Corrosion of Porous Gold Plating In Field and Laboratory Environments

By W.H. Abbott

Electroplated gold coupons with well-defined porosity were exposed in several classes of field environments for a few months to seven years. Parallel laboratory studies were conducted in dilute, flowing, mixed-gas environments. The results revealed that porous gold plating degrades at widely differing rates and by varying mechanisms, depending on the class of environment. Degradation from exposure to single gases as well as mixed gases containing only sulfur-bearing pollutants was relatively benign compared with field rates, even at concentrations of a few hundred parts per billion. Mixed gases of H₂S/NO₂/Cl₂produced corrosion at rates useful for accelerated tests and with realistic mechanisms.

n recent years, there has been considerable development and implementation of dilute, flowing, mixedgas tests for accelerated aging of contact finishes, components, and even systems. This has been coupled with a growing understanding of the chemical nature of field operating environments and their effects on materials.

For an accelerated aging procedure to be generally useful for reliability studies, the test should (1) reproduce the chemistry of field reactions, (2) reproduce the dominant mechanisms, (3) produce the correct kinetic and relative responses of materials, (4) have known acceleration factors, and (5) be practical to implement, control, and repeat.'

This paper represents one part of a comparison of field and laboratory reactions. It was designed to examine the chemistry of corrosion and reaction mechanisms of porous gold coatings in several types of field environments. The objective was to provide support for the development of improved laboratory tests employing flowing, mixed gas.

Materials and Procedures

The finish consisted of 0.75 μ m of cobalt-hardened acid gold over 1.25 μ m of sulfamate nickel, This combination was selected because it is typical of materials widely used for electronic connector finishes. The phosphor-bronze substrate was prepared to a standard surface roughness of about 0.01 μ m CLA. This procedure was used in an attempt to obtain a nearly constant porosity level for all test samples; it is well known that the substrate surface has a dominant effect on porosity.²The median porosity value was 4 \pm 2/cm² as defined by the SO₂ porosity test (ASTM B-583). This is a chemical test that uses a relatively short exposure (24 hr) and high concentrations of SO₂.³ Individual pore sites are "decorated" by corrosion products and can be counted at low magnification (10X).

Gold-plated samples were evaluated by contact resistance probing according to ASTM B-667-80, which has

> Reactive Chlorides Cl₂ Reactive Sulfides as H₂S

○ Reactive Ch
 △ Reactive Su
 □ SO₂
 ● Particulates

10.





Fig. 1-Reactivity distribution and metallic corrosion mechanisms of indoor electrical and electronic environments.

Fig. 2-Worldwide distribution of pollutant to which indoor electrical and electronic equipment is subjected.

been described by Antler.⁴ A solid, hemispherically ended gold rod probe (3.2 mm in diameter) was conditioned and verified against a tin-nickel standard prior to use. Fifty points/coupon were probed at normal forces of 50 to 500 g. In addition, select samples were examined by scanning electron microscopy, energy-dispersive X-ray analysis, and electron spectroscopy for chemical analysis.

Similar procedures were followed in laboratory experiments. All studies were conducted in a continuous flow system in which gas concentrations were continuously monitored. (All concentrations referred to here are for nominal values in the test environment.) Variations in measured concentrations for specific pollutants were as follows: ± 8 to 10 percent for H₂S and SO₂, \pm 10 to 15 percent for NO₂, and \pm 15 to 20 percent for Cl₂. Measurements were taken at 30 $\pm 2^{\circ}$ C and 70 ± 2 percent relative humidity.

Field Environments

The concepts of reactivity monitoring and environmental classes for describing field environments were published earlier.⁵¹⁶ Figure 1 shows the worldwide reactivity distribution for indoor electronic devices and indicates the relative severity of the four test sites used.

Figure 2 shows worldwide distributions of critical pollutants measured in and around operating electrical and electronic equipment' together with the characteristics of each of the four sites. Even though the average real pollutant levels are extremely low (a few ppb), rapid material corrosion and component failure may occur.

For the purposes of this paper, the term "sulfide" refers to corrosion products produced by reactive, reduced sulfur species in the gas phase of many possible sulfur-containing compounds. Hydrogen sulfide is believed to be the principal constituent causing corrosion of indoor electronic devices. "Chloride" refers to chlorine-retaining reaction products that may be produced by many organic and inorganic halogenated compounds.

Field Data

Figure 3 shows a typical set of data from four sites (A-D) after one year of exposure. It is clear that significant degradation occurred at three of the four sites. In fact, this prediction was evident even by visual examination of samples. The data also show a clear relationship between the degree of contact resistance degradation and environmental severity.



Chemical composition* Mechanism(s)

Reactivity level	Non-			
	Metallic	metallic Major Minor		
Α	_	— None None		
В	Ni, Cu	Cl, O, (S)** Pore –		
С	Cu, Ni	S, Cl, O Pore Creep		
D	Cu, (Ni)	S, (CI), (0) Creep Pore		

'Listed in order from largest to smallest amount.

"Parentheses indicate small to trace amounts.

degradation.



These points are further amplified by Fig. 4, which

describes the kinetics of degradation through three years

as measured by the 90th percentile from data such as those in Fig. 3. Only at Site A were the studies continued through

at least seven years of exposure with no measurable

Table 1 summarizes the field data in terms of the

Fig. 3—Contact resistance (100-g force) of porous gold (Au/Ni/Cu) after a year of field exposure at four reactivity levels.



3. 4—Kinetics of porous gold degradation in field environments at fou severity levels.

with the expected results shown in Fig. 1. Multiple corrosion mechanisms exist, depending on the severity of the operating environment.

The chemical data are likewise significant with respect to both the metallic. and non-metallic corrosion products. In all cases, major amounts of nickel were found in the corrosion products, particularly in the less severe environments. As severity levels increased, copper became dominant, but nickel was still a factor in the corrosion reactions. This finding is significant because it clearly demonstrates that nickel may not be regarded as a corrosion barrier. Classical laboratory tests often show just the reverse, with copper as the dominant, if not exclusive, corrosion product.

The dominant corrosion features and chemistries are shown in Figs. 5-7. The non-metallic constituents revealed shifts depending on the environmental class. In all cases, some chloride was found. These results cannot be overemphasized. Chlorides⁸¹⁹ and, more specifically, chloride/ sulfide synergisms and interactions^{67,10} have been shown to play an important role in virtually all corrosion reactions; our results were consistent with these findings.

Attempts must be made to simulate these effects for realistic laboratory tests. Data on variable corrosion mechanisms (Fig. 1) imply that multiple testing procedures must be developed. Furthermore, the proper choice of a procedure for component qualification should be based on some knowledge of the probable range of application environments.

Laboratory Results

Figures 8 and 9 show laboratory exposure data presented in a format similar to that used for the field tests in Figs. 3 and 4. The most technically important conclusions are as follows:

1. Neither the H_2S nor SO_2 single-gas procedures give reactions kinetically useful for accelerated tests. In other words, they are not severe relative to field data bases even at nearly 1 ppm.

2. Mixtures of H₂S and SO₂ are similarly benign.

3. Three-gas mixtures such as H₂S/SO₂/NO₂, although somewhat more severe, do not appear to satisfy modern testing requirements because they are unrealistic and too slow in causing corrosion.

4. Low-level sulfide/chloride mixtures of even a few ppb will degrade porous gold plating at significant rates and with realistic mechanisms.

These conclusions are further amplified by the results in Table 2. Porous gold plating degrades rapidly in many field environments, but the simple procedures commonly used in lab testing (Table 2) do not degrade these materials at



Fig. 5—Chemistry and morphology of Class II pore corrosion.



ig. 6-Chemistry and morphology of Class III pore corrosion and creep.

 Table 2

 Dominant Chemical Compositions and

 Degradation Mechanisms of Au/Ni/Cu

 In Laboratory Environments

Chemic	Chemical composition		Mechanism(s)	
Pollutant Metallic	Non-metallic	Major	Minor	
500 H ₂ S Cu	S, O	(Pore)	(Creep)*	
1000 SO ₂ Cu	S, O	(Pore)		
500 H ₂ S +				
1000 SO2 Cu	S, O	(Pore)	(Creep)	
100 H ₂ S + 100				
SO ₂ + 100 NO ₂ · Cu	S.O	(Pore)	(Creep)	
3-10 Cl ₂ . Ni, Cu	CI, O	Pore	<u>с</u>	
10 H ₂ S + 10 Cl ₂ Ni, Cu	CI. O. (S)	Pore	الأستين ال	
100 H ₂ S + 10 Cl ₂ Ni. Cu	S. CI, O	Creep	Pore	

*Parentheses indicate weak effects.



Fig.7-Chemistry and morphology or Class IV edge creep.

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significant rates. Even more important, however, is the fact that both the corrosion products and mechanisms produced by these procedures do not occur in the field.

These problems apparently can be overcome by proper use of the sulfide/chloride interactions. Furthermore, by adjusting the concentrations, both the dominant mechanisms and corrosion chemistry can be shifted to agree more closely with field data. The results in Fig. 9 show that proper use of these interactions can realistically accelerate the reactions to useful levels.

Conclusions

Conventional gold plating exposed as coupons will degrade rapidly in three classes of indoor environments. There is neither a single degradation mechanism nor a single dominant chemical composition of the corrosion products. However, these reactions can be grouped broadly into four environmental classes. Simulation of the reactions within each class and useful kinetic responses for materials must be an objective of laboratory simulation.

This study has shown that single-gas tests and many proposed multiple-gas tests will not meet multiple requirements. Field studies have shown that the strong sulfide/chloride interactions affect most natural degradation processes. The use of dilute H₂S/Cl₂ and possibly more complex mixtures may produce useful, realistic reactions in the laboratory. Dominant mechanisms and chemical compositions can be adjusted by changes in concentration levels.

Many of the reactions produced in such environments are severe. In view of this, there is an increasing need for a better understanding of the range of application environments in order to develop proper testing procedures.



Fig. 8-Contact resistance distributions of porous gold after laboratory exposure at 30° C and 70 percent relative humidity.

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Fig. 9—Kinetics of porous gold degradation in several laboratory environments at 30° C and 70 percent relative humidity.

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