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Effect of heat treatment with the mould on the super-elastic property of Ti–Ni alloy castings for dental application

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Tensile property of Ti–50.85Ni (mol %) alloy castings was investigated quantitatively in relation to the thermal behavior accompanied with phase transformation to evaluate the effect of heat treatment after casting with the mould in air. The heat treatment temperature was 713 or 773 K, and the period was 0.9, 1.8, or 3.6 ks. Apparent proof stress of the castings decreased with increasing period of heat treatment, and the decrease was larger with the treatment at 773 K. Residual strain also decreased by the heat treatment, however, it was low with the treatment for relatively short period, i.e. 713 K-0.9 and 1.8 ks, and 773 K-0.9 ks treatments. From the thermal behavior measured by differential scanning calorimetry (DSC), the ascent in the transformation temperatures and the increase in the thermal peak height appeared to influence the changes in the tensile property. These changes by heat treatment were believed to be effective to utilize more flexibility, less stress and less permanent deformation in dental castings.

1. Introduction

Ti–Ni alloy is a unique metallic biomaterial because of its special characteristics, such as shape memory effect and super-elasticity. Since this alloy also possesses high corrosion resistance [1] and good biocompatibility [2], its super-elasticity has been applied in the dental field to orthodontic arch wires [3, 4], coil springs [5], expansion appliance [6], flexible root canal files [7], ligature wires for intermaxillary fixation [8], and dental castings [9–11].

Although the special properties of Ti–Ni alloy were expected to be useful for cast dental appliances, it was difficult to cast Ti–Ni alloy by conventional dental casting techniques. 55-Nitinol castings prepared with conventional procedures were reported to be brittle and devoid of mechanical memory [12]. Due to the recent progress in the dental casting technology for titanium alloys including machines and mould materials [13], the problems originated from the high reactivity of titanium with melting atmosphere and mould materials have been reduced.

On the other hand, the mechanical property of Ti–Ni alloy is easily influenced by small changes in composition, impurities, heat treatment condition, etc. The influence of the composition and the purity of the materials on the tensile property of Ti–Ni alloy castings was reported [14]. In this study, the effect of a practical heat treatment in the mould immediately after casting on the tensile property of Ti–Ni alloy castings was investigated for clinical dental application.

2. Materials and methods

2.1. Specimen preparation

Ti–Ni alloy (NT-E4, Furukawa Electric, Japan) was used in this study, and its composition was Ti–50.85Ni in mol %. The alloy materials were melted on a water-cooled copper crucible in an argon arc melting furnace to make the alloy ingots for casting. To minimize the influence from the melting atmosphere, it was vacuumed until the degree reached less than 2.7×10^{-3} Pa after the air inside the chamber was replaced twice with high purity argon gas. Then, the argon gas was introduced again in the chamber as the melting atmosphere. Unalloyed titanium was used as the getter material before melting the Ti–Ni alloys.

The mould material used was a commercial phosphate-bonded silica investment (Snow White, Shofu, Japan). Wax patterns for test specimens were invested, and the moulds were made according to the manufacturer's instruction cooled down to room temperature.

Casting was performed with use of a modified argon arc melting and pressure casting machine (Castmatic-T, Iwatani, Japan) [10]. The air inside the melting and casting chambers was replaced with high-purity argon gas three times before it was vacuumed until the degree

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reached 0.63 Pa by a rotary pump. Then, the argon gas was introduced for the casting atmosphere.

Heat treatment was performed immediately after casting with the mould in a dental electric furnace in air atmosphere. The heat treatment temperature was 713 or 773 K, and the period was 0.9, 1.8, or 3.6 ks. The specimens were water-quenched and sandblasted. Five specimens were prepared for each condition.

2.2. Tensile test

The dumbbell-shaped specimens for tensile test were 2.0 mm in diameter at the parallel part gauged. The test was carried out at 310 K with a universal testing machine and a strain meter, 10 mm in gauge length, at a crosshead speed of 8.3 μm/s. After the specimens were stressed up to 3.0% strain, the stress was removed at the same speed. Then, the specimens were stressed again to fracture.

The tensile property was evaluated by apparent proof strength, residual strain, tensile strength and elongation. The apparent proof strength here was defined as the stress required producing a strain, 0.2% larger than the strain of elastic limit. The residual strain was the strain remained after being unloaded from 3.0% strain.

2.3. DSC measurement

The thermal behavior accompanied with the phase transformation of Ti–Ni alloy casting was measured by DSC. The specimens were cut from cast bars, 2.0 mm in diameter and 1.0 mm in thickness, and sealed in aluminum cells. The atmosphere of the measuring chamber 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, and liquid nitrogen was used for the cooling process.

2.4. Statistics

In the three tensile parameters of apparent proof strength, tensile strength and elongation, one-way factorial analysis of variance was used for the detection of the difference among groups. The differences between groups were detected by Tukey–Kramer test as the *post hoc* test. With respect to the residual strain, nonparametric tests were selected. Kruskal–Wallis test was used for the detection of the difference in residual strain among groups, and Mann–Whitney U test was performed to detect the differences between groups. Statistical significance was set at $p < 0.05$.

3. Results

3.1. Tensile properties

Figs 1 and 2 show typical stress–strain curves of Ti–50.85Ni alloy castings with heat treatments at 713 or 773 K. Thin line indicates the as cast specimen without heat treatment; dotted, dashed and solid thick lines indicate the specimens with heat treatments for 0.9, 1.8 and 3.6 ks, respectively. On every stress–strain curves observed in this study, the increase in stress per unit strain decreased after the elastic limit was exceeded, like permanent deformation in usual metals. However, the strain decreased considerably by being unloaded because of super-elasticity.

Fig. 3 shows the apparent proof stress values of the Ti–Ni alloy castings with each heat treatment conditions. The apparent proof stress decreased with increasing period of heat treatment. There were statistically significant differences within the same heat treatment temperature groups except between the conditions at 713 K for 1.8 and 3.6 ks. It was also observed that apparent proof stress of the 773 K group was lower than that of the 713 K group. Significant differences existed between the conditions for 0.9 ks and between the conditions for 3.6 ks. In the comparison of each treatment condition with the as cast condition, the apparent proof stress after heat treatment decreased except the 713 K-0.9 ks condition.

The residual strain values of the Ti–Ni alloy castings are shown in Fig. 4. Although the values were considerably scattered, the residual strain of the specimens with heat treatment was lower than that of the as cast specimens. Significant differences existed between

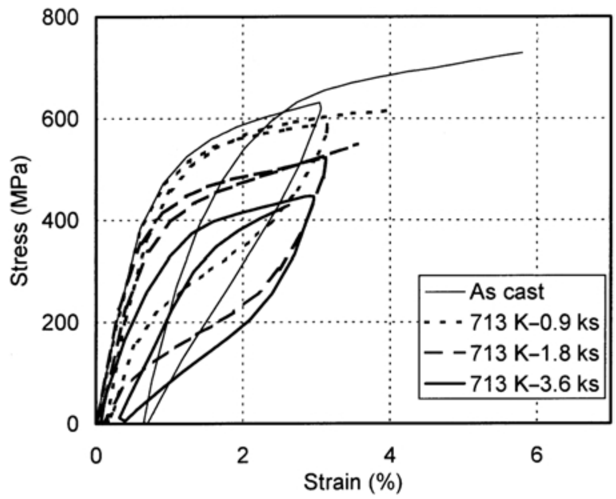

Figure 1 Typical stress–strain curves of the Ti–50.85Ni (mol %) alloy castings with heat treatment at 713 K for 0.9, 1.8 or 3.6 ks in comparison with as cast condition.

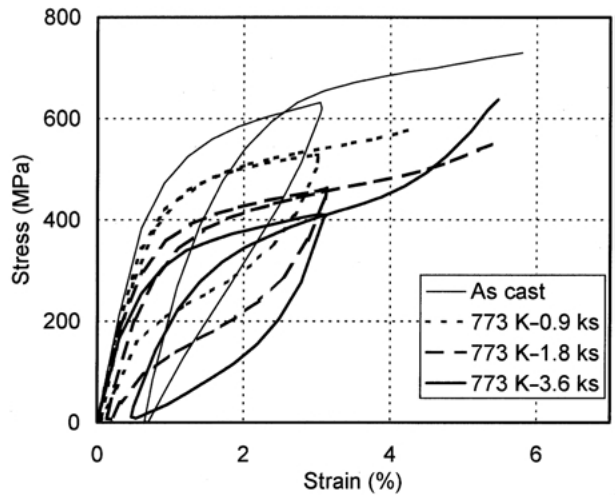

Figure 2 Typical stress–strain curves of the Ti–50.85Ni (mol %) alloy castings with heat treatment at 773 K for 0.9, 1.8 or 3.6 ks in comparison with as cast condition.

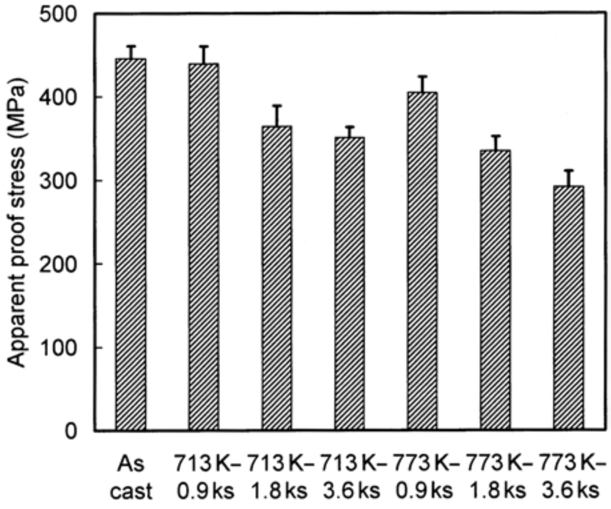

Figure 3 Apparent proof stress of the Ti–50.85Ni (mol %) alloy castings with heat treatment in comparison with as cast condition.

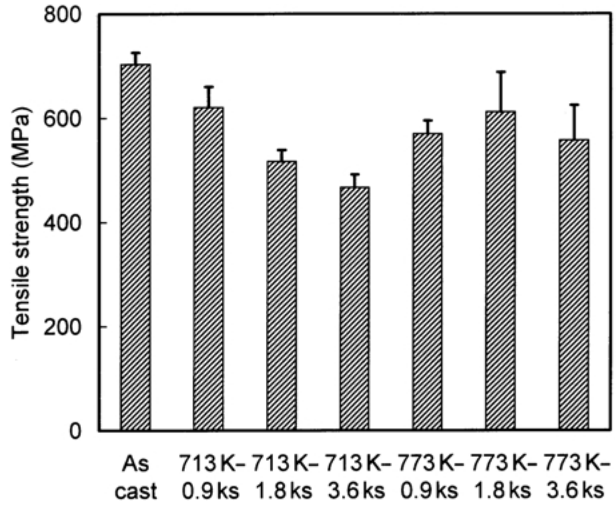

Figure 5 Tensile strength of the Ti–50.85Ni (mol %) alloy castings with heat treatment in comparison with as cast condition.

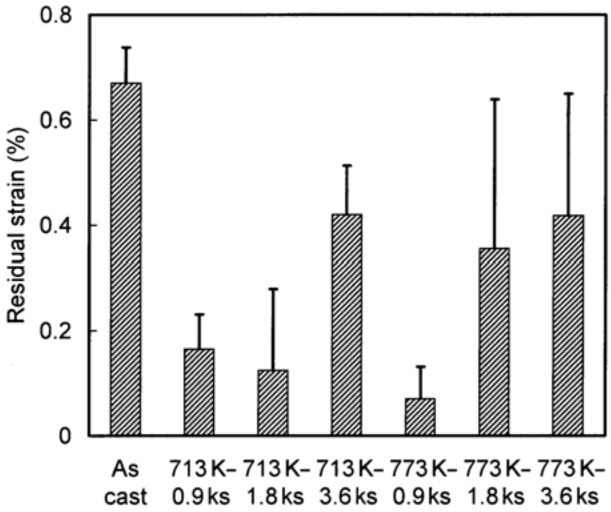

Figure 4 Residual strain of the Ti–50.85Ni (mol %) alloy castings with heat treatment in comparison with as cast condition.

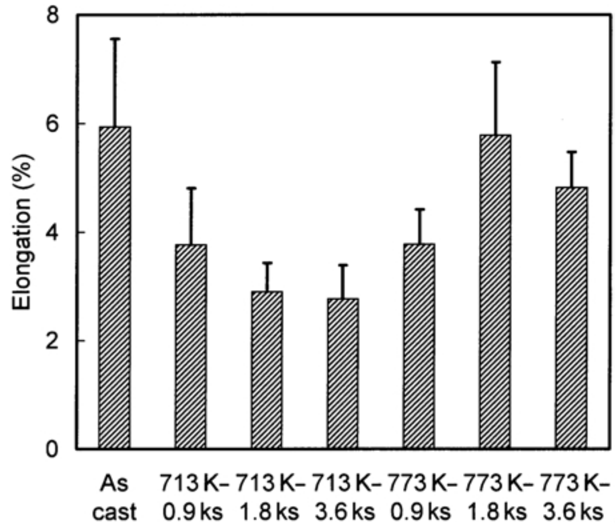

Figure 6 Elongation of the Ti–50.85Ni (mol %) alloy castings with heat treatment in comparison with as cast condition.

the as cast and the heat-treated conditions except the 773 K-3.6 ks condition. In the comparison among the treatment conditions, residual strain was low in the cases of short period treatments. In the 713 K group, the residual strain values for 0.9 and 1.8 ks conditions were statistically lower than that for 3.6 ks, while that for 0.9 ks was lower than those for 1.8 and 3.6 ks in the 773 K group.

Fig. 5 shows the tensile strength of the Ti–Ni alloy castings with each heat treatment conditions. The tensile strength decreased with heat treatment. Significant differences existed between the as cast and the heat-treated conditions except the 713 K-0.9 ks condition. There were statistically significant differences within the 713 K group, the tensile strength of 713 K-0.9 ks was higher than those of 713 K-1.8 ks and 713 K-3.6 ks, while no significant difference existed in the 773 K group. With respect to the elongation shown in Fig. 6, the values for the heat treatment conditions of 713 K-1.8 ks, 713 K-3.6 ks and 773 K-0.9 ks were statistically lower than that for the as cast condition.

3.2. Thermal behavior

Figs 7 and 8 show typical DSC curves of Ti–50.85Ni alloy castings with heat treatments at 713 K. The exothermic peaks indicate the exothermic reaction accompanying the martensitic transformation from parent phase to martensitic phase in the cooling process, while the endothermic ones were caused by the reverse transformation in the heating process. These thermal peaks shifted to the high temperature side by the heat treatment at 713 K with increasing treatment period. The exothermic peaks shifted considerably with the heat treatment for 1.8 ks or more. The height of the endothermic peaks increased with increasing period of the heat treatment.

Typical DSC curves of the Ti–Ni alloy castings with heat treatments at 773 K are shown in Figs 9 and 10. The thermal peaks associated with the martensitic and reverse transformations shifted in a similar manner to those with 713 K treatments. The peak height of the specimens with 773 K treatments was higher than that with 713 K treatments for the same treatment period.

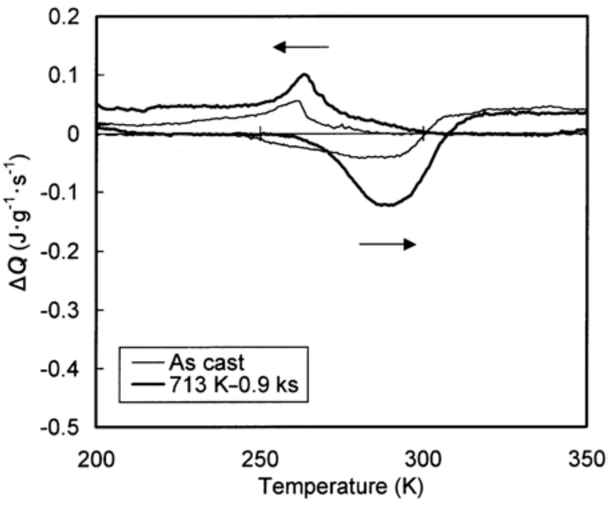

Figure 7 Typical DSC curves of the Ti–50.85Ni (mol %) alloy castings with heat treatment at 713 K for 0.9 ks in comparison with as cast condition.

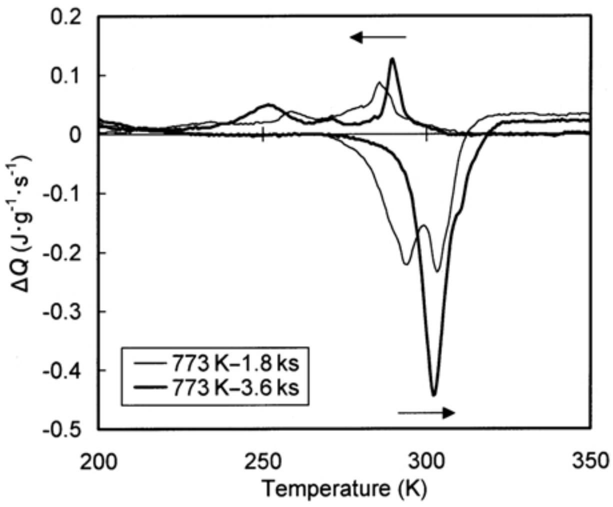

Figure 10 Typical DSC curves of the Ti–50.85Ni (mol %) alloy castings with heat treatment at 773 K for 1.8 or 3.6 ks.

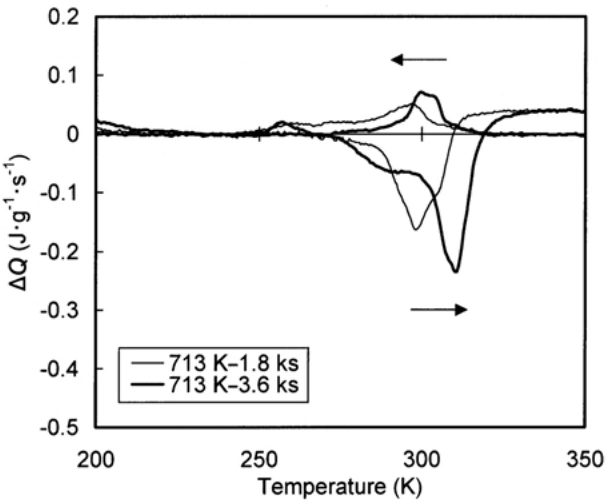

Figure 8 Typical DSC curves of the Ti–50.85Ni (mol %) alloy castings with heat treatment at 713 K for 1.8 or 3.6 ks.

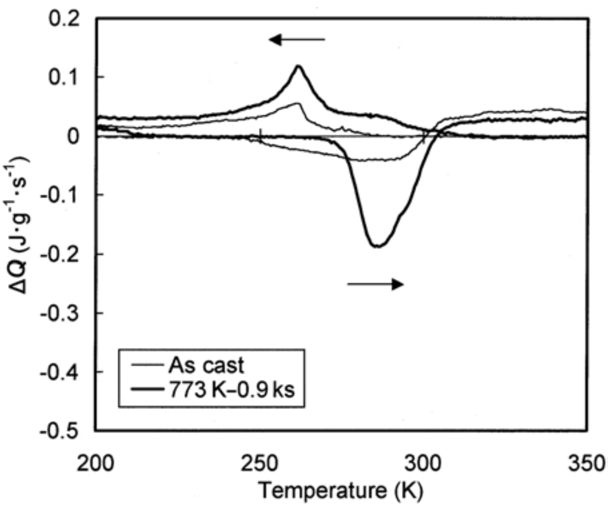

Figure 9 Typical DSC curves of the Ti–50.85Ni (mol %) alloy castings with heat treatment at 773 K for 0.9 ks in comparison with as cast condition.

The change in two transformation temperatures, martensitic transformation starting (M_s) temperature and austenitic transformation finishing (A_f) temperature, of Ti–50.85Ni alloy castings with different heat treatment conditions is shown in Fig. 11. These temperatures were determined at the intersection of the tangent of the peak slope and the base line. M_s temperature for the as cast condition was 273.3 K, which rised considerably with increasing period of heat treatment until 1.8 ks. With respect to the A_f temperature, slight ascent was observed with increasing treatment period.

4. Discussion

Typical stress–strain diagram of super-elastic alloy shows a hysteresis curve, on which the strain over elastic limit recovers considerably with decreasing stress. After the stress exceeds the elastic limit, the slope of the curve decreases in a manner similar to yielding. Apparent proof stress of Ti–50.85Ni alloy casting was decreased by the heat treatment at 713 or 773 K as shown in Fig. 3. One of the reasons for this change is thought to be the rise in M_s

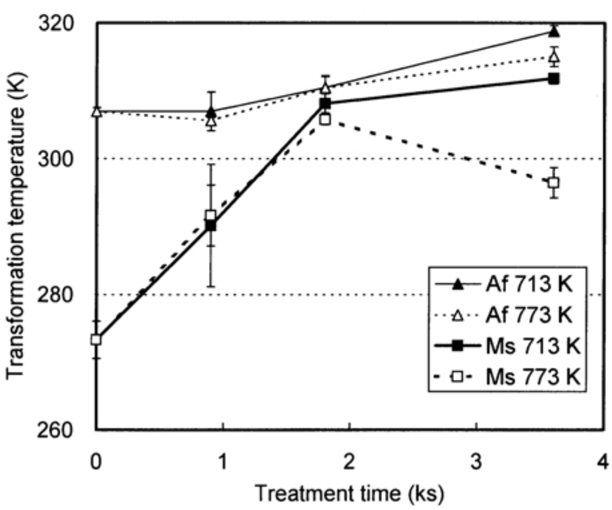

Figure 11 Transformation temperatures of the Ti–50.85Ni (mol %) alloy castings with heat treatment at 713 or 773 K.

temperature by the heat treatment, because it should cause the decrease in the stress required for the stress-induced martensitic transformation.

The residual strain, defined as the strain remained after being unloaded, decreased by the heat treatment as shown in Fig. 4, especially with the conditions of 713 K-0.9 ks, 713 K-1.8 ks and 773 K-0.9 ks. Since the A_f temperatures of these groups were close to that of the as-cast condition, there should be other reasons for the decrease in the residual strain. One of the probable factors would be the microstructural change by the heat treatment, which was suggested by the increase in the thermal peak height [15]. This is thought to be related with phase transformability of martensitic and reverse transformations.

With respect to the relatively high residual strain for the conditions of 713 K-3.6 ks, 773 K-1.8 ks and 773 K-3.6 ks, one of the probable reasons is the increase in the A_f temperature close to or above the testing temperature of 310 K. This is also believed to cause large variation in the residual strain for the 1.8 and 3.6 ks conditions. Although the stress-induced martensite transforms to the parent phase by removing the stress, this reverse transformation must be incomplete below the A_f temperature since a part of martensite still remains below this reverse transformation finishing temperature.

Tensile strength tended to decrease by the heat treatment, which appears to be related with the decreases in the apparent proof stress and the elongation. One of the possible reasons for the decrease in elongation is oxidation of the specimens during the heat treatment process. Considering the general procedure and equipment in dental laboratories, heat treatment after casting with the mould was chosen with use of a dental electric furnace in air. Since a small amount of oxygen causes the decrease in M_s temperature [16] and low elongation [14], heat treatment in a vacuum or a nitrate bath could be effective to increase the elongation.

It is known that three kinds of phase transformation can occur in Ti–Ni alloy [17]: $B2 \leftrightarrow R$, $B2 \leftrightarrow M$, $R \leftrightarrow M$, where $B2$, R and M indicate parent, rhombohedral and martensitic phases, respectively. The DSC curves for the conditions of 713 K-3.6 ks, 773 K-1.8 ks and 773 K-3.6 ks were observed to consist of two thermal peaks as shown in Figs 8 and 10. This suggested that R-phase transformation could occur for these conditions, although two stage yielding [18] was not observed in the stress–strain diagrams of the present study.

In conclusion, it was proved that the heat treatment of Ti–50.85Ni alloy castings with the mould in air was effective to change the tensile property of the castings in relation to the phase transformation behavior. The decrease in apparent proof stress and in residual strain is believed to be advantageous to utilize more flexibility, less stress and less permanent deformation in dental castings.

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