Desorption of Hydrogen from Palladium Plating

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ABSTRACT
Desorption of co-deposited hydrogen from Pd and Pd alloy platings may cause micro-cracking. The desorption process takes days to complete. To assure that hydrogen induced micro-cracking can be detected immediately after plating, several methods have been established for quick removal of hydrogen from Pd deposits.

INTRODUCTION
During plating of Pd or Pd alloy from an aqueous electrolyte, hydrogen is generated on the cathode if the plating efficiency is less than 100%. Hydrogen is co-deposited and diffuses into the Pd metal lattice forming an interstitial solid solution of PdH₅.

Pd has a face centered cubic sublattice. Hydrogen atoms partially fill the octahedral holes to form PdH₅. The fraction of interstitial sites occupied depends on the plating conditions such as temperature, partial pressure of hydrogen, etc. Although hydrogen atoms occupy only interstitial sites, the sublattice of metal atoms in PdH₅ is larger than and simply an expansion of the parent metal lattice. The PdH₅ lattice undergoes expansion or contraction as the Pd/H ratio changes.

Palladium metal has a lattice constant of 3.889 Å. If hydrogen is dissolved in Pd at room temperature, the lattice will increase gradually until an atomic ratio for H/Pd of 0.03 is reached. At this ratio, the PdH₅ is entirely in the α-phase and the lattice constant has increased to 3.895 Å. A higher hydrogen concentration will transform some of the α-phase to β-phase, which has a lattice constant of 4.04 Å and a H/Pd ratio of 0.57. Accordingly, the lattice constant of Pd plating is influenced by the amount of co-deposited hydrogen.

It is known that Pd plating with high hydrogen concentration causes micro-cracking. This can be explained by considering the difference in lattice constants of pure Pd, and the hydrogen containing α- and β-phases. The desorption of hydrogen from Pd plating must be expected to cause stresses in the plating because of the lattice contraction, especially during transformation from β-phase to α-phase. When the tensile components of this stress exceed the yield point the stress is relieved by cracking. To estimate a time interval for the onset of the stress relief, diffusion of hydrogen in palladium may be considered. The corresponding diffusion constant at room temperature is about $5.4 \cdot 10^{-7} \cdot \text{cm}^2 \cdot \text{s}^{-1}$. At this relatively high diffusion rate one should expect a very short transit time of a change in concentration of hydrogen across a Pd layer of a few μm. However, according to the experience of the authors residual hydrogen may not have been completely desorbed from Pd platings after days or even months. Trace impurities in the deposit, surface conditions and the mass transfer coefficient of hydrogen from the layer to the environment affect the diffusion process. Therefore, hydrogen induced micro-cracking may or may not be occurring immediately after plating.

Among the detrimental consequences of micro-cracking are poor adhesion, poor wear and high porosity. Therefore, it is highly desirable to find practical methods for accelerated removal of hydrogen from Pd deposits. In the study leading to this paper possibilities of identifying such procedures the following approaches were taken:

- Constant potential coulometry for the determination of the H/Pd atomic ratio,
- cyclic voltammetry,
- anodic polarization,
- vacuum extraction at elevated temperature,
- vapor phase desorption.

EXPERIMENTAL
The instrument used to control current and potential for the experiments performed in this study was an EG&G PARC.
model 173 potentiostat/galvanostat. Experiments involving constant potential were carried out using a model 173 with an EG&G PARC model 179 digital coulometer plug-in module. Cyclic voltammetry experiments used the model 173 with an EG&G PARC model 175 universal programmer and a model RE0074 X-Y recorder. The test cell for both types of experiments was an EG&G PARC model K0047 corrosion cell with a model 178 electrometer probe and 178/41 filter. All required specimens were prepared following the same general procedures. Copper research test paddles with an effective surface area of 10 cm² served as substrates.

The test paddle surface was first degreased in alkaline cleaner, rinsed in deionized water, electropolished in 10% sulfuric acid and rinsed again with deionized water. For constant potential coulometry the samples were air dried and weighed on a Sartorius model 2472 analytical balance. For the cyclic voltammetry tests this step was not performed. The sample was then plated in a palladium strike bath at room temperature for 45 s at a current density of 1 A/dm². The sample was rinsed in deionized water, electropolished in 10% sulfuric acid and rinsed again with deionized water. For continuous the bath temperature was increased to 75°C and tested. The palladium bath was first tested at 20°C and current densities of 1, 2, and 3 A/dm². Then the bath temperature was raised to 60°C, and samples plated at 1, 3, 6, and 10 A/dm². Subsequently the bath temperature was increased to 75°C and tested at 1, 3, 6, and 9 A/dm². All samples were plated to a thickness of 1.9 µm. At each current density three individual specimens were prepared. Each Pd-plated sample was then placed in the K0047 corrosion cell and anodized for 15 min at a potential of +0.750 V. The total electric charge, measured in coulombs (C; 1 C = 1 s · A), that passed during this time was recorded with the model 179 digital coulometer. After anodization, the sample was removed from the corrosion cell, rinsed in deionized water, air dried and weighed. From the charge passed and the mass of palladium plated, the atomic ratio of H to Pd was calculated. In

Table 1 the experimental parameters temperature and current density are listed together with the H/Pd atomic ratios. The latter are averages of the three samples for each current density.

<table>
<thead>
<tr>
<th>Bath Temperature °C</th>
<th>Current Density A/dm²</th>
<th>Atomic Ratio H/Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>0.212 ± 0.010</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.160 ± 0.008</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.165 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.144 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.122 ± 0.005</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>0.016 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.014 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.012 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.082 ± 0.002</td>
</tr>
<tr>
<td>75</td>
<td>1</td>
<td>0.005 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.101 ± 0.035</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.104 ± 0.011</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.118 ± 0.002</td>
</tr>
</tbody>
</table>

Cyclic Voltammetry

The procedure employed for this technique involved measuring the corrosion potential of a sample in a 1N sodium hydroxide solution and then scanning from a potential that was 100 mV more negative to a potential that was 1 V more positive than the corrosion potential and then back again while measuring the current carried by the cell. This cycle was repeated at least five times. The instruments for the various tasks are listed in Table 2.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Task</th>
</tr>
</thead>
<tbody>
<tr>
<td>175 Universal Programmer</td>
<td>to scan the potential</td>
</tr>
<tr>
<td>173 Potentiostat/Galvanostat</td>
<td>with 376 Logarithmic Converter Module to measure corrosion potential and current</td>
</tr>
<tr>
<td>RE0074 X-Y Recorder</td>
<td>to record output of scanning</td>
</tr>
</tbody>
</table>

When a sample of pure Pd was tested with this technique, no current passed through the cell. The corresponding scan is shown in Figure 1. Until the onset of oxygen evolution above a potential of +0.650 V no current is noticed. The same result was obtained on a two year old palladium plated part. In none of these samples hydrogen was expected. The results of the scan support this expectation. In the previous section it was mentioned that the palladium surface with the highest amount of hydrogen had been plated at a bath temperature of 20°C and a current density of 1 A/dm². Figure 2 shows the cyclic scan for a sample plated under these conditions. A high current is carried during the first anodic scan. It decreases with increasing number of scans until it reaches a value of virtually zero.

The results obtained here show that this technique can be used to determine the presence of hydrogen in a plated deposit. As the sample is anodized, it is observed that less and less hydro-
gen remains. This is in agreement with the results from the procedure used to determine the H/Pd atomic ratio. Because of these results from this point on the cyclic voltammogram was used to determine if other procedures had fully removed the hydrogen in the deposit.

Anodic Polarization

In the first two sections of this study two analytical methods were introduced:

(a) a method for quantitative determination of the H/Pd atomic ratio.

(b) a method for qualitative determination of presence of hydrogen in a Pd deposit.

It can be anticipated that, by combining the two processes, samples with low hydrogen content can be prepared in a short period of time. These samples would be expected to compare to older plated parts which had their hydrogen slowly escape over a long period of time. Anodic polarization offers an opportunity to remove the hydrogen from the deposit and cyclic voltammetry to determine how effective the anodic polarization had been.

Samples were prepared using the standard procedure described in the experimental section. They were plated to a thickness of 1.9 µm in the palladium bath at 20°C and at a current density of 1 A/dm². Subsequently each sample was rinsed and placed in the K0047 corrosion cell. A constant potential was applied to the sample for a set time after which it was shut off. A cyclic voltammetry scan was then performed on the sample. Figure 3 shows the anodizing potentials, the time periods, and the corresponding cyclic voltammogram. It can be seen that with increasing anodizing potential and duration a scan pattern is approached that appears to be identical to the scan of pure Pd. This was obtained at an anodizing potential of +0.750 volts for 90 minutes.

Vacuum Extraction at Elevated Temperature

This procedure was employed with the intent to remove the hydrogen from the deposit with vacuum and elevated temperature serving as driving forces. Again, samples were prepared following the standard procedure with the palladium bath at a temperature of 20°C and at a current density of 1 A/dm². After plating, the samples were rinsed and air dried. They were then placed in the vacuum oven which was already set at the desired temperature. The oven was closed, the vacuum applied and the time scale set to zero. Temperature and duration of exposure of the samples to the vacuum were varied. Two different temperatures, 100°C and 150°C, and several intervals of exposure time were chosen. After the desired duration of exposure had elapsed, the samples were removed from the oven, placed in the K00477 corrosion cell and cyclic voltammograms were obtained.

Figure 4 shows results of exposure of a sample to vacuum at 100°C for 60 minutes and at 150°C for 90 minutes. A noticeable amount of hydrogen is still present in the sample treated at 100°C for 60 minutes. The cyclic voltammogram of the sample exposed to 150°C in vacuum for 90 minutes is identical with that for pure Pd. To determine how effective the treatment in vacuum was, three samples were placed in the oven. Without applying vacuum the samples were heated to 150°C and left at this temperature for 150 min. The results of this test presented in Figure 4 show clearly that all three samples still contain hydrogen.

Vapor Phase Desorption

For this experiment three samples were prepared in the palladium bath at a temperature of 20°C and a current density of 1
A/cm². The samples were rinsed with deionized water, air dried and placed in the Hybrid Technology Corporation Phase Four Vapor Reflow system for 5 minutes. After their removal from the vapor phase reflow unit, cyclic voltammograms were obtained. They are presented in Figure 5. The scans for all three samples are identical and are also the same as found on pure Pd metal and on the two-year old plated samples. Two of the three samples had palladium flaking off in form of a very fine powder. This test yielded samples with no hydrogen in the deposit and induced cracking in two of them. Such behavior is expected with age removal of hydrogen.

**DISCUSSION**

The term cyclic voltammetry describes a variant of voltammetry whereby the potential is scanned periodically between two limits. In this study, the limits were selected only for observing oxidation and reduction of hydrogen. The data obtained by this method were verified by comparing them with data measured on samples of cast, of two-year old plated and of freshly plated palladium. As shown in Figures 1 and 2 a noticeable current was observed only on the fresh samples.

Because the neutral hydrogen atoms are oxidized to protons which diffuse rapidly to the bulk of the solution, the reverse reaction i.e. the reduction of H⁺ to neutral hydrogen is negligible. With increasing number of scans the current decreases until its value coincides with the base line. It was demonstrated that cyclic voltammetry can be used explicitly to monitor removal of hydrogen. Therefore, the method was also applied to evaluate other techniques that appear potentially useful for hydrogen desorption.

Electrochemical oxidation of hydrogen in palladium at a potential of 0.59 V relative to the SCE was reported previously. In order to accelerate the anodization, for the present study the potential was set slightly higher, namely to +0.75 V. The amount of hydrogen can be calculated from the total charge Q, which in turn is found by integrating over the current

\[ Q = \int_0^t i(\tau) \, d\tau \]

where

- \( i(\tau) \) = current as function of time,
- \( t \) = duration of current flow.

Estimated values of the partial pressure of H in PdH₀.₀₃ and PdH₀.₁ are listed in Table 3 for temperatures of 50, 160, and 200°C. These data show that with increasing temperature the removal rate of hydrogen from palladium deposits should also increase. Results of the study presented here and already reported above confirm this. It was found that at 150°C an exposure for 120 minutes is needed to complete the hydrogen removal under vacuum. This was reduced to 5 minutes at 215 °C under a perfluoro-hydrocarbon vapor shield.

**SUMMARY AND CONCLUSIONS**

The results of experiments presented in this study show that the following four methods are suitable for accelerated removal of hydrogen from palladium plated samples.
1. Cyclic voltammetry in 1N NaOH at a potential varying from −0.1 to 1.0 V relative to SCE.
2. Anodic polarization in 1N NaOH for 2 hours at a potential of +0.75 V relative to SCE.
3. Vacuum extraction at 150°C for 2 hours.
4. Vapor phase desorption at 215°C for 5 minutes.

Application of any of these methods resulted in a drastically reduced hydrogen content of newly palladium plated samples. The hydrogen content after such treatments was equivalent to the hydrogen content of pure Pd metal or to that of two year old palladium plated parts. All four methods offer the opportunity to remove hydrogen from a palladium deposit. Thermally activated extraction in vacuum and vapor phase desorption methods appear to be most suitable in a production environment. Application of each of the four methods presented in this study can contribute to negating the statement that hydrogen embrittlement must be expected to occur after palladium plated products are shipped. Some of the methods have been in use since 1985. They proved to provide consistent microcracking-free products and allowed shipment of billions of electronic contacts without any concern of delayed microcracking.

REFERENCES

I-Yuan Wei is AMP Consultant and Director, Contact Materials, in the Global Technology Group at AMP Incorporated, Harrisburg, Pennsylvania.

Dr. Wei holds a Bachelor of Science degree in chemistry from the National Taiwan Normal University, a Master of Science degree in organic chemistry from the National Taiwan University, and a Ph.D. in physical chemistry from Tufts University. He held positions as research and development manager at National Aluminum, as Scientist at Sprague Electric Company, and as Research Associate at the University of North Carolina at Chapel Hill. In 1981 he joined AMP as a Senior Development Engineer and served the Company in positions with increasing responsibilities as Project Manager, Manager Plating Research, and as Director, Contact Materials. During 1991 to 1994 Dr. Wei was chairman of the Electronics Finishing Committee of the American Electroplaters and Surface Finishers Society and received the Board Recognition Award of the Society in 1994. He is credited with the introduction of the Duragold plating process and is recognized for his contributions to the evaluation of non-precious metals as gold replacements. His present research interests focus on new contact finishes and finishing processes.

Jerry Brewer was a member of the Technology Group of AMP Incorporated when the work reported above was done.