The effects of additives such as Cu, Mo, and Mn on the corrosion resistance of Ni-Cr alloy were investigated in Ringer's solution by the polarization resistance method.

The corrosion potential became noble and the polarization resistance increased with the addition of Cu or Mo. Anodic polarization measurements showed that these two elements retarded the anodic reaction and enhanced the passivation of Ni-Cr alloy. Mn also reduced the corrosion rate of Ni-Cr alloy as well as Cu and Mo, although the inhibition mechanisms were different. Electrochemical measurements and microscopic observations showed that the presence of Mn did not contribute to the protectiveness of passive films but decreased the cathodic reaction rate of Ni-Cr alloys.

A good linear relationship was observed between average corrosion rate obtained from the weight loss measurement and average polarization conductance, and could be expressed as

$$i_{corr} = 25(mV)Y_{corr}.$$  

Key words: Ni-Cr alloy, Polarization resistance, Anodic polarization curve

INTRODUCTION

Due to the high cost of gold, nonprecious alloys such as Ni-Cr alloys have been introduced in dentistry as alternatives to gold base alloys for crowns and bridges. These nonprecious alloys, however, are less stable chemically than the noble alloys in the oral environment. Electrochemical corrosion in the oral cavity can reduce the mechanical strength of dental restorations and may release toxic, metallic compounds into the surrounding tissues. Thus corrosion resistance is important and there is a need for a quick, convenient corrosion test for screening and developing new dental alloys.

The objective of this study was to develop such an instantaneous method for the evaluation of corrosion resistance of dental alloys. The Square Wave Current Method\textsuperscript{1-3}, which is based upon the principle of the polarization resistance method derived by Stern and Geary in 1957\textsuperscript{4}, was employed to examine the corrosion behavior of Ni-Cr alloys. The effects of additives, such as Cu, Mo, and Mn on the passivation of Ni-Cr alloy were also investigated.

MATERIALS AND METHODS

1. Materials

Table 1 shows the nominal composition of Ni-Cr alloys examined in this study. Cu was added in 5 wt% increments to 30 wt% in the Ni-15Cr alloy. The effects of Mo and Mn on the passivation of Ni-Cr alloys were also examined. About 2.5 wt% of Si and Mn was added to
CORROSION RATE MEASUREMENT OF Ni-Cr ALLOYS

Table 1 Nominal composition of the experimental alloys

<table>
<thead>
<tr>
<th>No.</th>
<th>Ni (%)</th>
<th>Cr (%)</th>
<th>Cu (%)</th>
<th>Mn (%)</th>
<th>Si (%)</th>
<th>Mo (%)</th>
<th>others (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>80.9</td>
<td>14.3</td>
<td>0</td>
<td>2.4</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>76.9</td>
<td>13.6</td>
<td>4.8</td>
<td>2.4</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>72.8</td>
<td>12.9</td>
<td>9.5</td>
<td>2.4</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>68.8</td>
<td>12.1</td>
<td>14.3</td>
<td>2.4</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>64.8</td>
<td>11.4</td>
<td>19.0</td>
<td>2.4</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>60.7</td>
<td>10.7</td>
<td>23.8</td>
<td>2.4</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>56.7</td>
<td>10.0</td>
<td>28.5</td>
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<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>78.6</td>
<td>13.8</td>
<td>0</td>
<td>2.1</td>
<td>2.1</td>
<td>2.3</td>
<td>0.6</td>
</tr>
<tr>
<td>9</td>
<td>76.1</td>
<td>13.5</td>
<td>0</td>
<td>2.1</td>
<td>1.7</td>
<td>1.7</td>
<td>5.7</td>
</tr>
<tr>
<td>10</td>
<td>73.7</td>
<td>13.0</td>
<td>0</td>
<td>1.4</td>
<td>1.4</td>
<td>8.6</td>
<td>1.9</td>
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<tr>
<td>11</td>
<td>78.8</td>
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<tr>
<td>12</td>
<td>74.6</td>
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<td>2.4</td>
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<td>0</td>
</tr>
<tr>
<td>13</td>
<td>66.3</td>
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<td>0</td>
<td>19.5</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

every alloy as a deoxidizer. The cast specimens comprised a rectangular flat surface about 30×20×1 mm in size. After wet-grinding through 1,000 grid emery paper, the alloy specimens were washed in distilled water and degreased in acetone. The surface of the specimen to be exposed was 8 cm², and the other surfaces were coated with nail varnish. The specimens were stored in a desiccator before use.

2. Electrochemical corrosion test

2-1. Anodic potentiodynamic polarization measurements

Figure 1 shows the polarization cell for making electrochemical measurements. A 30×10×1 mm carbon plate was employed as a counter electrode. The standard reference electrode used was a saturated calomel electrode (SCE), which was connected electrically through a salt bridge to an electrolyte in the cell. The electrochemical characteristics of the alloys were examined in Ringer’s solution which contained reagent grade sodium chloride, calcium chloride, and potassium chloride.

The procedure used for making anodic potentiodynamic polarization measurements was similar to that of the ASTM Recommended Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements (G5-78).
Oxygen-free nitrogen was spurged through the test solution in the cell for 30 min before the specimen was introduced and then at a lower rate throughout the test. Sixty min after specimen immersion, polarization measurements were started from the open-circuit potential to +0.8 V (vs. SCE). The scan rate was 0.1 mV/s. After an anodic polarization curve had been obtained, the specimen was examined microscopically.

2-2. Polarization resistance measurements

By applying the Square Wave Current Method, the polarization resistance $R_{corr}$ was measured for 50 days, along with the corrosion potential $E_{corr}$. Although the electrical nature of the electrodes is basically nonlinear, linear approximation is feasible when polarization is small\cite{1}. The electrical equivalent of an electrode system with a linear approximation can be given as in Fig. 2, where $R_{corr}$ is the polarization resistance, $R_s$ the solution resistance, and $C_d$ the double layer capacitance. When a repetitive square wave current which is symmetrical with respect to zero current and has an amplitude $I$ is imposed on the above system, the following potential response is observed as shown in Fig. 3. The peak-to-peak value of the potential change can be theoretically expressed as\cite{1},

$$\Delta E_{p-p} = 2I_sR_{corr} \tanh \left( \frac{1}{4fC_dR_{corr}} \right) + 2IR_s$$ \hspace{1cm} (1)

![Fig. 2](image1.png) **Fig. 2** An electrical equivalent circuit of the corroding system.

![Fig. 3](image2.png) **Fig. 3** Square wave current and the potential response.
where \( f \) is the frequency of the square wave current. Since relation (2) and (3) are easily derived from Equation (1), \( R_s \) and \( (R_{corr} + R_s) \) can be determined by extrapolating \( f \) to infinity and zero, respectively.

\[
\lim_{f \to \infty} \Delta E_{p-p} = 2IR_s \\
\lim_{f \to 0} \Delta E_{p-p} = 2I(R_{corr} + R_s)
\]

Then the polarization resistance \( R_{corr} \) can be determined as the difference between Equations (3) and (2). Stern-Geary's theory expects proportionality between \( i_{corr} \) and \( 1/R_{corr} \),

\[ i_{corr} = K/R_{corr} \]

where \( K \) is a constant which is specific to the corroding system. It should be noted that \( R_{corr} \) was selectively extracted only from the peak-to-peak values of the changes in potential at high and low frequencies and that \( i_{corr} \) can be obtained from Equation (4). The applying current was 1 kHz for obtaining \( R_s \) and 0.001 Hz for \( (R_{corr} + R_s) \).

The corrosion potential measurements for each systems were made with an electrometer having an input impedance of \( 10^9 \Omega \). All electrochemical measurements were carried out at 37°C in a temperature-controlled enclosure. The electrolyte was renewed every week.

3. Weight loss measurement

The samples were weighed both prior to and subsequent to testing to obtain the weight loss value \( \Delta W \) during the test period. After a series of electrochemical measurements, the test specimens were taken out of the solution and then dipped in 15% hydrochloric acid solution for 2 minutes to remove corrosion products. Preliminary tests showed that corrosion of the test specimens during this treatment was negligible. The average corrosion rate was calculated from the weight loss of the test piece \( \Delta W \),

\[ i_{corr} = \frac{nF}{T \cdot S} \left\{ \frac{a}{100 m_{Ni}} + \frac{\beta}{100 m_{Cr}} + \frac{\gamma}{100 m_{Cu}} + \frac{\delta}{100 m_{Mn}} + \frac{\varepsilon}{100 m_{Mo}} \right\} \Delta W \]

where \( n \) is the number of electrons exchanged in the reaction; \( T, S, \) and \( F \) are the test period, surface area of the specimen, and the Faraday constant, respectively; \( m \) is the atomic weight and \( a, \beta, \gamma, \delta, \) and \( \varepsilon \) are weight percent of individual elements dissolved into the solution. In this calculation, the alloy was assumed to corrode uniformly and the oxidation state of metal ions to be divalent.

4. Metallurgical examination

Analytical scanning electron microscopy (SEM), which combines the examination of the surface morphology with element analysis by wavelength-dispersive X-ray techniques was used for the characterization of the corroded surface of the test specimens. This form of surface examination was performed only for Cu-containing alloys.

RESULTS

1. Anodic polarization behavior of Ni-Cr alloys

The effects of additives such as Cu, Mo, and Mn on the anodic polarization behavior of
the Ni-Cr alloy were investigated. Anodic polarization curves were obtained in duplicate. Figure 4 shows the typical features. A passive range was observed for the Ni-Cr-15Cu alloy from $-350$ to $-50$ mV (vs. SCE). Above this potential, a continuous increase in current density occurred. For the Ni-Cr-9Mo alloy, a short passive range was also observed. Compared to these two alloys, Ni-Cr and Ni-Cr-Mn alloys were characterized by a higher current density and no passive region was observed.

2. Corrosion behavior of Ni-Cr alloys in Ringer’s solution

Figure 5 shows the variations in corrosion potential and polarization resistance with time for the Ni-Cr-3Mo alloy. Corrosion potential $E_{\text{corr}}$ exhibited noble value just after immersion, and changed rapidly to a less noble direction, and then reached a steady-state value. Initial polarization resistance was relatively low, which indicated a high corrosion rate. As time elapsed, polarization resistance increased with a maximum after approximately 4 days then decreased gradually to a low value. Steady-state polarization resistance of the alloy was achieved after about 20 days in Ringer’s solution. Figures 6 and 7 show the variation in

![Fig. 4 Anodic polarization curves for Ni-Cr alloys in de-aerated Ringer's solution at 37°C.](image1)

![Fig. 5 Changes in polarization resistance and corrosion potential for Ni-Cr-3Mo alloy with time.](image2)
corrosion potential and polarization resistance with time for Ni-15Cr and Ni-Cr-15Cu alloys, respectively. These alloys showed almost the same behavior as the Ni-Cr-3Mo alloy, although absolute values of polarization resistance were quite different. For the Ni-Cr-20Mn alloy, however, the corrosion potential became noble as the polarization resistance decreased as shown in Fig. 8, suggesting that this corrosion process was controlled by a cathodic
3. Effects of additional elements on the electrochemical parameters and corrosion rate of Ni-Cr alloys

Polarization conductance which is an inverse of polarization resistance is expected to be proportional to the corrosion rate, and its average value over the test period was calculated from Equation (5),

\[ \bar{Y}_{corr} = \frac{1}{T} \int_0^T Y_{corr} dt \]  

where \( T \) is the test period. Figure 9 shows the dependence of the average polarization conductance and corrosion rate on the Cu content. Both polarization conductance and corrosion rate data suggest that the corrosion reaction was markedly reduced when the Ni-Cr alloy contained more than 10 wt% of Cu. As is shown in Figs. 6 and 7, the corrosion potential became noble as the Cu content increased. These results indicate that Ni-Cr alloys

Fig. 9  Dependence of average corrosion conductance and average corrosion rate over the test period on the Cu content of Ni-Cr alloy.

Fig. 10  Dependence of average corrosion conductance and average corrosion rate over the test period on the Mo content of Ni-Cr alloy.
became passive with Cu content.

Figures 10 and 11 demonstrate the effects of Mo and Mn on the corrosion resistance of the Ni-Cr alloy. The addition of a small amount of Mo to the alloy reduced the corrosion rate significantly. Although Mn also improved the corrosion resistance up to 10 wt%, the corrosion rate can be expected to increase for alloys having an Mn content exceeding 10

![Graph showing dependence of average corrosion conductance and average corrosion rate over the test period on the Mn content of Ni-Cr alloy.]

Fig. 11 Dependence of average corrosion conductance and average corrosion rate over the test period on the Mn content of Ni-Cr alloy.

![SEM image and characteristic X-ray images of Ni-Cr-30Cu alloy.]

Fig. 12 SEM image and characteristic X-ray images of Ni-Cr-30Cu alloy.
6. Surface characterization study

Representive SEM photomicrographs of the corroded specimen surfaces and the X-ray distribution map for Ni, Cr, and Cu revealed the presence of segregation. As is evident in Fig. 12, the phases which contained less Cu were subjected to attack, whereas the Cu-rich regions were corrosion resistant.

DISCUSSION

1. Effects of additional elements on the corrosion resistance of Ni-Cr alloy

Table 2 shows the electrochemical parameters of five Ni-Cr alloys in Ringer's solution 60 min after specimen immersion. The corrosion potential became noble and the corrosion rate was reduced by the addition of Cu. This behavior can be explained as follows.

Figure 13 shows the schematic Evans diagram\(^7\) of Ni-Cr alloys. In this figure, anodic polarization curves correspond to the dissolution of alloy elements,

\[
\text{Me} \rightarrow \text{Me}^{n+} + ne^- \quad (7)
\]

The cathodic polarization curve corresponds to the oxygen reduction reaction in the neutral solution,

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (8)
\]

Table 2 Electrochemical parameters of Ni-Cr alloys measured 60 min after immersing the specimen

<table>
<thead>
<tr>
<th>Alloys</th>
<th>E(_{\text{corr}}) (mV)</th>
<th>R(_{\text{corr}}) (k(\Omega)cm(^2))</th>
<th>Y(_{\text{corr}}) (S/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr</td>
<td>-295</td>
<td>60</td>
<td>1.67\times10(^{-8})</td>
</tr>
<tr>
<td>Ni-Cr-15Cu</td>
<td>-230</td>
<td>100</td>
<td>1.00\times10(^{-8})</td>
</tr>
<tr>
<td>Ni-Cr-9Mo</td>
<td>-250</td>
<td>85</td>
<td>1.18\times10(^{-8})</td>
</tr>
<tr>
<td>Ni-Cr-10Mn</td>
<td>-310</td>
<td>120</td>
<td>8.33\times10(^{-8})</td>
</tr>
<tr>
<td>Ni-Cr-20Mn</td>
<td>-370</td>
<td>70</td>
<td>1.43\times10(^{-8})</td>
</tr>
</tbody>
</table>

Fig. 13 Schematic anodic and cathodic polarization curves showing the effect of Cu and Mo on the corrosion behavior of Ni-Cr alloy.
In this diagram, corrosion rate $i_{corr}$ and corrosion potential $E_{corr}$ are given at the intersection of two lines. The addition of Cu to Ni-Cr alloy caused the anodic polarization curves to intersect the cathodic polarization curve at point C instead of point A and the corrosion potential was shifted in a noble direction. Thus the anodic reactions were retarded and the passivation of the Ni-Cr alloy was enhanced.

X-ray analysis on test specimens revealed Cu-segregation which might result in imperfect passivation. Since the homogeneity of the alloy microstructure exhibits a superior corrosion resistance, the corrosion rate of Cu-containing Ni-Cr alloys is expected to be reduced by appropriate heat treatment.

Mo also contributed the protectiveness of passivate films and to the reduction in the corrosion rate of Ni-Cr alloys as shown in Fig. 13. Mn, however, reduced the corrosion rate of Ni-Cr alloys by a different mechanism. Unlike Cu and Mo, the corrosion potential became less noble as the corrosion rate decreased with the addition of Mn. This behavior was due to the retardation of the cathodic reaction. Figure 14 shows schematically the effects of Mn on the cathodic polarization. In this case, the anodic polarization was unaffected, and the corrosion potential was shifted to a more negative value from $E_0$ to $E_{10\text{Mn}}$ with the corrosion rate being reduced with the addition of Mn. For alloys having an Mn content exceeding 10 wt%, anodic polarization curves were shifted in a lower-right direction which indicated the increase in corrosion rate and the decrease in corrosion potential compared to those of the Ni-Cr–10Mn alloy.

Meyer reported that Mo and Mn acted together in enhancing the tendency to passivation. Mo was considered to inhibit the anodic reaction, whereas Mn to reduce the cathodic reaction rate of Ni-Cr alloy.

The specimens were examined microscopically after completion of the anodic polarization curve. Figure 15 shows some low magnification photographs of the specimen surfaces. Pitting was observed on the surface of the Ni-15Cr and Ni-Cr-Mn alloys. On the contrary, Ni-Cr-Cu and Ni-Cr-Mo alloys were attacked more uniformly. Cu and Mo could increase the resistance to pitting in Ringer's solution. These results suggest that the addition of Cu

![Fig. 14 Schematic anodic and cathodic polarization curves. The cathodic polarization curve shifts from A to B with the addition of Mn.](image-url)
or Mo inhibits the anodic reaction and enhances the passivation of Ni-Cr alloy, while the addition of Mn does not.

2. Possibility of estimating the corrosion rate of Ni-Cr alloys using The Square Wave Current Method
Stern-Geary's theory expects proportionality between corrosion rate and polarization conductance. In practice, proportionality between these two variables was observed (Fig. 16), although the compositions of the alloy samples were different. Thus, these experiments prove that the polarization resistance determined by the present method correlate well with the actual corrosion rate. The proportionality constant $K$ obtained from the slope of the straight line was 25 mV.

The features of The Square Wave Current Method are that, (1) polarization resistance can be measured with sufficient accuracy within a short time, (2) the analysis of the collected data is simple, and (3) it is a nondestructive method, so that corrosion rate can be determined continuously without disturbing the corroding system.

**CONCLUSIONS**

A polarization resistance method was employed to investigate the effects of additional elements such as Cu, Mo, and Mn on the passivation of the Ni-Cr alloy. Weight loss measurement and X-ray analysis on the test specimens were performed as well as electrochemical tests.

1. The corrosion potential became noble and the corrosion rate was reduced with the addition of Cu or Mo which means that the tendency for Ni-Cr alloy to passivate was enhanced by these two elements.
2. These two elements also increased the resistance to pitting in a chloride containing electrolyte.
3. For Cu containing Ni-Cr alloys, segregation was observed on the test specimens and Cu-rich regions were corrosion resistant.
4. Cathodic reactions of Ni-Cr alloys were inhibited by the addition of Mn.
5. Polarization resistance could be determined with sufficient accuracy and reproducibility by the Square Wave Current Method.
6. A good linear relationship was observed between average corrosion rate ($i_{corr}$: $\mu$A/cm$^2$) obtained from weight loss measurement and average polarization conductance ($Y_{corr}$: $mS/cm^2$), and could be expressed as,

$$i_{corr} = 25(mV)Y_{corr}.$$ 

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分極抵抗法による歯科用 Ni-Cr 合金の腐食速度測定
遠藤一彦，平野 進，平澤 忠
鶴見大学歯学部歯科理工学教室

矩形波電流分極法を用いて Cu，Mo および Mn を含
有する Ni-Cr 合金の分極抵抗を 37℃ リンゲル液中で測
定し，耐食性を評価した。その結果，いずれの元素も
Ni-Cr 合金の耐食性を向上させることが明らかとなっ
た。腐食電位およびアノード分極曲線の測定結果から，
Cu，Mo は Ni-Cr 合金のアノード反応を抑制して安定な
不動態に寄与するのに対し，Mn はカソード反応を抑制
することが明らかとなった。また，Cu および Mn は Ni-
Cr 合金の耐孔食性を向上させるが，Mn にはその作用が
ないことが明らかとなった。

分極抵抗の測定結果と重量減少量から求めた腐食速度
の間には良い相関が得られた。Ni-Cr 合金では，分極抵抗
から腐食速度に変換する定数 K の値は 25 mV となった。

Succinoxy alkylene methacrylate の歯科用合金への接着性
福島忠男，堀部 隆
福岡歯科大学歯科理工学教室

レジンの歯科用合金への接着性を改善するために側鎖
長の異なる Succinoxy alkylene methacrylate を 4 種
合成し，合金への接着性と化学構造との関係を検討した。
すなわち，合成モノマーから調整した 4 種の Bonding
agent をサンドペーパー (600 番) で最終研磨した 4 種
の歯科用合金 (gold (Type IV)，Au-Ag-Pd，Ni-Cr，Co-Cr
合金) に薄く塗布し，その上から即時レジンを焼入して
作製した着着試料について，37℃ の恒温槽に 7 日間放置
後 (Dry)，および 37℃ の水中に 7 日間浸漬後 (Wet)，

切断接着試験より接着力を求めた。その結果，non-
precious 合金へのレジンの接着性は Bonding agent の
使用により著しく向上したが，precious 合金の場合は
Bonding agent の効果が認められなかった。Dry
での gold と nonprecious 合金 および Wet での
precious 合金への接着力と化学構造には相関が認めら
れてなかったが，その他ではやや側鎖長の短いものが優れ
た接着性を示した。

陶材焼付金属冠の色調に関する研究
（第 1 報）線塗溶射法の応用
寺田善博，姫野孝枝，平安英造
九州大学歯学部歯科補綴学第 1 教室

金合金およびニッケルクロム合金（金合金を線塗溶射
した試料と溶射しない試料）を用いて，オペレート陶材を
焼成した試料の色調を比較した。

オペレート陶材を焼成することによって下地金属の色を
効果的に遮断するという見地から，金合金および金合金
を溶射したニッケルクロム合金は，溶射をしていない
ニッケルクロム合金より下地金属として優れていた。金
合金と溶射合金の色の類似性についても明かである。結
論として，金合金とニッケルクロム合金の長所を合わせ
持つ線塗溶射法の応用は陶材焼付金属冠の優れた下地金
属を作るために非常に有効であることが明らかである。