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Introduction

There has been much investigation in the past concerning ways to eliminate the embrittling effects of hydrogen in galvanized steel components.[1] Such galvanized parts are used extensively in the automotive industry. One solution that is commonly used is to anneal the galvanized parts at approximately 200 degrees Celsius for 4 to 24 hours. This annealing process does restore the ductility. However, very few if any experiments have been done to measure the amount of hydrogen released and the temperature dependence of the hydrogen release. This investigation is part of an on going effort to measure the hydrogen released from galvanized steels at various temperatures up to 800 degrees Celsius.

The Method of Modulated Beam Mass Spectrometry

To study the temperature dependence of the hydrogen release rate in galvanized steels a highly sophisticated technique known as modulated beam mass spectrometry was used. This technique was originally developed by Holister *et al.*[2] and applied to uranium dioxide studies by Srivastava (aka Kumar) and Olander[3] and later used on copper and steels by Kumar.[4] It has a highly superior sensitivity for measuring desorption rates.

Figure 1 shows how conventional mass spectrometry is used in conjunction with modulated beam technology to produce a highly sensitive instrument that can measure desorption rates as low as hundredths of a nanogram per second (0.01 ng/s). The apparatus is contained in a stainless steel ultrahigh-vacuum system. The sample is placed in a platinum crucible where it is heated by a furnace. The desorbed gases that travel up through an orifice are chopped by a rotating blade before passing into the mass spectrometer. A lock-in amplifier is used to read that part of the AC signal which has the same frequency as the chopper blade. Also connected to the apparatus is an ion pump which maintains the ultrahigh-vacuum.

Before an experiment can be performed the mass spectrometer must be calibrated. A gas of a known pressure and volume is bled into the system through a valve which has a known flow rate for the pressure of the gas. The mass spectrometer signal is measured to obtain a relationship between the mass spectrometer and the flow rate.

The Embrittling Mechanisms of Hydrogen in Steels

It has been generally agreed upon that there is a relationship between the hydrogen content in steels and their embrittlement. Many theories have been proposed to attempt to explain this phenomenon but so far none have proven to be totally satisfactory.

One theory that is presently considered is that hydrogen forms small gaseous voids which can lower the strain energy surrounding a stress concentrator when the specimen is under tension.[5] The hydrogen lowers the stress energy by diffusing to the high energy region and forming a small void. The voids can act as microvoids in the void sheet mechanism of ductile failure.[6] This type of mechanism would require slow strain rates to allow the hydrogen to diffuse to the high energy regions of the material. This is consistent with the findings of past strain rate experiments of hydrogen charged specimens.[7] Slow strain rates were found to enhance the effects of hydrogen embrittlement, which is opposite the effects of most other types of embrittlement.

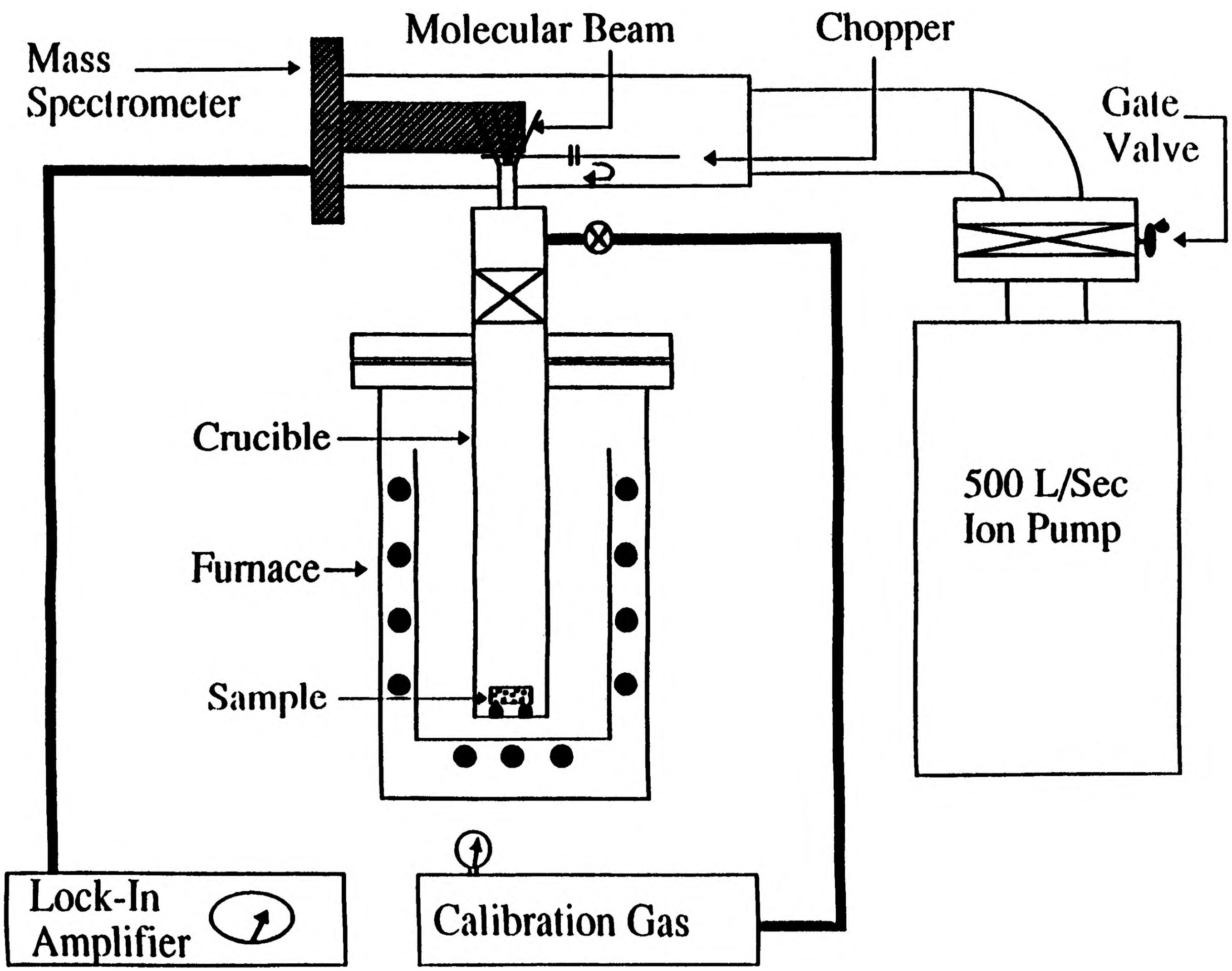

Fig. 1 Apparatus for Characterizing Gases

Another theory is the hydrogen induces embrittlement by migrating to the tips of existing microcracks. The hydrogen migrates to the crack tip through stress assisted diffusion. The high curvature tip of the microcrack has a high energy associated with it which due to the tendency of the tip of the crack to act as a stress concentrator. The highly mobile hydrogen lowers the free energy of the crack tip by migrating to it, which in turn lowers the cohesive force of the atoms surrounding the crack tip. This in turn lowers the strength of the material. This mechanism of embrittlement would also require slow strain rates for the hydrogen to diffuse to the cracks.

Results and Discussion

Galvanized steel seat belt holders and clips for automotive upholstery were analyzed for their hydrogen content. Three different types of samples were analyzed for each of the following: galvanized, galvanized then baked for four hours, and 'as received' which were the same as the other samples but had not been galvanized or baked. The three things listed above had been done by industry before the investigation began.

The 'as received' seat belt holder samples desorbed hydrogen only at temperatures in excess of 160 deg. C for 4 hours a total of 0.04 ppm (40 ng/g of sample of hydrogen was released. When the temperature was increased from 160 to 460 deg. C at 10 deg. C per minute a total of 0.175 ppm (175 ng/g of sample) was released. A galvanized sample (mechanically polished to remove Zn) was given the same treatment as the 'as received'. A total 0.488 ppm (488 ng/g of sample) of hydrogen was released with 80% coming out at temperatures above 160 deg. C.

When the results of the mechanically polished galvanized sample are compared to the results of a galvanized sample in which the Zn was removed with acid the hydrogen release is almost twice as much for the acid washed sample. It is concluded that the mechanical polishing removed not only the Zn plating but also some of the hydrogen rich layer on the steel surface.

A galvanized seatbelt holder sample (Zn removed with acid) was heated from room temperature to 200 deg. C at 4 deg. C per minute and maintained at 200 deg. C for 40 minutes. The total hydrogen release was 1.679 ppm (1679 ng/g of sample). In another experiment using the same sample the temperature was increased to 660 deg. C at 10 deg. C per minute and held for 40 minutes. The temperature was then increased at the same rate to 800 deg. C having a total annealing time of 8 hours with a total release of 13.11 ppm . The total release of from the sample in both experiments was 14.78 ppm of hydrogen.

Figure 2 shows hydrogen released from a galvanized seat belt holder with Zn left intact. When these results are compared with the results of a sample with the Zn removed with acid it is shown that Zn contains considerable hydrogen and also acts as a barrier to diffusion of hydrogen from the steel. In a 4 hour anneal a total of 5.08 ppm (5.08 micrograms per gram of sample) of hydrogen is released at 200°C in comparison to only 1.679 ppm for the sample with Zn removed by acid. Furthermore, the peak of the release curves occurs at ~3 hours from the start of the experiment as compared to only 50 min for the sample with the Zn removed with acid. Therefore, it appears that Zn plating delays hydrogen release and acts as a barrier for hydrogen diffusion.

Conclusions for galvanized clips are similar to those of seat belt holders. Figures 3 and 4 show hydrogen release rates up to 200°C from galvanized clips (Zn removed with acid) and galvanized clips with Zn plating intact, respectively. The total hydrogen release during 3 hours of annealing was 1.01 ppm for 'Zn removed' samples and 1.37 ppm for 'Zn not removed' samples. Just like the galvanized seat belt holders, the Zn plated clips contain a significant amount of hydrogen. Furthermore, the peak of the hydrogen desorption curve occurs at 140°C for

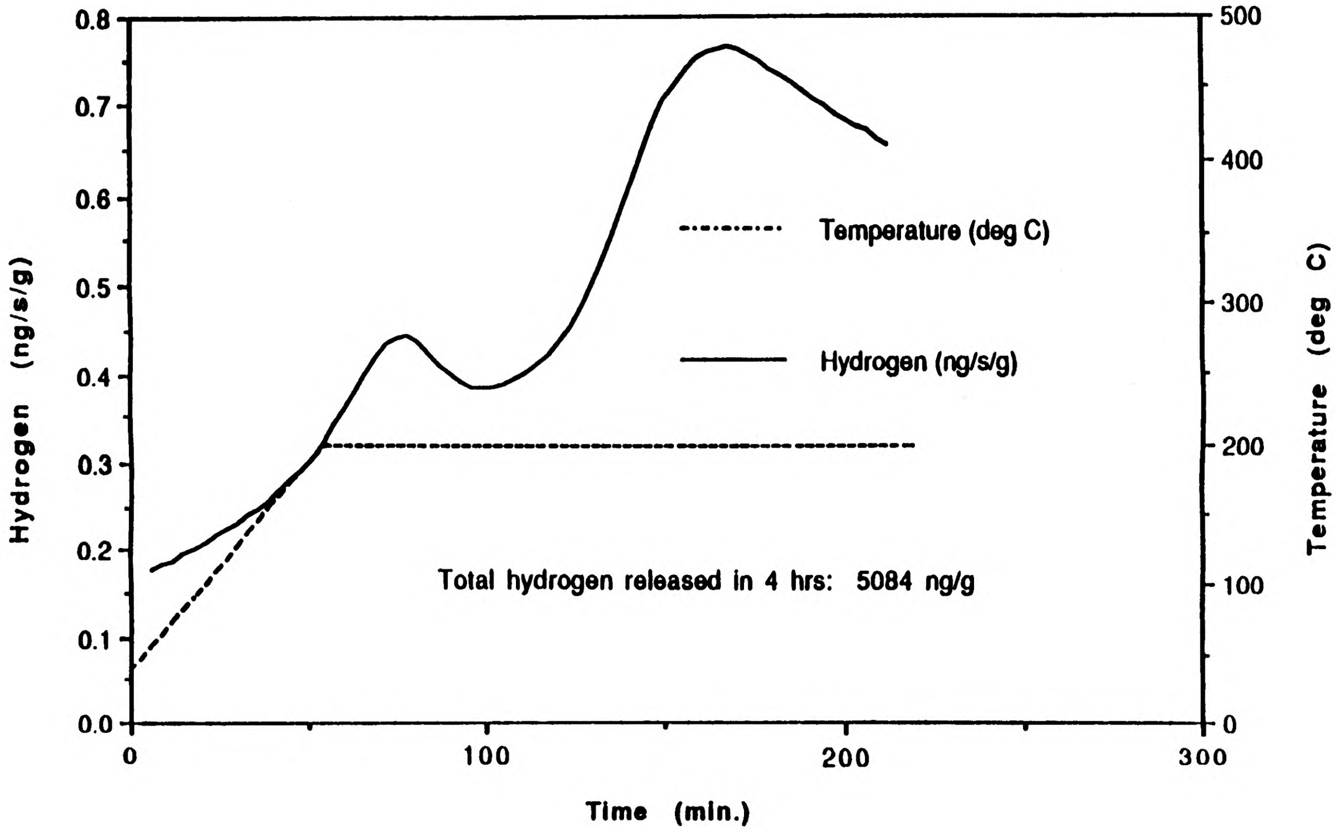

Figure 2. Galvanized seat belt holder. Zn not removed.

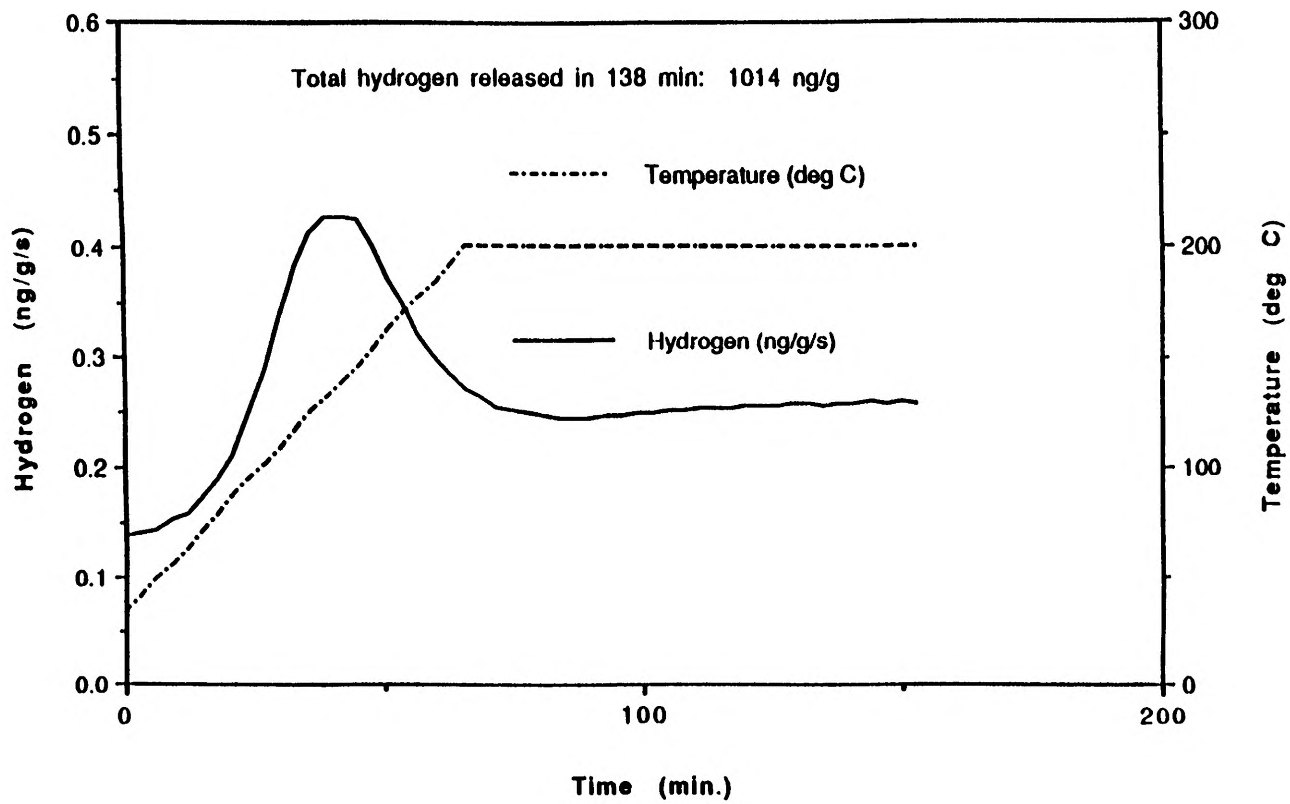

Figure 3. Galvanized clips. Zn removed with 1.5M HCl.

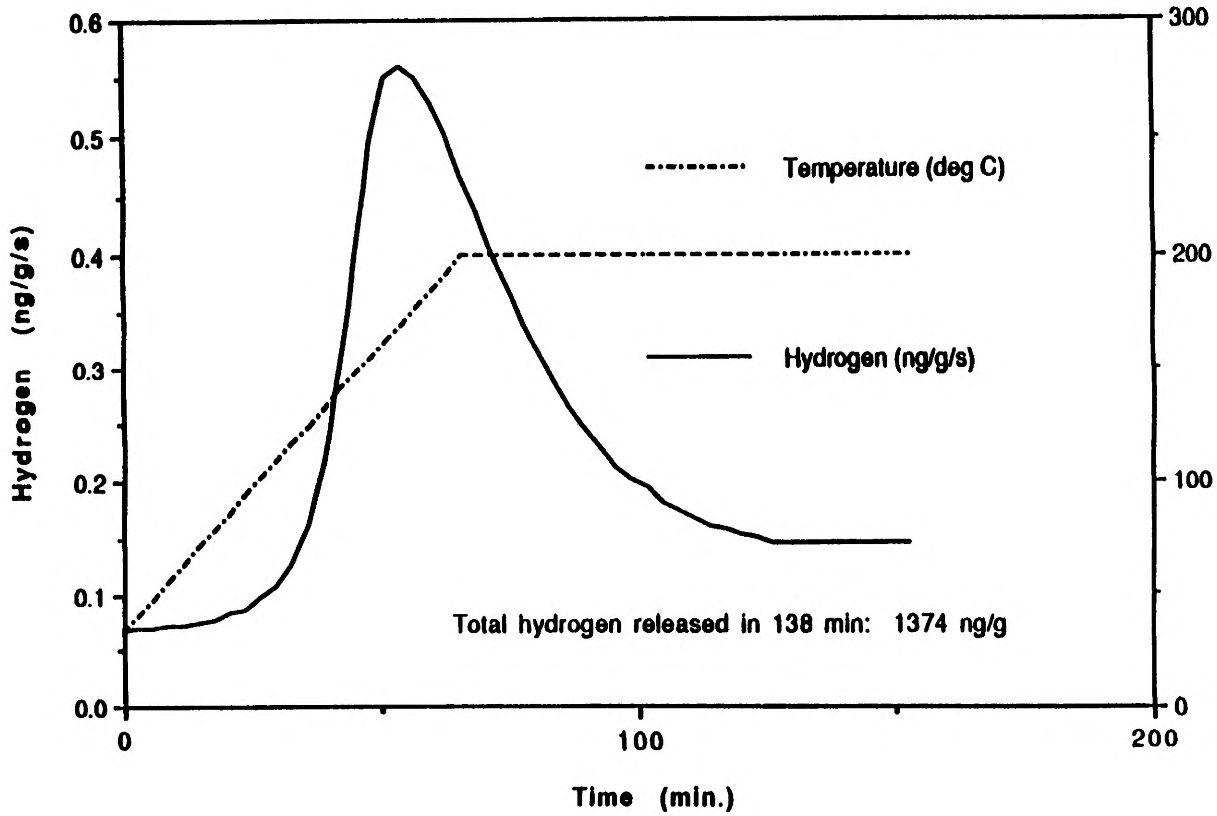

Figure 4. Galvanized clips, Zn not removed.

'Zn- removed' samples as opposed to 180°C for 'Zn not removed' samples. The shift in the peak to higher temperatures is an indication that the Zn plating acts as a barrier to hydrogen diffusion.

Figure 5 shows the hydrogen desorption curve up to 800°C from galvanized clips when the Zn is removed by acid (1.5 M HCl). A total of 3.13 ppm of hydrogen is released. This is considerably lower than 13.11 ppm for the seat belt holders (Zn removed with acid).

Conclusions

The following conclusions were drawn from the present work:

1. Modulated Beam Mass Spectrometry (MBMS) is capable of measuring hydrogen release rates of the order of 0.01 ng/sec. For one gram of sample, MBMS can conveniently measure concentrations of hydrogen on the order of a hundredth of 1 ppm.

2. The Zn plated layer contains a significant fraction (up to 20%) of the total hydrogen in the galvanized steels.

3. Zn plating acts as a barrier to hydrogen diffusion during annealing, requiring longer times or higher temperatures for hydrogen release.

4. Annealing at 200°C for 4 hours releases only a fraction of the total hydrogen uptake. The fraction is 30% for clips and only about 10% for seat belt holders.

5. Annealing at 200°C redistributes the high concentration of subsurface hydrogen into the bulk. This may be the reason why thicker (0.5 cm) seat belt holders release a lower fraction of hydrogen than the clips (radius ~0.1 cm).

6. The electroplated surface, with or without the Zn removed, acts as a barrier to hydrogen release. This promotes hydrogen redistribution in the bulk.

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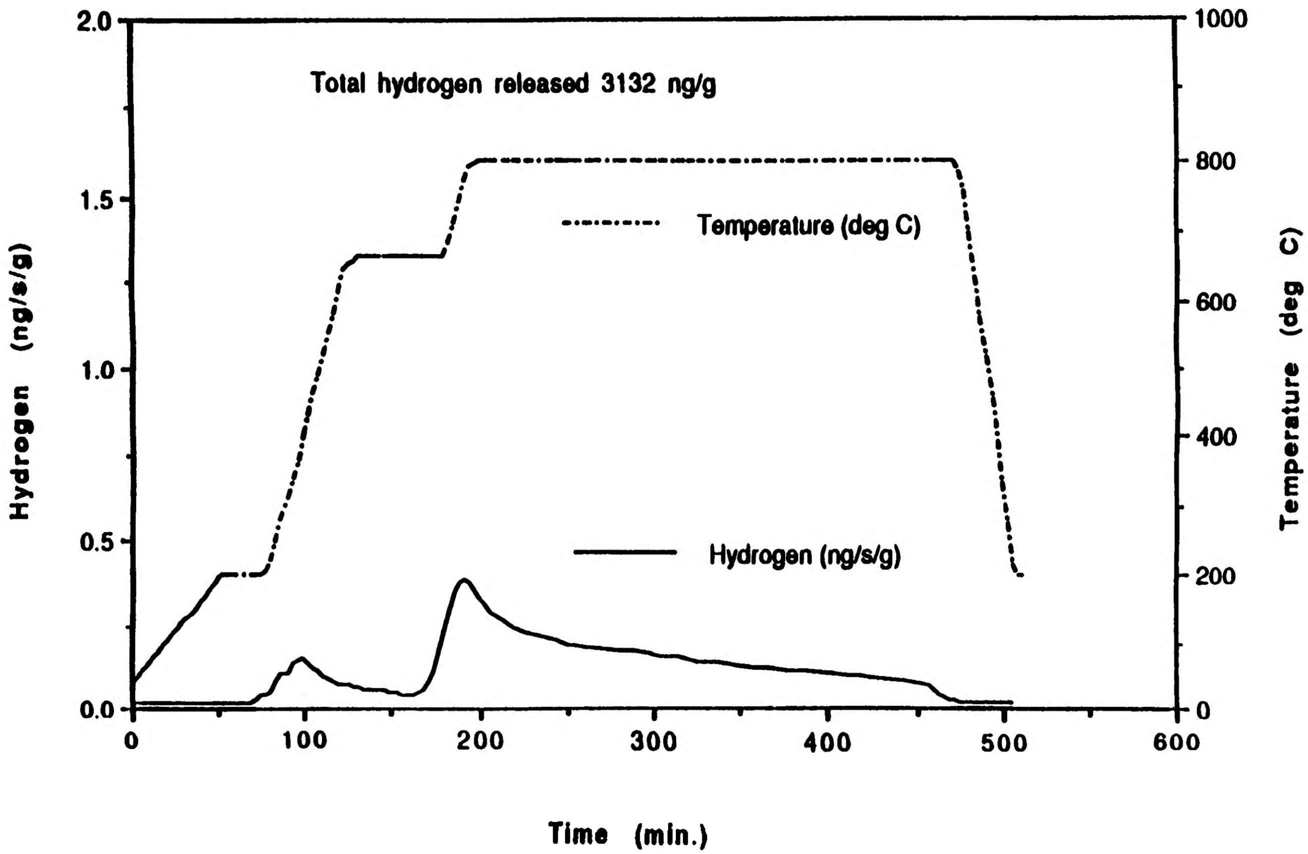

Figure 5. Galvanized clips. Zn removed with 1.5M HCl.