Technical Article

Hydrogen Embrittlement in Coating Technology – Measurement & Testing

Pre-treatment and electroplating for low alloy 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 behavior of differently prepared samples using a special constant load test, atomic hydrogen evolved during the coating process and penetrating into the basis metal is primarily trapped near the basis metalcoating interface. During baking after plating, the atomic hydrogen can be removed and effuse through the coating and also be more homogeneously distributed in the bulk of the basis 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.

Our current investigations using 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 provide enough information to point to process changes and test procedures so that hydrogen embrittlement can be avoided.

The pretreatment and plating processes for low-alloyed high-strength steels (such as those used in the aircraft industry) can be followed by hydrogen embrittlement. This is a concern in most industries as at least some, if not all parts, including fasteners, cams, pins, rivets and springs are susceptible. Hydrogen embrittlement occurs at the atomic level, within a metallic material. Therefore, there are no visible, external signs of potential failure. The consequences are much more devastating than corrosion because the failures are unexpected, occurring with no warning as the crack initiates at the atomic level, within the metal and below the surface. By

contrast, corrosion occurs only on the surface of the metal

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and can be visually detected.

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Fig. 1—Fracture rate of Zn-plated fuse holder rings with respect to annealing time at $220^{\circ}C$ ($428^{\circ}F$).



Nuts & Bolts: What This Paper Means to You

Pre-treatment and electroplating of low alloy high tensile strength steel aircraft components can be followed by hydrogen embrittlement, which can only be relieved by baking. Until now, there was no good way of finding where the hydrogen was. The coating? The steel? In between? Here the authors have come up with a way of doing just that, by glow discharge emission optical spectroscopy. The results provide enough information to point to process changes and test procedures so that hydrogen embrittlement can be avoided.



Fig. 3—Depth profile of a zinc layer deposited by hot dip galvanizing.



Fig. 4—Depth profiles of an electrolytically deposited Co-Pt-W layer: (a) as plated and (b) after annealing.

State of the Art

Controlling hydrogen embrittlement is technically challenging because of the need 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 metallic structure, strength and 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 were conventionally semi-bright zinc plated, heat treated and mounted on a cylindrical pin such that the stress was close to the yield point but below any plastic deformation. The fracture behavior as a function of the post-plating heat treatment after a two-month testing time is shown in Fig. 1.

Each point in the diagram represents the behavior of 100 samples and therefore fulfills statistical demands. The fracture rate first increases with bake-out time, up to a maximum and finally approaches zero with further time. The reason for this behavior is said to be an absorption-diffusion mechanism of hydrogen in the case of 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. It is thought however that the distribution is not uniform, and the highest concentration should be close to the zinc-basis metal interface. As the increased temperature exceeds the trapping energy, hydrogen diffuses primarily into the basis metal as the zinc itself forms an efficient diffusion barrier. As expected this is followed by a dramatic increase in the fracture rate up to unity. With increasing bake-out time, however, a new equilibrium is reached where, because of effusion and diffusion effects, the hydrogen content in the basis metal falls below the local critical concentration and no further embrittlement occurs. 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) has become available, hydrogen distribution profiles in metals can be measured.

Experimental Results

The analysis of samples containing gases is one of the more problematic aspects in solid sample analysis. As far as hydrogen detection is concerned, GD-OES and Nuclear Reaction Analysis (NRA) are among the very few analytical techniques capable of dealing with it. In the first case, the sample is sputtered using argon ions from a low pressure plasma, where, consequently, the sputtered atoms are excited and emit light. The second method uses the principle of resonance depth profiling, the resonance reaction ¹H(¹⁵N, $\alpha\gamma$)¹²C used for monitoring the spatial distribution of hydrogen in the material, up to 1 to 2 μ m (39 to 79 μ -in.) in depth. Easier, cost effective and designed especially for depth profiling of thick layers (such as zinc coatings in the range of several micrometers in thickness), GD-OES is a powerful tool for hydrogen analysis in metals. Figure 2 shows the experimental setup.

The glow discharge is optically analyzed by a UV-VIS polychromator, where the characteristic H_{α} -line of the Lyman series ($\lambda = 121.5 \text{ nm}$) is detected by a photomultiplier tube. A commercial surface depth profile GD-OES instrument^{**} was used with a Grimmtype glow discharge source (GDS) having a 2.5 mm anode diameter for the investigations.⁴ The hydrogen detection limit was 1 ppm.⁵



Fig. 5—Depth profiles of an electrolytically deposited cadmium-layer: (a) as plated and (b) after heat treatment. The cadmium signal is not shown.

It should be mentioned that in conventional GD-OES, a problem arises with hydrogen as a contaminant in the GDS from such sources as residual moisture, hydrocarbons from conventional oil pumps, leaks and the like. This hydrogen considerably effects the spectral and other properties of the GDS and also the sputter rate which results in a modified crater profile. Extensive studies into contaminant control have been performed in our laboratory and corrections are already commercially available. Similar alterations can be found that do not depend on a hydrogen source, as, *e.g.*, for the spectra of TiH, as a sample or Ti using an argon glow discharge containing

** LECO SDP-750, LECO Technik GmbH, Munich, Germany

small quantities of hydrogen.⁴ In both cases of hydrogen origin, a dissociation process of the molecular hydrogen takes place.

The following two examples will illustrate how powerful a tool GD-OES is in analyzing hydrogen in plated samples not necessarily related to the embrittlement problem. Figure 3 shows the depth profiling for a zinc layer on steel formed by hot dip galvanizing. As expected no hydrogen is found. Any hydrogen originating from the pickling pretreatment and penetrating the basis metal effuses during the high temperature galvanization. The minimal hydrogen signal detected at the surface of the sample is caused by contamination and is an indication of the sensitivity of GD-OES. The aluminum at the zinc-steel interface originates in the molten bath where it is added to avoid the formation of brittle alloy phases.

The second example involves a Co-Pt-W layer electrodeposited on a copper substrate. Figure 4a shows that GD-OES depth profiling shows significant hydrogen content in the coating. No hydrogen is found in the copper basis metal, which is known to form a very efficient diffusion barrier to hydrogen. After annealing the sample at 400°C (750°F) for 24 hours (Fig. 4b) hydrogen can no longer be detected.

The hydrogen distribution of a porous plated cadmium layer used in the aircraft industry (a low embrittlement coating) is shown in Fig. 5. Although the cadmium signal is not shown in the diagram, the interface can be clearly delineated from the iron signal of the basis metal. While hydrogen is incorporated in the cadmium layer the following maximum indicates that a significant amount of hydrogen is stored in the interface (Fig. 5a). After heat treatment at 220°C (428°F) for 8 hours, the hydrogen content in the layer is more or less unchanged showing that it is chemically bound and therefore not diffusible. In agreement with the model given above the maxi-

Sputtering Time, s mum at the interface disappears and the level within the basis metal is reduced. Hydrogen is now able to effuse and diffuse.

Figure 6 shows the profiles for a zinc-plated and blue-chromated sample in the as plated condition (Fig. 6a) and after heat treatment (Fig. 6b). Again chemically bound hydrogen is found in the semibright plated zinc layer. The carbon and sulfur comes from codeposited brighteners. In order to get information on the quantity of hydrogen in the zinc layer, additional NRA measurements were carried out.⁶ Because of the unavailability of certified standards containing hydrogen, the GD-OES quantification of hydrogen calibration curve can be derived by adding hydrogen in gaseous form in controlled quantities. For specially prepared samples, *i.e.*, electrolytic zinc coatings of 1 µm depth, NRA yields hydrogen concentration values of about 10 atomic %, homogeneously distributed in the zinc layer. Unfortunately, the zinc-steel interface could not be



Fig. 6—Depth profile of an electrolytically deposited and blue chromated zinc layer: (a) as plated and (b) after heat treatment.



Fig. 7—Depth profiles of an electrolytically deposited and blue chromated zinc layer with an intermediate nickel layer: (a) as plated and (b) after heat treatment.

evaluated, because the uncertainty of the localization of the reaction involving hydrogen at $\sim 1~\mu m$ depth was too high.

An innovative zinc-plating process of high interest has been developed, where a thin nickel layer is plated prior to zinc plating to avoid the post heat-treatment.⁷⁻⁹ For electrochemical reasons, related to the nickel plating process and the nickel surface itself, the process of hydrogen recombination to molecular hydrogen is preferred. As a result, the partial pressure of hydrogen at the surface is less and therefore hydrogen penetration into the basis metal is reduced. The hydrogen profile in Fig. 7a shows no significant hydrogen at the basis metal-nickel interface and similar results are noted at the nickel-zinc interface. As expected no change is found after heat treatment at 220°C (428°F) for 2 hours (Fig. 7b). 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 stress within a component is the deciding factor.

Conclusions

Depth profiling of hydrogen in electroplated components using GD-OES confirms the diffusion/effusion model based on sustained load fracture tests. For layers forming a barrier for hydrogen as zinc or cadmium, hydrogen is essentially trapped at the layer-basis metal interface. By heat treatment, hydrogen can be released and allowed to effuse as well as diffuse. This results in a more homogeneous distribution at a non-critical level. At the same time, the results show that hydrogen embrittlement associated with plating high strength materials can be controlled by co-plating appropriate samples such as fuse holder rings and testing them in a sustained load fracture test. This cost-effective procedure allows monitoring and documenting of data for every batch run through the plating processes.

Acknowledgments

The authors wish to thank FEM Schwäbisch Gmünd, Lufthansa, Enthone (all Germany) and Boeing (USA) for preparing the test samples used in this study. Support of the colleagues from laboratory I.41, Beam Analysis, BAM in performing the NRA analysis is also gratefully acknowledged.

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