The Adhesion Mechanism of Dental Adhesive Resin to the Alloy

— Relationship between Co-Cr Alloy Surface Structure Analyzed by ESCA and Bonding Strength of Adhesive Resin —

Hiroki OHNO, Yoshima ARAKI, and Masahiro SAGARA

Department of Dental Materials Science, School of Dentistry, Higashi-Nippon-Gakuen University, Ishikari-Tobetsu, Hokkaido, Japan

Received on March 12, 1986

A dental adhesive resin containing 4-META was bonded to three different surface states, an as-polished surface and two oxidized surfaces, of a 70 mass % Co-Cr alloy. The surface structure of the alloys was analyzed by ESCA and reflection electron diffraction. The relationship between the bonding strength and surface structures is discussed on the basis of the adhesion mechanism models.

A several-molecule thick layer of H₂O which is adsorbed on the Co₃O₄ layer of the oxidized surfaces lowers the bonding strength. This explains why the bonding strength of the resin on the as-polished surface, which is an amorphous passive film, is superior to the oxidized surfaces which are mainly composed of Co₃O₄.

Key words : Adhesive resin, Adhesion mechanism, Alloy surface structures

INTRODUCTION

Recently marked developments have been made in the studies on the adherence of dental adhesive resin to both human teeth and dental alloys¹⁻⁶⁾. Many studies have been made on the resin adhesion to dental alloys ; pioneering work by Tanaka on Ni-Cr alloys⁷⁻⁹⁾ and gold alloys¹⁰⁾ ; studies on Ni-Cr alloys¹¹⁻¹⁵⁾, Co-Cr alloys^{11,15-22)}, and precious metal alloys^{14,15,23-28)}. There have been, however, no reports on the relationship between the alloy surface structure and resin adhesion or the mechanism of the adhesion. A fundamental and practical understanding of the mechanism of adhesion would enable us to specify the alloy surface structure which would strongly adhere to the resin, and to establish the guide lines for both the development of alloys and preparation of the alloy surface to obtain strong bonds for the adhesive resin.

We examined the bonding strength of the dental adhesive resin to the Co-Cr alloys after the bonded specimens had been subjected to thermal stress by the thermal cycle method using liquid nitrogen to rapidly evaluate the adhesive strength. The alloy surface was characterized by X-ray photoelectron spectroscopy (ESCA) and reflection electron diffraction to clarify the relationship between the bonding strength and alloy surface structure. With ESCA the chemical state of the atoms can be determined in the top several 10 Å layer of a specimen, making it suitable for investigating the adhesion phenomena which are very sensitive to the surface state. The adhesive strength of the adhesive resin to the Co-Cr alloy was discussed using adhesion models based on the measured bonding strength and the details of the alloy surface structure.

EXPERIMENTAL METHODS

1. Materials

A 70 mass % Co-30 % Cr alloy was used. The alloy was prepared by melting Co and Cr of a purity better than 99.99 % in an alumina Tammann tube under an argon atmosphere using a high frequency induction furnace. The alloy was cut into small chips and the chips were soldered to a mild steel disk as shown in Fig. 1. The dental adhesive resin was the MMA-TBB resin* containing 4-META (4-methacryloxyethyl trimellitate anhydride)²⁾.

2. Pretreatment of Alloy Surfaces

The Co-Cr alloy specimens were polished metallographically to eliminate any mechanical factors affecting the bonding strength and given three different surface treatments: polished, or oxidized for 5 min in air at 300°C or 500°C. The specimens were stored in a desiccator with silica gel before the adhesion experiments, ESCA measurements, and reflection electron diffraction.

3. Adhesion Experiments

As shown in Fig. 1, the Co-Cr specimen and a 5 mm ϕ 18-8 stainless steel rod were attached with the adhesive resin for a tensile test to measure the bonding strength. Fig. 2

Fig. 1 Tensile test piece for bonding strength measurements. Co-Cr alloy specimen was bonded with adhesive resin to an 18-8 stainless steel rod. The U shaped piece was applied to the groove in the stainless steel rod for the testing.

Fig. 2 Adhesion apparatus used to bond the stainless steel rod vertically to the Co-Cr alloy surface and to maintain a constant 50 μm resin layer thickness.

* Super-Bond C & B, SUN MEDICAL Co., Ltd., Kyoto, Japan

shows the adhesion apparatus with a micrometer which was used for two purposes : to attach the stainless steel rod vertically to the Co-Cr alloy surface and to maintain a constant 50- μ m thick resin layer. The effect of the excess resin at the point of adhesion on the bonding strength can be eliminated by Scotch tape on the stainless steel rod as shown in Fig. 1.

4. Tensile Test and Thermal Cycle

The tensile test for the bonding strength measurement was carried out after keeping the specimen at room temperature for 24 hr after the adhesion treatment. The test was performed on a testing machine[†] with a load speed of 2 mm/min, after inserting a U shaped piece in the groove of the stainless steel rod (Fig. 1) and placing the test piece in the jig for the tensile test in Fig. 3. Before testing, the specimen was subjected to 20 thermal cycles from liquid nitrogen (-195.8°C) to water temperature (40°C), alternately for 1 min each.

5. ESCA Analysis and Reflection Electron Diffraction.

The ESCA measurements of the three different surface states were performed using an electron spectrometer[‡] with Mg $K\alpha$ radiation (1253.6 eV). The binding energies of the measured photoelectron peaks were calibrated by using the C (1s) peak of hydrocarbon contamination at a binding energy of 285.0 ± 0.2 eV. The alloy surface was subjected to argon ion etching at 2 kV and 20 mA under a pressure of 5×10^{-5} Torr in the spectrometer. The

Fig. 3 Jig for the tensile test.

[†] Auto-Graph IS-5000, Shimadzu Co., Kyoto, Japan

[‡] ESCA 750, Shimadzu Co., Kyoto, Japan

etching rate was ca. 1 Å/sec at these etching conditions. ESCA measurements and the argon ion etching were performed alternately to determine both the amounts and chemical states of the elements in the depth direction. The ESCA analysis was carried out by computer[§] in the ESCA spectrometer.

The amounts of Co, Cr, and O were computed according to equation (1)²⁹⁾. The intensity of a photoelectron, N , which is ejected from a shell in an element, 'a', in a thick specimen is expressed by :

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

where N_o is a constant, n_a the amount of atom 'a' per unit volume, σ the photoelectron cross section, λ the mean-free path, and S a spectrometer factor. In the present study, the photoelectron intensity of each element was measured from the peak areas of Co ($2p_{3/2}$), Cr ($2p_{1/2,3/2}$), O (1s), and C (1s). For example, the concentration of Cr, C_{Cr} , is performed by equation (2) :

$$C_{Cr} = \frac{n_{Cr}}{n_{Co} + n_{Cr} + n_o + n_c} \dots\dots\dots(2)$$

where n_{Co} , n_{Cr} , n_o , and n_c are the amounts of Co, Cr, O, and C calculated from equation (1). The quantitative error in the calculations is estimated to be $\pm 5-30\%$. Quantitative values obtained from equation (2) were separated into the metallic and oxidation states of Co and Cr by subtracting the metallic state component from the measured spectrum areas.

Reflection high energy electron diffraction patterns were determined with an electron microscope^{//} with 100 kV accelerating voltage. The camera constant was calibrated with the transmission diffraction pattern of a gold film immediately before and after taking the reflection patterns. The compounds on the alloy surface were identified from the JCPDS card-index on the basis of the measured spacings.

RESULTS

1. Bonding Strength

Figures 4, 5, and 6 are the measured bonding strengths for the tensile test obtained from the as-polished surface, and the surfaces oxidized for 5 min in air at 300°C, and at 500°C, respectively. The value shown in the left and right halves in each figure are the bonding strengths without (non-thermal cycle) and with the thermal cycle, respectively. The horizontal lines in the figures indicate the average of the repeated values. There were three failure types which are classified as in Table 1: Type I is a failure in the resin (cohesive failure); Type II is partly a cohesive failure and part interface failure at the alloy surface; and Type III is a cohesive failure and interface failure at the periphery of the adhesion to the alloy surface. At 500°C an oxide colored surface due to failure was observed on all alloy surfaces. This indicates the failure at the interface between the resin and the oxide. Table 1 lists the failure types and the notations used in Figures 4-6.

The bonding strength for the as-polished surface (Figure 4) is similar for both the

§ ESPAC 100, Shimadzu Co., Kyoto, Japan

// H-500, Hitachi Ltd., Tokyo, Japan

Fig. 4 Results of bonding strength measurements obtained from the specimens bonded to the as-polished Co-Cr alloy surface. The left half is the bonding strength without (non-thermal cycle) and the right with the thermal cycle. The horizontal line shows the average of the repeated tests.

Fig. 5 Results of bonding strength measurements obtained from the specimens oxidized at 300°C.

Fig. 6 Results of bonding strength measurements obtained from the specimens oxidized at 500°C.

Table 1 Observed failure types and their notations

Failure type	Observed figure	Notation in Figs.4-6
I		
II		
III

Fig. 7 Relationship between the bonding strength and area fraction of interface failure (Interface Fracture Ratio) at the periphery from the testes with the thermal cycle in Fig. 6.

non-thermal and thermal cycle specimens. With the non-thermal cycle, the specimens show only the Type I failure, while with the thermal cycle there are 5 Type III failures in addition to the Type I failures.

Figures 5 and 6 show that the specimens with surfaces oxidized at 300°C and 500°C and without the thermal cycle exhibit bonding strengths similar to the specimens with as-polished surfaces and that all the failures were of Type I except for a few cases of Type II failure. However, after the thermal cycle treatment the bonding strength decreased significantly with a wide scattering of values, and all failures are of Type III.

Figure 7 shows the relationship between the bonding strength, Y , and the area fraction, X , of interface failures at the periphery obtained from specimens subjected to the thermal cycles in Figure 6 (500°C), it is represented by equation (3):

$$Y = -6X + 435 \quad \text{.....(3)}$$

2. ESCA measurements

Figure 8 shows (a) the Co ($2p_{3/2}$) spectrum and (b) the Cr ($2p_{1/2,3/2}$) spectra obtained at different depths of the as-polished specimen, obtained by varying the argon ion etching time. The 'surface' spectrum was obtained from the polished surface without argon ion etching and the 20 sec and 40 sec spectra were obtained from depths of 20 Å and 40 Å as the etching rate is ca. 1 Å/sec. In Fig. 8 (a), the binding energy at the 20 Å and 40 Å deep Co ($2p_{3/2}$) peaks is 778.7 eV, which indicates a metallic Co. The 'surface' spectrum shows a doublet with a separation of approximately 2.9 eV, showing that the surface contains two different chemical states: The lower binding energy peak in the doublet is identified as a metallic Co while the other is an unknown state. Figure 8 (b) shows that the metallic Cr peak was obtained by the etching of 40 Å. The spectra obtained from the unetched surface had a shoulder indicating

Fig. 8 ESCA spectra at different depths of the as-polished specimens at varying argon ion etching times: (a) is the Co ($2p_{3/2}$) spectrum and (b) is the Cr ($2p_{1/2,3/2}$) spectra. The 'surface' spectra are from the surface without argon ion etching. The etching rate is ca. $1 \text{ \AA}/\text{sec}$.

the metallic state at 574.4 eV and the unknown state had a peak 2.8 eV higher than shoulder of the metallic state. The unknown states of Co and Cr will be discussed later.

Figure 9 shows a set of spectra obtained from different depths of specimens oxidized at 300°C , (a) is the Co ($2p_{3/2}$) spectrum and (b) is the Cr ($2p_{1/2,3/2}$) spectra. In (a), metallic Co was obtained by etching $120 \text{ \AA}$, which removed the oxides on the alloy surface. The peak at the unetched surface was 1.7 eV higher than the metallic state, and may be attributed to Co-oxide. At a longer etching time, the shoulder on the lower binding energy side of the peak at $40 \text{ \AA}$ developed to a well-shaped peak for the metallic state at $60 \text{ \AA}$, showing a mixture of Co-oxide and metallic Co. In (b), the all-metallic state appeared by etching to $180 \text{ \AA}$. The Cr ($2p_{3/2}$) peak on the unetched oxidized surface falls 2.5 eV higher than that of the metallic state. Metallic and oxidized Cr are mixed at $80 \text{ \AA}$ to $120 \text{ \AA}$.

In the specimens oxidized at 500°C , metallic states were obtained by etching $340 \text{ \AA}$ in Co and $500 \text{ \AA}$ in Cr, which shows that Cr-oxide is formed deeper than Co-oxide.

Figure 10 shows the depth variation of Co, Cr, and O calculated with eq. (2) for the as-polished specimen. The calculation was performed by including adsorbed carbon which is not shown in Fig. 10. The concentrations at etching time zero are those of the surface before etching. The Co and Cr concentrations became constant after etching $20 \text{ \AA}$ and oxygen decreased remarkably with increasing etching time.

The concentrations of Co and Cr in Fig. 10 were obtained from the mixture of the metallic and unknown states shown in Fig. 8. The two states could be separated and their concentrations determined. The spectra from the specimen in Fig. 9 (b) at 80 sec could be separated into these two spectra as shown in Fig. 11, the metallic state (fine solid line) and

Fig. 9 ESCA spectra at different depths of the 300°C oxidized specimen.

Fig. 10 Depth concentrations of Co, Cr, and O from the as-polished specimen. One sec of etching time is equivalent to ca. 1 Å etching.

Fig. 11 The observed Cr ($2p_{1/2,3/2}$) spectra (heavy solid line) after 80 sec argon ion etching of the specimen oxidized at 300°C resolved into the spectra for the metallic state (fine solid line) and Cr-oxide (dotted line). The area fraction of the spectra gives the concentration of the two states.

Fig. 12 Concentrations of the metallic and unknown states of Co (a) and Cr (b) in depth, obtained from the as-polished surface (Fig. 10).

Fig. 13 Concentrations of Co, Cr, and O in depth, from the 300°C oxidized specimen. One sec etching is equivalent to ca. 1 Å in depth.

the Cr-oxide (dotted line). The area fraction gives the concentration of the two states. In the same manner the concentrations of Co and Cr in Figure 10 could be separated into the metallic and unknown state as shown in Figure 12: The separated concentrations of Co and Cr are shown at (a) and (b). The metallic and unknown states of Co and Cr are present at the surface (etching time zero). The concentration of the Co unknown state becomes zero at a 20 Å depth, while the Cr unknown state reaches a maximum. The film thickness on the as-polished surface is 20-30 Å.

Fig. 14 Concentrations of the metallic and unknown states of Co (a) and Cr (b) in depth, obtained from the 300°C oxidized surface (Fig. 13).

Fig. 15 Reflection electron diffraction patterns from the surfaces of the as-polished (a) and 500°C oxidized specimens (b).

Figure 13 shows the concentrations of Co, Cr, and O in the depth direction, for the specimens oxidized at 300°C. In the same manner as in Fig. 11, the concentrations in Fig. 13 can be separated into the metallic and oxidized states as shown in Fig. 14 (a) for Co and (b) for Cr. The Co-oxide is rich at the surface, while Cr-oxide reaches a maximum at a depth of 60 Å. The oxide film is ca. 120 Å thick and contains metallic Co and Cr from 30–40 Å.

3. Reflection Electron Diffraction

Figures 15 (a) and (b), show the reflection electron diffraction patterns obtained from the surfaces of the as-polished and 500°C oxidized specimen. The pattern of the diffraction rings in the specimen oxidized at 300°C is similar to Fig. 15 (b) although more diffuse. There are no diffraction rings in (a), indicating that the as-polished surface is covered with an amorphous film. In Table 2, the observed lattice spacings and intensities of the diffraction rings

Table 2 Lattice spacings and intensities observed from diffraction rings (in Fig. 15(b)) with the data for Co_3O_4 from the JCPDS card-index. 'X' indicates the absence of an identification lattice spacing.

Observed values			Reference substance measured by X-ray		
			JCPDS card		
			Co_3O_4		
Ring No.	d Å	I	d Å	I/I ₁	hkl
1	4.71	m	4.666	20	111
2	2.88	s	2.860	40	220
3	2.46	vs	2.438	100	311
4	2.33	vw	2.333	12	222
5	2.03	s	2.021	25	400
6	1.86 X	vw			
7	1.65	w	1.6505	12	422
8	1.57	s	1.5559	35	511
9	1.44	s	1.4293	45	440
10	1.37 X	vw			
11	1.29	vw	1.2788	6	620
12	1.24	w	{1.2330	12	533
			{1.2191	8	622
13	1.18	vw	1.1671	4	444
14	1.14	vw	1.1321	4	711
15	1.09	w	1.0803	8	642
16	1.06	w	1.0524	16	731

in (b) are shown together with the data for Co_3O_4 from the JCPDS card-index, showing that the oxidized specimens are covered with Co_3O_4 . There is no identification lattice spacing at 'X' in the table, however, the diffraction intensity from the substance is very weak, which indicates a small amount.

DISCUSSION

1. Failure Types of Failure at the Points of Adhesion

Though failures appear in the adhesive resin after the tensile test, fractures do not occur in the covalent bonds of PMMA alone. The main factor in the bonding strength is not the strength of the covalent bond but intermolecular forces (hydrogen bond and Van der Waals force)³⁰⁾. However, when failure occurs in the resin, the bonding strength is not the full intermolecular force of PMMA. Because, in the adhesive resin layer, there are some factors³¹⁾ which make the bonding strength lower than the total intermolecular force of the resin. These include air bubbles, variation in the monomer-polymer ratio, impurities, and low molecular weight components. These factors are considered to cause the large scattering of the bonding strength values at the failure of the resin (Type I in Table 1) shown in Figs. 4-6.

In the adhesion tests of the specimens the different surface states were clearly shown by the thermal cycle. Without the thermal cycle there were no differences between the as-polished and oxidized surfaces. With the thermal cycle, for the oxidized surface, interface

failure occurred at the periphery of the adhesion (Type III in Table 1), and bonding strength decreased with increasing area fraction of the interface failure as shown in Fig. 7. Even with the thermal cycle, the as-polished samples show no change in bonding strength or failure type, showing that the as-polished surface is superior for adhesion.

In a butt joint as in the present study, thermal stress generated in an adhesive is considered to be a function of both diameter and thickness of the adhesive layer, and the stress is large at the periphery and zero at the center of adhesion³²⁾. Cracks at the resin/alloy interface propagate from the periphery to a point where the thermal stress balances with the adhesive force, producing a Type III failure.

2. Characterization of the Co-Cr Alloy Surface

Table 3 shows the oxide chemical shifts, ΔE_B (referred to the metallic state), of the energy level ($2p_{3/2}$) which have been reported for Co and Cr. Table 4 shows the chemical shifts ΔE_B for Co ($2p_{3/2}$) and Cr ($2p_{3/2}$), obtained in this study from the three alloy surfaces, as-polished, oxidized at 300°C, and oxidized at 500°C, all before argon ion etching. By comparing Tables 3 and 4, oxidation states of the unknown peaks in Fig. 8 (as-polished surface) are identified as divalent (II) for Co and trivalent (III) for Cr. On the surface oxidized at 300°C, however, Co can not be identified as Co (III) or Co (II + III) from ΔE_B because both Co chemical states are very close^{34,36)}. Chemical states on the surface oxidized at 500°C are the same as those oxidized at 300°C.

Reflection electron diffraction identified an amorphous layer on the as-polished surface and $\text{Co}_3\text{O}_4 + \text{X}$ (unidentified compound) on the oxidized surface. Table 5 shows the results obtained from ESCA and reflection electron diffraction.

Table 3 Reported oxide chemical shifts ΔE_B (eV) with reference to the metallic state

Element	Oxides	Oxidation states	Energy level	ΔE_B (eV) Data taken from literature
Co	CoO	II	$2p_{3/2}$	$2.9^{33)}$, $2.2^{36)}$, $2.5^{34)}$
	Co_3O_4	II + III		$1.8^{34)}$
	Co_2O_3	III		$1.6^{34)}$, $1.1^{36)}$
Cr	Cr_2O_3	III	$2p_{3/2}$	$3.0^{33)}$, $2.5^{35)}$, $2.4^{37)}$
	CrO_3	IV		$4.5^{33)}$, $4.9^{37)}$

Table 4 Measured chemical shifts ΔE_B (eV) of the unknown peak obtained from the surface before argon ion etching with reference to the metallic state

Surface pretreatment	Measured ΔE_B (eV)	
	Co $2p_{3/2}$	Cr $2p_{3/2}$
As-polished	2.9	2.8
300°C	1.7	2.5
500°C	2.2	2.3

Table 5 Characterization of the as-polished and oxidized surfaces of the Co-Cr alloy. X: the unknown substance, ?: chemical state not determined by ESCA

Surface pretreatments	ESCA	Reflection electron diffraction
As-polished	Co(II) + Co(O), Cr(III) + Cr(O)	Amorphous
300°C	Co(?), Cr(III)	Co ₃ O ₄ + X
500°C	Co(?), Cr(III)	Co ₃ O ₄ + X

(1) As-polished Surface

The film on the as-polished surface of the Co-Cr alloy is a so-called passive film, which also forms on stainless steel, Ni base alloys, and Co base alloys containing Cr above a certain content. A number of studies have reported passive films on these alloys, and proposed the rational formulas of $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ ³⁸⁾, $\text{Cr}(\text{OH}) \cdot \text{CrO}_4$ ³⁹⁾, Cr_2O_3 ⁴⁰⁾, $\text{Cr}(\text{OH})_3$ ⁴¹⁾, $2\text{CrO}(\text{OH}) \cdot 3\text{H}_2\text{O}$ ⁴²⁾, and $\text{CrO}(\text{OH}) \cdot \text{H}_2\text{O}$ ⁴³⁾. Hashimoto et al. have introduced a more general formula, $\text{CrO}_x(\text{OH})_{3-2} \cdot n\text{H}_2\text{O}$, hydrated chromium oxy-hydroxide^{44,45)}.

On stainless steel the film is amorphous and 30 to 60 Å thick⁴⁶⁾. Okada has proposed that the surface structure of chromium electroplating is a one molecule layer of the ol-compound coordinating six $-\text{OH}$ around a central Cr^{3+} ⁴⁷⁾. By studying the films formed by chromium electroplating, Uchida et al. found OH stretching and HOH bending vibration by infrared absorption spectroscopy⁴²⁾, and also confirmed the vaporization of water in the film up to 240°C by thermo-gravimetry and by the decrease in infrared absorption⁴⁸⁾. They concluded that the film structure is the ol-compound containing zeolitic water in addition to Okada's structure. Okamoto has proposed the structural model of the passive film on stainless steel in Figure 16, two dimensional inorganic polymers which coordinate O^{2-} , OH^- , and H_2O around Cr^{3+} (indicated as M)⁴⁹⁾.

Thus the structure of the passive film on the as-polished surface of the Co-Cr alloy in this study is considered to have a structure which is somewhat more complicated than in Figure 16. The film is amorphous, 20-30 Å thick, and the surface is rich in Co(II). In the inner part of the film, Co(II) decreased remarkably while Cr(III) increases. The states of the $-\text{OH}$ and

Fig. 16 Model of passivated surface on stainless steel (Okamoto)⁴⁹⁾.

H₂O on the as-polished surface can be determined as follows: The oxygen concentration in the passive film, $C_{OX(passive)}$, can be obtained by equation (4) from the Co and Cr concentrations, C_{Co} and C_{Cr} , assuming six coordinating $-OH$ and/or H_2O around Co and Cr.

$$C_{OX(passive)} = 3(C_{Co} + C_{Cr}) \quad \dots\dots\dots(4)$$

The concentrations, C_{Co} and C_{Cr} , can be obtained from Fig. 12 (unknown state). The calculated and measured (Fig. 10) oxygen concentrations are plotted in Fig. 17. The calculated values agree with those measured at the surface (etching time zero), showing that these metal ions have six coordinated $-OH$ and H_2O . The discrepancies in the inner part show that the coordination number here is below six.

The metallic Co and Cr detected on the surface without argon ion etching (Fig. 8) need not be caused by these metallic states at the top surface. Since the mean free path of a photoelectron ejected from the 2p shell of Co and Cr is $7-8 \text{ \AA}^{29}$, ESCA must detect metallic elements down to this depth.

(2) Oxidized Surface

On the oxidized specimens, the ESCA measurements could not determine the oxidation states of Co, Co (III) or Co (II + III), however, reflection electron diffraction revealed that Co_3O_4 is predominantly formed on the oxidized alloy surface. Though Co has a lower affinity for oxygen than Cr, Co was preferentially oxidized near the surface (Fig. 14) because of the high Co content.

Co_3O_4 has a normal spinel structure with Co^{2+} ions at the tetrahedral sites, and Co^{3+} ions at the octahedral sites⁵⁰. From the ESCA measurements, Co_2O_3 and Co_3O_4 which contain both Co^{2+} and Co^{3+} could not be distinguished by a chemical shift.

Fig. 17 Measured oxygen concentration (as Fig. 10) and calculated oxygen concentration for six coordinated $-OH$ and/or H_2O around the metal ions.

Fig. 18 Adsorbed $-OH$ and H_2O layer model for metal oxide (Bolger)⁵¹.

To increase the surface energy due to unsaturated bonds at the solid surface, the surface (decreasing free energy) is stabilized by arranging the atoms to the particular positions and adsorbing molecules. Therefore, the oxide surface is not directly exposed to air because it adsorbs mainly $-\text{OH}$ or H_2O . Bolger proposed the oxide model shown in Fig. 18⁵¹⁾: The oxide surface adsorbs a monolayer of $-\text{OH}$ directly, chemisorbed H_2O molecules in the middle, and physisorbed H_2O on the top of the adsorbed layer.

The thickness of these adsorbed layers on the surface oxidized at 300°C can be measured from the ESCA data: When Co and Cr concentrations to form Co- and Cr- oxides, C_{Co} and C_{Cr} , are known, the oxygen concentration in the oxides, $C_{\text{Ox(oxide)}}$, can be calculated from equation (5) assuming that the formed oxides are stoichiometric oxides of Co_3O_4 and Cr_2O_3 .

$$C_{\text{Ox(oxide)}} = 1.33 \times C_{\text{Co}} + 1.5 \times C_{\text{Cr}} \quad \dots\dots\dots(5)$$

Both C_{Co} and C_{Cr} are given in Fig. 14. The measured (Fig. 13) and calculated oxygen concentrations in the depth direction are plotted in Fig. 19. At the top layer (surface without etching), the measured value was 17 % higher than the calculated value. At $20\text{ \AA}$ (20 sec) below the top layer, the measured value increased slightly and the calculated value decreased markedly. These increases and decreases in oxygen concentration are considered to be due to the adsorbed $-\text{OH}$ and H_2O . Though sputtering yield by the ion etching and mean free path of ejected photoelectrons should be considered, it may be concluded that there is an adsorbed layer of ca. $20\text{ \AA}$ on the Co-Cr alloy surface oxidized at 300°C . The thickness is equivalent to a 5-8 molecule layer of adsorbed water.

3. Differences in the Adhesion Mechanisms for the As-polished and Oxidized Surfaces

Adhesion is the interaction of molecules through the interface between adhesive and

Fig. 19 Measured oxygen concentration (as Fig. 13) and oxygen concentration calculated to form Co- and Cr- oxides.

Fig. 20 Hydrogen bond model for the 4-META side-chain and adsorbed $-\text{OH}$ on metal (Masuhara)¹⁾.

substance. For the adhesion mechanism of PMMA resin containing 4-META on a metal surface, Masuhara has suggested the presence of hydrogen bonds between the 4-META and adsorbed $-OH$ on the metal as in Fig. 20¹⁾. Here, it is necessary to describe the difference in adhesion between the as-polished and oxidized surfaces of the Co-Cr alloy on the basis of the adhesion mechanisms.

The surface models in Figs. 16 and 18 help in understanding the adhesion mechanism of adhesive resin to the alloy surfaces. Figure 21 shows the possible adhesion mechanism models of the PMMA resin containing 4-META: Models (a), (b), and (c) for the as-polished surface were made according to Figure 16 and Models (d), (e), and (f) for the oxidized surface according to Fig. 18. Adhesion depends on the atomic interaction which is determined by the directly visible atoms less than $10\text{\AA}$ from the top surface⁵²⁾. Model (a) shows the possibility of primary atomic bonds for 4-META in the resin with the metallic Co and Cr existing in a $7-8\text{\AA}$ deep layer. Model (b) shows a hydrogen bond of 4-META and $-OH$ in the passive film. Model (c) is Van der Waals interaction between water molecule and metal ion with hydrogen bond of water molecule and 4-META. Model (d) shows the hydrogen bond of 4-META with hydroxyl groups on the top surface of oxide layer. Model (e) includes one water molecule between the hydroxyl group and 4-META. Model (f) which includes several molecules of water is not part of the model for the adhesion mechanism on the as-polished surface because the adsorption model of the as-polished surface coordinates six $-OH$ and H_2O around a metal ion and does not have a several-molecules thick layer of adsorbed water. In these

Fig. 21 Suggested adhesion model of PMMA resin containing 4-META on as-polished (a, b, and c) and oxidized (d, e, and f) surfaces: M is the metal atom, ... hydrogen bond or Van der Waals interaction. The chemical bonds which are similar in bond strengths are labeled by the same number at the bonding positions.

models the chemical bonds which have nearly equal bonding strengths are labeled by the same number at the bonding positions.

Differences in the adhesiveness to the as-polished and oxidized surfaces with the thermal cycle are as follows: (1) almost all cohesive failures in the resin for the as-polished surfaces (Figure 4), and (2) interface failures at the oxide/resin interface on the periphery of adhesion for the oxidized surfaces. These results and the adhesion model in Figure 21 indicate that the strength at the adhesion interface decreases in the order interface formed from (a), (b), and (c) > resin > interface formed from (d), (e), and (f).

The adhesive force depends on the strength of specific chemical bonds, the existence of specific chemical bonds, and the amount of bonds. Since the same dental adhesive resin was used for both the as-polished and oxidized surfaces, the incidence of chemical bonds for the as-polished surface are equivalent to those for the oxidized surface. Models (b) and (c), for the as-polished surface are considered to be in agreement with Models (d) and (e) for the oxidized surface in the chemical states of the bonds. Therefore, Models (a) and (f) are different for the two surfaces. Model (a) due to the primary atomic bond is stronger than Model (f). Furthermore, the probability of the existence of Model (f) is not small as there is a several-molecule layer of adsorbed water on the oxidized surface. Thus the existence of the chemical bond (f) is a factor that lowers the adhesion to the oxidized surface.

CONCLUSIONS

Dental adhesive resin was bonded to three different 70 mass % Co-30 % Cr alloy surfaces, as-polished, oxidized at 300°C in air, and oxidized at 500°C in air. The adhesion was examined by a tensile test with and without a thermal cycle using liquid nitrogen. These alloy surface structures were analyzed by ESCA and reflection electron diffraction. The relationship between the adhesion and the alloy surface structure is discussed by considering adhesion models, including hydrogen bonds with -OH and H_2O on the alloy surfaces.

The resin bond to the as-polished surface is stronger than that to the two oxidized surfaces. The thermal cycle showed clear differences in the surface states affecting the adhesion. There are no differences in adhesion for the two oxidized surfaces.

The structure of the as-polished surface is an amorphous passive film 20-30 Å in thickness, and considered to be made up to six -OH and/or H_2O coordinated around Cr^{3+} and Co^{2+} or Co^{3+} metal ions.

Co_3O_4 was predominant on the surfaces oxidized at 300°C and 500°C. On the 300°C surface, a several-molecule thick layer of water was adsorbed on the 120 Å thick oxide layer. The presence of chemical bonds including a several-molecule thick layer of adsorbed water between the oxidized surface and the 4-META side-chain was considered to be the reason why adhesion to the oxidized surface is inferior to that to the as-polished surface.

ACKNOWLEDGEMENT

The authors wish to thank Mr M. Tanabe (Shimadzu Co., Kyoto) for ESCA measurements.

REFERENCES

- 1) Masuhara, E. : A dental adhesive and its clinical applications, *Quintessence Books Co.*, 1982, pp. 11-68. (in Japanese)
- 2) Takeyama, M., Kashibuchi, S., Nakabayashi, N., and Masuhara, E. : Studies on dental self-curing resins, (Part 17) Adhesion of PMMA with bovine enamel or dental alloys, *J Japan Soc Dent Appar Mat* **19** (47) : 179-185, 1978. (in Japanese)
- 3) Nakabayashi, N., Takeyama, M., Kojima, K., and Masuhara, E. : Studies on dental self-curing resins, (Part 20) Adhesion mechanism of 4-META/MMA-TBB resin to dentine, *ibid.* **23** (61) : 34-39, 1982. (in Japanese)
- 4) Nakabayashi, N., Takeyama, M., Kojima, K., Mogi, M., Miura, F., and Masuhara, E. : Studies on dental self-curing resins, (Part 22) Adhesion of 4-META/MMA-TBB resin to enamel, *J Japan Soc Dent Appar Mat* **23** (61) : 88-92, 1982. (in Japanese)
- 5) Matsumura, H., Kojima, K., Kadoma, Y., and Masuhara, E. : Studies on dental self-curing resins, (Part 26) Effect of 4-META and 4-MET addition to the MMA-TBBO resin, *J J Dent Mat* **3** (4) : 480-489, 1984. (in Japanese)
- 6) Matsumura, H., Kojima, K., Kadoma, Y., and Masuhara, E. : Studies on dental self-curing resins, (Part 27) Adhesion of monomers with aromatic carboxylic group to the metals and alloys, *ibid.* **3** (6) : 810-820, 1984. (in Japanese)
- 7) Tanaka, T., Nagata, K., Nakabayashi, N., and Masuhara, E. : Application of 4-META on adhesive opaque resin, (Part 1) Adhesive strength and the stability, *J Japan Soc Dent Appar Mat* **20** (50) : 79-84, 1979. (in Japanese)
- 8) Tanaka, T., Nagata, K., Nakabayashi, N., and Masuhara, E. : Application of 4-META on adhesive opaque resin, (Part 2) Improvement of adhesive stability, *ibid.* **20** (52) : 221-227, 1979. (in Japanese)
- 9) Tanaka, T., Nagata, K., Takeyama, M., Atsuta, M., Nakabayashi, N., and Masuhara, E. : 4-META opaque resin — A new resin strongly adhesive to nickel-chromium alloy, *J Dent Res* **60** (9) : 1697-1707, 1981.
- 10) Tanaka, T., Nagata, K., Takeyama, M., Nakabayashi, N., and Masuhara, E. : Heat treatment of gold alloy to get adhesion with resin, *J Japan Soc Dent Appar Mat* **21** (54) : 95-102, 1980. (in Japanese)
- 11) Yamashita, A. and Yamami, T., : Procedures for applying adhesive resin (MMA-TBB) to crown and bridge restorations, (Part 1) The influence of dental non-precious alloys and the treatment of inner surface of metal to adhesion, *J Japan Prosth Dent* **26** (3) : 130-137, 1982. (in Japanese)
- 12) Yamashita, A., Yamami, T., Ishii, M., Yamaguchi, T., and Uramoto, T. : Procedures for applying adhesive resin (MMA-TBB) to crown and bridge restorations, (Part 3) The Ni-Cr alloys for adhesive resin and its adhesive strength and durability, *ibid.* **26** (6) : 22-31, 1982. (in Japanese)
- 13) Shinohara, N., Tojinbara, O., Akita, H., Kakiuchi, T., and Jimi, T. : Studies on the adhesive strength between adhesive resins and each metal surface treated by wire explosion spray (Part 2) Adhesive shear strength between Ni-Cr alloy surface treated by wire explosion spray and adhesive resin (Super Bond C and B), *J Japan Prosth Dent* **28** (5) : 165-169, 1984. (in Japanese)
- 14) Matsumura, H. : Adhesion of dental alloys, (Part 1) Effect of monomers with an acid anhydride group, *J J Dent Mat* **4** (5) : 421-429, 1985. (in Japanese)
- 15) Matsumura, H. : Adhesion of dental alloys, (Part 2) Effect of monomers with an acid anhydride or a carboxylic group, *ibid.* **5** (1) : 65-70, 1986. (in Japanese)
- 16) Mogi, T. : Studies on adhesion of methacrylic resin to cobalt-chromium alloy for denture base — Effect of 4-methacryloxyethyl trimellitate anhydride monomer, *J Japan Prosth Dent* **23** (4) : 76-92, 1979. (in Japanese)
- 17) Yasuda, N., Sasaki, M., Mogi, T., Matsumoto, M., and Ai, M. : Interface between metal and resin on the finishing line of cobalt-chromium denture, (Part 1) Effect of finishing line structure on the degree of dye penetration, *ibid.* **22** (3) : 15-18, 1978. (in Japanese)
- 18) Yasuda, N., Sasaki, M., Mogi, T., Ai, M., and Nakabayashi, N. : Interface between metal and resin on the finishing line of cobalt-chromium denture, (Part 2) Effect of 4-META on preventing dye penetration at the finishing line, *J Japan Prosth Dent* **22** (3) : 19-25, 1978. (in Japanese)
- 19) Sasaki, M., Yasuda, N., Mogi, T., and Ai, M. : Interface between metal and resin on the finishing line

- of cobalt-chromium denture, (Part 3) Studies on finishing line structure, *ibid.* **23** (2): 162-166, 1979. (in Japanese)
- 20) Yasuda, N., Sasaki, M., Mogi, T., and Ai, M.: Interface between metal and resin on the finishing line of cobalt-chromium denture, (Part 4) A clinical survey of cobalt-chromium dentures by 4-META coating system, *J Japan Prosth Dent* **23** (2): 167-172, 1979. (in Japanese)
 - 21) Sasaki, K., Yasuda, N., Mogi, T., and Ai, M.: Interface between metal and resin on the finishing line of cobalt-chromium denture, (Part 5) Changes of bonding strength caused by using adhesive resin, *ibid.* **24** (4): 7-10, 1980. (in Japanese)
 - 22) Yasuda, N., Sasaki, M., and Ai, M.: Interface between metal and resin on the finishing line of cobalt-chromium denture, (Part 6) A clinical survey of cobalt-chromium dentures by 4-META dough system, *J Japan Prosth Dent* **26** (2): 1-5, 1982. (in Japanese)
 - 23) Takaki, A., Fujiyama, E., Shimizu, H., Tanaka, T., and Asuta, M.: Study on bond strength between adhesive resin and Au-Ag-Pd alloy, *ibid.* **28** (5): 9-14, 1984. (in Japanese)
 - 24) Yamashita, A., Kondo, Y., and Fujita, M.: Adhesive strength of adhesive resin PANAVIA EX to dental alloys. (Part 2) Adhesive strength of precious alloys, *J Japan Prosth Dent* **28** (6): 43-53, 1984. (in Japanese)
 - 25) Etchu, Y., Nakamura, K., Ozonoe, Y., and Noguchi, H.: On oxidation treatment of alloy adherends for adhesion of dental cements, *J J Dent Mat* **4** (6): 692-700, 1985. (in Japanese)
 - 26) Varga, J., Matsumura, H., Tabata, T., and Masuhara, E.: Adhesive behaviour of the alloys 'AL-BABOND E' containing large percentage of Pd after various surface treatments, *Dent Mat J* **4** (2): 181-190, 1985.
 - 27) Shintani, H., Futagami, M., Yukihiko, A., Satou, J., Satou, N, Kai, M., Hayashihara, H., Inoue, T., and Seo, T.: Bond strength and marginal closure of newly developed adhesive cements, *Dent Mat J* **4** (2): 175-180, 1985.
 - 28) Doi, M.: Tensile adhesive strength of dental resin cements to dental alloy surface — Adhesion to Type II dental gold alloy —, *Jap J Consev Dent* **28** (3): 956-967, 1985. (in Japanese)
 - 29) Hirokawa, K.: Surface analysis by XPS, AES, and SIMS, *Bull Japan Inst Met* **21**: 885-890, 1982. (in Japanese)
 - 30) Imoto, M., (ed. by Inst Japan Adhesion): Adhesion handbook, *Nippon-Kogyo-Shinbun*, 1976, p. 7. (in Japanese)
 - 31) Hata, T.: *ibid.* p. 67. (in Japanese)
 - 32) Obata, Y., Inoue, Y.: Analysis of residual stress at adhesion layer, *J Chemi Industry* **61** (1): 39-42, 1958. (in Japanese)
 - 33) Holm, R. and Storp, S.: ESCA studies of chemical shifts for metal oxides, *Appl Phys* **9**: 217-222, 1976.
 - 34) Okamoto, Y., Nakano, H., Imanaka, T., and Teranishi, S.: X-ray photoelectron spectroscopic studies of catalysts — Supported cobalt catalysts —, *Bull Chem Soc Japan* **48** (4): 1163-1168, 1975.
 - 35) Bouyssoux, G. and Romand, M.: XPS and AES studies of anodic passive films grown on chromium electrodes in sulphuric acid baths, *J Elect Specro and Related Pheno* **11**: 185-196, 1977.
 - 36) Haber, J. and Ungier, L.: On chemical shifts of ESCA and auger lines cobalt oxides, *ibid.* **12**: 305-312, 1977.
 - 37) Asami, K. and Hashimoto, K.: The X-ray photo-electron spectra of several oxides of iron and chromium, *Corrosion Sci* **17**: 559-570, 1977.
 - 38) Sargent, G. J.: Electrolytic chromium, *Trans Amer Electrochem Soc* **37**: 479-497, 1920.
 - 39) Müller, E.: Die Wirkung von Fremdanionen auf die Elektrolyse wässriger Chromsäure-Lösungen, *Ztschr Elektrochem* **50** (8): 172-186, 1944.
 - 40) Weiner, R. and Schiele, C.: Elektronenbeugungsuntersuchungen an Kathodenfilmen bei der Elektrolytischen Reduktion der Chromsäure, *Z Physikal Chemi N F* **26**: 248-268, 1960.
 - 41) Solov'eva, Z. A. and Vagramyan, A. T.: Oscillographic investigation of film formation on the cathode surface in the electrolytic reduction of chromic acid, *J Phys Chem (USSR)* **36** (4): 751-756, 1962.
 - 42) Uchida, H., Kado, S., Yamada, K., and Ogasawara, T.: Structure of hydrated chromium oxide film on tin free steel, *J Japan Inst Metals* **33** (11): 1295-1299, 1969. (in Japanese)
 - 43) Kondo, Y. and Matsubayashi, H.: Structure of hydrated chromium oxide film formed by electrolytic reduction in chromic acid solution, *Kinzoku-Hiyoumen-Gijutsu* **28** (4): 223-227, 1977. (in Japanese)

- 44) Asami, K., Hashimoto, K., and Shimodaira, S.: An XPS study of the passivity of a series of iron-chromium alloys in sulphuric acid, *Corrosion Sci* **18**: 151-160, 1978.
- 45) Hashimoto, K.: Asami, K., Naka, M., and Masumoto, T.: Surface films formed on amorphous Co-Cr alloys in 1 N HCl, *Boshoku Gijutsu*, **28**: 271-277, 1979.
- 46) Rhodin, T. N.: Oxide films on stainless steels, *Corrosion NACE* **12**: 41-53, 1956.
- 47) Okada, H.: Electrochemical study on chromium and nickel plating, *Thesis of Hokkaido Univ* (No. 4473), 1961. (in Japanese)
- 48) Uchida, H., Kado, S., Yamada, K., and Kato, C.: Dehydration of hydrated chromium oxide film on tin free steel, *J Japan Inst Metals* **33** (11): 1290-1295, 1969. (in Japanese)
- 49) Okamoto, G. and Shibata, T.: Stability of passive stainless steel in relation to the potential of passivation treatment, *Corrosion Sci* **10**: 371-378, 1970.
- 50) Kiriyaama, R. and Kiriyaama, H.: Structural inorganic chemistry (I), *Kyoritu-Shuppan*, 1975, p. 144. (in Japanese)
- 51) Bolger, J. C. and Michaels, A. S.: Molecular structure and electrostatic interactions at polymer-solid interfaces, Interface conversion for polymer coatings (ed. by Weiss, P. and Cheever, G. D.), *Elsevier Publishing Co.*, 1968, pp. 3-60.
- 52) Nishiyama, Y.: Design of surface (Conversion of surface, ed. by Japan Chemical Soc), *Kagaku-Sousestu*, No. 44, 1984, pp. 1-6. (in Japanese)

cm², 50 kg/cm²と著明に低下した。これらの事実から、酸エッチングされたエナメル質にボンディング材を施す

際には出来る限り慎重におこなうべきであることが確認された。

接着性レジンと合金の接着機構の解明に関する研究

—— ESCA によって解析された Co-Cr 合金の表面構造とレジンの接着強さの関係 ——

大野弘機, 荒木吉馬, 相良昌宏

東日本学園大学歯学部歯科理工学教室

70 mass %Co-30 %Cr 合金の 3 つの異なる表面状態 (バフ研磨したまま, 300°C と 500°C で大気中で酸化) に対する接着性レジン (4-META 添加) の接着性について検討した。合金の表面構造は ESCA と反射電子回析で解析し, 接着性と表面構造の関係について接着モデルを仮定して論じた。

接着性は, 研磨したままの方が 300°C と 500°C で酸化したものより優れていた。この接着性の優劣は, 液体チッ素を用いた熱サイクルを施すことによって見出された。

研磨したままの表面構造は, 20~30 Å の非晶質の不動態被膜で, Cr³⁺ や Co²⁺ または Co³⁺ を中心にして -OH や H₂O が 6 配位で結合していると考えられた。また, 300°C の場合は, 120 Å の酸化被膜が形成され, その表面は, 主に Co₃O₄ から成っている。酸化層の表面には数分子の H₂O が吸着していると考えられ, この吸着水の存在が, 研磨したままの表面よりも接着性を低下させた原因と考えられた。

表面滑沢硬化処理床用レジンの耐摩耗性

山本昌雄*, 若狭邦男*, 松井 昌**, 笠原義人*, 二反田淳二*, 徐 崇仁***

*広島大学歯学部歯科理工学講座

**葵歯学研究所

***中国医薬学院

本研究では, 表面滑沢硬化処理した床用レジンの耐摩耗性を表面粗さ R_{max}, R_z, R_a 及びブラッシング消失量の観点から検討した。すなわち, 表面滑沢硬化処理剤, Linkle Coat (Coating 1) 及び Permacure Link (Coating 2) の 2 種類を用いて, それら処理したものと無処理のものとを

とを統計的に比較, 検討した。その結果, 表面滑沢硬化処理した場合, その耐摩耗性は無処理のコントロールよりもより優れており, とくに, Coating 1 による床用レジンの消失量は摩耗回数の増加にもかかわらず Coating 2 のものよりも少ないことが判明した。

金属メッシュプレートの義歯床への応用

川原春幸, 石崎順啓, 武田昭二, 今井弘一, 山形伸明

大阪歯科大学歯科理工学教室

床義歯装着時におこりうる床下粘膜組織にみられる弊害をできるだけ軽減し, 粘膜の生理機能を自然状態に保持できるような床用材料 TRUTISSU を試作し, いくつかの基礎実験を行なうとともにモニターによる臨床観察をも行ない, 以下のような評価を得た。1. TRUTISSU の成形性はよく, 成形後の適合性は良好であった。2. 口蓋粘膜に対する床の吸接着維持については他の材料と

くらべて同等の維持力が示された。3. 生物学的適合性については TRUTISSU の構成金属線に対して良好な細胞の接着ぬれを示し, 何らの変性も認められなかった。また, 口蓋粘膜をシミュレートした人工粘膜上の細胞について TRUTISSU 直下の細胞は正常な増殖を示した。4. コバルト・クロム床やレジン床との比較について, 装着感, 温度感および嗜好品に対する味覚などに