Corrosion Resistance of the Pt-Fe-Nb Magnets for Dental-casting

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Magnetic attachments have been used in clinical dental practice, but there is some difficulties associated with removable bridges. One possible solution is to make whole bridges of Pt-Fe magnet alloys and its abutment out of magnetic stainless steel by casting. In terms of castability and magnetic properties, the promising composition of the Pt-Fe-Nb magnet alloy is Pt-30.0 mass% Fe-0.6 mass% Nb and Pt-30.0 mass% Fe-0.5 mass% Nb-0.03 mass% Si. In the present study, the corrosion resistance of these alloys was investigated based on the elusion test, electrochemical behavior and surface characterization by EPMA analysis. The released elements from the Pt-Fe-Nb magnets were mainly Fe ions in quantities similar to that of stainless steel for biomedical use, and the Pt-Fe-Nb magnet alloy, the Pt-Fe-Nb-Si magnet alloy and platinum resembled each other in electrochemical behavior. The present findings suggest, that the Pt-Fe-Nb magnet alloy provides excellent corrosion resistance and has important clinical dental applications.

Key words: Pt-Fe-Nb magnet alloys, Dental casting, Corrosion behavior

INTRODUCTION

Ready-made magnetic attachments have been become increasingly more common in clinical dental practice in Japan¹–⁴. These attachments are made from rare earth permanent magnet with a magnetic stainless steel yoke, and they are covered and sealed completely by non-magnetic stainless steel⁵–⁷. However, there are some problems associated with the use of these attachments with removable bridges because there is not enough room to set a magnetic attachment at the crown for a vital molar. In addition, there are other problems when a magnetic attachment is applied to a non-vital tooth. Equipping a removable bridge with a magnetic attachment causes weakness in the bridge. Moreover, since the magnetic attachment is fixed with adhesives, there are concerns about separation of the attachment from the bridge by degradation of the adhesives. To solve these problems, we developed a new bridge system, made by a dental casting technique utilizing castable permanent magnet alloys⁸–¹¹. The Pt-Fe-Nb magnet alloys have previously been investigated as dental casting alloys⁸⁰. The magnet alloy of Pt-30.0 mass% Fe along with a few additional elements, had excellent magnetic properties and a reasonable castability by casting into titanium dental investment material in an argon atmosphere⁸⁰.
It was reported that Pt-30.0 mass% Fe-0.6 mass% Nb (Fe-39.5 mol% Pt-0.75 mol% Nb) could cast into titanium investment material using the high frequency melting vacuum pressure dental casting machine\(^{8,11}\). Furthermore, adding 0.03 mass% Si (0.1 mol% Si) to this alloy reduced surface roughness and casting defects of casting, and the casting of the alloy which added 0.03 mass% Si (0.1 mol% Si) showed adequate attractive force in which clinical applications may be possible\(^{10,11}\).

The purpose of the present was to investigate corrosion resistance of the dental casting of the Pt-30.0 mass% Fe-0.6 mass% Nb (Fe-39.5 mol% Pt-0.75 mol% Nb) and Pt-30.0 mass% Fe-0.5 mass% Nb-0.03 mass% Si (Fe-39.5 mol% Pt-0.65 mol% Nb-0.1 mol% Si) magnet alloy by elution, anodic polarization curve and natural potential in 0.9% NaCl and 1.0% lactic acid solution, and the surface characteristics.

**MATERIALS AND METHODS**

*Composition and specimens*

The alloys used for the experiments were Fe-39.5 mol% Pt-0.75 mol% Nb (Pt-Fe-Nb magnet casting) and Fe-39.5 mol% Pt-0.65 mol% Nb-0.1 mol% Si (Pt-Fe-Nb-Si magnet casting). They were prepared from 99.995% electrolytic iron (MAIRON-HP, Toho Zinc Co. Ltd., Tokyo, Japan), 99.9% platinum (Pt, Tanaka Kikinzoku Kogyo K.K., Tokyo, Japan), 99.9% niobium, and 99.5% silicon. An argon arc furnace (TAM-4S, Tachibanariko Co. Ltd., Sendai, Japan) in 99.999% argon gas was used to make the magnet alloys. To produce a homogeneous alloy, the metals were alternately inverted and melted at least four times. The dimensions of the specimens for the corrosion test were 7 × 7 × 3 mm rectangles. The specimens were made by dental casting, using the dental investment material for titanium crowns and bridges (Titavest CB, Morita Co. Ltd., Tokyo, Japan). The magnet alloys were cast using a high frequency melting vacuum pressure casting machine (Argoncaster T, Shofu Inc., Kyoto, Japan) at a mold temperature of 600°C. Subsequently, the specimen was vacuum-sealed in the silica tube and then heated for solution and aging anealing. The solution condition of the specimens was treatment for 30 min at 1,325°C, and quenched in ice salt water. The aging condition was for the maximum value of the maximum energy products (Pt-Fe-Nb magnet casting was 9 hr at 650°C, Pt-Fe-Nb-Si magnet casting was 7 hr at 600°C\(^{8-12}\)). After the heat treatment, the specimens were magnetized with a static magnetic field of 20 kGs for 60 sec.

*Elution*

The surfaces of casting specimens were polished with #800 emery paper and cleaned with acetone in an ultrasonic cleaner. The specimens were dipped into the capped polyester tube filled with 10 ml 0.9% NaCl solution or 1% lactic acid solution maintained at 37°C for 168 hr. Immediately after immersion, the solutions were saturated with oxygen (about 6.3 mg/l). The quantitative analysis of the immersing liquid was carried out on Fe, Pt and Nb using inductively coupled plasma atomic emission spectrometry (IRIS/IRIS-AP, Nippon Jarrell-Ash Co. Ltd., Kyoto, Japan). The amount of
dissolution converted the concentration of each ion into a dissolution mass per 1 cm². The experimental findings are shown as the average of 5 measurements.

**Electrochemical behavior**

Each specimen was embedded in epoxyresin, leaving one surface free, then the surface of the casting specimens was removed using #800 emery paper. After ultrasonic cleaning with acetone, the specimens were used for electrochemical measurement. The potential values against the Ag/AgCl reference electrode were converted into the potential values against the normal hydrogen electrode (NHE).

The natural potential and anodic polarization measurements were determined in 0.9% NaCl solution and 1% lactic acid solution at 37°C. Changes in the natural potential (n=3) were recorded against an Ag/AgCl reference electrode over 168 hr for each alloy in a solution saturated with a dissolved oxygen concentration of 6.3 mg/l. The anodic polarization measurement (n=2) was obtained at a scanning rate of 5.0 \( \times 10^{-4} \) V/sec in the 0.9% NaCl and 1% lactic acid at 37°C. The oxygen in the solutions was purged to a minimal concentration (<0.2 mg/l) using argon gas, to avoid the influence of a cathode reaction. The potential and current measurements were carried out in a cell with three electrodes: the specimen as the working-electrode, the platinum electrode as the counter-electrode, and a saturated calomel electrode against which the potential on the specimen surface was measured. After the free corrosion potential became stable, polarization measurements were started from the rest potential. To reduce of limit errors, the measurements were repeated twice using different specimens for each condition, and the lower breakdown potential of each condition was adopted. Electrochemical measurement was performed and compared under similar conditions with platinum.

**Surface characterization**

The polished specimens of the magnet alloys were observed under an optical microscope, and the composition was analyzed by EPMA (JX-8800, JEOL Ltd., Tokyo, Japan).

**RESULTS**

**Elution**

The results of the dissolution from the Pt-Fe-Nb magnet alloys in 0.9% NaCl solution or 1% lactic acid solution at 37°C are shown in Tables 1 and 2. In the 0.9% NaCl solution, dissolutions of all elements were below the detection limits in both the Pt-Fe-Nb magnet casting and the Pt-Fe-Nb-Si magnet casting. In the case of the 1% lactic acid solution, however, a very small amount of Fe ion and a trace of Nb ion were detected which were eluted from both the Pt-Fe-Nb magnet casting and the Pt-Fe-Nb-Si magnet casting. The Pt ion dissolution could not detected. The dissolution of the Fe ion was 1.1 \( \mu g/cm² \) from the Pt-Fe-Nb magnet casting, and 4.1 \( \mu g/cm² \) from the Pt-Fe-Nb-Si magnet casting. The dissolution of the Fe ion from the Pt-Fe-Nb-Si magnet
Table 1  Released elements from Pt-Fe-Nb magnet alloys and dental alloys in 0.9% NaCl corrosive solutions (over 168 hr)  

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Fe</th>
<th>Pt</th>
<th>Nb</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Ag</th>
<th>Cu</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Fe-Nb magnet casting</td>
<td>*</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.100±0.190</td>
</tr>
<tr>
<td>Pt-Fe-Nb-Si magnet casting</td>
<td>4.146±0.423</td>
<td>*</td>
<td>0.065±0.018</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.211±0.408</td>
</tr>
<tr>
<td>Stainless Steel (SUS316L)</td>
<td>2.490</td>
<td></td>
<td></td>
<td>0.160±0.200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.850</td>
</tr>
<tr>
<td>Stainless Steel (SUS447J1)</td>
<td>1.780</td>
<td></td>
<td></td>
<td>0.150</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td>1.930</td>
</tr>
<tr>
<td>Type IV Gold Alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.577±0.592</td>
</tr>
<tr>
<td>Detectable limit</td>
<td>0.001</td>
<td>0.011</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.169</td>
</tr>
</tbody>
</table>

*not detected (Average±S.D.)

The groups joined by the line were not significantly different by one-way ANOVA.

Table 2  Released elements from Pt-Fe-Nb magnet alloys and dental alloys in 1% Lactic acid corrosive solutions (over 168 hr)  

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Fe</th>
<th>Pt</th>
<th>Nb</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Ag</th>
<th>Cu</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Fe-Nb magnet casting</td>
<td>1.077±0.188</td>
<td>0.023±0.004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.000±0.188</td>
</tr>
<tr>
<td>Pt-Fe-Nb-Si magnet casting</td>
<td>4.146±0.423</td>
<td>*</td>
<td>0.065±0.018</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.211±0.408</td>
</tr>
<tr>
<td>Stainless Steel (SUS316L)</td>
<td>2.490</td>
<td></td>
<td></td>
<td>0.160±0.200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.850</td>
</tr>
<tr>
<td>Stainless Steel (SUS447J1)</td>
<td>1.780</td>
<td></td>
<td></td>
<td>0.150</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td>1.930</td>
</tr>
<tr>
<td>Type IV Gold Alloy</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>1.169</td>
</tr>
</tbody>
</table>

*not detected (Average±S.D.)

The groups joined by the line were not significantly different by one-way ANOVA.

casting in 1% lactic acid was larger than that from the Pt-Fe-Nb magnet casting.

Electrochemical behavior

Fig. 1 shows the natural potential changes in the Pt-Fe-Nb magnet alloys over 168 hr in 0.9% NaCl solution. For the purpose of comparison, the natural potential of platinum is shown in this figure. The change in the natural potential was measured three times at each condition and the curve of the low value was taken and shown as an example (Fig. 1). All natural potential curves of platinum were maintained between 0.5 and 0.7 (V vs. NHE), and all findings of the natural potential of the Pt-Fe-Nb magnet alloys were maintained between 0.35 and 0.5 (V vs. NHE). With the Pt-Fe-Nb magnet alloys, passivation occurred a few hours after immersion. For transition of the natural potential, statistical analysis by one-way analysis of variance (ANOVA: P<0.05) was performed every 24 hr, and the following results were obtained: the natural potential of the Pt-Fe-Nb magnet casting and the Pt-Fe-Nb-Si magnet casting was clearly lower than that of platinum, and only after 168 hr was the natural potential of the Pt-Fe-Nb-Si magnet casting lower than that of the Pt-Fe-Nb magnet casting.

Fig. 2 shows the natural potential changes of the Pt-Fe-Nb magnet alloys casting
and platinum over 168 hr in 1% lactic acid solution. All results of the natural potential of platinum were maintained between 0.75 and 0.85 (V vs. NHE), and both magnet alloys were maintained between 0.65 and 0.75 (V vs. NHE). The potential of these magnet alloys began rising quickly, and reached the maximum, and then the natural potential fluctuated slowly with time. The value followed a similar pattern to that
Fig. 3 Anodic polarization curves of Pt-Fe-Nb magnet alloys in 0.9% NaCl corrosive solutions.

Fig. 4 Anodic polarization curves of Pt-Fe-Nb magnet alloys in 1% lactic acid corrosive solutions.
observed with 0.9% NaCl solution. Consequently, the natural potentials of both magnet alloys were lower than those of platinum at all investigating points. Moreover, the natural potential of the Pt-Fe-Nb-Si magnet casting was low compared with the Pt-Fe-Nb magnet casting after 72 hr, and the potential of the Pt-Fe-Nb-Si magnet casting fluctuated with time.

Fig. 3 shows the potentiodynamic anodic polarization curve of the Pt-Fe-Nb magnet alloys in 0.9% NaCl solution. Within the stabilized activity range the dissolution potential of both the Pt-Fe-Nb magnet alloys were lower than that of platinum. A flat portion like passivation area was observed in both alloys from 0.5 (V vs. NHE) of the Pt-Fe-Nb-Si magnet casting and 0.2 (V vs. NHE) of the Pt-Fe-Nb magnet casting. Until the transpassive region above 1.2 (V vs. NHE) was reached, the current density was stabilized by the small density. There was little difference in the behavior of the two alloys. The values of the anode current of these magnet alloys were of a lower potential than those of platinum, but, in the transpassive region, the anodic polarization curves were similar to those of platinum.

Fig. 4 shows the potentiodynamic anodic polarization curve in 1% lactic acid solution. The anode current of both alloys began to flow from the higher potential compared with that in 0.9% NaCl solution, and was increased by activity dissolution from approximately 0.6 (V vs. NHE). Then, a flat portion like passivation area was observed until the potential reached the transpassive region around 1.2 (V vs. NHE). According to the anodic polarization behavior in 1% lactic acid solution, there was no significant change among the Pt-Fe-Nb magnet alloys.

Surface characterization
Figs. 5 and 6 show the microstructure of these magnet alloys observed under an optical microscope. The boundary was observed in both magnet alloys, and this bound-
Fig. 7 Maps of Pt, Fe and Nb on the surface of an aged Pt-Fe-Nb magnet casting by EPMA.

ary was observed by EPMA analysis. Fig. 7 shows the distribution of each element at the surface of the aged Pt-Fe-Nb magnet casting by EPMA. Each element was uniformly distributed according to composition. Neither segregation nor precipitation was observed in the microstructure. Fig. 8 shows the EPMA findings of the aged Pt-Fe-Nb-Si magnet casting. Fe was higher in the vicinity of the grain boundary. However, Pt and Nb decreased at the grain boundary, and Si was also slightly higher in the vicinity of the boundary.

**DISCUSSION**

**The corrosion resistance of the Pt-Fe-Nb magnet casting**

In both the 0.9% NaCl solution and the 1% lactic acid solution at 37°C, the anodic polarization curves of the Pt-Fe-Nb magnet casting showed natural potentials that were lower than those of platinum (Figs. 3 and 4). It was reported, however, that the natural potential of the Pt-Fe-Nb magnet of wrought alloy is equivalent to that of platinum in 0.9% NaCl solution and 1% lactic acid solution. The microstructure of the Pt-Fe-Nb magnet casting was uniform in composition, as shown in Fig. 8. EPMA
revealed neither segregation nor precipitation in the microstructure. It appears that the difference in the natural potentials between the casting and the wrought alloy depended on the ordering amount of the super lattice. However, the anodic polarization curves of the Pt-Fe-Nb magnet casting in 37°C, 0.9% NaCl solution and 1% lactic acid solution had high pitting potential and suggested excellent corrosion resistance.
In 37°C 0.9% NaCl solution, the natural potential of the Pt-Fe-Nb magnet casting reached 0.4 (V vs. NHE) several hours after immersion, and then became constant (Fig. 1). At this potential, the anodic polarization curve of the Pt-Fe-Nb magnet casting in 0.9% NaCl solution showed stable passivity. Therefore, the 0.9% NaCl solution appears to provide excellent corrosion resistance.

Fig. 2 shows the natural potential of the Pt-Fe-Nb magnet casting in 1% lactic acid solution. According to this, the natural potential reaches 0.7 (V vs. NHE) several hours after immersion, and there after remains almost constant. This potential of 0.7 (V vs. NHE) is also a passive state according to the anodic polarization curve of the Pt-Fe-Nb magnet casting in 1% lactic acid solution. Therefore, the corrosion resistance of the Pt-Fe-Nb magnet alloy casting in 1% lactic acid solution was also suggested to be excellent.

These findings agree with the elution test results. After immersing the Pt-Fe-Nb magnet casting in 0.9% NaCl solution at 37°C for 168 hr, no elution ions from the magnet were detected. Traces of the Fe and Nb ions were detected when the Pt-Fe-Nb magnet casting was immersed in 1% lactic acid solution, but the elution ion content was lower than that from SUS316L or SUS447J1 stainless steel in 1% lactic acid solution (Table 2)\textsuperscript{13–15}, and the total amount of these ion contents was equal to that from the Type IV gold alloy (Table 2)\textsuperscript{16}. Elution tests demonstrated that the Pt-Fe-Nb magnet alloy casting had superior corrosion resistance as a dental alloy.

Pt-Fe-Nb-Si magnet casting
The anodic polarization curve of the Pt-Fe-Nb-Si magnet casting in 0.9% NaCl solution or 1% lactic acid solution was in good agreement with those of the Pt-Fe-Nb magnet casting. There was no great difference between the natural potential of the Pt-Fe-Nb-Si magnet alloy casting and the Pt-Fe-Nb magnet alloy casting in 0.9% NaCl solution or in 1% lactic acid solution at 37°C for 168 hr. This suggests that the Pt-Fe-Nb-Si magnet casting may also have good corrosion resistance, which is comparable to the Pt-Fe-Nb magnet casting. No eluted ions were detected from the Pt-Fe-Nb-Si magnet casting, even when the Pt-Fe-Nb-Si magnet alloy was immersed in 0.9% NaCl solution at 37°C for 168 hr (Table 1). However, in the elution test for the Pt-Fe-Nb-Si magnet casting in 1% lactic acid solution, there was Fe ion elution, which was four-folds greater than for the Pt-Fe-Nb magnet casting, and approximately double that of the elution from stainless steel SUS316L\textsuperscript{13}. This can be attributed to the microstructure of the Pt-Fe-Nb-Si magnet casting. In the microstructure of the Pt-Fe-Nb-Si magnet casting, there was an iron rich layer along the grain boundary as shown in Fig. 7, and a small platinum rich layer was observed around it. The rest potential might be low at the iron rich layer. Therefore, this layer became an anode, and the Fe ion from the Pt-Fe-Nb-Si magnet casting might be eluted in the 1% lactic acid solution. The surface ratio of the iron rich layer was very low, and, therefore, there was no clear difference in the measurement of the natural potential and the anodic polarization curve. Thus, the elution of Pt-Fe-Nb-Si magnet casting appeared to be slightly inferior to that of the Pt-Fe-Nb magnet casting in 1% lactic acid.
solution. However, the eluted ion quantity from the Pt-Fe-Nb-Si magnet casting was not so great compared with that from dental casting Au-Ag-Pd alloys\(^\text{17}\). Fe ions may be relatively safe, and would not be expected to cause allergic reactions. Although the Pt-Fe-Nb-Si magnet casting may be useful as a dental alloy, attention must be paid to crevice corrosion which damages passivity.

**The contact corrosion**

Contact corrosion between the magnet castings and the stainless steel must be considered because the outer crown made from Pt-Fe magnet castings uses magnetic stainless steel as a keeper. The natural potential of SUS447J1 magnetic stainless steel is approximately \(0.2\) (V vs. NHE) in 0.9% NaCl solution for 36 hr\(^\text{17,19}\). It was lower than 0.4 V of the resting potential of the Pt-Fe-Nb magnet alloys. When these alloys contact each other, the SUS447J1 stainless steel becomes an anode, and the corrosion potential is expected to be in the range from 0.2 to 0.4 V\(^\text{20,21}\). The range of this potential is in the passivity area of the SUS447J1 stainless steel\(^\text{17,19}\), and is lower than the pitting corrosion potential 1.27 (V vs. NHE)\(^\text{17,19}\). Therefore, the Pt-Fe-Nb magnet alloys may be used with magnetic stainless steel SUS447J1 by contact in 0.9% NaCl solution at 37°C.

The contact corrosion in 1% lactic acid solution appears to be similar to that observed for 0.9% NaCl solution. It suggests the natural potential and pitting corrosion potential of each alloy are higher in the 1% lactic acid solution. The natural potential of the Pt-Fe-Nb magnet casting and the Pt-Fe-Nb-Si magnet casting were approximately \(0.7\) (V vs. NHE) in the 1% lactic acid solution for 168 hr (Fig. 2). Therefore, SUS447J1 stainless steel becomes an anode when the magnet castings contact with stainless steel in 1% lactic acid solution\(^\text{20,21}\). In the 1% lactic acid solution, the pitting potential of stainless steel is approximately 1.33 (V vs. NHE)\(^\text{14}\). In addition, for SUS447J1 stainless steel, it may be possible that the Pt-Fe-Nb magnet casting or the Pt-Fe-Nb-Si magnet casting contacts with the stainless steel in 1% lactic acid solution at 37°C.

**CONCLUSIONS**

Anodic polarization curves, natural potential change for 168 hr and elution of the Pt-Fe-Nb magnet casting showed excellent corrosion resistance in 0.9% NaCl solution and 1% lactic acid solution at 37°C.

Anodic polarization curves, natural potential change for 168 hr and elution of the Pt-Fe-Nb-Si magnet casting also showed good corrosion resistance in 0.9% NaCl solution and 1% lactic acid solution at 168 hr. However, the quantity of Fe ion eluted from the Pt-Fe-Nb-Si magnet casting in 1% lactic acid solution was greater than that from the Pt-Fe-Nb magnet casting.

From the view point of corrosion resistance, both the Pt-Fe-Nb magnet casting and the Pt-Fe-Nb-Si magnet casting can be useful for applications as dental magnetic attachments.
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