Quantitative & Localized Hydrogen Analysis of Electroplated Material

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Pre-treatment and electroplating of especially low alloyed high tensile strength steel components 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 the same time 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) and has been proven by localized glow discharge emission optical spectroscopy (GD-OES). Now quantitative and localized analysis of hydrogen is possible as certified reference materials have been developed. 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. Examples will be discussed.

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.



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

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. Glow Discharge Optical Emission Spectrometry (GD-OES) - an already well-established analytical technique routinely used for the in-depth elemental analysis of metallic coatings of thickness in the range of some μm – has been systematically applied for measuring of the hydrogen distribution in metals. One should note that the GD-OES depth profiles can be routinely quantified by means of calibration via certified reference materials (CRM) for almost all the elements of the periodic table. However, the quantification of hydrogen is not possible yet, due to the lack of reference materials with certified amounts of hydrogen. The basic problem in the certification process is the long-term stability of the hydrogen concentration, which is very poor according to the wellknown high diffusion coefficient of hydrogen even at room temperature. We have recently carried out a survey from which three classes of coatings have been selected as being suitable as (layered) CRM for hydrogen. One should also note that on the other hand, even the qualitative hydrogen depth profiles are often useful for individual applications.

3. Experimental Results

The analyse of samples containing gases can be considered as one of the problematic aspects in the solid sample analysis. As far as hydrogen detection is concerned there are only a very few analytical techniques capable to deal with:

Analytical method	Detection of H	Quantification of H	Limitations
HE	\checkmark	4	no local information (i.e., no depth profiles)
NRA	4	\checkmark	analysed depth of up to only 1-2 µm
ERDA	4	\checkmark	"
GD-OES	1	_	lack of H-CRM

For example Hot Extraction (HE) does not provide local information on the hydrogen concentration in a material. Both Nuclear Reaction Analysis (NRA) and Elastic Recoil Detection Analysis (ERDA) are able to quantify the in-depth distribution of hydrogen, however up to only 1-2 μ m depth, which is rather insufficient for many practical applications. In the case of GD-OES, the sample is sputtered using Argon ions from a low pressure plasma, where, consequently, the sputtered atoms are excited and emit light. Easier, cost effective and designed especially for depth profiling of thick layers (such as Zn coatings in the range of several μ m thickness), GD-OES constitutes a powerful tool for hydrogen analysis in metals. The experimental set-up of the commercial surface depth profile GD-OES instrument LECO SDP-750 (LECO Technik GmbH, Munich, Germany) is shown in ref. (4) and further analytical figures of merit of the method are comprised in the review ref. (5).

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 ⁽⁶⁾.

The hydrogen depth profile of a Zn-plated sample using a commercial semi-bright low acid electrolyte is represented in Figure 2.



Fig. 2 - 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. Analysis with Raman spectroscopy in order to identify the compounds containing hydrogen are in progress. For comparison Fig. 3 show the depth profile of a Zn layer produced by hot dip galvanizing , which obviously does not contain a remarkable hydrogen concentration.



Fig. 3 - Depth profiling of a Zinc layer deposited by hot dip galvanising

Coming back to the case of Zn coating *electrolytically* deposited, GD-OES depth profiling of samples being annealed for 24 hours in an argon atmosphere at 220°C (Figure 4) 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.



Fig. 4 – Depth profiles of H only in an electrolytically deposited Zn layer: (i) unannealed (black curve) and (ii) annealed (blue curve) 24 h, 220^oC in Argon.

An innovative Zn-plating process of high interest has been recently developed, where a thin Ni layer is plated preceding the Zn plating in order to avoid the heat post-treatment ⁽⁷⁻⁹⁾. For electrochemical reasons during the Ni plating process as well as at the Ni surface itself the hydrogen recombination process to molecular hydrogen is preferred. As a result the partial pressure of hydrogen at the surface is less and therefore hydrogen penetration into the base metal is reduced. The hydrogen profile in Figure 5a shows no significant hydrogen at the base metal-Ni interface and about the same at the Ni-Zn interface. As expected no change is found after a conventional heat treatment at 220°C for 2 hours (Figure 5b). Of course this result has to be

confirmed by sustained load tests as hydrogen embrittlement is a complex system property where the local hydrogen concentration in the area of critical tensile stresses within a component is deciding.



Fig. 5 - Depth profiles of an electrolytically deposited and blue chromated Zn-layer with a Ni intermediate layer (a) as plated and (b) after heat treatment.

A further example is given for a magnetic CoPtW-layer electrolytically deposited on a copper substrate. 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 CoPtW-layer as plated (a) and after annealing (b)

As already mentioned, in order to quantify the hydrogen signals found by GD-OES into concentrations one needs reference materials with *certified* amounts of hydrogen. At present

there is no CRM suitable for GD-OES calibration of H (www.comar.bam.de). Various trials in the past of production of bulk materials (charged with H) or hydride pellets have failed, as the H concentration was not stable over longer periods of time (even at room temperature). The reliable alternative has been proven to be some thick *coatings* containing H in *bound* form and hence unable to diffuse easily even at higher temperatures. An immediate example of such a potential reference coating is just offered by electrolytical Zn (see Figure 4). First test samples with various hydrogen concentrations in the Zn coating have been produced and supposed to homogeneity and stability investigations. The in-depth and lateral homogeneity of the H concentrations in the macroscopic range is tested by GD-OES (qualitatively only); the first ~1.5 μ m from the top surface are quantitatively analysed by ERDA and NRA, respectively. The results of the H concentrations for three different electrolytical Zn coatings can be put together as follows in Figure 7a.



Fig. 7 – GD-OES depth profiling of H of three various concentrations in electrolytically Zn coatings together with the absolute H concentrations as measured in the first ~1.5 μ m depth by ERDA and NRA, respectively (a); stability test after 5 months (b).

As one can see in Figure 7a, both ERDA and NRA quantitative results are in a good agreement each other and the correlation of the H concentrations with the H signals found in GD-OES is not linear. Further investigations related to this point are necessary, nevertheless matrix effects were expected. Exact determination of the sputter rates (necessary to be known for new CRMs) are planned, however they are difficult to be performed with high accuracy (by weighing). First stability measurements for this type of coatings have been performed by GD-OES after 5 month and show a quite good stability of the hydrogen concentrations (Figure 7b). Measurements of both in-depth and lateral homogeneity of the hydrogen concentration in the microscopic range by Secondary Ion Mass Spectrometry (SIMS) are in progress. An extension of the range of application of H-CRM for other analytical methods is obviously welcome.

In order to gain a better insight in the calibration curve of hydrogen, other matrices containing stable concentrations of bound H have been selected from our survey.



Fig. 8 – GD-OES depth profile of a W-DLC(H) coating deposited on steel (a); GD-OES depth profiles of H only for two different H concentrations determined by ERDA (b).

W-DLC hard coatings containing hydrogen, see Figure 8, have been established as a second class of coatings where the homogeneous concentration of H keeps stable.

Another suitable candidate of H-CRM can be Si(H), see Figure 9. The existent Si(H) layers are thin layers (having a thickness in the range of ~100-200 nm) destined for NRA; production of thicker layers is under discussion.



Fig. 9 – *GD-OES depth profile of a Si(H) layer on Si wafer.*

4. Conclusions

Hydrogen depth profiling 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. Nevertheless accurate quantified results for hydrogen are possible to be obtained only by means of calibration via reference materials. Due to the lack of existent CRM for H, a survey on potential candidates of CRMs for H have been carried out and three relevant coatings containing hydrogen in various concentrations have been selected. Systematic measurements on the homogeneity and stability of the hydrogen concentration in the selected coatings are in progress by using a combination of the few analytical methods able to detect hydrogen, namely GD-OES, ERDA and NRA, respectively.

5. References

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