Evaluation of a potential dental application of vapour deposition techniques for coating alumina with tin oxide

P. V. McCRORY, V. PIDDOCK, E. C. COMBE

Department of Restorative Dentistry, Turner Dental School, University of Manchester Dental Hospital, Manchester, M15 6FH, UK

S. TINSTON, R. D. ARNELL Department of Aeronautical and Mechanical Engineering, University of Salford, Salford, M5 4WT, UK

P. WEGLICKI, J. OWEN Department of Chemistry, University of Southampton, Highfield, Southampton, SO9 5NH, UK

Coatings of tin oxide have been deposited onto alumina using both physical vapour deposition (PVD) and chemical vapour deposition (CVD) techniques. Significant increases in bond strength were determined for certain of the PVD groups of samples. The PVD coatings proved amenable to colour modification by post-deposition oxidation. Sectioned coatings were examined by scanning electron microscopy and X-ray maps were produced which indicated the distribution of tin. This study supports earlier findings indicating the potential of such coatings for improved bonding of dental restorations.

1. Introduction

Alumina reinforced dental porcelains were first described by McLean and Hughes in 1965 [1], as a means of strengthening feldspathic glass crowns. Such materials contained approximately 40% by weight of free alumina. More recently, an aluminous porcelain has been manufactured with a greater proportion of alumina particles and has been shown to have improved tensile properties [2]. A system is now available which enables the fabrication of ceramic crown and bridge substructures which contain approximately 85% of free alumina and is claimed to possess a tensile strength far superior to conventional porcelains [3]. The sintered alumina substructure is infiltrated with molten glass to achieve a fully dense body. The alumina, in common with the glassy matrices of each of these dental ceramics, is incapable of bonding chemically to existing dental cements. Fixation of all-ceramic restorations currently relies on mechanical retention via acid etching and or physical abrasion of the ceramic to create a roughened surface. The application of organosilane coupling agents has also been shown to improve the bond strength of porcelain to resin-based dental cements in the short term [4] and such materials are routinely used for the bonding of ceramic veneers and inlays. However, the hydrolytic stability of these compounds is questionable [5]. Tin oxide has been shown to bond with glass ionomer cements [6] and certain resin-based composite cements [7], and unlike the aforementioned silanes, is believed to be chemically stable in the oral environment. The present authors have demonstrated previously that tin oxide coatings deposited onto a conventional alumina reinforced dental porcelain using a reactive ion plating technique, are capable of producing bond strengths to an adhesive composite resin such that in tension, failure occurs cohesively within the porcelain [8]. Tin oxide coatings have also been deposited on ceramic substrates by chemical vapour deposition [9].

Following the trend towards stronger, higher alumina content dental ceramics, the aim of the present study was to determine the tensile bond strength of a commercial resin-based cement to tin oxide coated recrystallized alumina, where the coating was applied by both PVD and CVD techniques.

2. Materials and methods

2.1. Initial preparation of samples

One hundred and forty alumina discs, 10 mm in diameter and at least 1 mm thick were cut from a rod of 99.9% pure recrystallized alumina (Goodfellow, Cambridge, England). One face of each disc was ground using 400 mesh abrasive powder (Carborundum powder, The Carborundum Co. Ltd., Manchester, UK) for 1 min and all discs were ultrasonically cleaned in a 2% proprietary solution containing anionic and non-ionic surfactants (Micro, International Products Corporation, Trenton, N.J., USA) for 5 min. Finally each sample was ultrasonically cleaned in distilled water for 5 min.

Discs prepared in this fashion were randomly allocated to 14 groups of 10 for further treatment as summarized below and detailed in Table I.

- Group 1 was retained as the control group, without any further surface treatment.
- Groups 2–7 were coated by reactive physical vapour deposition (RPVD).
- Groups 8-10 were treated by physical vapour deposition (PVD).
- Groups 11 and 12 were coated using a magnetron sputtering technique (MS).
- Groups 13 and 14 were treated by metal organic chemical vapour deposition (MOCVD).

2.2. Reactive physical vapour deposition

Three groups of 10 specimens (groups 2, 3 and 4) were placed in a stainless steel holder (Fig. 1) which permitted a standard area of 71 mm² to be treated. The holder was positioned centrally above the tin target in the chamber of an A700Q vacuum coating rig (Leybold-Heraeus GmbH, Hanau, Germany) with an electron beam evaporation system. The coating chamber was sealed and evacuated to a base pressure of 1.5×10^{-3} Pa and the electron gun evacuated to a pressure of 4×10^{-4} Pa. High purity argon was then bled into the chamber until the pressure increased to 0.3 Pa. In this atmosphere the samples and sample support were negatively biased with respect to the target using an RF power supply of 150 W. The power was applied for 5 min to sputter clean both the samples and sample support. The contaminated atmosphere was constantly replaced with clean argon.

After cleaning, oxygen was bled into the atmosphere, producing a run pressure of 4 Pa. At the same time the tin target was heated using an electron beam gun operating at 5 kW (20% of maximum power). The substrate-source (tin target) separation, measured from the centre of the holder, was 500 mm. The RF biasing power was again 150 W over an electrode

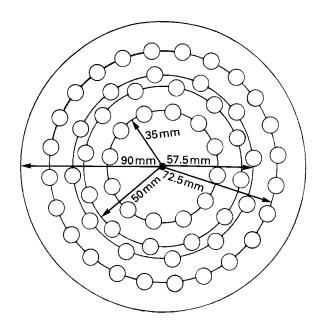


Figure 1 Specimen holder.

surface area of approximately 545 cm² giving a power density of 0.276 W cm⁻². Specimens were coated with tin oxide for 190 s, then allowed to cool in the coating chamber for a period of approximately 2 h prior to releasing the vacuum, to avoid any reaction occurring between heated specimens and the atmosphere. Similar cooling times were allowed for the other PVD techniques described below.

A further three groups (5, 6 and 7) were coated in the same way for 10 min.

Post-deposition oxidation of samples in groups 3 and 6 was carried out. The specimens were heated in air to 500 $^{\circ}$ C and held at that temperature for 5 min in a porcelain furnace (Multimat MC2, Dentsply, Brighton, UK).

Group Number	Coating type	Coating Method	Coating Time (min)	Substrate– target separation (mm)	Radial position on holder (mm)	Post- deposition treatment
1	None					
2	Tin oxide	RPVD	3.16	500	35	None
3	Tin oxide	RPVD	3.16	500	57	Oxidized
4	Tin oxide	RPVD	3.16	500	72.5	None
5	Tin oxide	RPVD	10	500	35	None
6	Tin oxide	RPVD	10	500	57	Oxidized
7	Tin oxide	RPVD	10	500	72.5	None
8	Tin	PVD	5	700		None
9	Tin	PVD	5	700		Oxidized
10	Tin	PVD	5	700		Oxidized
11	Tin	MS	5	100		None
12	Tin	MS	5	100		Oxidized
13	Tin oxide	MOCVD	15	N/A		None
14	Tin oxide	MOCVD	15	N/A		Oxidized

TABLE I Summary of coating groups

RPVD = Reactive ion plating

PVD = Non-reactive ion plating

MS = Direct current magnetron sputtering

MOCVD = metal-organic chemical vapour deposition

2.3. Non-reactive physical vapour deposition

Thirty alumina discs were coated in the manner described below using non-reactive ion plating to deposit a layer of metallic tin (groups 8, 9 and 10). The specimens were coated in the same ion plating rig as that used for the reactive ion plating samples and were held in the same stainless steel support.

The specimen holder was again positioned centrally above the target in the ion plating chamber. The chamber was evacuated to a base pressure of 1×10^{-3} Pa and the electron gun to a pressure of 1×10^{-4} Pa. Argon was then bled into the chamber raising the pressure to 0.4 Pa. In this atmosphere the samples and support were negatively biased with respect to the target using a d.c. power supply of 42 W to enable sputter cleaning for 20 min. The contaminated argon atmosphere was constantly replaced with clean argon.

After cleaning the samples, the tin target was heated using an electron beam gun operating at 5 kW. Coating with tin was carried out using a substrate-source separation of 700 mm and the run time was 5 min. The specimens were again allowed to cool prior to releasing the vacuum.

After coating, the specimens were processed as follows: group 8 was left un-oxidized, group 9 was oxidized in air for 30 min at $600 \,^{\circ}$ C and group 10 for 2 min at 900 $^{\circ}$ C.

2.4. Magnetron sputtering

Unlike the two PVD techniques detailed above, which used electron beam heating of the target to release metal atoms and ions into the coating atmosphere, the technique of magnetron sputtering employs a magnetic field to confine and direct a plasma towards the target material. Bombardment by the plasma results in the liberation of atoms and ions of the target material which in this case was tin. Twenty alumina discs were again placed in the circular support and cleaned in a 0.889 Pa argon atmosphere using a 150 W/400 V RF power supply applied for 5 min. During the cleaning process the target was biased at 240 V/0.2 A d.c. After cleaning, the argon pressure was maintained at 0.889 Pa and a 260 V/0.4 A power supply was applied to the magnetron to begin the tin coating process. The specimens were unbiased during the coating run which lasted for 5 min. On removal of the specimens from the chamber, the tin target was found to have melted.

The specimens were divided into two groups of ten. Group 11 received no further treatment and group 12 was oxidized for 5 min at 500 °C.

2.5. Metal organic chemical vapour deposition

Twenty alumina discs were placed in a laboratory CVD reactor as described previously by Weglicki [9]. The tin oxide precursor used was dibutyltin diacetate. This was maintained in the volatilizer at temperatures between $45 \,^{\circ}$ C and $50 \,^{\circ}$ C. The alumina disc substrates

were heated to $270 \,^{\circ}$ C at the onset of deposition. Precursor vapour was introduced into the reactor chamber in a stream of oxygen carrier gas at a flow rate of $100 \,\mathrm{cm^3 \, min^{-1}}$ and tin oxide deposition was allowed to proceed for a total of 15 min, after which time the substrate temperature had increased to $440 \,^{\circ}$ C. The total reactor pressure during the deposition was maintained at around 1.3 Pa.

The specimens were divided into two groups of ten. Group 13 received no further treatment and group 14 was oxidized according to the following schedule in an effort to eliminate the observed discolouration in the deposited layer: 5 min at 500 °C, then 5 min at 600 °C, followed by 5 min at 700 °C and finally 10 min at 800 °C.

2.6. Colour assessment

Each group of treated alumina specimens was examined for colour changes comparing coated samples with the original alumina surface.

2.7. Tensile bond testing

Rods of a beryllium-free nickel chromium metal-ceramic alloy (Wiron 99, Bego, Bremen, Germany) of diameter 8 mm and length 25 mm were circumferentially notched close to one end. This alloy had previously been shown to achieve very high bond strengths with the cement chosen for the study [8]. The opposite face was ground with 400 mesh abrasive for 1 min, then air polished using 50 μ m aluminium oxide powder followed by ultrasonic cleaning as described above for the alumina specimens. The surfaces so treated provided opposing adherends for bond testing.

Self-adhesive ring reinforcements each with a circular perforation of average area 23.4 mm^2 and 0.07 mm thick, were centrally located over the alumina discs and were applied to the treated surfaces.

A barium-containing polymeric dental cement (Panavia EX, Cavex Holland BV, The Netherlands) was mixed according to the manufacturer's instructions and applied to the exposed area of coating on each disc. An alloy rod, prepared surface down, was then pressed over the cemented area, ensuring that excess cement extruded from the periphery. This excess was removed and an oxygen barrier fluid (Oxyguard, Cavex Holland BV, The Netherlands) was applied to prevent oxygen inhibition of the polymerization reaction. The specimens were stored at room temperature for 7 days. The tensile bond strength of each specimen was measured using a universal testing machine (RDP-Howden, Learnington Spa, UK). A crosshead speed of 0.5 mm min⁻¹ was used to apply the load.

2.8. Preparation of samples for SEM and X-ray mapping studies

Following bond testing, selected samples were sectioned perpendicular to the coated surface and mounted in acrylic resin. The specimens were then polished to a $3\,\mu m$ finish with diamond paste and carbon coated to render them electrically conductive.

The samples were examined in a Cambridge 360 scanning electron microscope (Cambridge Instruments, UK). Both secondary and four-quadrant backscatter electron images were formed. Corresponding X-ray maps were produced for the elements barium, tin and aluminium.

3. Results

3.1. Colour of coatings

Samples from groups 2–7 showed distinct yellowbrown discolouration in the coatings suggesting the presence of partially oxidized tin. Following thermal oxidation, the discolouration in groups 3 and 6 was removed, as determined by visual inspection.

The non-reactive PVD tin coated samples initially exhibited a metallic sheen. However, the post deposition oxidation treatments rendered the coatings white in colour.

There was no significant discolouration apparent in the magnetron sputtered coatings.

The MOCVD coatings were very highly coloured with a pronounced brown hue. The samples in group 14 remained coloured after post-deposition oxidation, though there was a change to lighter yellow-brown shade.

3.2. Bond strength

The results of the tensile bond strength tests are presented in Table II. The data were subjected to statistical analysis using Tukey's HSD procedure and significant differences at the 5% level are given in Table III.

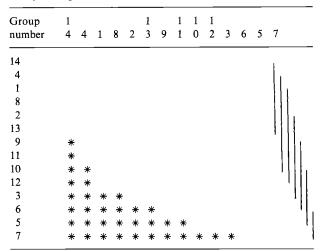
3.3. SEM and X-ray mapping studies

Difficulties were encountered in attempting to image the coatings of bond tested samples. However, X-ray mapping studies did give useful information. It proved possible to obtain X-ray maps for specimens in all categories of coating methods, except those coated

TABLE II Tensile bond strength results

Group	Number of Samples	Mean (MPa)	Standard Deviation	Standard Error
1	10	11.4	4.7	1.5
2	10	11.8	4.5	1.4
3	10	18.9	7.0	2.2
4	10	9.3	3.7	1.2
5	10	22.1	7.0	2.2
6	10	20.4	4.9	1.5
7	10	26.7	4.5	1.4
8	10	11.4	3.2	1.0
9	10	13.5	5.6	1.8
10	10	17.0	5.7	1.8
11	10	14.6	3.9	1.2
12	10	17.0	5.8	1.8
13	10	12.9	3.0	0.9
14	10	5.7	1.5	0.5

TABLE III Statistical analysis of bond strength data using the Tukey-HSD procedure



(*) denotes pairs of groups significantly different at the 0.05 level. Homogeneous subsets (subsets of groups, whose highest and lowest means do not differ by more than the shortest significant range for a subset of that size) are indicated by vertical bars.

using magnetron sputtering where the original intention had been to deposit a very thin coating.

Figs 2–6 are typical examples of X-ray maps produced. Image (a) of each figure shows the distribution of aluminium (predominantly from the substrate), (b) the distribution of tin (from the tin coating) and (c) the distribution of barium (from the cement). Each image represents an area approximately $30 \mu m$ square. The corresponding backscattered electron image for Fig. 2 is shown in Fig. 7.

4. Discussion

4.1. Colour of deposited coatings

The application of coatings to ceramic restorations, ideally should not have a deleterious effect on the aesthetic qualities. One of the criteria applied when selecting tin oxide as a bondable coating was its lack of colouration in its fully oxidized state.

The colours of the various coatings deposited in this study ranged from white to silver grey with shades of yellow and brown between. These colours coincided with those of tin and its oxides which are summarized in Table IV.

The deposition of tin (IV) oxide using reactive PVD techniques involves complex coating procedures. Therefore, variability in colour may arise as a result of differences in the degree of oxidation. Clearly, any discolouration of the ceramic is likely to impair the aesthetics of the restoration. Earlier studies involving the post deposition oxidation of tin oxide coatings on porcelain discs, indicated that it is possible to lighten highly coloured tin oxide coatings by heating in air [8]. However, as the untreated porcelain samples were quite strongly coloured, it was not possible to determine the full extent to which colour of the coating may be removed. In the present study, changes in colour were more readily observed against the white alumina background. However, it should be noted that in the ideal clinical situation, very thin coatings of the order

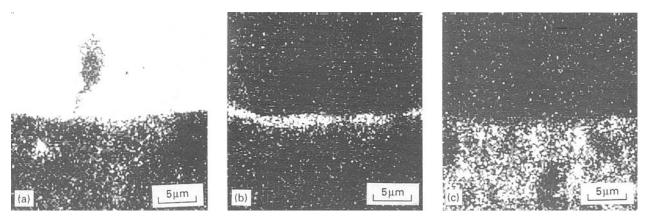


Figure 2 X-ray maps of elements: aluminium (a); tin (b); and barium (c) in a group 2 specimen.

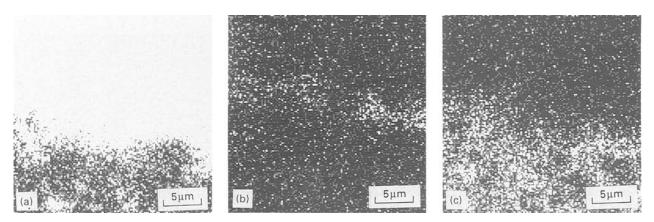


Figure 3 X-ray maps of elements: aluminium (a); tin (b); and barium (c) in a group 5 specimen.

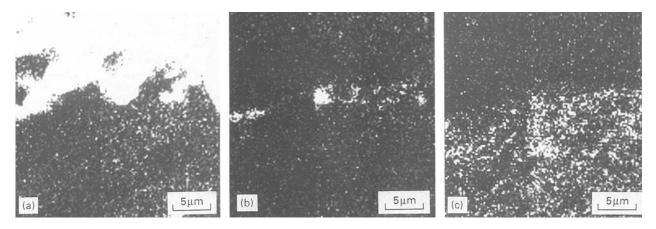


Figure 4 X-ray maps of elements: aluminium (a); tin (b); and barium (c) in a group 8 specimen.

of $0.1-1.0 \,\mu\text{m}$ would be deposited which would not interfere with fitting accuracy. In such circumstances, even coating materials with a high extinction coefficient may be expected to have a relatively small effect on the colour of the final restoration.

The discolouration observed in the samples from the reactive ion plated groups (2, 3 and 4 in particular) was almost certainly due to the presence of unoxidized and partially oxidized tin atoms. The post-deposition oxidation treatments successfully removed this discolouration for groups 3 and 6. The absence of colour suggested that there was no significant contamination by iron sputtered from the apparatus, though it was not possible to determine whether aluminium (used to line the chamber) contamination had occurred. However, to preclude the possibility of contamination of the control samples (group 1), these specimens were not sputter cleaned.

The metallic tin coatings on samples produced by d.c. sputtering were also successfully oxidized, the coatings being rendered virtually white. In order to confirm the presence of white tin oxide coatings, the electrical conductivity of some samples was demonstrated using a digital resistance meter, as tin oxide is

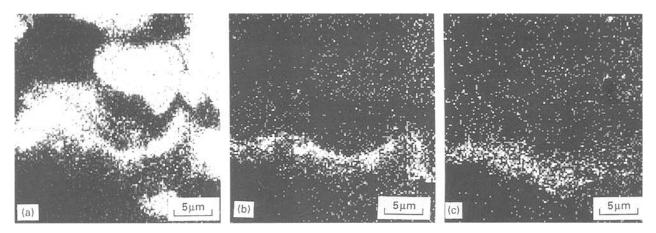


Figure 5 X-ray maps of elements: aluminium (a); tin (b); and barium (c) in a group 9 specimen.

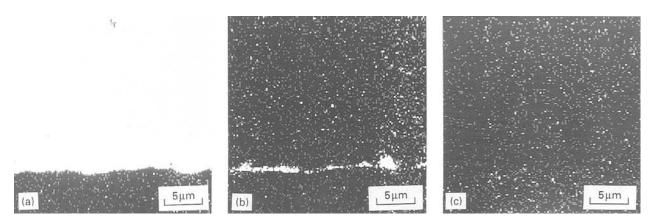


Figure 6 X-ray maps of elements: aluminium (a); tin (b); and barium (c) in a group 13 specimen.

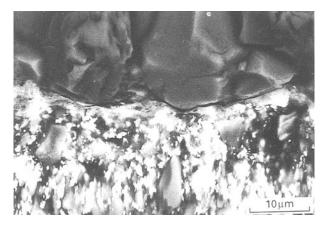


Figure 7 Back-scattered electron image of a sample from group 2 corresponding to Fig. 2.

known to be a conductor. It should be noted that the presence of tin in the coating was subsequently demonstrated by X-ray mapping. However, the question of whether some tin was lost by evaporation early in the post-deposition oxidation procedure, has yet to be resolved.

The magnetron sputtered coatings were essentially white in colour. This may have been due to the deposition of white tin rather than the more common grey allotrope or as a result of premature oxidation of

TABLE IV Colour of tin and some of its oxides [10]

Material	Colour	Atomic Structure	Density (g cm ⁻³)
Tin (Grey)	Silver-grey	Cubic	5.75
Tin (White)	White	Tetragonal	7.28
Tin (Brittle)	White	Rhombic	6.52
Tin (II) oxide	Black	Cubic (or tetragonal)	6.45
Tin oxide monohydrate SnO _{x.} H ₂ O	Yellow-brown		
Tin (IV) oxide	White	Tetragonal (also Hexagonal or rhombic)	6.95

the tin coating in air. The latter could occur in circumstances where the specimens were not adequately cooled prior to being removed from the vacuum chamber.

Therefore, it was concluded that for PVD deposited tin/tin oxide coatings, the oxidation state of the tin and the colour of the coatings may be modified by heat treatment in air.

Post-deposition oxidation of the MOCVD coatings merely altered the dark brown hue of the coating to a lighter shade. The original discolouration is probably attributable to a combination of the following contaminants: carbon from the precursor, unreacted precursor, tin oxide mono-hydrate and contaminants in the precursor. However, heat treatment of the postdeposition oxidized samples (group 14), is likely to have decomposed the monohydrate, and broken down any remaining precursor. Therefore, it seems likely that the main cause of discolouration in the coatings was carbon contamination.

4.2. Bond strength measurements

Samples coated for 190 s with tin oxide by RPVD in groups 2 and 4 did not exhibit a significantly different tensile bond strength compared with the uncoated controls. However, samples in group 3, which underwent subsequent thermal oxidation, showed a significant increase in bond strength. All RPVD samples coated for a period of 10 min produced significantly higher bond strengths. It would appear, therefore, that the coatings produced during the longer coating run time differed from those in groups 2 and 4. This may have been due to differences in chemistry or physical structure of the coatings. On the basis of the observed colours, it was concluded that the initial coatings of groups 2-4 were less well oxidized than those in groups 5-7. In the case of post-oxidized samples coated for 10 min (group 6) no further improvement in bond strength was achieved compared with group 7. Indeed, the greatest mean bond strength among all the groups was 26.7 MPa for group 7 discs which received no post-deposition oxidation. This value was similar to the maximum average tensile bond strength of 27.0 MPa reported for Panavia EX bonded to Ni-Cr-Be dental alloys ion sputtered with tin oxide by Tanaka et al. [7].

The bond strength data suggest that there is an optimal stoichiometric ratio of tin to oxygen of $\frac{1}{2} - x$ for such coatings where the requirement is for maximum adhesion. In the case of the PVD coatings, where oxygen diffuses into the coatings resulting in 'x' approaching zero, the tendency is for the bond strength to reach a value of approximately 20 MPa.

The effect of coating thickness alone on bond strength is difficult to determine. Although the surface characteristics of the substrate should be effectively shielded by a layer of tin oxide a few atoms thick, the coating itself will develop increasing numbers of flaws with increasing thickness, and bond strength might be expected to be dependent on coating thickness for this reason if failure then occurs within the oxide layer. Additionally, stresses associated with such flaws and the flaws themselves are likely to be modified by heat treatments.

The RPVD coatings produced by the longer regime appear to exhibit an optimum oxidation state which is not changed significantly by further thermal oxidation. The effect of specimen location within the sample holder did not appear to have a statistically significant effect for the plating configuration used in this study as indicated by the similarity in groups 2 and 4, and 5 and 7.

No significant improvements in bond strength were achieved by the application of tin coatings using the

PVD technique, with or without post-deposition oxidation. It is not clear whether the nature of the tin oxide coating on group 10 samples in particular, was very different from that of groups 3 and 6. It should also be noted that there was no statistically significant difference between groups 3, 6, 9 and 10 suggesting that post-deposition oxidation of initially unoxidized or partially oxidized tin coatings produces a standard bond strength.

No significant difference was found between the bond strengths for the oxidized and non-oxidized magnetron sputtered groups (11 and 12), nor between these two groups and the group 1 control. However, the group 12 mean did not differ significantly from all but the highest of the four groups with greater average bond strengths.

Post-deposition oxidation resulted in a trend towards a bond strength in the range 17–20 MPa for all PVD groups (3, 6, 10 and 12) except group 9 which had a mean bond strength of 13.5 MPa. There was no statistically significant difference between any of these groups.

The density data in Table IV indicates that there is a change in volume when the ratio of oxygen to tin is increased in incompletely oxidized coatings. Therefore, for a given coating (other than fully oxidized deposits), the magnitude of interfacial stress will be altered by post-deposition oxidation of the coating.

In the case of specimen groups 2 to 4, the original coatings were significantly more discoloured than groups 5 to 7 suggesting that the former were less well oxidized. This may also explain why cohesive failure was observed in the tin oxide layers of groups 2 and 4 but not in groups 3 (with post-deposition oxidation), 5, 6 and 7 which were less/not discoloured and pre-sumably better oxidized. However, for all cases of cohesive failure within the tin oxide, there was no suggestion of any tin oxide–alumina adhesive failure. It is reasonable to assume that tin is intimately incorporated into the substrate and probably relatively well oxidized at the interface by oxygen from the alumina lattice. One can envisage a gradation from pure aluminium oxide to pure coating.

The MOCVD coatings did not produce a significant change in bond strength compared with the control group 1. In addition, no significant difference was noted between the oxidized and non-oxidized groups (13 and 14). However, it is interesting to note that the oxidation treatment was associated with a lowering of the bond strength. Oxidation of contaminant carbon compounds in the coating and degradation of the bond between the coating and the alumina due to the heat treatment, may have contributed to the observed reduction in adhesion.

4.3. Comparisons of the various coating methods

It is clear that the PVD techniques employed in this study are superior to the MOCVD method used. However, refinement of the chemical vapour deposition process may be expected to improve coating quality. Physical vapour deposition techniques, especially those which employ active or self biasing of the substrate combined with sufficient power density, produce physical mixing of the substrate surface and the coating material. This graded interface is more desirable from the mechanical point of view as stress concentration is likely to be reduced. Although there were considerable differences between the various PVD group means, generally, the bond strength achieved appeared to be more dependent on the degree of oxidation of the tin itself rather than the particular method employed.

4.4. SEM and X-ray mapping

Generally it proved difficult to image the tin oxide coatings by SEM using either the back-scattered electron detector or secondary electron imaging. Therefore X-ray mapping procedures were adopted to highlight the presence of tin at the interface. Barium was used as a marker for the cement. X-ray mapping resolved tin containing layers for both reactive and non-reactive ion plating techniques. Despite the fact that the cohesive strength of the cement has been shown to be in excess of 39 MPa [8], all the bond tested PVD samples showed evidence of retained cement and therefore cohesive failure within the cement. This might be explained by rapid development of local stress concentration producing premature failure within the cement layer. The fact that bond failure was demonstrated to have occurred in the cement is encouraging, in that it indicates that the mechanical and adhesive performance of the coatings per se are not limiting factors in the tensile strength of the system.

The X-ray map for the sectioned sample from group 13 (CVD) indicates that failure occurred in the tin oxide layer (Fig. 6), as tin and aluminium were found, but barium was absent in the map.

To place these results in a clinical context, bond strengths to directly deposited tin oxide coatings would appear to compare favourably with chemically etched and silane treated ceramics. In a previous study on coated dental porcelain substrates, improvements in bond strength were masked by cohesive failure within the porcelain [8]. With the increasing interest in high strength dental ceramics, interfacial failure may become the dominant mode of breakdown and this study clearly demonstrates the potential benefits for high alumina systems.

5. Conclusions

It has been shown that alumina can be successfully coated with tin oxide by PVD techniques, and that such coatings can be rendered white by post-deposition oxidation. These results confirm the potential of this technique for improving bonding of dental ceramics, without adversely affecting the aesthetics of all-ceramic restorations. This study also indicates that PVD techniques may be superior to CVD methods for this application.

Acknowledgements

The authors wish to thank Mr Chris Roberts of the Department of Orthodontics, University of Manchester for his assistance with the statistical analysis.

References

- 1. J. W. McLEAN and T. H. HUGHES, Br. Dent. J. 119 (1965) 251.
- 2. V. PIDDOCK, Clin. Mater. 4 (1989) 349.
- 3. H. CLAUS, Die Quintessenz der Zahntechnik 4 (1991) 35.
- 4. R. M. HIGHTON, A. A. CAPUTO and J. MATYAS, J. Prosthet. Dent. 42 (1979) 292.
- 5. R. C. PRATT, J. O. BURGESS, R. S. SCHWARTZ and J. H. SMITH, *ibid.* 62 (1989) 11.
- J. W. MCLEAN and I. R. SCED, Aust. Dent. J. 21 (1976) 119.
 T. TANAKA, M. HIROANO, M. KAWAHARA, H. MAT-
- SUMURA and M. ATSUTA, J. Dent. Res. 67 (1988) 1376. 8. P. V. McCRORY, S. TINSTON, V. PIDDOCK, P. KELLY,
- E. C. COMBE and R. D. ARNELL, J. Dent. 19 (1991) 171. 9. P. S. WEGLICKI, PhD thesis, University of Salford, UK
- 9. P. S. WEGLICKI, PhD thesis, University of Salford, UK (1990)
- CRC Handbook of chemistry and physics, 1st student edition R. C. Weast, ed. (CRC Press, Boca Raton, FL, 1987) p. B-73

Received 8 April and accepted 23 November 1992