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Contact erosion of silver and Au/8% Ag following N^+ ion-beam treatment

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Comparison has been made between the contact erosion behaviour of Au/8% Ag and pure silver prior to and following N^+ implantation of surfaces to a dose of 2×10^{17} ion cm^{-2}. Details of the rate of erosive transfer between anode and cathode pairs were studied over a range of switching current with subsequent surface examination by scanning electron microscope. Significant reduction in erosion rate due to N^+ implantation occurred in Au/8% Ag at currents of $I < 100$ mA and in silver over an extended range of current (25 to 500 mA), conditions which corresponded to metal transfer by mechanical adhesion. The ion-beam treatments were observed to produce no qualitative change in the nature of the erosion process.

1. Introduction

Wrought alloys based on the noble metals gold, palladium or silver are used as electrical contacts in electromechanical devices such as relays and connectors operating in low-power conditions. For such contact surfaces, the principal property requirements are freedom from interfacial non-conducting films, thermal stability and electrical conductivity [1, 2]. In the case of switching contacts, which perform the function of repeated junction formation and separation, the integrity of the contact surfaces is also determined by the occurrence of metal transfer or erosion which causes a progressive disfigurement of the interface. Reduction in contact erosion has been sought by the minor addition of elements to form either the Au–Ag, Au–Ni or Au–Pd alloy systems for low level or dry circuit conditions or Ag–Pd in the medium level range [1]. Additions to binary alloys which produce characteristics of precipitation hardening are a further alternative [3]. Nevertheless, limitations arising in the use of alloying additions have recently been defined [4], including the possibility of selective oxidation of duplex nickel phases causing reduction in contact stability of Au–Ni alloys and the inability of the continuous solid solutions formed by the Au–Ag and Au–Pd systems to produce significant effects on either hardness or coefficient of adhesion.

In recent years, extensive interest has developed in the use of ion-beam modification of metal surfaces, particularly in the improvement of friction and wear properties of steels [5]. Ion implantation has also been reported to significantly increase resistance to sliding wear of non-ferrous materials such as pure aluminium [6] and alloys based on copper [7] and palladium [8]. The purpose of the present work was to examine the application of ion-beam techniques as a means of treatment of electrical contact surfaces either in combination with bulk alloying additions or as an alternative method. Substrates consisting of fine silver and Au/8% Ag were selected, representing preferred contact materials from the dry circuit and intermediate levels of switching current [4]. N^+ was used throughout as the implant species because of recognized tribological effects in other non-ferrous materials [7, 8]; preliminary studies using ion-beam mixing of titanium are also presented. Elemental titanium exhibits a lower coefficient of adhesion than either silver or gold [9] while showing comparatively low electrical resistivity in nitride form [10].

2. Experimental details

Specimen materials of pure silver (99.99 + %) and Au/8% Ag were obtained as dome-shaped rivets approximately 2 mm in diameter with microhardness of 84 HV and 104 HV, respectively. The Au/8% Ag alloy consisted of a layer ($\simeq 10\,\mu$m) roll-bonded onto an underlying base of Ag/30% Pd. The contact behaviour of these materials was assessed by operation in spring-loaded relays under resistive circuit conditions of 48 V. Individual values of current were 25 to 200 mA for the Au/8% Ag alloy and from 25 to 500 mA for the silver contacts, these values representing ranges of typical usage. The frequency of closure of the contact pairs was 7 Hz with tests continued until 5×10^6 operations with the contact force measured as 10 gf. Weight change during the test period was determined to an accuracy of $\pm 0.5\,\mu$g, while measurements of contact resistance were taken at intervals of 5×10^3 operations using a high-sensitivity Kelvin Bridge. Similar tests were also conducted on contact surfaces of fine silver and Au/8% Ag which had been implanted with N^+ to a dose of 2×10^{17} ion cm^{-2} at an energy of 100 keV; beam dimensions were 3.4 to 4.0 mm with a current density of 7.5 μA cm^{-2}. A further series of specimens of Au/8% Ag were used as a substrate for vacuum evaporation of pure titanium to a thickness of 20 nm with subsequent ion bombardment with N^+ using the same beam energy as above to create conditions of atomic mixing of the titanium.

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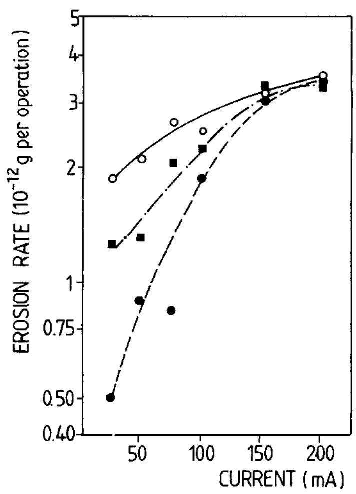

Figure 1 Measurements of the cathode erosion rate as a function of switching current for Au/8% Ag in (○) the untreated condition and (●) following N^+ implantation and (■) Ti–Au/8% Ag ion-beam mixing.

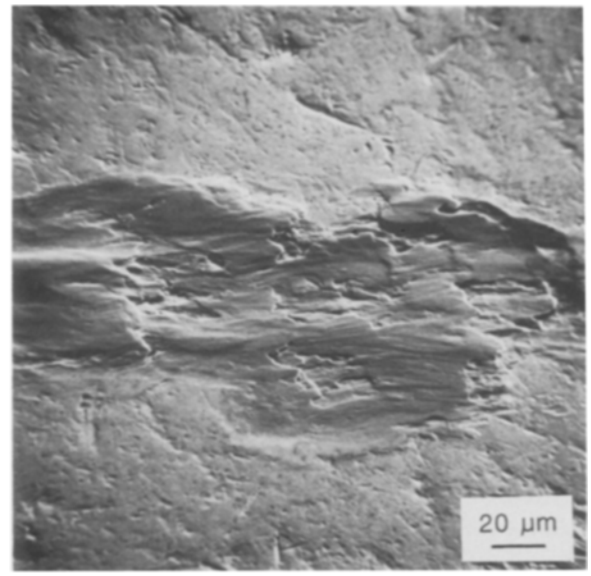

Figure 3 Scanning electron micrograph showing details of the erosion zone of the cathode for unimplanted silver following 4×10^3 cycles at 100 mA.

3. Results and discussion

Comparative measurements of the erosion rate of the cathode for both implanted and unimplanted specimens are plotted in Figs 1 and 2 as a function of switching current; in all cases examined, the cathode loss was equal to anode gain. Junctions which were comprised of combinations of N^+ implanted/unimplanted specimens were found to produce a higher degree of variability in erosion rate than N^+ implanted/N^+ implanted surfaces. As a consequence, all work quoted in the results was completed using N^+ implanted/N^+ implanted specimens.

Compared with the erosion characteristics of the base materials, a considerable reduction in erosion rate of implanted specimens was evident, mainly within the range < 100 mA in Au/8% Ag, see Fig. 1, but across the complete range of current in silver specimens (Fig. 2). Under these conditions, reductions in contact erosion rate due to N^+ implantation were similar in magnitude for both substrate materials; with ratios of approximately 4 : 1 for unimplanted to implanted specimens. However, for the Au/8% Ag alloy at $I \geqslant 100$ mA (see Fig. 1) a convergence of erosion rates was evident such that at 200 mA, differences between treated and untreated specimens were negligible. In the case of the Au/8% Ag alloy modified by ion-beam mixing, erosion rates were intermediate between those of the N^+ implanted and unimplanted specimens, again approaching a value similar to the unimplanted substrates at $I \geqslant 100$ mA.

Examination of the contact surfaces following extended operation confirmed the existence of a build-up at the anode and erosion of the cathode, topological features generally designated as "pip and crater" formation [11]. Detailed observation of the surfaces by scanning electron microscopy revealed two predominant forms of transfer. (i) At relatively low currents (< 100 mA), the contact region in both silver and Au/8% Ag was characterized by extensive shear and mechanical transfer between the surfaces, features which were most clearly defined during the early stages of operation such as shown in Fig. 3. Within the

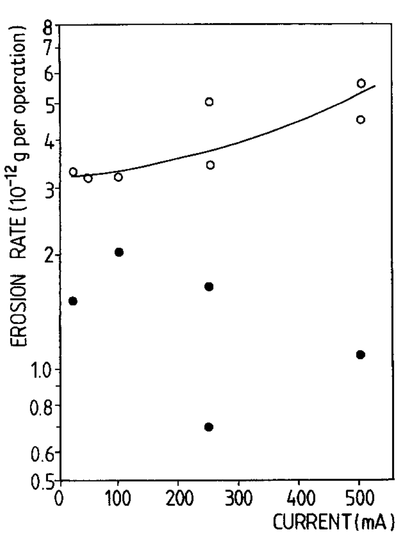

Figure 2 Measurements of cathode erosion rate as a function of switching current for silver in the (●) N^+ implanted and (○) unimplanted conditions.

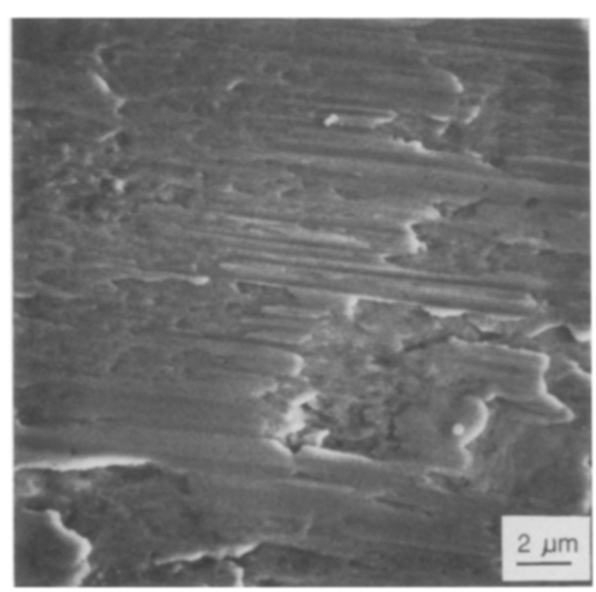

Figure 4 Scanning electron micrograph of the erosion zone of the cathode of N^+ implanted silver after 5×10^6 cycles at 100 mA.

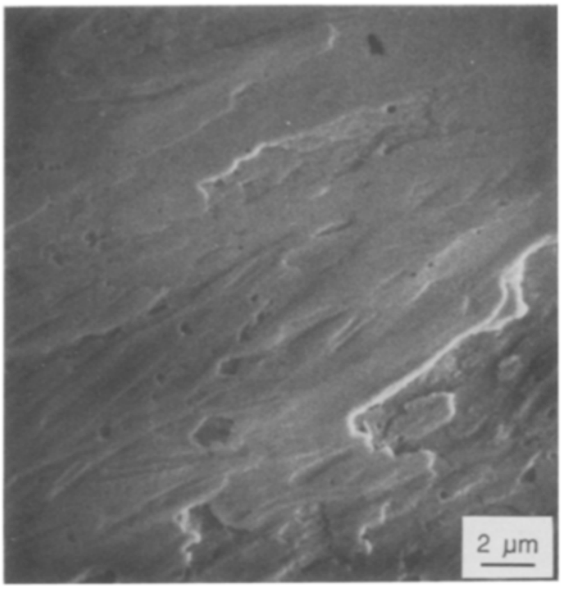

Figure 5 Scanning electron micrograph showing the erosion zone of the cathode for N^+ implanted Au/8% Ag after 5×10^6 cycles at 25 mA.

contact regions were a series of zones of overlapping plastic flow indicating the occurrence of a number of separate transfer events. The cumulative effect of transfer of this type was the formation of an anode protrusion comprising a layered structure of heavily strained material. Observations of the eroded cathode showed little discernable difference in surface features developed by the unimplanted (Fig. 3) and implanted specimens, Figs 4 and 5; some abrasion grooving due to sliding movement was also evident. Similarly, the erosion patterns developed by the N^+ implanted and unimplanted specimens of silver at currents of 250 and 500 mA showed a striated pattern as in Fig. 6, surface characteristics which are indicative of a process of adhesive transfer [12, 13]. (ii) At $\geqslant 100$ mA in Au/8% Ag, the erosion surfaces were characterized by the formation of fine spherical particles approximately 0.5 to 1.0 μm diameter such as illustrated in Fig. 7. The

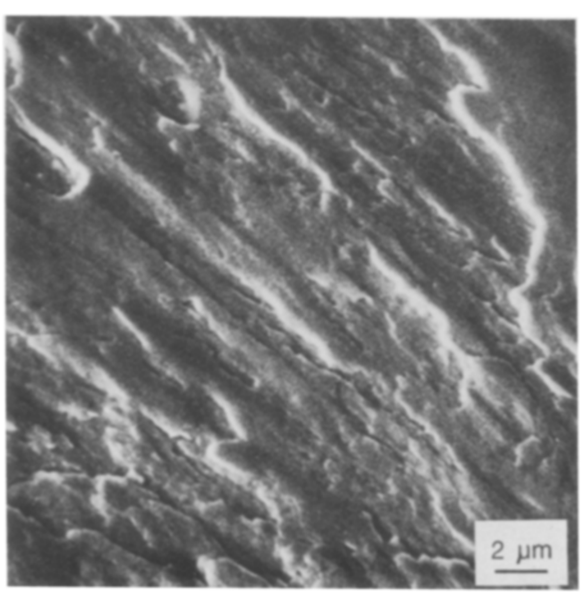

Figure 6 Scanning electron micrograph showing details of erosion of the cathode of N^+ implanted silver operated at 500 mA, 5×10^6 cycles.

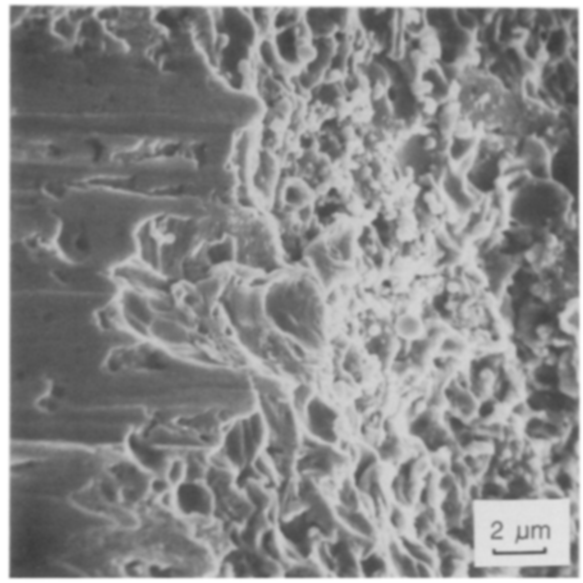

Figure 7 Scanning electron micrograph showing the anode deposit for unimplanted Au/8% Ag at 200 mA, 5×10^6 cycles.

deposits formed at the anode under these conditions were comprised of an accumulation of such particles which had been compressed by the sliding movement of the surfaces (Fig. 7). Observations of spherical particles give clear evidence of molten bridge formation, the rupture of the bridge being inevitably associated with the occurrence of a post-break electrical discharge of transient (msec) nature [14]. Similar features were also evident at the anode deposit of the ion-treated specimens as in Fig. 8.

Measurements of contact resistance of the junctions taken initially and at intervals during relay operation are summarized in Table I. The N^+ implantation of either substrate material produced negligible effect on contact resistance, a situation which remained unaltered during subsequent testing. Specimens of Au/8% Ag–Ti exhibited an initially high resistance which reduced gradually during operation, although remaining at an increased level compared with unimplanted surfaces.

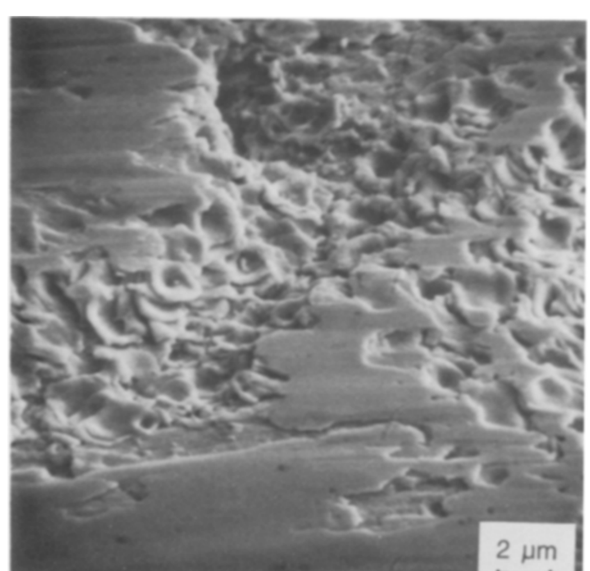

Figure 8 Scanning electron micrograph of the anode region of N^+ implanted Au/8% Ag after 5×10^6 cycles at 200 mA.

TABLE I Summary of measurements of contact resistance

Material	Contact Resistance (mΩ)		
	Initial	5×10^4 cycles	1×10^6 cycles
Au/8% Ag	16.5	15.3	15.0
N^+ implanted	15.8	15.5	15.3
Au/8% Ag–Ti	250 mΩ – 1 Ω	25.5	25.5
Fine silver	15.5	15.4	14.9
N^+ implanted	14.8	14.7	14.3

The results are of general significance in extending the range of known metals in which tribological effects of ion implantation have been observed. Because of the characteristics of chemical inertness and low hardness, sliding contact in silver [12] and Au/Ag alloys [13] is dominated by processes of adhesive transfer. Similarly, in the low-amplitude sliding movement examined in the present investigation, reductions in erosion rate due to N^+ implantation were confined to conditions coinciding with a progressive transfer by mechanical adhesion. Under these conditions, the magnitude of the N^+ implantation effect on transfer rate was equivalent in both the pure silver and the solid solution alloy Au/8% Ag, although producing no qualitative change in the nature of the erosion process. While it is difficult to predict quantitatively the effect of the implanted layer on the various stages of formation and separation of an individual junction, the strength of an adhesive junction is known to be sensitive to properties altered by ion implantation such as the hardness and ductility of the near surface regions [15] and the presence of small quantities of segregated solute [16]. Based on increase in surface mechanical strength, adhesive transfer at ion-implanted surfaces may be expected to occur with reduced area of initial contact at asperity junctions and with separation involving a lower adhesive force [17]. At the same time, the N^+ implantation produced an absence of any alteration in contact resistance of surfaces, an essential characteristic in applications of low-level switching.

In contrast, conditions which produced molten particle formation in the Au/8% Ag alloy ($I > 100$ mA), showed little influence of ion-beam treatment on erosion rate. Considered in terms of the processes of molten-bridge formation and post-break electrical discharge, the presence of the implantation layer evidently exerted only minor influence on physical properties such as melting point, thermal conductivity and surface energy [14] which control the magnitude of metal transfer during arcing. The observed occurrence of arcing in this alloy is consistent with the lower critical current for arc initiation in gold than in silver [11].

4. Conclusions

1. Nitrogen implantation of Au/8% Ag and pure silver to a dose of 2×10^{17} ion cm^{-2} produced a significant reduction in erosion rate of the substrate under conditions of metal transfer by mechanical adhesion.

2. In the range of current for which arcing occurred in the Au/8% Ag alloy, N^+ implantation produced negligible effect on erosion rate.

3. Surface treatments comprising the deposition of a thin titanium layer on Au/8% Ag substrates with subsequent processing by ion-beam mixing produced effects on erosion rate which were intermediate between those of ion-implanted and unimplanted specimens.

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References

1. H. C. ANGUS, *Met. Rev.* 141 **16** (1971) 13.
2. M. ANTLER, *Thin solid films* **84** (1981) 245.
3. A. BISCHOFF, R. SCHNABL and F. ALDINGER, IEEE *Trans on Components, Hybrids and Manufacturing Technology* Vol. CHMT-5, **1** (1982) p. 74.
4. R. SCHNABL and D. PÖSS, 33rd Relay Conference, April 1985, Still Water, Oklahoma, (National Association of Relay Manufacturers, Elkhart, IN, 1985) p. 17.
5. C. J. McHARQUE, *Met. Rev.* **2** (1986) 49.
6. P. B. MADAKSON and A. A. SMITH, Proceedings of Conference on Ion Beam Modification of Materials, edited by B. Biase, G. Destefanis and J. P. Gailliard, *Nuclear Instruments and Methods*, **209–210** (1983) 983.
7. S. SARITAS, R. P. PROCTOR, V. ASHWORTH and W. A. GRANT, *Wear* **82** (1982) 233.
8. M. ANTLER, C. M. PREECE and E. N. KAUFMANN, IEEE *Trans on Components, Hybrids and Manufacturing Technology*, Vol. CHMT-5, **1** (1982) 74.
9. M. SIKORSKI, *Wear* **7** (1964) 144.
10. A. GOLDSMITH, T. WATERMAN and H. HIRSCHHORN, "Handbook of Thermophysical Properties of Solid Materials", Vol, 4, (Pergamon Press, Oxford, 1962) p. 1XD–4.
11. R. HOLM, "Electric Contacts, Theory and Application", 4th Edn. (Springer-Verlag, New York, 1967) pp. 283, 304.
12. M. ANTLER, *Wear* **7** (1964) 181.
13. M. ANTLER and E. T. RATLIFF, IEEE *Trans on Components, Hybrids and Manufacturing Technology*, Vol. CHMT-6, **1** (1983) 3.
14. F. LLEWELLYN-JONES, Proceedings, Holm Conference on Electrical Contacts, Illinois, Chicago, (1978), (Illinois Institute of Technology, Chicago, 1978), p. 249.
15. N. GANE, P. F. PFAELZER and D. TABOR, *Proc. R. Soc. A* **340** (1974) 495.
16. J. FERRANTE and D. H. BUCKLEY, *ASLE Trans* **15** (1) (1972) 18.
17. N. E. HARTLEY, in "Treatise on Materials Science and Technology", Vol. 18 (Academic Press, Florida, 1980) p. 333.

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