

Do's & Don't's



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Hydrogen Embrittlement from Plating Processes

Do's and Don'ts to minimize and/or eliminate hydrogen embrittlement from high strength steels, copper alloys or other alloys.

What is hydrogen embrittlement? How does it form? What is the mechanism, *i.e.*, how does it take place? Why does hydrogen cause embrittlement? I really do not know the answer to the preceding four questions. There are numerous scientific papers dealing with these questions. I have read many of them over time and I still don't know. An excellent paper was given by Dr. Chris Raub¹ when he received the AESF Scientific Achievement Award at AESF SUR/FIN 1993, entitled "Hydrogen in Electrodeposits: Of Decisive Importance, But Much Neglected."

What I do know is that hydrogen embrittlement can cause catastrophic failure of high strength steel and other alloys. The failure is usually in the form of cracking or complete separation. It can also cause blisters in both the basis metal and at the plating interface, reduced ductility, internal voids and lower yield strength.

What steels are subject to hydrogen embrittlement? I have found controversy about this. In general, high-strength steels, including "low alloy steels" and some stainless steels are vulnerable. Often steels susceptible to embrittlement are related to their tensile strengths. Dini² indicates that steels with tensile strength values of 1240 to 2140 MPa (180,000 to 310,000 lb./in²) are susceptible to embrittlement. Other references indicate risk above 1100 MPa (160,000 lb./in²). In general, the higher the tensile strength of the steel, the more susceptible it is to hydrogen inclusion and embrittlement. Even austenitic alloys are susceptible. Maraging high-strength steels with tensile strengths of 2740 MPa (397,000 lb./in²) have higher susceptibility to hydrogen embrittlement.

In an article by Paatsch,³ ultra high strength steel fuse holder rings of C75 (German standard DIN 471) and were plated in various plating solutions and under a number of different preparation cycles. The results and conclusions are interesting. The processing used was as follows: an alkaline cleaner; followed by pickling in 12% HCl-inhibited acid for 0 to 600 seconds; followed by plating. The deposits studied included zinc plating in eight different zinc plating solutions, Watts nickel, sulfamate nickel, cyanide copper and acid copper. There were failures using a modified constant load test derived from ASTM F 519.⁴

A summary of the results shows that all of the samples using 60 sec or more pickle time failed at time intervals of up to 24 hr heating at 220°C (428°F) regardless of the plating solution used. Some samples required 70 hr of heat treatment after plating, to pass the tests. The samples that used less than 60 sec of inhibited HCl pickle showed no failures at all, regardless of the type of plating solution used.

A note about electroless nickel and hydrogen

Electroless nickel (EN) generates hydrogen as a part of the deposition reaction. Therefore, hydrogen embrittlement of high-strength steels can occur. What is different about electroless nickel deposits, you ask? Remember that electroplated deposits are crystalline. That is, they have grain boundaries from which hydrogen can escape during the baking process. Electroless nickel is virtually amorphous (without grain structure). Since there are

no grains, it is very difficult for hydrogen to pass through electroless nickel deposits, particularly thicker deposits where there is little or no porosity.

How then, can hydrogen relief take place? Sometimes EN deposits over 25.4 μm (0.001 in.) thick will crack on heat-treating at high temperatures or at low temperatures for long times. Hydrogen can then escape. But we usually do not want cracks because they may induce cracks in the basis metal. Another method is to mask a non-critical area so that there is an unplated area from which hydrogen can escape on baking. Also baking should start at very low temperature for a long time, followed by a gradual increase in temperature to the recommended level. EN deposits with thicknesses of 25.4 μm (0.001 in.) or higher are very likely to crack if heated to 300°C (572°F) or above. The cracking is due to the reduction in volume as the nickel phosphorus changes to crystalline (Ni₃P).

What did I learn from all this coupled with many years of experience? Here are a few precepts to consider:

Do's

Do be aware that hydrogen embrittlement can cause serious failures.

Do use appropriate heat relief of entrapped hydrogen. The time and temperature combination must be such that tests prove no failure.

Do test very soon after plating, one to three hr. Test another baked sample after many hours.

Do realize that the bake time and temperature required to do the job may be much more than the standards ask for. Always test.

Do use solvent degreasing, alkaline soak cleaning or anodic alkaline cleaning (if required for specific soils).

Do use inhibited acid for pickling, if pickling is really necessary. Not all inhibitors work well. Test the results.

Do consider shot grit blasting, vibratory cleaning and shot peening. Shot peening is good for lowering the surface stress.

Do consider alternative coating processes such as mechanical plating of zinc, Ti-cad or other suitable metals. There is also powder coating to consider.

Don'ts

Don't assume that just because you followed the recommended post plating bake cycle that the hydrogen is removed sufficiently to pass the tests.

Don't use strong or non-inhibited acid pickles.

Don't use the same bake cycle for electroless nickel deposits unless there is an unplated escape area on the part.

Don't rely on a simple bend test shortly after plating. Bend tests are not reliable for hydrogen embrittlement determination. There is no reliable quick test.

Don't use cathodic preplating treatments. A nickel strike for activation of stainless and other nickel-containing alloys may be required. Be assured that there will be significant infusion of hydrogen. A longer than usual bake cycle may be required.

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References

1. C.J. Raub, *Plating & Surface Finishing*, **80** (9), 30 (1993).
2. J.W. Dini, *Electrodeposition, The Material Science of Coating and Substrates*, Noyes Publications, Park Ridge, NJ, 1993.
3. W. Paatsch, *Plating & Surface Finishing*, **83** (9), 70 (1996).
4. ASTM F 519-06, *Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating/ Coating Processes and Service Environments*, ASTM International, W. Conshohocken, PA, 2006.

Fact or Fiction?

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anthrax. Ask someone in United's Red Carpet room to mail something for you, and they will say, "We are forbidden to do that because of anthrax."⁸

West Nile virus was the "bug du jour" of summer 2002 and perceived by the media as a great threat. Yet in comparison to our real killer bugs, only 284 people died. Again from Siegel, "There was no media memory. As West Nile faded in the fall, no one at any network or any newspaper thought to apologize for overstating the case. There were no retractions, no amendments, just simply no more front page coverage and no more headlines on cable TV."⁷

Smallpox was next on the scare chart in spite of the fact that it hadn't made anyone sick in the U.S. in over fifty years. "With smallpox, the greatest problem in the fall and winter of 2002 was an exaggerated sense of risk on all sides. The smallpox scare was a new category of absurd over-reaction when compared with the previous public health hypes."⁹

Severe Acute Respiratory Syndrome (SARS) arrived in 2003 and became almost synonymous with the word virus. There were only 7,000 cases in the world, and fewer than 100 in the United States. No one here died of SARS, but a lot of people worried unnecessarily. Siegel reports, "Many patients called me in the spring of 2003 convinced that the slightest cough was SARS. People were afraid to sit next to an Asian person or to eat in a Chinese restaurant."⁶

Siegel says this about bird flu, "According to a significant study published in the prestigious British journal *Nature* recently, the H5N1 bird flu virus is at least two large mutations and two small mutations away from being the next human pandemic virus. This virus attaches deep in the lungs of birds but cannot adhere to the upper respiratory tract of humans. Since we can't transmit the virus to each other, it poses little immediate threat to us."¹⁰

"Even the word 'pandemic' scares us unnecessarily. The word simply means a new strain of a virus appearing in several areas of the world at one time and causing illness. The last flu pandemic, in 1968, killed 33,800 Americans - slightly less than the number who usually die here of the flu in an average year. We certainly don't need to think in end-of-the-world terms for that kind of pandemic."¹⁰

Flu changes its shape and size and is a killer worthy of respect and attention. But the most contagious virus among humans is our fear.

Summary

"Media obsession not only misinforms but also, diverts attention from the real dangers. Misdirection means ignoring the fact that millions don't have health insurance and millions are malnourished. Mad cow is only a tiny risk. Only 150 deaths compared to other food borne illnesses. The media misdirects us away from 500,000 cases of salmonella food poisoning. They use an isolated incident to wrongly profess a trend."¹¹

As Siegel concludes, "We are scaring ourselves about the wrong things in a way that is clearly a terrorist's delight. (We do much of the work for them). In 2001, terrorists killed 2,978 people in the United States, including the five from anthrax, and we have been obsessed with terrorism and the supposed risks ever since."¹² P&SF

References

1. D. Ropeik & G. Gray, *Risk*, Houghton-Mifflin Company, New York, NY, 2002; p. 2.
2. B. Glassner, *The Culture of Fear*, Basic Books, New York, NY, 1999; p. xii.
3. K. Perina, "Cracking the Harvard X-Files," in *The Best American Science Writing 2004*, D. Sobel, Ed., Harper-Collins, New York, NY, 2004; p. 115.
4. W. Durodie, "The True Cost of Precautionary Chemicals Regulation," *Risk Analysis*, **23**, 389 (2003).
5. M. Siegel, *False Alarm*, John Wiley & Sons, New York, NY, 2005; p. 17.
6. M. Siegel, *False Alarm*, p. 18.
7. M. Siegel, *False Alarm*, p. 129.
8. "Travelers' Intercom," *International Travel News*, **30**, 11, (February 2006).
9. M. Siegel, *False Alarm*, p. 130.
10. M. Siegel, "A Pandemic of Fear," *The Washington Post*, March 26, 2006; p. B07.
11. M. Siegel, *False Alarm*, p. 57.
12. M. Siegel, *False Alarm*, p. 196.