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The effect of indium on porcelain bonding between porcelain and Au–Pd–In alloy

J. A. HAUTANIEMI
University of Turku, Department of Applied Physics, Itäinen Pitkäkatu 1, SF-20520 Turku, Finland

The effect of small In additions on oxide structure and porcelain adherence to Au–Pd alloys was studied. In was oxidized internally as In_2O_3. No uniform external oxide layer could be seen. Small In addition (1 at%) did not have any detectable effect on porcelain adherence ($\sim$12 MPa), whereas higher In concentration (5 at%) caused significant increase in bond strength ($\sim$26 MPa). This increase was probably a result of higher In_2O_3 concentration at the surface.

1. Introduction

Pd-containing alloys have become recognized as alternatives to high-Au and non-precious alloys for metal-ceramic restorations. The main reasons for the popularity of palladium alloys are good corrosion and tarnish resistance along with acceptable biocompatibility and the price of Pd, which is approximately one-half of that for Au. Pd-rich alloys suitable for metal-ceramic restorations can be roughly divided into following groups: Au–Pd–, Pd–Co–, Pd–Cu– and Pd–Ag-based alloys [1]. Considering the physical properties, processing characterics and the amount of precious metal components, the Au–Pd– system is very attractive because of the excellent compromise between these three factors [2].

The importance of the oxide layer on the bonding of metal to porcelain is generally accepted for all kinds of metal-ceramic materials. The theory of glass/metal-bonding was largely developed by Pask [3–5]. He postulated that chemical bonding across the interface is achieved by having therodynamically stable equilibrium in the interfacial zone and having both phases saturated with an oxide of the substrate metal. The oxide layer formed on metal by preoxidation is supposed to be dissolved by molten glass. The chemical bonding is maximized when a monomolecular oxide layer remains at the interface. The importance of oxide adherence to its alloy substrate has been emphasized by Mackert [6, 7], who found a correlation between oxide adherence and porcelain adherence to metal. The dental noble alloys are normally alloyed by base metals like In, Sn and Ga, which form an oxide layer on the alloy. Accumulation of oxidizing elements within a few micrometres of the metal/porcelain interface has been reported in several studies [8–13], in which concentration profiles of alloy components over a metal/porcelain interface were measured by electron microprobe. Such data are generally found to support the theory that chemical bonding mechanisms are controlled by oxidizing metal components. More detailed descriptions of possible bonding mechanisms are presented in the literature [14–18].

In a very few studies [19, 20] the structure and composition of the outermost surface oxide layers of noble alloys, formed during oxidation treatment, have been studied by surface sensitive methods like XPS (X-ray photoelectron spectroscopy). The depth sampled by this method is very thin, of the order of a few nanometres. This makes it possible to study much thinner oxide layers than by electron microprobe, whose sampling depth is around 1 μm. Ohno *et al.* [19] studied the role of indium on the adherence of Au–In(1 wt%) alloy on silica glass by XPS, known also as ESCA (electron spectroscopy for chemical analysis). The adherence of sessile drops of this gold alloy increased when heat treatment produced a thin oxide layer on the surface of the alloy. The authors concluded that the introduction of the non-bridging oxygen atoms and indium ions into silica glass was an essential factor in promoting good adherence between the gold alloy and silica glass. Hautaniemi *et al.* [20] studied the oxidation of various Pd-containing alloys. For Au–Pd–In–Sn alloy indium was preferentially oxidized, whereas for Au–Pd–In–Ga alloy gallium oxidized preferentially. No bond strength data were presented in these studies.

The objectives of the present work were to study the effect of small In additions (1 and 5 at%) on (1) the structure and composition of oxide layer and (2) porcelain adherence between porcelain and Au–Pd–In alloy. A further purpose (3) was to evaluate the correlation between the composition of outermost surface layers and the bond strength. Multitechnique analyses (SEM (scanning electron microscopy), EDX (energy-dispersive X-ray analysis), XRD (X-ray diffraction) and XPS) were used to determine the composition and the structure of the oxide layer formed during oxidation treatment. The bond strength of porcelain to alloy was measured by a four-point bending test.

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2. Experimental procedure

The compositions of the three alloys studied are given in Table I based on the weighted amounts of the component metals. The alloys were induction-melted under argon atmosphere in an alumina (Al_2O_3) crucible from elemental components of purity better than 99.95 wt %. Plate specimens (26 mm × 26 mm × 1.3 mm) were subsequently cast in a dental centrifugal machine. The surface to be veneered was ground by SiC-paper (up to 1000 grit). Oxidation and firing schedules are given in Table II.

A scanning electron microscope (Cambridge Stereoscan 200) equipped with an EDX system (LINK AN 10000) was used in the characterization of the sample surfaces.

X-ray diffraction (Philips) measurements were made with a diffractometer using CuK_α radiation. The oxides formed on the surface were identified on the basis of the *d*-values given by the diffraction data files.

The structure of the outermost part of the oxide layer was studied using XPS (Perkin-Elmer PHI 5400). The XPS-spectra were obtained using MgK_α radiation (1253.6 eV). The measured binding energies (BE) were calibrated by using as reference the BE of the $AU4f_{7/2}$ line (83.6 ± 0.2 eV). The take-off angle relative to the surface was 45 degrees. The concentration profiles were measured using Ar^+-bombardment with a beam voltage of 3 kV. The sputtering rate was measured to be less than 1 nm min^{-1} using a Ta_2O_5/Ta reference sample. A lower ion beam energy (1 keV) was used to detect possible initial changes in concentration profiles. Quantitative analyses were carried out using the following sensitivity factors given by the manufacturer of the spectrometer: O1s 0.711; $Pd3p_{1/2}$ 0.766; Au4f 6.250 and $In3d_{5/2}$ 4.359.

Alloy plates were cut into 6 mm × 8 mm × 1.2 mm test pieces and veneered with an opaque layer for the measurement of bond strength between alloy and porcelain. The first opaque layer was thin and the second one was built up to a total thickness of 0.5 mm. The specimens were glued with epoxy at 150 °C for 10 min to rectangular steel bars both on the porcelain and the metal side. Four-point bending was carried out at a crosshead speed of 1 mm min^{-1} using a standard machine for mechanical testing (Instron). A more detailed description of this method is presented elsewhere [21, 22].

TABLE I The compostion of the studied alloys (at %) (wt % in parenthesis)

Alloy	Au	Pd	In
AP	40.0 (55.2)	60.0 (44.8)	
API1	39.6 (54.8)	59.4 (44.4)	1.0 (0.81)
API5	38.0 (53.0)	57.0 (43.0)	5.0 (4.1)

TABLE II Firing procedures

Oxidation	$300\,^\circ C \xrightarrow{ca\ 4\ min} 980\,^\circ C/5$ min + air cooling
1st opaque[a]	$300\,^\circ C \xrightarrow{ca\ 4\ min} 950\,^\circ C/1$ min + air cooling
2nd opaque[a]	$300\,^\circ C \xrightarrow{ca\ 4\ min} 940\,^\circ C/1$ min + air cooling

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[a] vacuum (4000–5000 Pa) was applied during heating.

3. Results

3.1. XRD

X-ray diffraction measurements were carried out in order to identify the oxides formed during oxidation treatment. The measured *d*-values as well as those reported for bcc In_2O_3 in the literature are given in Table III. For both alloys (API1 and API5) the most

TABLE III The oxides identified by XRD prior to veneering

Oxide	*d*-values [30]	Measured *d*-values	Alloy
In_2O_3 cubic, bcc	2.92 2.53 1.79	– – –	API1
		2.94 2.54 1.80	API5

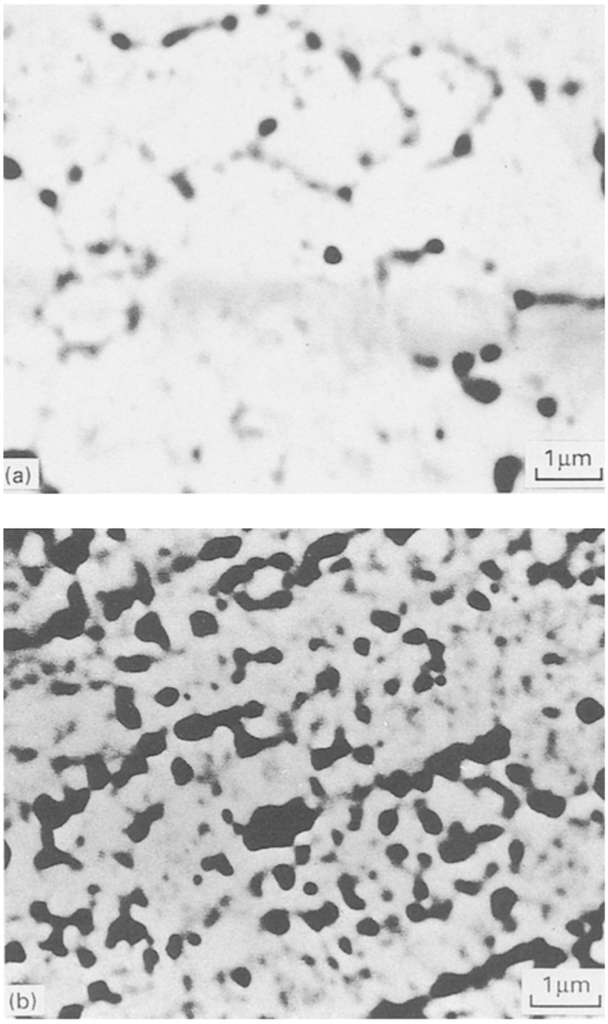

Figure 1 Backscattering (BS) images of oxidized alloys: (a) API1; (b) API5.

intense diffraction peaks were caused by the unoxidized matrix. For API1, no oxide reflections were seen whereas for API5, *d*-values corresponding to bcc In_2O_3 were detected (Table III).

3.2. SEM/EDX

The backscattering (BS) images of the sample surfaces after oxidation treatment are presented in Figs 1 and 2. Fig. 1 shows the surface of the sample after oxidation treatment, and Fig. 2 shows the cross-sections of the same specimens.

3.3. XPS

The XPS total spectra for oxidized alloys API1 and API5 are presented in Fig. 3. The measured binding energies (BE) are given in Table IV and values for the relevant oxides from the literature [23] in Table V. The composition profiles for alloy component as function of sputtering time are given in Fig. 4. The depth resolution of measurements during the first couple of minutes was increased using lower ion beam energy (1 keV), lower take-off angle (10 degrees), and shorter sputtering intervals. No indication of the existence of a continuous external oxide layer was seen.

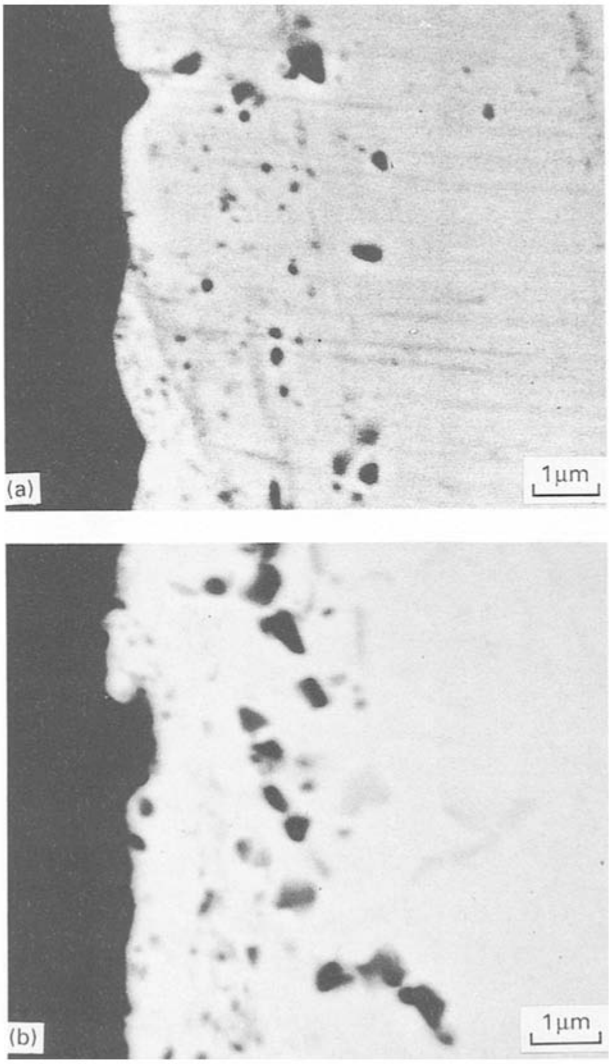

Figure 2 BS images of cross-section of oxidized alloys: (a) API1; (b) API5.

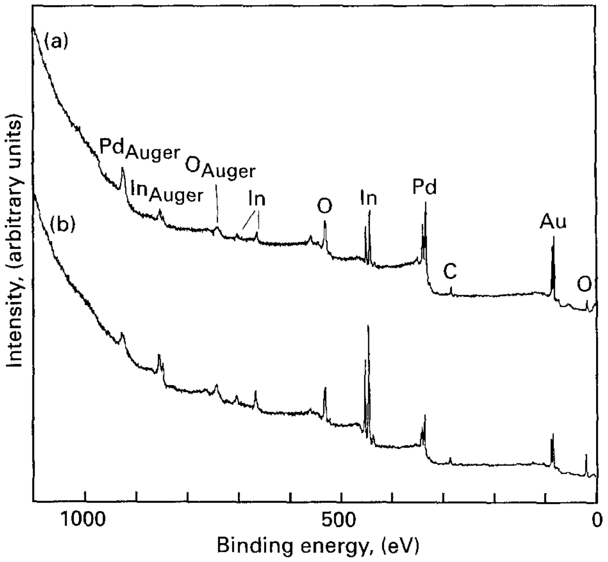

Figure 3 XPS total spectra for oxidized alloys: (a) API1; (b) API5.

TABLE IV BE values measured for oxidized alloys

Alloy	$Au4f_{7/2}$	$Pd3d_{5/2}$	$In3d_{5/2}$
AP	83.8	335.3	
API1	83.8	335.2	445.0
API5	83.8	335.3	445.0

TABLE V BE values given by literature [23]

Substance	Emission line	BE(eV)
Pd	$3d_{5/2}$	335.0
PdO	$3d_{5/2}$	336.3
Pd_2O	$3d_{5/2}$	337.9
In	$3d_{5/2}$	444.0
In_2O_3	$3d_{5/2}$	449.0

TABLE VI Bond strength measured by four-point bending

Material	Bond strength (MPa) ± SD	
AP	15.0	Average = 12.5 ± 2.3
	12.0	
	10.6	
API1	12.7	
	13.6	Average = 11.3 ± 3.4
	6.2	
	12.8	
API5	19.9	
	23.9	Average = 25.9 ± 5.0
	28.1	
	31.5	

Indium appeared as In_2O_3 for both alloys even after sputtering for 45 min. The BE of $Pd3d_{3/2}$ indicate that palladium existed as a metallic state for oxidized (Table II) In-containing alloys, and for non-oxidized Au–Pd alloy as well.

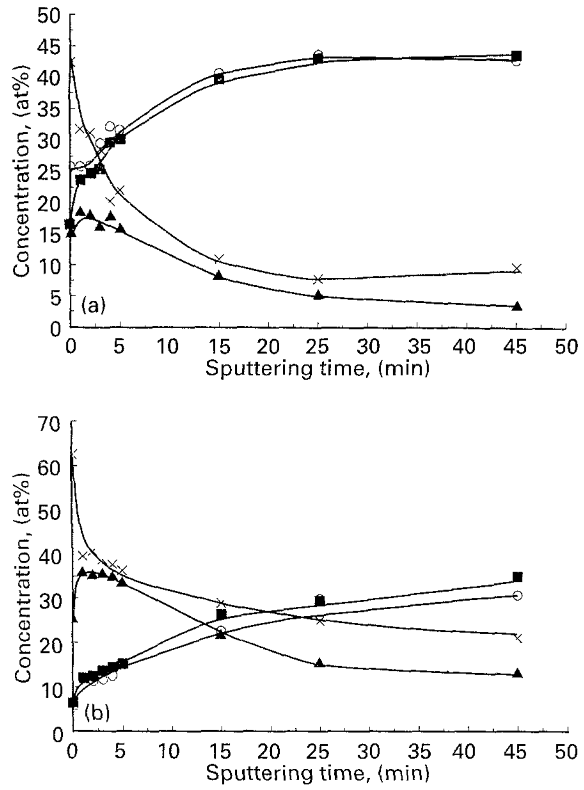

Figure 4 Composition depth profiles (XPS) for oxidized alloys: (a) API1; (b) API5. ■ Au, ○ Pd, × O, ▲ In.

3.4. Four-point bending

The results of four-point bending tests are given in Table VI. The calculation of fracture stress has been described elsewhere [24]. The bond strength was approximately the same (12.5 and 11.3 MPa) for AP and API1, but much higher for API5 (25.8 MPa). The analysis of variance (one-way ANOVA) demonstrated that there were significant differences between bond strength values as reflected by a $p \leqslant 0.001$.

4. Discussion

XPS measurements showed that In appeared as In_2O_3 even after sputtering for 45 min for both alloys. Also XRD measurements confirmed the existence of In_2O_3 for the API5 alloy. The concentration of In_2O_3 for API1 was probably too small to be detected by XRD. The determination of the composition of the dark regions (Fig. 1) by EDX was difficult because those areas were so small that emission of X-rays from the light matrix contributed to results. However, strong In signals were detected from the dark areas. On the basis of these measurements one can conclude that indium is oxidized as In_2O_3, and is located mainly in the dark areas of the BS micrographs in Figs. 1 and 2.

Oxidation of indium occurred internally. No uniform external oxide layer was seen either by XPS or SEM. The strong XPS Au and Pd signals can be seen in the XPS total spectra (Fig. 3). These signals were detected even at a very low take-off angle of 10 degrees. The inelastic mean free path λ [25] of Pd signals in oxide is about 2.5–3.0 nm. The vertical depth sampled is given [26] by $d = 3\lambda \sin \alpha$. The presence of $Pd3p_{1/2}$ signals, even at 10 degrees, seems to rule out the existence of a thicker (> a few nanometres) uniform external oxide layer. If such a layer existed, the XPS Au and Pd signals would be attenuated beyond observation. Furthermore, no decrease in In concentration was seen during initial sputtering. If thin uniform external In_2O_3 layer existed, a decrease in In concentration would have been seen at the beginning of the sputtering cycle, especially at low ion beam energy and low take-off angle. Since this was not observed, the outermost layers must consist of In_2O_3 and unoxidized Au and Pd. The thickness of the layer oxidized internally is a few micrometres and varies to some extent. No clear difference can be seen between API1 and API5. After the firing procedures the thickness of the layer oxidized internally (not presented) remained roughly the same for both alloys.

The strong surface segregation of In for oxidized samples can be seen for API1 and API5. The maximum amount of In is ~ 19 at % for API1 and ~ 36 at % for API5. The initial decrease in O concentration and increase in Au, Pd and In concentrations after sputtering for 1 min is likely caused by removal of adsorbed oxygen from the surface. The sputtering rate was estimated to be somewhat lower than $1\ \mathrm{nm\,min^{-1}}$. Thus, the thickness of the layer with higher In concentrations was a few nanometres. The strong segregation of In is due to its high oxygen affinity, which can be deduced from the negative Gibbs standard free energy change associated with formation of the oxide [27, 28]. The most common oxide of Pd is PdO, which is not stable at the oxidation temperature. The dissociation temperature of PdO in normal atmosphere is 877 °C [29], which means that PdO can only be formed during heating or cooling.

The proportion of oxidized area (dark areas in Fig. 1) for API5 is considerably higher than for API1. The XPS results confirm the same: the ratio In/(Au + Pd) is about 2.1 for API5 and 0.36 for API1. This indicates that In_2O_3 coverage of the API5 surface is much higher than for API1.

In the work of Ohno *et al.* [19] small In concentration (1.7 at %) caused better bonding (no percentage given) when the oxide layer was produced on the surface of the Au–In alloy. In this work a small In addition (1 at %) did not have any detectable effect on porcelain adherence, whereas a higher In concentration (5 at %) caused a significant increase in bond strength. This indicates that In_2O_3 concentration has to be above a certain level to produce adequate bonding. In this work this was obtained by higher bulk concentration of In.

The measured data for Au–Pd–In alloy support the theory that porcelain bonding is of chemical nature. The chemical bonding mechanism require sufficient amounts of surface oxides that are adherent to the alloy and bond to the porcelain.

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