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Surface analysis of dental amalgams by X-ray photoelectron spectroscopy and X-ray diffraction

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Short Title : Surface analysis of amalgams by XPS and XRD

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Abstract

Objectives : It is important to characterize the surface of dental amalgam in order to understand the process of mercury release from amalgam restorations in the oral. The mercury evaporation occurs not only from the newly made restoration but also from the set material.

Methods : The surfaces of four different types of amalgams, which had been well set, were analyzed with X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) and the relationship between surface compositions and mercury release was studied. Fresh amalgam surfaces as well as aged surfaces, which were stored for 30 days in air, were investigated using XPS and the chemical states of amalgam components and oxygen were studied. The aged surfaces were also characterized with XRD and grazing angle X-ray diffraction.

Results : With increased oxidation, the surface contents of tin and oxygen were increased in all amalgams. In contrast, the surface contents of copper and mercury were decreased. An increase of zinc or indium content were observed in zinc or indium containing amalgams, respectively. A surface layer enriched with indium and oxygen was clearly detected by XPS but not with grazing angle X-ray diffraction.

Significance : The thickness of the enriched surface layer is estimated to be in the order of few nanometer, which is approximately equal to the analysis depth of XPS. In addition, the presence of metallic elements, like tin and zinc, that readily form a stable oxide layer at the surface suppress the release of mercury

Keywords : Amalgam; Surface analysis; X-ray photoelectron spectroscopy, X-ray diffraction;

Mercury; Vapor

Introduction

The mercury evaporation from amalgam restorations in the oral cavity has been extensively debated in recent years. The evaporation occurs not only from the newly made restoration but also from the set material [1-14]. In an ongoing study, Berglund et al. studied the *in vitro* mercury evaporation from brushed surfaces of four different brands of amalgam. The conventional type of amalgam showed a more rapid decrease of mercury release after brushing compared to the other types. The mercury evaporation is closely related to the state of the amalgam surface. Therefore, an analysis of the chemical state of the amalgam surface is necessary in order to reveal the relationship between the mercury release and amalgam composition.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) provide the chemical state information on the surface layer and the depth composition profiles. Therefore, XPS and AES have been widely applied for the analysis of surface layer of amalgam. Hanawa et al. [15,16] revealed that the zinc containing amalgam forms a tin and zinc oxide layer on the surface and this layer suppresses the mercury evaporation. Nakajima et al. [17] using AES reported that the surface of indium containing amalgam was rapidly covered with both an indium and a tin oxide films. McDermott et al. [18] studied the surface of high copper amalgams using XPS and suggested a SnO₂ like surface oxide component in high copper amalgams.

The purpose of this study was to analyze the surface layers formed on four different brands of amalgams and estimate the relationship between the chemical state of surface layers and mercury release rates.

Materials and Methods

The dental amalgam alloys tested were ANA 68, ANA 2000, Dispersalloy and Indiloy (Table 1). The cylindrical specimens of each alloy (4 mm in diameter, 8 mm in height) were prepared by a specially trained person. This was carried out 5 years prior to the measurements of mercury release according to the procedures outlined in ISO 1559:1995 Dental materials-alloys for dental amalgam. The specimens were kept in dried air at room temperature. The specimens were thereafter cut into disks with a thickness of 1 mm. The surfaces were polished with silicon carbide paper through 600 grid and diamond paste (1 : m) and washed with acetone in ultrasonic bath.

The XPS spectra corresponding to Ag3d, Sn3d, Cu2p, Zn2p, In3d, Hg4f, O1s and C1s were measured with X-ray photoelectron spectroscopy (Axis Ultra, Kratos Analytical, New York, USA). The specimens were cooled below -100°C with liquid nitrogen to maintain the vacuum in the chamber. The binding energies were calibrated using the C1s peak of 285eV from advantageous carbon. For each specimen, XPS measurements were performed for the surface that was nearly non-oxidized and the surface that was fully oxidized, where the former was studied after that the surface had been scratched and subsequently exposed to less than 30 sec in air and the last was studied after that the surface had been polished and subsequently exposed to air for more than 30 days.

The relative concentration of atom i , C_i , was calculated from the integrated intensity for the photoelectron derived from atom i , I_i , and the atomic sensitivity factor of atom i , S_i , according to the following equation;

$$C_i = (I_i/S_i)/\{\sum(I_i/S_i)\}$$

The crystal phases of aged amalgam specimens were estimated using X-ray diffraction and grazing angle X-ray diffraction (JEOL JDX-3500, Tokyo, Japan). The analyzing depth of grazing angle X-ray diffraction can be varied by changing the incidence angle of the X-rays.

Results

The bulk composition (Table 1) and the surface composition of metallic elements measured by XPS (oxygen and carbon excluded) of nearly non-oxidized (fresh) and fully oxidized (aged) surfaces are shown in Fig.1. The oxygen content of fresh and aged surfaces were shown in Table 2. With increasing oxidation from a fresh surface to an aged surface, the surface content of tin and oxygen increased in all amalgams. In contrast, the surface contents of copper and mercury decreased. In the zinc containing amalgam Dispersalloy, the surface content of zinc was significantly increased for the aged specimen. Further, the enrichment of tin was relatively smaller than for ANA 68 and ANA 2000. The surface composition of indium containing amalgam (Indiloy) showed a typical enrichment of indium up to 80at% of the metallic element. The oxygen content in fresh surfaces was approximately 30-40at% regardless of the type of amalgam, while the oxygen contents increased up to around 60at% after aging. Indiloy showed the highest oxygen content (76at%) (Table 2).

Table 3 shows the binding energies of measured elements of fresh and aged surfaces. Also, published binding energy data are listed in Table 4 [19]. The binding energy of Ag3d and Hg4f of all specimen were assigned to the metallic state. The binding energy of In3d in both the fresh and the aged Indiloy specimen were assigned to the oxide state. It was difficult to identify the state of zinc from the binding energy, because the binding energies of zinc in the metallic and oxide state were too similar. In Fig.2 Sn3d_{5/2} and Cu2p_{3/2} spectra were deconvoluted into two components. These components derived from metallic and oxide state, according to Table 4. The

estimated ratios of metallic state of tin in each fresh and aged amalgam are shown in Fig.3. As shown in Fig.2 and Fig.3, tin was mostly in the oxide state and copper was mostly in the metallic state. The ratio of metallic tin decreased due to oxidation in all amalgams except for Indiloy. The fraction of copper in the oxide state was 15% for the fresh surfaces of ANA 2000, Dispersalloy and Indiloy. For the fresh surface of ANA 68 and all aged amalgams, deconvolution was difficult because the intensity of the Cu2p peaks were weak.

Fig.4 shows the X-ray diffraction spectra of the aged surface of amalgams, where the $\gamma_1(\text{Ag}_2\text{Hg}_3)$ and the $\eta(\text{Cu}_6\text{Sn}_5)$ phases were observed in all specimens. The $\gamma_2(\text{Sn}_7\text{Hg})$ and the $\gamma(\text{Ag}_3\text{Sn})$ were observed in ANA 68, while $\epsilon(\text{Cu}_3\text{Sn})$ was observed in ANA 2000, which is a high copper amalgam. Fig.5 shows the spectra, obtained using grazing angle X-ray diffraction and conventional diffraction, of an aged indium containing amalgam (Indiloy) surface. Grazing angle X-ray diffraction provides the crystal phases in a surface layer, where the thickness analyzed was varied by changing the incidence angle of the X-rays. Even in the diffraction spectrum with a low angle of X-ray irradiation, peaks were assigned to γ_1 and γ phases. There were no peaks derived from the phase containing indium.

Discussion

As shown in Fig.1, the amalgam surfaces were enriched either with tin, zinc, indium or two of these and oxygen with oxidation. The surfaces of conventional amalgam (ANA 68) and high copper amalgam (ANA 2000) were rapidly enriched with tin. The zinc containing amalgam Dispersalloy showed rapid increase of zinc content and a slow increase of tin content on the surface. The indium containing amalgam Indiloy showed a rapid increase of indium. The tin content for fresh surfaces and aged surfaces of Indiloy increased and decreased, respectively. The copper content decreased in all amalgams with oxidation which was typically observed in the high copper amalgam ANA 2000. The binding energies shown in Table 3 suggests that the state of silver and mercury were in the metallic state and tin and indium were mainly in oxidized state. As shown in Fig. 2 and Fig. 3, tin was mostly oxidized and the fraction of tin in the oxidized state increased with aging. In contrast, most of the copper was in the metallic state and about 15% was oxidized for the fresh surface. Concerning zinc, the identification of the state of zinc from the binding energy was difficult because the binding energies of zinc in the metallic and oxide state were too similar. Hanawa et al. [16] proposed that the zinc of the amalgam surface oxidized forming zinc oxide based on thermodynamic arguments.

The standard formation energy of oxide for amalgam components is shown in Table 5. The Gibbs formation energies of tin, indium and zinc oxide are significantly lower than those of other amalgam components. The Gibbs formation energy of copper is lower than those of silver and mercury. These formation energies suggests that tin, indium and zinc are oxidized prior to copper

while silver and mercury are seldom oxidized. In the present study, silver and mercury were determined to be in the metallic state, copper partially oxidized, tin and indium oxidized and zinc was probably also oxidized. This result is well understood on the basis of the formation energy of oxide. In Dispersalloy and Indiloy, zinc and indium were enriched prior to tin on each surface suggesting that zinc and indium were oxidized prior to tin. The Gibbs formation energies of oxide of tin, indium and zinc are in the order $\text{SnO} > \text{ZnO} > \text{In}_2\text{O}_3 > \text{SnO}_2$. Assuming that oxidation of zinc and indium occurred prior to tin indicates that SnO is the oxide on the Dispersalloy and Indiloy surfaces. McDermott et al [18] suggested SnO_2 as the surface oxide component in high copper amalgams. Therefore, the oxidation mechanism and the composition of the surface layer is probably strongly affected by addition of zinc or indium.

Hanawa et al. [15,16] characterized the surface of various amalgams using XPS and proposed that the high content of tin and zinc in the amalgam surfaces are the result of the migration of these elements towards the surface and their subsequent oxidation. In these reports, the thickness of the surface layers containing zinc and tin were estimated to be several nanometers. Nakajima et al. [17] reported that the surface of indium containing amalgams were rapidly covered with both indium and tin oxide film. The results of the present study are consistent with these reports.

Fast diffusion of elements is necessary for the rapid migration of tin, zinc and indium and for the evaporation of mercury. Table 6 shows the diffusion coefficient of metallic elements in silver at room temperature (25°C). Mercury, tin, zinc and indium shows a high diffusion coefficient compared to silver and copper.

As shown in Fig.1, Indiloy showed the most drastic change in surface composition. Therefore, the surface characterization using grazing angle X-ray diffraction was performed for the aged Indiloy. In the result of Fig.5, using a low incidence angle (0.2°), mainly the major phase (γ_1) was detected and phases of indium oxide were not detected. The effective thickness, which provides the 99 percent of diffraction X-rays compared to specimen with infinite thickness, is described as follows;

$$x = -\ln(1-0.99)/[\mu d\{\operatorname{cosec}a + \operatorname{cosec}(2\theta - a)\}]$$

where x is the effective thickness (cm), μ is the mass absorption coefficient (cm^2/g), d is the density (g/cm^3), a is incidence angle (degree) and 2θ is diffraction angle (degree). The mass absorption coefficients of silver and mercury, which are major components of amalgams, are reported as 218 and 216, respectively [22]. The estimated effective thickness where the incidence angle of X-rays is 0.2 is approximately 60 nanometers. The indium enriched surface layer after 30 days of aging was estimated to be considerably thinner than 60 nanometer. Therefore, the thickness of the enriched surface layer is estimated to be in the order of few nanometer, which is approximately equal to the analysis depth of XPS.

Berglund et al. studied the mercury vapor release from the brushed amalgam surfaces for the amalgams as shown in Fig.6. ANA 68 showed the most rapid decrease of mercury release which terminated within 15 minutes. Dispersalloy also showed a rapid decrease of mercury

release compared to the other two types of amalgams. In Fig.1, ANA 68 contained the highest tin content at the surface. Dispersalloy had smaller content of tin, but larger content of zinc. Therefore, tin and zinc plays an important role in suppression of mercury vapor release and zinc is also effective. Ferracane et al. [24] studied the relationship between the mercury release rate of various types of amalgams and their compositions. The mercury release decreased with an increased the tin content in the γ_1 phase. On the other hand, the effect of zinc was not as clear as that of tin. This report concluded the tin content in the γ_1 phase is the primary determinant of mercury vapor release. In the present study and in an ongoing study by Berglund et al., the formation of surface oxide layer consist of tin and zinc and their effect on mercury release were confirmed and that is consistent with the results of Ferracane et al.[24] In contrast, Indiloy which surface was rapidly covered by indium with oxygen, showed a higher mercury release in comparison with the other indium-free amalgams. Thus, the surface layer of indium was considered as not as effective for suppression of mercury release as tin and zinc. However, Okabe et al. [25] reported that the mercury release rate after trituration decreased with increasing indium concentration. The present study and the ongoing study by Berglund et al. were carried with the amalgam specimens made 5 years prior to the measurements. Therefore, the period after trituration may have influenced on the behavior of Indiloy.

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Table 1 Composition of dental amalgams in atomic per cent

| Element | ANA68 ¹ | ANA2000 ¹ | Dispersalloy ² | Indiloy ³ |
|---------|--------------------|----------------------|---------------------------|----------------------|
| Ag | 44.0 | 25.6 | 43.0 | 39.5 |
| Sn | 14.8 | 16.0 | 10.1 | 13.2 |
| Cu | 5.5 | 25.6 | 12.5 | 14.5 |
| Zn | 0.1 | 0.1 | 1.0 | — |
| In | — | — | — | 3.1 |
| Hg | 35.6 | 32.7 | 33.4 | 29.7 |

1 Nordiska Dental AB, Helsingborg, Sweden

2 Johnson & Johnson, Dublin, Ireland

3 Shofu Inc., Kyoto, Japan

Table 2 Oxygen content on fresh and aged amalgam surfaces in atomic per cent

| Specimens | fresh | aged |
|--------------|-------|------|
| ANA68 | 37 | 63 |
| ANA2000 | 33 | 52 |
| Dispersalloy | 33 | 58 |
| Indiloy | 39 | 76 |

Table 3 Binding energies (eV) of elements contained in amalgams

| Elements | ANA68 | ANA2000 | Dispersalloy | Indiloy |
|-----------------------------|--------|---------|--------------|---------|
| Hg4f _{7/2} (fresh) | 100.0 | 100.0 | 99.9 | 100.0 |
| Ag3d _{5/2} (fresh) | 368.0 | 368.0 | 368.1 | 367.8 |
| Sn3d _{5/2} (fresh) | 487.0 | 486.7 | 487.2 | 487.0 |
| | 485.2 | 485.1 | 485.4 | 485.5 |
| Cu2p _{3/2} (fresh) | 933.4 | 932.7 | 933.0 | 933.3 |
| | | 934.4 | 935.0 | 935.2 |
| Zn2p _{3/2} (fresh) | n.d. | n.d. | 1021.6 | n.d. |
| In3d _{5/2} (fresh) | n.d. | n.d. | n.d. | 444.4 |
| Hg4f _{7/2} (aged) | 100.0 | 100.0 | 99.9 | 100.0 |
| Ag3d _{5/2} (aged) | 368.0 | 368.0 | 368.0 | 367.9 |
| Sn3d _{5/2} (aged) | 487.1 | 487.1 | 487.4 | 487.8 |
| | 485.4 | 485.3 | 485.3 | 486.0 |
| Cu2p _{3/2} (aged) | n.d. | 932.9 | 933.1 | 932.9 |
| | | 934.8 | | |
| Zn2p _{3/2} (aged) | 1021.5 | n.d. | 1021.5 | n.d. |
| In3d _{5/2} (aged) | n.d. | n.d. | n.d. | 444.6 |

Table 4 Published binding energies

| Elements | Binding energy of metallic state (eV) | Binding energy of oxide state (eV) |
|---------------------|---------------------------------------|--|
| Hg4f _{7/2} | 99.5 ~ 100.0 | 100.5 ~ 101.0 |
| Ag3d _{5/2} | 368.1 ~ 368.3 | 367.3 ~ 368.0 |
| Sn3d _{5/2} | 484.6 ~ 485.2 | 486.0 ~ 486.8 (SnO) 486.4 ~ 486.9 (SnO ₂) |
| Cu2p _{3/2} | 932.5 ~ 932.9 | 932.3 ~ 932.8 (Cu ₂ O) 933.4 ~ 934.0 (CuO) |
| Zn2p _{3/2} | 1021.2 ~ 1021.6 | 1021.4 ~ 1021.8 |
| In3d _{5/2} | 443.6 ~ 444.0 | 444.3 ~ 444.8 |

Table 5 Standard free energies of oxidation reaction of amalgam components

| Reaction | $\Delta H^\circ(\text{kJ/mol})$ | $\Delta S^\circ(\text{J/mol})$ | $\Delta G^\circ_{298}(\text{kJ/mol})$ | Refer ence |
|--|---------------------------------|--------------------------------|---------------------------------------|---------------|
| $\langle \text{Ag} \rangle + 1/4(\text{O}_2) = 1/2\langle \text{Ag}_2\text{O} \rangle$ | -153 | -33.1 | -5.4 | [20] |
| $\{\text{Hg}\} + 1/2(\text{O}_2) = \langle \text{HgO} \rangle$ | -91 | -108 | -59 | [21] |
| $\langle \text{Cu} \rangle + 1/2(\text{O}_2) = \langle \text{CuO} \rangle$ | -156 | -93.1 | -128 | [21] |
| $\langle \text{Cu} \rangle + 1/4(\text{O}_2) = 1/2\langle \text{Cu}_2\text{O} \rangle$ | -85 | -47.7 | -71 | [21] |
| $\langle \text{Sn} \rangle + 1/2(\text{O}_2) = \langle \text{SnO} \rangle$ | -281 | -96.5 | -252 | [21] |
| $\langle \text{Sn} \rangle + (\text{O}_2) = \langle \text{SnO}_2 \rangle$ | -578 | -207 | -519 | [21] |
| $\langle \text{Zn} \rangle + 1/2(\text{O}_2) = \langle \text{ZnO} \rangle$ | -350 | -101 | -320 | [21] |
| $\langle \text{In} \rangle + 3/4(\text{O}_2) = 1/2\langle \text{In}_2\text{O}_3 \rangle$ | -456 | -147 | -412 | [20] |

phases : (gas), {liquid}, <solid>

Table 6 Diffusion coefficients of amalgam components in silver at 25°C [22]

The diffusion coefficient D_T at a temperature T(K) is given as $D_T = D_0 e^{-Q/RT}$

| Elements | Q | D_0 (cm ² /sec) | D_{298} (cm ² /sec) |
|----------|------|------------------------------|----------------------------------|
| Ag | 45.2 | 0.67 | 4.5×10^{-34} |
| Cu | 46.1 | 1.23 | 1.8×10^{-34} |
| Hg | 38.1 | 0.079 | 8.7×10^{-30} |
| In | 40.8 | 0.41 | 4.7×10^{-31} |
| Sn | 39.3 | 0.255 | 3.7×10^{-30} |
| Zn | 41.7 | 0.54 | 1.4×10^{-31} |

Figure Captions

Fig.1 Surface compositions of fresh and aged amalgams and calculated bulk compositions

Fig.2 $\text{Cu}2p_{3/2}$ and $\text{Sn}3d_{5/2}$ XPS spectra of the fresh surface of ANA2000

Fig.3 The determined fraction of tin in the metallic state of fresh and aged amalgams

Fig.4 X-ray diffraction spectra of aged amalgams

(A6 : ANA68, A2:ANA2000, DS:Dispersalloy, IN:Indiloy)

Fig.5 Grazing angle X-ray diffraction spectra of aged Indiloy surface

Fig.6 The time dependence of the mercury release rate from amalgams after brushing

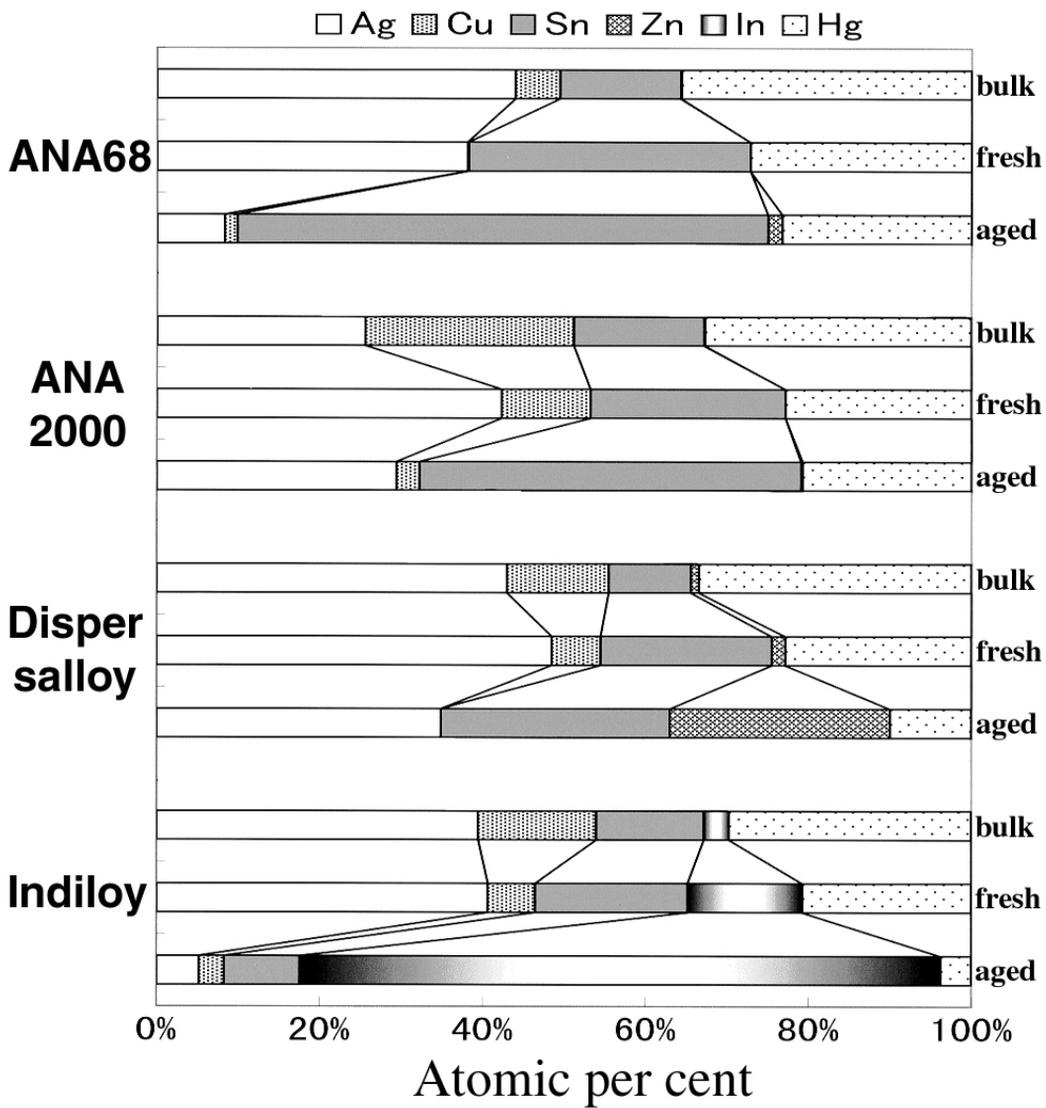


Fig.1

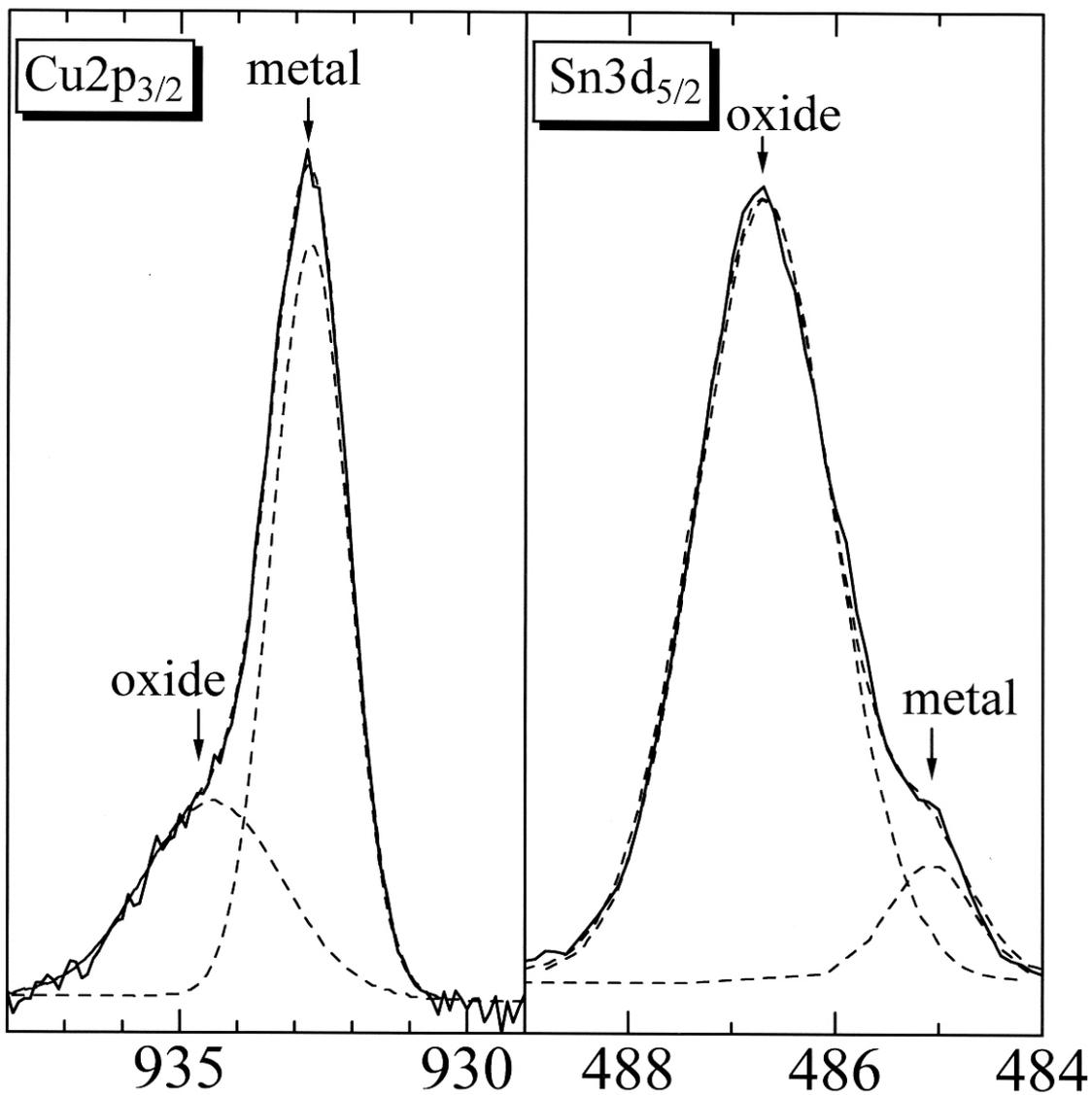


Fig.2

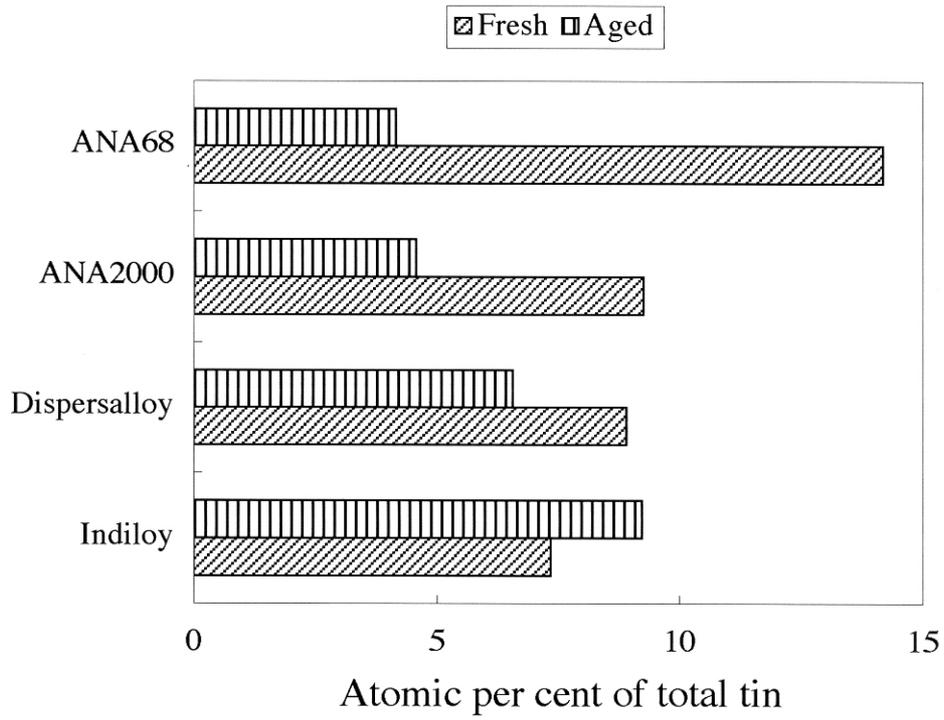


Fig.3

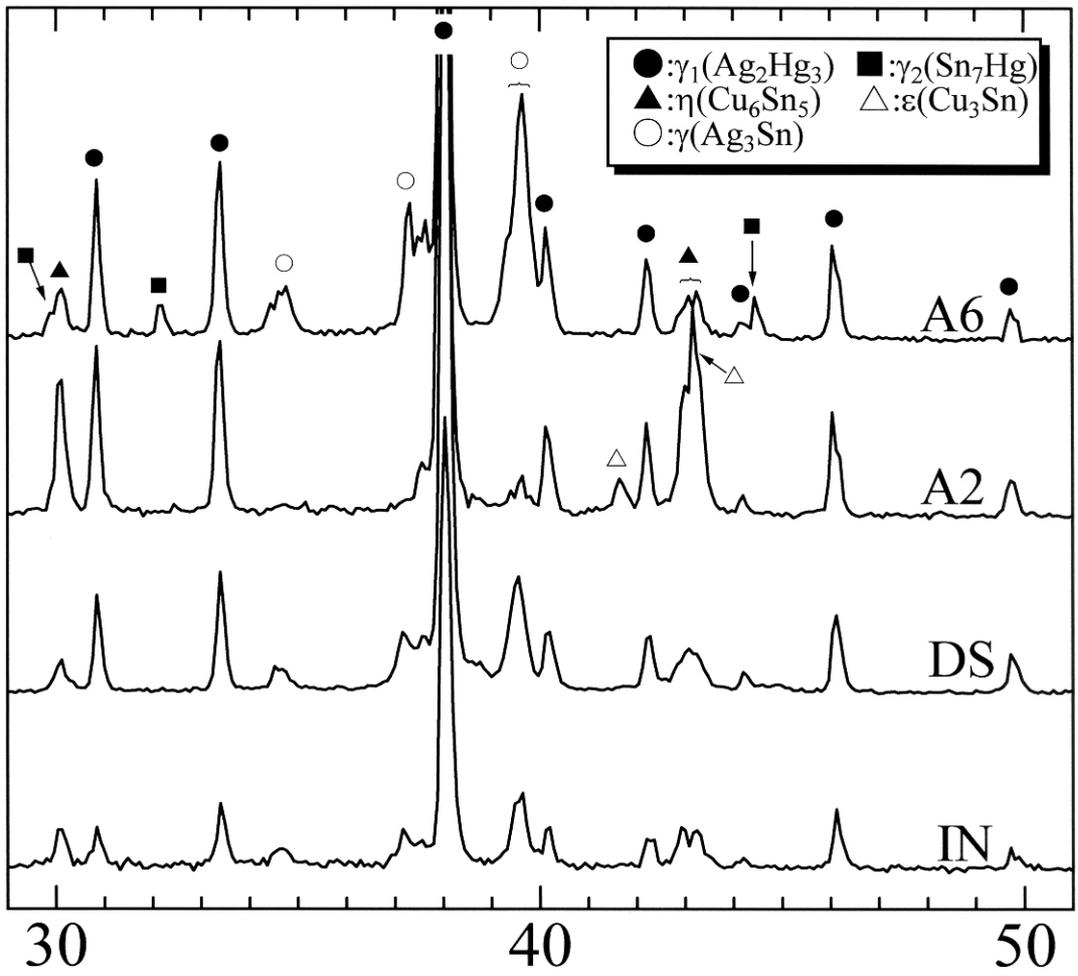


Fig.4

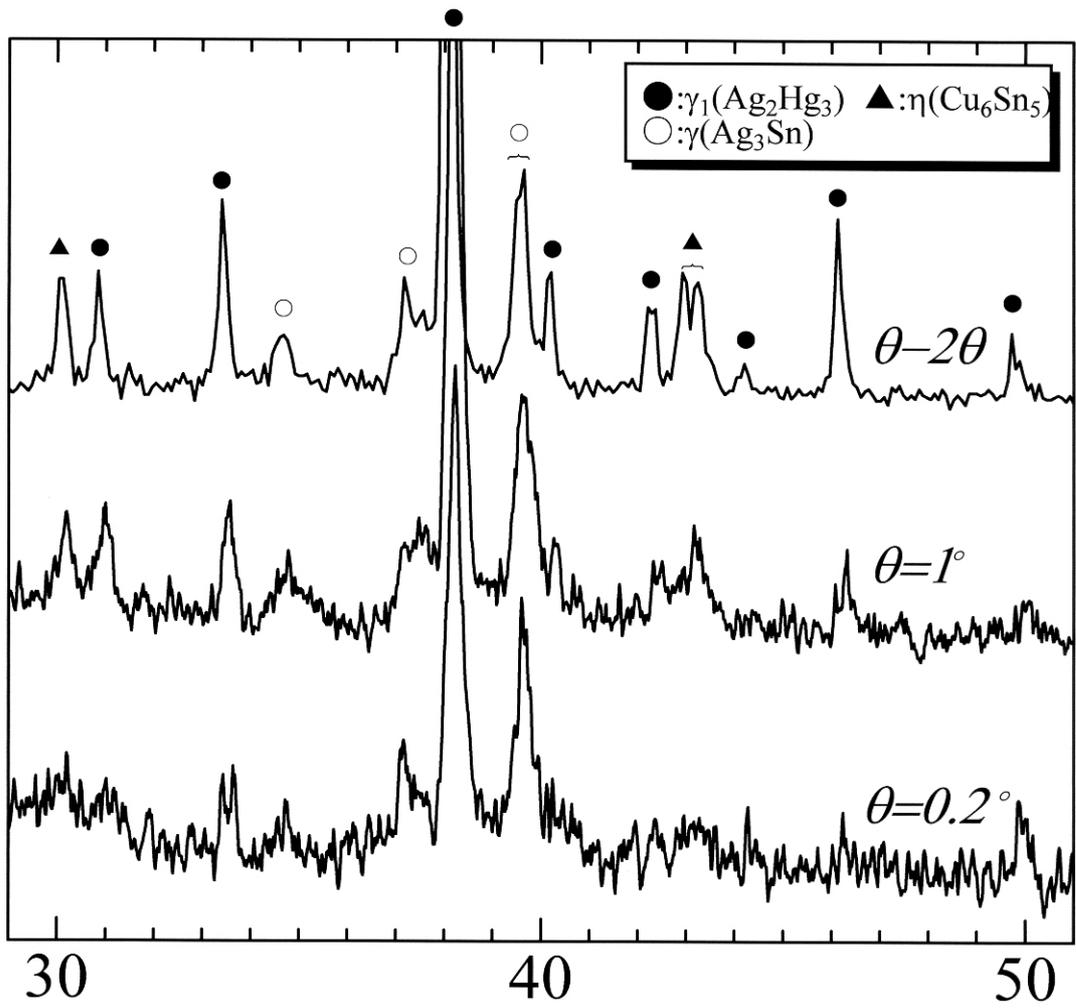


Fig.5

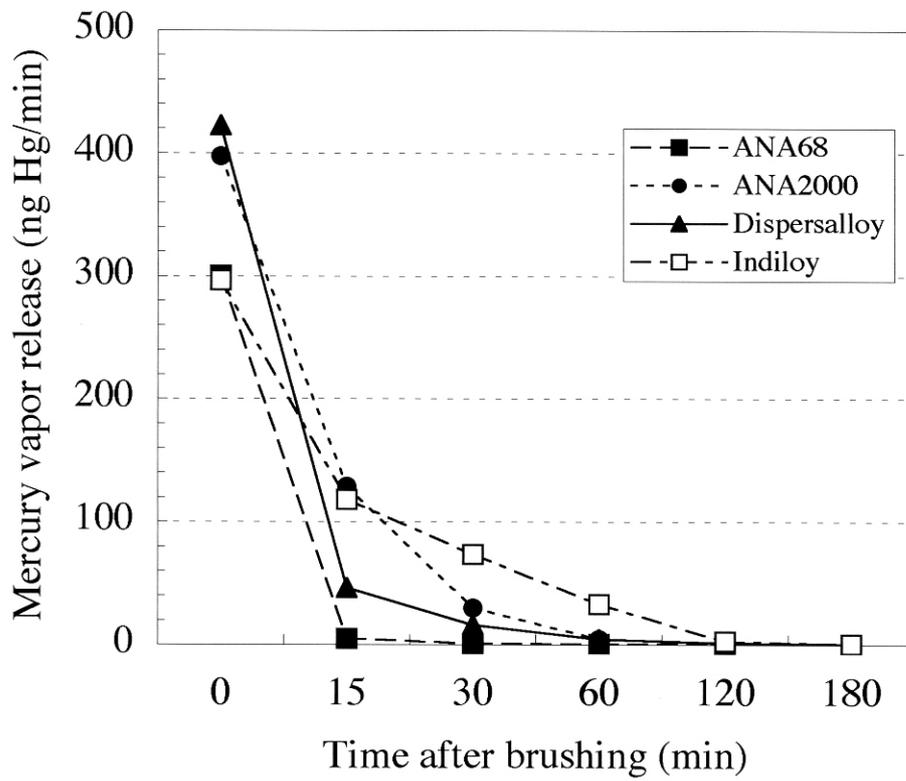


Fig.6