Fundamental Study on Porcelain-Fused-to-Metal High-temperature Oxidation Behavior of Sn and In in Gold Alloys under Various Oxygen Partial Pressures

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The oxidation behavior of gold alloys containing small amounts of Sn and/or In was investigated in order to analyze adherence mechanisms in the porcelain-fused-to-metal (PFM) system. Experimental gold alloys (99.5wt% Au-0.5wt% Sn, 99.5wt% Au-0.5wt% In and 99.0wt% Au-0.5wt% Sn-0.5wt% In) were oxidized over an oxygen partial pressure (P_{O_2}) range from 0.016 to 0.8atm and a temperature range from 700 to 900°C, and a commercial PFM alloy (Ceramic Gold) was done at $P_{O_2} \leq 0.2$ atm.

Both the concentrated amounts of In in Au-In alloy and of Sn and In in Au-Sn-In alloy on each alloy surface after oxidation increased at $P_{O_2} < 0.2$ atm by the transition from internal to external oxidation, and nodules consisting of alloy matrix were observed on the oxidized surface. The oxidation behavior of the commercial PFM alloy was similar to that of Au-Sn-In alloy. Indium in the alloy determined the oxidation behavior and surface characteristics.

Key words: Porcelain-fused-to-metal, High-temperature oxidation, Indium

I. INTRODUCTION

Porcelain-fused-to-metal (PFM) restorations have been extensively used in practical dentistry because of their strength, chemical stability and esthetics. A necessary condition for PFM systems is that the alloy surface adheres securely to the porcelain. There have been many reports¹⁻⁴⁾ in the ceramic industry on the adherence between metal and ceramics. Also in dentistry, many researcher⁵⁻²⁴⁾ have reported the adherence mechanisms, the strength of adherence and the reactions at the interface in PFM systems. It has been clarified that additive base metal components such as Sn and In are important for the adherence of precious PFM alloys. The detail adherence mechanism, however, is still unknown because the interface between the PFM alloy and dental porcelain is a very thin reactive layer and the alloys and porcelains have complex compositions.

Some researchers^{14,17,19-24)} have examined the adherence mechanism with respect to high-temperature oxidation of PFM alloys. Ohno et al.¹⁹⁻²²⁾ reported in detail the surface metal oxides and the high-temperature oxidation of gold alloys. In these studies, preferential oxidation occurred when the alloys were oxidized, and an internal oxide layer was present in the alloys containing small amounts of Sn and In¹³⁾, Fe and Sn²¹⁾, and In and Fe²²⁾.

This study investigated the high-temperature oxidation behavior of Sn and In in gold alloys at an early stage in order to analyze the adherence mechanism between metal and porcelain. Preoxidation treatment (a degassing treatment) of PFM alloy and/or a porcelain firing are usually carried out under reduced air pressure, but there are few reports^{15,16,18)}

on the oxidized surface of PFM alloy when the atmosphere in a furnace varies. In this study, the oxidation behavior of Sn and In was examined at various oxygen partial pressures (P_{O_2}). Binary and ternary experimental alloys were used to clarify the oxidation behavior of Sn and In. A commercial PFM alloy was also adopted and was compared with the experimental alloys.

II. MATERIALS AND METHODS

II.1. Preparation of alloys used

II.1.1. Experimental alloys

Three kinds of experimental alloys were prepared using Au, Sn and In with purities greater than 99.9wt%. (Table 1) Pure metals were sealed with argon gas in quartz glass tubes after weighing to give a 10 g ingot of each alloy and were melted at 1150°C in an electric furnace. After quenching, the ingots sealed in the tubes were kept in the furnace at 700°C for 3 hours to homogenize.

II.1.2. A commercial PFM alloy

Ceramic Gold, designated alloy C, was adopted as a commercial PFM alloy. The composition of alloy C in wt% is shown in Table 2. Delivered ingots of alloy C were sealed with argon gas in a quartz glass tube, and were melted in the furnace at 1250°C. After quenching, the ingot sealed in the tube was homogenized in a manner similar to that of experimental alloys.

II.1.3. Preparation of specimens

After each alloy was rolled out to 0.5 mm in thickness, specimens were trimmed in the size of 5 mm×5 mm×0.5 mm. They were sealed again with argon gas in the quartz tubes, and were heated at 700°C for 3 hours to remove the strains caused by rolling.

Specimens were polished metallographically with emery papers and alumina powder with water before oxidation.

Table 1 Materials used

Experimental Alloy	code
99.5wt% Au-0.5wt% Sn	Au-Sn
99.5wt% Au-0.5wt% In	Au-In
99.0wt% Au-0.5wt% Sn-0.5wt% In	Au-Sn-In
Commercial Alloy	
Ceramic Gold ^ℓ	alloy C

ℓ: Shofu Inc., Kyoto, Lot. 098315

Table 2 Composition of alloy C in wt%

Element	Au	Pd	Pt	Ag	In	Sn	Fe
wt % [§]	86.9	6.6	3.4	0.9	1.0	0.9	0.3

§: analyzed by EPMA with the ZAF method

II.2. Experimental methods

II.2.1. Oxidation of alloys

The oxidation conditions are shown in Table 3. P_{O_2} was controlled by reducing the pressure of the atmosphere in the furnace with a rotary pump at $P_{O_2} < 0.2$ atm, based on the assumption that P_{O_2} of the atmosphere is 0.2 atm. At $P_{O_2} \geq 0.2$ atm, it was regulated by mixing pure oxygen and nitrogen gas and the total flow rate of the mixed gas through furnace was 1000 cm³/min. The oxidized specimens were cooled in pure nitrogen gas. Fig. 1 shows the setup of the oxidation furnace in this experiment.

II.2.2. Observation and analysis of oxidized specimens

The oxidized specimens were observed by secondary electron images (SEI) with a scanning electron microscopy* and back scattered electron images (BEI) with an electron probe

Table 3 Oxidation conditions

Experimental Alloy	
Temperature (°C)	700–900
Oxygen partial pressure (atm)	0.016–0.8
Oxidation time (min)	10
Commercial Alloy	
Temperature (°C)	700, 900
Oxygen partial pressure (atm)	0.016–0.2
Oxidation time (min)	10

Figure 1 Setup of oxidation furnace.

(RP: rotary pump, G: vacuum gage, R: recorder, J: cold junction, C: mixing chamber, M: molecular sieves, Fm: flow meter, L: leak, S: specimen holder, P: thermocouple, Q: quartz glass tube, TC: digital temperature controller, F1: furnace (heating position), F2: furnace (cooling position))

*: JSM-T20, JEOL, Tokyo.

Table 4 Technical conditions for analysis

EPMA	Acc. voltage	20 kV
	Abs. current	15 nA
	Beam area	80 $\mu\text{m} \times 80 \mu\text{m}$
	Int. time	10 sec $\times$ 3
	Characteristic X-ray	AuL α , SnL α , InL α , OK α
ESCA	X-ray source	MgK α
	Tube voltage	7 kV
	Tube current	50 mA

microanalyzer (EPMA).**

The oxidation behavior of Sn and In concentrated on the specimen surface portion was measured by the detection of their characteristic X-rays using an area analysis of EPMA^{*}. Their characteristic X-ray intensities were compared with that of each standard sample with a purity greater than 99.9wt%. Five specimens were used in an oxidation condition, and the area analysis was performed at 3 positions in each specimen. That is, the mean relative intensity and standard deviation were calculated from 15 measured values.

Cross-sections perpendicular to the oxidized surface were also observed. Carbon film with a thickness from 30 to 40 nm was vaporized on the oxidized specimen prior to observation and measurement of characteristic X-rays.

The oxidation behavior in the top layer of the surface of the specimen was investigated by a X-ray photoelectron spectroscopy (Electron Spectroscopy for Chemical Analysis, ESCA).^{##} Table 4 shows the technical conditions for analysis by EPMA and ESCA.

It is necessary to clearly distinguish the surface in ESCA from that in EPMA. In the surface analysis by ESCA, the escape depth of photoelectrons in this experiment condition is nearly 1 nm.²⁵⁾ On the other hand, those of characteristic X-rays measured by EPMA generally range from 0.1 to 5 μm .²⁶⁾ The characteristic X-rays, therefore, include the X-rays from alloy matrix beneath the surface oxide layer in this experiment.

III. RESULTS

III.1. Oxidation behavior of experimental alloys

III.1.1. Observation of experimental alloy surface

Figures 2 to 4 show SEIs of oxidized surfaces of experimental alloys. Surfaces of Au-Sn were covered uniformly with the oxide layer, and folds on the surface were enlarged with increasing Po_2 . (Fig. 2) In Au-In, polygonal nodules appeared on the oxidized surface. (Fig. 3) These nodules were enlarged and/or partially fused to each other with increasing Po_2 and temperature. Surfaces of Au-Sn-In were analogous to those of Au-In. (Fig. 4)

** : JCXA-733, JEOL, Tokyo.

* : EMX-2A, SHIMADZU, Kyoto.

: JESCA-4, JEOL, Tokyo.

Figure 2 Secondary electron images of oxidized Au-Sn alloy.
(upper row: oxidation at 700°C, a, b and c are P_{O_2} —0.016, 0.2 and 0.8 atm, respectively., lower row: oxidation at 900°C, d, e and f are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively.)

Figure 3 Secondary electron images of oxidized Au-In alloy.
(upper row: oxidation at 700°C, a, b and c are P_{O_2} =0.016, 0.2 and 0.8 atm respectively., lower row: oxidation at 900°C, d, e and f are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively.)

Figure 4 Secondary electron images of oxidized Au-Sn-In alloy.
(upper row: oxidation at 700°C, a, b and c are $P_{O_2}=0.016$, 0.2 and 0.8 atm, respectively., lower row: oxidation at 900°C, d, e and f are $P_{O_2}=0.016$, 0.2 and 0.8 atm, respectively.)

Figures 5 to 7 show BEIs of oxidized surfaces of experimental alloys. In the same BEI photograph, an average atomic number of the light region is higher than that of the dark region, since the back scattering coefficient of a high atomic number element is larger

Figure 5 Back scattered electron images of oxidized Au-Sn alloy.
(upper row: oxidation at 700°C, a, b and c are $P_{O_2}=0.016$, 0.2 and 0.8 atm, respectively., lower row: oxidation at 900°C, d, e and f are $P_{O_2}=0.016$, 0.2 and 0.8 atm, respectively.)

Figure 6 Back scattered electron images of oxidized Au-In alloy. (upper row: oxidation at 700°C, a, b and c are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively., lower row: oxidation at 900°C, d, e and f are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively.)

Figure 7 Back scattered electron images of oxidized Au-Sn-In alloy. (upper row: oxidation at 700°C, a, b and c are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively., lower row: oxidation at 900°C, d, e and f are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively.)

than that of a low atomic number element.²⁷⁾ Oxide-rich regions, therefore, appear as dark regions in the BEI photograph. Numerous insular regions were present in the BEIs of Au-Sn. (Fig. 5) These regions conformed to convex regions on the oxidized surface ob-

served in the SEIs. In both Au-In and Au-Sn-In, light nodules appeared on the surface and many dark dots considered as oxides were dispersed on the surface. (Figs. 6 and 7) Results of line analysis by EPMA showed that the characteristic X-ray intensity of Au in-

Figure 8 Oxidation at grain boundaries (Au-Sn-In alloy, 700°C, $P_{O_2}=0.2$ atm).
 a: Secondary electron image of surface grain boundaries
 b: Back scattered electron image and characteristic X-ray images at grain boundaries (The grain boundaries in b differ from those in a.)

Figure 9 Relative intensity of Sn in oxidized Au-Sn alloy.

creased largely at a polygonal nodule on the oxidized surface of Au-Sn-In, but the intensities of Sn, In and O decreased.

Figures 8a and 8b show respectively the SEI of a grain boundary region and the concentration of Sn and In at grain boundaries in Au-Sn-In at 700°C and $P_{O_2}=0.2$ atm.

III.1.2. Relative intensities of Sn and In

Figures 9 to 11 show relative intensities of Sn and In concentrated on the alloy surface

Figure 10 Relative intensity of In in oxidized Au-In alloy.

Figure 11 Relative intensities of Sn and In in oxidized Au-Sn-In alloy.

portion over the P_{O_2} range from 0.016 to 0.8 atm. The relative intensity of Sn in Au-Sn tended to rather decrease with decreasing P_{O_2} . It increased significantly with rising temperature. (Fig. 9) The relative intensity of In in Au-In tended to decrease slightly with increasing P_{O_2} at $P_{O_2} \geq 0.2$ atm, however, it increased markedly with decreasing P_{O_2} at $P_{O_2} < 0.2$ atm. (Fig. 10) The relative intensities of Sn and In in Au-Sn-In increased with the decrease of P_{O_2} , and they markedly increased at $P_{O_2} < 0.2$ atm in a manner similar to that of Au-In. (Fig. 11) There was a significant difference between the behavior of Sn in Au-Sn and that in Au-Sn-In.

III.1.3. Observation of cross-sections of specimens

Figure 12 shows cross-sections of oxidized experimental alloys by BEI. The oxide layer on Au-Sn was not visualized clearly so that it appeared thin in this experiment. In both Au-In and Au-Sn-In, the oxide-rich regions (dark regions in photograph) penetrated the alloy matrices with the increase of P_{O_2} . In these alloys, the internal oxidation occurred obviously at high P_{O_2} . The nodules were not present on the oxide layer, but they were connected with the alloy matrix under the oxide layer.

III.2. Oxidation behavior of alloy C

III.2.1. Observation of alloy C surface

Figure 12 Cross-sections of oxidized experimental alloys (Back scattered electron images at 900°C).
(upper row: Au-Sn alloy, U1, U2 and U3 are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively., middle row: Au-In alloy, M1, M2 and M3 are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively., lower row: Au-Sn-In alloy, L1, L2 and L3 are P_{O_2} =0.016, 0.2 and 0.8 atm, respectively.)

Figures 13 and 14 respectively show SEIs and BEIs of oxidized alloy C. The nodules that were observed in Au-In and Au-Sn-In also appeared on the oxidized surface of alloy C. The oxidized surface became coarse and the number of nodules decreased with the decrease of P_{O_2} . Dark network patterns resembling grain boundaries appeared on the alloy.

When characteristic X-ray intensities of composition elements of alloy C were measured on a nodule, grain boundaries and a plain surface region, Au and Pt increased on the nodule, Sn, In and Fe increased on the grain boundaries and Pd and Ag increased on the plain region.

III.2.2. Relative intensities of Sn, In and Fe of alloy C

Figure 13 Secondary electron images of oxidized alloy C.

- a: at 700°C and $P_{O_2}=0.016$ atm,
- b: at 700°C and $P_{O_2}=0.2$ atm,
- c1: at 900°C and $P_{O_2}=0.016$ atm,
- d1: at 900°C and $P_{O_2}=0.2$ atm.
- c2 and d2 are respectively high magnification images of c1 and d1.

Figure 14 Back scattered electron images of oxidized alloy C.
a: at 700°C and $P_{O_2}=0.016$ atm, b: at 700°C and $P_{O_2}=0.2$ atm,
c: at 900°C and $P_{O_2}=0.016$ atm, d: at 900°C and $P_{O_2}=0.2$ atm.

Figure 15 Relative intensities of Sn, In and Fe in oxidized alloy C.

Figure 15 shows relative intensities of Sn, In and Fe of the oxidized alloy C. The intensities of Sn and In in alloy C were lower than those in experimental alloys, although alloy C contained larger amounts of Sn and In than experimental alloys. The relative intensity of In increased, and that of Sn slightly increased, particularly at 900°C, with decreasing P_{O_2} , but Fe was not affected by P_{O_2} . The behavior of Sn and In in alloy C were generally similar to that in Au-Sn-In.

III.2.3. Cross-sections of alloy C

Figure 16 shows BEIs of cross-section of oxidized alloy C. The internal oxides (dark regions) increased with the increase of P_{O_2} and dark networks resembling grain boundaries appeared in the alloy matrix. These networks became thick at 900°C. The cross-sections of alloy C were similar to those of Au-In or Au-Sn-In, but the internal oxides were still clearly present in the alloy matrix at $P_{O_2}=0.016$ atm.

III.3. Surface analysis by ESCA

III.3.1. Binding energies of Sn, In and Au

Binding energies of Sn3d5/2, In3d5/2 and Au4f7/2 photoelectrons, which have the highest photoionization cross-section²⁸⁾, were measured by ESCA and were compared with those of SnO₂ and In₂O₃ standard powders with purities greater than 99.9wt%. (Fig. 17)

Figure 16 Cross-sections of oxidized alloy C (Back scattered images).

a: at 700°C and $P_{O_2}=0.016$ atm,

b: at 700°C and $P_{O_2}=0.2$ atm,

c: at 900°C and $P_{O_2}=0.016$ atm,

d: at 900°C and $P_{O_2}=0.2$ atm.

Figure 17 Peak positions of Sn3d5/2, In3d5/2 and Au4f7/2 by ESCA.

Figure 18 ESCA peak intensity ratios (Au/In) of Au-In and Au-Sn-In alloys.

The top layer of oxidized Au-Sn consisted of SnO_2 . In_2O_3 and Au were identified in the top layer of oxidized Au-In, and SnO_2 , In_2O_3 and Au were noted in the top layer of oxidized Au-Sn-In. There were no significant shifts of binding energies in each element, when Po_2 and temperature varied. The $\text{In}3d_{5/2}$ lines of In_2O_3 , which were formed by oxidation, were more stable than the $\text{Sn}3d_{5/2}$ lines of SnO_2 formed by oxidation. The presence of $\text{Au}4f_{7/2}$ lines on both Au-In and Au-Sn-In suggested that the alloy matrix was partially exposed even after oxidation. This phenomenon could be related to the presence of nodules observed in SEI and BEI of Au-In and Au-Sn-In.

Before oxidation, Au, Pd, O (absorbed) and C were detected on alloy C by ESCA. After oxidation, Sn, In, O, Pd, Au and C were identified on the surface of alloy C, but Fe, Ag and Pt were not. The oxides in the top layer of the surface were SnO_2 and In_2O_3 . Identified Pd was not oxidized, because $\text{Pd}3d_{3/2}$ line after oxidation agreed with that of pure Pd plate (99.99wt%) which removed the surface oxides.

III.3.2. Peak intensity ratio between Au and In

ESCA data indicated that Au was present in the top layer of the oxidized surface of the alloys containing In. The peak intensity ratio between Au and In (Au/In) was adopted in this experiment in order to investigate the relation between the amount of Au on the oxidized surface and Po_2 .

Figures 18 and 19 respectively show the Au/In ratio in experimental alloys containing

Figure 19 ESCA peak intensity ratios (Au/In) of alloy C.

In and alloy C.

ESCA peak intensity was expressed by the following equation:²⁹⁾

$$I_i = F \cdot S \cdot N_i \cdot \sigma_i \cdot \lambda_i \cdot T_i [1 - \exp(-d/\lambda_i)] \quad (3.1)$$

where I_i is the intensity of i -photoelectrons of a given energy, F is the X-ray photon flux, S is the fraction of electrons detected by the spectrometer, N_i is the number of atoms per cubic centimeter emitting i -photoelectrons, σ_i is the atomic cross-section for i -level ionization, λ_i is the mean free pass length of i -photoelectrons, T_i is the transmission factor for i -photoelectrons through the surface contaminants and d is the thickness from which i -photoelectrons emerged. The relative intensity (I_i/I_j) for two different photoelectrons peak from the same sample is,

$$\frac{I_i}{I_j} = \frac{N_i}{N_j} \cdot \frac{\sigma_i}{\sigma_j} \cdot \frac{\lambda_i}{\lambda_j} \cdot \frac{T_i}{T_j} \frac{[1 - \exp(-d/\lambda_i)]}{[1 - \exp(-d/\lambda_j)]} \quad (3.2)$$

In this experiment, binding energies of the peak in each element did not significantly shift with varying Po_2 and temperature. When it is assumed that the contamination and surface roughness are constant, I_i/I_j is,

$$\frac{I_i}{I_j} = \frac{N_i}{N_j} \cdot \text{Constant} \quad (3.3)$$

Since σ , λ , T and d are not affected by Po_2 when the specimens were oxidized, Figs. 18 and 19 show the changes of the existence ratio of Au as a function of Po_2 . Po_2 affected particularly the ratio in Au-In. The ratio in alloy C decreased with decreasing Po_2 and temperature. The changes of the ratio are related with the number of Au-rich nodules observed in SEI and BEI.

IV. DISCUSSION

IV.1. Oxidation of experimental alloys

Surface oxides on experimental alloys could not be identified by X-ray diffraction analysis since oxide layers were very thin; thus, they were analyzed by ESCA. Surface oxides on Au-Sn and Au-In were SnO_2 and In_2O_3 , respectively. Both were formed on Au-Sn-In.

The concentration of Sn on the surface portion by oxidation varied with increasing temperature rather than Po_2 . The oxide layers on metal are of two types when the metal is oxidized at high temperature, a p-type and an n-type conducting protective oxide layer.³⁰⁾ It is generally agreed that SnO_2 in its undoped form is an n-type, wide-bandgap semiconductor.³¹⁾ The determination process of growth of the n-type oxide layer is a diffusion process of metal ion (Sn ions in this experiment) and electrons from metal/oxide to oxide/gas interface.³⁰⁾ The electrical conductivity of SnO_2 semiconductor was found to vary as $\text{Po}_2^{-1/a}$ with $a=6.5$ at high temperature and it rose markedly with rising temperature than with increasing Po_2 .³²⁾ In the case of oxidation of Au-Sn, the amount of Sn concentrated on the surface was affected by the change of temperature rather than that of Po_2 .

The relative intensity of In in Au-In increased at $P_{O_2} < 0.2$ atm, particularly at 900°C. Oxide particles and oxide networks were found in the alloy matrix. Internal oxidation is known to occur in alloys containing In.^{19, 22 33-35} Rapp^{34, 35} reported the transition from internal to external oxidation with changing P_{O_2} and content of In. Both BEIs of cross-section and measurements of relative intensity of In suggested the transition from internal to external oxidation in Au-In and that the transition point exists at $P_{O_2} < 0.2$ atm.

The internal oxidation is caused under the condition that a diffusion velocity of oxygen from surface to inner part of alloy is larger than that of metal atom (In in this experiment) from inner part to surface of alloy. Hence, In atoms unite with oxygen atoms at the inner part of alloy and then the internal oxide particles are formed there. However, the penetration of oxygen into the alloy decreases with reducing P_{O_2} , and the amount of In atoms diffusing to the surface increases relatively, and the oxides were formed near the surface. The exact transition point could not be determined in this experiment.

The oxidation behavior of Au-Sn-In was similar to that of Au-In. Both Sn and In in the alloy were oxidized and formed SnO_2 and In_2O_3 . Values of Gibbs standard energy of formation (ΔG) for SnO_2 are -150.54 kcal/mol at 700°C, -153.347 kcal/mol at 800°C and -156.423 kcal/mol at 900°C.³⁶ The values of ΔG for In_2O_3 are -244.588 kcal/mol at 700°C, -249.721 kcal/mol at 800°C and -255.234 kcal/mol at 900°C.³⁷ The values for In_2O_3 are smaller than for SnO_2 at each temperature. This difference indicates that In_2O_3 is formed easily in comparison with SnO_2 and that the formation of In_2O_3 is predominant at high temperature. The oxidation behavior of Au-Sn-In could be similar to that of Au-In because of the predominant oxidation reaction of In_2O_3 and its formation might inhibit the formation of SnO_2 on the surface.

A non-stoichiometric In_2O_3 was also the n-type semiconductor as SnO_2 and the interstitial ions were probably the predominant defects.³⁸ The oxidation behavior of Au-Sn differed from that of Au-In or Au-Sn-In, in spite of the similarity between SnO_2 and In_2O_3 in conductive property. It is necessary to further clarify this difference by measuring diffusion coefficients and electrical conductivities of oxide layers.

In the oxidized surface of Au-Sn-In at 700°C, Sn and In concentrated on the grain boundaries. (Fig. 8) Additive base metal elements in PFM alloy were oxidized particularly at grain boundaries.^{1, 6, 7} It is a widely accepted theory that self-diffusion in face-centered cubic metals occurs by a lattice vacancy mechanism.³⁹ There, however, are some short-circuit diffusion mechanisms that cannot be explained uniformly by the lattice vacancy mechanism in solid solution. One of them is grain boundary diffusion.⁴⁰ The grain boundary diffusion occurs easily in comparison with the lattice vacancy diffusion.⁴¹ Hoffman and Turnbull³⁹ reported that the grain boundary diffusion was predominant at low temperature but lattice diffusion was predominant at high temperature. In alloys containing a small amount of In, additive base metal elements would be transported easily through the grain boundaries from the inner part to surface, since the external oxide layers were not uniformly formed.

The nodules were found on the oxidized surface of Au-In and Au-Sn-In. Mackert et al.²³ found nodules on the oxidized surface of a Pd-Ag alloy containing Sn and In. They concluded that these nodules resulted from the "Nabarro-Herring creep" mechanism caused

by the internal oxidation. When oxides such as SnO_2 and In_2O_3 are formed in the alloy matrix, the molar volume of alloy matrix increases because the molar volume of oxide is larger than that of unoxidized alloy matrix. Nabarro-Herring creep (a diffusional creep) comes into existence at very high temperatures and very low stresses.⁴²⁾ The formation of nodules in this experiment could be through the mechanism above. It would contribute to the presence of $\text{Au}4f7/2$ lines on the oxidized surface of Au-In and Au-Sn-In. The nodules were not analyzed in detail, however, Murakami et al.²⁴⁾ reported, using a fine focus X-ray generator method, that Au classified as Miller's indices 111, 200, 311 and 222 was identified on the PFM alloys after the preoxidation treatment. The above finding suggests that these diffraction patterns of Au are generated from the nodules.

IV.2. Oxidation of a commercial PFM alloy

The oxidation behavior of alloy C was similar to that of Au-Sn-In or Au-In. It is suggested that In, one of the composition elements of alloy C, determines the type of oxidation and the surface characteristics. The internal oxide layers were formed after 1 hour at 1000°C in several commercial PFM alloys²⁰⁾ and in gold alloys for porcelain.^{19,21,22)} In this experiment the internal oxide layers were formed in 10 minutes. The amount of base metal elements in alloy C were larger than in experimental alloys, thus, the internal oxides in alloy C were also larger than those in experimental alloys. Therefore, the larger stresses yield in the alloy matrix and the large amount of nodules could be produced on the surface in a comparison with experimental alloys.

The alloy matrix of alloy C contained a large amount of internal oxides at $\text{Po}_2=0.016$ atm. Wagner³³⁾ theoretically analyzed the internal oxidation phenomenon. When the oxide, MO_x , is formed by the reaction between the metal composed alloy, M, and the oxygen diffusing from the surface to inner part of alloy, O, the condition that the internal oxidation occurs is,

$$N_M^0 < [(\pi g^*/2\nu) \cdot N_O^S \cdot (D_O V)/(D_M V_{OX})]^{1/2} \quad (4.1)$$

N_M^0 indicates the bulk concentration of M in the alloy, g^* is the critical volume ratio of oxide when the type of oxidation transits from internal to external, N_O^S is the molar fraction of oxygen on the alloy surface, D_O and D_M respectively are the diffusion coefficients of oxygen and metal M, and V and V_{OX} are the molar volume of the alloy and the oxide, respectively. On the other hand, the condition of external oxidation is,

$$N_M^0 > [(\pi g^*/2\nu) \cdot N_O^S \cdot (D_O V)/(D_M V_{OX})]^{1/2} \quad (4.2)$$

Equation (4.1) and (4.2) indicate that increasing N_M^0 and/or reducing N_O^S are necessary for a complete external oxidation. That is, the complete external oxide layer on alloy C is established under the condition that Po_2 decreases more than experimental conditions and/or that base metal components add to alloy C in large quantities.

IV.3. Oxidized surface and porcelain fusing

The type of oxidation of gold alloys containing a small amount of In is converted from internal to external with the decrease of Po_2 . The amounts of surface oxides on these alloys were affected by Po_2 , particularly at high temperature. The air pressure in a furnace is usually reduced in the preoxidation treatment before a porcelain firing. As the reduc-

tion of air pressure in the furnace decreases the P_{O_2} , the preoxidation treatment under reduced pressure should promote the formation of surface oxides on the alloys containing a small amount of In. Many dental porcelain manufacturers recommend reducing the pressure in the furnace during porcelain firing in order to prevent bubbles in porcelain. This procedure also should accelerate the formation of oxides at the interface between alloy and porcelain.

The adherence mechanisms between PFM alloy and porcelain consist of (1) mechanical bonding forces, (2) Van der Waals forces, (3) chemical bonding forces, and (4) compressive bonding forces.⁵⁾ Regardless of the mechanism, the affinity between alloy and porcelain is very important, especially for a good wetting (a high work of adhesion).¹⁻³⁾ Some investigators^{1,2,6,8-10)} emphasized that the presence of Sn or its oxides at the interface play an important role in good adherence. Nally et al.¹¹⁾ and Tsutsui¹²⁾ reported that the presence of In or In_2O_3 at the interface made a good adherence. Ohno et al.¹³⁾ found, using ESCA, that a thin oxide layer of In on the Au-In alloy plays an indispensable role in making a strong adherence of the alloy to silica glass. In either case, the reduction of P_{O_2} during preoxidation treatment and/or porcelain firing actively forms the oxides such as SnO_2 and/or In_2O_3 at the interface, if the alloy contains a small amount of In and then dental porcelain components would contact positively with the surface oxides on alloy.

Oxidized alloy matrices of Au-In, Au-Sn-In and alloy C at low P_{O_2} showed corroded aspects and oxidized grain boundaries. (Figs. 12 and 16) Espevik et al.¹⁴⁾ reported that the surface oxides and oxides at grain boundaries probably contributed to the good adherence. It is expected that a complex consisting of interdiffusing porcelain and surface oxides is interlocked in alloy matrix with the corroded aspect.

The surface roughness is enlarged by the nodules, but the formation of nodules reduces the existence ratio of oxides on the surface. It is still unknown how nodules contribute to the adherence. The contact area between porcelain and surface oxide is reduced by the nodules, but, the nodules may be one of the factors in mechanical and compressive bonding forces.

As one of base metal components Fe was added to alloy C but it could not be identified in the top layer of surface after oxidation. The presence of Fe did not participate in the adherence to porcelain¹²⁾ and the purpose of adding Fe to gold alloys was to increase the sag-resistance of alloy because Fe produced a FePt phase in alloy matrix.⁴³⁾ In this experiment, the oxidation behavior of Fe in alloy C did not affect the formation of surface oxides.

V. CONCLUSION

The oxidation behavior of experimental gold alloys containing small amounts of Sn and/or In was investigated and compared with that of a commercial PFM alloy. The following results were obtained:

(1) When Au-Sn was oxidized, the amount of Sn concentrated on surface was affected by temperature rather than P_{O_2} .

(2) The amount of In in Au-In and amounts of Sn and In in Au-Sn-In concentrated on surface increased at $P_{O_2} < 0.2$ atm and at higher temperature.

(3) The internal oxide layers were formed in both Au-In and Au-Sn-In alloy matrices by addition of In. The transition from internal to external oxidation occurred at $P_{O_2} < 0.2$ atm and caused a relative increase of surface oxides.

(4) The nodules consisting of alloy matrix were found on the oxidized surface of both Au-In and Au-Sn-In. A large amount of nodules at high P_{O_2} suggested that they are derived from internal oxidation.

(5) The oxidation behavior of alloy C was similar to that of Au-Sn-In and a small amount of In in alloy C determined the type of oxidation and oxidized surface characteristics.

It is concluded that the procedures under reduced air pressure such as preoxidation treatment and porcelain firing promote the formation of surface oxides and could promote positive contacts between porcelain and surface oxides on alloy, if PFM alloy contains a small amount of In.

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金属焼付ポーセレンに関する基礎的研究 各種酸素分圧下における金合金中のスズ及び インジウム的高温酸化挙動

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金属焼付ポーセレンの金属と陶材との接着機構を解析するための基礎的研究として、スズ或いはインジウムを少量含んだ金合金の酸化挙動に関する実験を行った。実験には三種の実験合金 (99.5 wt% Au-0.5 wt% Sn, 99.5 wt% Au-0.5 wt% In, 99.0 wt% Au-0.5 wt% Sn-0.5 wt% In) を作製し、酸素分圧 0.016~0.8 atm, 温度 700℃~900℃の範囲で酸化挙動を観察した。又、市販の焼付用合金 (セラミックゴールド) についても酸素分圧 0.2 atm 以下の酸化挙動について実験を行った。

Au-In 合金中のインジウム及び Au-Sn-In 合金中のスズ、インジウムの酸化後の表層部付近への集積量は酸素分圧 0.2 atm 以下では増加した。これは酸化様式が内部酸化傾向から外部酸化傾向に転換したためと考えられた。そしてこれらの合金の酸化表面には、合金マトリックスからなるノジュールが観察された。市販焼付用合金の酸化挙動は Au-Sn-In 合金の場合と類似していた。この合金では、インジウムが、合金の酸化挙動と表面性状に大きな影響を与えるものと考えられた。

レジン系セメントの接着性について

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歯質や金属と化学的に接着し、従来のセメントに比較して、接着力はもとより耐溶解性、耐酸性に優れ、さらに被膜厚さも改良されたレジン系セメントが開発された。

2種類の接着性レジン系セメント (Bis-GMA 系コンポジットレジンタイプ, 4-META タイプ) を用いて、金銀パラジウム合金の接着強さと2級インレー合着後の辺縁封鎖性をサーマルサイクリング後の色素浸透度により、従来のセメント (グラスアイオノマーセメント, リ

ン酸亜鉛セメント) と比較検討した。

従来のセメントに比べ、2種のレジン系セメントは著しく高い接着強さを示し、サーマルサイクリング後も同様の傾向を示した。

接着性セメントで合着したインレーの咬合面部および歯頸部のいずれにおいても、色素浸透度はエナメル質内に限局していた。リン酸セメントでは、窩底および歯髄腔まで浸透が認められ、グラスアイオノマーはその中間であった。

高パラジウム含有合金 “アルバボンド E” の 表面処理が接着挙動に及ぼす影響に関する研究

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高パラジウム含有合金 “アルバボンド E” を各種接着性レジンで接着する場合の合金の表面処理法について検討した。被着面は鏡面研磨、アルミナサンドブラスト、

電解エッチング, Sn 電析, シリコーター処理および400℃1回加熱処理とし、接着材は 4-META-MMA-TBB 系レジンとパナビア EX を使用した。比較のため、パラ