Corrosion Resistance and Surface Characterization of Electrolyzed Ti-Ni Alloy

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Ti-Ni alloy has been increasingly applied to medical and dental devices, such as coronary stents and orthodontic wires. This alloy contains nickel, which is known to give rise to cytotoxicity, metal allergy, and carcinogenicity. Therefore, the purpose of this study was to improve the corrosion resistance of Ti-Ni alloy by electrolytic treatment, whereby investigation was carried out using different acidic electrolyte compositions. As a result, specimens electrolyzed with lactic acid, water, and glycerol were found to show higher corrosion potential and release lower amount of titanium and nickel ions than mechanically polished specimens (p<0.05). With the electrolytic treatment, nickel concentration in the surface oxide layer of Ti-Ni alloy decreased, and the thickness of the surface oxide layer increased. Based on the results of this study, it was shown that electrolytic treatment with suitable electrolyte could improve the corrosion resistance of Ti-Ni alloy, which is effective to produce medical and dental devices that utilize shape memory effect or superelasticity with better biocompatibility.

Key words : Ti-Ni alloy, Electrolytic treatment, Surface characterization

INTRODUCTION

Titanium and titanium alloys, such as Ti-6Al-4V, Ti-6Al-7Nb, and Ti-Ni, are widely applied to dental and medical appliances7-14 due to their high corrosion resistance7-14 and good biocompatibility15. Since Ti-Ni alloy shows the special properties of shape memory effect and superelasticity, it is also used for special medical and dental appliances, e.g., orthodontic wires16,17, root canal files18, coronary stents19, and catheters20.

To date, many studies have investigated the corrosion behavior of Ti-Ni alloys20-27. It was reported that a higher amount of released ions was detected from Ti-Ni alloy than from unalloyed titanium or Ti-6Al-4V alloy27, thereby suggesting that the corrosion resistance of Ti-Ni alloy was not as good as the other two metals that show high corrosion resistance28. Further, the nickel element — which is contained in Ti-Ni alloys — is known to cause adverse reactions like cytotoxicity27,28, metal allergy12,27,29,30 and carcinogenicity27,31. Against this background of health concerns, it is necessary to improve its biocompatibility by reducing nickel ion release from the alloy.

Electrolytic treatment, such as anodic oxidation and electropolishing, is one of the methods to oxidize the surface of Ti-Ni alloys. With electropolishing, Trepanier et al.22 reported that this surface treatment method improved the corrosion resistance of Ti-Ni alloy. Likewise, Trigwell et al.31 studied the oxide layer of Ti-Ni sheet after polishing and etching treatments, and electropolishing produced a smooth surface with enriched titanium oxide. In these studies, however, details of the electropolishing conditions were not given clearly and fully. Although Cheng et al.34 anodized Ti-Ni in a methanolic electrolyte, its effect on corrosion resistance was not reported.

Since the electrolyte is one of the primary components of electrolytic treatment, different acidic electrolyte compositions were prepared in this study in search of suitable electrolytes against corrosion. Polarization test and immersion test were carried out to evaluate the corrosion resistance of the electrolyzed Ti-Ni alloy. In addition, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were performed to characterize the surface composition and structure of the electrolyzed Ti-Ni alloy.

MATERIALS AND METHODS

Specimen preparation

Cylindrical rods of Ti-Ni alloy (Ti-50.85mol%Ni, NT-E4, Furukawa Electric, Japan) were cut into discs (8 mm in diameter, 1 mm in thickness). Discs were polished and mirror-finished with 0.05-μm alumina paste, followed by ultrasonic cleaning in acetone, ethanol, and deionized water for 300 seconds each.

Electrolytic treatment was carried out using the electrolytes shown in Table 1. As shown, sulfuric acid, lactic acid, and phosphoric acid were selected from the electrolytic treatment of titanium, titanium alloy, and other metals35-38. Glycerol and ethanol were added as solvents for electrolytes to improve the efficiency of electropolishing39.

Specimens were treated with one of the following acidic electrolyte compositions: an electrolyte which

...
Table 1 Electrolyte compositions and electrolytic treatment conditions

<table>
<thead>
<tr>
<th>Specimen code</th>
<th>Component</th>
<th>Amount (vol%)</th>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>Time (min)</th>
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<tbody>
<tr>
<td>MP</td>
<td>Control (mechanical polishing)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GLSE</td>
<td>Glycerol</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
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<td></td>
<td>Water</td>
<td>16</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>GPE</td>
<td>Phosphoric acid</td>
<td>28</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>36</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

Glycerol: 84-87% (Japanese Pharmacopoeia, Kozakai Seiyaku)
Lactic acid: 85.0-92.0% (Guaranteed reagent, Kanto Chemical)
Sulfuric acid: 96.0% (Guaranteed reagent, Kanto Chemical)
Phosphoric acid: 85.0% (Extra pure, Kanto Chemical)
Ethanol: 99.5% (Extra pure, Kanto Chemical)

Specimens were put into polyethylene vessels with 20 ml of 1.0% lactic acid (JIS T 0304), and continuously shaken at 1.67 Hz. After immersion at 310 K for 30 days, quantification of released ions was carried out by means of an inductively coupled plasma emission spectrometer (ICP, PS3000, Leeman Labs, USA). Three specimens were tested for each condition (GLSE, GLW, GPE, and MP). Amounts of released component ions per unit surface area of the specimens were then calculated.

**XPS analysis**

XPS was performed with an electron spectrometer (SSX100, SSI, USA). The pressure during spectra acquisition was less than 2.3 × 10⁻⁷ Pa. All binding energies given in this paper were relative to the Fermi level, and all spectra were excited by monochromatized Al Kα radiation (energy: 1486.61 eV, voltage: 10 kV, and current: 30 mA). The spectrometer (pass energy: 20 eV) was calibrated against Au 4f7/2 (binding energy: 84.07 eV) and Au 4f5/2 (87.74 eV) of pure gold and Cu 2p3/2 (932.53 eV), Cu 2p1/2 (952.35 eV), and Cu Auger L₃M₅M₃ line (kinetic energy: 918.65 eV) of pure copper. Binding energies at the peaks observed in photoelectron spectra were further corrected using the value of the energy of C 1s level (285.0 eV) of contaminant hydrocarbon when the charging effect was clear. The energy values employed in this study were determined based on previously published data [40]. The take-off angle, defined as the angle between the direction of photoelectron path to the electron spectrometer and specimen surface, was 35°. As for the thickness of the oxide layer and the compositions of both the surface oxide layer and substrate, they were simultaneously calculated according to the method by Asami et al. [41,42]. Two specimens were analyzed for each condition (GLSE, GLW, GPE, and MP).

**AES analysis**

Depth profiles of the elements in the specimens were obtained by AES using an Auger electron spectroscope (JAMP-7100, JEOL, Japan) with argon ion
sputter etching. One specimen was analyzed for each condition (GLSE, GLW, GPE, and MP), and vacuum level of the analyzing chamber during measurement was at the order of $10^{-7}$ or $10^{-8}$ Pa. Accelerating voltage of the primary electrons for Auger electron excitation was 10 kV. Electron probe size was about 12 µm in diameter, and the current was $5 \times 10^{-7}$ A. After measuring the differential Auger electron spectra, their peak-to-peak (p-p) intensities were used for quantification. Peak-to-peak modulation voltage for the differential spectra was 5 eV. The KLL,KL2,3 transition peaks for carbon, oxygen, the L2M2.3M4.5 peak for titanium, and the L3M3.5M4.5 peak for nickel, were used for analysis. Quantification of the relative concentration was performed using a relative sensitivity factor of element $i$, $\alpha_i$. Concentration of element $i$, $X_i$, was then calculated using the following conventional equation:

$$X_i = \frac{I_i}{\alpha_i} \sum_{j=1}^{N} \frac{I_j}{\alpha_j}$$

where $I_i$ is an integrated intensity of Auger peak, $\alpha_i$ is the relative sensitivity factor of each element, $i$ and $j$ indicate elements $i$ and $j$ respectively, and $N$ is the number of elements.

Under the applied argon ion sputtering conditions (3 kV and 300 Am$^{-2}$ in $8 \times 10^{-2}$ Pa), etching rate for SiO$_2$ film on silicon was 0.1 nm s$^{-1}$. This value was used as the parameter to calculate the thickness of the oxide layers$^{32}$.

RESULTS

Macroscopic and microscopic observations

Macroscopic photographs are shown in Fig. 1(a). The color of MP and GLSE specimens was silver, while GLW and GPE specimens had gold-blue and blue surfaces. In addition, the surface of GLSE specimen was less mirror-like when compared with the other three. Through SEM observation, GLSE specimen showed a more irregular surface than the other three specimens as shown in Fig. 1(b).

Polarization test

Typical polarization curves of MP, GSLE, GLW, and GPE are shown in Fig. 2. Average open circuit potential ($E_{oc}$) and average corrosion potential ($E_{corr}$) values of MP, GLSE, GLW, and GPE are summarized in Table 2. As shown in Fig. 2, the current density at the passive region of GLSE was lower than that of MP. After the passive region, the current densities of GLSE and MP started to increase gradually. On the other hand, the current density values of GLW and GPE remained cathodic up to $E_{corr}$, and then became anodic and increased gradually without a passive region.

Immersion test

Fig. 3 shows the amounts of titanium and nickel ions released from the specimens during the 30-day immersion. Amount of released titanium ions was lowest from GLW, whereas it was highest from GPE. Moles of released titanium ions from GLSE and GLW were significantly less than that of MP (p<0.05). Likewise, moles of released nickel ions from the three electrolyzed groups were significantly less than that from MP (p<0.05) — in particular, the release amount was lowest from GLW. When comparing the amounts of released titanium and nickel ions within each group, there were no significant differences for MP (p=0.24) and GLSE (p=0.90). However, for GLW and GPE, the amount of the released nickel ions was less than that of titanium ions (p<0.05).

XPS analysis

Ti 2p XPS spectra of the specimens in the electron energy region, including 2p$_{1/2}$ and 2p$_{3/2}$ electron peaks, are shown in Fig. 4(a). The Ti 2p$_{3/2}$ peak of MP specimen gave four peaks according to valences of Ti$^0$, Ti$^{2+}$, Ti$^{3+}$, and Ti$^{4+}$. The binding energies of these valences were 454.2, 455.5, 457.5, and 458.6 eV respectively. Ti$^0$ peak was assigned to the metallic state in the substrate metal. Ti$^{2+}$, Ti$^{3+}$, and Ti$^{4+}$ peaks were derived from the oxidized titanium in the surface oxide layer$^{30}$. The integrated intensity of Ti$^{4+}$ peak was higher than any other valences. On the other hand, the Ti 2p$_{3/2}$ peak of all electrolyzed specimens (GLSE, GLW, and GPE) gave only one peak for the valence of Ti$^{4+}$, and the binding energies of these electrolyzed specimens ranged from 458.6 to 458.8 eV. Therefore, Ti$^{2+}$ and Ti$^{3+}$ in the oxide layer of MP specimen were oxidized to Ti$^{4+}$ by the electrolytic treatment, and titanium in the surface oxide layer became more thermodynamically stable$^{30}$.

Fig. 4(b) shows the decomposition results of the Ni 2p$_{3/2}$ electron region spectra of the specimens. The Ni 2p$_{3/2}$ peak of MP specimen gave three peaks that originated from Ni$^0$, Ni$^{2+}$, and satellite. The

<table>
<thead>
<tr>
<th>Specimen Code</th>
<th>MP</th>
<th>GLSE</th>
<th>GLW</th>
<th>GPE</th>
</tr>
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<tbody>
<tr>
<td>$E_{oc}$</td>
<td>$-0.425 \pm 0.020$</td>
<td>$-0.231 \pm 0.050$</td>
<td>$-0.151 \pm 0.021$</td>
<td>$-0.010 \pm 0.098$</td>
</tr>
<tr>
<td>$E_{corr}$</td>
<td>$-0.369 \pm 0.095$</td>
<td>$-0.228 \pm 0.048$</td>
<td>$0.974 \pm 0.066$</td>
<td>$1.174 \pm 0.013$</td>
</tr>
</tbody>
</table>

Average ± Standard deviation, N=3
Fig. 1 Macroscopic photographs (a) and SEM photographs (b) of specimens after each electrolytic treatment.
main peak was at 852.3 eV of binding energy, which was assigned to Ni^0 derived from nickel in the substrate metal. The second peak at 855.9 eV of binding energy was attributed to Ni^{2+} state, corresponding to Ni(OH)_2 in the surface oxide layer. The integrated intensity of Ni^0 was higher than Ni^{2+} for MP. As for the electrolyzed specimens, their Ni 2p_{3/2} peaks gave different peak intensity patterns compared to that of MP specimen. The integrated intensities of Ni^{2+} were higher than that of Ni^0 in GLSE and GLW; in particular, GPE specimen gave only Ni^{2+} peak and satellite without detectable Ni^0 peak. For GLW, the total integrated intensity of Ni^0 and Ni^{2+} peaks was lower than that of the other electrolyzed specimen groups.

Fig. 4(c) shows the results of the electron region spectra of O 1s of the specimens. The O 1s peak gave three peaks: the peaks at 530.1 and 531.7 eV were attributed to O^{2-} and OH^{-} respectively, while the peak at 533.2 eV was assigned to absorbed and/or bound water.

Table 3 shows the XPS results for the relative concentration and thickness of the surface oxide layer, which were calculated from the integrated intensity of each element. For all specimens, the dominant element in the surface oxide layer was oxygen, while nickel concentration decreased by electrolytic treatment. In particular, nickel reduction was remarkable when treated with the electrolyte composed of glycerol, lactic acid, and water (GLW). Sulphur existed in the surface oxide layer of GLSE at a binding energy of 169.0 eV, which was assigned to SO_4^{2-}, while phosphorus was observed in the surface oxide layer of GPE at binding energies of 133.1 and 134.2 eV, which were assigned to HPO_4^{2-} and H_2PO_4^{-} respectively. For the MP specimen, thickness of the oxide layer was 2.2 nm, while those of electrolyzed GLSE and GLW were 4.3 and 5.1 nm respectively. However, the thickness of the oxide layer for GPE could not be calculated since the photoelectrons of substrate metal were not detected.

AES analysis
Fig. 5 shows the AES depth profiles of the relative concentration of each element in the surface oxide layer of MP, GLSE, GLW, and GPE. For MP, the concentrations of titanium and nickel increased in a similar manner according to the depth, and the value for nickel was slightly lower than that for titanium. On the other hand, for GLSE, GLW, and GPE, nickel concentration was lower than titanium concentration at the surface region and increased gradually. The boundary between the oxide layer and substrate was defined as the depth where the oxygen concentration was the average value of its initial value at the outmost layer and the stable value in the substrate. Assuming that the etching rates of the surface oxide layer for the specimens were the same as that of SiO_2 film on silicon, the thickness of the surface oxide layer for MP specimen was calculated as 1.4 nm, while those of GLSE, GLW, and GPE were 5.6, 16.6, and 146.9 nm respectively.

DISCUSSION
In this study, E_{corr} values were different from E_{pzc} values in each specimen. In particular, GLW and GPE revealed relatively large differences. These specimens were covered with a thick and stable oxide film that acted as a strong protective film as well as provided insulation. This film prevented a flow of electricity between the alloy substrate and the electrolyte. Therefore, obvious differences were observed between the E_{corr} and E_{pzc} values of GLW and GPE. In the polarization curves, the current densities of GLSE and MP increased slightly in the passive region,
where the velocity of passive film generation was equivalent to that of passive film dissolution\(^{60}\). In the transpassive region after the passive region, the current density gradually increased due to metal dissolution and \(O_2\) evolution\(^{47}\). However, the oxide film on GLW and GPE specimens restricted metal dissolution. This thus explained the finding that the current density values of GLW and GPE remained cathodic between the open circuit potential and \(E_{corr}\) value, thereby leading to very high \(E_{corr}\) values for GLW and GPE. Consequently, there was no passive region for the GLW and GPE specimens. \(E_{corr}\) is one of the parameters that estimates the corrosion resistance of metals: higher \(E_{corr}\) shows better corrosion.
resistance. Therefore, based on the results of this study, the electrolytic treatments were shown to improve the corrosion resistance of Ti-Ni alloy.

With respect to the immersion test, the amounts of released titanium and nickel ions from GLW were lower than those from any other specimens, and the amount of released nickel ions was lower than that of released titanium ions. Although the amount of released nickel ions was also lower than that of released titanium ions for GPE, the amount of titanium ions was higher than the other electrolyzed groups. These results implied that the electrolytic treatment for GLW — with the electrolyte composed of lactic acid, water, and glycerol — was more effective in improving the corrosion resistance of Ti-Ni alloy than the other acidic electrolyte compositions.

In this study, thickness of the surface oxide layer was calculated by both the XPS and AES methods. In the XPS method, thickness of the oxide layer was based on the peak intensity of a metal element in the substrate. Therefore, limitation in thickness measurement stemmed from the detectable limit of photoelectrons. In the case of the surface oxide layer of GPE shown in Table 2, the thickness could not be calculated since the photoelectrons of Ni$^0$ in the substrate metal were not detected. On the other hand, in the AES method, thickness was calculated

<table>
<thead>
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<th>Specimen code</th>
<th>Relative concentration (mol%)</th>
<th>t (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Ni</td>
</tr>
<tr>
<td>MP</td>
<td>13.3±1.4</td>
<td>9.9±1.2</td>
</tr>
<tr>
<td>GLSE</td>
<td>16.1±0.2</td>
<td>7.6±2.1</td>
</tr>
<tr>
<td>GLW</td>
<td>19.6±0.6</td>
<td>1.6±0.4</td>
</tr>
<tr>
<td>GPE</td>
<td>14.7±2.8</td>
<td>2.9±1.1</td>
</tr>
</tbody>
</table>

Average ± Standard deviation, N=2

*Thickness exceeded detectable limit

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**Fig. 5** AES depth profiles of the relative concentrations of elements at the surface oxide layer of Ti-Ni alloy. Specimens were mechanically polished (MP) or electrolyzed (GLSE, GLW, and GPE), where: (a) MP, (b) GLSE, (c) GLW, and (d) GPE.
based on the relative concentration of oxygen. Due to these analytical differences, the thickness values of the surface oxide layer calculated by XPS and AES methods were different. Nonetheless, both methods showed a common tendency in the thickness of the surface oxide layers: highest value for GPE, followed by GLW, GLSE, and MP. This indicated that the electrolytic treatment caused the thickness of surface oxide layer to increase, and that the oxide layer thickness was dependent on the electrolyte composition.

As for the relative concentration of nickel in the surface oxide layer, it decreased after being subjected to electrolytic treatment (Table 2). The valence of nickel in the surface oxide layer was only Ni$^{2+}$ as shown in Fig. 4(b), which corresponded to Ni(OH)$_2$ – a thermodynamically stable substance in the presence of water and neutral or slightly alkaline solutions. On the other hand, Ni(OH)$_2$ dissolves easily in acidic solutions with the formation of nickel ion Ni$^{2+}$, or in very alkaline solutions with the formation of nickelite ion HNiO$_2$. Since the pH of electrolytes used in this study ranged from 0.73 to 1.4, it is suggested that Ni(OH)$_2$ selectively dissolved from the outmost surface oxide layer to the electrolytes during the electrolytic treatment. Consequently, nickel concentration in the surface oxide layer of the electrolyzed specimens was lower than that of MP specimen.

Ti$^{3+}$ and Ti$^{4+}$ in the surface oxide layer of MP specimen were oxidized to Ti$^{4+}$ by the electrolytic treatment as shown in Fig. 4(a). In other words, the oxidation process of TiO to trivalence occurred, and so did dehydoration. After Ti$^{2+}$O$_2$ was formed by the oxidation of TiO, its oxidation to tetravalence produced Ti$^{4+}$O$_2$H$_2$, and TiO$_2$ was formed by the dehydration of Ti$^{4+}$O$_2$H$_2$ according to the following reactions:

$$\text{Ti}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{TiO(OH)}_2 + 2\text{H}^+ + 2\text{e}^- \quad (\text{oxidation to tetravalence}) \quad (1)$$

$$2\text{TiO(OH)}_2 \rightarrow 2\text{TiO}_2 + 2\text{H}_2\text{O} \quad (\text{dehydration}) \quad (2)$$

TiO$_2$ is thermodynamically stable in the presence of water or aqueous solution. For GLW, the surface oxide layer consisted of Ti, O$^{2-}$, OH$^-$, absorbed and/ or bound water, and a slight amount of nickel. Therefore, it was possible that this surface oxide layer was more stable than that of the other specimens.

With respect to the electrolyte for GPE, almost all the phosphate ions existed as H$_2$PO$_4^-$ and HPO$_4^{2-}$ at pH $\leq$ 0.25. Therefore, the reaction between titanium and phosphate could be described as follows:

$$\text{TiO(OH)}_2 + 2\text{H}_2\text{PO}_4^- \rightarrow \text{TiO(H}_2\text{PO}_4)_2 + 2\text{OH}^- \quad (3)$$

$$\text{TiO(OH)}_2 + \text{HPO}_4^{2-} \rightarrow \text{TiO(HPO}_4)_2 + 2\text{OH}^- \quad (4)$$

H$_2$PO$_4^-$ and HPO$_4^{2-}$ ions were taken up in the surface oxide layer, which could be a reason for the increase in released titanium ions from GPE in the immersion test.

Weight loss of Ti-Ni alloy specimen was 1.3% when treated with GLSE electrolyte – which was composed of lactic acid, sulfuric acid, ethanol, and glycerol. As for GLW and GPE, the weight losses were 0.01% and 0.03% respectively. The authors speculated that the difference in weight loss could be attributed to TiO$_2$. This was because TiO$_2$ was the main component in the surface oxide layer of Ti-Ni alloy, and TiO$_2$ is soluble in sulfuric acid. In this connection, the thin surface oxide layer and the high nickel concentration in the oxide layer of GLSE specimen could be attributed to TiO$_2$ dissolution.

From the results of this study, it was shown that with a suitable electrolyte, electrolytic treatment could improve the corrosion resistance of Ti-Ni alloy. Therefore, it is thought that this is an effective means of producing medical and dental devices that utilize shape memory effect or superelasticity with better biocompatibility – advantageous properties that can be rendered by Ti-Ni alloy with improved corrosion resistance.

**CONCLUSIONS**

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

1. Electrolytic treatment was effective in improving the corrosion resistance of Ti-Ni alloy. In particular, the GLW treatment – with the electrolyte composed of glycerol, lactic acid, and water – showed high corrosion potential and yielded less amount of released titanium and nickel ions.

2. Titanium in the surface oxide layer of Ti-Ni alloy was oxidized to Ti$^{4+}$ by electrolytic treatment, and thus became more stable.

3. Thickness of the surface oxide layer of Ti-Ni alloy increased after being subjected to electrolytic treatment.

4. Nickel concentration in the surface oxide layer of Ti-Ni alloy decreased after being subjected to electrolytic treatment, especially by the GLW treatment.

5. Characteristics of the surface oxide layer of electrolyzed Ti-Ni alloy varied according to the electrolyte composition.

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