Electrochemical evaluation of the corrosion resistance of cup-yoke-type dental magnetic attachments

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The corrosion resistance of different magnetic assemblies —Magfit DX800 (Aichi Steel), Gigauss D800 (GC), Hyper Slim 4013, and Hicorex Slim 4013 (Hitachi Metals)— were electrochemically evaluated using anodic polarization curves obtained in 0.9% NaCl solution at 37°C. Stainless steels (444, XM27, 447J1, and 316L) composing the magnetic assemblies were also examined as controls. This revealed that all of the magnetic assemblies break down at 0.6–1.1 V; however, their breakdown potentials were all still significantly higher (p<0.05) than that of 316L. The distribution of elements in the laser welding zone between the yoke and shield ring was analyzed using EPMA; except with Magfit DX800, where the Cr content of the shield ring weld was greater than that of 316L. These magnetic assemblies are expected to have good corrosion resistance in the oral cavity, as their breakdown potentials are sufficiently higher than the 316L commonly used as a surgical implant material.

Keywords: Magnetic attachment, Corrosion resistance, Breakdown potential, Anodic polarization

INTRODUCTION

Dental magnetic attachments are generally composed of either a pair of magnets, or a magnet and a magnetic alloy1,2. In either instance, the attractive force generated between this pairing acts to retain dentures or the superstructures of dental implants in the oral cavity. The magnets are composed of a rare-earth magnetic core, which is covered with corrosion-resistant stainless steel or titanium to protect the more readily oxidized core2.

One kind of the magnet currently used is a magnetic assembly that forms a magnetic circuit using magnetic yokes. This magnetic circuit generates a large attractive force, and is therefore utilized for cup-yoke-type or sandwich-type magnetic attachments3,4. For example, Japanese cup-yoke-type magnetic attachments with a diameter of 3.5–4 mm and a thickness of 1.3 mm exhibit an attractive force of 5–7 N between the magnetic assembly and a keeper made of ferritic stainless steel5,6. This strong force of attraction, as well as the small, thin shape, ensures secure attachment of dental treatments.

Ferritic stainless steels such as SUS 444, SUS XM27 and SUS 447J1 are the most commonly used for the yokes and keepers of cup-yoke-type magnetic attachments (“SUS” is the Japanese Industrial Standard for stainless steels), also protecting the magnet core against corrosive environments. To complete the magnetic circuit, a shield ring of austenitic stainless steel (SUS 316 or SUS 316L) is laser welded in the boundary between the cup and the disk yoke5.

Although ferritic stainless steels have corrosion resistance better than that of SUS 316L, an alloy which is widely used for surgical implants7,8, the keepers are embedded in the precious alloys used for root cap clinical treatment by casting or cementing9. The authors have therefore previously examined whether these harsh environments cause a deterioration of the corrosion resistance of ferritic stainless steels, finding that contact with gold or silver dental alloys increases the number of Fe ions released10-12. Furthermore, heating to 700–800°C for more than 2 h was found to reduce the breakdown potential13.

In the oral cavity, both the magnetic assemblies and keepers are exposed to a complex process of galvanic corrosion. Despite this, however, few researchers have reported the corrosion behavior of magnetic assemblies with regards to the galvanic corrosion created by contact with dental alloys.

There are weld zone jointing ferritic and austenitic stainless steels in the magnetic assemblies. It is commonly known that the welding is likely to cause a localized reduction in corrosion resistance through sensitization by heating14; and thus, magnetic assemblies may exhibit corrosion behavior that is very different from homogenous ferritic stainless steel. Moreover, corrosion of the weld zone can lead to corrosion of the rare-earth magnet core, thereby releasing large numbers of ions15. It is therefore crucial to evaluate the corrosion resistance of magnetic assemblies in order to use them safely for dental implants and dentures. To this end, this study examines the corrosion behavior and electrochemical stability of cup-yoke-type magnetic assemblies, so as to evaluate their corrosion resistance when used in conjunction with dental precious alloys.
MATERIALS AND METHODS

From among the commercially available Japanese magnetic attachments, cup-yoke-type magnetic assemblies with a diameter of approximately 4 mm were selected: Magfit DX800 (Aichi Steel, Nagoya, Japan), Gigauss D800 (GC, Tokyo, Japan), Hyper Slim 4013 and Hicorex Slim 4013 (Hitachi Metals, Tokyo, Japan). These magnetic assemblies are hereafter referred to as Magfit, Gigauss, Hyper, and Hicorex, respectively. The yoke of each attachment was made of AUM20 (comparable to SUS 444), SUS XM27 or SUS 447J1, and the shield ring was made of SUS 316 or SUS 316L. Since the shape of each magnetic assembly is similar, an external view and a schematic cross-section of Hicorex is provided in Fig. 1 as an example. The size and composition of each magnetic assembly is given in Table 1.

The stainless steels SUS 444 (Nisshin Steel, Tokyo, Japan), SUS XM27 (Nippon Koshuha Steel), SUS 447J1 (Nippon Koshuha Steel) and SUS 316L (Nisshin Steel, Tokyo, Japan) were used as controls (hereafter referred to as 444, XM27, 447J1 and 316L, respectively). SUS 444 was used due to a lack of availability of AUM20, as the two alloys are comparable. The stainless steel samples were prepared by first rolling to a thickness of 1 mm, with the processing strain then removed by heating at 1,100°C for 30 min followed by water quenching. The chemical composition of each of the stainless steels is shown in Table 2.

The cup yoke of the magnetic assembly was prepared by connecting an electric lead to its upper surface with silver paste, and then embedding all but the bottom part (mating surface) in an epoxy-acrylic resin. After this, the specimens were ultrasonically cleaned in distilled water and rinsed with ethanol, and then used for electrochemical evaluation. The stainless steels were cut into 10 mm square specimens, which were polished using #180–#800 mesh carborundum paper, and then pretreated using a procedure similar to that used for the magnetic assembly.

The potentiodynamic anodic polarization curve of each specimen was measured in a 0.9% NaCl solution.

Table 1 Materials and sizes of the cup yoke type magnetic assemblies

<table>
<thead>
<tr>
<th>Product (Company)</th>
<th>Yoke</th>
<th>Shield ring</th>
<th>Size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magfit DX800 (Aichi Steel)</td>
<td>AUM20 (444)</td>
<td>316</td>
<td>φ 4.2×1.3</td>
</tr>
<tr>
<td>Gigauss D800 (GC)</td>
<td>XM27</td>
<td>316L</td>
<td>φ 4.0×1.3</td>
</tr>
<tr>
<td>Hyper Slim 4013 (Hitachi Metals)</td>
<td>XM27</td>
<td>316L</td>
<td>φ 4.0×1.3</td>
</tr>
<tr>
<td>Hicorex Slim 4013 (Hitachi Metals)</td>
<td>447J1</td>
<td>316L</td>
<td>φ 4.0×1.3</td>
</tr>
</tbody>
</table>

Table 2 Chemical compositions of the stainless steels

<table>
<thead>
<tr>
<th>Type</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>444</td>
<td>18.6</td>
<td>2.0</td>
<td>0.20</td>
<td>0.008</td>
<td>0.27</td>
<td>0.17</td>
<td>0.029</td>
<td>Bal.</td>
</tr>
<tr>
<td>XM27</td>
<td>26.0</td>
<td>1.0</td>
<td>0.17</td>
<td>0.002</td>
<td>0.34</td>
<td>0.09</td>
<td>0.019</td>
<td>Bal.</td>
</tr>
<tr>
<td>447J1</td>
<td>30.0</td>
<td>2.0</td>
<td>0.18</td>
<td>0.003</td>
<td>0.15</td>
<td>0.04</td>
<td>0.015</td>
<td>Bal.</td>
</tr>
<tr>
<td>316L</td>
<td>17.7</td>
<td>2.0</td>
<td>12.32</td>
<td>0.010</td>
<td>0.06</td>
<td>0.85</td>
<td>0.033</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Fig. 1 Example of a magnetic assembly (Hicorex Slim 4013).
with less than 0.2 ppm dissolved oxygen at 37°C \((n=3)\) using a potentiostat (Model 273, Princeton Applied Research, Tennessee, USA) equipped with a platinum counter electrode. Air free was carried out by bubbling the solution of 300 mL with argon gas. Measurement was started immediately after immersion from rest potential to 1.5 V (vs. NHE) at a scanning rate of \(5 \times 10^{-4}\) V/s. In order to obtain numerical values of the breakdown potential, it was defined as being a tenfold increase over the value of the current density, which moved upward almost vertically in the passive region of the anodic polarization curve. The breakdown potentials were statistically analyzed using ANOVA (Scheffe test) at a significance level of \(\alpha=0.05\).

The corroded areas created on the mating surface of each magnetic assembly by anodic polarization were observed through an optical microscope (GX-51, Olympus, Tokyo, Japan). Each new magnetic assembly was also cut at its median plane, as shown in Fig. 1(b); and after mirror polishing of the cut surface, the weld zone was qualitatively and quantitatively analyzed using an electron probe microanalyzer (EPMA) with wavelength-dispersive X-ray spectrometry (JXA 8900, JEOL, Tokyo, Japan) \((n=3)\). Quantitative analyses in the vicinity of the mating surface were performed five or more times per specimen. Color mapping images and the Cr, Ni and Mo content of the weld zone were obtained, and were statistically analyzed using ANOVA (Scheffe test) at a significance level of \(\alpha=0.05\).

**RESULTS**

Profiles of the anodic polarization curves for the various magnetic assemblies (solid lines) and stainless steels (short dashed line) are summarized in Fig. 2. The profiles of the stainless steels show a passive region, in which the current density undergoes only minimal change with an increase in scanning potential. Beyond this region the current densities abruptly increase, which is where the stainless steels broke down. The profiles of the magnetic assemblies show similar passive regions to those of the stainless steels. Passive current densities of each magnetic assembly are about ten times lower than those of each stainless steel composing it within the passive regions, respectively.

The breakdown potentials of the stainless steels and magnetic assemblies are shown in Fig. 3 (a) and (b), respectively. In Fig. 3 (a), the breakdown potentials of the stainless steels can be seen to rise in the following ascending order: 316L (Group A), 444 (Group B), XM27...
and 447J1 (Group C). With an increase in the Cr content of the stainless steel, the breakdown potential also rose; however, there is no significant difference (p>0.05) in the breakdown potentials of XM27 and 447J1.

As shown in Fig. 3 (b), there was no significant difference (p>0.05) in the breakdown potentials of Magfit, Gigauss and Hyper (Group B); the yokes of which were made of either 444 or XM27. However, the breakdown potentials of Hicorex (Group C), with a yoke of 447J1, were significantly higher (p<0.05) than those of Magfit. The breakdown potentials of all the magnetic assemblies were significantly higher (p<0.05) than those of 316L (Group A), despite having a welded 316 or 316L shield ring. As compared to the stainless steels composing the magnetic assemblies, the breakdown potentials of Magfit and Hicorex were significantly higher (p<0.05) than those of 444 and 447J1 composing them, respectively. No significant difference (p>0.05) could be found among the breakdown potentials of Gigauss, Hyper and XM27.

The corroded areas on the surface of each magnetic assembly are shown in Fig. 4. Serious corrosion is frequently observed in the vicinity of the weld zone on all surfaces following anodic polarization at 1.5 V. Small pits and cracks caused by corrosion are also evident in the weld zone of Hicorex covered with 447J1; however, the Hicorex shows less corrosion damage than the other magnetic assemblies.

Figure 5 shows the distribution of Cr and Ni in the weld zone on the surfaces of the magnetic assemblies. The composition images reveal that a weld bead covers the surface of the shield ring, and effectively prevents the exposure of shield rings made of 316 or 316L. The magnetic assemblies except Hicorex have one weld bead on the surface. On the other hand, Hicorex shows the connected two weld beads caused by welding twice. Magfit shows a thin pure Ni film in the boundary between the disk yoke and the shield ring, and the weld bead was alloyed with the yokes, the Ni film and the shield ring. The distributions of Cr and Ni in the weld bead are not appreciably different from those in the shield ring. In Gigauss, Hyper and Hicorex, however, the distribution of Cr and Ni in the weld bead is greater and less, respectively, than that in the shield ring.

Figure 6 shows the Cr, Ni and Mo distribution in the beads of all magnetic assemblies. The Cr content of Magfit (Group A) is significantly smaller (p<0.05) than that of the other magnetic assemblies (Groups B and C), but there is no significant difference (p>0.05) in the Cr content of Gigauss, Hyper and Hicorex (Groups B and C). The Cr content of all the magnetic assemblies is believed to be larger than that of 316L.

The Ni content of Magfit (Group A) is significantly greater (p<0.05) than that of the other magnetic assemblies (Group B), and there were no significant differences (p>0.05) between Gigauss, Hyper and Hicorex (Group B). In the case of the Mo content, there is no significant difference (p>0.05) evident between any of the magnetic assemblies.

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![Fig. 4](image_url) Surface appearance of magnetic assemblies after anodic polarization measurement to 1.5 V in 0.9% NaCl solution at 37°C.

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DISCUSSION

Dental magnetic assemblies are hybrid devices designed for coexistence with dental alloys. Therefore, it is necessary to evaluate their corrosion resistance in environments involving coexistence with dental alloys.

The breakdown potentials of ferritic stainless steels such as 444, XM27 and 447J1 was found to be higher than that of 316L due to the fact that they all contain more Cr. Figure 4 shows that the weld zones on the shield rings of all magnetic assemblies are preferentially corroded, however their breakdown potentials are higher (0.6–1.1 V) than those of the shield rings made of 316L according to the anodic polarization curves. This adverse effect is caused by the surface of the shield rings being covered by the weld bead, as the XM27 and 447J1 used for the yokes both contain more Cr (26 and 30 mass%, respectively) than 316L. This means that the beads of 316L alloyed with XM27 or 447J1 exposed at the surface have an increased Cr content, resulting in an increased breakdown potential in the shield ring. Given that deterioration in corrosion resistance often results from welding\(^\text{14}\), the very slight local heating induced by laser welding also contributes to the lack of deterioration in this instance because the cooling rate is too fast to precipitate the $\sigma$ or $\chi$ phase that triggers intergranular or pitting corrosion\(^\text{13}\).

In the case of the Magfit with yokes of 444, there were no differences in the distribution of Cr between the shield ring and the bead. Moreover, the Mo content, which is known to contribute to an increase in corrosion resistance\(^\text{16}\), also showed no appreciative difference. The higher breakdown potential of Magfit compared to 316L is therefore considered to be the result of surface treatments such as the passivation treatment\(^\text{14}\) that may have been applied prior to receiving it for testing. Some of the other magnetic assemblies also demonstrate breakdown potentials higher than those of the stainless steels composing their yokes, suggesting that this is not an isolated case. Hence, although the details are at best sketchy, it is suggested that magnetic assemblies should not be polished in clinical use, as the removal of surface treatments may reduce their corrosion resistance.
Takahashi et al.\textsuperscript{10} obtained corrosion potentials of 444, XM27, 447J1, and 316L in contact with a range of precious alloys commonly used for dental root caps by using their respective anodic and cathodic polarization curves. This revealed that the rest potentials of precious alloys, such as Type 3 and 4 gold and silver alloys, are less than or comparable to 0.35 V; and that they therefore do not reach the breakdown potential of 316L, even when the surface area ratio of the precious alloy is tenfold the size of that of the stainless steel.

The results of this study clearly show that cup-yoke-type magnetic assemblies have a higher breakdown potential than 316L, a material that is already used in surgical implants exposed to oxidizing environments containing chloride ions that are conducive to pitting corrosion. Thus, when magnetic assemblies come into contact with precious alloys used for dental root caps, either directly or by way of the keepers, the corrosion potential cannot be increased beyond their breakdown potential. The corrosion potentials therefore clearly exist in a passive region of electrochemical stability, and so the magnetic assemblies are expected to maintain an excellent corrosion resistance. However, given that the weld zones are slightly less corrosion resistant than the yokes, it is preferable to select a combination of dental alloys that will raise the corrosion potential as little as possible.

**CONCLUSION**

Cup-yoke-type magnetic assemblies composed of 444 (comparable to AUM20), XM27 and 447J1 demonstrated breakdown potentials sufficiently higher than the 316L of the shield ring to ensure excellent corrosion resistance. In addition, these assemblies should maintain their stable corrosion resistance in an oral cavity, because their breakdown potential levels are sufficiently higher than the corrosion potential generated by contact with precious alloys used for root caps in clinical treatments. Despite this, it is preferable to select a combination of dental alloys that will give the lowest overall increase in corrosion potential, so as to ensure that the magnetic assemblies are adequately protected from serious galvanic corrosion damage over time.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge NEOMAX ENGINEERING Co., Ltd., and GC Co., Ltd., for providing the dental magnetic attachments. This study was partially supported by Grants-in-Aid for Scientific Research (B) (18390511) and Challenging Exploratory Research (25670830) in JSPS, and a NEDO grant (05IS051).

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