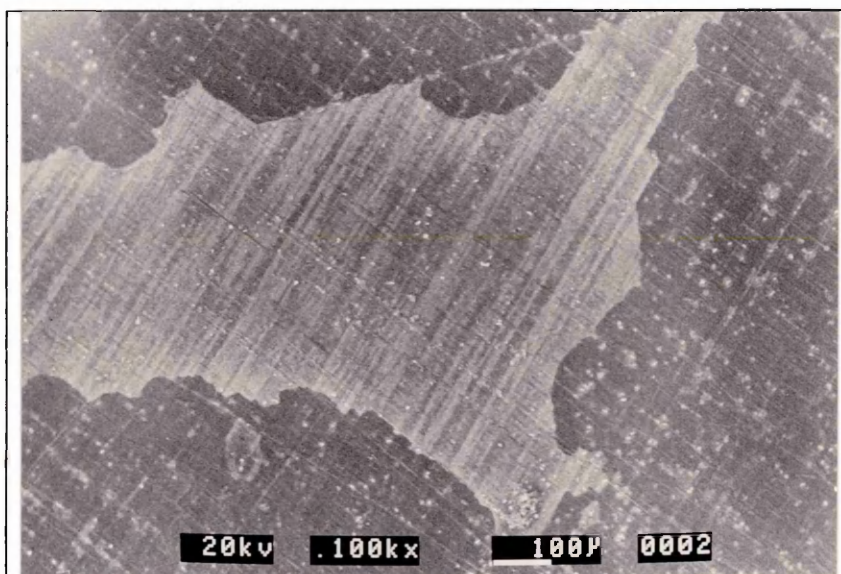


Photo. 5.4 Surface after 10 min contact exposure.

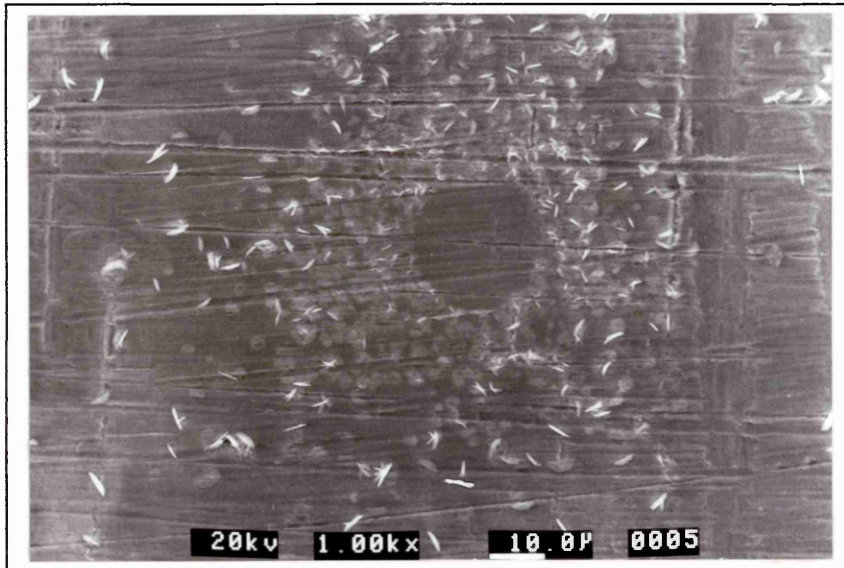


Photo. 5.5 Zinc hydroxide whiskers around the probable site of a hydrogen bubble.

5.3.2 Contact Deposits From Single Salt and Plating Solutions

The following observations were made on the appearance of contact deposits.

- ◆ **Nickel Sulphate:** Visually, the surface of the specimen exposed to nickel sulphate solution, revealed a burnished effect, giving a slight gilt colour to the surface. Photograph 5.6 shows the electron micrograph of the surface, with a relatively thick coating covering the surface scratches. The deposit partially covers what appears to be pitting, similar to that in Photograph 5.8, but with a much thicker deposit.
- ◆ **Zinc Sulphate:** The zinc sulphate solution left a uniform, matt, grey-white coating on the steel surface. Photograph 5.7 shows a relatively thick deposit with many zinc hydroxide whiskers on the surface. No sign of pitting was observed.
- ◆ **Plating Solution:** Visually, little or no change was observed from the original steel surface. Photograph 5.8 shows a very thin deposit with no sign of zinc hydroxide whiskers, although zinc was indicated from XPS analysis. Extensive pitting of the surface was apparent, indicating localised corrosion. Since zinc was detected at the surface of the zinc-nickel sulphate sample, despite there being no visual evidence of zinc hydroxide whiskers, it seems reasonable to conclude that the combined salts modified each other to produce a deposit containing both zinc and nickel species, but significantly thinner than either.

It was noted that whereas the nickel single salt solution produced pitting, there was no evidence of such pitting on the specimen exposed to the zinc single salt solution. Pitting in the specimen from the plating solution seems to indicate an influence from the nickel, although XPS analysis (see spectra referring to mc200.dat) indicate a predominance of zinc(II) species in the deposit

Scratches on the surface of each specimen from the surface preparation were largely covered by relatively thick deposits from the single salts, but not so from the plating solution. This seems to indicate that the deposit from the plating solution is thinner than those from the single salts, or that the modified deposit is finer in texture and more evenly distributed, thereby not filling in surface defects and irregularities.

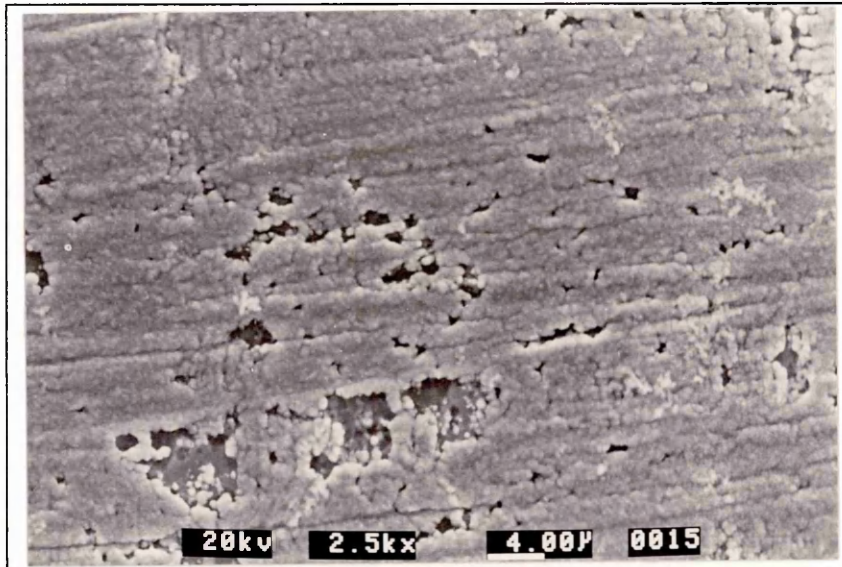


Photo. 5.6 Contact deposit from 0.52M nickel sulphate solution.

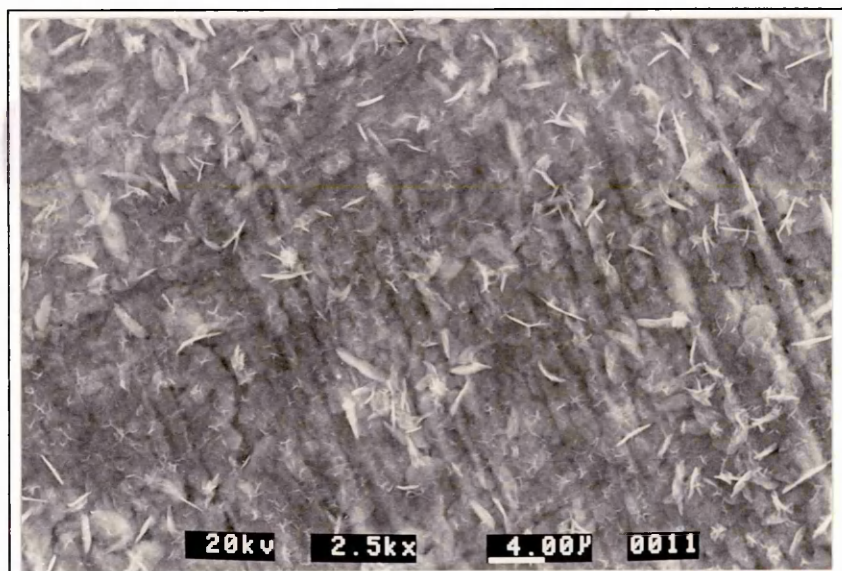


Photo. 5.7 Contact deposit from 0.98M zinc sulphate solution.

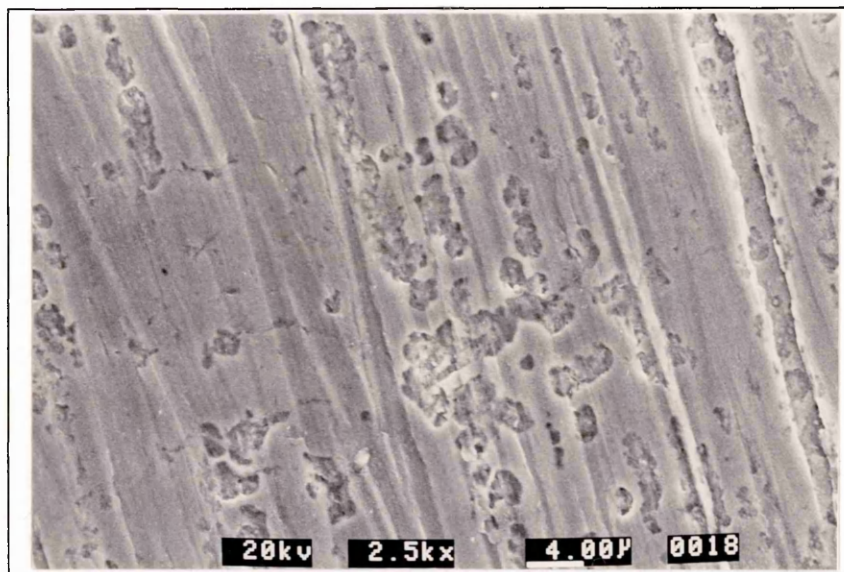


Photo. 5.8 Contact deposit from 0.52M nickel sulphate solution and 0.92M zinc sulphate plating solution.

5.3.3 Chemical Precipitation from Solution Using Sodium Hydroxide.

Table 5.2, below, summarises the observations and tests conducted on precipitates obtained by slowly adding sodium hydroxide solution into an excess amount of the solutions indicated in the left hand column of the table.

Original Solution	Appearance	Dimethyl Glyoxime Test	X-ray Analysis
0.98M Zinc Sulphate	White crystalline powder	Negative	Zinc hydroxy sulphate present
0.52M Nickel Sulphate	Bright (apple) green powder	Bright red colouration at powder surface. Red colour remains even after washing three times in boiling water	Amorphous
Plating Solution of mixed salts	Pale white-green powder	Pink colouration at powder surface. Pink colour remains even after washing three times in boiling water	Zinc hydroxy sulphate present Nickel not detected

Table 5.2 Summary of the chemical precipitation tests

Previous investigators^[86] have conducted X-ray diffraction on the surface of electrodeposited zinc-nickel alloy and on the zinc hydroxide whiskers present on the surface of the electrodeposit. Zinc hydroxy sulphate had been identified as being present, but no nickel had been detected. This investigation confirms the presence of zinc hydroxy sulphate in the chemical deposit.

These results, together with the results of the XPS analyses, show that nickel was in fact also present, even though it is present in much smaller quantities than the zinc hydroxide. However, the nickel is present in an amorphous form that would not have been detected by the X-ray diffraction in the earlier works.

The agreement about the zinc hydroxy sulphate in this work and earlier investigations, together with the identification of nickel in both contact deposits (XPS analyses) and chemical precipitates, justifies the use of sodium hydroxide to obtain precipitates for analysis. That the nickel hydroxide is amorphous is significant in understanding why nickel had not been identified during earlier investigations.

5.3.4 Examination of the Interlayer of Electroplated Specimens.

Fig. 5.6 shows concentration profiles through a thin, electrodeposited layer from a solution at a pH of 2.

The graph represents concentration in terms of Atomic Percent versus depth below the surface of the electrodeposit and is measured in terms of seconds of etch time.

It is a regrettable feature of this method that, by etching the surface for a prolonged time, errors can be introduced by the following mechanisms..

- Initially, an exchange of momentum between the argon ion beam and specimen surface can force atoms deeper into a matrix rather than remove them from the surface. Thus some atoms will be "detected" in layers below that from which they originated.
- Atoms, once removed may ionise and re-attach themselves to the surface either by settling or by being electrostatically attracted back to the target sample.
- The surface and interlayers are rough by the standards of such a technique, and so sampling is taken over a range of depths.
- Argon ion beam etching does not remove a planar layer.

These factors help to explain why no sharp boundary between layers was found, but a diffuse boundary was obtained in the region of 5000 seconds.

It is significant to note that as the value of zinc atom percentage begins to decrease, the value of nickel atom percentage starts to increase. The actual size of the increase is small, but when taken in context, concentration of nickel at the interface is twice that at the surface. Thus the postulation that there would be an increase in concentration of nickel at the interface is demonstrated to be correct.

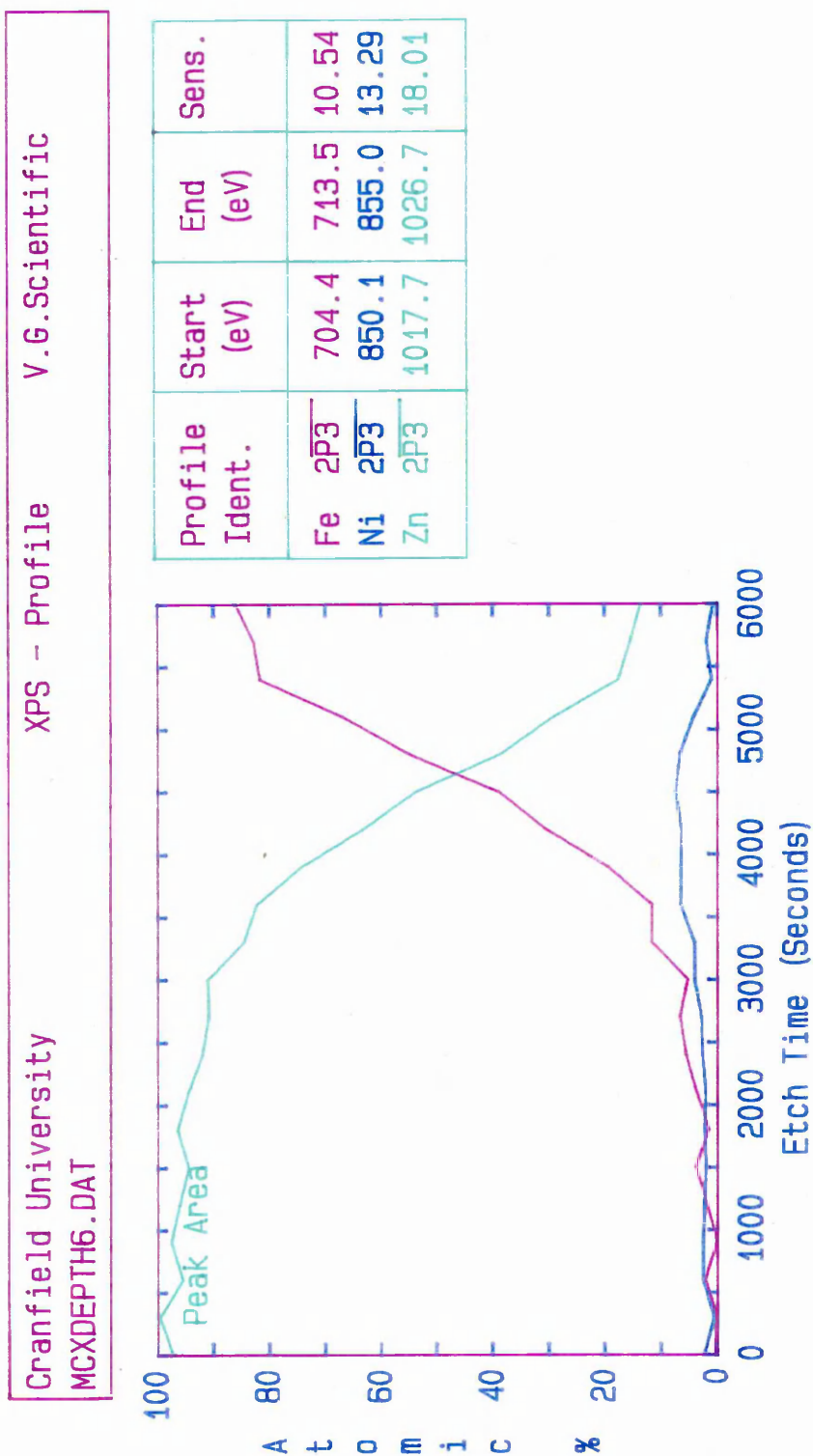


Fig. 5.6 Depth profile through an approximately 0.2 μ m electroplated deposit at pH2, showing nickel enrichment adjacent to the substrate.

Photographs 5.9 to 5.13 show the distribution of the elements, oxygen, zinc, nickel and iron across the wall of the pit and therefore through the electrodeposit.

Careful examination of these photographs shows that oxygen is more abundant at the surface and decreases towards the steel substrate. Zinc forms a relatively thick band, just below the oxygen rich surface, but does not maintain an equally high concentration down to the surface of the steel. Adjacent to the steel surface, just below and merging with the zinc layer a thin, nickel rich layer was found, as had been postulated.

The evidence of this depth profiling is such that, plating at pH2, requires a significantly longer time and hydrogen current density to raise the pH of the solution at the electrode surface to that critical value to produce zinc hydroxide precipitation than at higher pH. During this time delay, before the onset of anomalous co-deposition, nickel metal is preferentially deposited, possibly as the pure metal but probably as a nickel rich zinc-nickel alloy. This nickel rich layer is responsible for a very efficient barrier to hydrogen absorption in spite of the fact that the environment is much more aggressive in favour of hydrogen absorption

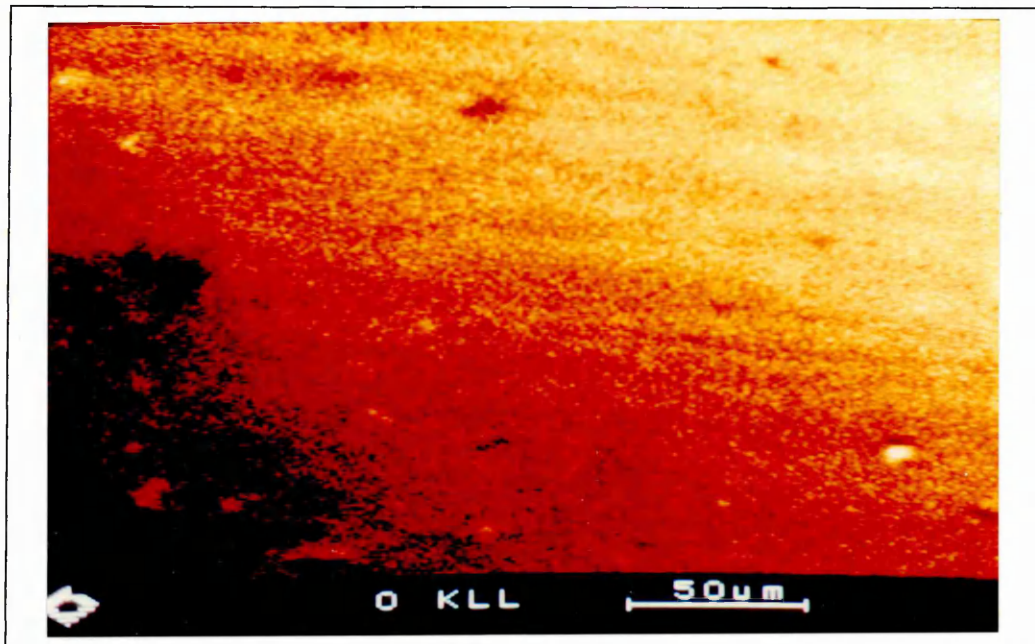


Photo. 5.9 Atomic map of oxygen distribution.

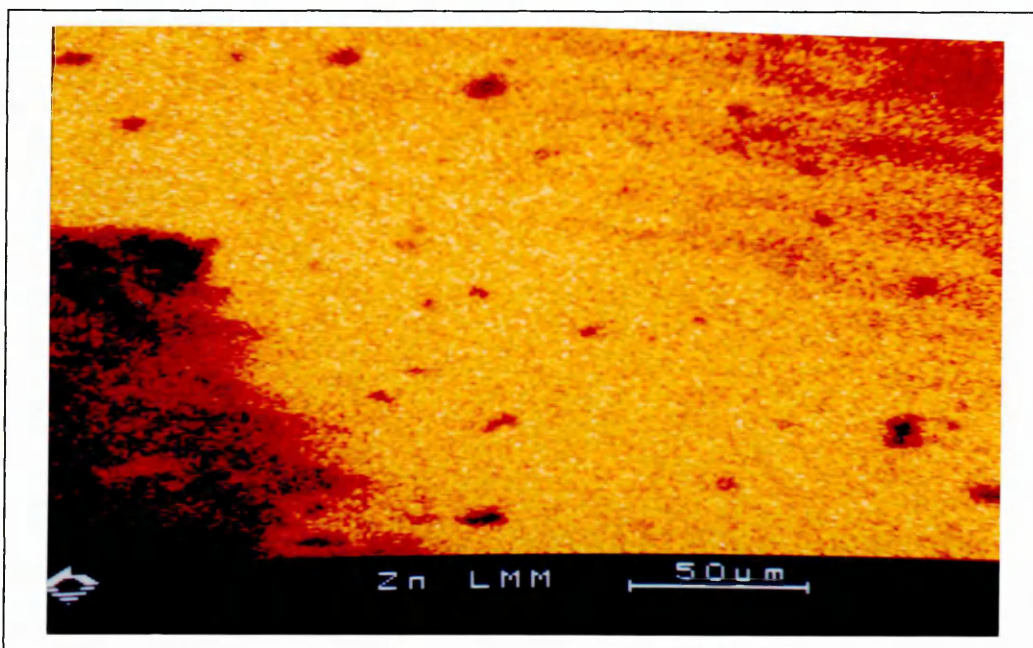


Photo. 5.10 Atomic map of zinc distribution.

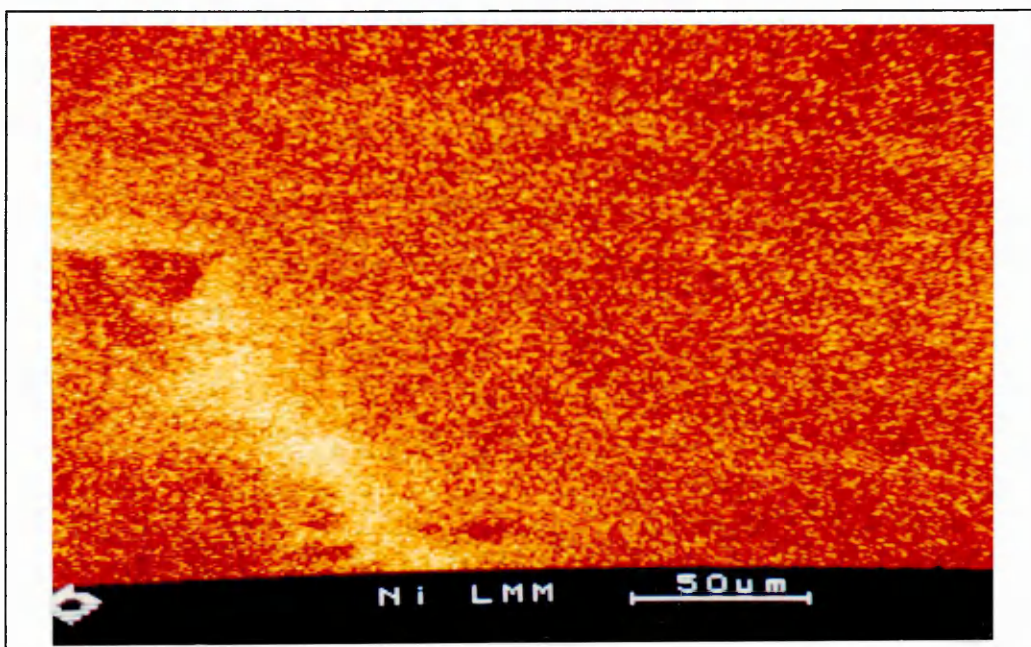


Photo. 5. 11 Atomic map of nickel distribution.

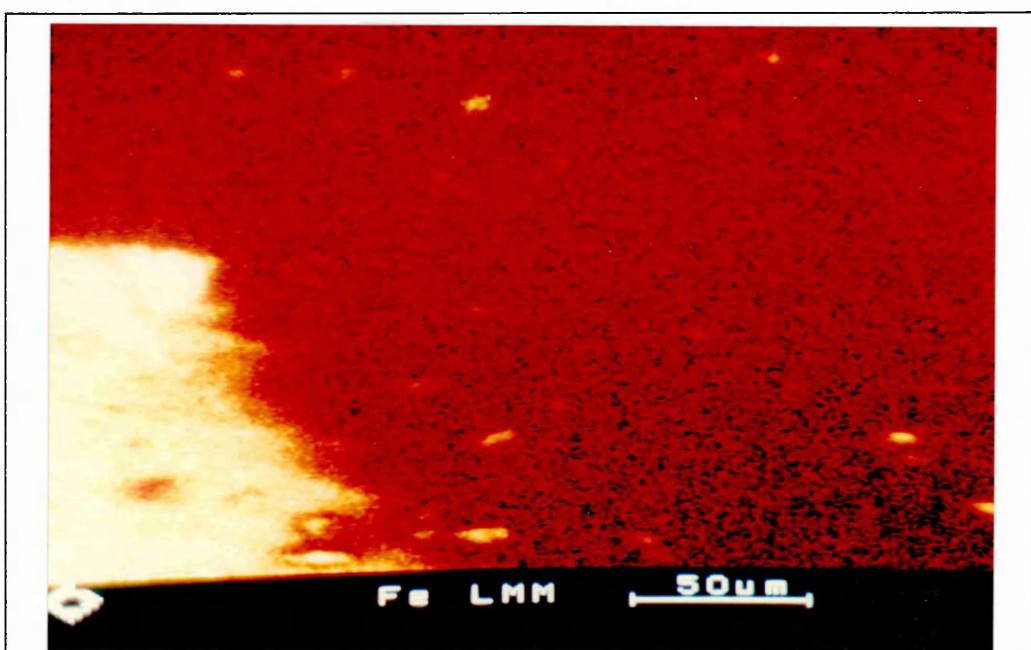


Photo. 5.12 Atomic map of iron distribution.

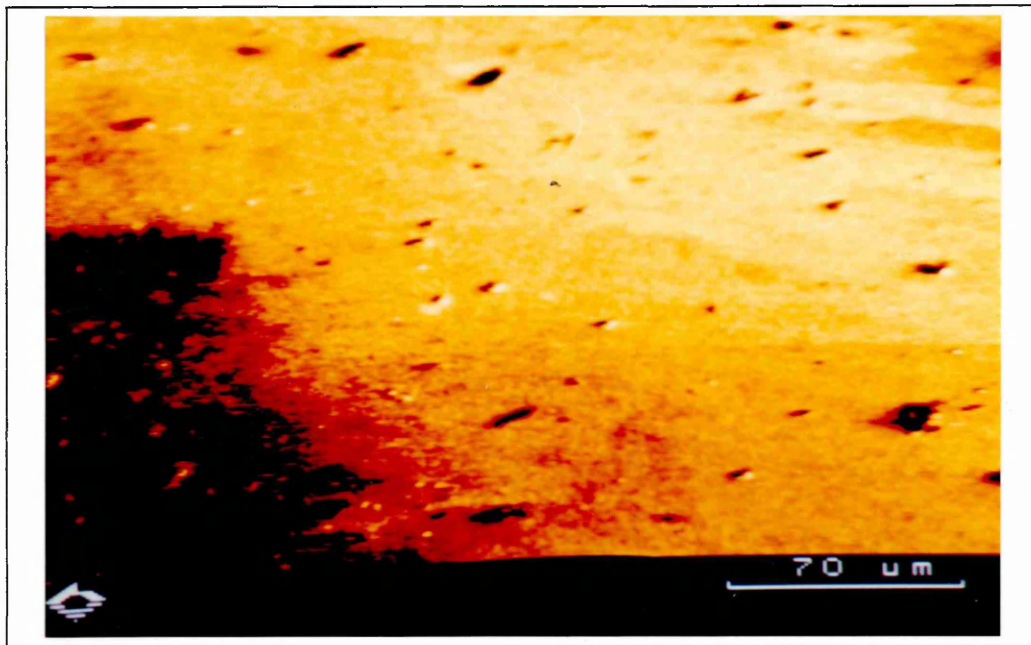


Photo. 5.13 SEM micrograph of the surface used in element mapping.

5.4 Summary of the Findings from Surface Analysis

It has been confirmed that contact deposits of two different compositions are deposited on a steel surface due to chemical processes and that the composition of the deposit is related to pH.

At relatively high pH, the deposit is essentially based on zinc hydroxide and appears to contain trace amounts of nickel, whereas at relatively low pH values, the deposit contains significantly more nickel. As nickel provides a good barrier to hydrogen permeation, the deposit formed at low pH gives rise to a more efficient hydrogen barrier. This explains the unexpected, and apparently anomalous observation, that less hydrogen would permeate a shim electrode when plating was performed at lower pH than at a higher pH, even though more hydrogen is produced electrolytically at the surface of the shim.

It is postulated that the contact deposit is of the same nature and similar composition to the deposit which is a pre-requisite of anomalous co-deposition. This statement is supported by the discovery of a predicted, very thin nickel or nickel rich layer adjacent to the substrate.

Examination of contact deposits from single salt and plating bath solutions indicates that the deposit formed from the plating solution may be thinner than either of the single salt solutions. This would seem to suggest that the zinc hydroxide, which forms the larger component, may absorb nickel ions from aqueous solution.

Production of larger quantities of the hydroxides by precipitation from solution support the findings that nickel is contained as an integral component in the hydroxide obtained from the plating solution. Furthermore, although the zinc hydroxide deposit is crystalline, giving a recognisable X-ray diffraction pattern, the chemically precipitated nickel hydroxide is amorphous. If then, the nickel hydroxide formed in this way is identical to that formed on the steel surface, this finding alone would explain why nickel has not been detected in the hydroxide deposits obtained during anomalous co-deposition by earlier investigators.^[86]

6 Summary Discussion

6.1 Overview of Results

It has been clearly demonstrated from slow strain rate tests, that cadmium electroplate is more embrittling than zinc-nickel alloy. The degree of embrittlement with zinc-nickel alloy has also been shown to be related to the pH of the solution and therefore to the current efficiency.

Permeation studies have provided indications that a nickel or nickel rich layer may exist adjacent to the substrate at pH values below pH3. Depth profiles of the surface using XPS and Auger analyses confirm that zinc hydroxide is present at the surface, but that at lower pH values, an extremely thin nickel deposit has been identified, as predicted, adjacent to the substrate.

XPS analyses of deposits from solutions at pH2 and pH4.4 confirm that zinc hydroxide is present in both cases. A nickel species, probably an oxide or hydroxide, is confirmed to be present in the deposit at pH2, but the presence of such species at pH4.4 has not been confirmed. If present, the nickel content of the pH4.4 deposit is very small.

Single salt solutions of either zinc or nickel sulphate produce an oxygen rich contact deposit, on a mild steel surface, containing zinc or nickel ions respectively. However, a contact deposit from a double zinc-nickel sulphate solution onto mild steel produces what appears to be a very much thinner deposit with some characteristics of both single deposits. This observation implies that zinc and nickel hydroxide may co-deposit together, in a single phase. Further evidence of this zinc-nickel hydroxide deposit is provided by chemical precipitation reactions and X-ray analysis. Again a zinc hydroxide species, as zinc hydroxy sulphate, was identified, but X-ray analysis of the nickel(II) hydroxide indicated an amorphous structure. Assuming that this test produces precipitates of comparable structure to those formed on the electrode surface, this would explain why nickel hydroxide has not previously been detected by X-ray analysis.

Together with the evidence from other investigators, it is now possible to propose a modification to the hydroxide suppression theory in which nickel suppression is not simply a physical process.

6.2 Anomalous Co-deposition - Double Hydroxide Mechanism

6.2.1 The production of a hydroxide deposit.

The classical hydroxide suppression mechanism, as proposed by Dahms and Croll,^[84] and investigated by Fukushima and others,^[88-92] relies on a zinc hydroxide deposit forming on the surface of the electrode. This deposit provides an abundant supply of zinc ions while forming a diffusion barrier for nickel ions. Consequently nickel deposition is suppressed.

The formation of a zinc hydroxide deposit is not questioned here. However, it is suggested that a small quantity of nickel ions are also deposited with the zinc hydroxide, possibly in a proportion that is dependent on pH.

For nickel hydroxide to be deposited, the required pH is calculated to be pH6.5.^[110] However, this value only represents the equilibrium conditions between particular values of aqueous Ni^{2+} , H^+ ions and solid NiO hydrate, or $\text{Ni}(\text{OH})_2$. Other equilibria will exist at other pH values. Furthermore, in a revision of the potential-pH diagram for nickel, Silverman^[111] indicates that the $\text{Ni}(\text{OH})_2$ may be stable over wider potential and pH ranges than considered by Pourbaix.^[110] Calculations of the pH at which $\text{Ni}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ are deposited are based on single substances. It is not known what effect, if any, nickel ions will have on the zinc hydroxide deposit at the pH and temperatures in question.

Evidence from X-ray analysis and the dimethyl glyoxime test on hydroxide precipitates from the plating solution, demonstrates that Ni^{2+} ions are present and integral with the zinc hydroxy sulphate precipitates. It follows that the hydroxide precipitate on the electrode surface may contain a small, pH dependent, quantity of nickel, within what is principally a zinc hydroxide matrix.

Reduction of the $\text{Ni}(\text{OH})_2$ within the deposit would then follow a parallel path to the reduction of $\text{Zn}(\text{OH})_2$. Assuming that both the metal and hydrogen ions are reduced simultaneously, the electrode potential of the alloy during deposition would be intermediate between that of $\text{Ni}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$ and H^+ . The exact value of the deposition potential would be the average of the potentials of the three species, taking account of their discharge ratio.^[112]

6.3 Permeation and Mechanical Studies

The permeation technique developed by Devanathan and Stachurski is usually performed in order to provide data on bulk hydrogen diffusion through a metal. In diffusion experiments, a clean metal surface is electrolytically charged with hydrogen until the efflux current has reached a plateau. In order to achieve reproducible results that are not adversely affected by irreversible traps, a number of precautions should be taken.^[39]

1. The membrane should not be less than approximately 250 μm . Ensuring a minimum thickness minimises the effect of the high concentration of traps situated in the surface regions of any metal surface while maximising the bulk diffusion effects.
2. The membrane should be precharged to fill any irreversible traps that would give an artificially long breakthrough time and shallow rising transient.
3. The exit side of the electrode should ideally be treated to eliminate oxide layers which may be oxidise the permeating hydrogen chemically, rather than allowing the hydrogen to be oxidised electrolytically.
4. Finally, where possible, the solutions should be pre-electrolysed to remove impurities which may affect either the influx of hydrogen or provide small currents on the efflux side of the electrode other than hydrogen oxidation.

In this work these precautions have been noted, but are considered not to be applicable for the following reasons.

1. The influence of the electrodeposit is a surface feature, therefore it is inappropriate to negate the surface effects by using a thicker specimen. In addition, because hydrogen entry is very much smaller than typical permeation studies, a much thinner specimen provides a greater diffusion gradient to produce a higher flux.

2. It was not the purpose of this investigation to collect bulk diffusion data, but to measure the quantity of hydrogen that permeated a steel shim. Assuming a constant trap density and consistent thickness of the shim electrode, it is reasonable to assume that the quantities of hydrogen measured would provide a "rank order" for the amount of hydrogen entering a steel surface as a function of time for different plating conditions. The rank order would then be expected to identify plating conditions likely to be embrittling.
3. For obvious reasons it would be inappropriate to pre-electrolyse a plating solution, and as the depletion of the electrode took up to three days, this was considered to be sufficient pre-electrolysis.
4. The oxide film on the depletion side would be present due to passivation of the steel. After the period of depletion, it was considered that the extent of the passive layer would be consistent from one experiment to another, and as a "rank order" for permeation was being sought, this was considered to be acceptable.

The slow strain rate method has clearly indicated its usefulness in detecting hydrogen embrittlement due to hydrogen ingress from an electrodeposit. By comparing times to failure at the same slow strain rate for similar tensile specimens, the extent of embrittlement can be determined. Again a rank ordering of plating conditions can be ascertained.

It was found that the rank ordering of both the electrochemical and mechanical methods provided results in very close agreement, each method confirming the results of the other. Both test methods, therefore, appear to produce equivalent results although each test is totally independent.

To test a single tensile specimen requires less time than to perform a single permeation experiment. However, due to each tensile specimen being unique from the point of view of crack initiation sites, it is necessary to strain a number of specimens to obtain a statistical population.^[76,77] Since a single permeation experiment is more reproducible and does not depend on a stochastic failure of the specimens, this is all that is required to assess the likelihood of hydrogen embrittlement being a problem for a particular set of plating conditions. This method, then, offers a cheap, quick and reliable method for assessing the embrittlement characteristics of plating baths.

The transition current density is pH dependent,^[90,91] occurring at higher current densities for lower pH. This is due to the need for more hydrogen to be reduced at the cathode surface to produce a pH of 5.5 for anomalous co-deposition. Thus it was expected that plating would become progressively more embrittling as the pH of the solution decreased.

This was found not to be the case over the range pH5 to pH2 in this investigation.

It was discovered that two factors play an important role in the embrittlement of steel due to zinc-nickel electroplating.

Firstly, pH is relevant, not solely due to the hydrogen ion concentration, but also to the nature of the initial chemical deposit left on the steel surface. This deposit is richer in nickel content at pH values below pH3. Nickel is known to be an efficient barrier to hydrogen absorption.^[104,105] Hence at low pH, much less hydrogen is absorbed than would otherwise be expected. Above pH3, a deposit rich in zinc hydroxide is deposited. This deposit is not as efficient at inhibiting the ingress of hydrogen, but thicker deposits are found to inhibit more hydrogen than thinner ones.

The second factor affecting hydrogen uptake, and hence embrittlement, is the time for which the electrode was in contact with the plating solution before plating commenced. During this contact time, a deposit was left on the surface of the electrode due to chemical action. pH played an important role in the nature of the deposit, in that above pH3, the deposit was essentially zinc hydroxide in composition, produced by a change in pH at the electrode surface as a result of the free corrosion of the steel surface. Thicker deposits were found to reduce the total hydrogen permeating the electrode. Below pH3, the pH of the solution was too low to allow the deposition of zinc hydroxide. Consequently, a very thin layer of nickel metal was deposited from solution by a simple displacement process. Longer contact times in this more aggressive case resulted in a greater quantity of hydrogen permeating the electrode. It is believed, however, that the increase in permeation is not due to the fact that the chemically deposited nickel provides less of a barrier than does the zinc hydroxide, but that the activity of hydrogen ions in solution is greater. From an examination of the transient between contact with the solution and starting electrodeposition, a significant quantity of hydrogen is found to permeate the electrode for contact times over 30 secs.

6.4 Chemical considerations

It would be expected that mild steel, in an oxygenated, acidic solution would corrode. SEM micrographs show that this is the case here. Since corrosion is an electrochemical process, it can be assumed that any process taking place at a cathodic site, during corrosion, is analogous to what happens at a cathode undergoing electrolysis at a very low current density. Thus the contact deposit can be considered to be a special case of the deposition mechanism, in which a hydroxide deposit is formed, but no reduction to the metallic phase occurs.

The hydroxide suppression mechanism, which is widely accepted as at least a partial explanation of anomalous co-deposition, requires that zinc hydroxide precipitates onto the steel surface. This is believed to be due to the co-deposition of hydrogen from solution at the cathode surface giving rise to an increase in pH at the steel surface. The contact deposit shows similar characteristics and it is suggested, therefore, that a study of the contact layer would help to explain, not only the effect of contact time on hydrogen permeation, but also the mechanism of anomalous co-deposition itself.

Since the zinc hydroxide layer formed during electrodeposition is both very thin and temporary, lasting only as long as it takes to convert the hydroxide deposit into zinc, it is difficult to examine in situ. The contact deposit above pH3 is, according to all observations, of the same nature as the hydroxide precursor to the electrodeposit but, in the absence of a plating current, is permanent and can be thickened to some extent for elemental and depth profile analyses simply by allowing it to grow in contact with the plating solution. Although the assertion here is that the contact deposit and the hydroxide deposit formed during electrodeposition are of the same nature, it is not asserted here that they are necessarily of the same composition. That is, any contact deposit will be based on zinc hydroxide, but the amount of nickel within that deposit may vary if, for example, the rate at which nickel is absorbed is constant with time. Such a case could arise if zinc hydroxide is deposited rapidly to a maximum thickness, determined by boundary layer diffusion of hydrogen ions, but nickel ingress into this matrix is constant with time. In the absence of any evidence, therefore, a constant ratio of zinc to nickel cannot be assumed for different contact deposits.

The compositions of both the contact deposit and the plating hydroxide deposits appear to be, primarily, pH dependent. This can be seen directly in XPS analyses of the contact deposits produced at pH2 and pH4.4, the results of which were presented earlier in Section 5. Significantly more nickel was evident in the surface deposit at the lower pH value. With regard to the hydroxide deposited during electrodeposition, a pH dependence can be inferred from an examination of the composition versus current density graphs, demonstrated in Fig. 2.20 as determined by Fukushima and others.

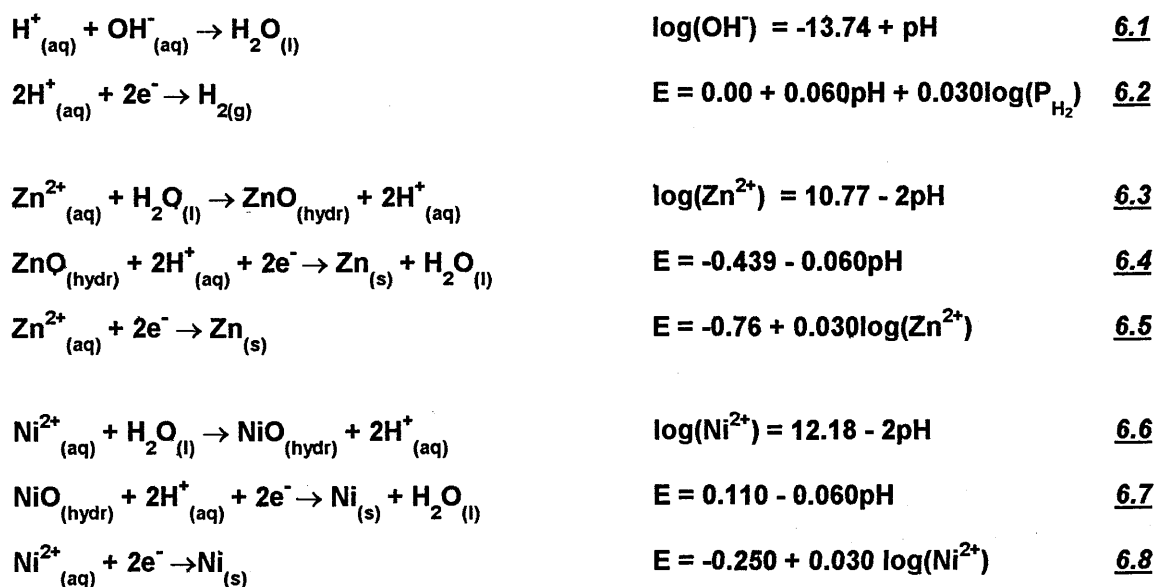
From Fig. 2.21, it can be seen that nickel content in Region I decreases with increasing current density. At the same time it will be noted that the current efficiency is very low, indicating a high level of hydrogen evolution. Since the current efficiency is relatively constant over this region, it seems reasonable to assume that the decrease in nickel content of the electrodeposit is compensated by an increase in the deposition of zinc. Presumably this zinc is reduced, not directly from zinc aqua ions, but from zinc hydroxide deposited due to pH changes due to hydrogen ion reduction. A mechanism to explain this is described overleaf.

Using equation 6.4, overleaf, obtained from Pourbaix,^[99,110] zinc hydroxide is calculated to be precipitated from a 0.92M aqueous zinc ion solution at a pH of 5.4. Since some zinc hydroxide will form in the absence of a plating current at a pH>3, it is reasonable to assume that some zinc hydroxide will form, even at low plating current densities. At the small current densities of Region I, it is postulated that the electrode potential is insufficient to allow a significant reduction of zinc hydroxide, even though zinc hydroxide is formed and a small amount is reduced to zinc. Reduction of nickel ions will predominate, since, within Region I, the zinc hydroxide is insufficient to produce an effective barrier to nickel ions and the potential at the electrode is insufficient to reduce large amounts of zinc hydroxide. With increasing current density, a more stable and thicker zinc hydroxide forms, increasing ohmic polarisation and resulting in a higher electrode potential to drive the current. As the potential increases, zinc hydroxide can be reduced faster and the proportion of zinc in the electrodeposit increases. This accounts for the previously unexplained occurrence of zinc-nickel alloy with a high nickel content below the transition current density, with zinc content increasing as the transition current density is approached

At the transition current density, the diffusion boundary layer becomes stable and buffered at pH 5.4 by the deposition of zinc hydroxide. At this point, the electrodeposition process becomes essentially that of zinc hydroxide reduction allowing for the continued removal of hydrogen ions to maintain the lower pH without actually producing embrittling hydrogen. The chemical mechanism of this process is discussed overleaf. The reduction of any nickel hydroxide within the zinc hydroxide matrix would follow an equivalent reaction path.

It will be noticed at this transition point, that the composition of the alloy changes in a rapid stepwise fashion, marked by a dramatic reduction in nickel content and a corresponding increase in zinc content of the alloy. A simultaneous increase in current efficiency is noted at this point. The efficiency increase cannot mean that hydrogen ions are no longer being reduced, since the pH would rapidly decrease making the zinc hydroxide unstable, therefore the reduced hydrogen ions must take some part in the final reduction of zinc hydroxide to zinc metal and water. Such an explanation would allow for the pH to remain relatively high at the cathode surface whilst simultaneously accounting for the significant reduction in hydrogen embrittlement of the steel substrate of zinc-nickel alloy compared with nickel metal.

A proposed mechanism, based on the equilibrium equations of Pourbaix is given below.



In his work on zinc, Pourbaix^[99,110] equated zinc hydroxide, $\text{Zn}(\text{OH})_{2(\text{s})}$ to hydrated zinc oxide, $\text{ZnO}_{(\text{hydr})}$ and nickel hydroxide, $\text{Ni}(\text{OH})_{2(\text{s})}$ to hydrated nickel oxide, $\text{NiO}_{(\text{hydr})}$. The thermodynamic equations relating to the ϵ -form of zinc hydroxide, which is the form of zinc hydroxide closest to that observed in this investigation, Pourbaix labelled "a". The equations above are written in the form used by Pourbaix but their thermodynamic values have been modified to take into account the change in temperature from 25° to 30°C. It should be mentioned that the numbering of the named equations is not the same as used by Pourbaix.

It can easily be shown that equations 6.3 and 6.4 above can be combined to produce equation 6.5, which is the reduction of aqueous zinc ions from an aqueous solution. Similarly equations 6.6 and 6.7 above can be combined to produce equation 6.8.

After an initial pH change, at the electrode surface, due to the reduction of hydrogen ions, the reduction of zinc ions proceeds in two steps, firstly, the chemical precipitation of the hydroxide and secondly, the electrolytic reduction of the hydroxide to zinc.

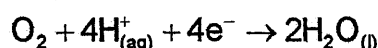
The reduction of hydrogen ions raises the pH, allowing reaction 2 to proceed with the release of hydrogen ions in a chemical buffering capacity. However the effect of the applied potential drives reaction 3 in the forward direction. In this way, the freshly produced hydrogen ions are used to facilitate the reduction of zinc hydroxide. Thus hydrogen is behaving as a catalyst under the influence of the applied potential. Hydrogen ions need only be reduced to hydrogen atoms, or to hydrogen gas in order to account for the inward diffusion of hydrogen ions.

Consequently a high pH is maintained without embrittlement and the plating current is very efficient. This mechanism appears to explain the changes, across Regions I and II of Fig. 2.21, in the composition of the alloy with increasing current density. In addition, the mechanism predicts that, when plating is commenced at a current density within the anomalous region, Region II, a short time will pass before the pH at the cathode surface reaches its critical value allowing the formation of a stable diffusion boundary layer and zinc hydroxide deposit. During this time, the composition of the electrodeposited alloy will vary. Section 5 presents analyses which verify this prediction in the case of a deposit from a solution at pH2. Tests from a solution at pH4 or higher were not conducted due to the time available. A diagrammatic representation of the mechanism is given in Fig. 6.1, for the non-plating, freely corroding steel, and in Fig. 6.2 for the case of the electrodeposit.

The mechanism, as described, seems to suggest a current efficiency of 100%. In practice, a current efficiency less than 100% would be expected, since some hydrogen ions would be reduced to hydrogen gas in order to compensate for maintaining a diffusion boundary layer close to the steel surface. Current efficiency would, therefore be expected to be lower in those solutions with the lower pH. This is what is found experimentally, as illustrated in Fig. 4.2, which examines the hydrogen current efficiency, rather than plating current efficiency, as a function of solution pH.

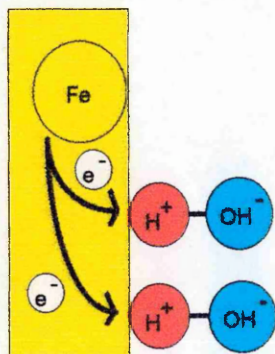
The compositions of the hydroxide deposits from contact and plating both appear to be pH dependant. Contact deposits exhibit an increased proportion of nickel with longer exposures and therefore thicker deposits. If it could be demonstrated at a later date that the thickness of hydroxide is related in some way to a plating current density, then a more detailed analysis of concentration profiles through a contact deposit may give an indication of the Zinc-Nickel ratio in the alloy electrodeposit.

Reduction of dissolved oxygen as an alternative to hydrogen ion reduction cannot be dismissed without some consideration. Ohnaka and Furutani^[115] observed that the permeation current through a Type 304 stainless steel in an aerated solution was less than in a de-aerated solution under otherwise identical conditions. Oxygen reduction according to the reaction...



...would have the same effect of increasing local pH as hydrogen ion reduction, but without hydrogen production and absorption. This would have the effect of not being embrittling. However, the conditions under which Ohnaka and Furutani observed the greatest reduction in hydrogen permeation were 95°C and pH10. These authors note that under conditions similar to those in a crevice, hydrogen reduction is favoured. Thus low pH and oxygen depletion would favour hydrogen reduction. In the plating solutions used in this work, the pH was certainly acidic, and the zinc hydroxide deposit would itself occlude the metal surface, making diffusion of oxygen into the surface difficult. Oxygen, then, would be diffusion limited through the hydroxide layer in the same way that current theories suggest that nickel is diffusion limited. If oxygen reduction was responsible for the hydroxide deposit, then pH5 conditions would be expected to be less embrittling than pH3, where hydrogen reduction would be more favourable. The converse is found to be the case.

Ohnaka and Furutani record that a critical potential (E_{crit}) of -0.90V (SCE) or less is necessary for the uptake of hydrogen. Plating in the anomalous region has been measured to be in the region of -1.2V (SCE)^[80] for the current densities of 20 mA cm⁻² used in this work.



Iron atoms are oxidised as
hydrogen ions are reduced.

(a)



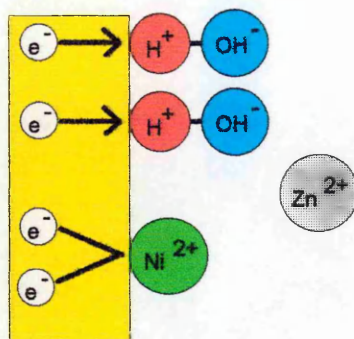
Iron dissolves as iron(II) ions.

Loss of hydrogen ions raises the pH
of the solution adjacent to the steel.

Zinc hydroxide is deposited onto
the steel surface, inhibiting further
corrosion of the steel.

(b)

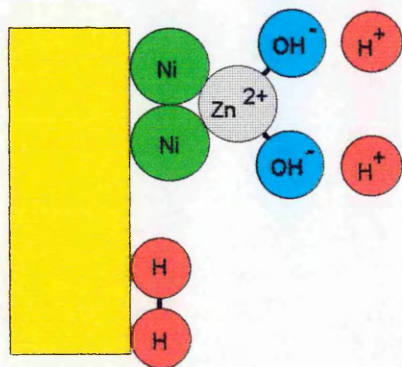
Fig. 6.1 Schematic mechanism for contact deposit formation.



Initially, hydrogen ions are reduced, raising the solution pH adjacent to the cathode surface.

In the absence of zinc hydroxide in the early stages, nickel is also reduced directly.

(a)

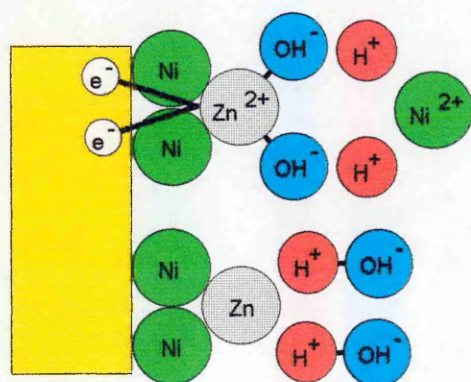


Zinc hydroxide is deposited.

More hydrogen ions must be reduced to maintain the high pH adjacent to the cathode surface.

Molecular hydrogen is formed in the initial stages only.

(b)



Once zinc hydroxide covers the electrode nickel is inhibited and is not reduced directly from solution.

Hydrogen ions are involved in the reduction of zinc hydroxide to metallic zinc, thereby maintaining both high pH and current efficiency.

(c)

Fig. 6.2a Schematic representation of anomalous alloy deposition.

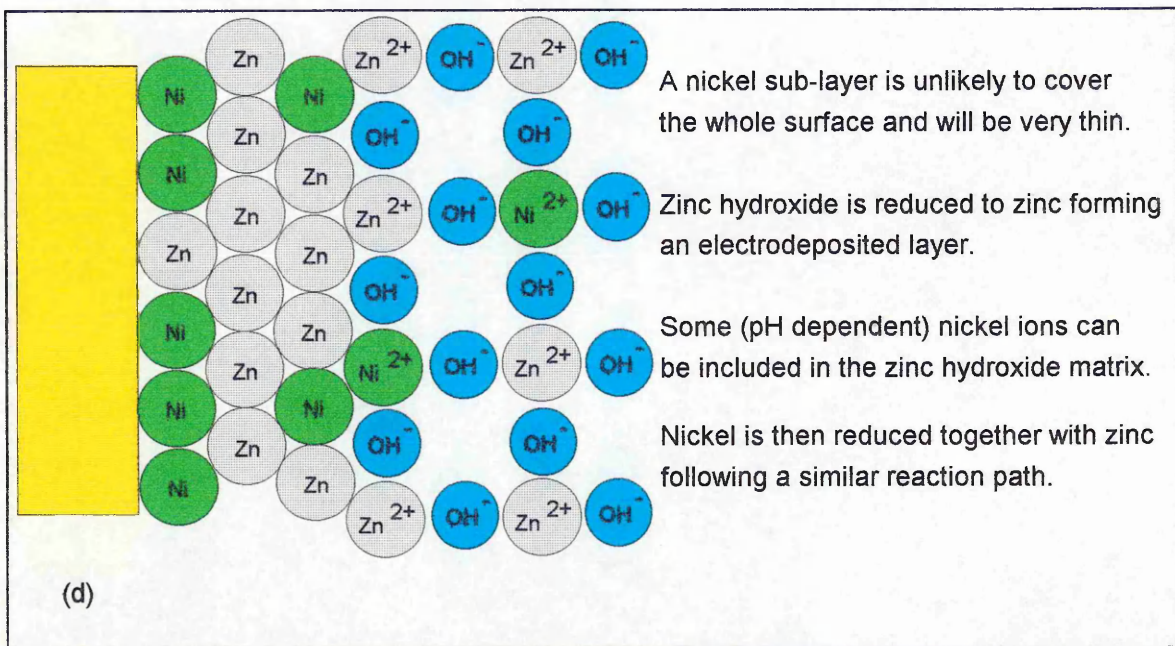


Fig. 6.2b Schematic representation of anomalous alloy deposition continued.

In concluding this section on the reduction of zinc (II) species, the theory just described may be extended to explain Region III in Fig. 2.21 in the following way.

As the current density increases, a limiting case of reduction of zinc hydroxide would arise, necessitating that hydrogen ions are once again reduced to hydrogen gas. This would account for the rapid fall in current efficiency across Region III. Furthermore, once hydrogen ions are reduced beyond the rate of zinc hydroxide reduction, the pH of the solution adjacent to the electrode would again be expected to rise.

Zinc hydroxide is amphoteric, and would be expected to dissolve once the pH had risen above pH10.^[99] Before this, however, in the region of pH9, zinc ions form the soluble bizincate ion (HZnO_2^-).^[99] This bizincate ion would then be able to diffuse away from the cathode surface. A decrease in pH away from the cathode surface would allow the formation once again of zinc hydroxide. However, forming away from the cathode surface, this zinc hydroxide would be loose and therefore not in sufficiently good electrical contact with the electrode to allow for efficient reduction to zinc metal, if at all. Thus, surface resistance will increase, forcing the electrode potential to increase in order to maintain the current. As the current efficiency falls once again, a deposit rich in nickel is formed.

To date, the hydroxide suppression mechanism has not offered a detailed explanation for the reduction of zinc hydroxide while maintaining the high surface pH and simultaneous high current efficiency, nor has it attempted to explain the behaviour of Region III.

So far, the explanation of anomalous co-deposition has been considered from the viewpoint of explaining why zinc is predominant in the deposit and not nickel. It is now time to consider the presence of nickel in the alloy deposit.

The deposition of nickel, according to the conventional hydroxide suppression mechanism, is somewhat opportunistic, with nickel aqua ions being impeded in their progress towards the cathode by the zinc hydroxide deposit. X-ray diffraction analyses had failed to detect the presence of any nickel(II) hydroxide on the surface of the electrodeposit and so was assumed not to be present. This investigation, however, has demonstrated a number of previously overlooked properties that go some way towards explaining more fully how the nickel is deposited.

- Zinc hydroxide, chemically deposited from plating solution contains nickel(II) ions that are integral with the crystal structure, and the X-ray diffraction pattern is identical to a chemically deposited sample of zinc hydroxide obtained in the absence of nickel.
- This zinc hydroxide deposit contains zinc hydroxy sulphate, a compound identified as being present in the zinc hydroxide whiskers formed during electrodeposition
- A solution of nickel(II) sulphate produced a nickel(II) hydroxide deposit that was shown to be amorphous by X-ray diffraction. Thus, if any nickel(II) hydroxide had been present in earlier work on electrodeposition, it now seems possible that it may have been amorphous; therefore nickel (II) hydroxide would not have been observed by electron diffraction.

Since nickel and zinc ions are similar in size, and of the same electrical charge, it is physically possible that nickel ions may substitute for zinc ions in the zinc hydroxide lattice. Since the readiness to form any hydroxide deposit is related to pH, and assuming that nickel enters the zinc hydroxide as a time dependent process, this would suggest that the nickel content of the deposit would increase with time. Since nickel is an effective barrier to hydrogen permeation, this seems to agree with the observations of a barrier to hydrogen permeation as contact time increases, at pH values above pH3. At lower pH values, the zinc hydroxide would not form so readily, and a contact deposit might be expected to have a different composition, perhaps one of nickel metal as was originally postulated. This different deposit, richer in nickel, would explain the overall decrease in hydrogen permeation at low pH, but with more hydrogen permeating at longer contact times.

6.5 Hydrogen Entry and Permeation

It is beyond the scope of this work to offer a detailed mathematical analysis of hydrogen permeation through a medium of increasing thickness. However, some comments can be made based on the observed transients.

It is assumed, as has been stated already, that some hydrogen ions are reduced at the electrode surface to produce hydrogen atoms. These hydrogen atoms may then combine to form molecular hydrogen, or diffuse into the surface of the electrode.

The surface upon which the hydrogen is deposited is complex and a number of simplifications must be assumed.

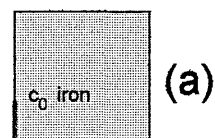
1. It is assumed that the hydrogen is reduced at a metal surface, implying either that the metal surface is not completely covered by the zinc hydroxide, or it is thin enough for the hydrogen to diffuse through it to reach the metal substrate.
2. The metal upon which the hydrogen is reduced will have recently been reduced by the reduction of hydroxide. Therefore a fresh metal surface, clear of any impurities is available.
3. Once the hydrogen is deposited the thickening electrodeposit may grow around the surface hydrogen, thereby accelerating absorption. A high hydrogen current, due to low pH conditions would be expected to produce hydrogen bubbles, but a low hydrogen current would not.

From permeation experiments, it is clear that the electrodeposit acts as a reservoir for hydrogen, continuing to release hydrogen into the substrate long after the plating current has been switched off. Also, because the transient continues to rise for about 30 minutes after the current has been switched off, the concentration of hydrogen in the electrodeposited layer must be very much higher than the substrate and the transfer of hydrogen from the electrodeposit to the substrate must be slow.

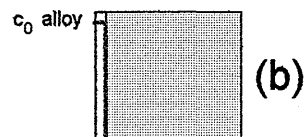
That the electrodeposit acts as a reservoir of hydrogen is not surprising, as the solubility of hydrogen in zinc is high, and hydrogen diffusivity is low,^[103,114] probably explaining the above observations. The presence of nickel in a deposit would further influence the amount and rate of hydrogen transfer to the substrate, since the diffusivity of hydrogen in nickel is very low and nickel is known to form a barrier to hydrogen, possibly with the formation of hydrides.

Assuming that the hydrogen current and rate of deposition are constant, and that the rate of diffusion of hydrogen through the electrodeposit is slow, then hydrogen profiles through the composite electrode would look something like those in Fig. 6.3, below...

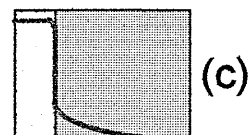
Initial situation - Bare substrate, hydrogen adsorbed on the surface.



Alloy is deposited, concurrently with hydrogen. Hydrogen concentration is initially constant.



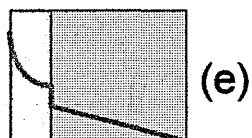
Hydrogen concentration in the alloy is higher than in the steel due to differences in hydrogen solubility between the metals. Hydrogen begins to diffuse into the substrate. Permeation is determined by the diffusion through steel.



The concentration gradient in the electrodeposit is greater than in the steel due to the low diffusivity in the alloy. Hydrogen concentration is not necessarily the same on both sides of the interface, again due to differences in solubility.



After an appreciable time, the concentration at the outer surface of the alloy begins to decrease. The interfacial concentration of also decreases. Permeation is determined by the diffusion through alloy layer.



The concentration gradient through the steel effectively remains constant, even though the gradient in the alloy does not.

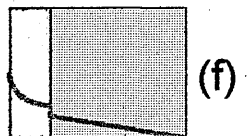


Fig. 6.3 Suggested, schematic hydrogen diffusion profiles during permeation experiments.

7 Conclusion

It was the purpose of this work to determine a rank order for the degree of embrittlement caused to a high strength steel, AISI 4340, due to zinc-nickel alloy electrodeposition and in so doing compare and contrast the embrittlement resulting from cadmium electrodeposition. Both the "as plated" and de-embrittled situations were considered.

This task was approached in two very different ways...

(i) A mechanical method of plating tensile specimens was used both with and without de-embrittlement using the slow strain rate method. This technique proved to be highly successful in detecting embrittlement, giving a degree of embrittlement in the form of the easily measured time to failure. Weibull statistical analysis was also successfully used to demonstrate the scatter in results for a given experimental regime.

The Weibull slope was found to change under certain conditions. These conditions were found to be pH dependent, indicating that two different processes resulted in two very different degrees of hydrogen uptake. It was surprising to discover that the plating conditions which were expected to produce embrittlement, that is lower pH and less efficient current density, were in fact the least embrittling conditions of those tested.

Examining the cross sectional area of failed specimens gave a numerical value for the degree of embrittlement in the form of an embrittlement index.

Whenever specimens were plated under pH conditions which were associated with either one the two different regimes of embrittlement, a low standard deviation was obtained. At a pH value intermediate between the two extremes, a high standard deviation was obtained, indicating that the sensitivity of the steel to embrittlement may be either

- very sensitive to pH, or
- surface features of the test specimen itself may play a role which becomes critical at this pH.

It has been demonstrated thoroughly that although cadmium electroplate is extremely embrittling, a de-embrittling bake will give what appears to be a 100% recovery in terms of degree of embrittlement. Under the worst conditions, zinc-nickel alloy can be almost as embrittling as cadmium, but with a greater scatter in times to failure. Again a de-embrittling bake allows 100% recovery. Most promising of all of the results is that if the plating solution is maintained at a pH of about 3, little or no embrittlement is observed. Thus by careful monitoring of the plating solution pH a commercial plating solution could be developed which would not require a de-embrittlement process. This would save time and reduce production costs.

(ii) Permeation studies designed, not to measure bulk diffusion parameters, but the amount of hydrogen entering and permeating a shim electrode, also indicated the presence of a barrier to hydrogen entry at lower pH values. A rank order for the amount of hydrogen entering and permeating a steel electrode closely matched the rank ordering from the mechanical tests.

From Permeation studies it was established that a chemical deposit was at least partially responsible for the barrier effect, since the time taken between pouring in the plating solution and switching on the plating current had a pronounced effect on the total amount of hydrogen permeating the shim electrode. The trend in the effect of this "contact time" was reversed between pH values below and above pH3, in that above pH3, the increasing contact time reduced hydrogen uptake while below pH3, increasing contact times increased the total amount of hydrogen permeating the electrode.

The evidence of both mechanical and permeation experiments lead to the postulation that nickel formed an initial deposit on the surface of the electrode before the alloy electrodeposit was established, but that two distinct, pH dependent deposits may be present.

Surface analysis using Auger and XP Spectroscopy successfully identified that the postulated barrier under pH2 plating conditions was in fact nickel, or a nickel rich deposit, immediately adjacent to the steel substrate. The contact deposit at pH2 was found to be richer in nickel than was the deposit formed at pH4.4. More nickel was detected in the contact deposit formed at pH4.4 after longer contact times. This may simply mean that the contact deposit had thickened sufficiently for the nickel content to be measured, or it may indicate that nickel ions are absorbed, or dissolve in the zinc hydroxide matrix, as a function of time.

Samples of hydroxide precipitates obtained by slowly adding sodium hydroxide solution to solutions of zinc sulphate, nickel sulphate and plating solution revealed some significant facts.

- The structure of the zinc hydroxide was, according to X-ray analysis, effectively identical to that found on the surface of anomalous co-deposits, that is, zinc hydroxy sulphate.
- The nickel hydroxide precipitate was amorphous.
- Using dimethyl glyoxime to test for the presence of nickel in the precipitate obtained from the plating solution proved that nickel was present in the deposit.

From these experiments, it was felt that the results could be used to shed fresh light on the hydroxide suppression mechanism of anomalous co-deposition and a model for the mechanism was presented.

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Appendix

A1 Statistical Analyses

A1.1 Weibull Statistical Analysis

In the absence of a notch in the tensile specimens, failure will occur randomly at sites of surface imperfections, or significant subsurface defects. Such failures produce individual results which, due to their random nature, cannot be expected to be reproducible. However, with large populations of results, patterns of behaviour will be repeated and a statistical distribution can be obtained which can be used in analysis.

Weibull analysis^[61] was originally developed for the analysis of the times to failure for the brittle failure of ceramics and glass. Fracture of these materials was dependant upon the size and distribution of imperfections throughout the material. Yokobori^[62] adapted the technique to the brittle failure of steel.

An application of Weibull analysis to the probability of survival of a tensile specimen similar to those used in this report is given in more detail, elsewhere,^[63,64] but a brief explanation is given below.

Weibull analysis assumes that the scatter in times to failure is due to a time dependant mechanism according to the relationship :-

$$P_s = e^{-x(t-t_i)}$$

Where	P_s	=	Probability of Survival of a specimen
	t	=	Time to failure, in hours.
	t_i	=	Incubation time, in hours, below which there are no failures. ($P_s = 1$)
	x	=	The Weibull slope, representing the probability of a failure occurring within a given time, in hours ⁻¹

Further useful relationships can be identified, such as:-

$$\begin{aligned} t &= \text{Mean time to failure.} \\ &= t_i + 1/x \end{aligned}$$

Figure A1, overleaf, illustrates these terms.

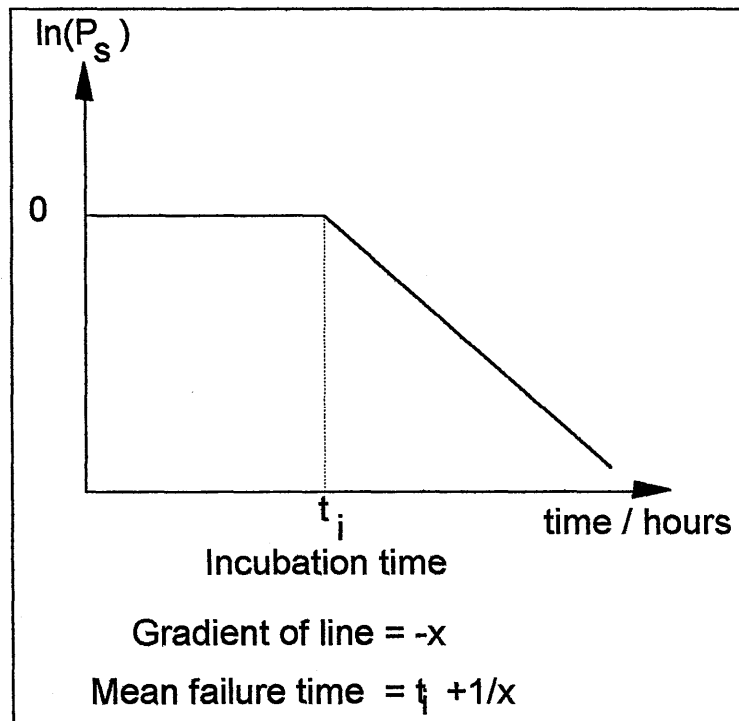


Fig. A.1 Schematic representation of the Weibull Analysis as applied to slow strain rate times to failure.

In a situation in which hydrogen is introduced into a specimen prior to testing and the extent of hydrogen embrittlement is due to the time dependence of the hydrogen diffusing to incipient crack nucleation sites, then the value of t_i will be a measure of susceptibility to embrittlement. The Weibull slope, x , gives the scatter of failure times and is an indication of the range of defect sizes within the specimens.

Statistical scatter in results is expected and found. Where the scatter is due to a single anomalous measurement, apparently inconsistent with the remainder of the group, it is possible that this may be due to experimental error, an unusually large difference in the sizes of the most significant stress raising defects within that specimens, or an excessive ingress of hydrogen for reasons which have not been accounted, resulting in a substantial difference in the time to failure. Where the scatter is large over the whole population of results, this is considered to be due to variations in mobile hydrogen within the specimen. Such scatter is indicative of the randomness associated with hydrogen embrittlement due to the complex nature of hydrogen uptake, diffusion into the substrate and interaction with randomly distributed stress raising defects.

A1.2 Student's t-Test

In a given population of values, it is expected that there will be a normal distribution of the values. Taking a second, small population, also with a normal distribution, it could be determined if the second population could belong to the first or not. Variances of the two groups may be compared statistically to see how close their population parameters lie. If the parameters lie within acceptable limits then the two populations may be considered, with some justification, to belong to the same population.

To state that any two groups of numbers belong, with certainty, to the same population is impossible. It is possible, however, by examining the variance of the two groups to determine a probability that they belong to the same group, thus giving a statistical confidence in linking the groups.

Let two groups of numbers be referred to by subscripts as 1 and 2.

Standard deviation	=	σ
Variance	=	σ^2
Mean value of the population	=	μ

Taking a random sample from each of two populations, of sizes n_1 and n_2 , the sample variance of these smaller, representative groups can be determined.

Standard deviation of the small group	=	s
Variance (small group)	=	s^2
Pooled standard deviation of both groups combined	=	s_p
Mean value of the small group	=	$\bar{x}$

If α represents the significance factor, that is the probability of the two groups belonging to the same distribution, then the two samples are considered **not** to be from the same population if...

$$t > \frac{(x_1 - x_2) - (\mu_1 - \mu_2)}{s_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

$$s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$$

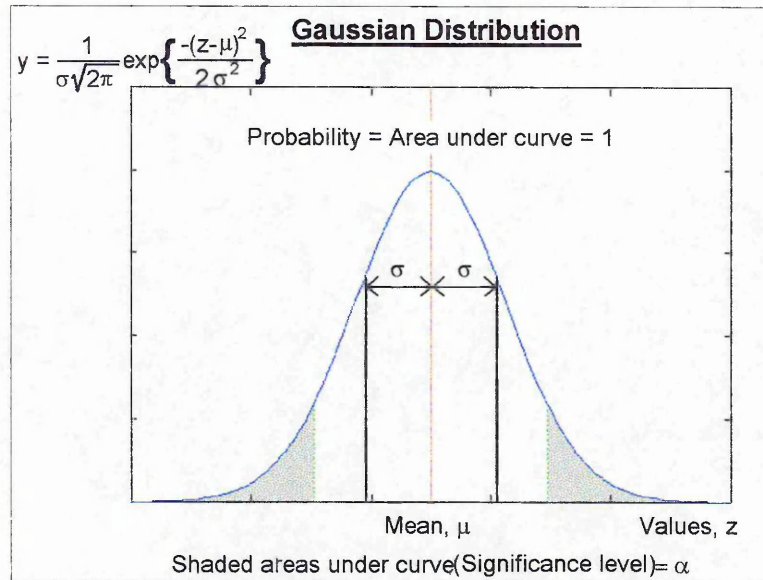


Fig. A.2 Normal distribution and the Student t-test.

For a given pair of samples, the degree of freedom, v , is given by ...

$$v = n_1 + n_2 - 2$$

For any given values of α and v , a limiting value for the t-statistic can be determined from tables. If the calculated value of $t(n_1 + n_2 - 2, \alpha)$ from experimentally determined values is less than the tabular value, then it is reasonable to assume that the two sample are from the same distribution with a probability of $100(1 - \alpha)\%$.

In this work, α is taken to be 0.05, thus the probability of the two samples belonging to the same distribution is $100(1 - \alpha)\%$, or 95%. This is the value generally used in this type of work.

A.2 Hydrogen Diffusion at a Right Angled Corner

Diffusion of hydrogen into a semi infinite medium bounded by parallel sides is described by the following boundary conditions...

$$0 < x < L \quad c = 0 \text{ at } t = 0$$

$$x = 0 \text{ and } x = L \quad c = c_0 \text{ at } t > 0$$

The solution of Fick's Second Law of Diffusion with these boundary conditions is given by^[50]...

$$c = c_0 \left[1 - 4 \sum_{k=1}^{\infty} \frac{1}{(2k-1)\pi} \sin\left(\frac{(2k-1)\pi x}{L}\right) \exp\left(\frac{-(2k-1)^2 \pi^2 D t}{L^2}\right) \right]$$

The hydrogen profile created by a computer calculation using this equation is given in Fig. 1, below...

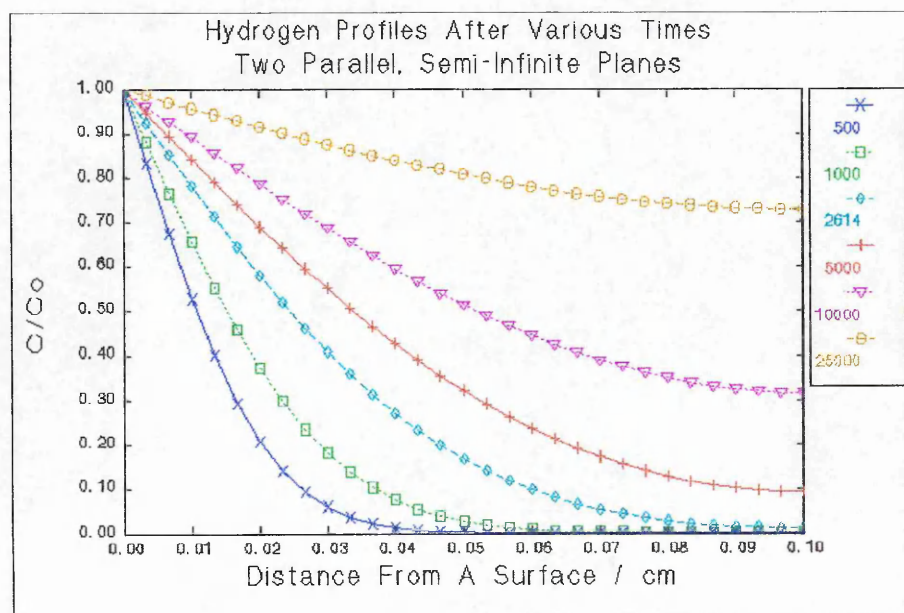


Figure A.3 One dimensional diffusion.

The solution above applies to hydrogen influx to a wide sheet where the effects of corners can be neglected. However, at a right angled corner, with hydrogen diffusing into the material normal to all faces, hydrogen concentrations would be expected to be greater in the those areas where the perpendicular diffusion fronts overlap.

Carslaw and Jaeger^[41] have calculated the analogous diffusion of heat **efflux** from a right angled corner and have given the function as...

$$v = f(x,a).f(y,b)$$

...for all surface temperatures kept at zero.

Where...

a and b denote the lengths of the sides of the rectangle

v denotes the resultant temperature at points (x,y) throughout the specimen.

x and y represent displacements along orthogonal faces of the rectangle.

Mathematically, under the assumptions of Fick's Laws, temperature can be replaced by hydrogen concentration, providing that the constant for diffusion is also changed. In addition, Carslaw and Jaeger point out that the profile for **influx** of heat (hydrogen) to a material would be given by...

$$f_{in}(x,y) = 1 - f_{out}(x,y)$$

Functions $f(x,a)$ and $f(y,b)$ for efflux are related to that given earlier for a semi infinite medium bounded by parallel sides and are given by...

$$c_{x,a} = c_{0,a} \cdot 4 \sum_{k=1}^{\infty} \frac{1}{(2k-1)\pi} \sin\left(\frac{(2k-1)\pi x}{a}\right) \exp\left(\frac{-(2k-1)^2 \pi^2 D t}{a^2}\right)$$

$$c_{y,b} = c_{0,b} \cdot 4 \sum_{n=1}^{\infty} \frac{1}{(2n-1)\pi} \sin\left(\frac{(2n-1)\pi y}{b}\right) \exp\left(\frac{-(2n-1)^2 \pi^2 D t}{b^2}\right)$$

Where k and n are integers and D is the coefficient of diffusion.

Profiles for various times are given in Figs A.5 to A.10. These graphs show a number of hydrogen profiles for various times and depths into a tensile specimen. The representation is as if viewed from a direction perpendicular to the x -axis, as shown in Figure A.4 Each graph considers displacements up to the mid-point of a specimen only, since the profile is symmetrical about the plane normal to the centre of each face. Thus, Hydrogen diffuses into the medium along the x -axis in a positive direction. Each line represents a profile at a different depth and each graph represents a different time interval from the start of diffusion. Calculations are based on a tensile specimen with a cross-sectional area of 2×2 mm and a diffusion coefficient of $2.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

Although all positions on the surface are at equal hydrogen concentration, just below the surface, hydrogen profiles rise more rapidly towards the corner. Thus at any given time, the corner section has the higher hydrogen concentration and is therefore more likely to include the site of a brittle fracture. This is borne out by the fracture surfaces of tensile specimens.

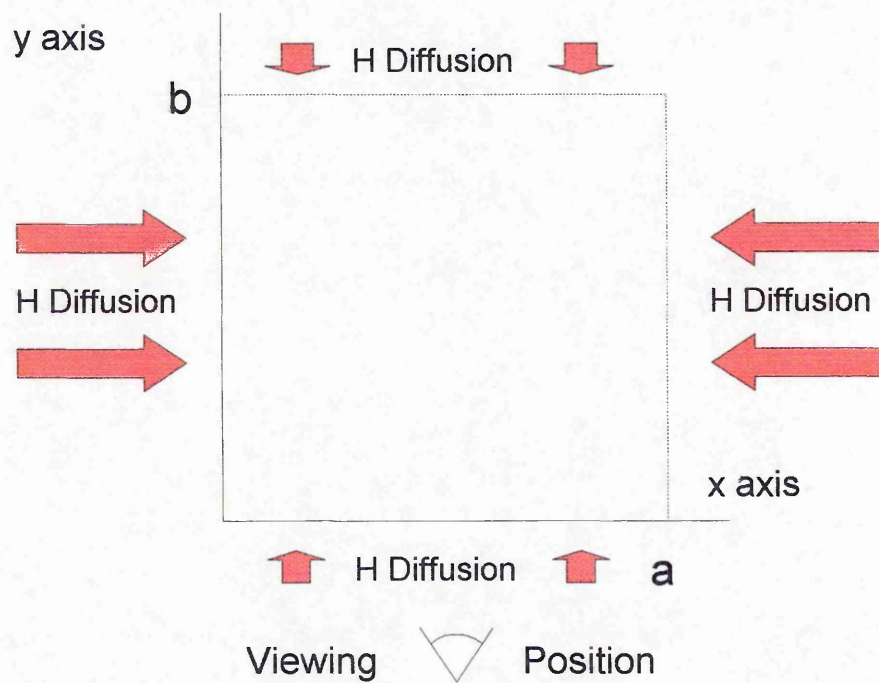


Fig. A.4 Cross-section through a tensile specimen showing the viewpoint for the graphs in Figs A.5 to A.10

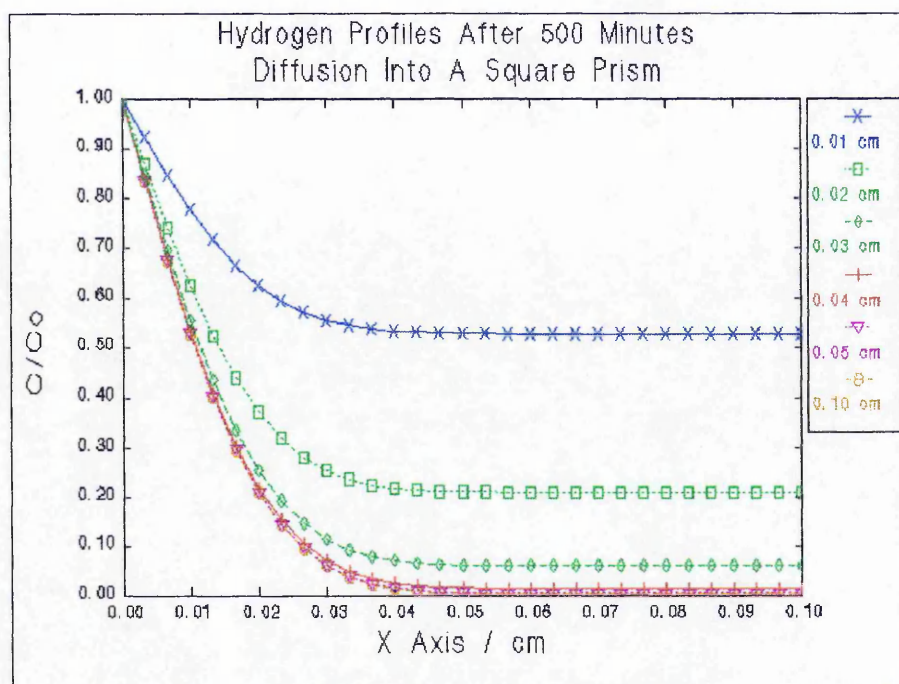


Fig. A.5 Hydrogen profiles - 500 minutes.

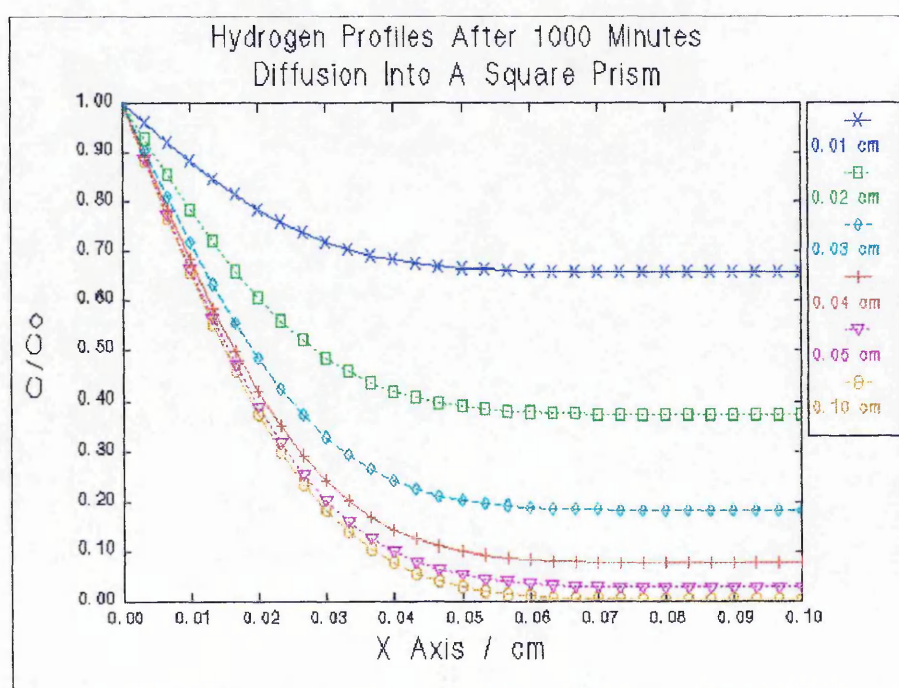


Fig. A.6 Hydrogen profiles - 1000 minutes

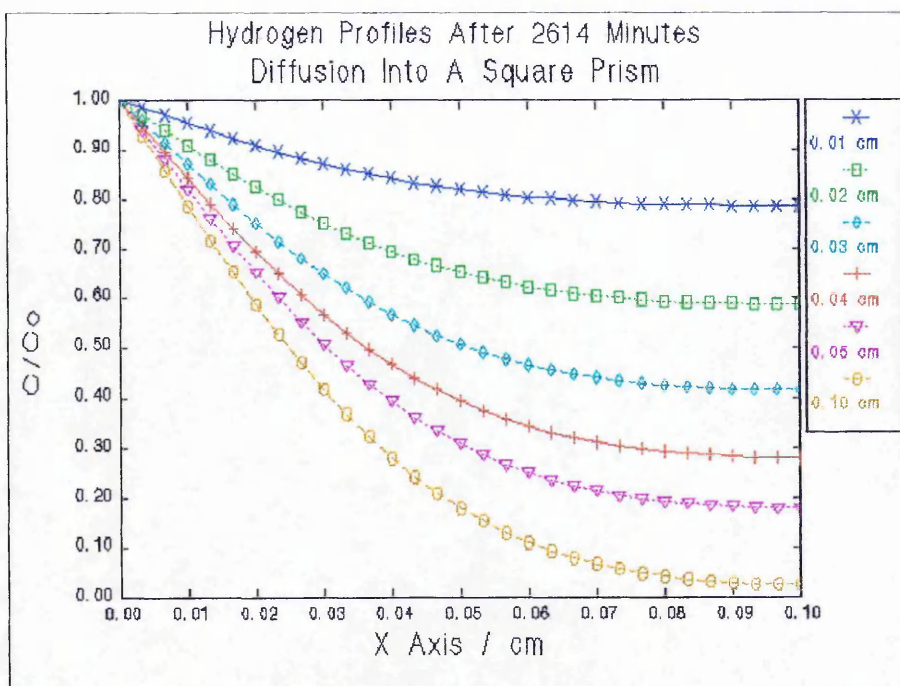


Fig. A.7 Hydrogen profiles - 2614 minutes

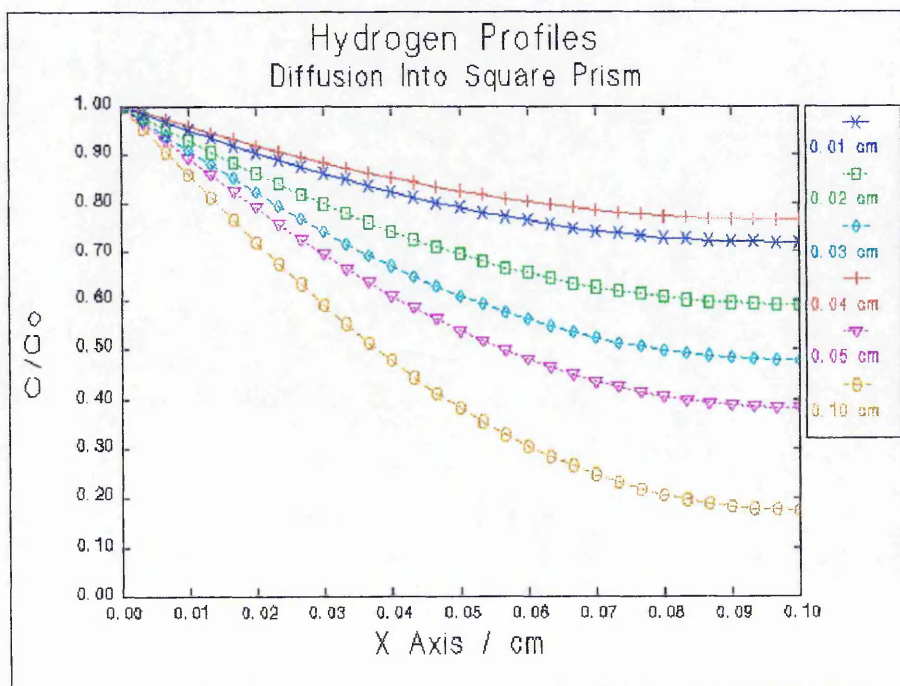


Fig A.8 Hydrogen profiles - 5000 minutes

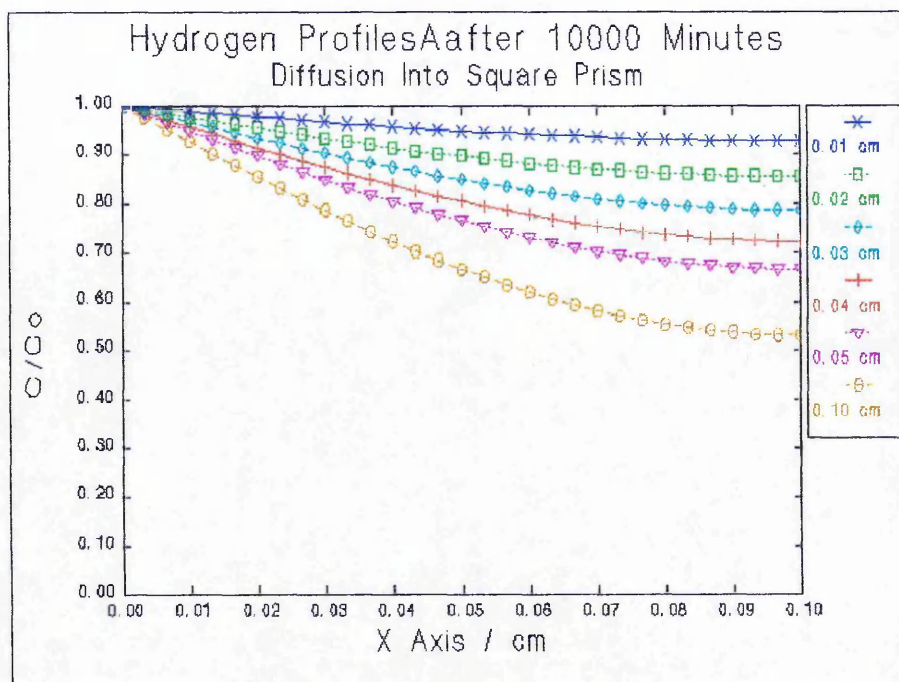


Fig A.9 Hydrogen profiles - 10000 minutes

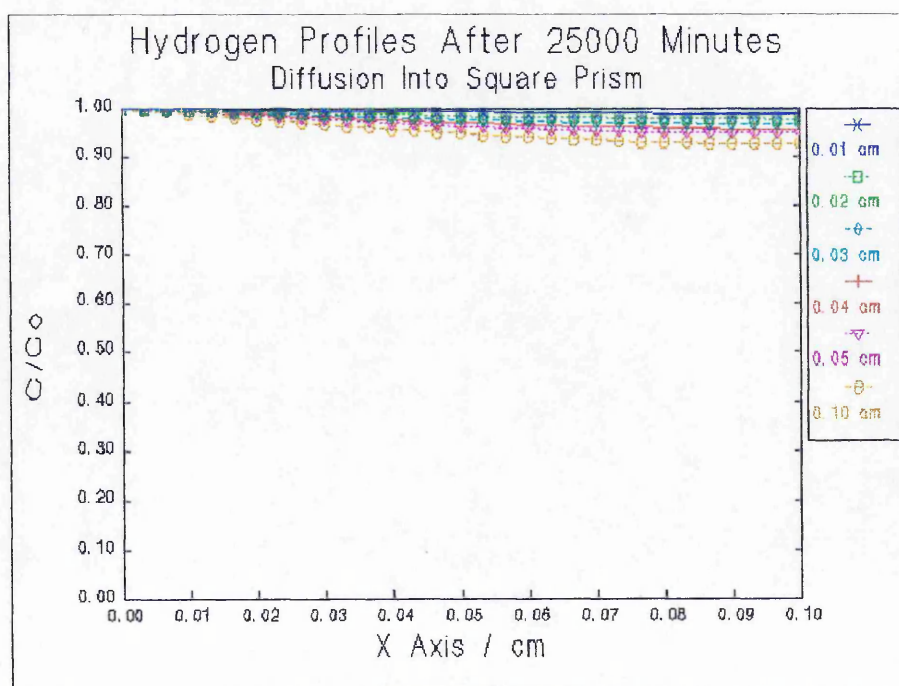


Fig A.10 Hydrogen profiles - 25000 minutes

A3 Current Efficiency by pH Measurement

This method assumes that the only cathodic reaction, other than the deposition of the metal involves the removal of hydrogen ions. It is also assumed that removal of an amount of hydrogen ions involves an equivalent amount of cathodic electrons, not simply a chemical reaction such as neutralisation.

$$\begin{array}{llll} \text{Initial pH} & = & A & \text{Initial } [\text{H}^+] & = & 10^{-A} \\ \text{Final pH} & = & B & \text{Final } [\text{H}^+] & = & 10^{-B} \\ \text{Change in } [\text{H}^+] & = & 10^{-B} - 10^{-A} \text{ moles dm}^{-3} & & & \\ \therefore \text{Amount of } \text{H}^+ & = & V(10^{-B} - 10^{-A}) \text{ moles} & & & \\ \text{Where } V & = & \text{Volume of solution in dm}^3 & & & \end{array}$$

If the current produced 100% hydrogen reduction...

$$\begin{array}{llll} \therefore \text{Amount of } \text{H}^+ & = & i t / z F \\ \text{Where } i & = & \text{total applied current in amps} \\ t & = & \text{time during which the current is passed in seconds} \\ z & = & \text{ionic charge} & = & 1 \\ F & = & \text{Faraday constant} & = & 96487 \text{ C mole}^{-1} \end{array}$$

Efficiency of the hydrogen reduction is given by...

$$\therefore \text{Hydrogen Efficiency} = z F V (10^{-B} - 10^{-A}) / i t \times 100\%$$

$$\text{or Plating Efficiency} = (1 - z F V (10^{-B} - 10^{-A}) / i t) \times 100\%$$