

博士論文

Polyacrylic acid-metal adhesive bond joint
characterization by x-ray photoelectron
spectroscopy

(X線光電子分光法によるポリアクリル酸-金属
接着界面の化学状態分析)

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The adhesive force to human tooth and metallic restoration of dental cements which contain polyacrylic acid (PAA) is found to be stronger than that of previous cements. Chemical interaction at the interface between metals and carboxylate groups of PAA were studied by x-ray photoelectron spectroscopic method combined with Ar^+ -ion beam etching technique to examine the mechanism of adhesion. A 2.5 wt% aqueous solution of PAA was painted on the surface of metal plates which are usual elements of dental alloy. Ar^+ -ion etching was used to scrape off *in situ* the PAA film coated on the metal plate gradually in the sample chamber of the ESCA equipment. After a few minutes of etching, ESCA spectra were observed. The profile of the spectra and binding energy of $4f_{5/2}$ and $4f_{7/2}$

levels of Au coated with PAA show little change by the Ar^+ -ion etching, and remain in the same state as those of uncoated Au. Similar behaviors were obtained in case of Pt. There are three chemical states on Sn plate coated with PAA. The lowest binding energy peak is assigned to pure Sn. The middle one is assigned to SnO_2 . The highest one corresponds to Sn combined with carboxylate groups of PAA. The chemical reaction corresponding to the highest binding energy peak seems to contribute to the strong adhesive force of these cements to Sn. These aspects of spectra corresponded to McLean's results which showed that these cements had weak adhesion to Au and Pt, but strong adhesive force to tinned Au and Pt.

INTRODUCTION

The whole phenomenon of the adhesion of dental cements is complex. The cement, in the setting process after mixing, contacts the metal restoration and the tooth substance. Many things are occurring at the same time,¹⁻³ so that adhesive force is composed of many factors. The electrostatic contribution and chemical contribution are of course only a portion of the total forces acting. But these contributions are very important from the standpoint of margin closure and endurance of bond joint. Carboxylate groups of polyacrylic acid seem to react with the metal restoration and calcium in tooth enamel, as a basis of strong adhesive force of the cements containing PAA. D. C. Smith described the adhesion mechanism of dental cements which contain PAA.^{4,5} PAA has been assumed to chelate with calcium in enamel. D. R. Beech showed that PAA reacts with calcium ions in enamel powder in his infrared spectroscopic study.⁶ There have been several investigations about the chemical reaction between polyacrylic acid and metal⁷⁻¹¹ or metal

oxide.¹² But few experiments have been performed concerning the chemical interaction at the intact bond joint of metal and polyacrylic acid. A technique is presented in which the chemical state of intact bond joints can be studied using x-ray photoelectron spectroscopy (ESCA), ESCA technique offers information of the chemical state on a solid surface to a 10–40 Å depth.¹³ Different chemical states of an atom give chemical shifts in ESCA spectra.¹⁴ Therefore, ESCA technique is a suitable technique to perform the chemical state analysis of PAA–metal adhesive bond joints.¹⁵ Ar⁺-ion beam etching was applied to the metal plate coated with PAA to scrape the PAA gradually in the sample chamber of ESCA equipment. After a few minutes of etching, ESCA spectra were measured. Thus the chemical state of the metal near the interface between the PAA and metal was analyzed to examine the chemical constituent of the strong adhesive force of the cement.

MATERIALS AND METHODS

Specimen preparation

Gold, platinum, silver, copper, cobalt, chromium, tin, and indium which are elements of dental alloys were selected for study. These were supplied by Hirano Metal and Alloy Corporation, Tokyo, Japan. The metal purity was upward of 99.9 wt%. Metals were prepared in a plate shape, 5 × 12 × 0.5 mm. These metal plates were polished with No. 600 emery paper, and then painted with a 2.5% by weight aqueous solution of PAA, and dried in a desiccator for 24 h. The standard metal compounds used to assign the peaks in the ESCA spectra were supplied by Wako Pure Chemical Industries, Osaka, Japan.

Argon ion etching

Ar⁺-ion etching was used to gradually scrape off the PAA film coated on the metal surface in the sample chamber of an ESCA spectrometer. A schematic illustration of argon ion etching is shown in Figure 1. High purity argon gas was led in to the ionization chamber at about 5×10^{-5} mm Hg. The argon ion beam was generated with a PHI Model 04-161 Sputter Ion Gun

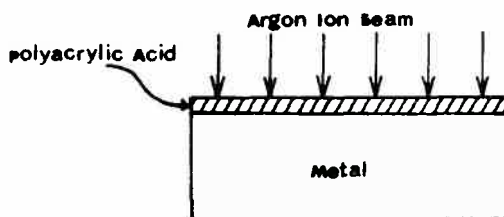


Figure 1. Schematic figure of argon ion etching of metal surface coated with PAA.

which was operated with a beam potential of 1.5 kV and electron emission current of 20 mA.

ESCA measurement

Experiments were performed in the AEI ES 200 electron spectrometer using Mg K_α radiation (1253.6 eV). The Au ($4f_{5/2}$, $4f_{7/2}$) binding energy, 87.74 eV, 84.07 eV, was used for calibration of the equipment. Oil diffusion pumps fitted with cold traps produce a vacuum of 5×10^{-8} mm Hg. After a few minutes of argon ion beam etching, the ESCA spectra were measured. Wide range ESCA spectra (binding energy: 0 to 1000 eV) was measured first, and a level of the largest intensity peak was chosen for chemical state analysis. The measurement was performed within the 10 eV range with centers of peaks at 0.1 eV steps. The argon ion beam etching and ESCA measurement were repeated alternately. When the PAA was removed from the metal surface by the etching, the ESCA measurement was concluded. Experimental spectra which were deconvoluted into separate components assumed Gaussian distribution. Thus the chemical states of the metals near the interface between PAA and metal were analyzed.

RESULTS AND DISCUSSION

Gold and platinum

Experimental ESCA spectra of Au coated with PAA are illustrated as a function of Ar^+ -ion etching duration in Figure 2. The abscissa shows binding energy of the photoelectron released from the sample. The ordinate shows the intensity of the photoelectron in an arbitrary unit. The profile of the spectra and binding energy of $4f_{5/2}$ and $4f_{7/2}$ levels of Au coated with PAA do show little change by Ar^+ -ion etching and remain in the same state as those of uncoated Au. Binding energy of electron in $4f_{5/2}$ and $4f_{7/2}$ orbitals are 87.74 eV and 84.07 eV, respectively. The ESCA spectra of Pt coated with PAA are illustrated in Figure 3. Similar results to Au were obtained in the case of Pt. Binding energy of electrons in $4f_{5/2}$ and $4f_{7/2}$ orbitals are 74.60 eV and 71.29 eV, respectively. These results show that the chemical reaction with chemical shift in ESCA spectra does not occur at the interface when Au and Pt are coated with PAA, and correspond with a previous observation that the cements have weak adhesive strength to Au and Pt.¹⁶

Silver and copper

Experimental ESCA spectra of Ag coated with PAA are illustrated as a function of Ar^+ -ion etching duration in Figure 4. The profile of Ag $3d_{5/2}$ level on the unetched sample shows a peak at 368.05 eV and a shoulder at

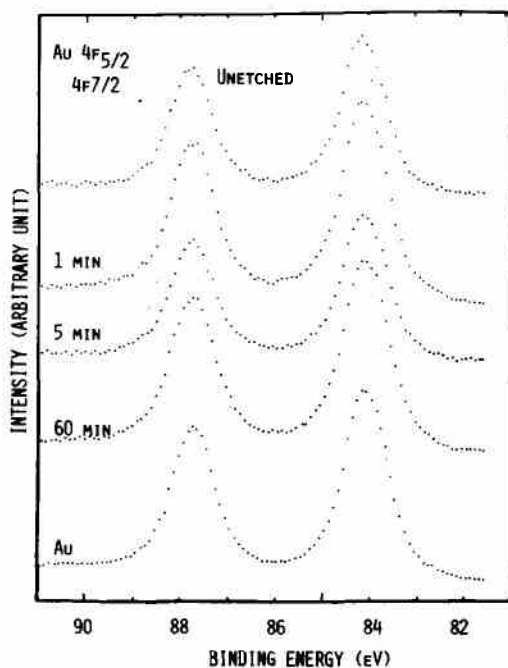


Figure 2. X-Ray photoelectron spectra of Au 4f_{5/2}, 4f_{7/2} levels of Au coated with PAA and etched by argon ion beam for 1, 5, and 60 min and pure Au metal.

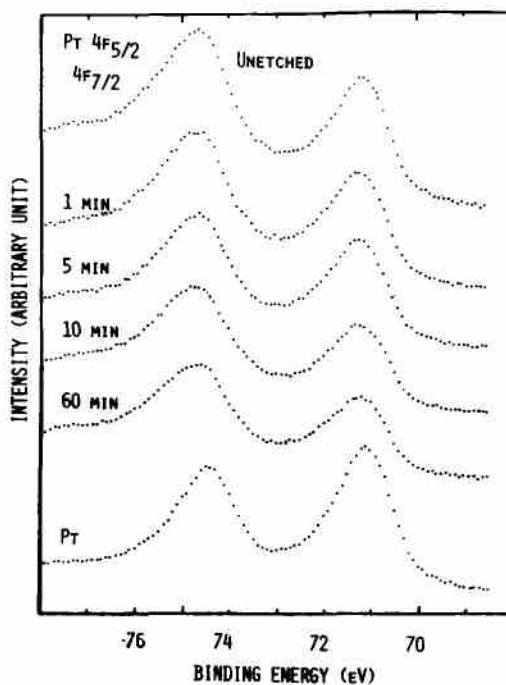


Figure 3. X-Ray photoelectron spectra of Pt 4f_{5/2}, 4f_{7/2} levels of Pt coated with PAA and etched by argon ion beam for 1, 5, 10, and 60 min and pure Pt metal.

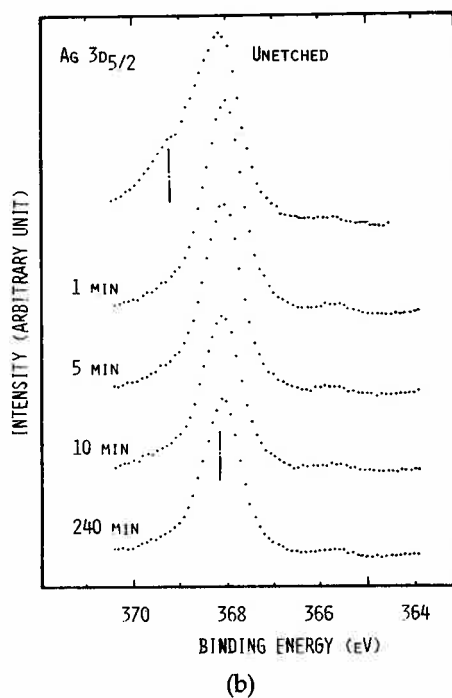
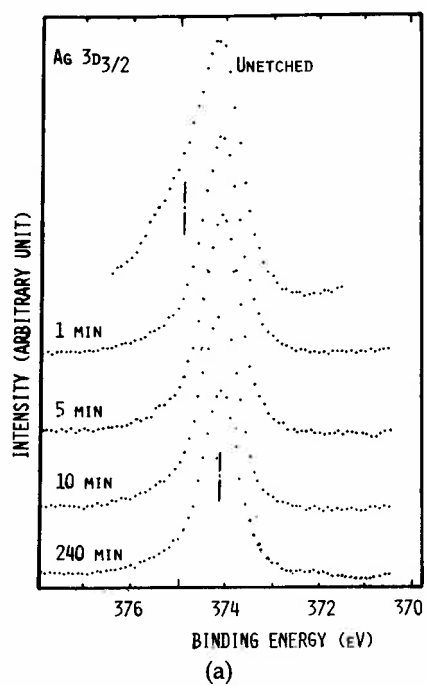


Figure 4. X-Ray photoelectron spectra of Ag 3d_{3/2}, 3d_{5/2} levels of Ag coated with PAA and etched by argon ion beam for 1, 5, 10, and 240 min.

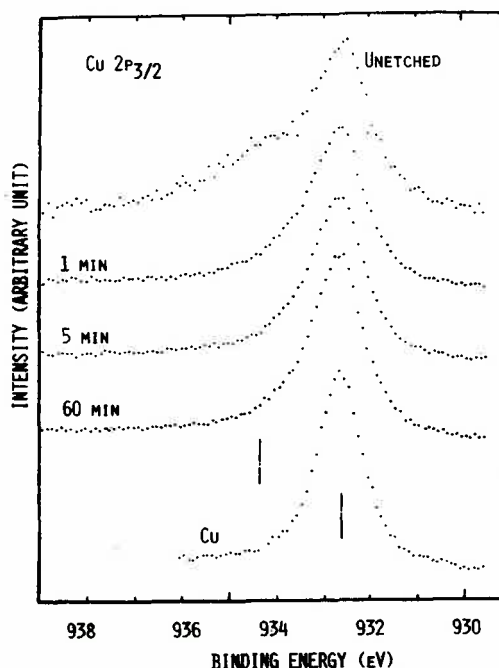


Figure 5. X-Ray photoelectron spectra of Cu $2p_{3/2}$ level of Cu coated with PAA and etched by argon ion beam for 1, 5, and 60 min and pure Cu metal.

369.15 eV. This shoulder disappeared gradually because of the Ar^+ -ion etching. Profile of Ag $3d_{3/2}$ level does not show good symmetry. S. Evans showed that no significant change occurred in the 3d signal throughout the oxidation other than some loss of intensity.¹⁷ So it seems that binding energy of this shoulder in the $3d_{5/2}$ signal does not correspond to that of silver oxide, but a product of the chemical reaction between polyacrylic acid and the silver surface. Medium adhesive strength of silver¹⁶ to the cements is caused by the chemical reaction between PAA and the silver surface.

Experimental ESCA spectra of Cu coated with PAA are illustrated as function of Ar^+ -ion etching duration in Figure 5. The profile of Cu $2p_{3/2}$ level on the unetched sample shows a peak at 932.53 eV and shoulder at 934.38 eV. This shoulder disappeared gradually by Ar^+ -ion etching. The binding energy at the peak corresponds to a pure Cu metal state. The binding energy of the shoulder is larger than that of Cu_2O and CuO in the literature^{17,18} and does not coincide with the satellite peak of copper oxides. H. P. Gregor, L. B. Luttinger et al. showed the following reaction of Cu and PAA:¹⁰



The shoulder of the spectrum seems to correspond to the product of this reaction. Ida et al. showed that the adhesive force of these cements to copper is strong.¹⁶ The chemical reaction corresponding to the shoulder in the spectrum seems to contribute to the strong adhesive force of these cements to Cu.

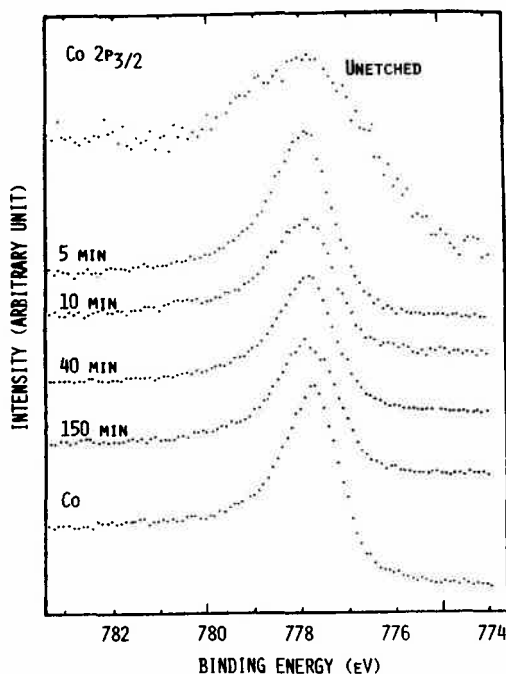


Figure 6. X-Ray photoelectron spectra of Co $2p_{3/2}$ level of Co coated with PAA and etched by argon ion beam for 5, 10, 40, and 150 min and pure Co metal.

Cobalt and chromium

Experimental ESCA spectra of Co coated with PAA are illustrated as a function of Ar^+ -ion etching duration in Figure 6. Profile of Co $2p_{3/2}$ level on the unetched sample shows a peak at 777.85 eV and two shoulders at 779.55 eV and 782.35 eV. These shoulders disappear by Ar^+ -ion etching for 5 min. Binding energy of the peak corresponds to that of metallic state of Co.¹⁹ These shoulders correspond to cobalt oxides in the literature.¹⁹ Previous work shows that the adhesive force of these cements to cobalt is slight.¹⁶ The reason is that the cobalt oxide film is very weak allowing the oxide film to peel off easily from the metal matrix. Adhesive forces of these cements to cobalt oxide seem to be strong, but the cobalt oxide film peels off easily producing weak adhesion to the metal.

Experimental ESCA spectra of Cr coated with PAA are illustrated as a function of Ar^+ -ion etching duration in Figure 7. Profile of Cr $2p_{1/2}$ level on an etched sample for 1 min show a peak at 583.61 eV and two shoulders at 586.08 eV and 588.25 eV. A profile of Cr $2p_{3/2}$ level show a peak at 574.23 eV, and two shoulders at 576.48 eV and 578.25 eV. These peak and shoulders correspond to Cr, Cr_2O_3 , and CrO_3 , respectively in a previous work.²⁰ The profile of a spectrum on a sputtered sample of 10 min shows an unsymmetric figure which has a swelling at the high binding energy side. A symmetric profile can not be obtained from a polished pure chromium surface which

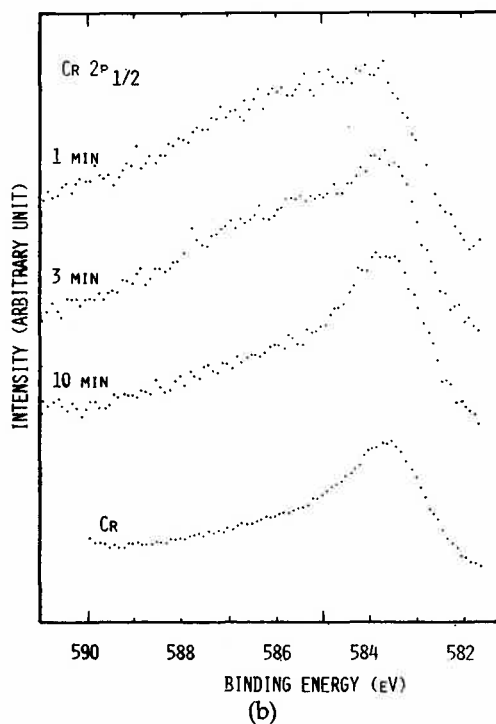
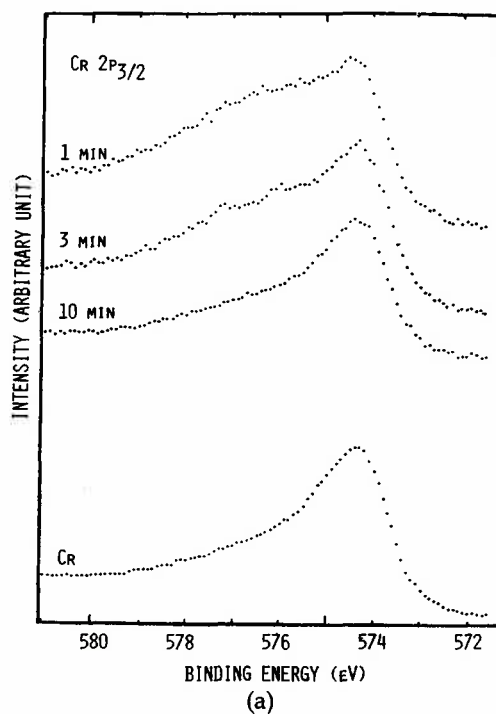


Figure 7. X-Ray photoelectron spectra of $\text{Cr } 2p_{1/2}$, $2p_{3/2}$ levels of Cr coated with PAA and etched by argon ion beam for 1, 3, and 10 min and pure Cr metal.

also was sputtered by Ar^+ -ion beam for a very long time. This shows that a passive film of chromium oxide is formed on metal matrix firmly. S. M. Skinner and B. Yamaguchi et al showed that the adhesive force of dielectric adhesive materials to oxidized metals is strong,^{21,22} for the surface potential of metal oxide is higher than that of pure metal surface. This result corresponds to previous work that the adhesive force of these cements to chromium is strong.¹⁶ These results explain the strong adhesive force of the cements to stainless steel and to cobalt-chromium alloys.²³

Tin and indium

Experimental ESCA spectra of Sn coated with PAA are illustrated as function of Ar^+ -ion etching duration in Figure 8. The profile of a $3d_{3/2}$ level on unetched sample shows three peaks at 493.33 eV, 495.47 eV, and 497.30 eV. Profile of $3d_{5/2}$ level on unetched sample show three peaks too at 484.89 eV, 487.08 eV, and 488.78 eV. With increased etching time, the highest binding energy peak diminished first. The middle binding energy peak disappeared second, and the lowest binding energy peak persisted longest. This suggests that three different chemical states of the Sn atom are located at the interface between PAA and metal surface. ESCA spectra of standard Sn compounds are measured to assign these peaks. The lowest binding energy peak is assigned to the pure Sn metal state as shown in Figure 9. The middle binding energy peak corresponds to the Sn state in SnO_2 . The highest binding energy peak, marked by an arrow in Figure 8, is assigned to a signal originated from Sn atoms combined with carboxylate groups of PAA. The strong adhesive force of the cements to Sn metal is derived from the chemical reaction corresponding to the highest binding energy peak. The present experimental results explain McLean's observation that the cements have very small adhesive strength to Au and Pt, but have strong adhesive forces to tinned Au and Pt.²⁴

Experimental ESCA spectra of In coated with PAA are illustrated as a function of Ar^+ -ion etching duration in Figure 10. A profile of In $3d_{3/2}$ level on unetched sample shows three peaks at 451.15 eV, 452.55 eV, and 454.40 eV. Profile of In $3d_{5/2}$ level on unetched sample show three peaks at 443.70 eV, 445.01 eV, and 446.76 eV. With increased etching time the highest binding energy peak diminish first. The middle binding energy peak disappeared second, and the lowest binding energy peak remained. This demonstrates that three different chemical states of In atoms are located at the interface between PAA and metal surface. ESCA spectra of standard In compounds were measured to assign these peaks. The lowest binding energy peak is assigned to the pure In metal state as shown in Figure 11. The middle binding energy peak corresponds to the In state in In_2O_3 . The highest binding energy peak, marked by an arrow in Figure 10, is assigned to a signal originated from In atoms combined with carboxylate groups of PAA. The strong adhesive force of the cements to Ag-In alloy²³ is certainly contributed by the chemical reaction producing the highest binding energy peak.

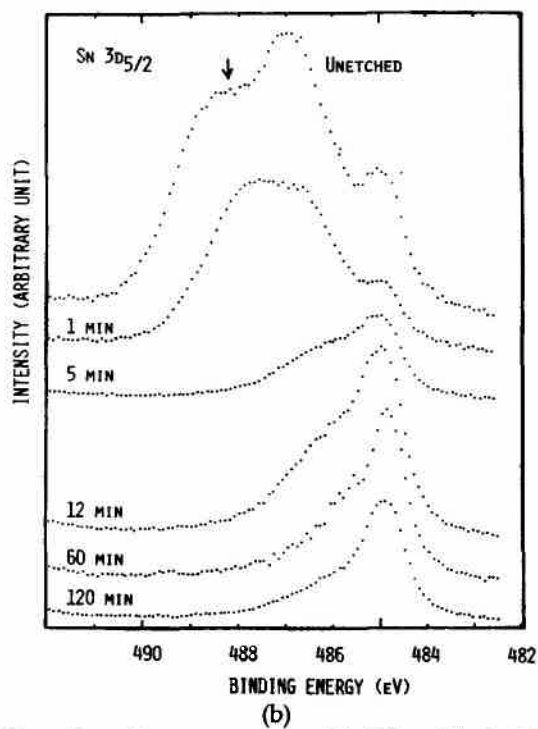
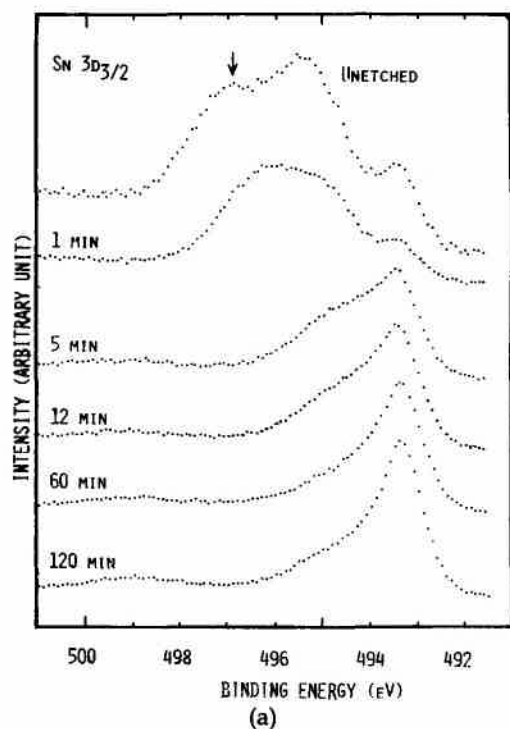


Figure 8. X-Ray photoelectron spectra of Sn $3d_{3/2}$, $3d_{5/2}$ levels of Sn coated with PAA and etched by argon ion beam for 1, 5, 12, 60, and 120 min.

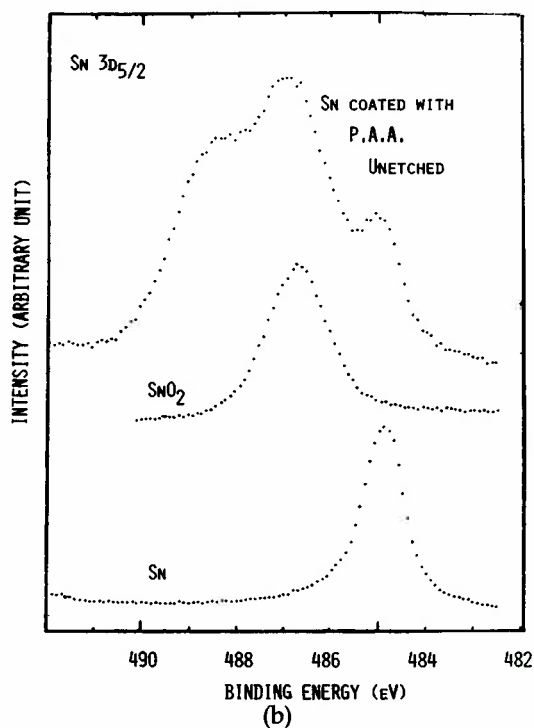
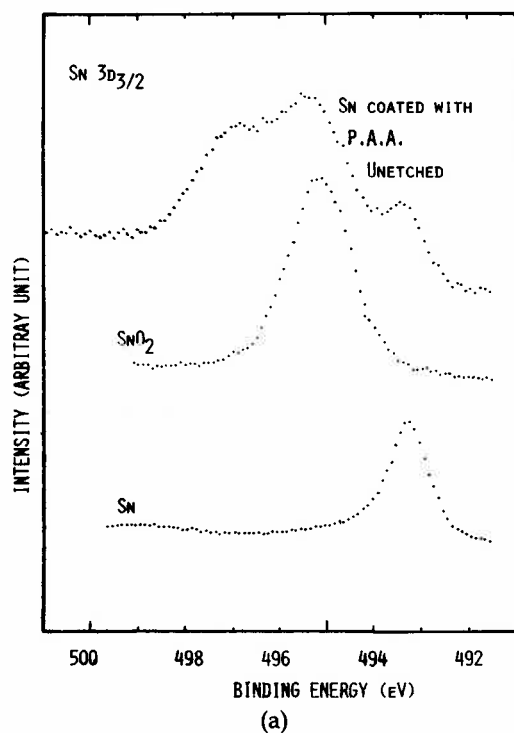


Figure 9. X-Ray photoelectron spectra of $\text{Sn } 3d_{3/2}$, $3d_{5/2}$ levels of Sn coated with PAA, SnO_2 , and pure Sn metal.

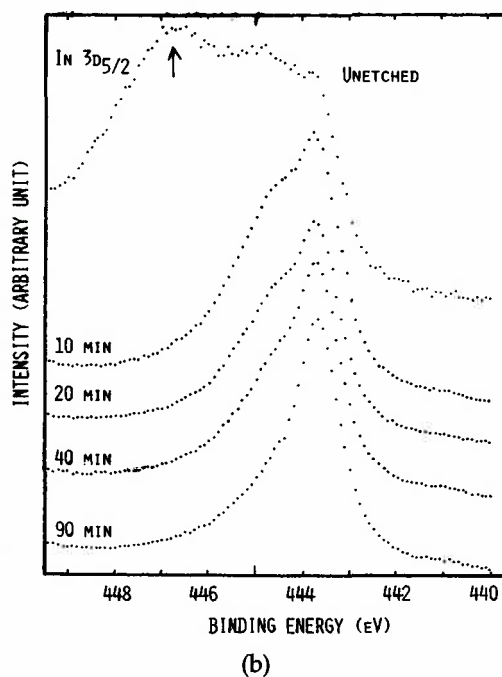
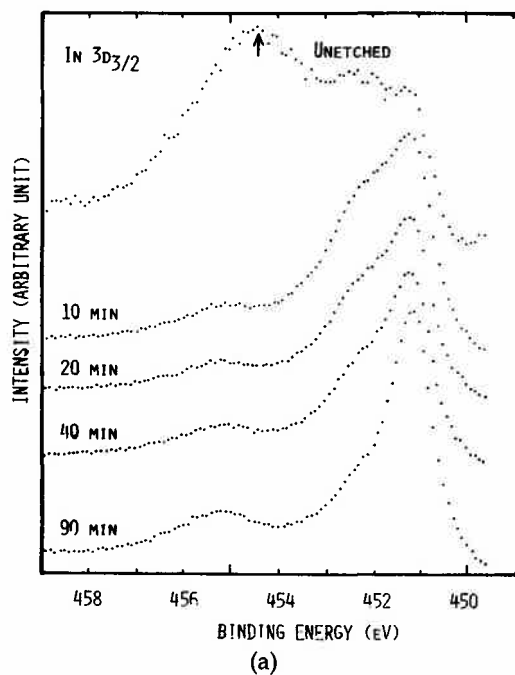


Figure 10. X-Ray photoelectron spectra of In $3d_{3/2}$, $3d_{5/2}$ levels of In coated with PAA and etched by argon ion beam for 10, 20, 40, and 90 min.

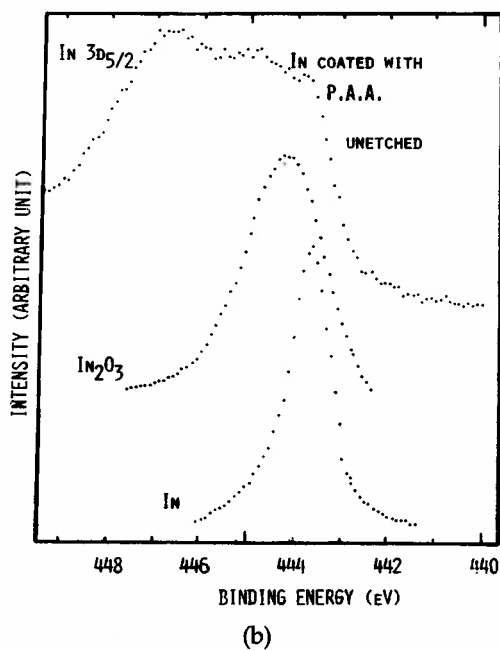
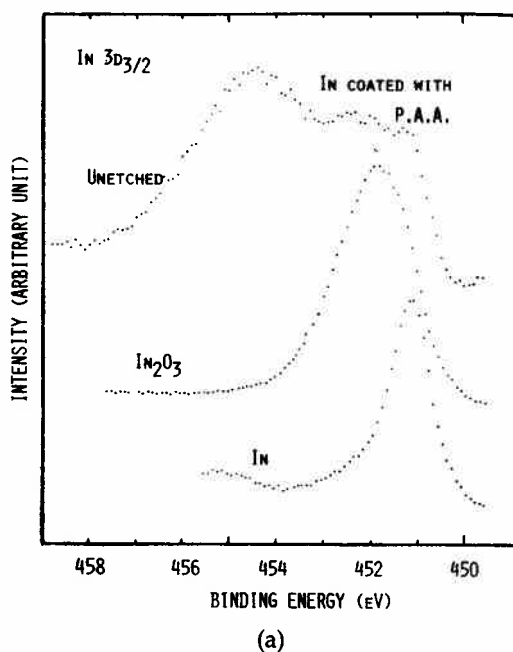


Figure 11. X-Ray photoelectron spectra of In $3d_{3/2}$, $3d_{5/2}$ levels of In coated with PAA, In₂O₃ and pure In metal.

Comparison of the experimental results with actual cementation

The ESCA measurement in electron spectrometer requires very high level of vacuum, so the metal samples were dehydrated after painting of PAA. It is a different point compared with actual cementation process with water.

In an actual cementation during dental treatment an aqueous solution of PAA is mixed with the cement powder. During mixing, free carboxylate groups of PAA react with metal ions in the cement powder and form a salt.¹² The amount of free carboxylate groups decreases rapidly with time after mixing.²⁵ When metal and tooth substance contact the PAA after mixing of the cement, there is a diminished number of free carboxylate groups available to react with the metal and tooth substance. It is expected that the large majority of carboxylate groups of PAA react with metal ions in the cement powder, and the minor part of carboxylate groups of PAA react with the metal restoration and tooth substance. This might be able to explain why the adhesive force of the cement is not as that suggested by the chemical reaction with PAA and metal restorations demonstrated by the ESCA measurement of this study.

CONCLUSION

ESCA spectra of metal coated with PAA were measured as a function of Ar^+ -ion beam etching duration. The adhesion mechanism of the cements was examined by comparison of ESCA results and adhesive strength of the cements to various metals studied in previous work. The following conclusions were obtained:

1. Chemical reactions with chemical shifts in ESCA spectra did not occur when Au and Pt were coated with PAA. This could explain the weak adhesive strength of the cements to the noble metals, Au and Pt.
2. When silver was coated with PAA, it reacted with the carboxylate groups of PAA. This chemical reaction contributed to the medium adhesive force of silver to PAA. The chemical reaction of copper and PAA resulted in a strong adhesive force.
3. When cobalt and chromium were coated with PAA, oxides were formed on the metal matrix. But the binding force of cobalt oxide and the cobalt matrix is very weak, allowing the oxide film to peel off easily, so the adhesive force of the cements to cobalt is very small. A passive film of Cr_2O_3 adheres on the chromium matrix firmly, so the adhesive force of these cements to chromium is very strong.
4. When tin and indium are coated with PAA, SnO_2 and In_2O_3 are formed. Chemical product of Sn and In with PAA are formed over the oxide film, these reaction contributes to a strong adhesive force of the cements to Sn and In.
5. In an actual cementation, it is expected that the large majority of carboxylate groups of PAA react with metal ions in the cement powder, and the minor part of carboxylate groups of PAA react with the metal restoration.

This might be able to explain why the adhesive force of the cement is not as that suggested by the chemical reaction with PAA and the metal restorations demonstrated by the ESCA measurement of this study.

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