Effect of (–)-epigallocatechin gallate on electrochemical behavior and surface film composition of Co-Cr alloy used in dental restorations

Guangyan QIAO^{1,2}, Jiansheng SU¹ and Meifeng HE³

¹Department of Prosthodontics, School of Stomatology, Tongji University, Shanghai 200072, China

²Department of Prosthodontics, Shanghai Stomatological Disease Center, Shanghai 200001, China

³State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200240, China

Corresponding author, Jiansheng SU; E-mail: g_y_qiao@126.com

The aim of this study was to investigate the electrochemical behavior of Co-Cr alloy in artificial saliva containing (–)-epigallocatechin gallate (EGCG) and to characterize the composition and structure of the passive film formed by potentiodynamic polarization. Electrochemical measurements ranked the corrosion resistance of Co-Cr dental cast alloy as follows when exposed to artificial saliva containing different concentrations of EGCG: 4.0 g/L > 2.0 g/L > 0 g/L > 0.5 g/L > 1.0 g/L. This showed that the concentration of EGCG in artificial saliva affected the corrosion behavior of Co-Cr alloy. X-ray photoelectron spectroscopy (XPS) results revealed that the outermost surface layer on Co-Cr alloy was mainly composed of Cr₂O₃ and EGCG-Cr (III) ion complex, which were formed by redox and complex formation reactions respectively. When the redox reaction was dominant, Co-Cr alloy exhibited high corrosion resistance in EGCG-containing artificial saliva. On the contrary, when the complex formation reaction was dominant, Co-Cr alloy exhibited low corrosion resistance.

Keywords: (–)-Epigallocatechin Gallate (EGCG), Dental material, Co-Cr alloy, Corrosion resistance, XPS

INTRODUCTION

Cast Co-Cr alloy is the material of choice for prosthodontic restorations, especially in developing countries, because of these cost- and function-related advantages: good physical and mechanical properties, excellent corrosion resistance, high biocompatibility, and low cost^{1–4}. Though well-known for their excellent corrosion resistance in the human body, Co-Cr alloys could undergo electrochemical corrosion when exposed to an electrolyte-rich fluid medium in the oral cavity^{5,6}.

The corrosion properties of metal alloys depend on a number of factors: alloy composition, potential values, strain rate, surface roughness, degree of oxidation, acidity (pH) and temperature of media, mixing velocity of solution, and the presence of corrosion inhibitors⁷. The oral cavity, on the other hand, is a dynamic environment that often undergoes rapid and substantial changes in temperature and pH, typically instigated by changes in the diet and unconscious regular contact with metal ions (arising from contact with fixed orthodontic appliances such as brackets, bands, and archwires). It is also a complex environment involving biological interactions contributed by a continuous flow of saliva and microbiological activity. Other factors that place severe demands on restorative materials in the oral cavity include occlusal loading, which results in mechanical wear and corrosion⁸.

Corrosion of a metal prosthesis in the mouth releases metal ions, which then come into contact with cells and tissues in the immediate environment, and are

subsequently distributed throughout the entire body^{9,10}. Metal ions released from dental cast alloys not only produce adverse effects on the morphology, viability, and proliferation rate of gingival fibroblasts, they also result in increased cytokine levels of Interleukin 2 (IL-2) and Interleukin 6 (IL-6)^{11–15}.

Tea has been consumed in many countries for a very long time. It is ranked as the second most popular beverage in the world after water. Today, there is an intense growing interest in the health benefits of tea, as evidenced by the many published reports on how tea could help prevent several chronic diseases. (–)-Epigallocatechin-3-gallate (EGCG) is the most important bioactive component in green tea and reportedly exhibits antimutagenic, antibacterial, antioxidant, antitumor, and cancer-preventive activities^{16–20}.

Many researches have focused on the interactions of catechins with metal ions and their biological significance^{21–23}. It was found that catechins could engage in redox reactions or chelating interactions with metal ions, especially transition metal ions, under different conditions²⁴, consequently changing their metabolism and bioactivities. In the oral environment, Co-Cr alloys have regular contact with tea beverages. Such contact or interaction may affect the corrosion resistance of Co-Cr alloys, causing metal ions to be released from alloys during tea drinking. However, the effect of tea drinking on the corrosion resistance and metal ion release behavior of Co-Cr dental cast alloys in artificial saliva containing EGCG remains to be investigated.

The aim of this study was to investigate the corrosion behavior of Co-Cr alloy in artificial saliva

Color figures can be viewed in the online issue, which is available at J-STAGE.

Received Jul 25, 2011; Accepted Mar 27, 2012

doi:10.4012/dmj.2011-159 JOI JST.JSTAGE/dmj/2011-159

containing EGCG and to characterize the composition and structure of the passive film formed on the surface by means of X-ray photoelectron spectroscopy (XPS). The concentrations of metal ions released from Co-Cr alloy in artificial saliva with different concentrations of EGCG were measured using inductively coupled plasma mass spectrometry (ICP-MS).

MATERIALS AND METHODS

Co-Cr alloy sample preparation

In the present study, the selected Co-Cr dental cast alloy was composed of 61.0 wt% Co, 26.0 wt% Cr, 6.0 wt% Mo, 5.0 wt% W, and 2.0 wt% of other elements (Wirobond, BEGO, Germany). To prepare the alloy samples, investment casting was done using a sheet wax pattern of 10 mm diameter $\times$ 1.5 mm thickness. Alloy melting was done in a vacuum arc melting furnace under a protective argon gas atmosphere. All the alloy ingots were melted three times to ensure homogeneity.

Prepared alloy samples were mechanically polished using increasing finer grades of silicon carbide papers (400-, 600-, 800-, 1000-, and 1200-grit), followed by polishing with 1- μ m diamond paste. After polishing, the samples were successively cleaned with acetone, alcohol, and deionized water in an ultrasonic bath. Drying was done in a stream of warm dry air²⁵.

Electrochemical measurements

The corrosion behavior of Co-Cr alloy was investigated using three different electrochemical techniques: open circuit potential (OCP), potentiodynamic polarization (PD), and electrochemical impedance spectroscopy (EIS). All electrochemical measurements were conducted using an electrochemical workstation (PARSTAT 2273, Princeton Applied Research, USA). A three-electrode electrochemical cell was used. It comprised a saturated calomel electrode (SCE) as the reference electrode, a platinum foil as the counter electrode, and Co-Cr alloy as the working electrode. The Co-Cr alloy working electrode was placed in a flat cell such that only 0.785 cm² of surface area was exposed to the electrolyte solution. Calibration temperature was maintained at 37 $\pm$ 0.5°C by immersing the test cell in a water bath. All electrochemical tests were conducted only after Co-Cr alloy sample was immersed in the electrolyte for 24 h.

The electrolyte was modified artificial saliva^{26,27} of the following composition: KCl (0.4 g/L), NaCl (0.4 g/L), CaCl₂·2H₂O (0.795 g/L), NaH₂PO₄·2H₂O (0.78 g/L), Na₂S·2H₂O (0.005 g/L), and urea (1 g/L). The electrolyte solution was prepared using analytical-grade reagents and deionized water. pH value of artificial saliva was adjusted to 6.5 using NaOH.

The recommended daily green tea intake is 6–16 g, and it varies with age^{28,29}. About 20–30% of the total dry weight is green tea polyphenols, of which EGCG accounts for 60–80%. To investigate the effects of different EGCG concentrations on the corrosion behavior of Co-Cr dental alloy, five concentrations of EGCG (0 g/L, 0.5 g/L, 1.0 g/L, 2.0 g/L, 4.0 g/L) were prepared. 0.5 g/L of EGCG was

equivalent to 4–6 g/L of low-concentration tea solution; 1.0 or 2.0 g/L of EGCG was equivalent to 8–13 g/L of tea solution; and 4.0 g/L of EGCG was equivalent to 17–25 g/L of high-concentration tea solution.

OCP measurements were performed for 1,800 s, respectively, in artificial saliva containing five different EGCG concentrations (0, 0.5, 1.0, 2.0, 4.0 g/L). Potential was recorded as a function of measurement time. EIS and PD measurements were performed after OCP measurement. EIS measurements were carried out at respective OCP values with a sinusoidal signal amplitude of 5 mV over a frequency range of 100 kHz to 10 mHz. PD scans started from a cathodic potential of –1,000 mV/SCE relative to OCP and stopped at an anodic potential where the anodic current increased dramatically. Scanning rate was 1 mV/s. At least three measurements were performed for each EGCG concentration to confirm the validity of the measured polarization curves and EIS data.

Ion release measurement

ICP-MS (VG-X7, Thermo Electron Corp., USA) was used to measure the possible release of Co, Cr, and Mo ions into the electrolyte. For each EGCG concentration, a sample of the electrolyte solution was taken from the electrochemical cell after each OCP test to measure the concentrations of Co, Cr, and Mo ions released. At least three replicate measurements were performed for each solution sample. Ion release measurement results (given in μ g/L) were converted into μ g/cm² to be expressed in terms of per unit surface area of Co-Cr alloy.

Surface analysis

Using an X-ray photoelectron spectrometer (PHI 5000, Versa Probe, Japan) with monochromatized Al K α radiation (1486.6 eV), XPS measurements were performed to analyze the chemical compositions of and oxidation states of elements in the passive film after electrochemical measurements. Photoelectron take-off angle was set at 45° with reference to the sample surface. Vacuum in analyzing chamber was maintained at a level of 10^{–8} Pa during analysis. Binding energy was normalized to the C 1s peak (E_b =284.8 eV) of EGCG or complex on the sample. XPS data were converted to VAMAS format and imported into the XPSPEAK software package for manipulation and curve-fitting.

Statistical analysis

All measured data —namely, E_{corr} , E_b , ΔE , R_{ct} , and ion release measurement results of Cr, Co, and Mo ions— were statistically analyzed using one-way analysis of variance (ANOVA) and multiple comparisons test (LSD *post hoc* test) to examine the effect of the factor of EGCG concentration. Group means of 95% difference were considered to be statistically different.

RESULTS

Open circuit potential (OCP)

Figure 1 shows the potential *versus* time curves of Co-Cr

Fig. 1 Variation of open circuit potential (OCP) values of Co-Cr alloy in artificial saliva with different concentrations of EGCG.

dental cast alloy, which was exposed to artificial saliva containing five different concentrations of EGCG, over an immersion duration of 1,800 s. During the initial 400 s, the OCP values of Co-Cr alloy in different EGCG concentrations changed with time conspicuously. After the initial 400 s of immersion, the OCP values of Co-Cr alloy became stable in EGCG-containing salivary electrolytes.

During the entire immersion duration, the alloy sample exposed to 1.0 g/L of EGCG consistently showed the highest OCP among the five EGCG concentrations. At the end of 1800-s immersion period, the OCP value stabilized at around -169 mV/SCE. In sharp contrast, the sample exposed to 0 g/L of EGCG consistently showed the lowest OCP. At the end of immersion period, its OCP value stabilized at around -268 mV/SCE, to be followed by the OCP of sample exposed to 0.5 g/L of EGCG.

The alloy sample exposed to 4.0 g/L of EGCG showed active OCP variations, where OCP varied rapidly from its initial high value at -171 mV/SCE to a relatively stable value at -190 mV/SCE. The sample exposed to 2.0 g/L of EGCG showed moderate OCP variation from -233 mV/SCE to -247 mV/SCE.

OCP values attained with EGCG-containing salivary electrolytes were higher than that exposed to 0 g/L of EGCG. Relative OCP stability observed for EGCG-containing salivary electrolytes after 400 s of immersion illustrated that there were some slow and regular reactions on the surface of Co-Cr casting alloy. This could reflect the adsorption of electrolyte on alloy surface to reach a stable and saturated state.

Potentiodynamic polarization (PD) curves

Figure 2 shows the representative PD curves of Co-Cr alloy in artificial saliva containing different concentrations of EGCG over a potential range of $-1,500$ mV to $+1,500$ mV. The cathodic polarization

curves represented the cathodic hydrogen evolution reaction through water reduction, while the anodic ones represented the dissolution process of Co-Cr alloy.

The corrosion potentials (E_{corr}) in Fig. 2 were different from the OCP values in Fig. 1. Surface conditions of the electrodes could be modified by potentiodynamic polarization because potential sweep was applied from $-1,500$ mV; therefore, the potential drifts were reasonable³⁰. This is a common phenomenon in many electrochemical systems. Although the cathodic polarization curves satisfy the Tafel relation, drifts in corrosion potentials (E_{corr}) of the Co-Cr alloy samples resulted in their cathodic current densities not having a reference value.

In all the PD curves, the visible anodic current density plateau was attributed to the formation of some protective film on the surfaces of all the alloy samples. Then, the anodic portions of the PD curves exhibited a similar curve shape with a pronounced breakdown potential (E_b). After which, current densities were observed to increase rapidly with little associated increase in potential. Passive current density is defined as the minimum current density required to maintain passivity³¹. The passive current (corrosion rate with anodic protection) can be evaluated from anodic potentiodynamic polarization curves such as in Fig. 2. Passive current densities do not represent the steady-state values, which are lower, but rather a close approximation.

Table 1 shows the potential differences (ΔE) of Co-Cr alloys in artificial saliva containing different concentrations of EGCG. As EGCG concentration increased from 0 to 1.0 g/L, ΔE increased from $1,309.50 \pm 8.82$ to $1,416.00 \pm 21.64$ mV/SCE. As EGCG concentration increased from 2.0 to 4.0 g/L, ΔE decreased from $1,271.75 \pm 28.03$ to $1,223.00 \pm 54.89$ mV/SCE. Therefore, Co-Cr alloy exhibited the highest corrosion resistance in artificial saliva with a low concentration of EGCG at 1.0 g/L. Conversely, Co-Cr alloy exhibited the lowest corrosion resistance in artificial saliva with a high concentration of EGCG at 4.0 g/L.

Electrochemical impedance spectroscopy (EIS)

Changes in corrosion potential in artificial saliva containing different concentrations of EGCG should also be reflected in the electrochemical impedance properties of films formed on alloy surfaces. Figure 3 shows the EIS results of alloy samples in artificial saliva containing different concentrations of EGCG (0, 0.5, 1.0, 2.0, 4.0 g/L). Bode impedance plots of Co-Cr alloys clearly revealed the dependence of impedance on EGCG concentration in the base solution (artificial saliva), which was also reflected in the change in diameter of semicircles in the Nyquist plots.

For a better understanding of the controlled corrosion process, Fig. 4 shows the equivalent circuit for EIS measurements in this study. High frequency capacitance loop was mainly related to the characteristics of electric double layer formed at the interface between the metal surface and electrolyte, which can be

Fig. 2 Potentiodynamic polarization (PD) curves of Co-Cr alloy in artificial saliva with different concentrations of EGCG: (a) 0 g/L, (b) 0.5 g/L, (c) 1.0 g/L, (d) 2.0 g/L, and (e) 4.0 g/L.

Table 1 Values of E_{corr} , E_b , and ΔE of Co-Cr alloys in artificial saliva containing different concentrations of EGCG (mean $\pm$ SD, $n=4$)

	E_{corr}		E_b		ΔE	
0 g/L EGCG	-763.13 $\pm$ 22.99	A	546.50 $\pm$ 19.36	a	1309.50 $\pm$ 8.82	a'
0.5 g/L EGCG	-777.88 $\pm$ 12.89	A	564.88 $\pm$ 22.86	a	1346.75 $\pm$ 13.72	b'
1.0 g/L EGCG	-799.65 $\pm$ 21.11	A	605.10 $\pm$ 31.20	b	1416.00 $\pm$ 21.64	c'
2.0 g/L EGCG	-723.75 $\pm$ 34.80	B	548.00 $\pm$ 16.04	c	1271.75 $\pm$ 28.03	d'
4.0 g/L EGCG	-711.13 $\pm$ 67.39	B	512.00 $\pm$ 27.39	c	1223.00 $\pm$ 54.89	e'

Different letters (A–B, a–c, a'–e') indicate statistical differences between values within a vertical column (determined by one-way ANOVA ($p<0.05$)).

Fig. 3 Nyquist and Bode plots of Co-Cr alloy in artificial saliva with different concentrations of EGCG: (a) 0 g/L, (b) 0.5 g/L, (c) 1.0 g/L, (d) 2.0 g/L, and (e) 4.0 g/L.

Fig. 4 Equivalent circuit for EIS measurements in artificial saliva with different concentrations of EGCG.

described by R_{ct} and CPE^{32} . R_{ct} was the charge transfer resistance parameter which represented the resistance of electron transfer during electrochemical reactions at the interface between the electrode and solution³³, while CPE was the constant phase element. Taking the rough metal surface into account, CPE_{dl} was used instead of the electric double layer capacitance. R_s referred to the solution resistance.

As seen in Fig. 3, the Nyquist plots of both experimental and simulated data showed very good agreement. Table 2 shows the simulated data which were

Table 2 Values of the equivalent elements in the equivalent circuit of Co-Cr alloys in artificial saliva containing different concentrations of EGCG (mean±SD, $n=4$)

	R_s ($\Omega \cdot \text{cm}^2$)	CPE_{dl} ($\mu\text{F}/\text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	
0 g/L EGCG	131.65±20.83	35.08±11.17	5.291E5±1.419E5	A
0.5 g/L EGCG	112.40±49.07	25.00±8.13	1.074E6±0.717E6	A
1.0 g/L EGCG	130.16±25.96	38.78±13.27	3.245E6±1.385E6	B
2.0 g/L EGCG	149.48±57.47	48.95±20.03	1.754E4±0.774E4	A
4.0 g/L EGCG	157.38±39.53	67.76±43.55	8025±1496	A

Different letters (A, B) indicate statistical differences between values within a vertical column (determined by one-way ANOVA ($p<0.05$)).

Table 3 Concentrations of Co, Cr, and Mo ions released from Co-Cr alloys in artificial saliva containing different concentrations of EGCG (mean±SD, $n=4$)

	Cr ($\mu\text{g}/\text{cm}^2$)		Co ($\mu\text{g}/\text{cm}^2$)		Mo ($\mu\text{g}/\text{cm}^2$)	
0 g/L EGCG	2.83±0.38	A	9.49±0.73	a	0.45±0.039	a'
0.5 g/L EGCG	2.11±0.16	B	7.32±0.50	b	0.35±0.050	b'
1.0 g/L EGCG	1.42±0.28	C	4.47±0.86	c	0.22±0.045	c'
2.0 g/L EGCG	4.01±0.32	D	12.63±1.48	d	0.54±0.034	d'
4.0 g/L EGCG	4.98±0.30	E	16.86±1.28	e	0.69±0.073	e'

Different letters (A–E, a–e, a'–e') indicate statistical differences between values within a vertical column (determined by one-way ANOVA ($p<0.05$)).

Table 4 Concentrations of elements of the outermost surface layer on Co-Cr dental cast alloys after electrochemical corrosion in artificial saliva containing 0 and 1.0 g/L EGCG and before argon ion sputtering

Specimen (before argon ion sputtering)	Element concentration (at% and wt%)							
	Cr2p3	Co2p3	Mo3d	C1s	O1s	Si2p	W4f	Fe2p3
0 g/L EGCG (at%)	9.24	3.69	0.81	24.72	51.87	4.60	0.57	4.50
(wt%)	20.40	9.24	1.89	12.60	35.24	5.47	4.45	10.70
1.0 g/L EGCG (at%)	11.99	0.42	1.47	18.98	64.32	0.67	1.62	0.54
(wt%)	26.72	1.06	3.47	9.76	44.11	0.80	12.78	1.30

obtained using ZSimpWin software for the equivalent circuit elements. As EGCG concentration increased from 0 to 1.0 g/L, R_{ct} increased from $(5.291 \pm 1.419) \times 10^5$ to $(3.245 \pm 1.385) \times 10^6$. As EGCG concentration increased from 2.0 to 4.0 g/L, R_{ct} decreased from $(1.754 \pm 0.77) \times 10^4$ to 8025 ± 1496 . Therefore, Co-Cr alloy exhibited higher corrosion resistance in artificial saliva with a low concentration of EGCG (0–1.0 g/L). Conversely, Co-Cr alloy exhibited lower corrosion resistance in artificial saliva with a high concentration of EGCG (2.0–4.0 g/L).

Taken together, results of electrochemical measurements in this study unanimously ranked the resistance corrosion of Co-Cr dental cast alloy as follows according to its exposure to artificial saliva containing different concentrations of EGCG: 4.0 g/L < 2.0 g/L < 0 g/L < 0.5 g/L < 1.0 g/L.

Ion release

Table 3 shows the concentrations of Co, Cr, and Mo ions released from Co-Cr alloys in artificial saliva containing different concentrations of EGCG (0, 0.5, 1.0, 2.0, 4.0 g/L). At 4.0 g/L of EGCG, the highest concentrations of Co, Cr, and Mo ions were released from Co-Cr alloy. Conversely at 1.0 g/L of EGCG, the lowest concentrations of metal ions were released. These results were in good agreement with the results of electrochemical measurements above.

X-ray photoelectron spectroscopy (XPS)

Table 4 lists the compositions of the outermost surface layers on Co-Cr alloys, as determined by XPS, after electrochemical corrosion in artificial saliva containing 0 and 1.0 g/L of EGCG. Figure 5 shows the full XPS survey spectra of Co-Cr dental alloy surfaces after electrochemical corrosion in artificial saliva containing

0 g/L and 1.0 g/L of EGCG and before argon ion sputtering. At 1.0 g/L of EGCG, the dominant elements were O, C, and Cr at 64.32, 18.98, and 11.99 at% respectively (Table 4). The C 1s peak at 284.8 eV could be attributed to C-C or C-O bonding, stemming from the artificial saliva containing EGCG. At 0 g/L of EGCG, the concentrations of Co and Cr increased, while those of Cr and O decreased.

Before argon ion sputtering, Co was not found in the XPS spectrum for 1.0 g/L of EGCG. Figure 6 shows the high-resolution XPS spectra of Co after sputtering. Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks were decomposed into two peaks respectively. Co⁰ and Co²⁺ (CoO) peaks in Co $2p_{3/2}$ and Co $2p_{1/2}$ spectra indicated the presence of metallic and oxidation states respectively. The Co⁰ peaks in Co $2p_{3/2}$ and Co $2p_{1/2}$ spectra at 778.40 eV and 793.30 eV corresponded to the metallic state in Co-Cr alloy. The Co²⁺ peaks in Co $2p_{3/2}$ and Co $2p_{1/2}$ spectra at 780.70 eV and 796.21 eV corresponded to the oxidation state in CoO.

Figure 7 shows the high-resolution XPS spectra of Cr before and after argon ion sputtering. Before sputtering, the spectra revealed two dominant peaks: Cr³⁺ $2p_{3/2}$ at 577.55 eV and Cr³⁺ $2p_{1/2}$ at 587.27 eV. After 120 s of argon ion sputtering, the dominant Cr $2p_{3/2}$ and Cr $2p_{1/2}$ peaks decomposed into two peaks respectively. Cr⁰ and Cr³⁺ peaks in Cr $2p_{3/2}$ and Cr $2p_{1/2}$ spectra indicated the presence of metallic and oxidation states respectively. The Cr⁰ peaks in Cr $2p_{3/2}$ and Cr $2p_{1/2}$ spectra at 575.21 eV and 585.01 eV corresponded to the metallic state in Co-Cr alloy.

Figure 8 shows the curve-fitted high-resolution spectra of C 1s core level before argon ion sputtering, which consisted of three peaks. According to reported data³⁴⁾, peak 1 at 284.78 eV was assigned to the carbon

Fig. 5 XPS survey spectra of Co-Cr dental cast alloys after electrochemical corrosion in artificial saliva containing 0 and 1.0 g/L of EGCG before argon ion sputtering.

Fig. 6 High-resolution XPS spectra of Co after 120 s of argon ion sputtering.

Fig. 7 High-resolution XPS spectra of Cr: (a) before sputtering, and (b) after 120 s of argon ion sputtering.

atoms in aliphatic amino acid side chains (C-C or C-H). Peak 2 at 286.24 eV was attributed to photoelectron emission of carbons bonded with a single bond to oxygen (C-O). Peak 3 at 288.64 eV was attributed to the carbon atoms in coordinate (O-C=O) or (O-C=O) group. After argon ion sputtering, no C peaks were detected.

Figure 9 shows the curve-fitted high-resolution spectra of O 1s core level before and after argon ion sputtering. Before sputtering, the spectra consisted of three peaks (Fig. 9(a)). Peak 1 corresponded to the oxidation state in Cr_2O_3 . Peak 2 was attributed to hydroxyl or hydroxide, OH^- . Peak 3 was assigned to adsorbed water, H_2O . After sputtering, the spectra also consisted of three peaks (Fig. 9(b)).

DISCUSSION

OCP results showed that after a few minutes of immersion, E_{corr} stabilized at a constant value, indicating that a stable passive film was formed on the alloy surface. This passive film was mainly composed of Cr_2O_3 , as determined by XPS. A good correlation was found between the OCP and PD results. In all the PD curves, a visible anodic current density plateau was observed for the five different EGCG concentrations, indicating the formation of some protective film on all the alloy surfaces. After which, a broad passive region spanning over a large potential range was observed for all the EGCG concentrations, which was prior to the occurrence of localized pitting corrosion at a high potential above 500 mV. Within the passive region, current density was maintained at a steady, low level. Passive current varied slightly with the different concentrations of EGCG, indicating that the addition of EGCG affected the corrosion behavior of Co-Cr alloy.

Fig. 8 High-resolution XPS spectra of C 1s before argon ion sputtering.

Co-Cr alloy exhibited higher corrosion resistance in artificial saliva with a low concentration of EGCG (0–1.0 g/L). Conversely, Co-Cr alloy exhibited lower corrosion resistance in artificial saliva with a high concentration of EGCG (2.0–4.0 g/L). Based on results gleaned from three electrochemical measurement techniques, the corrosion resistance of Co-Cr dental cast alloy according to the different concentrations of EGCG was as follows: 4.0 g/L < 2.0 g/L < 0 g/L < 0.5 g/L < 1.0 g/L. Further, ICP-MS results confirmed that Co-Cr alloy released the highest amounts of Co, Cr, and Mo ions in artificial saliva containing 4.0 g/L of EGCG, but the least metal ions in artificial saliva containing 1.0 g/L of EGCG.

Fig. 9 High-resolution XPS spectra of O 1s: (a) before sputtering, and (b) after 120 s of argon ion sputtering.

Fig. 10 Schematic diagram illustrating the complex formation reaction between EGCG and Cr (III) ion.

It was reported that metallurgical heterogeneities of alloys contributed to localized corrosion³⁵. In the present study, it was determined by XPS that the outermost surface layer on Co-Cr alloy consisted mainly of Cr_2O_3 after electrochemical corrosion; in other words, the major constituent was Cr (about 90% Cr oxides)^{36–38}. In the passive film, Cr was present mainly as Cr (III) oxide and in a smaller amount as Cr (III) hydroxide³⁶. Cr (III) hydroxide decomposed into Cr (III) metal ion in the EGCG-containing salivary electrolytes. While the oxides of Cr formed the major constituent of the outermost surface layer, the oxides of Co were dissolved. Hence, XPS spectra of the passive film before argon ion sputtering did not detect Co in the outermost layer. However, the metallic and oxidation states of Co were detected after 120 s of argon ions sputtering. Thus, it could be concluded that Co was not very significant in either the formation of oxides or the corrosion behavior. Apart from Co oxides, another minor constituent of

the passive layer were Mo oxides. Although Mo is less important than Cr, alloys with less Mo are more susceptible to pitting³⁹.

XPS results also revealed that the composition of the outmost surface layer included EGCG-Cr (III) ion complex. The complexing behaviour of EGCG with metal ions such as Al^{3+} and Mn^{2+} has been previously reported^{40–42}. Significant differences exist between the complex formation properties of EGCG and other polyphenols lacking the gallate ring (D-ring). Major coordinate bonds in EGCG metal complexes are formed by the gallate ring, while the galocatechin ring (B-ring) has a secondary coordination effect^{40–42}. In the present study, it seemed probable that the central $-\text{OH}$ group of B-ring was deprotonated and coordinated to Cr^{3+} ion. When $-\text{O}^-$ atom of the B-ring was coordinated to the same Cr^{3+} ion which was bonded to two $-\text{O}^-$ atoms of the D-ring, a large strain was induced in the coordinated EGCG molecule. Figure 10 is a schematic diagram which

illustrates the probable complex formation reaction between EGCG and Cr (III) ion.

The corrosion process which took place in EGCG-containing artificial saliva was essentially a redox reaction. It is noteworthy that EGCG and hydroquinone belong to the same of polyphenols. During the redox reaction between Cr (VI) ion and EGCG, Cr (VI) was reduced to Cr_2O_3 and hydroquinone (H_2Q) was oxidized to semiquinone ($\text{HQ}^\cdot$). In a second oxidation step, semiquinone ($\text{HQ}^\cdot$) was oxidized to quinone (Q) by Cr (VI) ion, culminating in the formation of Cr_2O_3 . A higher Cr_2O_3 content in the passive film resulted in higher corrosion resistance.

Redox reaction led to the formation of Cr_2O_3 , thus inhibiting the corrosion of Co-Cr alloy in artificial saliva containing EGCG. Complex formation reaction between EGCG and Cr metal ion enhanced the corrosion reaction of Co-Cr alloy. Therefore, when the redox reaction was dominant, Co-Cr alloy in artificial saliva containing EGCG would exhibit high corrosion resistance. On the contrary, when complex formation reaction was dominant, Co-Cr alloy would exhibit low corrosion resistance.

CONCLUSIONS

Within the limitations of the current study, the following conclusions were drawn:

1. When the redox reaction was dominant and Cr_2O_3 was the major constituent of the passive film formed on alloy surface, Co-Cr alloy exhibited high corrosion resistance in artificial saliva containing EGCG.
2. When complex formation reaction was dominant and EGCG-Cr (III) ion complex was the major constituent of the passive film formed on alloy surface, Co-Cr alloy exhibited low corrosion resistance.
3. Tea intake should not exceed the recommended daily intake especially for those who wear restorations made of Co-Cr alloy. This is because high concentrations of tea might accelerate the corrosion process of and release of metal ions from Co-Cr alloys in the mouth.
4. EGCG concentration in artificial saliva affected the corrosion resistance of Co-Cr alloys because it determined the dominant reaction and hence passive film composition. Cascading effects include the types of metal ions released and the corrosion speed. Further studies need to be conducted to investigate the corrosion mechanisms induced by different EGCG concentrations and the corrosion products thereof.

ACKNOWLEDGMENTS

This study was supported by funding through the National Natural Science Foundation, China (Grant No. 30970726), Shanghai Municipal Health Bureau Youth Fund (Grant No. 20114Y053), Shanghai Postdoctoral

Sustentation Fund, China (Grant No. 11R21414700), and the National Science Foundation for Post-doctoral Scientists of China (Grant No. 20110490715).

REFERENCES

- 1) Eliasson A, Arnelund CF, Johansson A. A clinical evaluation of cobalt-chromium metal-ceramic fixed partial dentures and crowns: A three- to seven-year retrospective study. *J Prosthet Dent* 2007; 98: 6-16.
- 2) Viennot S, Dalard F, Lissac M, Grosgeat B. Corrosion resistance of cobalt-chromium and palladium-silver alloys used in fixed prosthetic restorations. *Eur J Oral Sci* 2005; 113: 90-95.
- 3) Mulders C, Darwish M, Holze R. The influence of alloy composition and casting procedure upon the corrosion behaviour of dental alloys: an *in vitro* study. *J Oral Rehabil* 1996; 23: 825-831.
- 4) Ardlin BI, Dahl JE, Tibballs JE. Static immersion and irritation tests of dental metal-ceramic alloys. *Eur J Oral Sci* 2005; 113: 83-89.
- 5) Berzins DW, Kawashima I, Graves R, Sarkar NK. Electrochemical characteristics of high-Pd alloys in relation to Pd-allergy. *Dent Mater* 2000; 16: 266-273.
- 6) Wylie CM, Shelton RM, Fleming GJ, Davenport AJ. Corrosion of nickel-based dental casting alloys. *Dent Mater* 2007; 23: 714-723.
- 7) Geis-Gerstorf J. *In vitro* corrosion measurements of dental alloys. *J Dent* 1994; 22: 247-251.
- 8) Lu Y, Chen W, Ke W, Wu S. Nickel-based (Ni-Cr and Ni-Cr-Be) alloys used in dental restorations may be a potential cause for immune-mediated hypersensitivity. *Med Hypotheses* 2009; 73: 716-717.
- 9) Faccioni F, Franceschetti P, Cerpelloni M. *In vivo* study on metal release from fixed orthodontic appliances and DNA damage in oral mucosa cells. *Am J Orthod Dentofac Orthop* 2003; 124: 687-694.
- 10) Agaoglu G, Arun T, Izgi B. Nickel and chromium levels in the saliva and serum of patients with fixed orthodontic appliances. *Angle Orthod* 2001; 71: 375-379.
- 11) López-Alías JF, Martínez-Gomis J, Anglada JM, Peraire M. Ion release from dental casting alloys as assessed by a continuous flow system: Nutritional and toxicological implications. *Dent Mater* 2006; 22: 832-837.
- 12) Issa Y, Brunton P, Waters CM, Watts DC. Cytotoxicity of metal ions to human oligodendroglial cells and human gingival fibroblasts assessed by mitochondrial dehydrogenase activity. *Dent Mater* 2008; 24: 281-287.
- 13) Wataha JC. Alloys for prosthodontic restoration. *J Prosthet Dent* 2002; 87: 351-363.
- 14) Shettlemore MG, Bundy KJ. Assessment of dental material degradation product toxicity using a bioluminescent bacterial assay. *Dent Mater* 2002; 18: 445-453.
- 15) Schmalz G, Garhammer P. Biological interactions of dental cast alloys with oral tissues. *Dent Mater* 2002; 18: 396-406.
- 16) Thomas R, Kim MH. Epigallocatechin gallate inhibits HIF-1 α degradation in prostate cancer cells. *Biochem Biophys Res Commun* 2005; 334: 543-548.
- 17) Nishikawa T, Nakajima T, Moriguchi M, Jo M. A green tea polyphenol, epigallocatechin-3-gallate, induces apoptosis of human hepatocellular carcinoma, possibly through inhibition of Bcl-2 family proteins. *J Hepatol* 2006; 44: 1074-1082.
- 18) Annabi B, Currie JC, Moghrabi A, Béliveau R. Inhibition of HuR and MMP-9 expression in macrophage-differentiated HL-60 myeloid leukemia cells by green tea polyphenol EGCG. *Leuk Res* 2007; 31: 1277-1284.
- 19) Noda C, He J, Takano T, Tanaka C, Kondo T, Tohyama K, Yamamura H, Tohyama Y. Induction of apoptosis by

- epigallocatechin-3-gallate in human lymphoblastoid B cells. *Biochem Biophys Res Commun* 2007; 362: 951-957.
- 20) Thangapazham RL, Singh AK, Sharma A, Warren J, Gaddipati JP, Maheshwari RK. Green tea polyphenols and its constituent epigallocatechin gallate inhibits proliferation of human breast cancer cells *in vitro* and *in vivo*. *Cancer Lett* 2007; 245: 232-241.
 - 21) Hayakawa F, Kimura T, Hoshino N, Ando T. DNA cleavage activities of (-)-epigallocatechin, (-)-epicatechin, (+)-catechin, and (-)-epigallocatechin gallate with various kinds of metal ions. *Biosci Biotechnol Biochem* 1999; 63: 1654-1656.
 - 22) Hoshino N, Kimura T, Hayakawa F, Yamaji A, Ando T. Bactericidal activity of catechin-copper (II) complexes against *Staphylococcus aureus* compared with *Escherichia coli*. *Lett Appl Microbiol* 2000; 31: 213-217.
 - 23) Furukawa A, Oikawa S, Murata M, Hiraku Y, Kawanishi S. (-)-Epigallocatechin gallate causes oxidative damage to isolated and cellular DNA. *Biochem Pharmacol* 2003; 66: 1769-1778.
 - 24) Esparza I, Salinas I, Santamaria C, Garcia-Mina JM, Fernandez JM. Electrochemical and theoretical complexation studies for Zn and Cu with individual polyphenols. *Anal Chim Acta* 2005; 543: 267-274.
 - 25) Wang QY, Zheng YF. The electrochemical behavior and surface analysis of $Ti_{50}Ni_{47.2}Co_{2.8}$ alloy for orthodontic use. *Dent Mater* 2008; 24: 1207-1211.
 - 26) Zavanelli RA, Guilherme AS, Pessanha-Henriques GE, de Arruda Nóbilo MA, Mesquita MF. Corrosion-fatigue of laser-repaired commercially pure titanium and Ti-6Al-4V alloy under different test environments. *J Oral Rehabil* 2004; 31: 1029-1034.
 - 27) Zavanelli RA, Pessanha Henriques GE, Ferreira I, De Almeida Rollo JM. Corrosion-fatigue life of commercially pure titanium and Ti-6Al-4V alloys in different storage environments. *J Prosthet Dent* 2000; 84: 274-279.
 - 28) Boehm K, Borrelli F, Ernst E, Habacher G, Hung SK, Milazzo S, Horneber M. Green tea (*Camellia sinensis*) for the prevention of cancer. *Cochrane Database Syst Rev* 2009; (3): CD005004.
 - 29) Feng J, Hou CY. Study on the release of fluoride in tea. *Food Sci Technol* 2006; 9: 93-95.
 - 30) Chang JK, Chen SY, Tsai WT. Electrodeposition of aluminum on magnesium alloy in aluminum chloride ($AlCl_3$)-1-3-Methylimidazolium chloride (EMIC) ionic liquid and its corrosion behavior. *Electrochem Commun* 2007; 9: 1602-1606.
 - 31) Foroulis ZA. Fundamental studies on anodic protection. Alloy 20 in sulfuric acid. *Ind Eng Chem Proc Des Dev* 1964; 3: 84-88.
 - 32) Morlidge JR, Skeldon P, Thompson GE, Habazaki H, Shimizu K, Wood GC. Gel formation and the efficiency of anodic film growth on aluminum. *Electrochim Acta* 1999; 44: 2423-2435.
 - 33) Song GL. Effect of tin modification on corrosion of AM70 magnesium alloy. *Corros Sci* 2009; 51: 2063-2070.
 - 34) Flaminia R, Lanza G, Salvi AM, Castle JE, Tamburro AM. Conformational study and hydrogen bonds detection on elastin-related polypeptides using X-ray photoelectron spectroscopy. *Biomacromolecules* 2005; 6: 1299-1309.
 - 35) Goff AHL, Joiret S, Abourazzouk D. Raman investigation of crevice corrosion in Ni-Cr dental alloys containing beryllium. *Electrochim Acta* 1998; 43: 53-62.
 - 36) Hodgson AWE, Kurz S, Virtanen S, Fervel V, Olsson COA, Mischler S. Passive and transpassive behavior of CoCrMo in simulated biological solutions. *Electrochim Acta* 2004; 49: 2167-2178.
 - 37) Kocijan A, Milosev I, Pihlar B. Cobalt-based alloys for orthopedic applications studied by electrochemical and XPS analysis. *J Mater Sci Mater Med* 2004; 15: 643-650.
 - 38) Kelly JR, Rose TC. Nonprecious alloys for use in fixed prosthodontics: a literature review. *J Prosthet Dent* 1983; 49: 363-370.
 - 39) Geis-Gerstorfer J, Weber H. *In vitro* corrosion behaviour of four Ni-Cr dental alloys in lactic acid and sodium chloride solutions. *Dent Mater* 1987; 3: 289-295.
 - 40) Navarro RE, Santacruz H, Inoue M. Complexation of epigallocatechin gallate (a green tea extract, egcg) with Mn^{2+} : nuclear spin relaxation by the paramagnetic ion. *J Inorg Biochem* 2005; 99: 584-588.
 - 41) Ohyoshi E, Sakata T, Kurihara M. Complexation of aluminium with (-)-epigallocatechin gallate studied by spectrophotometry. *J Inorg Biochem* 1999; 73: 31-34.
 - 42) Inoue MB, Inoue M, Fernando Q, Valcic S, Timmermann BN. Potentiometric and (1) H NMR studies of complexation of $Al(3+)$ with (-)-epigallocatechin gallate, a major active constituent of green tea. *J Inorg Biochem* 2002; 88: 7-13.