COATING TECHNOLOGY OF HIGH STRENGTH STEELS WITHOUT HYDROGEN EMBRITTLEMENT

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ABSTRACT

Pre-treatment and electroplating of especially low alloyed high tensile strength steel components (such as those used in the aircraft industry) can be followed by a delayed hydrogen-induced fracture known as hydrogen embrittlement. The entire coating process has to be controlled to avoid any failure. As estimated by the fracture behaviour of differently prepared samples using a special constant load test, atomic hydrogen being evolved during the coating process and penetrating into the base metal is mainly trapped close to the interface base metal-coating. During a baking procedure after plating, the atomic hydrogen can effuse through the coating as well as being more homogeneously distributed in the bulk of the base metal, both reducing the risk of embrittlement. This effect seems to be evident by tensile tests (sustained load tests and incremental step load tests) but up to now there has been no analytical proof. Now investigations using the glow discharge optical emission spectroscopy (GDOES) show that the hydrogen distribution in the coating, at the interface and within the bulk material, can be directly measured. The results give an improved knowledge and enable one to work out process parameters and test procedures for coating techniques to be more effective to avoid hydrogen embrittlement.

KEYWORDS

high strength steel, electroplating, corrosion protection, hydrogen embrittlement, glow discharge optical emission spectroscopy, GDOES

INTRODUCTION

Electrochemical pre -treatment and plating processes of especially low-alloyed high-strength steels (such as those used in the aircraft industry) can be followed by hydrogen embrittlement. However almost every known industry is concerned as at least some, if not a substantial quality of susceptible parts as fasteners cams, pins, rivets, springs are used everywhere. Hydrogen embrittlement occurs at the atomic level, within a metallic material. Therefore, there are no visible, exterior signs of potential failure of a part, product, or structure. The consequences are much more devastating than corrosion because failures are unexpected, occurring with no warning as the crack initiates at the atomic level, within the metal, below the surface (area of three dimensional plastic deformation), whereas corrosion occurs on the surface of the metal and can be visually detected.

STATE OF ART

Controlling hydrogen embrittlement is technically challenging because of the requirement of trying to measure the interaction of the smallest atom in the periodic table, hydrogen, on an atomic level within metals. Besides the concentration of atomic hydrogen the metal structure and strength as well as the tensile stresses (residual and applied) are the most important parameters. Classically, time-to-failure sustained load tests are conducted to evaluate the threshold stress of a component, above which the delayed fracture will occur and below which fracture will never occur. A new test method to measure the threshold stress in an accelerated, economical and quantitative way has been developed applying the Incremental Step Loading technique[1].

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In recent investigations[2] high strength fuse holder rings where conventionally semi-bright zinc plated, heat treated and mounted on a cylindrical pin that way, that the stress was close to the yield point but below any plastic deformation. The fracture behaviour, depending on the post -plating heat treatment after a two - month testing time is shown in Figure 1. Each point in the diagram represents the behaviour of 100 samples and therefore fulfils statistical demands.

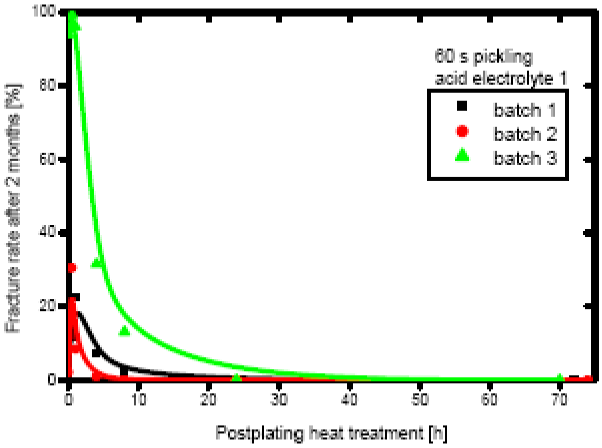

Fig. 1 - Fracture rate of Zn -plated fuse holder rings with respect to the annealing time at 220°C

The fracture rate first increases with bake-out time, up to a maximum and finally approaches zero with further increasing time. The reason for that behaviour is supposed to be an absorption-diffusion mechanism of hydrogen for bright or semi-bright zinc coatings[3]. According to electrochemical hydrogen permeation measurements and hydrogen concentration measurements using the hot extraction technique, a large amount of hydrogen is trapped in the zinc coating area. It is supposed that the distribution is not uniform however, and the highest concentration should be close to the zinc-base metal interface. With increasing temperature hydrogen diffuses mainly into the base metal as the zinc itself forms an efficient diffusion barrier. As expected this follows in a dramatical increasing of the fracture rate up to unity. With increasing bake-out time, however, a new equilibrium is read where, due to effusion and diffusion effects the hydrogen content in the base metal falls below the local critical concentration and no embrittlement occurs further on. Up to now however no analytical proof for this reasonable interpretation of the tensile test experiments has been given. Now, as efficient Glow Discharge Optical Emission Spectroscopy (GDOES) is available, hydrogen distribution in metals and profiles can be measured. The knowledge of the local distribution of hydrogen during the plating process and in the plated component is essential for the procedure to avoid any embrittlement.

EXPERIMENTAL RESULTS AND DISCUSSION

The analyse of samples containing gases can be considered as one of the problematic affects in the solid sample analysis. As far as hydrogen detection is concerned there are only few techniques and GDOES is the most favourable for detecting hydrogen in thick metal coatings like Zn coatings plated for corrosion protection.

In this technique the sample is sputtered using Argon ions from a low pressure plasma, where, consequently, the sputtered atoms are excited and emit light. Figure 2 shows the experimental setup.

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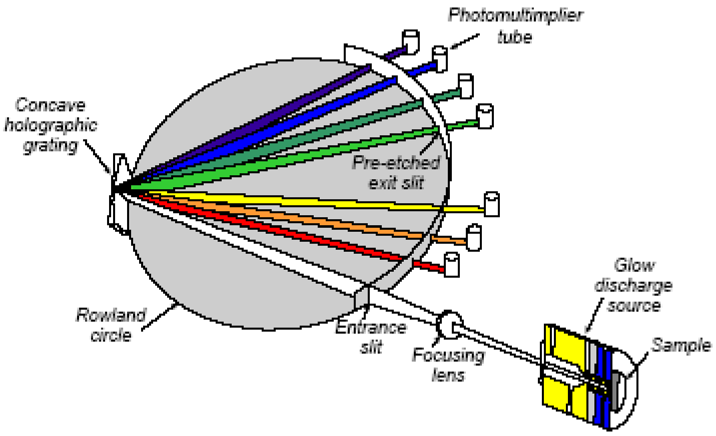

Fig. 2 - The Grimm-type GD-OES source and the UV-VIS polychromator, as the commercial LECO SDP -750 spectrometer

The glow discharge is optically analysed by an UV-VIS polychromator, where the characteristic H-line of the Lyman series (λ = 121.5 nm) is detected by a photomultiplier tube. A commercial surface depth profile GDOES instrument LECO SDP-750 (LECO Technik GmbH, Munich, Germany) was used with a Grimm-type glow discharge source (GDS) having a 2.5 mm anode diameter for the investigations[4]. The hydrogen detection limit is 1 ppm. The hydrogen depth profile of an embrittlement-free Zn-plated sample using a commercial semi-bright low acid electrolyte is represented in Figure 3.

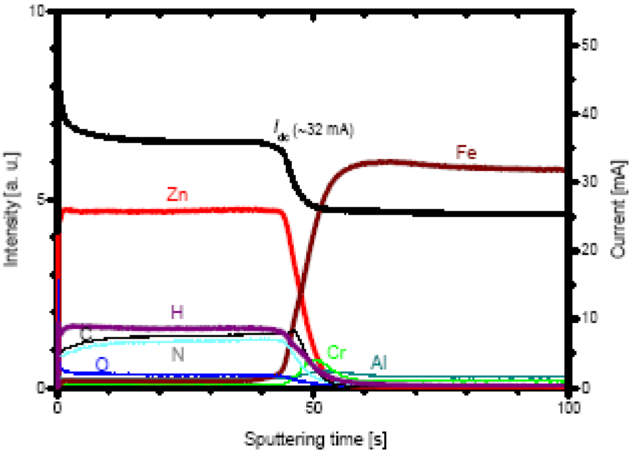

Fig. 3 - Depth profiling of an electrolytically deposited Zn-layer on steel substrate

Following the profile of Zn and Fe it can be concluded that a high and constant hydrogen content is detected within the Zn layer and no significant hydrogen is present in the base metal. Obviously hydrogen is incorporated into the layer, probably as $Zn(OH)_2$ and organic additive derivates respectively.

The hydrogen distribution of a Cd-plated sample according to the aircraft regulations with a semibright appearance and therefore porous structure (low-hydrogen-embrittlement Cd) is shown in Fig. 4

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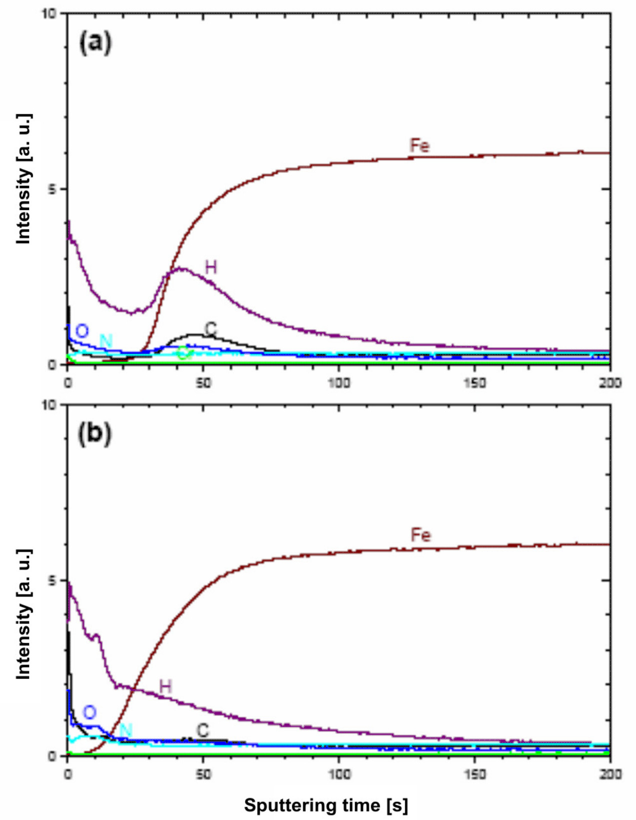

Fig.4 – Depth profiling of a Cd-plated steel substrate as plated (a) and after baking (b).
(The Cd-Signal is not shown)

Although the Cd-Signal is not shown, the coating-substrate interphase can be recognized by following the Fe-scan. In the as-plated situation (4a) obviously Hydrogen is stored in the Cd-layer and a maximum is shown in the interphase area. After a baking procedure at 200 ° C for 8 hours (4b) the hydrogen content in the layer remains approximately constant as an indication, that this hydrogen is chemically bound e.g. as hydroxide not being diffusionable. The maximum however vanishes and the hydrogen content in the base metal decreases in agreement with the model discussed above.

Similar behaviour can be expected for Zn electrodeposition. Fig. 5 shows the results for a Zn – plated and passivated (blue chromate) sample.

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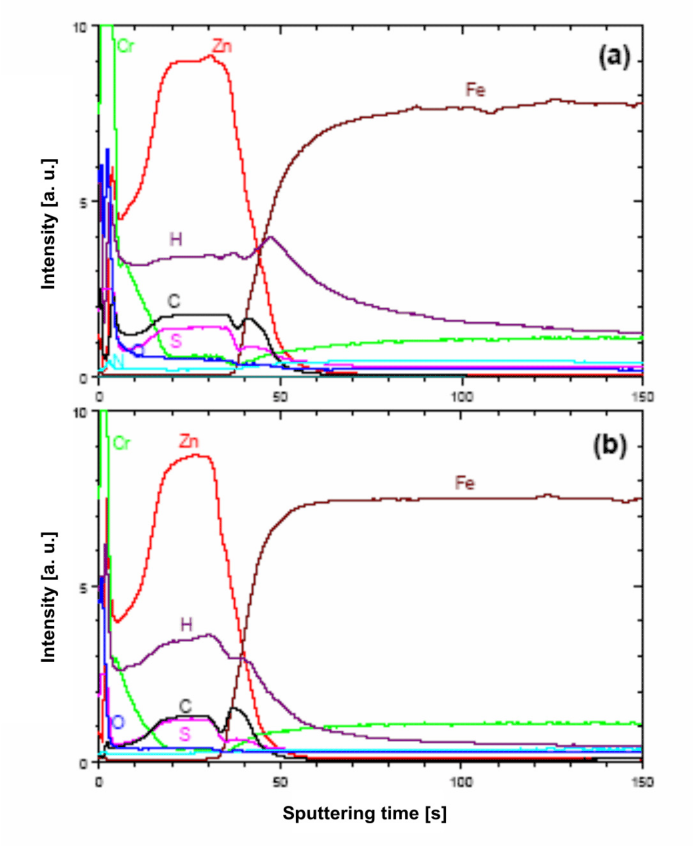

Fig. 5 – Depth profiling of a Zn-plated and passivated (blue chromate) steel substrate as plated (a) and after baking (b)

Hydrogen in the layer again comes from incorporated hydroxide and the carbon content represents incorporated organic brightners used for plating a bright Zn layer. The hydrogen maximum at the interphase in the as plated sample (5a) again vanishes and the amount of hydrogen in the substrate is decreased and more homogeneously distributed after the baking procedure (5b).

Of high interest is to plate a thin Ni layer (1 – 2 µm) on the substrate succeeded by the Zn plating process. Because of kinetic electrochemical reasons (hydrogen overvoltage, hydrogen recombination behaviour) less hydrogen will be stored at the Ni-Fe-interphase and further on during the Zn plating on the Ni-covered steel substrate [4]. This however is topic of ongoing experiments. The result could be, that a baking procedure can be reduced or even will be not necessary any more. Fig 6 shows the result for a Ni and Zn plated steel substrate.

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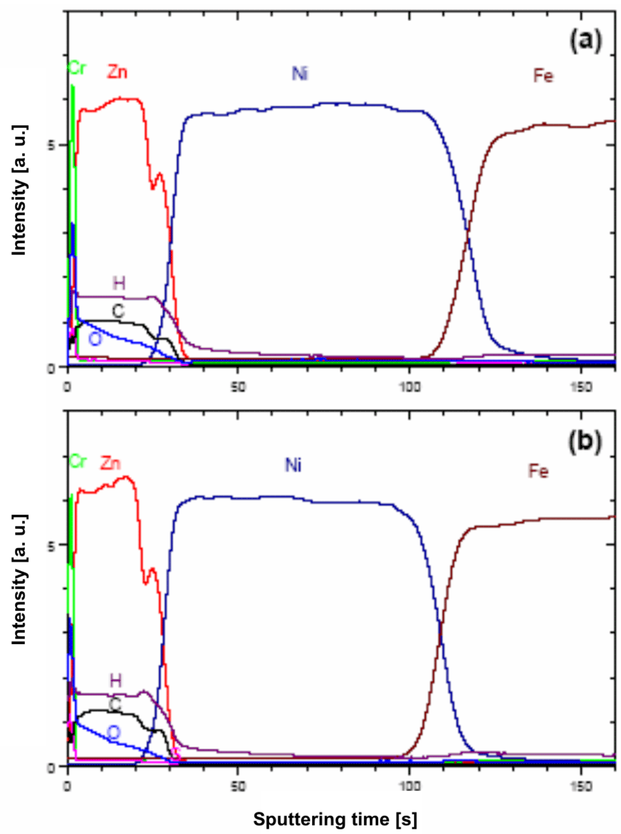

Fig. 6 – Depth profiling of a passivated (blue chromate) Zn plated steel substrate with a thin Ni interlayer as plated (a) and after baking(b)

The depth profile of hydrogen (6a) clearly shows no significant enrichment at the Ni-substrate interphase. The level is about the same as in the unaffected bulk material. The profile at the second interphase Zn-Ni is very similar, supporting overall the electrochemical considerations presented above. As expected the depth profile is not influenced by the baking procedure (6b). In addition similar results have been received in plating a ZnNi-alloy of about 12 to 15 percent Ni, which can be used as a replacement for Cd in aircraft industry. There is indication, that in both cases a baking procedure will be not necessary to avoid any hydrogen embrittlement. Ongoing experiments should prove this in near future.

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