Electronic structure of the L-cysteine films on dental alloys studied by ultraviolet photoelectron spectroscopy

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Abstract. The valence electronic structures of the dental alloys, type 1, type 3, K14, and MC12 and their interaction with L-cysteine have been studied by ultraviolet photoelectron spectroscopy with synchrotron radiation. It was found that the electronic structures of the type-1 and type-3 dental alloys are similar to that of polycrystalline Au, while that of the K14 dental alloy is much affected by Cu. The electronic states of the MC12 dental alloy originate dominantly from Cu 3d states and Pd 4d states around the top of the valence bands, while the 4–7-eV electronic structure of MC12 originates from the Ag 4d states. The peak shift and the change in shape due to alloying are observed in all the dental alloys. For the L-cysteine thin films, new peak or structure observed around 2 eV on all the dental alloys is suggested to be due to the bonding of S 3sp orbitals with the dental alloy surfaces. The Cu-S bond as well as the Au-S and Au-O bonds may cause the change in the electronic structure of the L-cysteine on type 1, type 3 and K14. For MC12, the interaction with L-cysteine may be dominantly due to the Pd-S, Cu-S, and Ag-O bonds, while the contribution of the Ag-S bond is small.

1. Introduction
Dental casting alloys are categorized into noble and base metal alloys. Noble dental alloys consist of Au, Ag, Cu, Pd, Pt, and other elements\cite{1}. Anti-corrosive nature of the noble metals is the reason of their use with a long history. However, they are not completely immune to corrosion. When these alloys are used for dental restoration, they are repeatedly exposed to proteins contained in foods. It is therefore interesting to investigate the valence electronic structures of the dental alloys and their interaction with amino acids.

Amino acids are building blocks of protein, which is the dominant component of the living things. They are normally restricted to twenty kinds of L-form \(\alpha\)-amino acids and only two of them contain sulfur\cite{2}. Cysteine \([\text{HS-CH}_2\text{-CH(NH}_2\text{)-COOH}]\) is one of the two such amino acids, and contains a sulfanyl group in its \(-\text{CH}_2\text{SH}\) side chain. The sulfanyl group (-SH) plays essential and ubiquitous roles in biology and bioelectronics\cite{3}. For examples, the proteins involving an amino-acid cysteine are related to the movement of living cells and ion channel cell\cite{4}. The formation of a disulphide bond between two cysteine residues results in the unraveling of the \(\alpha\)-helix and the distortion of the ligand-binding groove\cite{5}. In order to investigate the functionality of cysteine, we measured the electronic structures of L-cysteine using ultraviolet photoelectron
spectroscopy (UPS) with synchrotron radiation[6]. It was revealed that the highest occupied molecular orbital (HOMO) of L-cysteine consists mainly of the S 3sp orbitals.

Recently, much interest from the basic bioscience and bioelectronics focuses on the amino-acid cysteine on well-defined metallic surfaces and its adsorption geometry, chemical reaction, electrical function, and so on. Experimental and theoretical investigations on the cysteine/Au system showed interesting findings[7–11]. Beerbom et al. conducted a UPS measurement on L-cysteine film prepared by dipping on polycrystalline Au[7]. Although they succeeded to observe the photoelectron spectrum of L-cysteine thick film which fairly agrees with that in the present study, they had a difficulty in observing a weak signal from the interface between L-cysteine and the substrate. Canepa et al. performed metastable deexcitation spectroscopy (MDS) for L-cysteine thin films on the surfaces of Au, Ag, and Cu single crystals[8, 9]. Since MDS is very sensitive to the molecular orbitals protruding on the vacuum side from the film surface only, they could not detect the interfacial state between L-cysteine and the substrates. Therefore, there is still a lack of thorough investigation on the valence electronic structures of L-cysteine thin films on metallic surfaces so far. Previously, we measured the photoelectron spectra of the thick and thin L-cysteine films on the dental alloy, type 1, and found the difference between them due to the interaction of L-cysteine with the dental alloy surface[12]. In order to study the interaction of L-cysteine with the dental alloy surfaces in more details, the UPS spectra of the L-cysteine films with the thickness of 3 Å on four dental alloys including type 1 have been carefully measured under the same conditions in the present study[13].

2. Experimental
UPS experiments were carried out at the Saga-University beamline BL13 in the Saga Light Source[14]. Synchrotron radiation was provided from the 1.4-GeV storage ring and monochromatized using a plane-grating monochromator[15]. For photoelectron spectroscopy, a hemi-spherical electron analyzer, MBS A-1, was used with a pass energy of 10 eV, corresponding to a resolution of about 40 meV. UPS spectra were obtained with the photon energy (hν) of 40 eV, where the overall resolution involving the monochromator and photoelectron spectrometer was checked by measuring the Fermi edge of Au to be about 100 meV.

Four types of dental casting alloys, type 1, type 3, K14 and MC12[1], were studied in the present study. type 1 (Casting Gold M.C. Type I), K14 (M.C. Gold Alloy) and MC12 (Castwell M.C. Gold 12 %) were purchased from GC Corporation (Japan), while type 3 (Casting Gold M.C. Type III) was obtained from ISHIFUKU Metal Industry Co., Ltd. (Japan). The compositions of the alloys supplied from the manufacturers are shown in Tab. 1. Four polycrystalline metallic plates, Ag, Cu, Pd, and Au were purchased from Nilaco Corporation (Japan). Before measurements, the surface of these alloys and metals was cleaned up by Ar⁺ ion sputtering with 0.5 kV in the sample-preparation chamber whose base pressure was about 8 × 10⁻⁸ Pa. The samples were transferred from the sample-preparation chamber to the analyzing chamber without exposing to air. UPS measurements were carried out in the analyzing chamber whose base pressure was about 4 × 10⁻⁸ Pa. The UPS spectra of polycrystalline Au, Ag, Pd and Cu plates were measured under the same conditions for comparison.

The L-cysteine films were prepared on the dental alloys by means of vacuum deposition. Powder samples of L-cysteine were purchased from Wako Pure Chemical Industries, Ltd. (Japan). The evaporation chamber was evacuated with a turbo molecular pump to about 4 × 10⁻⁵ Pa. A quartz thickness gauge was used to monitor the thickness of the deposited films. The deposition rate was set to be 0.3 Å/s. The L-cysteine films prepared on the alloys were transferred in situ to the analyzing chamber. It has already been confirmed with Raman scattering and atomic force microscopy that smooth L-cysteine films can be formed without decomposition in the present vacuum deposition method[6].
Table 1. The composition of the type-1, type-3, K14, and MC12 dental alloys.

| Alloy | Composition (atomic%) |
|-------|-----------------------|
|       | Au  | Ag  | Pt  | Pd  | Cu  |
| type 1| 69  | 18  | 0   | 0   | 13  |
| type 3| 54  | 14  | 2   | 3   | 24  |
| K14   | 37  | 19  | 0   | 4   | 41  |
| MC12  | 6   | 43  | 0   | 19  | 32  |

3. Results and discussion

Figure 1 shows the UPS spectra of the four dental alloys taken at $h\nu=40$ eV. The UPS spectra of polycrystalline Au, Ag, Pd, and Cu are also shown. Each UPS spectrum of the dental alloys and metals shows characteristic structures reflecting different valence electronic states. In the spectrum of polycrystalline Au, there are Au $5d_{5/2}$ and Au $5d_{3/2}$ peaks about 3.0 and 6.0 eV, respectively[16,17]. A peak about 4.2 eV and a shoulder about 6.6 eV observed on polycrystalline Ag are attributed to Ag $4d_{5/2}$ and Ag $4d_{3/2}$, respectively [16,18]. The Pd $4d$ states have the large density of states in the range of 0–4 eV. For polycrystalline Cu, a prominent peak from 3d states locates at 2.7 eV [17,19]. We can understand the electronic structures of the dental alloys by comparing the UPS spectra in Fig. 1 and also by referring the existing reports on the electronic structures of metals and alloys[16–19].

The spectral features of type 1 and type 3 in the range of 2.0–8.0 eV are very close to each other, and also they are in good agreement with that of polycrystalline Au because of the large content of Au, but the details are slightly different between them. In the present study, we synthesized the spectra for each alloy by simply summing the observed spectra of polycrystalline metals weighted according to the composition listed in Tab. 1. The synthesized spectrum for type 1 fairly agrees the features of the observed one with some exceptions (not shown). The peak at ~6 eV in the synthesized spectrum was much smaller than that in the observed one. The difference may be due to the peak shifts of Au $5d$ and Ag $4d$ states upon alloying[16]. The discrepancy between the observed and the synthesized spectra for type 3 was much bigger than for type 1. One of the differences is the shoulder around 1.0–2.0 eV which may be due to peak shift upon alloying of the Cu 3d states increased in type 3[17]. On the other hand, the peaks and shoulders are observed in the range of 1.0–8.0 eV for the UPS spectra of K14 and MC12 which are not similar to that of polycrystalline Au. Since the shoulder around 1.9 eV in the spectrum of K14 is close to that of polycrystalline Cu, it may be due to the Cu 3d states with a small energy shift just as observed for type 3. Since the Au 5d states appear in the range of 2.0–8.0 eV and also the peaks due to the Ag $4d$ states exist at 3.8–7.7 eV, the peaks in the range of 2.3–8.0 eV in the K14 are attributed to the mixture of Au $5d$ and Ag $4d$ states with small shifts and changes in shape. Since the Pd $4d$ and Cu 3d states have the large density of states in the range of 0–4 eV and 2–4 eV, the structure of MC12 in the range of 1–4 eV may be due to the Pd $4d$ and Cu 3d states. The peaks at ~5.0 and ~6.3 eV are due to these Ag $4d$ states. In summary, the electronic states of type 1 originate dominantly from Au and additionally from Ag and Cu as constituents, and those of type 3 originate dominantly from Au and largely from Cu with additional contribution from Ag. The electronic states of K14 originate from Au, Ag, and Cu, while those of MC12 originate dominantly from the Cu 3d and Pd $4d$ states around the top of the valence bands and the 4–7-eV structure originates from the Ag $4d$ states. The electronic structures of the dental alloys are not a simple sum of those of the constituents, showing energy shifts and changes in shapes upon alloying.
Figure 1. Photoelectron spectra of the dental alloys, type 1, type 3, K14, and MC12 taken at $hν=40$ eV. Photoelectron spectra of polycrystalline Au, Ag, Pd and Cu measured under the same conditions are also shown for comparison.

Figure 2. Photoelectron spectra of the L-cysteine thick and thin films on the dental alloys, type 1, type 3, K14, and MC12 taken at $hν=40$ eV. Photoelectron spectra of the L-cysteine thin films on polycrystalline Ag, Cu, Pd, and Au taken under the same conditions are also shown for comparison. At the bottom is the total and partial photoelectron spectra of L-cysteine molecule which are calculated by using the molecular orbital calculation and photoionization cross sections. Vertical lines are drawn as a mere guide to eyes.

Figure 2 shows the UPS spectra of L-cysteine thin films on the dental alloys with the thickness of 3 Å. The contribution of the substrates and the background due to inelastic scattering were subtracted on the assumption that the intensity just below the Fermi edge is due to the dental alloys and the background due to inelastic scattering is sufficiently smooth with no structure. In Fig. 2, the spectra of the L-cysteine thin film on polycrystalline Au, Ag, Pd, Cu and of the L-cysteine thick film (60 Å), which were measured under the same conditions, are also shown for comparison. The spectra of the L-cysteine thin films are apparently different from that of the thick film, which clearly indicates that they exhibit the electronic structures of L-cysteine interacting with the substrate dental alloys at interface. An additional peak appears around 2 eV for type 1, type 3, K14 and an additional structure appears for MC12 similar to polycrystalline Pd. The peak around 5 eV shifts to the lower binding energy side for type 1, type 3, and by 0.2 eV, while the peak for K14 shifts only by 0.1 eV. There is no appreciable shift for MC12. The structure around 7 eV changes for type 1 and MC12, but not for type 3 and K14. The peaks at 9 and 13 eV are relatively insensitive to the substrates. These discrepancies are due to the different interaction between the L-cysteine thin films and the substrate surfaces as explained below.
In order to understand the interaction, the electronic structure of L-cysteine molecule is required. In the previous study, the photoelectron spectra and HOMO and lowest unoccupied molecular orbitals of L-cysteine molecule were calculated using a molecular-orbital (MO) calculation and the photo-ionization cross section[6]. The MO calculation was carried out using the Gaussian03 program with the DFT B3LYP/6-311+G(d, p) method. The values of the photo-ionization cross section were taken from the well-known data[20]. The good agreement between the calculated and observed spectra of L-cysteine showed that the C3 geometry may be the most probable geometry among the seven possible geometries of cysteine molecule (C1~C7). The calculated UPS spectra of L-cysteine molecule is shown in Fig. 2. The partial photoelectron spectra of constituent elements of O and S are also shown for convenience. Figure 2 clearly shows that the HOMO originates from the S 3sp orbitals, and the peaks around 5.0 and 7.4 eV are due to the O 2sp orbitals.

The additional peak at ~2 eV on the L-cysteine thin films in Fig. 2 locates at the position very close to the valence states derived from the Au 5d and Cu 3d states in Fig. 1 and the S 3sp orbitals of L-cysteine in Fig. 2. Therefore, the formation of orbital bonding may occur between the Au 5d and Cu 3d states and S 3sp orbitals. The peak at 5 eV on the L-cysteine thick film shows some shifts to 4.9 eV and 4.8 eV on the thin films because of the interaction with the substrates. The O 2sp orbitals of L-cysteine exist around 5.0 eV as shown in Fig. 2. The large density of states (DOS) originating from the Au 5d and Ag 4d states exist around 4 eV. So, the interaction between the Au 5d and/or Ag 4d states and O 2sp orbitals may cause the shift of the 5-eV peak. The structure around 7 eV changes for type 1, MC12 and polycrystalline Au, but not for type 3, K14 and polycrystalline Ag. The DOS originating from the Au 5d and Ag 4d states extend in this energy as in Fig. 1. The O 2sp orbitals are dominant in the energy range in Fig. 2. Therefore, the interaction of the Au 5d states with O 2sp orbitals may change the 7-eV structure in type 1. The interaction of the Ag 4d states with the O 2sp orbitals may also change the 6~8 eV structure because MC12 has a strong peak mainly due to the Ag 4d_3/2 states at 6.3 eV upon alloying with Cu and Pd while the interaction between the Ag 4d states and O 2sp orbitals may be weak on polycrystalline Ag.

In conclusion, for the L-cysteine thin film on type 1, the new peak around 2 eV, the energy shift of the 5-eV peak, and the 7-eV shoulder structure are due to the Au-S, Au-O, and Au-O bonds, respectively according to the discussion above. Similar Au-S and Au-O bonds may be formed for the L-cysteine thin film on type 3, resulting in the 2-eV new peak and the shift of the 5-eV peak. The Cu-S bond may also contribute to the 2-eV peak, and a little more Cu atoms on the surface may hinder the formation of Au-O bond, resulting in the smaller 7-eV shoulder. For the L-cysteine thin film on K14, the energy position of the 2-eV peak is slightly different with others. The energy shift of the 5-eV peak is smaller for K14, even though the amount of Ag in K14 is not so different from those in type 1 and type 3. The 7-eV shoulder is not appreciable on K14. These differences may be due to the contributions from Cu since its composition is much higher. So, the Cu-S bond may contribute to the 2-eV peak, and Cu atoms on the surface may hinder the formation of Au-O bond, resulting in the small shift of the 5-eV peak and the smaller 7-eV shoulder just as for type 3. For the L-cysteine thin film on MC12, the spectrum shows only a small and broad structure around 2 eV just as the thin film on polycrystalline Ag. Therefore, it is supposed that the Ag-S bond is not strong, although Ag is the most dominant component in MC12. This may be due to the energy difference between the Ag 4d states and S 3sp orbitals and the shielding effect by conducting electrons from Cu and Pd components in MC12. The interaction of the S 3sp orbitals with Pd 4d and Cu 3d states may result in the broad structure around the top of the valence band. The energy shift of the 5-eV peak is not observed in Fig. 2. This may be due to the strong interaction of the Ag 4d states with the O 2sp orbitals. The interaction of the Ag 4d states with the O 2sp orbitals may also change the 6~8 eV structure.
4. Summary
The electronic structures of the dental alloys, type 1, type 3, K14, and MC12 and their interaction with L-cysteine have been studied by UPS using synchrotron radiation. It was found that the electronic structures of type 1 and type 3 are similar to that of polycrystalline Au, while that of K14 and MC12 are much affected by Cu and Ag, respectively. The peak shifts and the changes in shape upon alloying are also observed in all the dental alloys. It should be noted that these electronic structures play an important role for the chemical interaction of the dental alloys with L-cysteine.

For the L-cysteine thin film on type 1, it was found that the electronic structure is almost identical with that on polycrystalline Au and is close to those on type 3 and K14 with some differences. A new peak or structure was observed around 2 eV for the L-cysteine thin films on all the dental alloys and elemental metals, while the 5-eV peak shifted to the lower binding energy side on type 1 and type 3 by 0.2 eV and on K14 by 0.1 V, and there was no appreciable shift on MC12. The 7-eV shoulder was observed on type 1 and MC12. It is suggested that the new peak or structure observed around 2 eV for the L-cysteine thin films on all the dental alloys may be due to the bonding of S 3sp orbitals with the dental alloy surfaces forming Au-S, Cu-S and Pd-S bonds, while the contribution of the Ag-S bond is small. The Au-O bond may be responsible for the shift of the 5-eV peak and the 7-eV shoulder. We believe that the deeper understanding of the electronic structure of L-cysteine films on the dental alloys leads to the improvement of dental alloy toward perfect anti-corrosive nature against amino acids.

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