JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 11 (2000) 695–700

Tensile properties and transformation temperatures of Pd added Ti-Ni alloy dental castings

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The effect of palladium (Pd) addition to Ti-Ni alloy as the third element was investigated to improve the super-elasticity of the alloy castings at body temperature for dental application. Ti-50.8Ni (at %) alloy, which exhibited super-elasticity at 310 K in castings, was used for comparison. 5.0, 7.5, 10.0 and 15.0 at % Pd was added to Ti-50.0Ni alloy by the substitution for Ni. The change in the proportion of Ti and Ni was also examined at the fixed Pd addition of 7.5 at %. The properties of the alloys were investigated in tensile test and differential scanning calorimetry (DSC). Ti-42.5Ni-7.5Pd alloy castings showed good super-elasticity among the examined alloys from the viewpoint of residual strain and elongation. Moreover, apparent proof stress could be changeable by the proportion of Ti and Ni with residual strain being kept low. Ti-42.5Ni-7.5Pd alloy castings exhibited better super-elastic flexibility than Ti-50.8Ni alloy, which is proven by lower apparent proof stress and larger elongation. This flexibility appears to be caused by its relatively high martensitic transformation starting temperature point. It is suggested that this flexibility with super-elasticity could widen the clinical application of the alloy casting in dentistry.

1. Introduction
Much attention has been paid to Ti-Ni alloy due to its unique characteristics, such as shape memory effect and super-elasticity. In the dental field, these applications of Ti-Ni alloy have been reported: orthodontic arch wires [1–3], super-elastic wires for removable orthodontic appliances [4] and expansion appliances [5, 6], orthodontic cast retainers [7], root canal files [8], prefabricated root canal posts [9], ligature wires for intermaxillary fixation [10, 11], super-elastic cast clasps [12, 13], shape memory pin bridge system [14] and shape memory dental implants [15]. Among these applications, super-elastic clasps and orthodontic retainers are made through the casting process. Recent developments in dental casting technology for titanium have enabled the utilization of the unique mechanical properties of Ti-Ni alloy in castings [16, 17].

The unique mechanical properties of Ti-Ni alloy originate from its thermoelastic martensitic transformation and the associated reverse transformation. The transformation temperatures are sensitively changed by chemical composition of the alloy, method of fabrication, heat treatment, etc., which have great influence on the bending property of Ti-Ni alloy [3, 18, 19]. Transformation behavior related to third transition elements such as iron, cobalt and copper, which were substituted for Ni, has been previously reported [20–22]. According to the binary phase diagram [23], Ni and Pd make a complete solid solution with decrease in melting point. Pd addition to equiatomic Ti-Ni alloy decreased transformation temperatures up to about 7.5 at % Pd [24]. In this study, the effect of Pd addition to Ti-Ni alloy as the third element was investigated to improve the super-elasticity of the alloy castings at body temperature for further development of its dental application.

2. Material and methods
2.1. Alloy composition
The alloy compositions used in this study are shown in Table I. The compositions of Ti-50.0Ni, Ti-50.4Ni and Ti-50.8Ni (at %) were used for the binary system, among which Ti-50.8Ni exhibited super-elasticity at 310 K in castings [25]. 5.0, 7.5, 10.0 and 15.0 at % Pd was added to the equiatomic Ti-Ni alloy by substitution for Ni (series A). The change in the proportion of Ti and Ni was also considered at the fixed Pd addition of 7.5 at % (series B).

2.2. Ingot preparation
Sponge titanium ($>$ 99.8 mass % purity), electrolytic nickel ($>$ 99.97 mass %) and palladium ($>$ 99.9 mass %) were used to make the Ti-Ni and Ti-Ni-Pd alloy ingots for castings. Sponge titanium was melted in an argon arc furnace with a non-consumable tungsten electrode and a water-cooled copper hearth. Then, it was weighed and melted again with precise amount of

TABLE I Composition of the alloys used in this study (at %)

	Ti	Ni	Pd
Binary	50.0	50.0	—
	49.6	50.4	—
	49.2	50.8	—
Series A	50.0	50.0	—
	50.0	45.0	5.0
	50.0	42.5	7.5
	50.0	40.0	10.0
	50.0	35.0	15.0
Series B	50.0	42.5	7.5
	49.9	42.6	7.5
	49.8	42.7	7.5
	49.7	42.8	7.5
	49.6	42.9	7.5

nickel and palladium. Each alloy was turned over and remelted three times to ensure chemical homogeneity.

2.3. Specimen preparation

The dimensions of the dumbbell-shaped tensile test specimen used in the tensile test are shown in Fig. 1. Molds were made with a phosphate-bonded investment (Snow White, Shofu, Japan) according to the manufacturer's indication. Casting was carried out with a modified type [17] of an argon arc melting and pressure casting machine (Castmatic-T, Iwatani, Japan). The castings were water-quenched and sandblasted. Five specimens were prepared for each condition.

2.4. Tensile test

Tensile test was performed at a cross-head speed of 1.0 mm/min with a universal testing machine and a strain gage extensometer with 10 mm gage length at 310 K. After loading to 3.0% strain, the specimens were unloaded to 0 MPa stress at the same speed, then they were loaded again to fracture. The unloading strain of 3.0% was considerably larger than the elastic limit, and consequently suitable to distinguish super-elasticity from shape memory effect or plastic deformation by evaluating residual strain and the transformation temperatures [25]. Properties of apparent proof stress (0.2%), tensile strength, residual strain and elongation were obtained from the stress-strain diagrams. F-test and sequential student's t-test were used for statistical analysis.

2.5. Differential scanning calorimetry measurements

Transformation temperatures of Ti-Ni and Ti-Ni-Pd alloy castings were measured by a differential scanning calorimeter (DSC). Specimens were cut with a diamond saw from the cast bars of 2.0 mm in diameter, and their weight was approximately 20 mg. They were sealed in aluminum cells, and α-Al_2O_3 was used as the reference material. The atmosphere of the measuring chamber was argon gas. The scanning temperature was between 173 K and 423 K. The heating rate was 0.17 K/s. Liquid nitrogen was used for the cooling process.

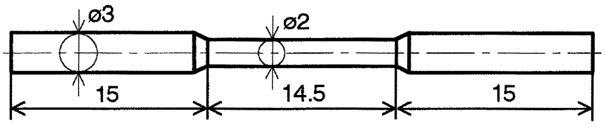

Figure 1 Dimensions of the tensile test specimen (mm).

3. Results

3.1. Tensile properties

Fig. 2 shows typical stress-strain diagrams of binary Ti-Ni alloy castings. Ti-50.8Ni alloy casting showed significantly lower residual strain ($p < 0.01$), 0.71 ± 0.20%, higher apparent proof stress ($p < 0.01$), 367.8 ± 21.4 MPa, and lower elongation ($p < 0.05$), 3.6 ± 1.2%, than Ti-50.4Ni or Ti-50.0Ni alloy casting.

Typical stress-strain diagrams of 50.0Ti-Ni-Pd alloy castings are shown in Fig. 3, and the tensile properties in the series A are shown in Fig. 4. While there was no significant difference in residual strain among Ti-Ni, 5.0Pd and 15.0Pd alloy castings ($p < 0.01$), 7.5Pd and 10.0Pd castings showed statistically lower residual strain ($p < 0.01$) and lower apparent proof stress ($p < 0.05$) than the binary alloy. Moreover, 7.5Pd castings showed better toughness than 10.0Pd castings with statistically higher tensile strength and larger elongation ($p < 0.01$). This was the reason why the series B started from this composition, Ti-42.5Ni-7.5Pd, considering the tensile properties in the series A.

Fig. 5 shows typical stress-strain diagrams of Ti-Ni-7.5Pd alloy castings in the series B, and the tensile properties are shown in Fig. 6. With the increase of Ni from 42.5 to 42.9 at %, significantly higher apparent proof stress was observed ($p < 0.01$). On the other hand, there was no significant difference in residual strain with the increase of Ni from 42.5 to 42.8 at % ($p < 0.01$). Besides, Ti-42.5Ni-7.5Pd alloy castings showed statistically larger elongation with no less tensile strength than the others in the series B ($p < 0.01$). Therefore, Ti-42.5Ni-7.5Pd alloy casting was evaluated to exhibit good super-elasticity as well as high toughness both in the series A and B.

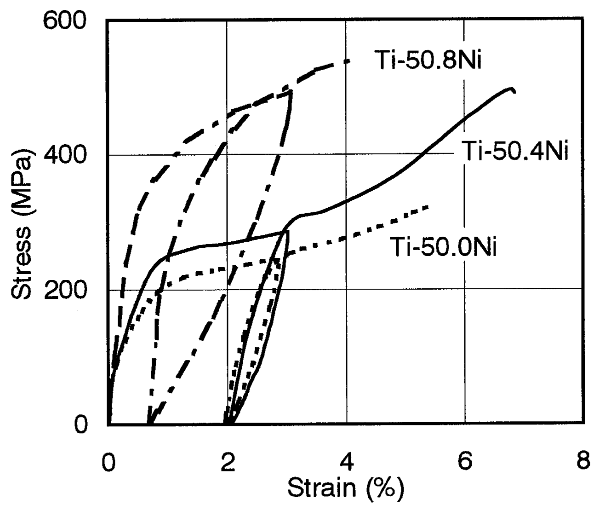

Figure 2 Typical stress-strain diagrams of Ti-Ni binary alloy castings of different compositions.

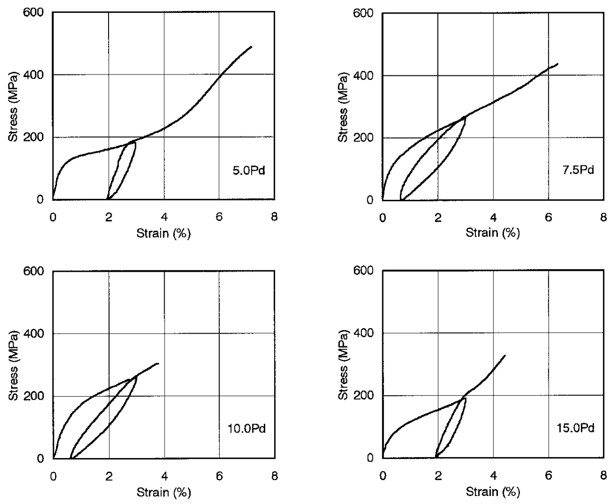

Figure 3 Typical stress-strain diagrams of 50.0Ti-Ni-Pd alloy castings with different Pd contents.

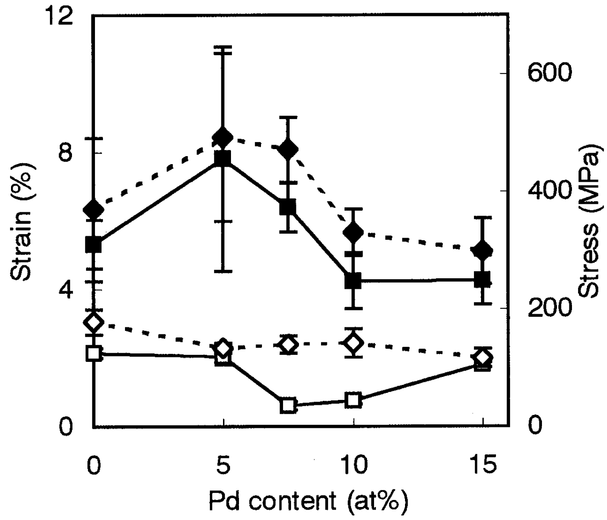

Figure 4 Tensile properties of 50.0Ti-Ni-Pd alloy castings with different Pd contents. (◇) apparent proof stress, (◆) tensile strength, (□) residual strain, (■) elongation.

3.2. Transformation temperatures

To evaluate the transformation temperatures, two parameters were taken from the DSC curves: the martensitic transformation starting temperature (M_s) and the reverse transformation finishing temperature (A_f). In the binary compositions shown in Fig. 7, both the M_s and the A_f points decreased almost linearly with the increase of Ni content. The constant difference between M_s and A_f points suggested that the change of the thermodynamical transformation, such as R-phase transformation which precedes the martensitic transformation [26], was not observed in this condition.

Change in transformation temperatures of 50.0Ti-Ni-Pd alloy castings is shown in Fig. 8. The M_s and A_f points of Ti-Ni-5.0Pd casting decreased from those of the binary alloy ($p < 0.01$). M_s points showed no significant difference among 5.0, 7.5 and 10.0 at% Pd addition ($p < 0.01$), but the A_f point of 7.5Pd was statistically the lowest, 333.2 ± 4.5 K ($p < 0.05$). The M_s and A_f points of 15.0Pd increased again from those of 10.0Pd ($p < 0.01$).

Similar to the Ti-Ni binary alloy, the M_s and A_f points

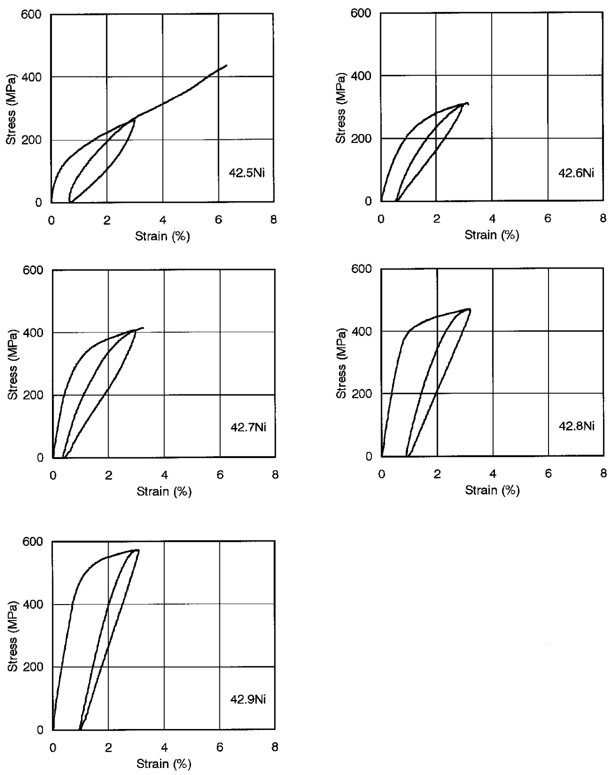

Figure 5 Typical stress-strain diagrams of Ti-Ni-7.5Pd alloy castings with different compositions.

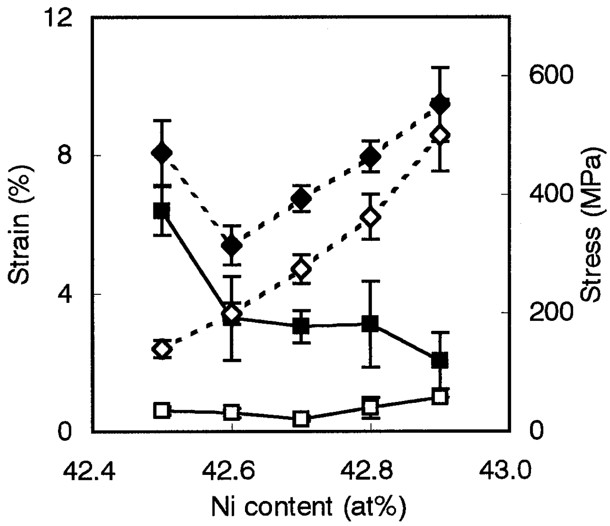

Figure 6 Tensile properties of Ti-Ni-7.5Pd alloy castings with different compositions. (◇) apparent proof stress, (◆) tensile strength, (□) residual strain, (■) elongation.

of Ti-Ni-7.5Pd alloy castings in the series B decreased almost linearly with increasing Ni content (Fig. 9). It was suggested that the similar mechanism might depress the transformation temperatures with the increase of Ni content.

4. Discussion

Super-elasticity of Ti-Ni alloy occurs through the process of stress induced martensitic transformation by loading and the reverse transformation by unloading. It is observed at a temperature above A_f point, because the

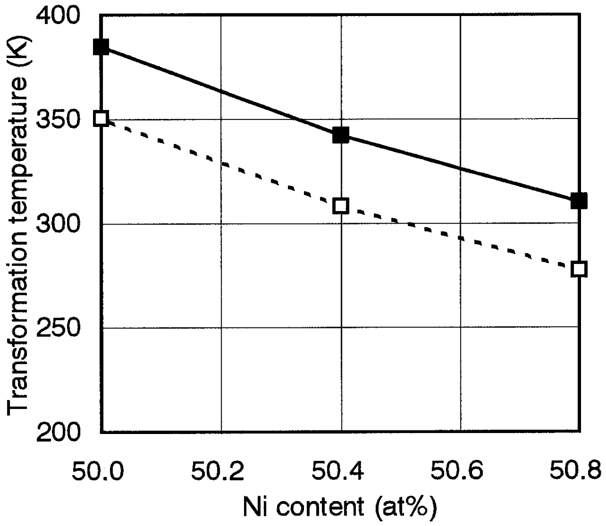

Figure 7 Transformation temperatures of Ti-Ni binary alloy castings. (□) M_s = martensitic transformation starting temperature, (■) A_f = reverse transformation finishing temperature.

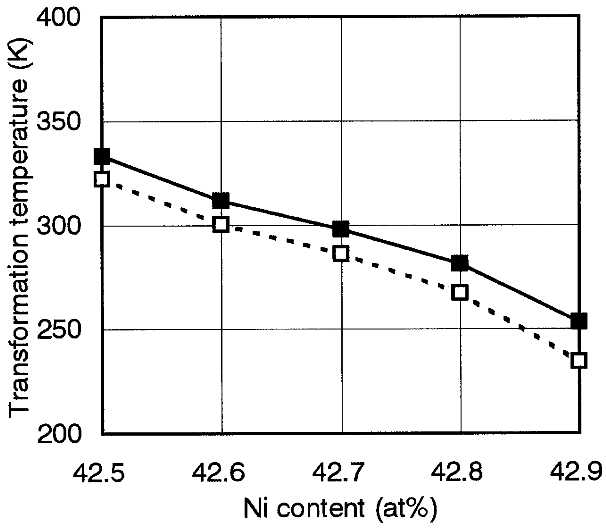

Figure 9 Transformation temperatures of Ti-Ni-7.5 Pd alloy castings with different compositions. (□) M_s, (■) A_f.

deformed martensite should be transformed reversely to the parent phase to recover its original shape. The relation between the alloy temperature and M_s point relates to the minimum stress to induce martensitic transformation. Therefore, M_s and A_f points are important factors to evaluate super-elasticity of the castings together with the mechanical parameters of apparent proof stress and residual strain.

In the stress-strain curves of Ti-50.0Ni and Ti-50.4Ni alloy castings in Fig. 2, the strain did not recover by unloading at body temperature except the elastic recovery, because their A_f points were above 310 K as shown in Fig. 7. Since the shape recovery due to the thermoelastic martensitic transformation is achieved by the reverse transformation to the parent phase, it can be observed above the A_f point. On the other hand, the curve of Ti-50.8Ni alloy casting showed low residual strain, which was caused by its lower A_f point. Increasing apparent proof stress with the increase of Ni content appears to be associated with the decrease in transformation temperatures according to the thermodynamic Clausius-Clapeyron relation [27]. This suggests a limit to lower the apparent proof stress with super-elasticity in the binary Ti-Ni alloy.

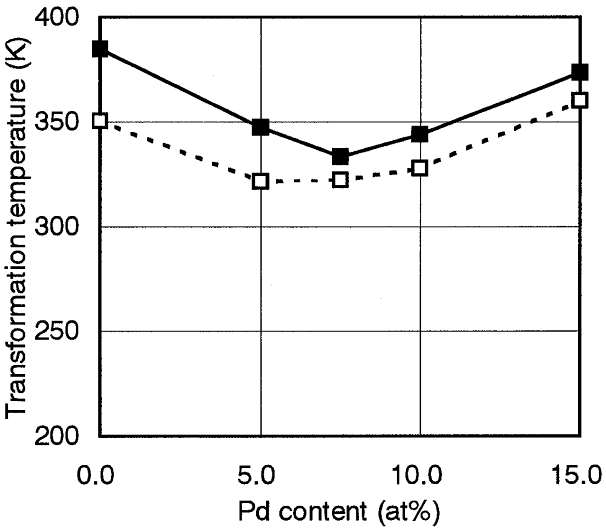

Figure 8 Transformation temperatures of 50.0Ti-Ni-Pd alloy castings with different Pd contents. (□) M_s, (■) A_f.

In the series A with different Pd contents, 7.5 Pd and 10.0 Pd showed low residual strain (Figs 3 and 4). Relatively low A_f points and the thermodynamically less difference between M_s and A_f points for these compositions appear to be the reasons for this change. Although the difference between the two transformation temperatures were statistically constant among 7.5Pd, 10.0Pd and 15.0Pd ($p < 0.01$), the A_f point of 15.0Pd was much higher than the others, which caused the large residual strain for this composition. Another factor may exist in the crystallographical mechanism of martensitic transformation, B2 → B19 → B19′ [24]. According to the investigation with X-ray diffraction [28], boundary between monoclinic martensite and orthorhombic martensite existed at 7 ∼ 8 at % Pd addition. Besides, in the orthorhombic martensite for 8 ∼ 20 at % Pd addition, the lattice parameter exhibited the enlargement of anisotropy with the increase of Pd addition. This appears to cause the larger elongation of 7.5Pd than 10.0Pd or 15.0Pd, while less difference between M_s and A_f points and low apparent proof stress suggest the smooth generation of orthorhombic martensite from parent (cubic) phase B2.

From the results on the tensile properties in the series B, it was suggested that apparent proof stress could be changeable by the proportion of Ti and Ni at the fixed 7.5 at % Pd addition with residual strain being kept low. To control the apparent proof stress would be effective in designing cast removable appliances. Low apparent proof stress is desirable in the cases with severe undercuts on abutment teeth, while high apparent proof stress is required to maintain considerable retentive force with regular undercuts. Although high apparent proof stress could obtained in the compositions of 42.8 and 42.9 at % Ni, their residual strain were considerably high. Therefore, combined use of binary Ti-50.8Ni alloy and ternary Ti-42.5 ∼ 42.7Ni-7.5Pd alloy was evaluated to be suitable to utilize the super-elasticity with different levels in apparent proof stress in dental castings.

From the biomechanical aspect, super-elastic Ti-Ni

TABLE II Efficiency for energy storage of Ti-Ni and Ti-Ni-Pd alloy castings: E1 = energy density per unit volume dissipated during one cycle; E2 = energy density per unit volume stored and available upon unloading; $\eta = E2/(E1 + E2)$ = efficiency for energy storage

Composition (at %)	E1 (MJ/m^3)	E2 (MJ/m^3)	η (%)
Ti-50.0Ni	5.1 ± 0.5	0.8 ± 0.1	12.8 ± 1.4
Ti-50.8Ni	7.8 ± 0.4	4.5 ± 0.2	36.6 ± 2.2
Ti-42.5Ni-7.5Pd	3.3 ± 0.3	2.6 ± 0.2	43.9 ± 3.3

Mean $\pm$ S.D.

alloy showed similar stress-strain behavior to living tissues, such as bone, tendon and hair [29]. In the dental prostheses, super-elasticity and shock absorptive characteristics [30] of Ti-Ni alloy would be useful to reduce excessive stress against periodontal tissues. Besides, Ti-42.5Ni-7.5Pd alloy castings exhibited better super-elastic flexibility than Ti-50.8Ni alloy, which is proved in lower apparent proof stress and larger elongation. This flexibility is believed to be caused by its relatively high M_s point, and would be effective to preserve the abutment teeth. Since the elastic modulus of cobalt-chromium (Co-Cr) alloy is higher than that of dental gold alloys, the rest-proximal-I bar system is frequently chosen in designing free-end saddle dentures. In these cases, Ti-42.5Ni-7.5Pd alloy could be applied with the advantage of flexible support as well as excellent fatigue property [13].

Table II shows the efficiency for energy storage [31] of Ti-Ni and Ti-Ni-Pd alloy castings. The efficiency η of Ti-50.0Ni alloy casting was significantly lower because of its typical shape memory effect. Ti-42.5Ni-7.5Pd alloy showed super-elasticity with better efficiency for energy storage than Ti-50.8Ni alloy castings ($p < 0.01$). The functional force by super-elasticity is applied to physiological tooth movement in orthodontic treatment [2]. Better efficiency for energy storage of Ti-42.5Ni-7.5Pd alloy indicates high functional force in spite of its low apparent proof stress. This property appears to also be advantageous to the retention devices in dental prostheses.

Several reports demonstrated excellent corrosion resistance [32] and good biocompatibility [29, 33] of Ti-Ni alloy. Furthermore, evaluation of the short-term biological safety of Ti-Ni alloys showed no cytotoxic, allergic or genotoxic activity [34]. However, careful consideration in Ni and Pd allergy is indispensable for the clinical application of Ti-Ni-Pd alloy castings.

5. Conclusion

While there was no significant difference in residual strain among Ti-50.0Ni, 5.0Pd and 15.0Pd alloy castings, 7.5Pd and 10.0Pd castings showed lower residual strain and lower apparent proof stress than Ti-50.0Ni alloy. Relatively low A_f points and less difference between M_s and A_f points for these compositions appear to be the reasons for this change. Moreover, 7.5Pd castings showed higher tensile strength and larger elongation than 10.0Pd castings. With the increase of Ni from 42.5 to 42.9 at % at the fixed 7.5 at% Pd addition, both M_s and A_f points decreased almost linearly and apparent proof stress increased. It was suggested that apparent proof stress could be changeable by the proportion of Ti and Ni at the fixed 7.5 at % Pd addition with residual strain being kept low. Ti-42.5Ni-7.5Pd alloy castings showed larger elongation than the other four. Ti-42.5Ni-7.5Pd alloy castings exhibited better super-elastic flexibility than Ti-50.8Ni alloy, which is proved in lower apparent proof stress and larger elongation. This flexibility is believed to be caused by its relatively high M_s point. It is suggested that this property could widen the application of super-elasticity to dental appliances.

Acknowledgments

The authors would like to thank Professor H. Hamanaka, Tokyo Medical and Dental University for his valuable guidance and discussions throughout this research.

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Received 2 December 1998
and accepted 21 June 1999