Long-delay Hydrogen Embrittlement Phenomena In Plating High-strength Steel Components

This is an edited version of the Garland Award paper delivered at the 32nd AESF Aerospace/Airline Plating Forum, Tulsa, OK (1996).

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Electrochemical pretreatment and plating processes of especially low-alloyed high-strength steels can be followed by hydrogen embrittlement. Damage may occur, particularly with unfavorable values of the surface/volume ratio and contingent on the hardening conditions of the components. This is the case for conventional zinc plating but also for new zinc alloy coatings often used as replacement for cadmium. In this study, the long-delay embrittlement behavior of Zn-plated fuse holder rings was investigated. This phenomenon can be significantly correlated with the pickling procedure and the post-coating heat treatment. Additional factors influencing surface roughness, texture and morphology of the components can be observed, however. The mechanism seems to be of electrochemical nature, affecting the rate of atomic hydrogen evolution during the plating process. A test procedure for evaluating long-delay embrittlement has been developed.

Low-alloyed high-strength steels must be protected against corrosion by proper surface treatment. Atomic hydrogen evolved during pretreatment and metal deposition, as well as corrosion processes, can penetrate the base metal and cause embrittlement phenomena. If proper parameters for construction design, and for the pretreatment and plating process, including a post-plating baking for embrittlement relief are chosen, hydrogen embrittlement can be avoided for all applications. Components with unfavorable values of the surface/volume ratio are regarded as critical because a large surface allows much hydrogen to penetrate the substrate. Therefore, high-strength fuse holder rings were plated and tested in constant load tests up to one year for embrittlement failures.

Sample Preparation

Fuse holder rings of C75 steel (referring to German Standard DIN 471) with an outer diameter of 5 mm and thickness of 0.5 mm were used for the experiments. For an inner diameter of 4.7 mm, the surface/volume ratio was about 6 mm^{-1}. The samples were tempered to a hardness value of about 550 HV, as listed in the table. Four different batches of equal chemical composition but differently tempered and, therefore, different surface roughness characteristics were used. Two batches with high roughness values were polished electrochemically for reference purposes.

The fuse holder rings were first degreased for 10 min in an alkali hydroxide and alkali silicate solution at 50 to 60 °C, followed by a pickling procedure from 0 to 600 sec in 12-percent HCl and at 20 °C. In all cases, a pickling inhibitor was used, which, according to hydrogen-permeation experiments, reduced hydrogen uptake of the steel base material.

For practical applications, the fuse holder rings were plated using eight different zinc electrolytes. Six were taken from the production line while two were made directly for the experiments. Three electrolytes were cyanidic, two were alkaline and cyanide-free, and three were of low acid character. All layers deposited were semi-bright. The current density for the barrel plating process was 1 A/cm^2 and the layer thickness was between 12 and 15 µm. Thickness and morphology of the coatings were monitored by cross section and weight measurements.

Normally, heat treatment after the pickling and plating process (bake-out) was performed at 220 °C between 15 min and 72 hr. For the entire investigation, 175,000 fuse holder rings were plated and tested for hydrogen embrittlement.[1]

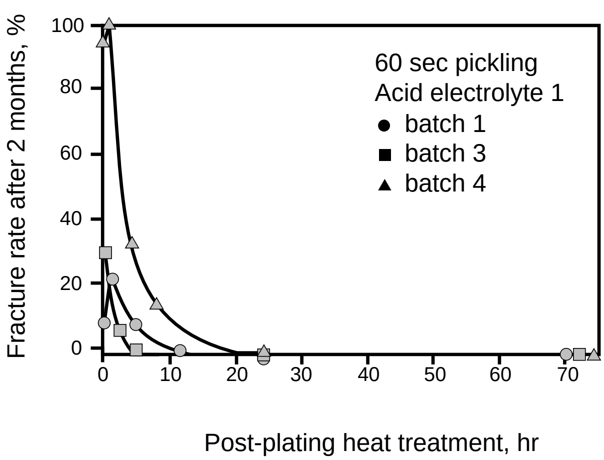

Fig. 1—Fracture dependence on post-plating heat treatment at 220 °C.

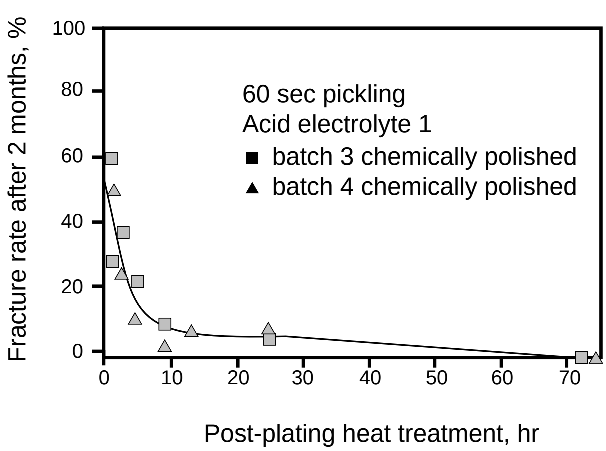

Fig. 2—Fracture dependence on post-plating heat treatment at 220 °C.

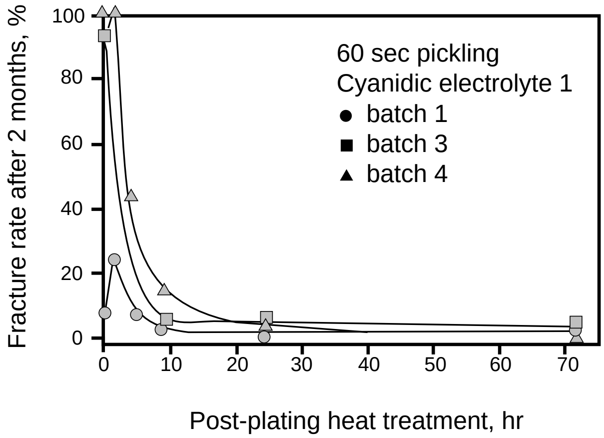

Fig. 3—Fracture dependence on post-plating heat treatment at 220 °C.

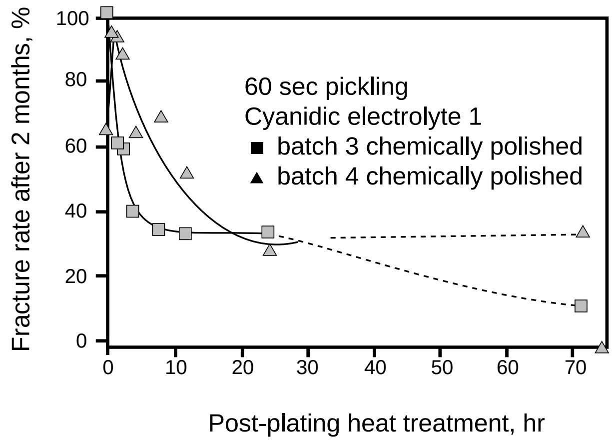

Fig. 4—Fracture dependence on post-plating heat treatment at 220 °C.

Results

Several test methods are available to demonstrate low hydrogen embrittlement properties of electroplated components.[2] They include ASTM 200 h: 75-percent Ultimate Tensile Strength; constant load tests, as defined in ASTM Standard F 519; the notched C-ring test; and a slow strain rate extension-to-fracture test. For the experiments reported, a special constant-load test was used that is easily applicable close to the production line and that allows analysis of long-delay embrittlement phenomena: The fuse holder rings with an inner diameter of 4.68 ±0.01 mm were mounted on a cylindrical pin with a diameter of 5.0 mm. According to calculations,[3] the stress is close to the yield point but below any plastic deformation.

The fracture behavior, dependent on post-plating heat treatment after a two-month testing time for three steel batches pretreated and plated in the same manner, is given in Fig. 1. Each point in the diagram represents the behavior of 100 samples. The fracture rate first increases with bake-out time, up to a maximum, then approaches zero with increasing time. The reason for that is the absorption-diffusion mechanism of hydrogen for bright or semibright zinc coatings.[4] According to hydrogen permeation and hydrogen concentration measurements, a very large amount of hydrogen is stored in the zinc coating. The distribution is not uniform, however, and the highest concentration is found close to the zinc/base-metal interface. With increasing temperature, this hydrogen diffuses mainly into the base metal as the zinc layer itself forms an efficient diffusion barrier. This is followed by a dramatically increasing fracture rate. With increasing bake-out time, however, a new equilibrium is reached where, because of diffusion effects, the hydrogen content in the base metal obviously falls below the critical concentration.

Figure 1 also shows the influence of the surface morphology of the samples on the fracture behavior. The fracture characteristic for electropolished fuse holder rings is shown in Fig. 2. With respect to SEM-investigation, the surface of batches 3 and 4, after the polishing process, did not show any significant difference. Both samples typically show a reduced fracture rate for low bake-out times, whereas the rate is relatively high in the long time period. The data seem to be reasonable inasmuch as the polishing results in a smooth, homogeneous and stress-free surface. On one side, this leads to a reduced concentration of hydrogen on the base metal surface during the plating process and, on the other side, the more uniform zinc coatings formed on the polished substrate form a more efficient hydrogen barrier. Comparable and even more significant results are obtained if zinc is deposited using a cyanide electrolyte (see Figs. 3 and 4).

The influence of different pickling times on the fracture behavior is shown in Fig. 5. For this experiment, all other process parameters (degreasing, plating, heat treatment) were kept constant. For a pickling time between 15 and 60 sec, the values for the fracture rate do not differ much and can be represented by the dashed area in Fig. 5. Only if very long pickling times were used did high fracture rates occur, even

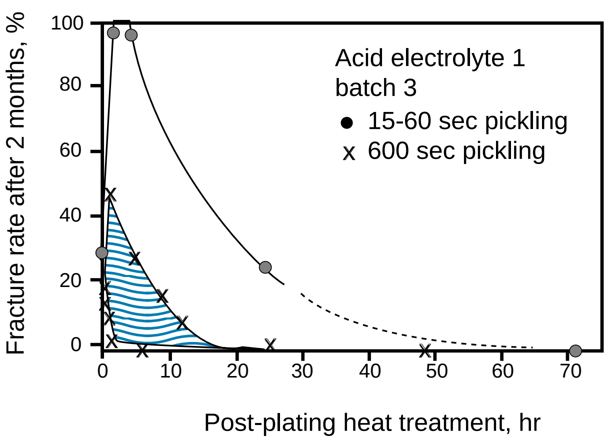

Fig. 5—Fracture dependence on post-plating heat treatment at 220 °C.

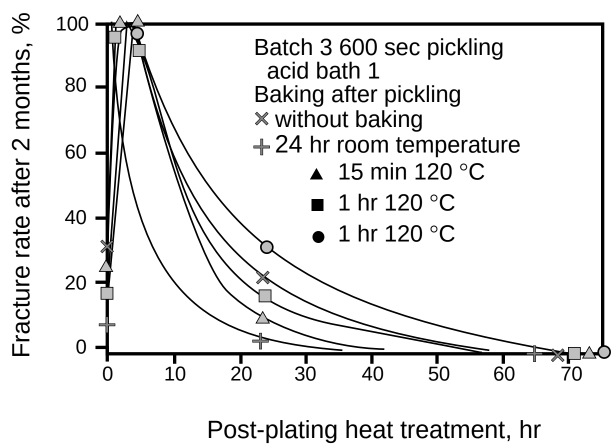

Fig. 6—Fracture dependence on post-plating heat treatment at 220 °C.

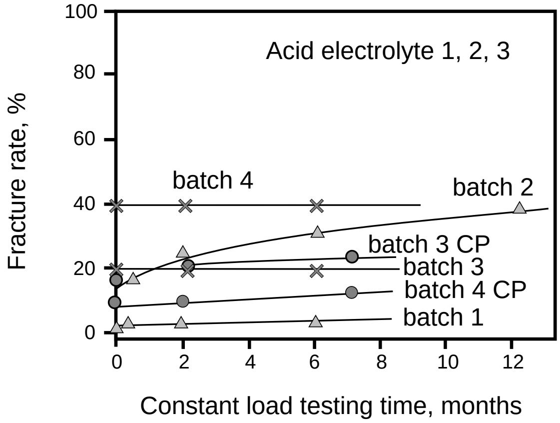

Fig. 7—Fracture dependence on testing time (CP: chemically polished).

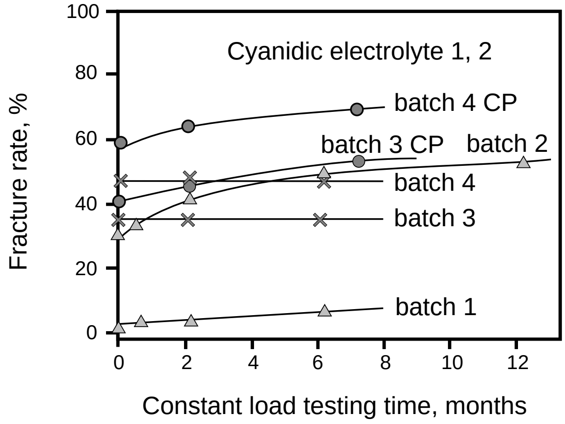

Fig. 8—Fracture dependence on testing time (CP: chemically polished).

after long bake-out times, up to 70 hr. Remarkably, a heat treatment after the long pickling procedure does not significantly reduce the fracture rate of plated and heat-treated samples, as can be seen from Fig. 6. Therefore, long pickling times should be avoided in any case.

Fracture events occurring after long testing times are dangerous and therefore of great interest. There is continual discussion of the minimum testing time necessary to be on the safe side with respect to hydrogen embrittlement. For that reason, the constant load tests were extended up to one year. The overall results show that the fracture rate was mainly dependent on the batch and the surface preparation. Therefore, an averaging for all the samples, respecting the differing pickling and deposition, as well as heat treatments, was possible. Figures 7 and 8 show the results for 36,900 and 21,000 samples respectively. Because of averaging, however, it is the tendencies, not the absolute values, that must be analyzed. A constant fracture rate with time shows that all fracture events were achieved within 24 hr. If the fracture rate is time dependent, failures are to be expected after a month, although the 24 hr result might have been satisfactory. The mechanism behind these results is not understood at present. Probably very slow structural changes lead to critical situations. Remarkably, those failures seem to be connected with a smooth surface morphology; this is of some significance with the experiments discussed above (see Figs. 1 to 4).

Conclusions

High-strength steel components with unfavorable values for the surface/volume ratio behave critically with respect to hydrogen embrittlement. Most important is the pickling procedure. If the time is less than 60 sec, embrittlement can be avoided in any case if the plating process is followed by an adequate heat treatment. The experiments show, however, that bake-out times up to 70 hr and more are necessary for a heating temperature of 220 °C. In addition to the steel structure, the pickling time and the deposition parameters, the surface morphology is of significant influence. An important result is that fracture events are possible even after some months' testing time. The mechanism itself is not understood at present. This behavior can be evaluated, however, if the time dependence of the fracture rate is followed for about two months.

Sample Characteristics

Criteria	Batch 1	Batch 2	Batch 3	Batch 4
Steel	C75	C75	C75	C75
Hardness HV 0.2	530 ±30	570 ±30	540 ±20	540 ±20
Surface roughness	smooth	very smooth	rough	very rough
Tempering conditions	vacuum	vacuum	inert gas	inert gas

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