Bull. Tokyo Med. Dent. Univ., 40: 167–172, 1993

INFLUENCE OF MOLD MATERIALS AND HEAT TREATMENT ON TENSILE PROPERTIES OF Ni-Ti ALLOY CASTINGS

BY

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ABSTRACT

The influence of mold materials and heat treatment on the tensile properties and the transformation temperatures of Ni-Ti alloy castings was investigated by tensile test and differential scanning calorimetry (DSC) in order to apply the special properties of the alloy to dental field. The compositions of the two alloys examined were 49.0 and 49.2 at% Ti. A silica investment and a magnesia investment were used as the mold materials. Heat treatment at 440 °C for 1.8 ks was performed.

Apparent proof strength decreased in both compositions, and residual strain increased in Ni-49.2Ti by the heat treatment. Elongation increased in Ni-49.0Ti with use of the magnesia mold or by the heat treatment. The transformation temperatures of Ni-49.2Ti increased with use of the magnesia mold. The change by the heat treatment suggested a structural change. The development of a suitable method for the casting of the alloy is expected to bring about the development of new devices and therapy in dentistry.

Key words: Ni-Ti alloy, Dental casting, Mold material, Heat treatment, Tensile property

INTRODUCTION

Ni-Ti alloy is a functional biomaterial due to its shape memory effect and super-elasticity. Andreasen and Hilleman [1] introduced the Nitinol alloy into orthodontics. Then, Watanabe [2] investigated the super-elasticity of Ni-Ti alloy orthodontic wire, and Miura *et al.* [3] reported on the orthodontic application of this wire. Since Ni-Ti alloy has good biocompatibility (Castleman *et al.* [4]) and high corrosion resistance (Speck and Fraker [5]), it is anticipated to develop new devices and therapy in the medical and dental fields.

The special properties of Ni-Ti alloy castings are also expected to be useful for dental prostheses. However, the alloy is difficult to be cast by conventional dental casting techniques; the special properties of Ni-Ti alloy are easily lost through the casting process. Civjan *et al.* [6] tried to cast the 55-Nitinol and mentioned that the castings prepared with conventional procedures were brittle and devoid of mechanical memory.

Recently, dental casting of titanium and titanium alloys has made great progress,

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Received for publication, November 1, 1993.

especially in mold materials and casting machines. These developments can also apply to the casting of Ni-Ti alloy. Hamanaka *et al.* [7] found that Ni-Ti alloy could be cast without losing shape memory effect and super-elasticity in tensile test, and Takahashi *et al.* [8, 9] investigated the properties in bending and fatigue tests.

It is known that the mechanical properties and the surface condition of titanium and titanium alloys are influenced by mold materials because titanium is very reactive at high temperatures. Ida *et al.* [10] found that the properties of the titanium castings with a magnesia investment were much better than those with a phosphate-bonded silica investment. Besides, heat treatment has a great influence on the mechanical properties of Ni-Ti alloy. Therefore, the authors investigated the influence of mold materials and heat treatment on the tensile properties and the transformation temperatures of Ni-Ti alloy castings to apply it in clinical dentistry.

Materials and Methods

The materials of Ni-Ti alloy ingots were a high grade sponge titanium (SSU, Osaka Titanium Co., Ltd., Osaka, Japan) and an electrolytic nickel (Sumitomo Metal Mining Co., Ltd., Tokyo, Japan); the purity was higher than 99.8 mass% Ti and 99.95 mass% (Ni+Co), respectively. The composition of the alloy used in this study was Ni-49.0 and 49.2 at% Ti. In this paper, the composition is expressed in at%. The sponge titanium was melted on a water-cooled copper crucible in an argon arc melting furnace (Daia Shinku Giken, Tokyo, Japan) and weighed. Then, the nickel was weighed accurately for the aimed composition and melted again with the titanium. The weight of the Ni-Ti alloy ingots was around 12 g.

Two kinds of mold materials were used. One was a commercial phosphate-bonded silica investment (Summa Vest, Shofu Inc., Kyoto, Japan), and the other was a magnesia investment (MD-105, Iwatani & Co., Osaka, Japan). The former was more reactive with molten titanium than the latter. The liquid/power ratio of the silica investment was 0.20 cm^3/g, and the water/powder ratio of the magnesia investment was 0.15 cm^3/g. The firing temperatures were 800 °C for the silica mold and 900 °C for the magnesia mold. The molds were kept at the temperatures for 1.8 ks, then cooled slowly to the room temperature.

Casting was performed with an argon arc melting and pressure casting machine (Castmatic-T, Iwatani & Co., Osaka, Japan), developed by Hamanaka *et al.* [11]. The castings were quenched with water and sand-blasted. Heat treatment was performed in a bath of nitrate (Durferrit AS-140, Parker Netsushori Kogyo, Tokyo, Japan) at 440 °C for 1.8 ks. Five specimens were prepared for each test.

The tensile test specimens were 2.0 mm in diameter between the gage marks and 40 mm in length. Tensile test was carried out at 37 °C with a universal testing machine (Model 1112, Instron, High Wycombe, UK) and a strain meter, 10 mm in gage length, at a cross-head speed of 8.3 μm/s. The specimens were once stressed up to 3.0 % strain, and the stress was removed at the same speed. Then the specimens were stressed again to fracture. The tensile properties evaluated were apparent proof strength, residual strain, tensile strength and elongation. The apparent proof strength here was defined as the stress required to produce a strain, 0.2 % larger than the strain of elastic limit. The residual strain was the strain after unloading from 3.0 % strain.

The transformation temperatures of Ni-Ti alloy castings were measured by differential scanning calorimetry (DSC). The specimens were cut with a diamond saw from cast bars; the size was 2.0 mm in diameter and 1.5 mm in thickness. They were sealed in aluminum cells and put into the measuring chamber of a differential scanning calorimeter (DSC-7000, ULVAC, Yokohama, Japan), The atmosphere of the measuring chamber was argon gas, and alpha alumina powder was used as the reference material. The scanning temperature was between − 100 °C and 100 °C. The heating rate was 0.17 °C/s. Liquid nitrogen was used for the cooling process.

RESULTS

Fig. 1 shows typical stress-strain curves of Ni-49.0Ti alloy castings on three conditions. Symbol A indicates the as cast specimen with the silica mold, B the as cast specimen with the magnesia mold and C the heat-treated specimen with the silica mold. The as cast specimens with the silica mold (A) showed low elongation; most of them could not unload from 3.0 % strain. However, the others (B and C) showed large elongation of 5 % and hysteresis curves at body temperature. After the elastic limit was exceeded, the slope of the curve decreased like plastic deformation in usual alloys. However, the strain recovered close to zero after unloading due to superelasticity. The heat-treated specimens showed lower yield stress than the as cast specimens, and the slope increased at 4 % strain.

Fig. 2 shows typical stress-strain curves of Ni-49.2Ti alloy castings on the three conditions; the symbols represent the same conditions as in Fig. 1. In this composition, the change in the stress-strain curves by the mold materials and the heat treatment was small compared with Ni-49.0Ti specimens. The slope of heat-treated specimens increased at 4 % strain similar to Ni-49.0Ti.

Figs. 3–6 show the change in mechanical properties of Ni-Ti alloy castings by the composition, the mold materials and the heat treatment. Lower apparent proof strength, larger residual strain and elongation were exhibited in the composition of Ni-49.2Ti than Ni-49.0Ti. Apparent proof

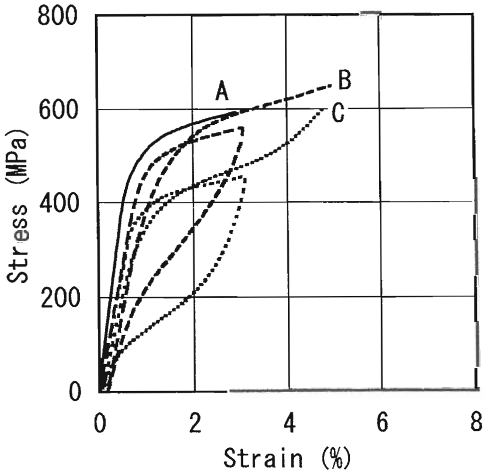

Fig. 1 Typical stress-strain curves of Ni-49.0 at% Ti alloy castings at 37 °C. A (solid line): as cast with silica mold, B (broken line): as cast with magnesia mold, C (dotted line): heat-treated at 440 °C for 1.8 ks after cast with silica mold.

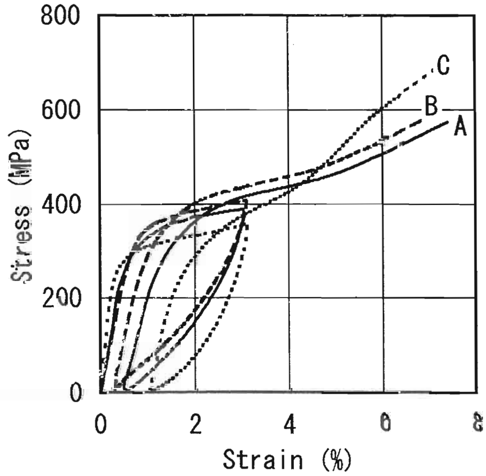

Fig. 2 Typical stress-strain curves of Ni-49.2 at% Ti alloy castings at 37 °C. A (solid line): as cast with silica mold, B (broken line): as cast with magnesia mold, C (dotted line): heat-treated at 440 °C for 1.8 ks after cast with silica mold.

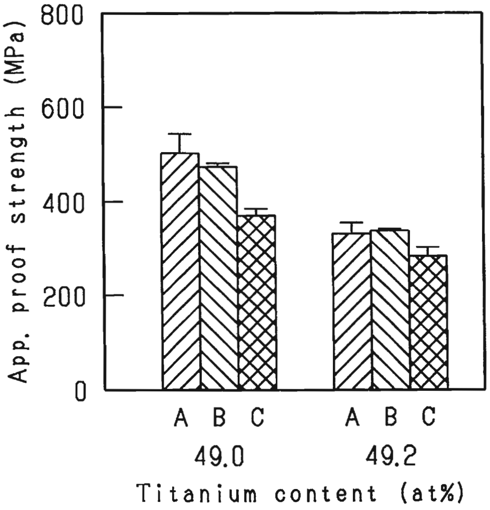

Fig. 3 Apparent proof strength of Ni-Ti alloy castings. A: as cast with silica mold, B: as cast with magnesia mold, C: heat-treated at 440 °C for 1.8 ks after cast with silica model.

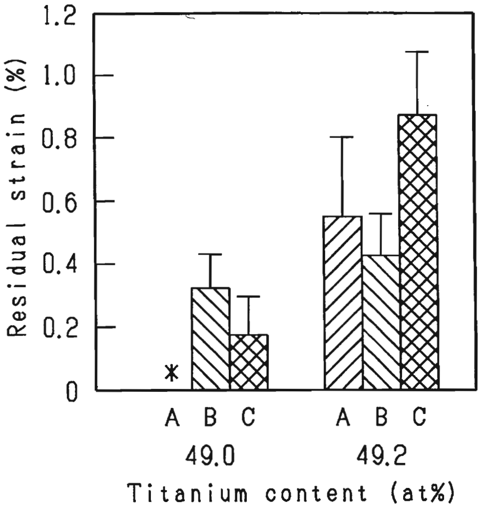

Fig. 4 Residual strain of Ni-Ti alloy castings. A: as cast with silica mold, B: as cast with magnesia mold, C: heat-treated at 440 °C for 1.8 ks after cast with silica mold. *shows no statistical datum obtained.

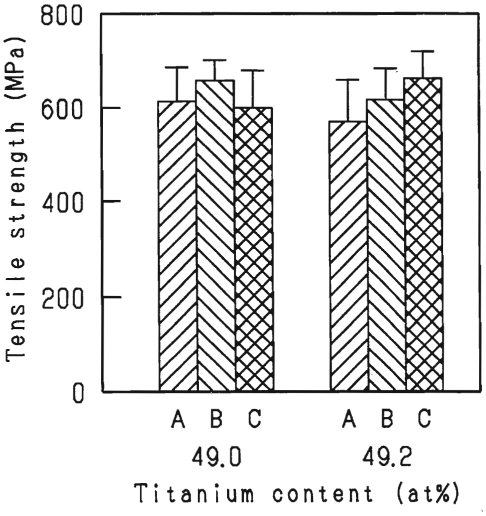

Fig. 5 Tensile strength of Ni-Ti alloy castings. A: as cast with silica mold, B: as cast with magnesia mold, C: heat-treated at 440 °C for 1.8 ks after cast with silica mold.

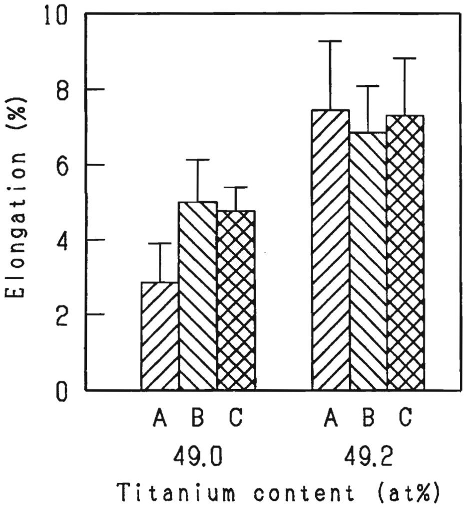

Fig. 6 Elongation of Ni-Ti alloy castings. A: as cast with silica mold, B: as cast with magnesia mold, C: heat-treated at 440 °C for 1.8 ks after cast with silica mold.

strength was almost unchanged by the mold materials and decreased by the heat treatment as in Fig. 3. The heat-treated Ni-49.2Ti specimens showed larger residual strain than the as cast ones. There was no significant differrence in tensile strength among all conditions. The elongation of the as cast Ni-49.0Ti specimens with the silica mold was especially low.

The change in the transformation temperatures of Ni-49.2Ti alloy castings by the mold materials and the heat treatment is shown in Table 1. The M_s and A_f points of the as cast specimens with the silica mold were lower than those with the magnesia mold by 3 °C and 10 °C, respectively. The M_s point decreased, and A_f point increased by the heat treatment at 440 °C for 1.8 ks.

DISCUSSION

Ni-Ti alloy is a promising biomaterial because of its shape memory effect and super-elasticity characteristics. These properties occur in association with the thermoelastic martensitic transformation. Shape memory effect is a phenomenon occurring through the transformation temperature range. The alloy is soft and easy to change in shape below the martensitic transformation temperature; the distorted alloy recovers its original configuration when it is heated through the reverse transformation temperature range. On the other hand, super-elasticity is a phenomenon at a temperature above the reverse transformation temperature range, associated with the stress-induced martensitic transformation. Ni-Ti alloy exhibits high flexibility and wear resistance owing to this property.

The transformation temperatures of Ni-49.2Ti alloy castings increased with use of the magnesia mold as in Table 1. The main reason for this change is thought to be the impurities from the molds. Since titanium reacts with oxygen more easily than silicon, titanium is oxidized and contaminated with silicon in the process of casting into silica molds. The reaction between molten titanium and mold materials is reduced with use of the molds with magnesia, alumina, calcia, zirconia, etc. These oxides have been used for dental casting of titanium.

The transformation temperatures were also changed by the heat treatment at 440 °C for 1.8 ks. Miyazaki and Otsuka [12] found that the R-phase was observed by aging after solution treatment of Ni-49.4Ti and that the M_s point was depressed. Since the M_s point decreased, and the A_f point increased by the heat treatment as in Table 1, a process like the R-phase transition seemed to occur by a structural change.

As for the influence of the mold materials and the heat treatment on tensile properties of Ni-Ti alloy castings, the change in apparent proof strength and elongation was greater in the composition of Ni-49.0Ti than Ni-49.2Ti. Okamoto *et al.* [13] found that the 440 °C-annealing reduced the yield stress of Ni-49.0Ti wires. As in Figs. 1–3, the apparent proof strength of the as cast specimens (A) decreased by the heat treatment (C), while it was almost unchanged with use of the magnesia mold (B). Since all the specimens before testing were in the parent phase of B2, yielding process was due to the stress-induced martensitic transformation. Taking into account the change of the M_s point, some factor other than transformation temperatures probably influenced the change in the apparent proof strength.

The residual strain was the most sensi-

Table 1. Transformation Temperatures of Ni-49.2 at% Ti Castings

Code	Mold material	Condition	M_s point (°C)	A_f point (°C)
A	Silica	As cast	3.4±4.7	30.9±4.2
B	Magnesia	As cast	6.2±3.2	40.7±2.8
C	Silica	Heat treated	−1.5±7.0	34.1±4.5

Mean±SD, n=5

tive parameter of the four used in this study. Small scatter in the material and the casting condition seemed to affect this property. It was low in Ni-49.0Ti and high in Ni-49.2Ti because of the difference in the reverse transformation finishing temperature, and tended to increase by the heat treatment in Ni-49.2Ti. As for the tensile strength, no marked difference was observed among all conditions. The elongation of the as cast Ni-49.0Ti specimen with the silica mold was lower than those of the other two as shown in Fig. 6. One of the reasons was the high apparent proof strength due to the composition and the reaction with the silica mold.

In conclusion, the influence of the reactivity of mold materials on tensile properties of Ni-Ti alloy casting was small except for elongation in the composition of low titanium content. Moreover, the properties can be changed by the heat treatment. The casting of Ni-Ti alloy is expected to bring about the development of new devices and therapy in dentistry.

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