TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

BULLETIN N° 61 MARCH 1990 FIRST QUARTER

T.I.C. meeting in Brussels

As requested by the membership during the last General Assembly, there will be an informal meeting of delegates in Brussels on April 27th 1990. The meeting will be held at 40 rue Washington, 1050 Brussels, at 14.30, and will include reports on the work and decisions of the Executive Committee and the progress of the group studying powder test standards, followed by discussions on topics of interest to the members. There will not be an officially convened General Assembly on this occasion as it is intended to provide an opportunity for delegates to meet each other and discuss developments in the association and the industry in a less formal way. The Thirty-first General Assembly will take place on November 6th 1990 (see President's letter).

On the morning of April 27th, the members of the Executive Committee will meet, and a meeting of the group working on the establishment of powder test standards is also planned.

All delegates are invited to lunch at 13.00, preceding the forum, and coffee will be available after the meeting. A small charge will be made to cover expenses.

Invitations will be sent to the voting delegates of member companies; anyone from a non-member company who might be interested in attending should contact the Secretary General, T.I.C., 40 rue Washington, 1050 Brussels.

President's letter

Since the last President's letter some significant changes have taken place in the tantalum industry. After many years, Fansteel decided to limit substantially their activities in tantalum and columbium, as has been reported in detail in the metals press.

Hellwarth Lahusen, Managing Director of Hermann C. Starck Berlin, retired after many years in this industry, as did another longstanding member of the industry, Chet LeRoy, Vice President of Teledyne Wah Chang Albany. Both served as official delegates of their respective companies at the T.I.C., and we wish them well in their retirement.

AVX, one of the largest capacitor manufacturers, was merged with Kyocera, a world renowned Japanese company mainly concerned with ceramics and other modern electronic materials.

On an experimental basis, an informal meeting of members follows the Executive Committee meeting on April 27th 1990 and we hope that all who can attend will do so.

The programme is shaping up well for the next General Assembly to be held in Perth, Western Australia, on November 5th, 6th and 7th : full details will appear in the next Bulletin. I hope you are all making plans to attend this very important meeting.

George J. Korinek
President

EDITORIAL :
The education of a technical adviser

When I took on this job in October last year, I was very conscious of my ignorance of much of tantalum and niobium technology. I am a metallurgist by training and I have been associated with the tantalum industry for some thirty years, but it has been through tin smelting and the tantalum-bearing tin slags which are a major source of the world's tantalum (and, in the early years, of niobium). Clearly a self-designed crash course was needed.

A very good summary of the extraction and uses of the two metals has been recently written by Dr Albrecht (1) from the long-standing member company Hermann C. Starck Berlin. In the course of fourteen pages he covers all the essentials, and whenever I needed to go into a particular subject more deeply, I found that most of my questions could be answered by searching in the pages of the 1988 Symposium Proceedings (2).

The problem thereafter has been to keep abreast of innovation at a time of very rapid technological advances. For this we have to look to the world's technical literature including patents; in this, T.I.C. members are aided by a headline service listing each month's references to our two subject metals. In the last three quarters of 1989 there was an average of 114 articles or patents each month which referred to either tantalum or niobium (or occasionally both). Out of such a mass of information all one can do is select articles on applications of the metals which might use them in significant quantities or which catch the imagination.

In the first category, I have been reading about niobium triselenide, which can be used with lithium in rechargeable cells giving a performance appreciably better than nickel/cadmium (3). Then there are cobalt magnet alloys containing tantalum or niobium (4) which would have particular application in tape or disc recorders, and thin film transistors using tantalum gate electrodes and a Ta_2O_5 anodic oxidation film for use with liquid crystal displays (5). In this electronic world, we all have equipment using such items : perhaps one or more of these inventions will prove a new outlet for our metals.

The longer shots but those which catch my fancy use niobium materials mixed with fluororubber to improve its chemical and heat resistance (6), with synthetic fibre to produce a wear-resistant and electrically conductive fabric (7), or with glass to make it non-fogging (8). Niobium is also proposed for the manufacture of synthetic gemstones (9). But best of all is the niobium substance mixed with chalk in toothpaste to prevent tooth decay (10). Tin fluoride had a good run some years back in the same role until it became too expensive or lost its novelty : is it now niobium's turn ?

1. W.W. Albrecht, Lanthanides, tantalum and niobium; publ. Springer, 1989; pp. 345-358.
2. Proceedings of the International Symposium on Tantalum and Niobium, Orlando; November 1988 (publ. T.I.C.).
3. F.A. Trumbore, J. Power Sources 26 (1989), 65-75.
4. Yokogawa-Hewlett Packard, Japanese Patent 63 270 440.
5. Sharp K.K., European Patent 312 389.
6. Kurasawa, Japanese Patent 63 312 336.
7. Kurasawa, Japanese Patent 01 006 111.
8. Kurasawa, Japanese Patent 63 307 143.
9. Zhongshan University, Chinese Patent 85 108 154.
10. Kurasawa, Japanese Patent 01 013 014.

T.I.C. statistics

TANTALUM

PRODUCTION AND SHIPMENTS 1989

(quoted in lb Ta_2O_5 contained)

Production	*1st quarter*	*2nd quarter*	*3rd quarter*	*4th quarter*	*Total*
Tin slag (2 % and over)	253 751	253 714	192 136	275 938	975 539
Tantalite (all grades), other materials	125 712	303 795	119 779	111 613	660 899
Total	379 463	557 509	311 915	387 551	1 636 438
Response	15/17	17/17	15/17	14/18	

Shipments	*1st quarter*	*2nd quarter*	*3rd quarter*	*4th quarter*	*Total*
Tin slag (2 % and over)	94 944	126 760	121 777	125 139	468 620
Tantalite (all grades), other materials	171 109	228 772	103 263	114 352	617 496
Total	266 053	355 532	225 040	239 491	1 086 116
Response	15/17	17/17	15/17	14/18	

Note :

The companies which reported included the following, whose reports are essential before the data may be released : Datuk Keramat Smelting, Greenbushes, Malaysia Smelting, Mamoré Mineração e Metalurgia, Metallurg Group, Tantalum Mining Corporation of Canada,Thailand Smelting and Refining

PROCESSORS' SHIPMENTS 1989

(quoted in lb Ta contained)

Material	*1st quarter*	*2nd quarter*	*3rd quarter*	*4th quarter*	*Total*
Ta_2O_5, K_2TaF_7	22 510	19 746	24 009	17 962	84 227
Alloy additive	20 628	17 413	50 170	31 298	119 509
Carbides	138 313	193 166	130 338	171 334	633 151
Powder/anodes	229 587	202 132	189 882	211 263	832 864
Mill products	89 203	82 277	73 955	71 936	317 371
Scrap, ingot, unworked metal, other	19 712	13 703	14 120	19 071	66 606
Total	519 953	528 437	482 474	522 864	2 053 728
Ta_2O_5 equivalent	710 937	713 390	651 340	705 866	2 772 533
Response	16/16	16/16	15/15	14/15	

Notes :

1. Reports by the following companies are essential before the data may be released : Cabot Corporation - Electronic Materials and Refractory Metals, Fansteel, W.C. Heraeus, Kennametal, Metallurg Group, Mitsui Mining and Smelting, NRC Inc., Showa Cabot Supermetals, Hermann C. Starck Berlin, Treibacher Chemische Werke, Vacuum Metallurgical Company, V Tech
2. Reports were made in lb tantalum contained.

Capacitor statistics

U.S. TANTALUM CAPACITOR SALES 1989

(thousands of units)

	1st quarter	*2nd quarter*	*3rd quarter*	*4th quarter*	*Total*
Foil	163	220	181	195	759
Metal-cased	29 000	25 499	21 673	21 553	97 725
Moulded	80 679	68 464	61 282	58 978	269 403
Dipped	97 082	98 237	90 663	87 218	373 200
Chips	47 650	48 859	48 822	56 821	202 152
Wet slug	2 079	2 052	1 729	1 963	7 823
Total	256 653	243 331	224 350	226 728	951 062

(Data from EIA)

EUROPEAN TANTALUM CAPACITOR SHIPMENTS

(thousands of units)

3rd quarter 1989	160 227

(Data from ECTSP)

JAPANESE TANTALUM CAPACITOR PRODUCTION AND EXPORTS

(thousands of units)

	Production	*Of this, exports*
3rd quarter 1989	889 050	242 893

(Data from JEIDA)

TANTALUM

QUARTERLY PRODUCTION ESTIMATES
(quoted in lb Ta_2O_5 contained)

Estimate made in third quarter 1989

LMB quotation :	*US $ 30*	*US $ 40*	*US $ 50*
4th quarter 1989	243 500	333 500	351 500
1st quarter 1990	273 500	373 500	401 500
2nd quarter 1990	266 500	355 500	406 500
3rd quarter 1990	256 500	355 500	406 500
4th quarter 1990	246 500	355 500	406 500

Estimate made in fourth quarter 1989

LMB quotation :	*US $ 30*	*US $ 40*	*US $ 50*
1st quarter 1990	273 500	373 500	401 500
2nd quarter 1990	266 500	375 500	406 500
3rd quarter 1990	255 500	375 500	426 500
4th quarter 1990	243 500	373 500	421 500
1st quarter 1991	243 500	373 500	421 500

Note :

The quarterly production estimates are based on information available, and do not necessarily reflect total world production.

Tantalum powder dopants and the effect of their residues on tantalum oxide quality of low oxygen tantalum surfaces

This paper was written by John VanVoorhis, James Bates and Frédéric Brindel of Sprague Technologies, Inc., Sanford, Maine, U.S.A., and presented by Mr VanVoorhis during the technical session following the Thirtieth General Assembly on October 19th 1989

ABSTRACT

For some time, the capacitor grade tantalum powder industry has recognized the beneficial effects of adding trace amounts (typically less than 100 ppm) of certain dopant elements to the product. Materials such as phosphorus, boron and sulfur have demonstrated the ability to inhibit surface diffusion and the related loss of powder surface area during sintering, thereby allowing the capacitor maker to achieve ever greater efficiency in terms of capacitance per unit of weight.

In contrast to these and other well-documented beneficial effects, we have found that the quality of the tantalum oxide film can be severely degraded due to unanticipated chemical reactions which occur exclusively at tantalum surfaces which are relatively low in thermal oxide thickness. Such conditions are commonly found at the tantalum lead wire connection of the capacitor. A lack of proper understanding of this phenomenon could possibly result in the incorporation of a defective dielectric film into the construction of the device, compromising performance and reliability.

INTRODUCTION

The manufacture of capacitor grade tantalum powders has, from its beginnings, involved the production of high purity surfaces which are capable of electrolytic formation of the dielectric, tantalum oxide (Ta_2O_5). Extreme purification can be accomplished by repeated vacuum arc melting or electron beam melting of solid tantalum metal. Volatile impurities are evaporated by the application of high metal currents which generate heat sufficient to melt the material at temperatures greater than 3000°C. The resulting powder has typically less than 50 ppm of total impurities, but limited efficiency (1,000-4,000 μfV/g) due to the inherently low surface area which is a consequence of the hydriding and grinding processes used to generate the powder from the solid ingot.

The introduction of sodium reduction technology allowed the creation of new generations of nodular-morphology tantalum powders, compromising absolute purity but allowing sizeable gains in surface area. The residual impurities (100-200 ppm) can be a direct result of salt or solvent compounds which remain after cleaning and leachates which originate in the processing equipment itself.

During the late 1970's the sodium reduction processes in use throughout the industry became more sophisticated. Manufacturers found that it was possible to produce high surface area tantalum powders by carefully controlling the conditions of the reduction process. The usual method of producing these high surface area materials involved significant reductions in the average particle diameter. In an effort to overcome the natural difficulties associated with using these new fine powders, tantalum producers and capacitor makers began to experiment with making deliberate additions of various elements and compounds to the material.

A primary concern is the excessive shrinkage and loss of surface observed when very pure, high surface area tantalum powders are pressed into anodes and sintered. The potential gains in surface area per unit of weight achieved by decreasing the average particle diameter are compromised by this effect. Inventors at first disclosed that by adding known amounts of certain dopant elements (nitrogen, silicon, phosphorus, boron) or their compounds to the pure tantalum powder, a measurable increase in the stored charge (CV) per unit of weight was realized (1). It was further stated that the observed increase was in proportion to the amount of additive used. The level of addition originally amounted to an equivalent of 200 to 3000 parts per million (by weight).

A number of disclosures concerning the addition of dopant elements to tantalum powder followed this work. In the forefront were the major powder producers, who developed and began to market materials containing a variety of additive impurities.

Phosphorus additions in the range of 5-400 ppm are known to enhance the capacitance retention of anodes by 10 %-30 % (2). Boron additions of 5 to 500 ppm perform the same function, and in addition are reported to improve the dielectric quality of the resultant tantalum oxide film, particularly when formed at temperatures below 85°C (3). Some work regarding the use of a combination of boron and phosphorus has been disclosed (4), where the particular processing stage where the dopants are added is purported to enhance the dielectric performance. Quantities of 10-600 ppm of phosphorus and 10-500 ppm of boron are involved here.

Sulfur additions have also been explored. Capacitance retention in the sintered anode can be improved by the addition of 20-500 ppm of elemental sulfur (5). A combination of sulfur, nitrogen and carbon has been reported to have beneficial effects in terms of both sintering inhibition and dielectric properties (6), the amount being preferably in the 150-2000 ppm range.

Of peripheral interest to this discussion, other additives have been disclosed in the patent literature. Additions of silicon dioxide (SiO_2) have been made in order to enhance the flow and die-fill properties of tantalum powder (7). Molybdenum, tungsten and tantalum di-sulfides as well as boron and silicon nitrides have been used to provide an inorganic material for die lubrification during anode pressing (8). (Some unique claims have been made concerning superior reverse voltage characteristics of the dielectric formed on such powders.) Interestingly, similar surface area preservation effects have always been described whenever an additive impurity was used in the tantalum powder.

The physical mechanism whereby the presence of these so-called "sintering inhibitors" perform their function has not been addressed in the literature. It is generally assumed that these elements interfere with the normal interparticle coalescence which occurs at temperatures greater than 1400°C in tantalum, at conditions where surface diffusion dominates the sintering process (9). The claimed effects of the inhibitors decline for sintering temperatures exceeding 1700°-1800°C, except in cases where the amount of dopant is quite high. At this point, it is postulated that bulk diffusion of the dopant into the tantalum (or, depending on the vapor pressure of the particular compound, the actual evaporation of the dopant from the surface into the vacuum) serves to mitigate any further effect.

Some of the claims concerning dopant elements include evidence attesting to a significantly *better* dielectric characteristic of the tantalum oxide film formed on the sintered anode. This improvement is typically expressed in terms of lower specific leakage current, higher breakdown voltage or even, in some instances, as improved failure rate or leakage stability on hot aging and accelerated voltage testing. The physical mechanism for this behavior has not been satisfactorily explained, and there is little recent confirming data. One disclosure refers to the additives as "probably acting as intermetallic alloy phase which has a particularly advantageous influence on the electrical properties of the dielectric oxide layer" (10). There is not unanimous agreement on this point, however. Life test data presented by one researcher support the view that the addition of dopant materials can be detrimental to the reliability of the capacitor if not carried out according to the preferred method (4).

Even if the evidence of enhanced dielectric performance is disputed, it is commonly inferred that the impurities intentionally added into tantalum powder, if done according to the methods and procedures specifically defined, have no detrimental effects on the capacitor made from it. Bulk analysis of finished anode bodies generally reveals little or no trace of the particular element(s) involved and it is assumed that the relatively high temperature of sintering under vacuum is sufficient to reduce the concentration to less than the detectable limits. There has been no direct observable influence of the dopants on the pellet surface or the consequent dielectric oxide film.

There is, however, one rather critical aspect of this process which has not been reported on heretofore. The tantalum riser wire, which serves as the anode connection of the capacitor, is necessarily of a completely different nature from the tantalum metal making up the anode body. First of all, it is a nearly solid mass, with virtually no porosity. It also is typically very low in oxygen content (less than 100 ppm), and has seen, at most, a single heat treatment following drawing to final size. This is normally a desirable characteristic, since the wire should be able to resist oxygen-related embrittlement during sintering.

As such, we have found that the wire can be, depending on the methods and practice of capacitor manufacture, unusually susceptible to alloying reactions. In fact, unpassivated tantalum wire (and foil) has been shown to form various alloys with phosphorus and boron vapors emanating from the outgassing of the dopant elements residing in the nearby anodes during sintering. We have also found that, under standard formation conditions, the nature of the tantalum oxide formed where such alloys are present is significantly degraded, both visually and electrically. The tantalum powder itself, as manufactured according to most versions of the doping procedure, has seen multiple heating cycles and has accumulated a substantial thermal oxide before exposure to the dopants (certainly to a level of more than 1000 ppm oxygen). Therefore, it is likely that almost all powders would be immune from any related effect, having a passivating oxide layer sufficient to prevent alloying from occurring.

EXPERIMENTAL

Standard available capacitor grade tantalum powder samples with the following chemical compositions were prepared or obtained :

1. Phosphorus additions :
   a. 0 ppm /Electron Beam melted, Control
   b. Doped, level unknown/Sodium Reduced, 10 000 CV/gram (less than 100 ppm)
   c. 50-100 ppm/Sodium Reduced, 15 000 CV/gram
   d. 50 ppm (as a., doped with ammonium di-hydrogen phosphate)
2. Boron additions :
   a. 0 ppm/Electron Beam melted, Control
   b. Doped, level unknown/Electron Beam melted, 5 000 CV/gram (less than 100 ppm)
3. Sulfur additions :
   a. 0 ppm/Electron Beam melted, Control
   b. 100 ppm/Sodium Reduced, 20 000 CV/gram
   c. 100 ppm (as a., doped with elemental sulfur/powder)

Capacitor grade tantalum wire (0.020" diameter) and foil (0.001" thickness) were prepared by degreasing (warm trichlorethylene), washing (deionized water), rinsing in acetone and air drying.

Sample pellets were prepared from each of the powders described above. Approximately 250 units of 0.2 grams each comprised the total loading of 50 grams.

The pellets and the unpassivated tantalum wire or foil were placed in tantalum sintering trays. One piece of wire or foil was covered with pellets on the top and bottom side, while the other was placed by itself, no more than 5 centimeters away. (See diagram, Figure 1).

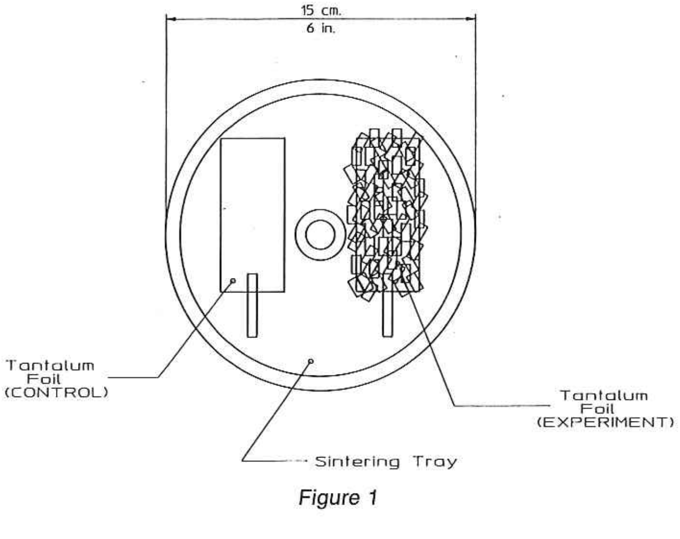

Figure 1

Tantalum wire samples were sintered in vacuum (approximately 10^{-6} torr) at five different temperatures : (1500°C, 1600°C, 1700°C, 1800°C and 1900°C). Tantalum foil samples were sintered at 1700°C only. The sintering temperature was held for a total of fifteen minutes.

Following sintering, the samples were cooled in helium until reaching room temperature and removed from the vacuum. The samples were taken from the trays and anodized together in a common electrolyte bath. The composition of the electrolyte was 0.1 % (volume) nitric acid or phosphoric acid at 80°C. A formation rate of approximately 2 v per minute was used to form the wires and foils to a final voltage of 80 v. This voltage was held for one hour before the samples were removed, rinsed in deionized water and air dried.

RESULTS / DISCUSSION

1. Anodized tantalum foil samples which have been exposed to phosphorus vapors in accordance with the experimental procedure described above clearly show discoloration of the tantalum oxide film on the surface of the foil. Submicroscopic examination reveals that not only is the thickness and refractive index of the oxide affected, but that the outer surface of the film has taken on an unusual rippled or bumpy appearance. The range of effect is surprisingly small, since the same material located no more than a few inches away shows no unusual behavior. Foils and wires sintered with undoped pellets are normal as well.

   Tantalum wire samples similarly treated also exhibit this discoloration and surface irregularity. A comparison of the different sintering temperatures reveals the defective oxide to be most severe at 1500°C sinter (extreme crystallization), and decreasing in intensity until it disappears at 1800°C.

   Tantalum wire samples which were passivated by repeated sintering at 2000°C in vacuum and exposure to atmosphere were also studied. As the amount of oxygen added to the wire increases as a result of multiple exposures (about 50 ppm each time), the alloying effect and the associated defective oxide film begin to dissipate. By the time the overall oxygen content of the wire reaches about 200-250 ppm (after three or four exposures) there is no further observable change in the oxide film after sintering in the presence of phosphorus vapors. It is apparent that a thermal oxide film of relatively small extent is sufficient to retard the alloying reaction between elemental tantalum and phosphorus vapors.

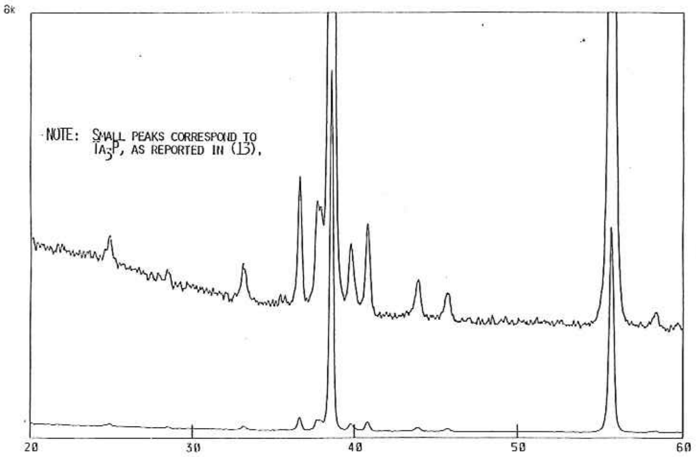

Figure 2
X-ray diffraction spectrum : anodized tantalum wire samples, exposed to phosphorus vapors (1700°C)

   By means of X-ray diffraction measurements, we were able to confirm the existence of Ta_3P in tantalum wire samples which were sintered in the presence of phosphorus bearing powders at 1700°C (Figure 2). The identity of at least three tantalum phosphide alloys has been established (11, 12). TaP, Ta_2P and Ta_3P are known to exist and the available literature reports that the alloying reaction begins at temperatures as low as 950°C. As temperatures increase, there is a tendency to progress from the TaP through Ta_2P and, when temperatures enter the 1660°-1720°C area, the Ta_3P phase begins to dominate (13).

   The inferior nature of the discolored and irregular tantalum oxide film formed on tantalum wires was confirmed by back-plating the wires in a copper sulfate solution. This practice has been established to identify common failure modes of solid tantalum capacitors in other contexts (14, 15).

2. Anodized tantalum foil samples which have been exposed to boron vapors in accordance with the experimental procedure defined above again show discoloration of the tantalum oxide film. SEM

examination of this surface reveals an extremely convoluted, nodular structure which is roughened, but on a much smaller scale than that of the phosphorus samples.

A series of sintering temperatures from 1500°C to 1900°C was tested for this group of samples. As we observed with the phosphorus-exposed tantalum wires, we found that the deleterious effect of the boron has dissipated once the sintering temperature reaches or exceeds 1800°C.

The literature describes reactions between tantalum and boron which are significant when the temperature reaches 950°C (16, 17). Five intermediate phases are known up to about 1650°-1750°C, where TaB_2 becomes dominant. This compound is extremely refractory with a melting point in excess of that of tantalum itself (>3000°C). No X-ray diffraction studies have as yet been done to confirm the presence of TaB_2 as was the case with Ta_3P.

Again, copper back-plating confirms the inferior nature of the discolored and irregularly formed areas of tantalum oxide.

3. Experiments with sulfur additions have failed to provide any evidence of the formation of tantalum sulfides in unpassivated materials. Oxide films formed over foils and wires sintered in the presence of sulfur-bearing powders (100 ppm nominal) are completely normal. The literature refers to reactions between sulfur and tantalum beginning at about 700°C (18, 19), and various alloy forms are known to exist (TaS, TaS_2, TaS_3). Under the conditions of this experiment, no adverse effects of the presence of sulfur were detected, in contrast to the performance of both phosphorus and boron.

CONCLUSIONS

Given the fact that two of the most common commercially used dopant elements in tantalum powders are capable of forming tantalum alloys under the right conditions, particularly at the surface of unpassivated tantalum wires, and that these alloys cause a disruptive and detrimental effect when the dielectric tantalum oxide is formed thereon, it is incumbent upon the capacitor maker to take these phenomena into account and to avoid the incorporation of such defective oxide into the device. The progressive drive to improve tantalum efficiency is leading capacitor designers into an area where the dangers of the formation of these defective oxide films are more and more likely, namely the progression of sintering conditions to temperatures less than 1800°C and the necessity of using doped powders to retain a maximum amount of surface area in the finished anode.

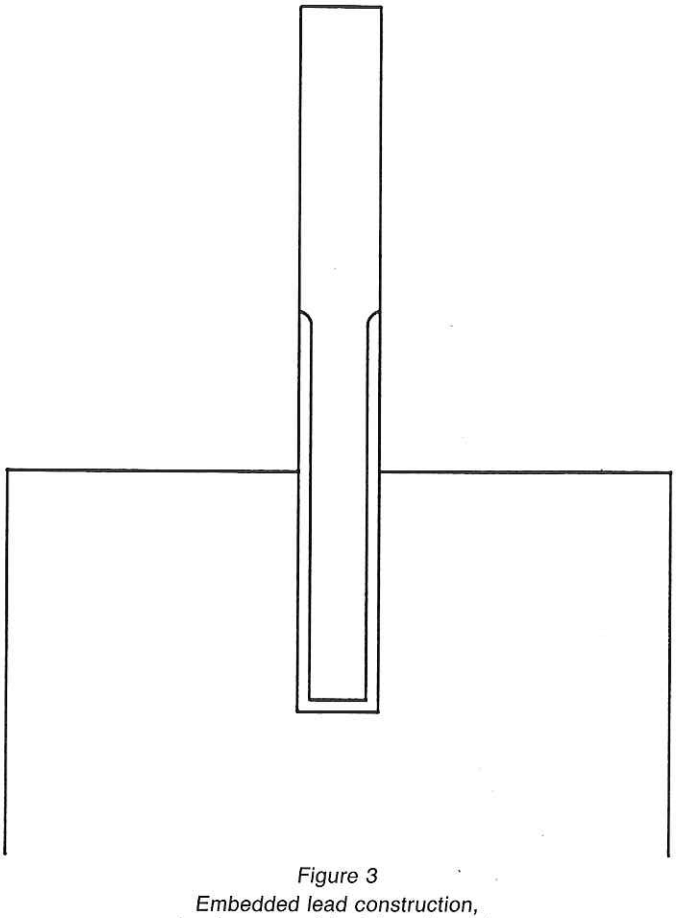

Figure 3
Embedded lead construction,
showing area of tantalum riser wire
susceptible to alloying and defective oxide

Of the two known configurations of the solid tantalum capacitor, the most risk is involved when a choice of an embedded lead wire is made. As in Figure 3, it may be seen that where an unpassivated lead wire is directly exposed to the doped tantalum powder (both inside the pellet and just slightly above it), there will undoubtedly be some exposure to vapors and significant alloying at the surface. Should this alloyed region of the tantalum lead wire be anodized and subjected to a sufficient electric field during use (as would be the case if the deposition of the counter electrode manganous oxide is efficiently carried out) one would infer that an increase in leakage current and an increased likelihood of premature parametric or catastrophic failure would arise.

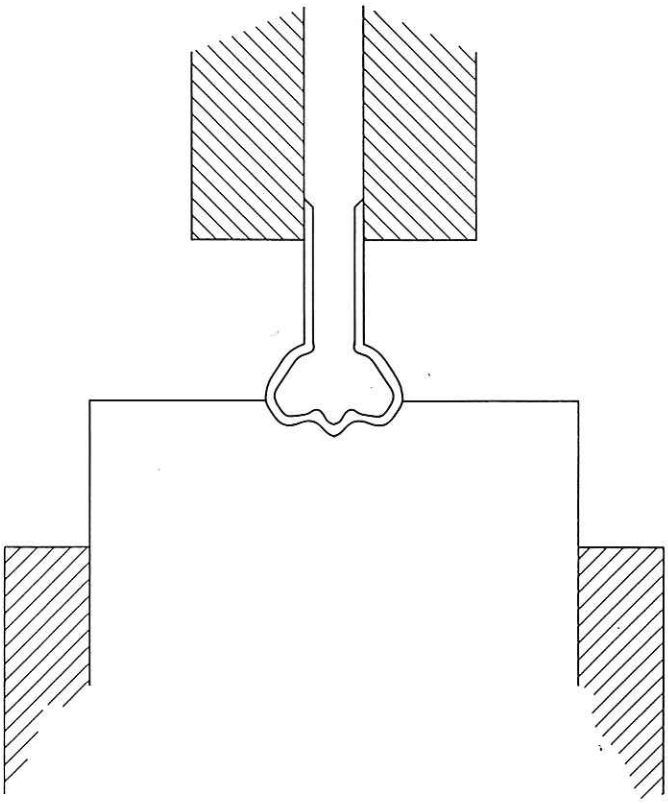

Figure 4
Welded lead construction,
showing area of tantalum riser wire
normally receiving passivating thermal oxide during heating

In the case of welded tantalum lead wires, the situation is more favorable, particularly when the welding is accomplished in air. Figure 4 depicts a sketch of the typical configuration. The wire segment and pellet are gripped by electrodes and brought into physical contact. A current is passed through the assembly, melting the tantalum wire which is then forced into the anode body. The total heat involved is actually quite small when properly done and the increase of temperature in the region of the lower part of the wire (beyond the clamps) is just sufficient to form a passivating thermal oxide layer without unduly increasing the bulk oxygen content of the anode itself. It has been demonstrated that the amount of oxidation involved in a typical welding cycle (in air) effectively blocks the alloying tendency of the tantalum surface during sintering in the presence of vapors from residual dopant elements. What is more, the preferred practice of construction of tantalum capacitors with welded lead wires requires that the pressed or "green" pellets be sintered prior to the actual welding step, which serves to dissipate at least a portion of the volatile dopant elements before the wire is exposed to vapors during the final sintering phase.

In conclusion, we have found that despite the demonstrated beneficial aspects of the practice of adding dopant elements to capacitor grade tantalum powders, there are significant side effects which have not been reported previously. The surface alloying of phosphorus and boron with tantalum at sintering temperatures now commonly used in capacitor manufacture, even at doping levels of less than 50 ppm, creates a situation which is incompatible with the formation of high quality dielectric tantalum oxide films. Although the practical effects of these phenomena on the quality and reliability of the finished capacitor have not yet been accurately determined, and indeed may be greatly influenced by the nuances of the particular manufacturing processes being used, there is reason to be concerned as to the possibility of creating such defective oxides without being aware of it. Such possibility is enhanced because of the relatively short range of influence of the alloying effect and the use of manufacturing methods which tend to incorporate such defects into hidden areas of the capacitor.

Although it may be argued that the area of affected dielectric is quite small compared to the total surface area of the anode, the lead wire is particularly sensitive as a low resistance path which carries relatively high currents during device operation. Considering persistent reports of inferior reliability results associated with the use of high CV tantalum powders, a careful analysis of these secondary effects may reveal that the source of the problems is not solely the high level of efficiency being sought, but may be at least partially caused by such unanticipated situations as those described here.

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