Bending Property of Super-Elastic Ti-Ni Alloy Dental Castings with Different Heat Treatments

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Bending property of Ti-Ni alloy dental castings was evaluated in comparison with that of Co-Cr alloy in a cantilever test. Heat treatment effect on the bending property was also investigated in relation to phase transformation. Ti-50.85Ni (mol%) alloy was used, and the shape of bending test specimens was half-rounded in cross section, 2.0 mm in diameter. The bending test was carried out at 310 K. Distance between the loading point and the grip edge was 5.0 or 10.0 mm. Maximum bending deflection was 0.50 mm. Thermal behavior accompanying phase transformation of Ti-Ni alloy was examined by differential scanning calorimetry. Load-deflection diagrams of Ti-Ni alloy castings in the bending test showed elastic and super-elastic deformation, while those of Co-Cr castings showed elastic and permanent deformation. Maximum bending load and residual deflection of the Ti-Ni castings were lower than those of the Co-Cr castings and were decreased by heat treatment under a high-stress condition at the 5-mm loading point. Transformation temperature was increased by heat treatment, which was thought to influence the change in bending property. Super-elasticity of the Ti-Ni alloy castings in bending was shown to be improved by heat treatment, offering the potential to improve the design and clinical performance of cast dental prostheses. [doi:10.2320/matertrans.48.428]

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1. Introduction

Super-elasticity is one of the most attractive mechanical properties of Ti-Ni alloy in medical and dental treatment. This phenomenon occurs at a temperature above the reverse transformation temperature range, associated with stress-induced martensitic transformation. The functional force generated by the super-elasticity is stable over a wide range of strain, deflection and/or torsion, which recovers remarkably. Since the alloy possesses high corrosion resistance as well as good biocompatibility, it has been increasingly applied to medical and dental appliances, including venacava filters, self-expanding stents, orthodontic wires and coilsprings, guidewires for catheters, endodontic rotary instruments and intermaxillary ligature wires. With respect to the production of Ti-Ni alloys, research on sputter-deposited thin films, melt-spinning technique and ultrafine laminates has been reported.

Super-elasticity of Ti-Ni alloy is also useful for dental prostheses, especially for denture retainers such as clasps and bars. The range of large shape recovery strain and of stable stress of super-elastic Ti-Ni alloy are considered to be useful for the fabrication of dental retainers with less stress to the abutment teeth and good esthetic appearance. Dental prostheses are generally made by precision casting. Although casting Ti-Ni alloy is difficult using conventional dental casting techniques, advances in dental casting technology for titanium alloys has made it possible to cast Ti-Ni alloy with super-elasticity.

Dental prostheses are used under repetitive stress conditions and studies of the fatigue property of Ti-Ni alloy castings showed superior fatigue property in a placement-and-removal test and a tensile test. It was also reported that heat treatment of Ti-Ni alloy castings improved super-elasticity in a tensile test, and decreases in apparent proof stress and residual strain were observed. However, in order to evaluate the mechanical properties of dental cast retainers from the clinical viewpoint, bending property is thought to be one of the suitable parameters of clinical performance considering the direction and condition of the applied force on the retainers. In the present study, bending property of Ti-Ni alloy dental castings was evaluated quantitatively in a cantilever test and compared with that of Co-Cr alloy, the most commonly used base metal casting alloy for partial denture framework. In order to improve bending property so as to achieve better shape recovery, the heat treatment effect on bending property was investigated in relation to phase transformation.

2. Experimental Procedures

Ti-Ni alloy ingots for casting were prepared using Ti-50.85Ni (mol%) alloy (NT-E4; Furukawa Electric, Japan) with use of an argon arc furnace. Wax patterns for test specimens were invested with a commercial phosphate-bonded silica investment material (Snow-white; Shofu, Japan). Molds for casting were made by melting the wax in the investment and firing it at 1073 K for 7.2 ks according to the manufacturers’ instructions. An argon arc melting and centrifugal casting machine (Ticast Super R; Selec, Japan) was used for casting. The casting conditions were 8 mm of distance between the electrode and the ingot, 180 A of electric current, and melting and pouring the alloy 30 s and 40 s after the start of rotation. The molds were water-quenched or heat-treated immediately after casting. Heat treatment was performed within the mold in an electric
furnace at 713 or 773 K for 1.8 ks in air, which was reported to be effective in previous studies.\textsuperscript{20,22} The specimens were water-quenched after heat treatment, and the specimen surface was polished with SiC paper #600 with minimum surface removal.

The shape of bending test specimens was half-rounded in cross section, 2.0 mm in diameter, 45 mm in length. A cantilever bending test was carried out at 310 K with a special jig fixed to a servo-hydraulic testing machine (Servopulser EHF-FB1; Shimadzu, Japan). Bending load was applied to the flat surface of the specimens. The distance between the loading point and the grip edge was 5.0 or 10.0 mm. The maximum bending deflection at the loading point was set at 0.50 mm in consideration of the standard undercut value for denture retainers. Since maximum deflection was constant, at the 5-mm loading point higher bending stress was applied to the specimens than at the 10-mm loading point. The loading and unloading speed was 0.02 mm s\textsuperscript{-1}. Bending property was evaluated by the parameters of maximum load value and residual deflection after being unloaded, obtained from load-deflection diagrams. Co-Cr alloy (Cobaltan clasp; Shofu, Japan) castings made with conventional techniques were used for comparison. Four specimens were prepared for each condition. One-way factorial analysis of variance was used for the detection of differences among groups. The Tukey-Kramer test was performed as the \textit{post hoc} test for the detection of differences between groups, where statistical significance was set at $p < 0.05$.

Thermal behavior accompanying phase transformation of Ti-Ni alloy casting was examined by differential scanning calorimetry (DSC). The specimens (approximately 30 mg) were cut from the castings and sealed in aluminum cells. The atmosphere of the measuring chamber of the differential scanning calorimeter (DSC-7000; ULVAC, Japan) was argon gas, and alpha alumina powder was used as the reference material. The scanning temperature was between 173 and 373 K. The heating rate was 0.17 K s\textsuperscript{-1}, and liquid nitrogen was used for the cooling process. Transformation temperatures were obtained from the DSC diagrams.

3. Results and Discussion

Typical load-deflection diagrams of the alloy castings at the 10-mm loading point are shown in Fig. 1; the thick solid line indicates the Ti-Ni cast specimen without heat treatment (TN-ac), dashed and dotted lines indicate the Ti-Ni specimens with heat treatment at 713 K (TN-713) and 773 K (TN-773), respectively, and the thin line indicates the Co-Cr specimen. All three Ti-Ni specimen groups showed a nearly linear relation between load and deflection, suggesting that the strain condition was within the elastic range of these Ti-Ni castings. In contrast, the Co-Cr specimen showed a gradual decrease in ratio of load to deflection in the loading process, which suggested yielding occurred for Co-Cr castings under this bending condition. This agreed with the permanent deflection remaining after being unloaded. The ratio of load to deflection in the loading process was much higher for Co-Cr alloy than Ti-Ni alloy castings, which is thought to be caused mainly by differences in their elastic moduli.

Figure 2 shows typical load-deflection diagrams of the castings in the bending test at the 5-mm loading point. All Ti-Ni castings showed a gradual decrease in the ratio of load to deflection in the loading process, similar to the Co-Cr casting at the 10-mm loading point; however, the deflection was considerably recovered in the unloading process. This recovery in deflection is thought to be caused by super-elasticity. Load value in the loading process tended to decrease after heat treatment. One possible reason for this change in load value was thought to be recrystallization by heat treatment.\textsuperscript{23} With respect to the Co-Cr specimens, the decrease in ratio of load to deflection started at a low deflection, and a large permanent deformation remained after being unloaded.

Maximum load values of the alloy castings in the bending test are shown in Fig. 3. These values were recorded at 0.50-
mm deflection, and the distance between the loading point and the grip edge was 5.0 or 10.0 mm. Although the maximum bending load of Ti-50.85Ni castings tended to decrease by heat treatment, the values were not significantly different at the 10-mm loading point. At the 5-mm loading point, however, the maximum load of 773-K treated Ti-Ni specimens was significantly lower than that of the as cast specimens. One of the reasons for this difference is thought to be the deformation modes of Ti-Ni alloy under these bending conditions. When bending stress exceeding the elastic limit is applied to super-elastic Ti-Ni alloys, the increase in load per unit deflection decreases, like permanent deformation. Therefore, the linear load-deflection relations of Ti-Ni specimens at the 10-mm loading point in Fig. 1 implied deformation within the elastic range, while the apparent yielding observed at the 5-mm loading point in Fig. 2 suggested deformation of these specimens exceeded the elastic limit. Since the latter includes elastic and twin deformations, the parameter of apparent yielding stress seemed to influence the maximum load value as well as the elastic modulus. With respect to the comparison between Ti-Ni and Co-Cr alloys, the maximum load was statistically higher for the Co-Cr specimens at both the 5-mm and 10-mm loading points. However, the maximum load of Co-Cr alloy at the 5-mm loading point was not proportionally higher than that at the 10-mm loading point when compared with the values of Ti-Ni alloys. This appeared to be caused by the less elastic range in deflection of Co-Cr alloy than Ti-Ni alloy.

Figure 4 shows the residual deflection values of the alloy specimens at the 5- and 10-mm loading points in the bending test. The residual deflection value was defined as the deflection remaining after being unloaded in order to evaluate the shape recovery of the cast specimens after being bent. The residual deflection values of the Ti-50.85Ni castings at the 10-mm loading point were not significantly different among the three conditions; however, at the 5-mm loading point this value was decreased significantly by heat treatment. The shape recovery of the Ti-Ni specimens at the 10-mm loading point was within the elastic deformation range, whereas at the 5-mm loading point the deformation range included elastic and super-elastic ranges. This difference in deformation mode is thought to influence the effect of the heat treatment on the residual deflection values of the Ti-Ni castings. The residual deflection value of the Co-Cr alloy casting was much larger than those of the Ti-Ni castings. Two of the main reasons for this difference are considered to be the low elastic range in deflection of Co-Cr alloy and the super-elastic shape recovery of Ti-Ni alloy.

Heat treatment was reported to effectively change the tensile property of Ti-Ni alloy casting in relation to phase transformation, although it was possible that oxidation of the specimens by heat treatment deteriorated the mechanical properties. The martensitic transformation of Ti-Ni alloy from parent phase to martensitic phase is accompanied by exothermic reaction, while the reverse transformation from martensitic phase to parent phase is accompanied by endothermic reaction. The change in transformation temperatures of the Ti-Ni alloy castings by heat treatment is shown in Table 1, where $M_s$, $M_f$, $A_s$, and $A_f$ indicate martensitic transformation starting and finishing temperatures, and austenitic transformation starting and finishing temperatures, respectively. Transformation temperature tended to increase by heat treatment, although the change was considerably

![Fig. 3 Maximum load values of Ti-50.85Ni (mol%) castings: as cast (TN-ac), heat-treated at 713 K (TN-713), heat-treated at 773 K (TN-773), and Co-Cr castings at the 5- or 10-mm loading point in the bending test. Values indicated by the same superscript letter were not significantly different ($p > 0.05$).](image1.png)

![Fig. 4 Residual deflection values after being unloaded of Ti-50.85Ni (mol%) castings: as cast (TN-ac), heat-treated at 713 K (TN-713), heat-treated at 773 K (TN-773), and Co-Cr castings at the 5- or 10-mm loading point in the bending test. Values indicated by the same superscript letter were not significantly different ($p > 0.05$).](image2.png)

<table>
<thead>
<tr>
<th>Condition</th>
<th>$M_s$ (K)</th>
<th>$M_f$ (K)</th>
<th>$A_s$ (K)</th>
<th>$A_f$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TN-ac</td>
<td>281.6 ± 3.1</td>
<td>243.6 ± 7.7</td>
<td>260.7 ± 5.7</td>
<td>320.9 ± 0.4</td>
</tr>
<tr>
<td>TN-713</td>
<td>301.1 ± 1.0</td>
<td>268.4 ± 8.9</td>
<td>286.0 ± 2.4</td>
<td>324.1 ± 1.2</td>
</tr>
<tr>
<td>TN-773</td>
<td>288.1 ± 2.3</td>
<td>271.6 ± 8.2</td>
<td>282.3 ± 2.2</td>
<td>322.8 ± 0.9</td>
</tr>
</tbody>
</table>
small for $A_t$. The increase in martensitic transformation temperature by heat treatment is thought to be one of the reasons for the decrease in maximum load, because it causes decrease in the stress required for stress-induced martensitic transformation.

The height of the thermal peaks increased after heat treatment. This may influence the change in bending property due to possible microstructural change including recrystallization. For all specimen conditions in the present study, the DSC diagrams showed the thermal reaction with combined two thermal peaks, which suggested the appearance of R-phase. Therefore, it is also possible that R-phase transformation influenced the bending property of the specimens.

The results obtained in the present study suggest that the bending property of Ti-Ni alloy castings was improved by heat treatment. The bending force delivered was much lower in the Ti-Ni alloy castings than in the Co-Cr alloy, which is widely used in clinical settings. This finding indicates that the design and application of denture retainers could be extended. In addition, the superior shape recovery of Ti-Ni castings will likely improve the clinical performance and reliability of dental prostheses.

4. Conclusions

Investigation of the bending property and heat treatment effect of Ti-Ni alloy dental castings in relation to phase transformation yielded the following conclusions.

(1) Load-deflection diagrams of Ti-Ni alloy castings in the bending test showed elastic and super-elastic deformation, while those of Co-Cr castings showed elastic and permanent deformation.

(2) Maximum bending load value of Ti-Ni alloy castings was lower than that of Co-Cr castings and was decreased by heat treatment under a high-stress condition at the 5-mm loading point.

(3) Residual deflection value of Ti-Ni alloy castings was much lower than that of Co-Cr castings and was decreased by heat treatment under a high-stress condition.

(4) Transformation temperature rose by heat treatment, except for $A_t$. The increase in $M_s$ is thought to influence the reduction in maximum bending load by heat treatment.

(5) Super-elasticity of Ti-Ni alloy castings in bending was improved by heat treatment, which is useful for improving the design and clinical performance of cast dental prostheses.

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REFERENCES