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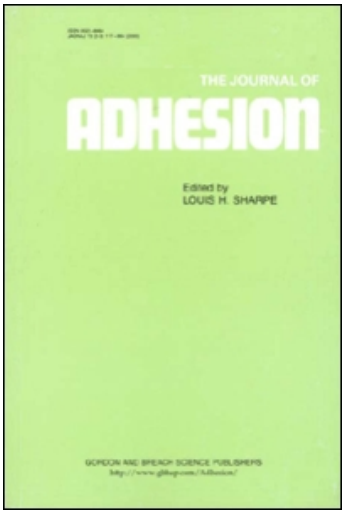

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K. W. Allen[a]; Tiow Lin Tan[a]
[a] Adhesion Science Group, City University, London

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Surface Preparation of Tantalum for Encapsulation and Adhesive Bonding

K. W. ALLEN and TIOW LIN TAN

Adhesion Science Group, City University, London EC1V 0HB

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A number of methods of surface preparation of tantalum for encapsulation in silicone rubber and for structural adhesive bonding were explored. The only ones which could be generally useful were boiling for 24 hours in distilled water (28% improvement) or boiling for 4 hours in 20% sodium hydroxide solution followed by boiling for 2 hours in dilute hydrochloric acid (34% improvement). An alternative, which could sometimes be used, was heating in air for at least 2 hours at 100°C.

KEY WORDS Tantalum; surface preparation; encapsulation; silicone rubber.

INTRODUCTION

Tantalum is one of the less common transition metals. Like aluminium it is an extremely reactive metal which, in its normal form, is greatly resistant to chemical attack due to the presence of a strongly coherent film of oxide. This film is the pentoxide which may be amorphous, crystalline or a mixture of the two. The crystal structure is complex, although the powder diffraction pattern has been indexed on the basis of an orthorhombic unit cell.

If the metal is heated above 150°C in air then oxidation occurs through chemisorption of oxygen at the surface followed by diffusion of the oxygen into the bulk of the metal with formation first of a variety of ill defined sub-oxides and eventually of the pentoxide Ta_2O_5.

The generally high resistance to corrosion or attack by the vast majority of aggressive reagents has the consequence of limiting possible etching solutions to fluoride formulations.[1,2]

Tantalum has been used extensively for a variety of prosthetic devices implanted within the body including plates, pins and screws for orthopaedic purposes. It is well established in this field as having very satisfactory mechanical properties and being highly resistant to attack by body fluids as well as causing no untoward tissue reactions. With the development of neural prostheses it has attracted further attention because of its electrical properties.

The simplest forms of electrodes transmit electrical impulses to or from the nerve fibres by straightforward conduction, but there are limitations on their use because of electrolytic reactions which are induced. These limitations may be overcome by using capacitive electrodes which have been shown to be able to transmit signals of higher power over much longer periods of time without adverse effects. The capacitive electrodes which have been most extensively used are porous Ta/Ta_2O_5 units.[3] In all neural prosthetic devices it is necessary to encapsulate all or some parts in silicone rubber both to provide hermetic sealing and insulation as well as to make them less irritant and more acceptable to the body tissues.

It was for this reason that techniques for producing satisfactory adhesion and encapsulation (which requires good adhesion) of tantalum were explored.

MATERIALS AND METHODS

Substrate

The tantalum used was supplied by Metal Crystals Limited, Harston, Cambridge, England and was described by them as 99.9% pure Ta. The high cost of tantalum was a significant factor so that all the initial studies were made with foil 0.025 mm thick stuck to aluminium carriers. Only the final studies used sheet metal 0.5 mm thick.

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Encapsulant and Adhesive

The encapsulant studied was a one-part, room temperature curing silicone rubber (Dow Corning 3140). This cross-links by hydrolysis with atmospheric moisture through alkoxy rather than acetoxy groups, so that it liberates alcohol rather than acid. It has been designed particularly for electrical applications where the corrosive action of liberated acid (from acetoxy groups) would be a serious disadvantage. Normal curing is complete in five days at room temperature.

For exploring structural adhesive bonding a conventional polyvinyl formal/phenol formaldehyde resin on a light weight non-woven nylon carrier (Ciba-Geigy Redux 775 RN) was used. This requires to be heated to $150 \pm 5°C$ for 30 minutes under a pressure of 70 kN m^{-2} for curing.

Joint Design

All the testing of adhesive strength was done with single lap joints with an overlap of 10 mm × 15 mm. The early stages of the work were done with tantalum foil 0.025 mm thick stuck with an epoxy adhesive (Ciba-Geigy Araldite AV100/HV100) to aluminium strips 1.5 mm thick. In the first series the tantalum measured 10 mm × 15 mm and corresponded exactly with the area of overlap. In the second series this was increased to 10 mm × 20 mm so that it extended beyond the region of critical stress at the end of the overlap. For the third and final series, unsupported tantalum specimens 0.55 mm thick and 10 mm × 40 mm were used.

Cleaning and Nature of Surface

Three methods for the initial cleaning of the tantalum surface were investigated.

1. Swabbing with toluene, rinsing with acetone and immersion in a solution containing 5% trisodium orthophosphate hydrate ($Na_3 PO_4 \cdot 12H_2O$) and 1% sulphonate alcohol detergent (Shell "Teepol"); followed by thorough rinsing in distilled water and drying.[4]
2. Following the above process (1) by heating for 30 minutes at 700°C in air.
3. Following the above process (1) by bombardment with plasma in oxygen.

The outcome of these three regimes was explored and compared with an untreated "as received" tantalum surface by Zisman's technique of measuring contact angle for a range of liquids and extrapolating to derive the critical surface free energy γ_c. Unfortunately most of the contact angles were small so that the errors involved were considerable, with the result that it was not possible to discriminate between the state of the surfaces to any meaningful extent. However it was evident that they were all effectively wetted by water so none of them had any significant contamination.

In later adhesive studies an initial cleaning by the above process (1) was followed by a variety of chemical treatments. The effects of several of these treatments were investigated by diffraction of both X-ray and electron beams and the results compared with standard data from the ASTM powder diffraction file. In an attempt to get information about the surface layer, glancing angle techniques were used in both cases in spite of the known problems with this technique. Again the results were unexpectedly inconclusive and no clear identification of the nature of the surfaces was possible. This was partly due to somewhat inadequate reference data; probably because of the large number and variable composition of the oxides of tantalum. It was only possible to conclude that the surface was probably a mixture of oxides with a significant amorphous component.

An ESCA (or XPS) examination together with an argon ion etching of an "as received" tantalum surface revealed:

1. A layer of adsorbed, contamination, containing mainly carbon, oxygen and silicon, about 30–40 Å thick.
2. A layer of oxide, essentially Ta_2O_5 with small amounts of excess oxygen and a little carbon, 40–100 Å thick.
3. The base of Ta metal containing a small amount of carbide TaC which continuously diffuses into the surface layer of oxide.

ADHESION TESTING

Preliminary Testing

It was recognised that with the somewhat unusual components of the lap joints and the nature of the silicone rubber adhesive, there were several possible sources of inconsistency. These included:

i irregularities in the bonding of the tantalum to the carriers, leading to bowed or distorted surfaces instead of planar ones

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ii misalignment of the two components of the final joint.
iii irregularities in the thickness of the glue line of the silicone rubber
iv rate of strain applied to the joints

In order to validate the procedures a preliminary series of tests was carried out.

A set of thirty single components was made by sticking 10 mm × 15 mm pieces of foil to the end of 1 mm × 10 mm × 100 mm aluminium strips, with Araldite AV100/HV100 using a hand roller. These were left to cure for 24 hours at room temperature under a weight of 1 Kg (equivalent to 6.6×10^3 Kg m^{-2}). The overall thickness of each one of these was measured at five points; each corner and the middle. Of this batch, only 4 had a difference greater than 0.03 mm between any of these measurements and these 4 were discarded.

Joints were made using the silicone rubber as adhesive with 2 mm lengths of wire in the glue line of different diameters to control the glue line thickness.

The alignment of these, and similar joints laps, was carried out very carefully. Each one was laid-up individually over a grid so that the risk of misalignment was very small. These joints were allowed to cure for 6 or 7 days under a light weight before they were tested.

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Glue-line thicknesses of 0.05, 0.07, 0.25 and 0.30 mm were used and the shear strengths were not significantly different with an overall mean value of 1.45 MNm^{-2}.

In order to both investigate the effect of strain rate in testing and the overall precision which might be obtained, a set of sixty similar joints was made. These were divided into four groups and were tested at 7, 20, 40 and 70 mm/min. No systematic variation was observed in the shear strength with the tenfold change in strain rate. However it was clear that even with 15 replicates the best precision which could be achieved in the strength was 2~3%.

Thus it was demonstrated that the sources of inconsistency which had been anticipated were not significant, and that the overall consistency should be perhaps 5% using a modest number of replicates.

First Series of Tests

A series of tests were carried out using various surface treatments of the tantalum foil. In each case the treatment was carried out after the washing procedure and before sticking the foil to the aluminium carriers. This last step was carried out by a careful "no-touch" technique using appropriate forceps. Otherwise the joints were prepared in the way which has already been described.

The details of the treatments, the resulting shear strengths and comments thereon are given in the following Tables I to III. Each of them needs to be considered by comparison with a Mean shear strength and Standard Error of the Mean (SEM) of 1.58; 0.17 MNm^{-2} and a cohesive failure of 50% for joints which have had no surface treatment except the washing procedure.

As Table I shows clearly, heating increases strength, but above 100°C the effect appears to be constant. This change is taking place at too low a temperature to be associated with removal of organic material and may perhaps be associated with the removal of water. The locus of failure of each joint was established as a percentage

TABLE I
Strength and locus of failure of joints made with silicone rubber 3140 after heating in air for 30 minutes at various temperatures

Temperature °C	Shear strength mean; SEM MNm^{-2}	% Cohesive failure
50	1.86; 0.06	80
100	2.13; 0.29	95
200	2.18; 0.03	90
300	2.12; 0.20	90
400	2.16; 0.11	80

cohesive failure within the adhesive (as distinct from apparent adhesive failure at the interface) and a mean value given for each batch of similar specimens.

These results in Table II bear out the results given in Table I and suggest that prolonged heating is advantageous, giving a 65% improvement but this heating may not always be possible for a particular component. Transmission electron micrographs suggest that the oxide layer is increased in thickness.

As Table III illustrates, evidently immersion in boiling water for 30 minutes or more gives a significant increase in bond strength and a considerable change in the locus of failure, although the apparent deterioration beyond 180 minutes is unexplained.

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TABLE II
Strength and locus of failure of joints made with silicone rubber 3140 after heating in air at 100°C for various periods of time

Time minutes	Shear strength mean; SEM MNm^{-2}	% Cohesive failure
30	2.13; 0.29	95
60	2.17; 0.13	95
120	2.63; 0.43	100
150	2.61; 0.33	100

TABLE III
Strength and locus of failure of joints made with silicone rubber 3140 after immersion in boiling distilled water for various periods of time

Time of immersion minutes	Shear strength mean; SEM MNm^{-2}	% Cohesive failure
0	1.58; 0.17	50
30	1.84; 0.07	90
60	1.95; 0.23	90
90	1.82; 0.10	90
120	1.83; 0.13	90
150	1.88; 0.18	90
180	2.12; 0.26	90
210	1.63; 0.05	80
240	1.63; 0.07	80

Transmission electron micrographs suggest that debris is removed from the surface, but no other change was apparent.

While tantalum is generally resistant to corrosion or attack by many reagents, a variety of solutions have been suggested for etching the metal, so several of these were tried.

Immersion in solutions of ammonium fluoride of concentrations ranging from 10% to 50% at 60°C for 5 minutes and of 20% concentration at 80°C for times from 6 minutes to 50 minutes generally gave some increase in shear strength. However no systematic pattern was apparent and the increases ranged from a few percent to 30% in a random manner. The addition of an oxidising agent, either hydrogen peroxide or nitric acid, to the ammonium fluoride did not lead to any improvement; indeed at longer times of immersion with nitric acid there was a clear reduction in joint strength of up to 50%. Electron microscopy showed etching along the grain boundaries together with the deposition and recrystallisation of some material.

Similar results were obtained with ammonium fluoride and sulphuric acid mixed solutions.

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Second Series of Tests

For a second series of tests the joints were modified both in their dimensions and in the detail of their construction. While the aluminium carriers remained unchanged, the pieces of tantalum foil were extended in length to 20 mm so that they extended beyond the area of overlap by 5 mm. In the process of manufacture, the pieces of foil were degreased, immersed in boiling phosphate/detergent solution for 15 minutes and then were rinsed in boiling distilled water. Finally they were stored over aluminium shot in order to minimise contamination with organic materials.[5] They were bonded to the carriers with Araldite AV100/HV100 and put into a hydraulic press under a pressure of 123×10^6 Kg m^{-2} for 5 minutes, followed by a day under a weight giving a pressure of 6.6 Kg m^{-2} at room temperature.

These specimens showed significantly less variation in thickness than the first series.

Finally before they were assembled into lap joints they were cleaned in an ultrasonic bath of acetone for one minute. The joints were made with silicone rubber 3140 with 0.3 mm spacers, exactly similar to the first series.

A set of eight joints prepared by this second technique were compared with a similar set prepared by the technique of the first series.

The mean shear strengths and SEMs for these two sets were:

First series joint design	1.52; 0.10 MNm^{-2}
Second series joint design	1.55; 0.05

Thus, although the strength remains unchanged, the variability was markedly reduced.

Then several pre-treatments were used on the tantalum before making into specimens. First it was immersed in boiling water for various periods of time, the results of which are given in Table IV. Thus the effect of immersion in boiling water, observed in the first series, is confirmed with the shear strength increasing by about

TABLE IV
Strength and locus of failure of joints made with silicone rubber 3140 after immersion in boiling distilled water for various periods of time

Time of immersion hours	Shear strength mean; SEM MNm^{-2}	% Cohesive failure
0	1.55; 0.05	50
1	1.38; 0.14	50
3	1.75; 0.05	70
5	1.92; 0.10	80
7	1.53; 0.08	70
9	1.65; 0.03	70
11	1.74; 0.06	80
13	1.61; 0.05	70
24	1.99; 0.16	90

28% and the mode of failure changing to a greater proportion of cohesive failure in the rubber. It is noticeable that the drop in shear strength at beyond 3 hours, noted in Table III is not apparent here.

Since none of the reagents used in the first series of tests showed any considerable improvement in joint strengths, a formulation suggested by Propp and Young[6] was tried. This consisted of a mixture of 5 volumes concentrated sulphuric acid, 2 volumes concentrated nitric acid and 2 volumes 42% hydrofluoric acid, used at room temperature. The etching was followed by immersion in boiling water for 24 hours. The results of this treatment are given in Table V.

Electron microscopy showed some etch pits and clearly, except for the briefest treatment, this resulted in considerably weaker bonds with a preponderance of adhesive failure.

Since the ESCA examination had indicated that the surface coating of untreated metal was anhydrous tantalum pentoxide, it was decided to attempt to hydrate this, although it was known to be difficult.

Degreased pieces of tantalum foil were immersed for 4 hours in boiling 20% sodium hydroxide solution. A first batch was removed, rinsed in distilled water and dried. The remaining pieces were then immersed for 2 hours in boiling dilute hydrochloric acid and a second batch was removed and rinsed in distilled water and

TABLE V
Strength and locus of failure of joints made with silicone rubber 3140 after immersion in mixed sulphuric, nitric and hydrofluoric acids

Time of immersion seconds	Shear strength mean; SEM MNm^{-2}	% Cohesive failure
0	1.55; 0.05	50
1	2.05; 0.17	80
2	1.27; 0.03	30
3	1.17; 0.18	30
4	1.20; 0.19	10
5	1.30; 0.30	10

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dried. The final batch was immersed for 2 hours in boiling water before drying. All these pieces were then assembled into joints and tested. The results are shown in Table VI.

Scanning electron microscopy of the second and third batches showed a surface structure with well defined grain boundaries with some indications of recrystallised oxide along these boundaries.

This gave an improvement of about 34% over the value (1.55 MNm^{-2}, Table V) for a degreased but otherwise untreated specimen. It was probably the most promising treatment for improving the bonding which had been explored.

Third Series of Tests

In order to extend the investigation to include a conventional structural adhesive, thicker tantalum sheet was used which could be made into lap joints without the need for aluminium carriers. Specimens 0.55 mm thick and 10 mm × 40 mm were cut and carefully polished on abrasive paper to remove burrs and give an entirely flat surface.

These were degreased in toluene and acetone, washed in boiled phosphate/detergent solution and well rinsed in distilled water. They were then subject to various pre-treatments before being assembled into single lap joints.

For comparison with the previous results silicone rubber 3140 was used, being allowed to stand for 7 days at room temperature under a weight giving a pressure of 5.6×10^3 Kg m^{-2}. The results of this study are given in Table VII which showed a 45% improvement over the specimen which had only been degreased.

Several sets of joints were made using Redux 775 RN which was cured for 30 minutes at 150°C under a pressure of 7 Kg m^{-2}. The results of this are given in Table VIII.

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TABLE VI
Strength and locus of failure of joints made with silicone rubber 3140 after attempted hydration of surface oxide coating

	Shear strength mean; SEM MNm^{-2}	% Cohesive failure
Boiled in NaOH	1.29; 0.11	20
Boiled in NaOH followed by HCl	2.11; 0.06	70
Boiled in NaOH and HCl, followed by boiling in water	2.04; 0.13	70

TABLE VII
Strength and locus of failure of joints made with silicone rubber 3140, using thick Ta sheet

	Shear strength mean; SEM MNm^{-2}	% Cohesive failure
Polished but no other treatment	0.99; 0.07	20
Polished and degreased etc	1.33; 0.09	50
Polished, degreased and 24 hours in boiling water	1.94; 0.08	80

TABLE VIII
Strength and locus of failure of joints made with Redox 775 RN, using thick Ta sheet

Treatment	Shear strength mean; SEM	% Cohesive failure
Polished but no other treatment	12.5; 0.7	10
Polished and degreased etc	25.3; 1.3	50
Degreased and 24 hours in boiling water	29.9; 1.3	80
Degreased and heated in air 1 hour		
100°C	24.3; 2.0	85
200°C	24.9; 0.8	95
400°C	25.6; 1.3	90
Degreased and immersed $H_2SO_4/HNO_3/HF$		
1 second	21.5; 0.9	75
5 seconds	18.2; 0.9	70
20 seconds	18.6; 1.1	70

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DURABILITY STUDIES

The durability of any adhesive joint is always an important criterion, and it is vitally important in the encapsulation of materials which are implanted within the body. Hence joints made both with the silicone rubber 3140 and with Redux 775 RN were studied. From the previous results it was decided to prepare the surface by immersing in boiling water for 24 hours. In addition some were treated with a 1% solution of γ-glycidoxy propyl trimethoxy silane (Union Carbide 187) which is an extremely well known coupling agent used to enhance durability of adhesive joints in water.[7]

The results of the tests involving silicone rubber are shown in Table IX. These results show the joints remaining in air, whether at 20°C or 38°C, increasing in strength by 10–15% over the first 3 weeks and then remaining constant. This is presumably due to a gradual completion of curing through cross-linking. On the other hand, if the joints are immersed in water at 38°C there is a marked decrease in strength. Surprisingly, this is the case whether a silane coupling agent is used or not, although this reduces the overall effect from 45% to 20%.

TABLE IX
Durability of tantalum/silicone rubber 3140 joints.
Mean Shear Strength (MNm^{-2}) after various periods of time

	Initial	7 days	14 days	21 days	28 days	49 days	56 days	112 days
Tantalum boiled in water								
Air 20°C	2.01	2.37	—	2.17	—	2.05	—	2.35
Air 38°C	2.01	2.59	2.18	—	2.33	—	2.44	2.38
Water 38°C	2.01	1.77	1.59	—	1.29	—	1.15	1.09
Tantalum boiled in water + silane treatment								
Water 38°C	2.06	1.89	1.66	—	1.64	—	1.59	—

TABLE X
Durability of tantalum/Redux 775 RN joints.
Mean Shear Strength MNm^{-2} after various periods of time

	Initial	7 days	21 days	35 days
Tantalum boiled in water at 38°C	29.9	12.8	11.0	10.08
Tantalum boiled in water and silane treatment in water at 38°C	29.4	12.4	11.9	11.9

A similar series of tests were made using Redux 775 RN and the results from these are given in Table X. While the effect of water in reducing the bond strength by 65% is not surprising in the absence of any coupling agent, it is quite unexpected that the use of a silane coupling agent had almost no effect.

DISCUSSION

From all this there arises the indication that simply heating tantalum in air at 100°C for at least 2 hours produces a surface condition which gives adhesive bonds of the maximum strength with silicone rubber—not only as measured by the shear strength but also by totally cohesive failure of the rubber.

Alternatively immersion in boiling water for a considerable period also gives bonds of significantly increased strength and an increase in the extent of cohesive failure.

Unfortunately it did not prove possible to provide adequate explanations of the mechanisms associated with these improved joint properties.

Generally none of the chemical etching processes which were tried showed any improvement in joint behaviour.

Apart from the apparent and unexplained failure of a silane coupling agent to give the expected improvements, the durability study gave results which might have been reasonably expected.

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