A Comparison of Precious Metal Contact Materials

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A COMPARISON OF PRECIOUS METAL CONTACT MATERIALS
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ABSTRACT

Two of the preferred methods of reducing the cost of electronic connectors are: a) to minimize the thickness of the precious metal contact materials and b) to select lower cost materials. Although the search continues for a suitable non precious contact material, the requirements of high reliability connectors dictate the selection of precious metals for most applications. Although gold remains the industry standard, gold and gold alloys added as a cover over palladium and palladium silver alloys continue to gain acceptance as lower cost alternatives.

Pure gold has optimum nobility for contact corrosion resistance. When lower cost alternatives are used, their performance in potentially corrosive environments is of major concern and interest. In this work, a series of gold and gold alloys, palladium, palladium silver and gold, palladium silver combinations were produced as inlay clad materials and exposed to Battelle environmental gas mixtures containing H₂S, Cl₂, and NO₂. The data subsequently generated is offered for possible assistance in contact material selection.

Precious metal performance was compared by measurement of contact resistance. To avoid the complication of creep corrosion products from copper alloy base metals, all precious metal combinations were inlaid into a wrought nickel. A manufacturing sequence typical of inlay cladding for connector spring materials was used for all metal combinations. Precious metal thicknesses of 30, 50 and 100 microminches were evaluated. The following alloys, listed in order of increasing contact resistance, were tested: Au, Au "capped" Pd40Ag, Au "diffused" Pd40Ag, Au "Ni" capped "Pd40Ag, Au "Ni" diffused "Pd40Ag, WE/1" capped "Pd40Ag, WE/1, Au25Ag, WE/1 "diffused" Pd40Ag, 70Au24Ag6Cu, Pd, and Pd40Ag.

INTRODUCTION

Pure gold has long been the industry standard as the premium electronic contact material. In the past decade, due to the increases in gold prices, design engineers have been challenged with the task of finding a suitable, cost effective replacement for pure gold.

Earlier work in this area demonstrated that there are material systems which equal pure gold as high reliability contact materials. In fact, Bader found the performance of DGR156 (gold diffused PdAg) "virtually indistinguishable from that of plated gold." His results are reported here for reference in Figure 1.
Bader's results, as indicated by change in resistance, are as follows (best to worst), (1) Au, (2) Au30Ag, (3) Au diffused PdAg, (4) Pd40Ag, (5) Au48Pd32Ag, (6) Au36Pd24Ag, (7) Au60Pd, (8) Au diffused Pd, (9) Pd, (10) Au80Pd. The above materials were evaluated after exposure in a 70 ppb Cl₂ atmosphere which may not be representative of a field condition. This data is presented as a comparison only.

Figure 1: Contact Resistance of inlays after 26 days exposure, 70 ppb Cl₂, and 80% Relative Humidity.

Other than the aforementioned work, there is a virtual absence of published data concerning the corrosion behavior of these alternate contact materials. The purpose of this investigation is to provide the designer with realistic information, using standardized (Battelle) environments, to aid in the selection of these lower cost materials.

Several of the most commonly used contact alloys, including gold, were evaluated at 30, 50 and 100 microinches. A series of tests allowed examination of the effect of precious metal porosity on contact resistance.

Nine different metal combinations, both single layer and multilayer, were evaluated. Table I lists the metal systems tested. The selection process for the alloys was an arbitrary one. Many other alloy combinations and thicknesses are possible, but those included here represent the most widely used material systems.

Table I: Material Systems Evaluated.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>THICK., u'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>35</td>
</tr>
<tr>
<td>Au</td>
<td>56</td>
</tr>
<tr>
<td>Au</td>
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<td>32</td>
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<td>53</td>
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<td>Au25Ag</td>
<td>109</td>
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<td>Pd</td>
<td>109</td>
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<tr>
<td>Pd40Ag</td>
<td>57</td>
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<tr>
<td>Pd40Ag</td>
<td>107</td>
</tr>
<tr>
<td>Au&quot;diffused&quot;Pd40Ag**</td>
<td>101</td>
</tr>
<tr>
<td>Au&quot;capped&quot;Pd40Ag***</td>
<td>108</td>
</tr>
<tr>
<td>WE#1&quot;diffused&quot;Pd40Ag**</td>
<td>105</td>
</tr>
<tr>
<td>WE#1&quot;capped&quot;Pd40Ag***</td>
<td>105</td>
</tr>
<tr>
<td>Au4N1&quot;diffused&quot;Pd40Ag**</td>
<td>98</td>
</tr>
<tr>
<td>Au4N1&quot;capped&quot;Pd40Ag***</td>
<td>111</td>
</tr>
</tbody>
</table>

* WE#1 is the trade name for the 69Au25Ag6Pt gold alloy.
** The gold or gold alloys in these systems were diffused into the PdAg alloy.
*** The gold or gold alloys in these systems remained as distinct layers over the PdAg alloy. This combination is also referred to as gold "capped" PdAg.
This study was designed to evaluate the performance of contact materials under established and standard sets of environmental conditions and to suggest suitable alternatives to pure gold. The environmental conditions are considered representative of locations where electronic components may be expected to function. Flat coupon studies are useful for comparing contact materials and ranking the materials against each other.

Actual connector performance can not be directly predicted without consideration of such factors as component geometry, housing design and use of lubricants or other protective films.

**EXPERIMENTAL PROCEDURES**

**MATERIALS**

Because of the relative ease of producing precious metal alloys in wrought form, the clad metal systems are able to incorporate a wide variety of contact material combinations. Precious metals can be combined as distinct layers, or one metal alloy can be diffused into another to obtain the optimum benefit of minimized cost and improved performance.

The precious metal alloys used for this investigation were wrought metals. Chemistries were held constant for all precious metal alloys in each material system. The base metal selected was wrought nickel. This alloy was selected to avoid the possible migration of base metal corrosion products via creep on to the contact surfaces. The clad metal systems were all processed through the same heat treatment and cold working operations to yield a half hard temper in the wrought nickel. All samples were cut to length and cleaned prior to shipment to Battelle Laboratories for exposure in environmental chambers.

**TESTING**

Three samples, 0.010" thick by 0.750" wide by 4.000" length, of each material system were tested to develop meaningful statistical data. Samples were exposed to Battelle Class II and Class III environments to simulate 2, 5, 10 and 20 years exposure for Class II and 1, 2, 5 and 10 years for Class III. These conditions were selected because they represent realistic field environments. The compositions of each environment are listed below:

<table>
<thead>
<tr>
<th>Class</th>
<th>Gas Concentrations (ppb)</th>
<th>RH(%)</th>
<th>Temp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>100 100 20</td>
<td>70</td>
<td>25</td>
</tr>
<tr>
<td>III</td>
<td>100 200 20</td>
<td>75</td>
<td>30</td>
</tr>
</tbody>
</table>

Additional samples were exposed at 150°C, Relative Humidity 45% for 250 and 500 hours to determine the oxidation characteristics of each metal system.

The test method used to evaluate the corrosion resistance of the contact materials was Low Level, Contact Resistance. Each material's stability was determined by the change in resistance after a planned exposure. The tests were done with a 4-wire system having a 10 mA test current and an open circuit voltage of 10mV.

Two different loads were used for these tests. A 20-gram load was used to detect small changes in resistance and a 100-gram load was used as a typical industry standard.

Mixed gas exposure was conducted at Battelle Laboratories, Columbus, Ohio. Low Level Contact Resistance testing and all sample preparation were done at Technical Materials, Incorporated, Lincoln, Rhode Island.
RESULTS AND DISCUSSION

I. Porosity

Table II lists the porosity results of the precious metal alloys investigated in this experiment. This data is included for comparison with contact resistance data which is presented later.

Table II

Porosity vs. Material system evaluated. Porosities were measured using Paper Electrographic method per ASTM B741-85. Pores less than .002" diameter were excluded. Total area tested per sample was 5.643 cm².

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Thickness (u&quot;)</th>
<th>Porosity, Pores/sq.cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>35</td>
<td>43</td>
</tr>
<tr>
<td>Au</td>
<td>56</td>
<td>15</td>
</tr>
<tr>
<td>Au</td>
<td>108</td>
<td>6.8</td>
</tr>
<tr>
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<td>17</td>
</tr>
<tr>
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<td>Pd</td>
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<tr>
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<td>107</td>
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</tr>
<tr>
<td>Au&quot;diffused&quot;Pd40Ag</td>
<td>101</td>
<td>4.4</td>
</tr>
<tr>
<td>Au&quot;capped&quot;Pd40Ag</td>
<td>108</td>
<td>1.0</td>
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<tr>
<td>WE#/1&quot;diffused&quot;PdAg</td>
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</tbody>
</table>

Changes in contact resistance are attributable to two primary factors in this study: (1) precious metal porosity and (2) changes in surface chemistry of the metal as a result of the mixed gas exposure. Precious metal porosity is, by definition, a discontinuity in the precious metal layer exposing the base metal. Porosity is a function of the manufacturing process and as the following graph demonstrates, porosity rapidly increases as precious metal thickness decreases.

Figure II

Porosity vs. Precious Metal Thickness
II. Elevated Temperature Exposure

Table III lists the contact resistance data generated from the materials tested for 250 and 500 hours at 150°C in air. Data in milliohms, n = 20 tests per sample minimum.

Contact resistance remained very stable for all precious metal inlays except for the gold-silver-copper alloy. Contact resistance for this alloy was immeasurable because the material rapidly oxidized. It is surmised that the copper in the alloy oxidized internally creating a non conductive material. Change in resistance was below 4 milliohms for all other material systems. [A typical industry standard requires less than a 10 milliohm change after some form of stress test.]

<table>
<thead>
<tr>
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<th>Thickness, u&quot;</th>
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<th>250 Hr.</th>
<th>500 Hr.</th>
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<td></td>
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<td>4.4</td>
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<td>2.4</td>
<td>5.7</td>
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</table>

TABLE III: CONTACT RESISTANCE AFTER EXPOSURE AT 150°C, 45% RH.
III. Class II Battelle Environmental Exposure

Table IV lists Contact Resistance Data for Class II; 2, 5, 10 and 20 years simulated exposure. Data in milliohms, n = 20 tests per sample minimum.

Resistance remained very stable for gold alloys up to and including 5 years with a 20-gram load and up to and including 20 years with the 100-gram load. The maximum change in resistance for the gold alloys, at 100 u", was less than 16 milliohms (less than 11 milliohms with 100 grams). Pd and Pd40Ag alloys became unstable after just 2 years simulated exposure. In this experiment Pd was more stable than Pd40Ag. It is surmised that the silver in the Pd40Ag alloy was attacked by the H,S in the gas mixtures to form a silver sulfide. Because of the sulfide degradation, the corrosion resistance of the Pd40Ag system was inferior to the Pd system, in this environment. Further work is necessary to analyze the surface compositions of the above materials.

All gold and gold alloy PdAg combinations remained stable up to and including the 20-year simulated exposure at 100-gram load. Some slight degradation (still less than 20 milliohm change) occurs when using a 20-gram load.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Thick., u&quot;</th>
<th>0 Year</th>
<th>2 Year</th>
<th>5 Year</th>
<th>10 Year</th>
<th>20 Year</th>
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<td>2.8</td>
<td>5.2</td>
</tr>
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<td>4.1</td>
<td>7.2</td>
</tr>
<tr>
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<td>2.3</td>
<td>4.8</td>
<td>2.8</td>
<td>6.5</td>
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</table>

174
IV. Class III Environmental Exposures

The data developed in Class III tests closely resembles the data generated in Class II, except that for some alloys the onset of instability quickened. The data again demonstrates gold’s ability to resist attack by corrosive atmospheres.

Table V lists the Contact Resistance Date for Class III; 1, 2, 5 and 10 years simulated exposure. Data in milliohms, n = 20 tests per sample minimum.

Comparable to 100 microinches pure gold, up to and including 10 years simulated exposure, are the multilayer Au/Pd40Ag metal systems. Both the Au"diffused"PdAg and Au"capped"PdAg metal systems differed less than 7 milliohms from the single layer gold material with the 20-gram load. With a 100-gram load, the difference between single layer gold and the multilayer Au/PdAg systems is less than 3 milliohms. Both of the Au4Ni/Pd40Ag systems compared favorably to the Au/Pd40Ag systems.

The diffused WE$1$ PdAg system showed acceptable stability (< 10 milliohm

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**TABLE V: CONTACT RESISTANCE AFTER CLASS III ENVIRONMENTAL EXPOSURE**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Thickness (µ)</th>
<th>0 Year 20 g</th>
<th>1 Year 100 g</th>
<th>2 Year 20 g</th>
<th>5 Year 100 g</th>
<th>10 Year 100 g</th>
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<tr>
<td>Au</td>
<td>35</td>
<td>3.7 2.1</td>
<td>4.1 2.6</td>
<td>8.1 3.0</td>
<td>8.1 3.8</td>
<td>&gt;100 &gt;100</td>
</tr>
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<td>Au</td>
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<td>3.5 2.1</td>
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<td>6.9 3.0</td>
<td>6.1 4.3</td>
<td>60.5 6.1</td>
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<td>3.6 2.5</td>
<td>4.3 2.6</td>
<td>3.8 3.0</td>
</tr>
<tr>
<td>WE#1</td>
<td>43</td>
<td>3.8 2.3</td>
<td>6.5 4.1</td>
<td>77.6 3.7</td>
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<td>&gt;100 &gt;100</td>
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change) through 5 years simulated exposure but became degraded considerably after the simulated 10 year exposure. This is considered to be a result of the relatively large volume of silver at the surface and its instability in H₂S environments.

The WE#1 capped PdAg also performed comparably to the other Au or Au alloy systems up to and including the 10 years simulated exposure.

In summary, all gold or gold alloy "capped" PdAg systems remained very stable up to and including 10 years exposure when tested with the 100 gram load and up to and including 5 years with the 20-gram load. The WE#1 single layer system also remained stable up to and including 5 years with the 100-gram test load at 50 and 100 microinches. [Up to 10 years at 100 microinches with a 100-gram load.] As found with Class II environments, the Pd and PdAg systems degraded much more rapidly than the Au containing systems with Pd being superior to PdAg.

CONCLUSIONS

This study was designed to evaluate various precious metal contact alloys that are widely used in the telecommunications, electronics, and computer industries. Testing was designed to investigate contact materials only, independent of such variables as connector geometry (design), lubrication, and fabrication methods.

Our results indicate:

1. "Gold Capped" combinations of Au/PdAg, WE#1/PdAg and Au4Ni/PdAg are excellent replacement materials for pure gold. The use of less expensive precious metals in these combinations allows contact costs to be reduced without compromising reliability by reducing precious metal thickness.

2. Precious metal performance, as measured by corrosion resistance, is rated best to worst, as follows; Au, Au"capped"Pd40Ag, Au "diffused"Pd40Ag, Au4Ni"capped" Pd40Ag, Au4Ni"diffused" Pd40Ag, WE#1"capped"Pd40Ag, WE#1, Au25Ag, WE#1"diffused"Pd40Ag, 70Au24Ag6Cu, Pd and Pd40Ag.

3. As precious metal thickness increases so does contact reliability, as measured by contact resistance.

4. Pd and Pd40Ag were unstable for all mixed corrosive gas conditions evaluated.

5. Pd was more stable than Pd40Ag for all environmental conditions in this experiment. The poor performance of Pd40Ag is surmised as being the result of sulfide degradation of the silver.

6. Flat coupon studies are useful as benchmarks for selecting good performers and eliminating poor ones. These tests compare precious metal alloys only. They do not indicate how each alloy will function in specific applications.

7. Further work is required to analyze for surface corrosion products produced during environmental exposures.

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Mr. Wiegard graduated from Lehigh University in 1984 with a B.S. degree in metallurgy and materials engineering. He has been with Technical Materials, Inc. since that time where he has been responsible for application development and process engineering. His current position is staff metallurgist.

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Dr. Williams graduated from the University of Wales with a B.S. degree in chemistry/physics followed by a Ph.D. in chemical engineering. After working on process and product development of specialty strip products for British Steel Corporation, he joined TMI (UK) Ltd. as general manager in 1979. He transferred to TMI USA in 1981 and became vice president, engineering in 1983. Dr. Williams has authored papers at the IEEE-Holm Conferences on Electrical Contacts, the Electronic Components Conferences and the Electronic Connector Study Group Conferences.