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[Original]

ESCA Study on Improvements in Adhesive Ability of Dental Adhesive Resin to Ni-Cr Alloy Treated by HNO₃ Solution

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Abstract

The adhesive ability of dental adhesive resin(4-META/MMA-TBB) to Ni-Cr alloy improves remarkably when the alloy surface is treated by conc. HNO₃ solution. Both as-polished and conc. HNO₃ treated alloy surfaces were analyzed by Electron Spectroscopy for Chemical Analysis(ESCA) to explain the superior adhesive ability of the alloy surface treated with HNO₃.

The surface of the HNO₃ treated specimen contains 25 at % Cr and 13% Ni and the as-polished specimen contains 17% Cr and 21% Ni. It shows that Cr, which has a good chemical affinity for 4-META resin, is concentrated on the alloy surface.

The O 1s spectra can be separated into three components: Component I is due to oxygen bonded with chromium in the passive film, Cr-O-Cr; II is due to oxygen bonded with both chromium and hydrogen in the passive film, Cr-OH · · · OH₂; and III is due to oxygen in physisorbed water molecules on the passive film. The area fractions are in the order II>I>III for the as-polished surface and I>II>III for the HNO₃ treated surface, indicating that a firm passive structure is formed on the surface treated by HNO₃ solution. This is the cause of the increase in the adhesive ability of the 4-META resin on the passive film.

Key words: ESCA study, Ni-Cr alloy, HNO₃ treatment

I. Introduction

The adhesive ability of dental adhesive resin containing 4-META to Ni-Cr alloy improves remarkably when the alloy surface is treated by conc. HNO₃ solution after sand-blasting.^{1,2)} The adhesive ability to both as-polished and conc. HNO₃ treated surfaces without surface irregularities has been investigated in the previous paper,³⁾ examining only the chemical adhesive effect: Adhesion to the alloy surface treated by conc. HNO₃ solution shows excellent adhesive ability, comparable with the as-polished Co-Cr alloy, and protects against the severe thermal cycle using liquid nitrogen.

In the present study, both the as-polished and conc. HNO₃ treated alloy surfaces were analyzed by Electron Spectroscopy for Chemical Analysis (ESCA) in order to clarify why the alloy surface treated by conc. HNO₃ solution is superior in adhesive ability to the as-polished surface. The adhesive abilities of both are discussed on the basis of differences in the surface structure.

II. Experimental Methods

1. Materials

The composition of the alloy used in this study was 70 mass % Ni- 30% Cr. Pure metals of a purity higher than 99.99% were used to manufacture the alloy. The melting was done in an alumina Tammann tube using a high frequency induction furnace in an argon gas atmosphere. The alloy was cut in 9 mm ϕ × 1 mm slices for ESCA analysis.

2. Surface Treatment of Alloy

The specimens were polished with a series of three emery papers and then by alumina abrasive with buffing cloth dampened with distilled water. The conc. HNO₃ treatment was performed by immersing the as-polished specimen in conc. HNO₃ solution (60%) for 15 min at room temperature. Both the as-polished and conc. HNO₃ treated specimens were rinsed with distilled water and then kept in a silica gel desiccator for 2 hr before ESCA measurements.

3. ESCA Measurement

ESCA measurements were performed using an ESCA-850 electron spectrometer † with Mg K α radiation (1,253.6 eV). Alloy specimens were fixed on the ESCA sample holder by setting and pressing indium metal between the specimen and the holder to maintain electric conductivity. The alloy surface was subjected to argon ion etching for 0.3 min at 2 kV and 20 mA under a pressure of 5×10^{-4} Pa in the spectrometer. ESCA measurements were performed at a pressure of 2×10^{-6} Pa evacuated by a turbo-molecular pump. The measurements and the argon ion etching were performed alternately to determine both the amounts and chemical

† Shimadzu, ESCA-850, Kyoto, Japan

states of the elements (Cr, O, and Ni) in the depth direction. The amounts of the elements in the depth direction were calculated by considering only the photoelectron cross section by a computer in the ESCA spectrometer.

The chemical shift of the Cr and Ni spectra was measured on the basis of the peak position of metallic states after the argon ion etching. A standard sample of Cr_2O_3 was obtained by heating Cr of purity better than 99.99% at 300°C in air. NiO as standard sample was not used because NiO is reduced by the argon ion etching.⁴⁾

III. Results and Discussion

1. As-polished Alloy Specimen

Figure 1 shows (a) the Cr $2p_{1/2,3/2}$ spectra, (b) the O 1s spectra, and (c) the Ni $2p_{3/2}$ spectra obtained at different depths of the as-polished specimen, by varying the argon ion etching time (in min). The 0 min spectrum was obtained from the polished surface without argon ion etching. In (a), the peaks of the binding energy at 574.3 eV, obtained by etching for 2.7 min, indicates Cr $2p_{3/2}$ from the metallic state. The Cr $2p_{3/2}$ spectrum obtained from the as-polished surface without etching (0 min) has a peak 3.0 eV higher than the metallic 574.3 eV peak and a shoulder at 574.3 eV, indicating that the surface contains two different chemical states of Cr: The lower binding energy shoulder is identified as a metallic Cr while the other is an unknown state in a passive film which will be discussed later.

The O 1s spectrum in (b) obtained from the unetched surface has a peak at 531.8 eV and a shoulder 1.5 eV lower than the peak, showing different chemical states of oxygen. By etching for 0.3 min, the peak at 531.8 eV disappears rapidly and the shoulder on the lower binding energy side developed into a small peak. The O 1s spectrum disappears by subsequent etching.

Metallic Ni is indicated by the peak at 852.8 eV in all the spectra in (c). The unetched surface (0 min) has a peak at 852.8 eV of the metallic state and a shoulder 3.2 eV higher than the metallic one.

The depth variation of concentration (at %) of Cr, O, and Ni for the as-polished specimen is shown in Fig. 2, showing that oxygen decreases remarkably and Ni increases by etching for 0.3 min.

2. Specimen Treated by Conc. HNO_3 Solution

Figure 3 shows a set of spectra obtained from different depths of a specimen treated by conc. HNO_3 solution, (a) is the Cr $2p_{1/2,2/3}$ spectra, (b) the O 1s spectra, and (c) Ni $2p_{3/2}$ spectra. At the unetched surface, there is a difference in both intensity ratios of a peak at 577.3 eV or 576.8 eV vs. a shoulder at 574.3 eV in the Cr $2p_{3/2}$ spectrum and a peak at 530.1 eV vs. a shoulder at 531.6 eV in O 1s spectrum between the as-polished (Fig. 1 (a) and (b)) and conc. HNO_3 treated specimens. This will be discussed later.

Figure 4 shows the concentration variations of Cr, O, and Ni in the depth direction for the

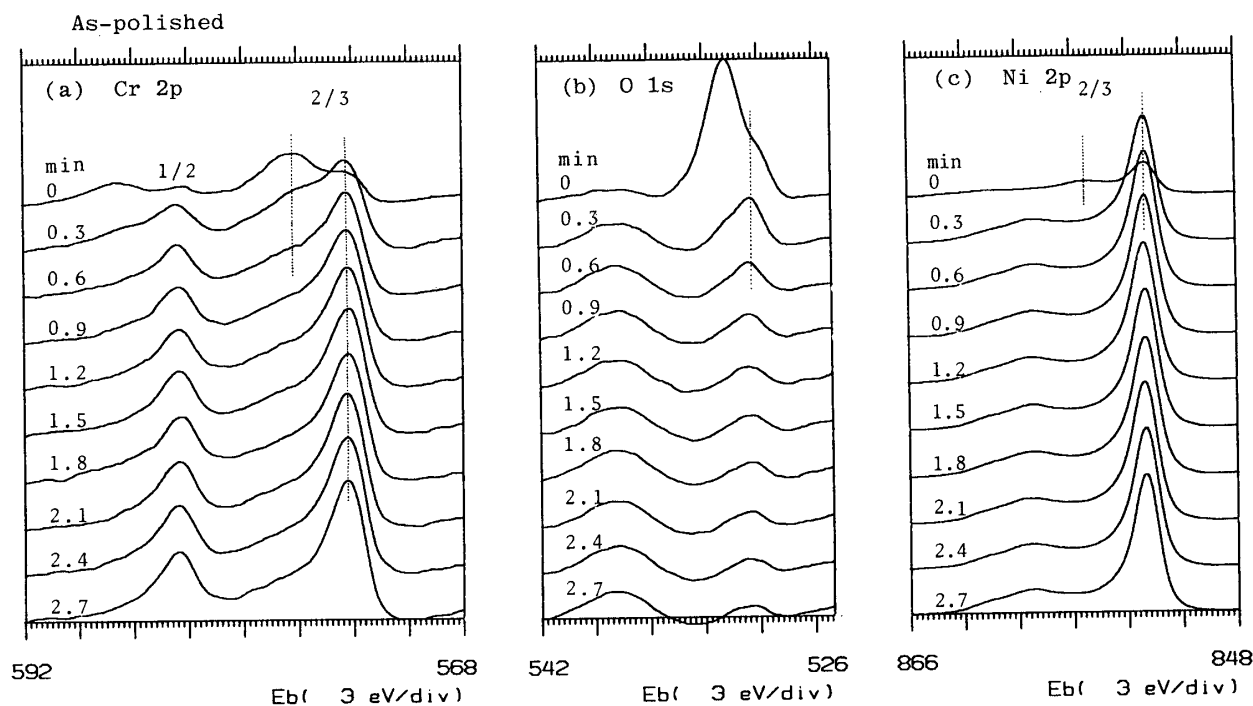


Fig. 1 Cr 2p(a), O 1s(b), and Ni 2p(c) spectra at different depths obtained from as-polished specimen, by varying the argon ion etching time(in min).

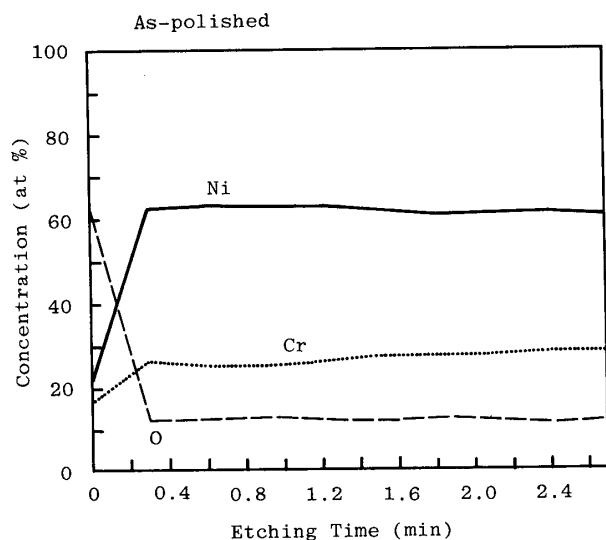


Fig. 2 Depth variation of concentration(at %) of Cr, O, and Ni for as-polished specimen.

specimen treated by conc. HNO_3 solution. At the unetched surface(0 min), concentrations of Cr and Ni are 25% and 13% for the conc. HNO_3 treated specimen and 17% and 21% for the as-polished specimen(Fig. 2). It shows that Cr concentrates at the alloy surface by treatment with conc. HNO_3 solution. With argon ion etching, the oxygen concentration of Fig. 4 decreases slower than that of Fig. 2 for the as-polished specimen, indicating that a thicker passive film forms on the alloy surface after treating with conc. HNO_3 solution.

3. Chemical Changes of Chromium by Treatment with Conc. HNO_3 Solution

For comparison with the chemical states of Cr, Fig. 5 shows a set of Cr 2p spectra obtained from four specimens, the unetched surface of the as-polished specimen in Fig. 1(a) and the HNO_3 treated specimen in Fig. 3(a), Cr_2O_3 , and metallic Cr. A 2.5 eV chemical shift is observed between Cr^{3+} and the metallic Cr state. The major peak of Cr $2p_{3/2}$ for the HNO_3 treated specimen coincides with the peak of the Cr^{3+} state. The as-polished specimen of Cr $2p_{3/2}$ has a peak of 0.5 eV higher binding energy than the Cr^{3+} state, indicating a higher oxidation state than the Cr^{3+} state. Both Cr $2p_{3/2}$ spectra of the as-polished and HNO_3 treated

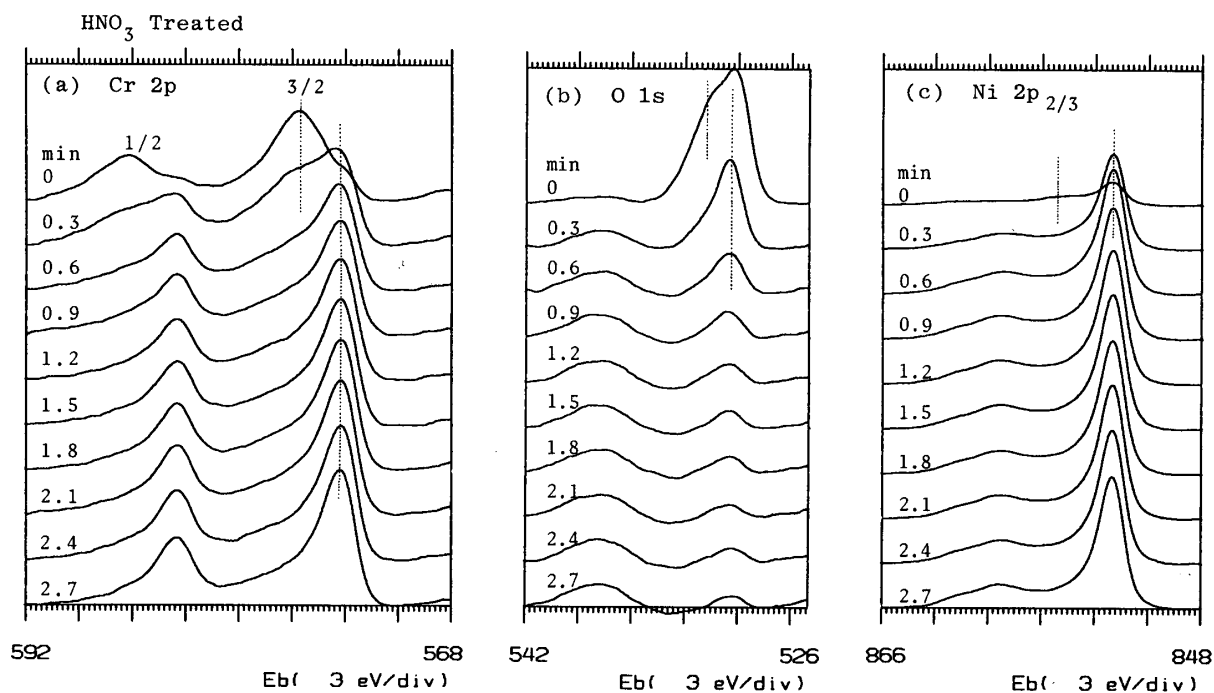


Fig. 3 Cr 2p (a), O 1s (b), and Ni 2p (c) spectra at different depths obtained from as-polished specimen, by varying the argon ion etching time (in min).

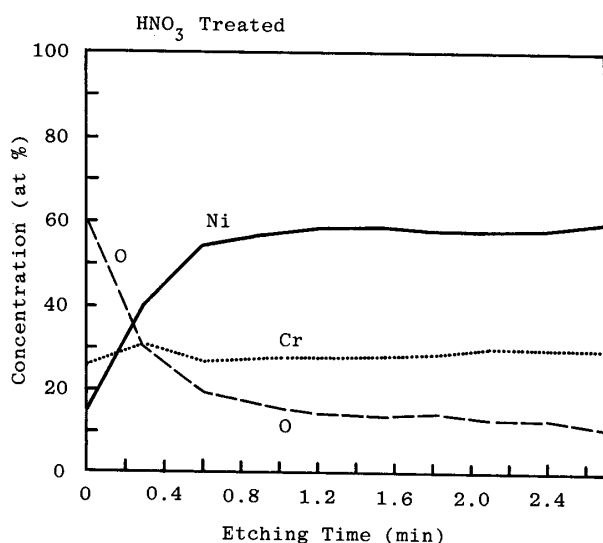


Fig. 4 Depth variation of concentration (at %) of Cr, O, and Ni for HNO₃ treated specimen.

specimens have a shoulder at the position of the metallic state. The intensity ratio for the as-polished specimen, metallic/oxidation state, is larger than that for the HNO₃ treated specimen.

On stainless steel the passive film is amorphous and 30 Å to 60 Å thick. The passive film is a two dimensional inorganic polymer which coordinates O²⁻, OH⁻, and H₂O around Cr³⁺.⁵⁾ It appears that the metallic Cr was detected from the substrate under the passive film, and the detection of the metallic Cr in both the specimens shows the formation of a film of ca. 10 Å because the mean free path of the

photoelectron ejected from the Cr 2p shell is ca. 10 Å.⁶⁾ However, the lower intensity ratio of the metallic/oxidation state for the HNO₃ treated specimen than that for the as-polished specimen shows a thicker film on the HNO₃ treated surface than on the as-polished surface.

4. Chemical Changes of Oxygen by Treatment with Conc. HNO₃ Solution

To clarify the changes of the oxygen chemical state, Fig. 6 shows a set of O 1s spectra obtained from the unetched surface of the as-polished in Fig. 1(b) and the HNO₃ treated specimen in Fig. 3(b) with O 1s obtained from Cr₂O₃. For the HNO₃ treated surface the major

peak position coincides with the peak of Cr_2O_3 and the shoulder agrees with the major peak of the as-polished specimen. The spectrum for the as-polished surface has a shoulder at the peak of Cr_2O_3 . This shows different oxygen chemical states: One is O^{2-} state and the other is an unknown state.

By use of the data analysis system included in the ESCA spectrometer, separation of oxygen states on the O 1s spectra was performed by assuming that the spectra are approximated by a Gaussian function. Figures 7 and 8 show the separated spectra of O 1s, obtained from the as-polished and HNO_3 treated specimen as shown in Fig. 6. Both O 1s spectra can be separated into three components indicated by the dotted line. The solid line, the observed spectra, agrees well with the chained line which is composed of the three components. Table 1 lists the peak position and area fraction of the components. The peak positions show the chemical states of oxygen and the area fractions give the amount of each chemical state. The O 1s spectra component I is the same chemical state as the oxygen in Cr_2O_3 as shown in Fig. 6. The oxygens of components II and III exist in the upper part of component I oxygen because these oxygens decrease remarkably by only a little argon ion etching as shown in Figs. 1(b) and 3(b).

From the above, the origins of these oxygen states are estimated as follows: Component

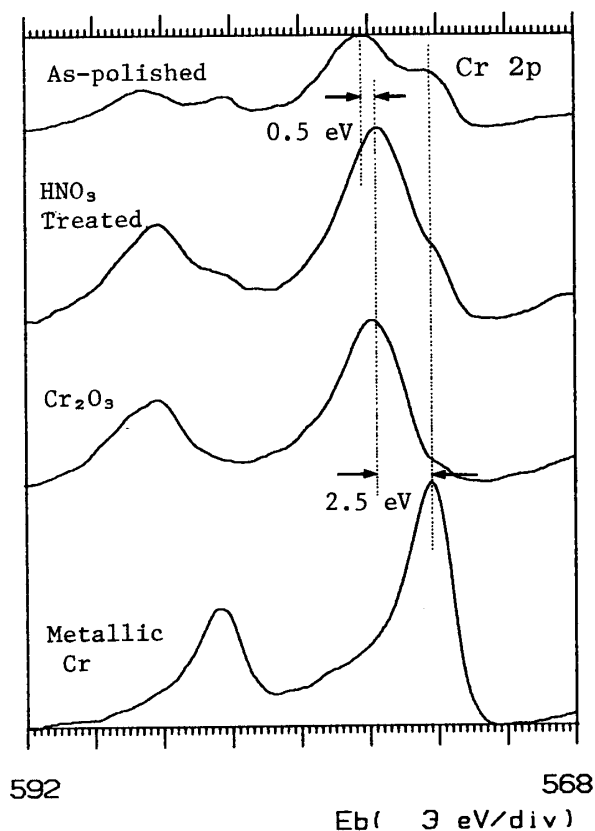


Fig. 5 Cr 2p spectra obtained from four specimens, as-polished alloy surface (unetched), HNO_3 treated alloy surface (unetched), Cr_2O_3 , and metallic Cr.

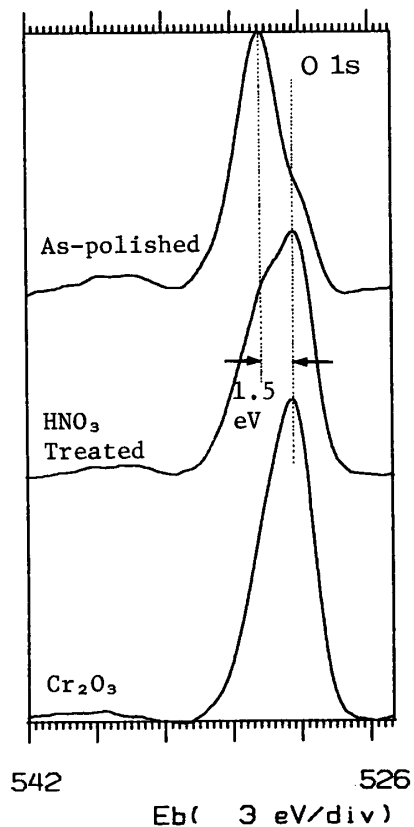


Fig. 6 O 1s spectra obtained from three specimens, as-polished alloy surface (unetched), HNO_3 treated alloy surface (unetched), and Cr_2O_3 .

I is due to oxygen bonded with chromium in the passive film, Cr-O-Cr; Component II is due to oxygen bonded with both chromium and hydrogen in the passive film, Cr-OH · · · OH₂; Component III is due to oxygen in physisorbed water molecules on the passive film. The area fractions are in the order II>I>III for the as-polished surface and I>II>III for the HNO₃ treated surface, indicating that a firm passive structure is formed on the surface treated by HNO₃ solution.

5. Surface Structure and Adhesive Ability

Adhesion depends on the atomic interaction which is determined by the atoms less than 10 Å from the top surface.⁷⁾ We have examined the adhesive ability of the 4-META resin on the clean metallic surface without passive or oxide films, obtained by the reduction method by use of hydrogen gas.⁸⁾ This clarified the chemical interaction between metal atom and polarity of the 4-META side-chain: The adhesive ability to metallic Ni is lower than that to metallic

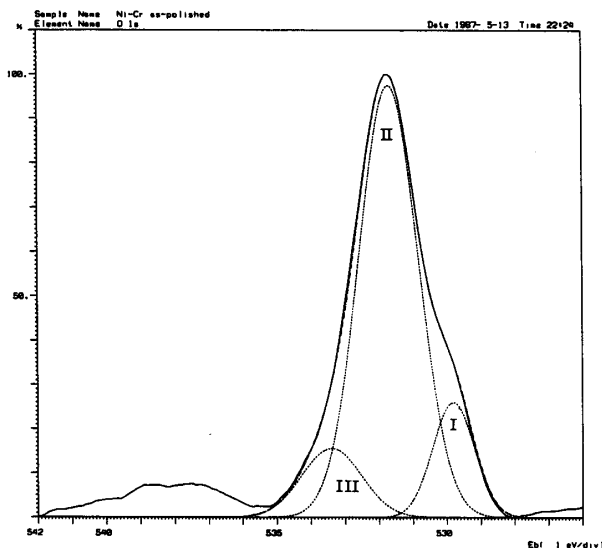


Fig. 7 O 1s spectra obtained from as-polished specimen (unetched), separated into three components.

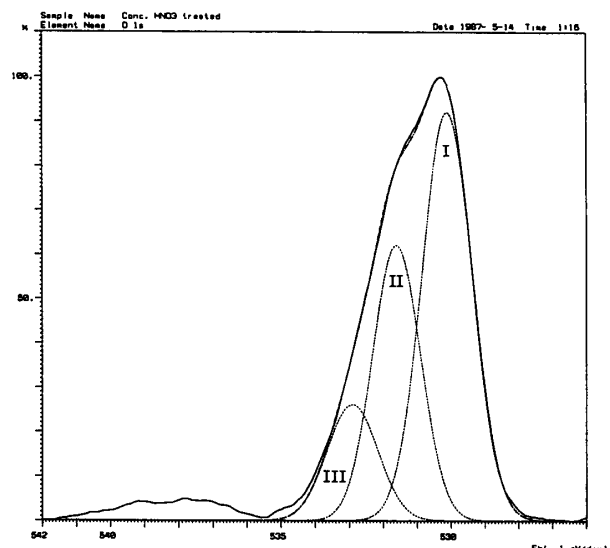


Fig. 8 O 1s spectra obtained from HNO₃ treated specimen (unetched), separated to three components.

Table 1 Peak position and area fraction of three components in O 1s spectrum shown in Figs. 7 and 8.

O1s Spectra Component	As-polished		HNO ₃ Treated	
	Peak Position (eV)	Area (%)	Peak Position (eV)	Area (%)
I	529.8	14	530.1	52
II	531.7	74	531.6	33
III	533.4	12	532.9	15

Cr.

The Ni content decreases at the alloy surface by Ni eluting to the HNO₃ solution, so that Cr which has a good chemical affinity for the 4-META resin concentrates on the alloy surface, resulting in the formation of a firm and thick passive film. This leads to an increase in the adhesive ability of the 4-META resin on the passive film.

ACKNOWLEDGMENT

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Ni-Cr 合金の濃硝酸処理による接着性向上の ESCA による解析

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Ni-Cr 合金を濃硝酸で処理すると研磨したままの場合よりも接着性レジン (4-META/MMA-TBB) に対する接着性が著しく向上する。その理由を解明するために硝酸処理と研磨したままの合金表面をX線光電子分光分析装置 (ESCA) で分析し、両者の表面構造を解析した。

研磨したままの合金表面における Ni と Cr の濃度は、Ni 21at%, Cr 17% であるが、硝酸処理を施すと Ni 13%, Cr 25% になった。硝酸処理によって合金表面で、4-META レジンに対する親和性の劣る Ni が減少し、親和性の優れた Cr が増加した。また、O 1s スペクトルを解析すると、次の3つの酸素に由来する成分に分解された。成分 I は不動態被膜の Cr-O-Cr に由来する酸素、II は不動態被膜中の Cr-OH \cdots H₂O に由来する酸素、III は被膜上に存在する吸着水に由来する酸素である。これらの成分の存在比は、研磨したままでは、II > I > III の順であるが、硝酸処理では、I > II > III になった。これらは、硝酸処理によって、4-META レジンに対する接着性が優れている不動態被膜が強固に形成していることを示す。