Abstract: The aim of this study was to investigate the electrochemical behavior of Ti$_{49.6}$Ni$_{45.1}$Cu$_5$Cr$_{0.3}$ (TiNiCuCr) alloy in artificial saliva solutions with a wide range of pH values and to characterize the surface passive film after polarization tests. This article represents the ideal, static environment and associated electrochemical response and comparison values. The corrosion behavior of TiNiCuCr alloy was systematically studied by open circuit potential, potentiodynamic, potentiostatic, and electrochemical impedance techniques. Potentiodynamic and potentiostatic test results showed that the corrosion behavior of TiNiCuCr was similar to that of NiTi alloy. Both corrosion potential ($E_{\text{corr}}$) and pitting corrosion potential ($E_{\text{b}}$) showed a pH-dependent tendency that $E_{\text{corr}}$ and $E_{\text{b}}$ decreased with the increase of the pH value. X-ray photoelectron spectroscopy results revealed the composition of the passive film consisted mainly of TiO$_2$ with a little amount of Ni oxides (NiO/Ni$_2$O$_3$) that was identical with NiTi alloy. Besides Ni, a Cu enriched sub-layer was also found. The nickel ion release rate showed a typical time-related decrease as examined by ICP/OES. In conclusion, the addition of Cu and Cr had little effect on the corrosion behavior of NiTi or on the composition and the structure of the passive film.

INTRODUCTION

Shape memory effect and superelasticity of equiatomic NiTi alloys are widely employed in various medical devices, for example, dental archwire, endodontic file, orthopedic instruments, and cardiovascular stents, and so forth. A review of the corrosion resistance of NiTi alloys in simulated human fluids has been reported, and the authors conclude that nickel-containing dental alloys do not pose a risk to patients or members of the dental team. The biocompatibility of metallic materials is closely related to their corrosion behavior. Large amounts of metal ions released from the metallic biomaterials are generally harmful for human health. The release of ions may cause unwanted reactions in the human tissues. This ion release behavior of the alloy is related with its corrosion rate.

Corrosion resistance of titanium and its alloys relies on the presence of a passive film on the surface, which is commonly recognized as TiO$_2$. This thermodynamically stable oxide film prevents the matrix from corrosion and provides good corrosion resistance and excellent biocompatibility in physiological environments. But the release of metal ions also takes place accompanied by the growth of the oxide film. Once the ion release rate equals to the growth rate of the passive film, the thickness of the film stabilizes at a constant scale. In spite of the protection, localized corrosion such as pitting corrosion and crevice corrosion may also occur due to its inhomogeneity.

Third and fourth alloying elements were added to NiTi alloy to enhance its mechanical or corrosion properties. Ma and Wu have found that the addition of Ta improves the corrosion resistance of NiTi in simulated body fluids, and decreases the Ni ion release rate under a corrosive environment. The substitution of Ni by Cu will result in the variance of the martensitic transformation sequence. With the increase of Cu content above 7.5%, the parent phase with a B2 structure can transform to a B19 martensite phase, and then to a B19$'$ martensite. Cu addition will also reduce the stress-hysteresis in the pseudoelasticity and stabilize the superelastic characteristics against cyclic deformation. Five to six percent addition of Cu will increase the strength and...
reduce the energy lost as measured by the area within the first and second plateau regions. Most of the earlier mentioned aspects are beneficial for orthodontic use.

Superelastic NiTiCu alloys have been developed as potential orthodontic archwire materials recently, unfortunately little published works can be found as far as concerning the corrosion behavior and the structure of the passive film. The aim of this study is to investigate the corrosion behavior of Ti_{49.6}Ni_{45.1}Cu_{5}Cr_{0.3} alloy (throughout this article the alloy compositions subscripts are atomic fractions), hereafter referred to as TiNiCuCr alloy, with NiTi as reference as well as the characterization of the passive film formed on the surface by means of X-ray photo-electron spectroscopy (XPS).

**MATERIALS AND METHODS**

TiNiCuCr alloy ingots were prepared by vacuum arc melting furnace protected by argon atmosphere. All the metal elements were at commercially pure level. The purity of each element, given as a mass fraction is as follows: 99.9% for Ti, 99.98% for Ni, 99.95% for Cu, and 99.98% for Cr. The alloy ingots were melted three times to ensure homogeneity. After melting, they were hot rolled at 850°C into sheets with about 1 mm in thickness. The sheets were then annealed at 850°C for 30 min and quenched into water. For electrochemical study, the hot rolled sheets were cut into (10 × 10) mm² squares by electro-spark cutting machining and polished to 2000 grit by SiC paper and then to mirror finish by means of Al₂O₃ with mean diameter of 2.5 μm. Before each measurement, the samples were ultrasonically cleaned in acetone, alcohol and deionized water, successively.

All the electrochemical measurements were conducted by Solartron 1287 Electrochemical Interface connected to a computer using Corrware as the control software. A platinum foil was used as counter electrode and potentials were controlled with respect to a saturated calomel electrode (SCE). All the measurements were carried out at (37 ± 0.5)°C by maintaining the test cell in a water bath. Before each test except electrochemical impedance spectrometry (EIS), the specimen was immersed into the electrolyte for 30 min. The sample area exposed to the electrolyte was 0.5 cm². The Ti-50.8 at. % Ni alloy samples were used as control.

The electrolyte was modified Fusayama artificial saliva. Its composition is as follows: NaCl (0.4 g/L), KCl (0.4 g/L), CaCl₂ (0.78 g/L), NaH₂PO₄·H₂O (0.69 g/L), Na₂S·9H₂O (0.005 g/L), KSCN (0.3 g/L), and Urea (1 g/L). All the chemical reagents were in analytical purity. The solution was prepared with analytically pure reagents and deionized water. The pH value of the neutral artificial saliva equaled to 5.3, and lactic acid and NaOH were used to adjust the pH value to 2.4 and 6.2, respectively.

Open circuit potential (OCP) measurement was conducted for 12 h in three different solutions with pH value equaling to 2.4, 5.3, and 6.2, respectively. The potential was recorded as a function of measuring time. Polarization tests were carried out by Potentiodynamic technique with a scanning rate of 1 mV/s; the working potential ranged from −500 mV to 1600 mV versus SCE. The test cell was purged for 30 min with high purity nitrogen (the purity larger than 99.999%) before and during the whole test. The polarization tests were repeated three times for each testing condition. Potentiostatic technique was performed for 1.8 ks in pH = 5.3 artificial saliva solution. The results were recorded as current density versus polarization time curve. The electrochemical impedance (EIS) measurements were performed with sinusoidal AC voltage amplitude of 10 mV above the OCP. The frequency ranged from 100 KHz to 10 mHz. Before EIS tests, samples were immersed in the solution 1 h for stabilization.

The specimens for ion release behavior study were sealed with room temperature curing denture base resin leaving an area of 1 cm² exposed to the saliva solution. The specimens were immersed into 50 mL of modified Fusayama artificial saliva solution at 37°C for different periods of time (1, 3, 5, and 7 days). The Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Optima 5300DV was used to measure the Ni ions concentrations.

XPS was used to characterize the surface film after polarization. The XPS data were taken on an AXIS Ultra instrument from Kratos Analytical. The data were converted into VAMAS file format and imported into CasaXPS software package for manipulation and curve-fitting.

**RESULTS**

Figure 1 shows the potential versus time curves of TiNiCuCr alloy carried out in three different pH values. We note that, at the beginning of the immersion, the $E_{corr}$ changes a lot. As the immersion went on, it tended to be constant. After 12 h, the potential stabilized at $-0.05$, $-0.094$, and $-0.34$ V in pH = 2.4, pH = 5.3, and pH = 6.2 solutions, respectively. It’s obvious that $E_{corr}$ decreases with the increase of the pH value.

Figure 2(A) shows the representative potentiodynamic polarization results of TiNiCuCr alloy in three different pH values of deaerated electrolytes including pH equaling to 2.4, 5.3, and 6.2 at 37°C which are similar to that of NiTi.
alloy (Figure 2(B)). As can be seen, the pitting corrosion occurred (indicated in the figures) at high potentials for both TiNiCuCr and NiTi alloys. It is obvious that both breakdown potential ($E_b$) and corrosion potential ($E_{corr}$) decrease with the increase of the pH values. Though it changes a little with the pH value, the passive current density keeps at a low level within the passive state.

Potentiostatic polarization technique was performed in pH = 5.3 artificial saliva solution. According to the potentiodynamic results, both TiNiCuCr and NiTi samples are under passive state at 500 mV versus SCE. So 500 mV was applied on the samples to acquire a stable passive film. As we can see from the results (Figure 3), both of the two current densities drop sharply to a lower level at the beginning; after a few hundreds of seconds, they stabilize, approaching a nearly constant level. The current density of NiTi sample, which is $3.09 \times 10^{-6} \text{ A/cm}^2$, is as six times high as that of TiNiCuCr sample.

EIS results demonstrate little difference among different artificial saliva solutions as shown in Figure 4 (Nyquist plot). It’s obvious that each Nyquist plot exhibits only one time constant, and the electrochemical behavior might be represented by a resistance $R_p$ and a capacitance $C$ in parallel. The resistance $R_p$, known as the polarization resistance, is inversely proportional to the corrosion rate and is thus an indicator of corrosion resistance. $R_p$ can be calculated from the diameter of the Nyquist plot for the systems with one time constant. The circle fitting results showed all the three Nyquist plots diameter were under the same magnitude. $R_p$ values for the pH = 2.4, 5.3, and 6.2 electrolytes are as follows: 0.28, 0.31, and 0.29 MΩ cm$^2$.

The Ni ion release rate decreased with the increase of the immersion time during the measuring period, as shown in Figure 5. This time-related decrease is similar to the results found by other researcher on the in vitro corrosion evaluation of NiTi alloy.9,10

The typical XPS survey spectra of the polarized TiNiCuCr alloy are shown in Figure 6. It can be found that, before sputtering, the dominant surface elements are O, C, and Ti, and they occupy the percentage of 38.09%, 43.95%, and 7.92%, respectively (Table I). The main component of C$_1$s peak at 284.251 eV is related to C—C bonding, and its presence is attributed to atmospheric
It is obvious that the concentration of Ni is less than that of Ti as can be seen from Table I. After sputtering, the Ni and Ti concentrations increased, while the O and C concentrations decreased sharply. The ratio of Ni:Ti is about 0.27:1 on the outermost surface, and it changed to about 2.57:1 after 300 s argon ion sputtering. Cu2p peaks appeared as can be seen in Figures 6(B) and 7(E) with a concentration of 3.58%.

The high resolution spectra of Ti exhibit two dominant peaks before argon ion sputtering, namely Ti 2p3/2 at 458.32 eV and Ti 2p1/2 at 463.99 eV with concentration of 5.00% and 2.49%, respectively. Both of them are corresponding to TiO2. There is also a little amount of metallic Ti corresponding to intermetallic NiTi at 453.68 eV and 459.22 eV. After argon ion sputtering for 300 s, there is only intermetallic Ti can be found as can be seen in Figure 7(C). On the outmost layer, there are little amount of NiO and Ni2O3 except metallic Ni [indicated by lines in Figure 7(B)]. But after sputtering, similar to Ti, there is only metallic Ni can be found as can be seen in Figure 7(D). It is notable that metallic Cu appeared after sputtering while it was absent on the outmost layer. Cr was not detectable either on the outmost layer or after argon ion sputtering.

**DISCUSSION**

The OCP results show that after a few hours immersion, the \( E_{corr} \) stabilized at a constant value, indicating a stable passive film had formed on the surface of the sample. This passive film consists of mainly TiO2 as examined by XPS. The final potentials after 12 h immersion decreased with the increase of the pH values. This is consistent with the results of potentiodynamic measurements. Though a little difference is observed, both TiNiCuCr and NiTi alloys possess a large range of passive region before the localized pitting corrosion occurs at high potentials above 1000 mV, indicating the good corrosion resistance. The pitting potential is high enough to stand against localized corrosion in vivo.11 The pH value of the electrolytes has limited influence on the corrosion behavior of the TiNiCuCr alloy similar to the NiTi alloy. We can see that both corrosion potential (\( E_{corr} \)) and breakdown potential (\( E_b \)) decrease with the increase of the pH values as shown in Figure 2, indicating that the pH value of the corrosion media may affect the corrosion resistance and the passive film stability of the alloys. Rondelli12 found the similar pH effects on

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<th>Survey Conditions</th>
<th>Element Concentration (%)</th>
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<tr>
<td></td>
<td>( \text{Ni}_{2p} )</td>
</tr>
<tr>
<td>Before sputtering</td>
<td>1.99</td>
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<td>After 300 s sputtering</td>
<td>61.43</td>
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pitting corrosion potential of NiTi alloy. But his results are opposite to ours, that is, the pitting potential increases with the increase of the pH values. This may be due to the different corrosion electrolytes used in our studies.

According to the potentiostatic results, the passive current density of NiTi alloy is much higher than that of TiNiCuCr alloy, indicating TiNiCuCr alloy would possess a lower corrosion rate than NiTi alloy as the passive current density is directly proportional to the corrosion rate by Faraday’s law. EIS results show little difference of $R_p$ of TiNiCuCr alloy immersed in three pH values saliva solutions. The Nyquist plots exhibit one time constant (virtually the same for each) indicating the presence of a single oxide layer on the surface that is the same for each test condition.

The XPS results confirmed that the composition of the outmost surface layer of the studied samples is TiO$_2$ with little amount of Ni/NiO/Ni$_2$O$_3$. Whereas there exists a Ni/Cu enriched layer between the outmost oxide film and the matrix as can be seen in Figure 6. This Ni enrichment phenomenon under the outmost layer has also been observed by others.13,14 Besides Ni, we also found Cu enriched below the oxide film. We believe that the Ti on the outermost surface is oxidized firstly by oxygen and is not released into the electrolyte while Ni and Cu remain unchanged.14,15 Both of them may diffuse into the sublayer or release into the electrolytes. At the mean time, the TiO$_2$ film prevents Ni and Cu from diffusing into the electrolytes as a barrier. Thus a structure consisting of the outmost oxide layer, the Ni and Cu enriched sublayer and the matrix formed on the surface.

CONCLUSIONS

This article represents the ideal, static environment and associated electrochemical response and comparison values. The actual situation with orthodontic archwire and engagement with the bracket will be dramatically different (dynamic, including crevice) than the corrosion response described in this article. We have investigated the corrosion behavior of Ti$_{49.6}$Ni$_{45.1}$Cu$_5$Cr$_{0.3}$ alloy and the characteristics of its passive film with NiTi alloy as reference. Electrochemical measurements results showed that the TiNiCuCr alloy has a similar corrosion behavior to that of the NiTi alloy under the same corrosion conditions. The pH value of the electrolyte has a little effect on the $E_{corr}$ and the $E_b$. Both $E_{corr}$ and $E_b$ decrease with the increase of the pH value. Ion release rate measurements confirmed that TiNiCuCr alloy had a similar corrosion behavior with NiTi alloy that exhibited a time-related decrease of release rate of Ni. XPS results revealed that the passive film consists mainly of TiO$_2$ with a little amount of Ni oxides (NiO, Ni$_2$O$_3$). Besides Ni, a Cu enriched sublayer was also found. All of the earlier results may conclude that the addition of Cu and Cr to change the superelastic characteristics of NiTi does not change the corrosion resistance of NiTi alloy in artificial saliva.

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