

The Effect of Test Environment on the Creep of Base Metal Surface Films Over Precious Metal Inlays

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Abstract—The selective deposition of precious metals for electronic connector contacts typically leaves adjacent areas of base metal exposed. In aggressive environments such as those containing H₂S-NO₂-Cl₂ species, the common connector materials, i.e., nickel and copper (alloys) could be attacked. Under extreme conditions, copper sulfide films may creep across the surface of the combined metals. The contact finish and the reactivity of the metal substrate can have a major influence on the creep process. Because pure gold does not form oxides or readily tarnish, it shows little resistance to the creep of the sulfide corrosion products. Other precious metals, such as palladium, have shown better resistance as have certain base metals which are characterized by stable surface oxide films.

This work will report upon an evaluation of two precious metal inlays, WE#1 (69Au25Ag6Pt) and diffused gold-palladium-silver, in combination with several base metals (C72500, C52100, C65400, C17200) which were exposed to a range of severe environments. The materials were exposed as a) bare coupons and b) assembled connectors. The environmental exposures were carried out in a laboratory chamber using Battelle Class II and III atmospheres, respectively. The chamber test periods simulated outdoor life exposures of two to twenty years for Battelle Class II and one to ten years for Battelle Class III. Sample coupons and connectors were characterized by measurements of contact and low-level circuit resistance, respectively.

The beneficial effects of a protective layer over copper alloys to prevent creep of corrosion products were demonstrated. Two methods were used to retard corrosive attack and creep. They were a) the use of a commercial lubricant and b) the shielding of a connector housing.

INTRODUCTION

THE SUBJECT of corrosion product film creep as a potential failure mechanism of electrical contacts continues to receive increasing attention. This is largely as a result of recent advances in the understanding of the chemistry of real-life service environment to which components may be subjected. Large-scale field studies, undertaken by Battelle Laboratories, Columbus, OH, as part of the "Environmental Studies Group" sponsored research project, have resulted in the identification of four broad categories of indoor electrical and electronic environments [1]. Continuing work will likely further identify important subgroups of these major categories. From the information gained in field studies it was possible to develop laboratory environments which reproduced field corrosion mechanisms in an accelerated time frame. Additionally the studies identified that:

- a) no single test could simulate all site conditions;

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- b) only by using multicomponent gas mixtures could field site corrosion mechanisms be reproduced;
- c) inclusion of reactive chlorides was essential to reproduce the majority of corrosion rates and mechanisms;
- d) gas concentrations of only 10 to 100 ppb were sufficient to produce corrosion film thicknesses which could result in potential contact failures.

The four broad environmental categories and their dominant corrosion mechanisms were defined by Battelle [1] as follows:

- Class I Benign—no dominant mechanism.
- Class II Pore Corrosion.
- Class III Pore and Creep Corrosion.
- Class IV Severe Film Creep—uncontrolled industrial.

The increased understanding of the effect of different environments upon pore corrosion and film creep will assist in the development of improved component and product designs. However, it is also important to understand the relationships of corrosion mechanisms to component failure. Bell Laboratories [2] found in an extensive study of field service failures that connectors almost never failed in telecommunication applications due to pore corrosion mechanisms when a degree of control was exercised over the environment. Other connector users [3] have reported that the migration of corrosion products onto gold surfaces is the least observed mechanism of corrosion-related field failures. In contrast, the studies undertaken at Battelle [1] indicated that in as many as 15-20 percent of field sites worldwide film creep could be the dominant corrosion mechanism.

For corrosion product film creep to occur there must exist a reactive base metal whose corrosion products can grow over adjacent contact surfaces. Copper alloys used in the majority of electrical connectors and switches are prone to such reaction mechanisms when exposed to severe environments. The life of components manufactured from reactive base metals within these severe corrosive environments can be improved by several means [4].

- 1) Cover all surfaces with a thick nonporous coating of (expensive) noble metal(s).
- 2) Protect reactive surfaces with a corrosion-inhibiting lubricant.
- 3) Shield the contact interface by appropriate component housing design.
- 4) Cover reactive surfaces with a base metal such as tin or nickel whose corrosion products do not creep. This option typically will also require a further coating of precious metal.

This work was designed to evaluate the performance of several copper-alloy base metals and two precious metals in the two corrosive environments within which most telecommunications, computer, and general business machine components may be located, i.e., Battelle Classes II and III. Since covering all surfaces with a thick nonporous noble metal can be prohibitively expensive, the precious metals were deposited as selective clad inlay stripes. This allowed study of pore corrosion effects by using two different inlay thicknesses and of creep corrosion effects from adjacent copper-alloy surfaces. The first phase of the work was an evaluation of cleaned coupons exposed to Battelle Class II and Class III environments. The results were compared to other studies [1], [5] of similar materials. The second phase evaluated the corrosion-inhibiting effect of a commercial electronic contact lubricant on the same set of coupons. Finally, all materials were evaluated in the form of mated rack and panel connectors (lubricated and unlubricated). All connectors were subjected to durability cycling before and after exposure to the test environments. All mixed gas testing was carried out in environmental chambers at Battelle Laboratories.

MATERIALS

The base metals selected for evaluation were traditional connector and switch spring materials: C72500 (copper-nickel-tin alloy), nickel-clad C72500, C52100 (phosphor-bronze), and C17200 (beryllium-copper). A recent new connector material C65400 (ultronze-high-strength bronze) was also included. Tarnish film creep studies involving copper-nickel-tin alloy have previously been reported upon by Abbott [1] and studies using phosphor-bronze and beryllium-copper were described more recently by Rau *et al.* [5].

The two precious metals selected were WE#1 (69Au25Ag6Pt) and diffused gold-palladium-silver (Au/60Pd40Ag). These materials represent two of the preferred inlay contact materials for connector and switch applications. The WE#1 alloy offers increased hardness over pure gold while reducing precious metal costs. Gold alloys have also been found to show a lower susceptibility to corrosion-product creep than pure gold. Palladium or palladium-silver alloys have also shown still further improvement in resistance to creep. Gold-palladium-silver alloys [6] offer further opportunities to reduce precious metals costs while, at the same time, maintaining the necessary nobility and durability for high-reliability applications.

Fig. 1 illustrates the inlay-base metal configurations used in all studies.

All materials were manufactured as strip in coil form using commercial inlay bonding processes at Technical Materials, Inc. The thicknesses of the WE#1 and diffused gold inlays were 1.25 and 2.0 μm , respectively, for all base metal combinations. Diffused gold-palladium-silver was selected as the thicker inlay since its reduced cost allows such use to improve reliability without compromising the economics of contact specification.

The lubricant selected was a five-ring polyphenyl ether which has been used extensively in commercial connector contact applications. A 1-percent concentration in 1, 1, 1

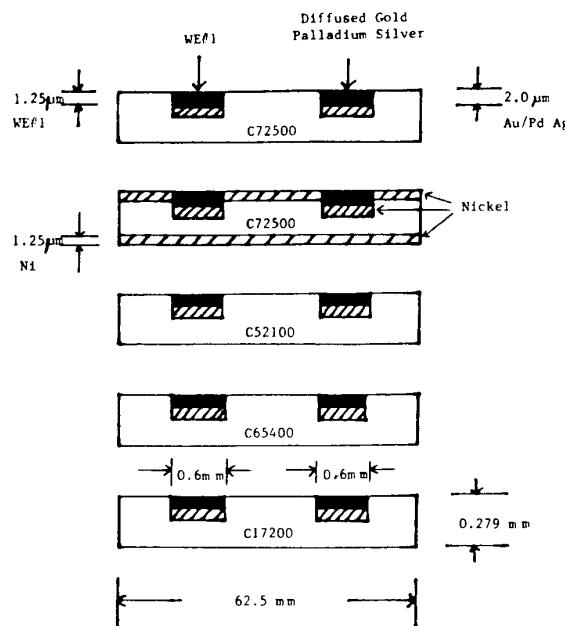


Fig. 1. Inlay-base metal combination.

trichlorethane was used for both coupon and connector studies.

The connector used as a test vehicle was a commercial 34-pin rack and panel connector, as shown in Fig. 2.

The temper and normal force for each base metal are shown in Table I.

The connector sockets were manufactured from the inlaid base metals. The surface roughnesses (rms) of the inlays were 0.175 and 0.125 μm for the WE#1 and diffused gold inlays, respectively. The connector pins were 1.58-mm-diameter phosphor-bronze electroplated with 2.5- μm nickel and 1.5- μm cobalt hardened gold.

EXPERIMENTAL

Multicomponent Gas Environments

All material combinations were exposed to both Class II and Class III environments at Battelle Laboratories. The composition of the environments was as follows:

Class	Gas Concentrations (ppb)			RH (percent)
	H ₂ S	NO ₂	Cl ₂	
II	10–15	200	10	75
III	100	200	20	75

Coupon Studies

The dimensions and configuration of each sample coupon are illustrated in Fig. 3.

Each coupon was ultrasonically cleaned using 1, 1, 1 trichlorethane (TCE) prior to lubricant application. The lubricant was applied by dipping each coupon to half its depth in a 1-percent solution of polyphenyl ether. All combinations of inlays and base metals were subjected to 96, 240, 480, and

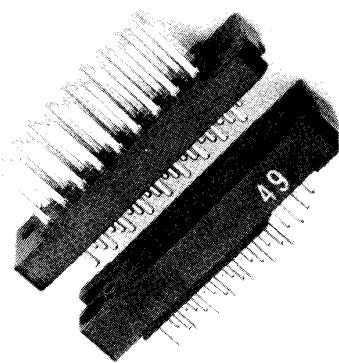


Fig. 2. Rack and panel connector.

TABLE I
CONNECTOR SOCKET NORMAL FORCE

Base Metal	Composition	Temper	Normal Force (g)
C72500	88.2Cu9.5Ni2.3Sn	spring	195
(Ni Clad)	88.2Cu9.5Ni2.3Sn	spring	205
C52100	91.8Cu8Sn0.2P	hard	200
C65400	95.5Cu3.0Si1.5Sn0.1Cr	3/4 hard	185
C17200	97.9Cu1.9Be0.2Co	1/4 HM	225

960 h in the Class II environment and for 48, 96, 240, and 480 h in Class III. Forty-eight hours of exposure in a laboratory chamber is equivalent to approximately one year of field service. Copper and silver control samples were used during each exposure sequence to ensure compliance with the appropriate Battelle environment.

Corrosion effects were evaluated by comparing the electrical contact resistance of inlays before and after environmental exposure. Surfaces were also examined using optical microscopy and using SEM/EDS analysis.

Connector Studies

Six combinations of inlaid base metal were selected for connector studies. They were: diffused gold-palladium-silver inlay in each of C72500; nickel-clad C72500, C52100, C65400, and C17200 base metals; and WE#1 inlay in C52100. Each of the above was evaluated in both Class II and Class III environments and for the same durations as described for coupon studies. All connectors were evaluated both unlubricated and lubricated. A total of 96 connectors were used in the study.

The normal forces of each spring material were determined using a force transducer system which enabled the relationship of the normal force (in grams) to be correlated with the deflection of the contact tynes.

The connectors were subjected to a combination of durability wear cycling and environmental exposure. Prior to any cycling, all connectors were thoroughly cleaned with a solution of 1, 1, 1 TCE, freon TS, and isopropyl alcohol using a three-step procedure:

- 1) immersion in boiling liquid

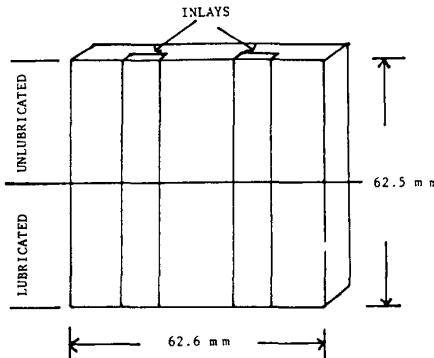


Fig. 3. Configuration of lubricated sample coupons.

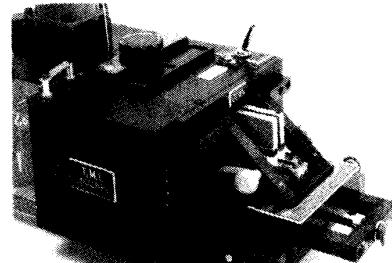


Fig. 4. Contact resistance tester.

- 2) immersion in hot vapors
- 3) a final cold spray rinse.

Connectors were evaluated both unlubricated and with addition of lubricant. When lubricant was used both pins and sockets were separately dipped into the 1-percent polyphenyl ether solution.

The procedure for durability and environmental exposure testing for each material was as follows:

- 1) Clean.
- 2) Apply lubricant to specified connectors.
- 3) Mate connectors.
- 4) Measure low-level circuit resistance (LLCR), 10 contacts per connector.
- 5) 200 cycles of unmating/remating.
- 6) Remeasure LLCR.
- 7) Expose to Battelle Environments.
- 8) Remeasure LLCR.
- 9) Unmate and remate one time.
- 10) Remeasure LLCR.
- 11) Unmate and remate four times.
- 12) Remeasure LLCR.

Corrosion effects were evaluated by comparing LLCR data at each stage of the test program and by optical microscopy and SEM/EDS analysis of individual contacts at the end of the environmental and durability test program.

Contact Resistance

Measurements of the electrical contact resistance of the precious metal inlays in coupon form were made using a standard four-wire system with a Hewlett-Packard Type 4328A milliohmmeter. The contact resistance unit, Fig. 4,

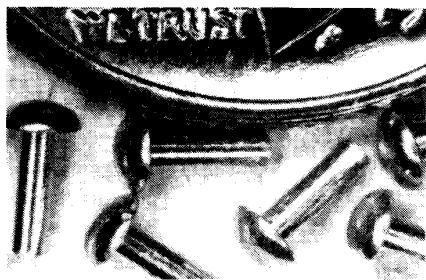


Fig. 5. Contact probes.

TABLE II
CONTACT RESISTANCE OF WE#1 AND DIFFUSED Au/PdAg INLAYS EXPOSED IN A CLASS II ENVIRONMENT

Base Metal	Inlay	Inlay Thickness	Maximum Values of Contact Resistance (mΩ) Time of Exposure (h)				
			0 h	96 h	240 h	480 h	960 h
C72500	WE#1	1.25 μm	3.75	3.50	5.88	11.42	16.12
C72500	Au/PdAg	2.00 μm	4.25	3.5	5.66	12.10	8.68

was of a double-probe design. The double-probe unit has demonstrated improved sensitivity and reproducibility for the measurement of thin films (0–10 mΩ) at low contact loads (15–20 g) when compared to a single-probe device. The unit is designed to have zero wipe during contact measurements.

The probes, Fig. 5, were solid gold of 3.175-mm radius and the distance between the probes was fixed at 2.54 mm. A contact load of 50 g was used for all measurements.

Low-Level Circuit Resistance

Four wire measurements were made according to MIL-STD-1344, Method 3002 with a 10-mA test current and an open-circuit voltage of 20 mV.

Measurement of Corrosion Film Creep

By contact-resistance probing, Abbott [1] determined that the visible front of an advancing creep corrosion film was in close agreement with the actual film. This was confirmed in the present work. Measurement of film creep was determined from the visible films using an optical comparator.

RESULTS AND DISCUSSION

Coupon Studies

1) *Class II Environment:* Table II details contact resistance values for WE#1 and diffused gold-palladium-silver inlays subjected to up to 980 h of chamber exposure. Measurements were taken (10 per coupon) in the region of the center of the inlay stripes.

Little change in contact resistance occurred for exposures up to 240 h. Between 480 and 960 h, the resistance increased, however, the maximum change was less than 12.5 mΩ. The highest values occurred for WE#1 inlay but differences between the two precious metals were not considered significant. Increases in contact resistance are considered to be due to the products of pore corrosion. The porosities of the as-

manufactured inlays were <3 pores/cm² for WE#1 inlay and <2 pores/cm² for diffused gold-palladium-silver. Porosities were measured using Paper Electrography to ASTM B741-85.

Table III illustrates the contact resistance differences for WE#1 inlay in each of the base metals. By definition the Battelle Class II environment is designed to promote pore corrosion and not result in any significant creep. In this work, some samples after 960-h exposure exhibited evidence of film creep as shown by high contact resistance values in Table III. There was no difference between C72500 and nickel-clad C72500 in the Class II environment as determined by contact resistance measurements.

The protection afforded by a lubricant film is clearly illustrated by the stable contact resistance up to and including the simulated twenty-year life exposure, Table III.

2) *Class III Environment:* The Class III environment is designed to promote both creep and pore corrosion. Fig. 6 compares film growth over WE#1 and diffused gold-palladium-silver inlays. Up to the 96-h stage, the diffused-gold inlay exhibited greater resistance to film creep than the WE#1. From 240 to 480 h, the difference between them was not significant, however, overall the diffused gold inlay fared slightly better.

The protective influence of a lubricant film was again demonstrated, Table IV, by the stable contact resistance of the inlays after exposure. Fig. 7 illustrates further the dramatic effect of a lubricant inhibiting film creep in what was otherwise a worst case 480-h Class III exposure.

Fig. 8 illustrates the influence of different base metals upon film growth. The results are in good general agreement with other data [1] and show little difference between the alloys. Although base metals containing elements that can form stable oxides (Ni, Sn, Si, Be) might be expected to exhibit resistance to the film growth the differences observed were minor within the severe Class III environment. The beryllium-copper alloy was pickled, as is commercial practice, to remove all but an

TABLE III
MAXIMUM VALUES OF CONTACT RESISTANCE OF WE#1 INLAY IN
DIFFERENT BASE METALS EXPOSED IN CLASS II ENVIRONMENT

Base Metal	Coupon Protection	Contact Resistance (mΩ)				
		0 h	96 h	240 h	480 h	960 h
C72500	none	3.75	3.50	5.88	11.42	16.12
C72500	lubrication	3.75	5.88	5.02	5.32	5.52
C72500	Ni clad (no lubrication)	3.75	4.08	4.70	10.90	12.06
C52100	none	3.90	3.88	4.90	>100.0	>100.0
C65400	none	3.85	4.10	6.56	8.40	90.80
C17200	none	3.90	4.04	20.76	>100.0	>100.0

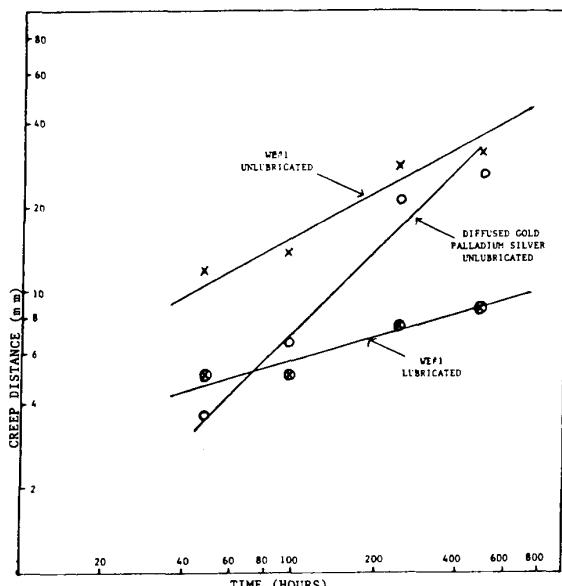


Fig. 6. Resistance of WE#1 and diffused gold-palladium-silver to corrosion product creep in Battelle Class III environment.

ultra-thin film of BeO from the surface. None of the other base metals received a final pickle or cleaning operation. They were used in the as-rolled condition.

In general, the corrosion performance of each of the base metals could be categorized as follows: the phosphor-bronze alloy was more readily attacked than copper-nickel-tin. The highest copper content alloy, beryllium-copper, suffered the greatest attack. The performance ranking over >480 h (> 10-year simulated lifetime) was C72500 (best performance) > C65400 > C52100 > C17200.

No significant difference in the resistance to corrosion product creep was observed between C72500 and nickel-clad C72500 with this environment. Although nickel corrosion products show little evidence of creep, the chloride/sulfide corrosion products of copper alloys will creep over nickel surfaces [1].

The dominant chemistry of creep products was confirmed as copper sulfide formation by SEM/EDS analysis. However, EDS analysis showed chloride, rather than sulfide, to be the predominant species in the thin film which composed the advancing front of the corrosion product.

Connector Studies

The purpose of this phase of the work was to examine the effect of the connector housing as a means of protection against corrosion product creep. To simulate actual connector qualification testing and to produce realistic contact performance requirements all connectors were subjected to 200 cycles of mating and unmating prior to environmental testing. Since all connectors were tested in the mated condition, two further durability tests were performed after exposure. A single unmating/remating was carried out to produce new contact interfaces and additional four cycles were performed to allow for wiping of any corrosion products adjacent to the contact area back into the region and actual contact interface.

Table V illustrates the LLCR results for all inlay-base metal combinations at all stages of the most severe environmental exposure, i.e., unlubricated connectors exposed to the Class III environment for 480 h. The LLCR values reported are the maximum readings obtained from measurements taken on ten contacts per connector.

The protection afforded by the housing is very significant. The results shown in Table V are typical of those found for every connector combination under all test conditions. Fig. 9 illustrates the pin and socket from a disassembled connector after 480 h of Class III exposure. The protection was such that the worst case evidence of corrosion of exposed copper alloys within the housing section was only a light discoloration.

SEM/EDS analysis of wear tracks of sockets and pins showed general metal transfer from pins to sockets as expected. Wear tracks showed little evidence of debris and lubricated connectors exhibited the smoothest burnished wear surfaces. There was no evidence of wear through the precious metals on pin or socket contacts.

CONCLUSIONS

These studies were designed to evaluate selective precious inlays clad to copper-alloy base metals in severe environments. They were also designed to go further and examine the protection afforded by a) a contact lubricant and b) a connector housing under realistic connector qualification conditions. A summary of the major findings is as follows:

1) Differences in film creep between the base metals and precious metals were observed to be in general agreement with other studies [1], [5]. These differences were, however, minor when compared to the complete inhibition afforded by the connector housing even in the most severe environment.

2) The rack and panel connector used in this work was 100 percent effective in eliminating corrosion of contact areas of both pins and sockets, and illustrated the importance of the total connector design in optimizing performance and reliability.

3) The results obtained in this work may not be directly applicable to unmated connectors, or other connectors of more open design, exposed to such aggressive environments.

4) The five-ring polyphenyl ether lubricant was effective in significantly reducing corrosion and film creep. Advances continue to be made in lubricant chemistry [7] and further studies are required to identify optimum requirements for corrosion protection.

TABLE IV
MAXIMUM VALUES OF CONTACT RESISTANCE OF WE#1 AND DIFFUSED Au/PdAg INLAYS EXPOSED IN A CLASS III ENVIRONMENT

Base Metal	Inlay	Inlay Thickness	Protection	0 h	Contact Resistance (mΩ)			
					48 h	96 h	240 h	480 h
C72500	WE#1	1.25 μm	lubrication	4.10	6.92	5.00	4.34	6.74
C72500	Au/PdAg	2.00 μm	lubrication	4.65	6.18	4.94	6.40	9.42

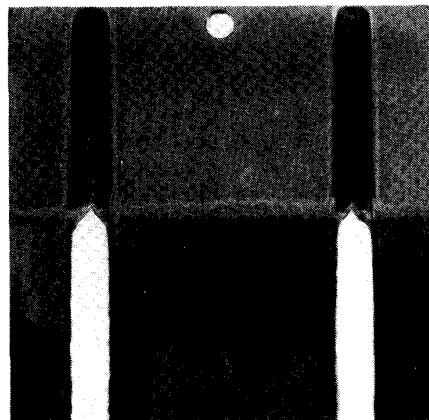


Fig. 7. Lubricant protection against corrosion product creep.

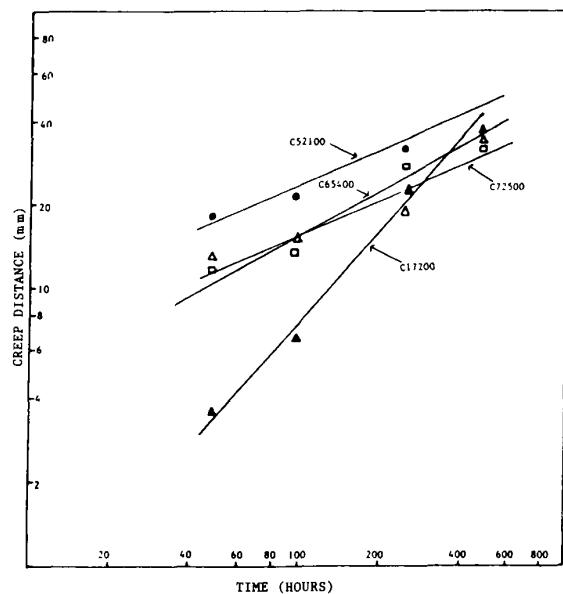


Fig. 8. Comparison of corrosion product creep for different base metals in Battelle Class III environment.

5) Corrosion product film growth over WE#1 and diffused gold-palladium-silver inlays occurred at similar rates, with the diffused-gold inlay being slightly superior.

6) Both WE#1 and diffused-gold-palladium-silver inlays exhibited excellent durability over 200 cycles of unmating and remating.

7) With some material combinations the Class II atmosphere appeared to promote film growth. Studies are planned to evaluate these effects further.

TABLE V
MAXIMUM VALUES OF LLCR MEASUREMENTS AFTER 480 h CLASS III EXPOSURE AND DURABILITY CYCLING

Base Metal	Initial	200 Cycles	480 h	480 h + 1 Cycle	480 h + 5 Cycles
			Class III		
C72500	5.4	5.6	5.1	5.1	5.3
C52100	5.5	5.9	5.1	5.1	5.2
C65400	6.3	6.8	6.3	6.4	6.5
C17200	5.2	5.6	4.8	4.9	5.0

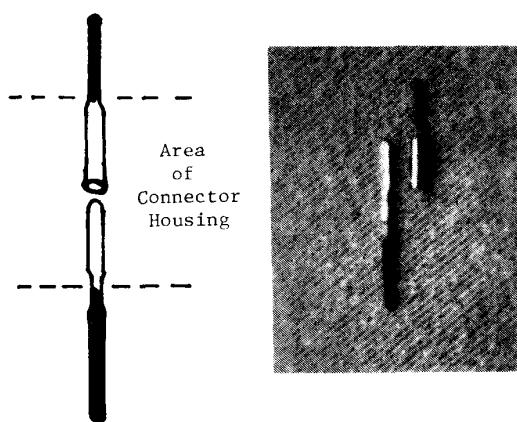


Fig. 9. Disassembled pin and socket showing protection against corrosion afforded by connector housing.

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