

The Development and Application of Palladium Contact Materials

RECENT WORK ON TELECOMMUNICATIONS CONNECTORS

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Palladium-based contact materials are replacing gold finishes on the contacts of many separable connectors used in telecommunications systems in the United States of America due to their lower cost. Before this was possible, however, methods had to be developed for: inhibiting the corrosive attack of palladium by certain chlorine-containing compounds in the atmosphere, retarding the formation of insulating frictional polymers on palladium, and improving its wear resistance. Also, improved manufacturing techniques for palladium contact materials were necessary. An alloy, clad 60 per cent palladium-40 per cent silver having a small amount of gold diffused into its near surface region, and a new palladium electroplating process which is used with a thin gold overplate, were developed. The technology behind these developments is described, and an example of the application of the new materials in a major connection system is given.

Gold has been the traditional contact material for high reliability, long lived separable electronic connectors used in telecommunications systems. However, escalation in its cost, together with rapid growth in the use of connectors and printed circuit boards, spurred a search for replacement contact materials which would be less expensive but equal to gold in reliability (1). Palladium was clearly the most attractive alternative due to its availability, from favourable early results in some telecommunications (2) and computer connection products (3), and because of the extensive experience gained with it on the contacts of wire spring relays in older electromechanical switching systems. There were, however, several questions concerning the suitability of palladium for the contacts of separable connectors. Since it is less noble than gold, any susceptibility to corrode might degrade its behaviour in low voltage circuits. In addition insulating frictional polymers were known to contaminate palladium surfaces at some conditions (4),

while its sliding wear was relatively unexplored. Finally, processes for fabricating palladium-based contact materials in high volume had to be developed.

Many organisations have contributed to the technology of palladium connector contacts. An historical account of early developments was published here recently (5). The present paper focuses primarily on work in the U.S.A. which has led to the growing acceptance of palladium in major products for the telecommunications industry. An important influence in this work was the recognition from studies of wire spring relays that the considerably less expensive 60 palladium-40 silver alloy was comparable to pure palladium in many of its properties (6).

Environmental Effects

A field study which included many noble contact materials and base metals was conducted by AT&T Bell Laboratories from 1974 to 1980 to determine the extent to which they were affected by the environment (7, 8).

Degradation of the bulk materials, corrosion at pores in noble metal coatings on non-noble substrates, and the spreading of tarnish films were all examined.

Various materials were exposed in air conditioned and non-air conditioned buildings located in different geographic regions. Visual observations for corrosion were supplemented by analysis with a contact resistance probe, a method that is very sensitive to the presence of insulating films on metals (9). The major finding was that palladium and 60 palladium-40 silver are tarnished by traces, that is to say less than 10^{-9} parts by volume, of certain gaseous chlorine-containing air pollutants when the relative humidity exceeds 60 per cent. Below this humidity, there is little or no effect.

The contact resistances at a load of 100g for clad palladium, 60 palladium-40 silver and electroplated cobalt-gold controls after 3 to 4 years of field exposure are shown in Figure 1. The contact resistances increased in all cases from the initial levels. Small amounts of dust particles contributed to these changes. Palladium and 60 palladium-40 silver which had been exposed in air conditioned locations were practically unaffected by corrosion. The tarnish films on 60 palladium-40 silver had slightly higher contact resistances than the films on palladium.

An Auger surface analysis with sputter depth profiling of palladium and 60 palladium-40 silver samples showed that the films contained chlorine (10). The tarnish subsequently was identified as $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ (11). From specimens that had been exposed for different lengths of time at a non-air conditioned site in an urban industrial location, it was found that the growth of the chloride films followed parabolic kinetics, and that palladium was more reactive than 60 palladium-40 silver. The rate constant k in the equation, $x^2 = kt$, where x is chloride film thickness and t is exposure time, is: for palladium, 1.11×10^{-11} cm^2/month and for the alloy, 5.82×10^{-13} cm^2/month . A concurrent study of 40 palladium-60 silver alloy showed more rapid contact resistance degradation than palladium due to the formation of

films containing silver and chlorine, as well as $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ (7, 10).

The greater nobility of 60 palladium-40 silver compared to palladium did not make its after-exposure contact resistance more stable because the alloy is both harder and has a higher bulk resistivity; these accentuate the influence of insulating films on contact resistance (7).

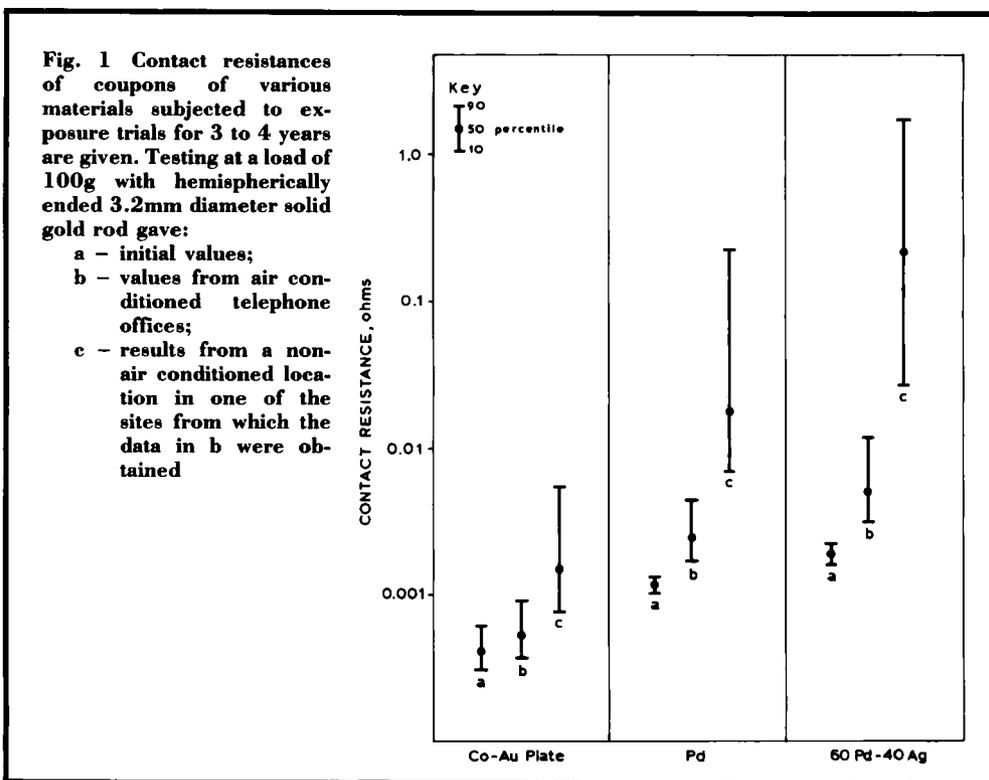
The effect of chlorine on palladium and palladium-silver alloys was confirmed by a subsequent study of samples that were exposed in a multiplicity of indoor environments and in shelters out-of-doors (8). Contact resistances in excess of 1000 ohms were measured on samples after 1 to 12 months of exposure in cases where pure gold controls were relatively unaffected.

Further studies of the reaction chemistry (12) showed that [a] gaseous chlorine produced the same tarnish film as the unidentified chlorine-containing air pollutants, [b] the severity of attack increased with both relative humidity and chlorine concentration, [c] gaseous hydrochloric acid was unreactive (13), and [d] mated contacts were less susceptible to chemical attack due to shielding of their surfaces by the connector housing, yet there was still significant risk of contact deterioration when palladium and palladium-silver were used.

In summary, traces of chlorine-containing compounds that had heretofore not been realised to exist are nearly always present in urban and industrial environments, and these compounds can rapidly tarnish palladium and some of its alloys under humid conditions. If the relative humidity cannot be controlled below 60 per cent, palladium may not be a satisfactory contact material. It was therefore evident that palladium-based contacts which contain some gold might have improved performance; these studies summarise the development of low gold-palladium contact materials.

Contact Materials with Thin Gold Surfaces Manufacturing Processes

Two palladium contact materials containing a small amount of gold were studied extensively. These were a clad alloy and an electrodeposited



pure palladium with a thin gold coating. One role of the gold is to attenuate the reactivity of palladium; but to be cost effective, the amount that is used must be small by comparison with the gold content in the original contact that it replaces.

Sheet metal is an especially attractive substrate from which to make connector contacts. Strip copper alloy such as CA 725 (88 copper-10 nickel-2 tin) is stamped and formed to the finished part, for example a contact receptacle with integral springs. By inlaying the precious metal in the correct location on the sheet, it will appear selectively at the contact region and in this way can be used very efficiently. An inlay is made by machining a groove in the substrate and inserting the metal before rolling it thin. Diffused gold, 60 palladium-40 silver cladding, designated DG R-156, is made from a three-layer material of gold foil on 60 palladium-40 silver and a nickel carrier, with thickness ratios in the range of approximately 1:10:30 to 50

(14). The combined thickness of gold and 60 palladium-40 silver in the final contact is in the range of 1.25 μm to 2.5 μm . Multiple passes of the composite through the rolls is usually necessary, depending on the desired thickness and substrate temper, and the metal is annealed between each rolling. This causes interdiffusion of the gold and 60 palladium-40 silver so that the composition of DG R-156 at the surface is 55 to 85 per cent gold, the balance being palladium and silver. The gold content diminishes in the body of the palladium-silver alloy; but by concentrating the gold near the surface it is utilised more effectively than if the alloy were homogeneous. DG R-156 has the colour of palladium.

Electroplated palladium has attracted interest and several commercial processes are now available which can give sound deposits with good contact properties. Methods for co-depositing palladium with nickel (15) or silver (16) have been developed. A significant

advance in palladium plating technology (17) involved the development of a new system based upon stable solutions that are easy to replenish and to maintain, and which can be prepared inexpensively from simple salts. This system will produce crack-free deposits under a wide range of conditions of barrel, rack, and continuous high speed strip plating (for example, at current densities from about 0.05 to 20 A/dm²). The tendency of palladium deposited from conventional solutions to crack originates in co-deposited hydrogen which forms β -PdH; this phase is unstable and loses hydrogen spontaneously (18). Internal stresses that develop in the deposit cause the cracking. The new process is 100 per cent current efficient, does not generate hydrogen, and is based on a non-ammoniacal bath involving a palladium chelate with an alkaline phosphate buffer (19). A thin gold overplating is applied to the palladium deposit, and a nickel subplate is used to improve the wear resistance of the finish, similar to practices with thick cobalt-gold deposits. This plating process is used extensively for connector and printed circuit contacts in the telecommunications industry.

Corrosion Tests

Laboratory tests and field exposures confirmed the corrosion resistance of DG R-156 and gold coated palladium plate, compared to the parent materials without gold. For example, in evaluating the inlay, coupons were placed in laboratory environmental chambers at 80 per cent relative humidity, with chlorine at a concentration of from 70 to 380×10^{-9} parts by volume in air, or to 380×10^{-9} parts of chlorine mixed with 100×10^{-9} parts of hydrogen sulphide (12). Exposures were for various durations and the characteristics of the resulting films were determined with a contact resistance probe at a load of 50g, as described above. In a typical experiment, the contact resistance of a 1.25 μ m thick DG R-156 inlay was comparable to that of the widely used connector contact alloy, 70 gold-30 silver, and was significantly less than that of palladium or of 60 palladium-40 silver.

The migration of corrosion films over the surfaces of selectively coated contact materials is of interest. The films originate in the copper based alloy at the edge of the coating. This has not been observed in telephone central offices (7), but it can occur in highly aggressive environments. Using dilute mixtures of hydrogen sulphide, nitrogen dioxide and chlorine, the rate of migration of corrosion films on DG R-156 was found to be similar to that over gold and 75 gold-25 silver alloy (20). Creep is not as extensive over less noble materials, such as palladium and 60 palladium-40 silver, because the tarnish that forms inhibits this movement.

Wear and Friction

In general, ductile noble contact materials with a hardness below about 300 kg/mm² are not desirable when mated with themselves in connectors that are engaged with a wiping or sliding action. Such materials experience high frictional forces, metal transfer, and wear. This observation assumes that the metals are employed in the usual range of thickness (0.5 to 5 μ m), that the normal force of the contact spring is from 100 to 300g, and that the numbers of engagements is greater than 10. Thus, DG R-156, palladium and 60 palladium-40 silver, as well as pure gold, are unsatisfactory. This generality excludes most cobalt- and nickel-containing gold platings from cyanide baths; they are relatively brittle, and asperity junction growth at the interface—which contributes to friction and wear—is inhibited (21). There are a number of ways to improve the sliding performance of DG R-156 and of palladium including the use of an opposing contact that is thickly plated with cobalt-gold, by using supplementary organic lubricants or a metallic film lubricant. In detail, a cobalt-gold opposing contact which is less hard than DG R-156 or palladium results in superficial metal transfer, thereby giving a cobalt-gold to cobalt-gold couple (22). An effective organic lubricant reduces the asperity welding tendency of the contact metals; and, like a thin metallic film lubricant (such as gold), involves the interposition of an easily sheared low friction

material at the interface. Boron ion implantation was found to increase the superficial hardness of palladium and 60 palladium-40 silver by from 25 to 45 per cent to values in excess of 300 kg/mm² (23), which reduced the excessive wear of the parent materials; however, ion implantation is too expensive to be acceptable for general connector applications.

Recent work has demonstrated the effectiveness of a thin gold overplate in lowering the wear and friction of palladium plate (24). This was extended to DG R-156 mated to gold coated palladium (25), where it was found that both thin pure gold and cobalt-gold platings are effective, as shown in Figure 2. Cobalt-gold is the preferred material, because if it is inadvertently plated to a thickness greater than the optimal level of about 0.05 μm the performance of the system is not seriously degraded, as is the case with a thick pure gold layer. In addition, the benefit of using a supplementary fluid lubricant is demonstrated in the Figure.

The Effect of Fretting

Although mated connector contacts are nominally at rest, sometimes small interfacial movements occur due to variation of the ambient temperature or to external vibrations. Adsorbed organic air contaminants polymerise on the surface of catalytically active metals, especially palladium, to form insulating solids called frictional polymers. It was therefore important to evaluate the effect of such movements on contact materials and new test equipment was constructed for this work (26). The significant findings are that the levels of organic pollutants in ordinary room ambients are sufficient to cause rapid changes of contact resistance, values in excess of 1000Ω occurring with palladium to palladium contacts in only a few thousand cycles under some conditions (27). The larger the amplitude of movement and the lower its frequency, the fewer the numbers of cycles required to achieve a given change of contact resistance. However, if the normal force between palladium contacts exceeds about 200g, the polymers are penetrated and cause only a small rise of contact resistance. The 60

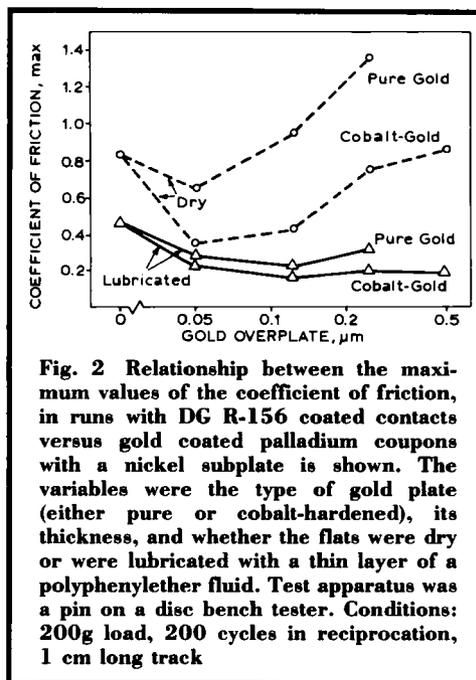


Fig. 2 Relationship between the maximum values of the coefficient of friction, in runs with DG R-156 coated contacts versus gold coated palladium coupons with a nickel subplate is shown. The variables were the type of gold plate (either pure or cobalt-hardened), its thickness, and whether the flats were dry or were lubricated with a thin layer of a polyphenylether fluid. Test apparatus was a pin on a disc bench tester. Conditions: 200g load, 200 cycles in reciprocation, 1 cm long track

palladium-40 silver alloy is much less susceptible than palladium to form polymers. An opposing gold or gold alloy which is softer will transfer to the palladium, resulting in an all-gold system; gold has little tendency to form polymers. A thin gold plating on palladium inhibits polymer formation until the gold is worn through. Supplementary organic lubricants, especially if used in relatively thick layers, can stabilise contact resistance because the polymers which form are nonadherent. Some of these findings are illustrated in Figure 3.

Thermal Stability

Palladium and its alloys are recognised to be thermally stable. This was verified with DG R-156, 60 palladium-40 silver, and electro-deposited palladium which were found to have stable contact resistances, well beyond the temperatures at which they would be used in practical connector applications. Coupons of these materials were aged in ovens and then probed with a gold rod at a load of 100g. The contact resistances following 1000 hours of ageing in air at 200°C were within 1 mΩ of their

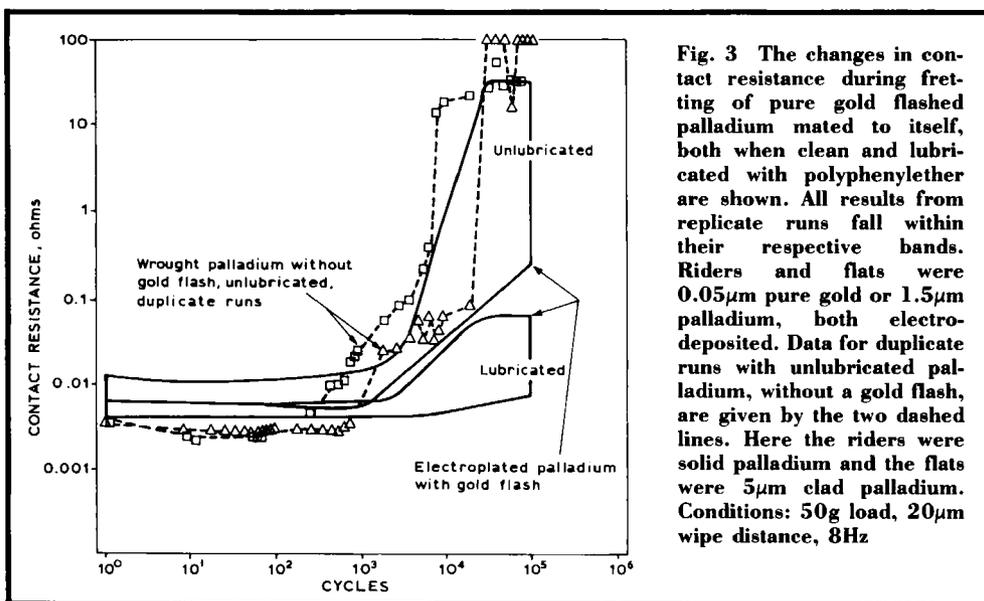


Fig. 3 The changes in contact resistance during fretting of pure gold flashed palladium mated to itself, both when clean and lubricated with polyphenylether are shown. All results from replicate runs fall within their respective bands. Riders and flats were $0.05\mu\text{m}$ pure gold or $1.5\mu\text{m}$ palladium, both electrodeposited. Data for duplicate runs with un lubricated palladium, without a gold flash, are given by the two dashed lines. Here the riders were solid palladium and the flats were $5\mu\text{m}$ clad palladium. Conditions: 50g load, $20\mu\text{m}$ wipe distance, 8Hz

initial values for $1.25\mu\text{m}$ thick DG R-156 and 60 palladium-40 silver, for 0.6 and $2.5\mu\text{m}$ electrodeposited palladium on nickel underplate on copper, and for $2.5\mu\text{m}$ of palladium plate on copper. Only thin ($0.6\mu\text{m}$) palladium on copper deteriorated, with contact resistance rising to $11.5\text{ m}\Omega$ from an initial value of $1\text{ m}\Omega$. The thermal stability of palladium electroplate with a $0.05\mu\text{m}$ thick gold coating was verified by product quality control tests carried out using connectors which

incorporated this material on their contacts.

In contrast to these results, 200°C is well beyond the thermal stability of typical cobalt-gold (0.1 to 0.3 per cent cobalt) electrodeposits which cannot be heated for more than a few hours at this temperature (28). Even below 125°C , the co-deposited elements and base underplate or substrate materials in gold may diffuse to the surface and cause the contact resistance to increase. In summary, palladium, 60 palladium-40 silver, and palladium alloys that contain a small amount of gold are preferred contact materials for elevated temperature applications.

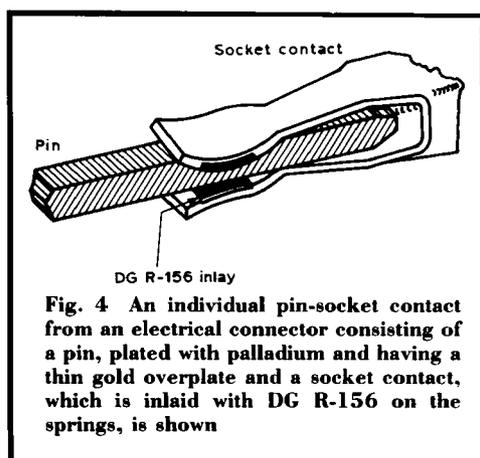


Fig. 4 An individual pin-socket contact from an electrical connector consisting of a pin, plated with palladium and having a thin gold overplate and a socket contact, which is inlaid with DG R-156 on the springs, is shown

An Application of Palladium Connector Contact Materials

The advances in palladium materials technology have been exploited in a number of telecommunications products. An important example involves the connector contacts of the AT&T Fastech® packaging system (29). This consists of a standard set of printed circuit boards, connectors, and other hardware for mounting and interconnecting electronic components to build shelves of equipment. The contact pins are pressed into plated through

holes of a printed circuit board backplane. A compliant section of the pin retains it in the board without solder. The back ends of the pin are terminated by solderless wrap connectors or by pluggable cables.

The contact system illustrated in Figure 4 consists of a socket contact and a 0.63mm square pin. The socket is CA 725 alloy inlaid with DG R-156 in the contact springs, and the CA 725 pin is plated with 0.05µm of cobalt-gold and 0.6µm palladium on a nickel underplate. The contacts are lubricated by immersion or by spraying with a solution of 2 per cent by weight of a 6-ring polyphenylether lubricant in a volatile solvent (30). On evaporation, a residual thin layer of the lubricant remains. A

qualification study of the connector with an earlier version of the contact materials has been reported (31). Exposure to laboratory chamber environments involving chlorine and hydrogen sulphide was used to simulate the effects of aggressive atmospheres; cycling temperature and mechanical vibrations were used in fretting tests; ageing at elevated temperature was used to induce stress relaxation of the spring materials; and 200 insertions and withdrawals were made to evaluate the durability of the connection. This packaging system has been in production since 1980; DG R-156 was introduced in 1981; gold coated palladium electroplate in 1984; and the present contact lubrication practices implemented in 1986.

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