Hydrogen Embrittlement in Coating Technology – Measurement & Testing

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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 metals is mainly trapped close to the interface base metal-coating. During a baking procedure after plating the atomic hydrogen can be removed from the traps and 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 emission optical spectroscopy (GD-OES) 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.

1. 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.

2. State of the 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).

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. 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 exceeding the trap energy, 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 (GD-OES) is available, hydrogen distribution in metals and profiles can be measured.

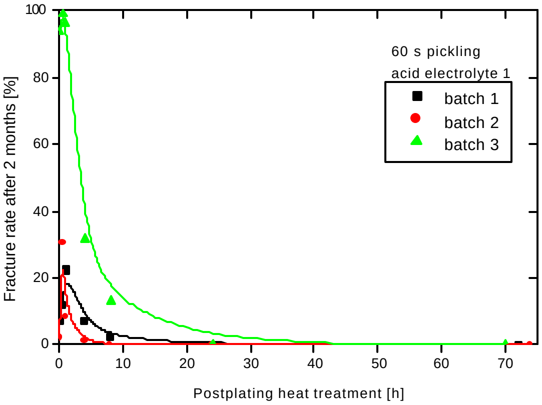

Fig. 1- Fracture rate of Zn-plated fuse holder rings with respect to the annealing time at 220°C

3. Experimental Results

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 especially GD-OES and Nuclear Reaction Analysis (NRA) are the very few analytical techniques capable to deal with. In the first case, the sample is sputtered using Argon ions from a low pressure plasma, where, emit light. The second method uses the principle of resonance depth profiling, the resonance reaction $^{1}H(^{15}N, \alpha\gamma)^{12}C$ being able to be used for monitoring the spatial distribution of hydrogen in material, however up to 1-2 µm in depth. Easier, cost effective and designed especially for depth profiling of thick layers (such as Zn coatings in the range of several µm thickness), GD-OES constitutes a powerful tool for hydrogen analysis in metals. Figure 2 shows the experimental setup.

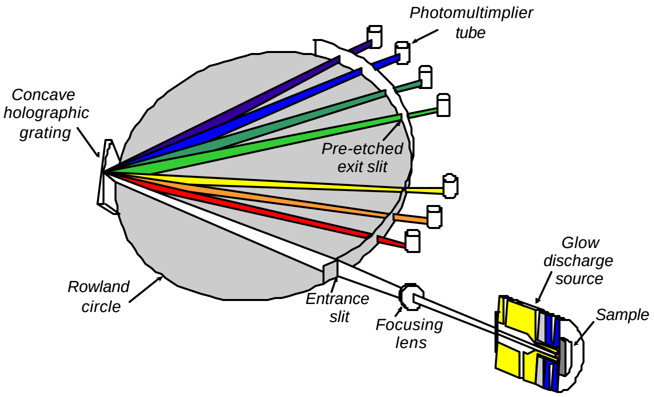

Fig. 2 - The Grimm-type GD-OES source and the UV-VIS polychromator, as the commercial LECO SDP-750 spectrometer

The glow discharge is optically analysed by an UV-VIS polychromator, where the characteristic H_α-line of the Lyman series (λ = 121.5 nm) is detected by a photomultiplier tube. A commercial surface depth profile GD-OES 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. It should be mentioned that in conventional GD-OES a problem with hydrogen arises as contaminations in the GDS such as residual moisture, hydrocarbures from conventional oil pumps, leak, etc. generates hydrogen which affects considerably the spectral and other properties of the GDS and the sputter rate resulting in a modified crater profile. Extensive studies dedicated to the control of the contamination have been performed in our laboratory and corrections are already implemented. Similar alterations can be observed independent of the H-source as e.g. for the spectra of TiH_2 as a sample or Ti using an argon glow discharge containing small quantifies of hydrogen(4). Obviously in both cases of hydrogen origin, a dissociation process of the molecular hydrogen takes place.

The hydrogen depth profile of a Zn-plated sample using a commercial semi-bright low acid electrolyte is represented in Figure 3.

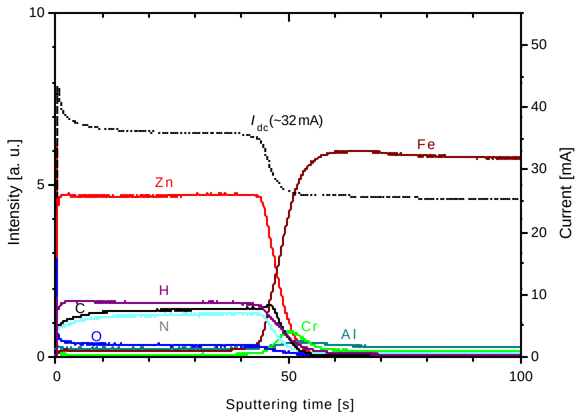

Fig. 3 - Depth profiling of an electrolytically deposited Zn-layer

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. For comparison the Figures 4 and 5 show the depth profile of a Zn layer produced by hot dip galvanizing and a bulk zinc sample, both not containing a remarkable hydrogen concentration.

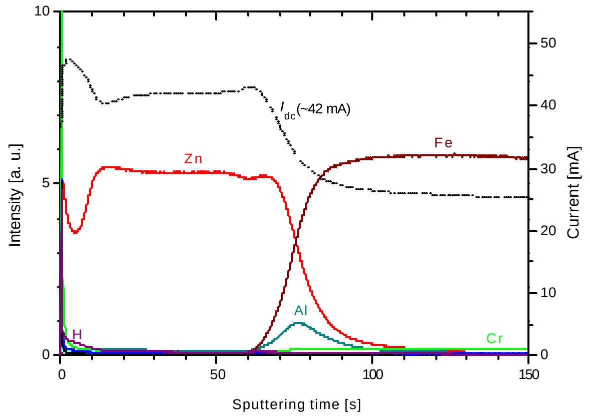

Fig. 4 - Depth profiling of a Zinc layer deposited by hot dip galvanising

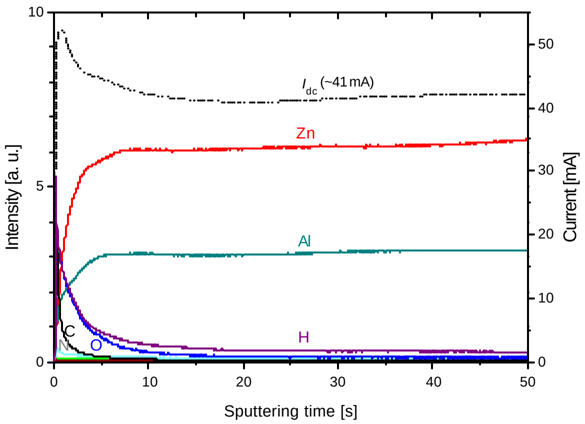

Fig. 5 - Depth profiling of a bulk Zn-sample

A further example is given for a CoPtW-layer electrolytically deposited on a copper substrat. Figure 6a shows that GD-OES depth profiling results in a remarkable hydrogen content within the coating. No hydrogen can be found in the copper base metal, which is known to form a very efficient diffusion barrier for hydrogen. After annealing the sample at 400°C for 24 h (Figure 6b) no hydrogen can be detected any more, indicating its vanishing due to an effusion process.

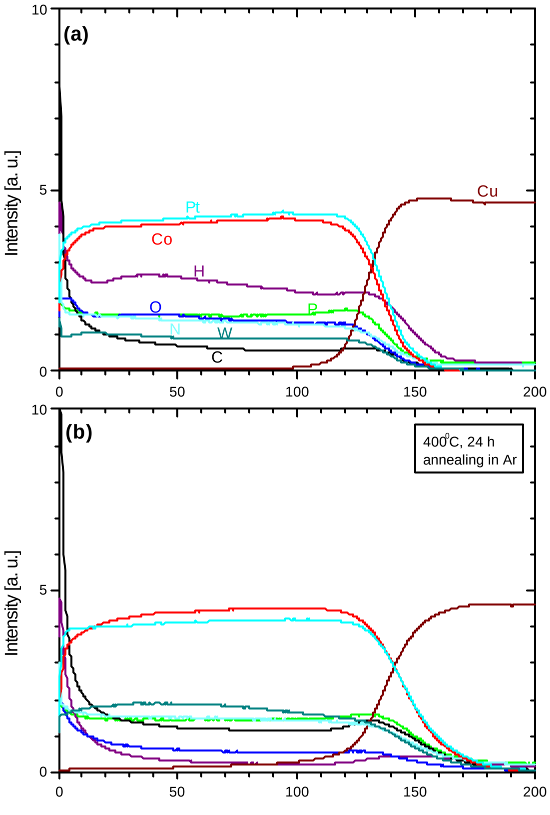

Fig. 6 - Depth profiling of an electrolytically deposited CoPt-layer as plated (a) and after annealing (b)

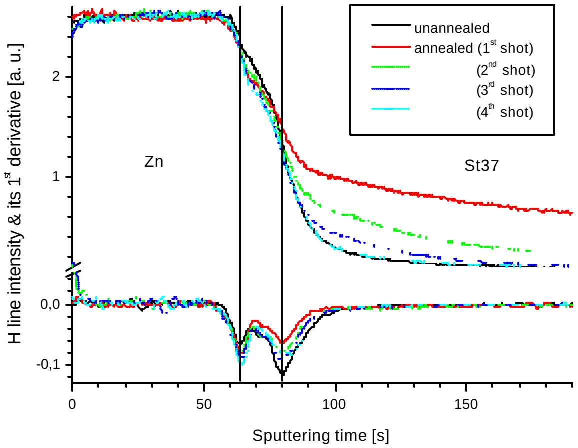

Fig. 7 – Depth profiles of electrolitically deposited Zn layer: (i) unannealed (black curve) and (ii) annealed (red curve) 24 h, 220^{0}C in Argon.

Depth profiling of samples being annealed for 24 hours in an argon atmosphere at 220°C (Figure 7) gives evidence that the hydrogen chemically bound in the layer itself is not influenced. Further on hydrogen being trapped in the layer–base metal interface diffuses and effuses resulting in a lower concentration and more homogeneous distribution in the base metal. Thus following the interpretation of the results of sustained load test experiments.

4. Conclusions

Depth profiling of hydrogen of electrolytically deposited Zn layers confirm the diffusion/effusion model based on sustained load fracture tests. This is supporting the procedure, that the zinc plating process of especially high strength material can be controlled with respect to hydrogen embrittlement by co-plating sensible samples such as fuse holder rings and testing them in a sustained load fracture test. The advantage of this cost-effective procedure is that the plating process of every batch necessary can be monitored and documented even with respect to statistical demands.

5. References

1. ASTM F 519: *Standard Test Method for Mechanical Hydrogen Embrittlement Evaluating of Plating Processes and Service Environments*

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