Adhesion of Adhesive Resin to Dental Precious Metal Alloys Part II The Relationship between Surface Structure of Au-In Alloys and Adhesive Ability with 4-META Resin

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Adhesion of 4-META to Au-In alloy was improved by adding In equivalent to 15% of Au content. On the basis of the results of Au-In alloys analyzed by XPS, the present study investigated the reason why adhesion of the Au-In alloy was improved. The O 1s spectrum could be separated into three oxygen chemical states, In_2O_3 , chemisorbed H_2O , and physisorbed H_2O . The amount of chemisorbed H_2O decreased remarkably with increasing amount of In. It is considered that the poor adhesive ability of the pure gold and alloys containing only small amounts of In was due to the chemisorbed H_2O molecules and insufficient indium oxide on the alloy surface. It was established that excellent adhesion requires an oxide with chemical affinity for 4-META to cover at least 50% of the alloy surface.

Key words : Adhesion, 4-META, XPS

INTRODUCTION

Silver based alloys containing In, Zn, and/or Sn have excellent adhesive ability to 4-META, although 4-META resin does not adhere strongly to pure silver, indicating that the adhesive ability could be affected by the presence of the base metals¹⁾. The water durability and bonding strength of 4-META resin to binary alloys of Au, Ag, Cu, or Pd containing In, Zn, or Sn were studied to determine the most effective kinds and amounts of base metals to add to dental precious metal alloys. Dental precious metal alloys with excellent adhesive ability to 4-META resin were developed in the previous study: Addition of In was the most effective, giving the best water durability improvements²⁾ at 15% in gold.

In the present study, the surface structure of Au-In alloys was analyzed by X-ray Photoelectron Spectroscopy (XPS) to determine the relationship between the adhesive ability and surface structure.

EXPERIMENTAL METHODS

Materials

Binary alloys of Au with 5, 10, 15, and 20 mass% In were made. Metals of purity

higher than 99.9% were melted in an alumina crucible covered with graphite using a high frequency induction furnace in an argon gas atmosphere. Weight loss by melting was less than 0.02%. The alloy specimens for XPS were 4 mm diameter with the surfaces metallographically polished to a mirror-like finish with sandpaper and buffed with a wet abrasive of aluminum oxide powder.

Surface analysis of Au-In alloys by XPS

The XPS measurements were performed with an electron spectrometer (ESCA-850, Shimadzu Co. Ltd., Kyoto, Japan) with Al K_{α} radiation (1486.6 eV) under a pressure of 2×10^{-6} Pa evacuated with turbo-molecular pumps. The alloy surface was subjected to argon ion etching at 2 kV and 20 mA under a pressure of 5×10^{-4} Pa in the spectrometer, giving an etching rate of 0.1 nm/sec with pure silver. The XPS measurements and argon ion etching were performed alternately to determine both the amounts and chemical states of the elements in the depth direction.

The quantitative analysis of the elements was carried out according to equation (1). Here the intensity of a photoelectron, N , ejected from a shell in an element, 'a', in a thick specimen is expressed by:

$$N = N_o \cdot n_a \cdot \sigma \cdot \lambda \cdot S \quad (1)$$

where N_o is a constant, n_a is the number of atoms of 'a' per unit volume, σ is the photoelectron cross-section, λ is the mean free-path, and S is a spectrometer factor. Since $\lambda \cdot S$ approximates unity for ESCA-850, the amounts of the elements could be calculated with only the photoelectron cross-section. The error in the calculations was estimated to be $\pm 5-30\%$ ³⁾.

The binding energies of the measured photoelectron peaks were calibrated by the C 1s peak of hydrocarbon contamination at a binding energy of 285.0 eV.

RESULTS

Surface analysis by XPS

Fig. 1 shows the concentration variations of In in the depth direction for 95Au-5In (mass%), 90Au-10In, 85Au-15In, and 80Au-20In alloys. The In concentration of the 95Au-5In alloy at the surface was similar to the concentration of the alloy matrix. However, the surface concentrations of In in the alloys containing more than 10 mass % In were twice those of the alloy matrix.

Fig. 2 shows the In 3d spectrum obtained from the as-polished Au-15In (mass%) alloy surface before argon ion etching. The spectrum had a wide half width value due to the mixture of metallic In and oxidation states identified as In_2O_3 ²⁾.

Fig. 3 shows a set of O 1s spectra obtained from the surface without argon ion etching for pure gold(a) and Au-In binary alloys containing 5(b), 10(c), 15(d), and 20(e) mass% In. The O 1s peak was at 532.8 eV for pure gold(a) and at 531.9 eV for the Au-15In (mass%) alloy(d). With increasing In concentration, the intensity of the lower binding energy increased, indicating that the shoulder at 530.0 eV was due to

Fig. 1 Concentration variations of In in the depth direction for 95Au-5In (mass %), 90Au-10In, 85Au-15In, and 80Au-20In alloys.

Fig. 2 In 3d spectrum obtained from as-polished Au-In alloy surface.

In_2O_3 . The chemical shifts of the higher binding energy peak of the Au-15In (mass%) alloy and pure gold were 1.9 eV and 2.8 eV with reference to the In_2O_3 state.

To clarify the changes in the oxygen chemical state, the data analysis system in the XPS spectrometer was used to separate the oxygen states on the O 1s spectra by assuming that the spectra could be approximated by a Gaussian function. Fig. 4 shows the O 1s spectra obtained from the Au-15In (mass%) alloy: (a) shows the separated spectra of O 1s, obtained from the spectrum without argon ion etching: The O 1s spectrum could be separated into three components indicated by the dotted lines. The solid line, the observed spectrum, agreed well with the chained line which is a composite of the three components. Among the O 1s spectra component I was the same chemical state as the oxygen in In_2O_3 as noted for Fig. 3. Fig. 4(b) shows the separated spectra of O 1s, obtained from the spectrum after argon ion etching for 0.05 min. The oxygen state indicated at 531.9 eV (II) was decreased strongly by the argon ion etching. It could be surmised that the oxygen of components II and III were present in the upper part of component I oxygen, because the oxygen due to II and III was decreased remarkably by the very limited argon ion etching.

DISCUSSION

Chemical states of oxygen

To decrease the surface energy due to free valence of metal atoms at the solid surface, the surface is stabilized (decreasing free energy) by arranging the atoms into particular positions and by adsorbing molecules. Metal surfaces immediately adsorb oxygen and water vapor if exposed to the air. With reactive metals there is initially

Fig.3 O 1s spectra from the surface, without argon ion etching, of pure gold and of Au-based binary alloys containing 5, 10, 15, and 20 mass% In.

some chemisorption that soon gives way to chemical reactions and the formation of oxides or hydroxides. There may be rearrangement of the surface atoms of the metal during the early stages of oxide growth⁴⁾. Therefore, the surface is not directly exposed to air because it is covered with -OH groups or a layer of H₂O, while the base metal bonds with oxygen to form oxide.

Bolger *et al.*⁵⁾ have proposed the oxide model on the metal shown in Fig. 5: The oxide surface directly adsorbs a monolayer of -OH, and there are H₂O surface layers tightly bonded to the surface hydroxyl groups and additional H₂O layers on top, their

Fig. 4 (a): Separated O 1s spectra obtained from Au-15In (mass%) alloy without argon ion etching in Fig. 3. (b): Separated O 1s spectra obtained from Au-15 (mass%) In alloy after argon ion etching for 0.05 min.

Fig. 5 Bolger's metal surface model⁴⁾. The oxide surface is covered with -OH groups as monolayer; there are H₂O molecules tightly bonded to surface hydroxyl groups in the middle and additional H₂O layers on top of the adsorbed layer.

Table 1 Binding energy (eV) and area fraction (%) of oxygen chemical states

	argon ion etching	oxygen chemical states		
		I (In ₂ O ₃)	II	III
pure gold	without	—	532.1 eV (34%)	533.6 eV (66%)
85Au-15In alloy	without	530.1 eV (27%)	531.9 eV (55%)	533.4 eV (18%)
85Au-15In alloy	with	530.1 eV (54%)	531.8 eV (35%)	533.2 eV (11%)

thickness depending on temperature and relative humidity.

The area fraction of oxygen chemical states shown in Fig. 4 gives the amount of each chemical state. Table 1 shows binding energy (eV) and area fraction (%) of oxygen chemical states, obtained from pure gold and Au-15In (mass%) alloy (Fig. 4). Since the II and III components were removed by argon ion etching, component I increased from 27% to 54%. With argon ion etching, component II decreased from 55% to 35% and component III decreased from 18% to 11%: The decrease in the amount of component II was bigger than that of component III, indicating that component II is on top of component III.

Sham *et al.*⁶⁾ have reported a study on clean and hydrated TiO₂ (rutile) surfaces by XPS, here the chemical shifts of oxygen species corresponding to the II and III components mentioned above were 1.4 eV and 2.8 eV with reference to the TiO₂ state. The oxygen of component II decreased when the sample was kept in an ultrahigh vacuum for a week. Healy *et al.*⁷⁾ have also discussed hydration and preferential molecular adsorption on titanium: Here the major peak was attributed to oxygen of

TiO₂ with the subpeaks at 1.5 and 3.0 eV higher than the O 1s of TiO₂. Healy *et al.* assigned the peak at $\Delta 1.5$ eV as physisorbed H₂O and that at $\Delta 3.0$ as chemisorbed H₂O. From the above, the origins of these oxygen states were estimated as follows: Component I is due to oxygen bonded with In in In₂O₃; Component II is due to physisorbed H₂O molecules; and Component III is due to the oxygen in the chemisorbed H₂O molecules.

Oxygen adsorbed on the pure Au was mainly due to chemisorbed H₂O molecules as shown in Table 1. On the Au-15In (mass%) alloy, the amount of oxygen from component II due to physisorbed H₂O molecules decreased remarkably and the oxygen from component I due to In₂O₃ increased strongly after argon ion etching for 0.05 min. There was a little change in oxygen from component III due to chemisorbed H₂O molecules.

Surface structure and adhesive ability

The effect of In addition to Au on the water durability at the adhesion interface has been demonstrated as shown in Fig. 6²⁾. Larger peeled areas (%) indicate lower water durability. Adding In was the most effective to improve the adhesive ability of gold, and water durability improved by addition of more than 15 mass% In.

Fig. 7 shows the atomic distribution of Au(white) and In(black) at the adhesion surface, the surface before argon ion etching, obtained from the quantitative analysis shown in Fig. 1: (a) Au-5In (mass%) alloy having poor adhesive ability, and (b) Au-15In (mass%) alloy having excellent adhesive ability. The atomic % of Au and In at the top surface were 90Au-10In on (a) and 56Au-44In on (b). Indium atoms bond with oxygen to form In₂O₃, and to obtain excellent adhesive ability it is necessary that the

Fig. 6 Results of the water durability tests at the adhesion interface, obtained from Au-In binary alloys²⁾.

Fig. 7 Atomic distribution of Au(white) and In(black), from the quantitative analysis in Fig. 1; (a) Au-5In (mass %) alloy with poor adhesive ability and (b) Au-15In (mass %) alloy with excellent adhesive ability.

alloy surface is covered with the In-oxide.

The surface of alloys containing In were covered with indium oxide, while pure gold was not covered with oxide. The energy at the gold surface is decreased by arranging the atoms and also by adsorbing the chemisorbed and the physisorbed H_2O molecules described above. To create excellent adhesion after removing the water molecules, there has to be a chemical interaction between the metal surface and the polar trimellitic group in 4-META.

Mogi⁸⁾ has reported the absence of adhesive ability of pure gold to 4-META resin. However, 4-META resin bonding with pure gold has been obtained by heating in flowing hydrogen gas, and also when the adhesion procedure was performed in a polyethylene chamber filled with ultra-high purity argon without oxygen or water molecules. The fracture appearance was a mixture of interface and cohesive failure with bonding strengths of about 300 kgf/cm^2 ⁹⁾. The adhesive ability obtained from the cleaned gold surface was quite different from the result in the atmosphere, showing that water molecules absorbed on the pure gold surface lead to poor adhesive ability.

The poor adhesive ability of the alloy containing only small amounts of In or pure gold as shown in Fig. 6 was due to chemisorbed H_2O molecules and insufficient indium oxide on the alloy surface. The atomic distribution shown in Fig. 7 does not show the top surface, but indicates the mean atom distribution in the photoelectron mean free path. However, the distance related to adhesion was nearly equal to the photoelectron mean free path by XPS because adhesion depends on atomic interactions which are determined by atoms less than 1 nm from the top surface¹⁰⁾. To obtain excellent adhesion of 4-META resin with a gold alloy, there must be no chemisorbed H_2O molecules on the alloy surface and the oxide element with chemical affinity for 4-META must cover at least 50% of the alloy surface as shown in Fig. 7(b).

CONCLUSION

Oxides on dental precious metal alloys play very important roles in the adhesion with 4-META. The present study described the reasons why adhesion of binary alloys was improved by adding In equivalent to 15% of Au content. The adhesive ability of 4-META to the Au-In binary alloys was discussed on the basis of the water durability at the adhesion interface. The Au-In alloy surface was analyzed by XPS to establish the relationship with adhesive ability. The XPS O 1s spectra were separated to clarify the changes in the oxygen chemical states. The adhesive ability was discussed in terms of the separated oxygen states, oxygen due to In_2O_3 , chemisorbed and physisorbed water molecules.

With In in Au based alloys, the In_2O_3 on the alloy surface plays a very important role in the adhesion with 4-META. It was established that to obtain excellent adhesion, the element of an oxide having chemical affinity for 4-META must cover at least 50% of the alloy surface. The poor adhesive ability of 4-META resin to pure gold is considered to be caused by chemisorbed H_2O molecules on the surface.

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