Bending property and phase transformation of Ti–Ni–Cu alloy dental castings for orthodontic application

M. YAMAMOTO, T. KURODA
Maxillofacial Orthognathics, Department of Maxillofacial Reconstruction and Function, Graduate School, Tokyo Medical and Dental University, 1-5-45 Yushima, Bunkyo-ku, Tokyo 113-8549, Japan

T. YONEYAMA*, H. DOI
Department of Metallurgy, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan
E-mail: yoneyama.met@tmd.ac.jp

Bending property of Ti–Ni–Cu alloy castings was investigated in a three-point bending test for orthodontic application in relation to the phase transformation. The compositions of the alloys were Ti–50.8Ni and Ti–40.8Ni–10.0Cu (mol %), and four cross-sectional shapes of the specimens were selected. Heat treatment was performed at 713, 753 or 793 K for 1.8 ks. The bending load changed by the cross-sectional size and shape mainly because of the difference in the moment of inertia of area, but the load–deflection relation did not differ proportionally in the unloading process. The difference between the load values in the loading and the unloading processes was relatively small for Ti–Ni–Cu alloy. With respect to the residual deflection, there was no significant difference between Ti–Ni and Ti–Ni–Cu alloys with the same treatment condition. The load values in the loading and the unloading processes decreased by each heat treatment for Ti–Ni alloy; however, the decrease in the load values for Ti–Ni–Cu alloy was not distinct. It is proved that Ti–Ni–Cu alloy castings produce effective orthodontic force as well as stable low residual deflection, which is likely to be caused by the high and sharp thermal peaks during phase transformation.

1. Introduction

Ti–Ni alloy is a promising functional material because of its special mechanical properties of shape memory effect and super-elasticity. Since Ti–Ni alloy also has high corrosion resistance [1] and good biocompatibility [2], it has been applied in the medical and dental fields as well. One of the most successful applications of this alloy in dentistry is the super-elastic alloy orthodontic wire introduced in 1982 [3, 4]. This wire showed super-elasticity providing light continuous force for physiologic and efficient tooth movement [5–7]. Successively, rectangular wires [8], bending method [9] and coil springs [10] of Ti–Ni alloy were developed for orthodontic treatment. With respect to the relation between mechanical properties and phase transformation of Ti–Ni alloy wires, a thermomechanical property [11], and difference between the wires [12, 13] were reported. The effect of heat treatment on the super-elastic property of Ti–Ni alloy was also examined [14, 15].

On the other hand, it was reported that Ti–Ni alloy castings prepared with conventional procedures were brittle and devoid of mechanical memory [16]. However, recent advancement in dental casting technology for titanium enables casting of Ti–Ni alloy without losing its special property [17, 18]. In addition, flexible super-elasticity in tensile test [19, 20] and the crystal structure [21] of Ti–Ni–Cu alloy were reported, which was thought to be advantageous to orthodontic treatment. In this study, the bending property of Ti–Ni–Cu alloy castings was investigated in a three-point bending test in relation to the phase transformation in differential scanning calorimetry (DSC) for new orthodontic application.

2. Materials and methods

2.1. Specimen preparation

Pure metals of titanium (> 99.58 mass %), nickel (> 99.97 mass %) and copper (99.99 mass %) were used to make Ti–Ni alloy and Ti–Ni–Cu alloy ingots for castings. They were weighed precisely and melted on a water-cooled copper hearth in an argon arc furnace with

*Author to whom all correspondence should be addressed.

a non-consumable tungsten electrode. Each alloy ingot was turned over and melted five times to ensure chemical homogeneity. The compositions of the alloys were Ti–50.8Ni (mol %) and Ti–40.8Ni–10.0Cu (mol %).

The molds were made of a phosphate-bonded investment (Snow White, Shofu, Japan) according to the manufacturer's indication. Casting was carried out with a gas-pressure casting machine (Autocast HC-III, GC, Japan). Casting conditions were 7.5 mm of electrode–ingot distance and 200 Å of electric current. The castings were water-quenched and sandblasted. Heat treatment was performed in a bath of nitrate at 713, 753 or 793 K for 1.8 ks.

2.2. Three-point bending test

To investigate the bending property of Ti–Ni and Ti–Ni–Cu alloy castings a three-point bending test [22] was carried out. The cross-sectional shapes of the bending test specimens were round with diameters of 0.6, 0.8 and 1.0 mm, and half-rounded with 1.5 mm diameter.

The center pole of the testing apparatus was combined with a load cell to measure the load on a specimen, and the two side poles were mounted on a movable stage connected with a displacement transducer to measure the deflection. The distance between the center pole and a side pole was 7.0 mm. The specimens were loaded until the deflection reached 2.0 mm, then unloaded. The deflecting speed was approximately 0.2 mm/s. The temperatures of the specimens and the apparatus were kept at 310 K.

To compare the bending property of the castings, one-way factorial analysis of variance was used for the detection of the differences among conditions. Tukey–Kramer test was performed as the *post hoc* test for the detection of the differences between conditions. Statistical significance was set at $p < 0.05$.

2.3. DSC measurement

Thermal behavior of Ti–Ni and Ti–Ni–Cu alloy castings was studied by a differential scanning calorimeter (DSC-7000, ULVAC, Japan). Specimens were 4.0 mm in diameter and 0.5 mm in thickness. They were sealed in aluminum cells, and alpha alumina powder was used as the reference material. The atmosphere of the measuring chamber was argon gas. 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.

3. Results

3.1. Load–deflection relation

Typical load–deflection diagrams of Ti–50.8Ni and Ti–40.8Ni–10.0Cu (mol %) castings in as cast condition are shown in Figs 1 and 2, respectively. Thin broken and solid lines indicate the specimens with rounded cross-sectional shape, 0.6 mm and 0.8 mm in diameter. Thick dashed and solid lines indicate the ones with the cross section of half-round (1.5 mm in diameter) and round (1.0 mm in diameter), respectively. In every load–deflection curve observed in this study, the increase in load per unit deflection decreased after the elastic limit was exceeded, like permanent deformation in usual metals. However, the deflection decreased considerably by being unloaded because of super-elasticity.

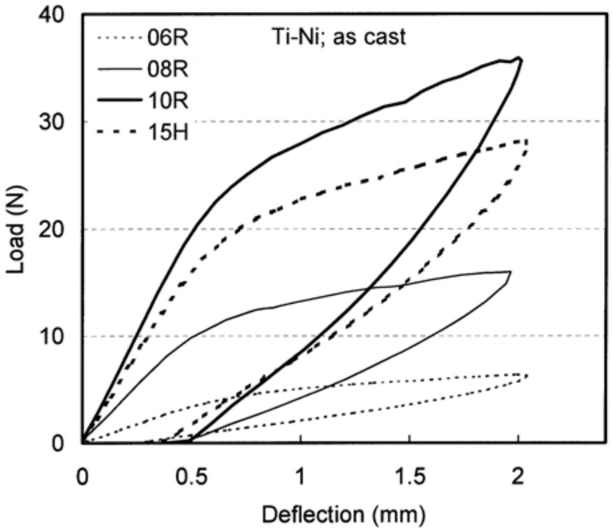

Figure 1 Typical load–deflection diagrams of Ti–Ni alloy castings with different cross-sectional configuration (as cast).

The load levels in the loading process were highest in the cross-sectional configuration of 1.0 mm round, and decreased in the order of 1.5 mm half-round, 0.8 mm round and 0.6 mm round in both the alloys. The difference in the load levels between the loading and unloading processes was smaller in Ti–Ni–Cu alloy than in Ti–Ni alloy. There were cross points of the curves in the unloading process in some conditions.

Figs 3 and 4 show the load–deflection diagrams of the castings with heat treatment at different temperatures. The load level in the loading process decreased considerably by the heat treatment in Ti–Ni binary alloy in comparison with the copper-added alloy. The load level of Ti–Ni–Cu alloy tended to be kept higher than that of Ti–Ni alloy during the unloading process. The residual deflection appeared to decrease by the heat treatment in both compositions.

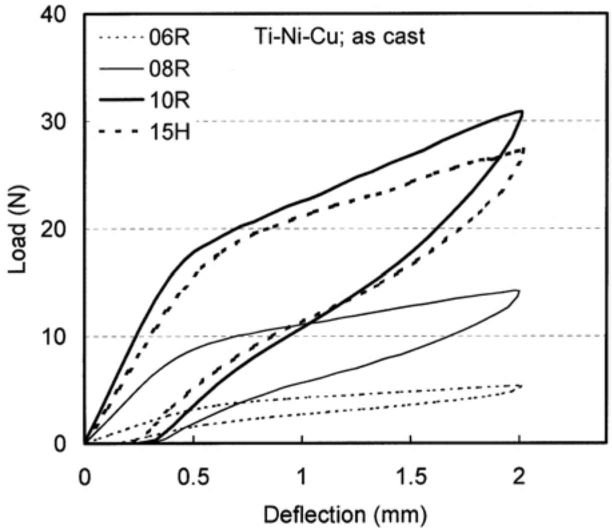

Figure 2 Typical load–deflection diagrams of Ti–Ni–Cu alloy castings with different cross-sectional configuration (as cast).

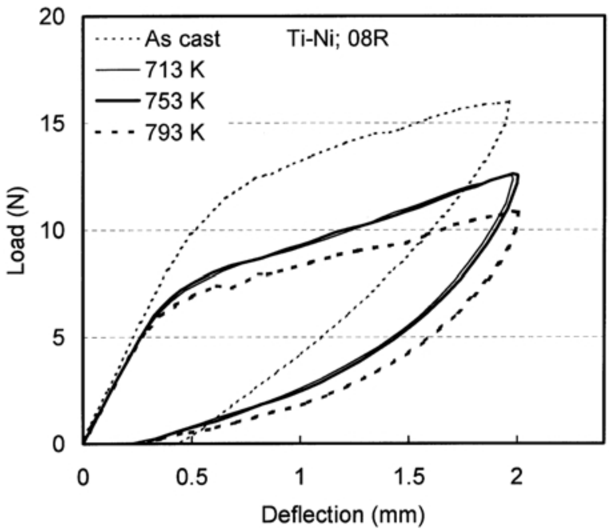

Figure 3 Typical load–deflection diagrams of Ti–Ni alloy castings with heat treatment. Cross-sectional configuration was round shape, 0.8 mm in diameter.

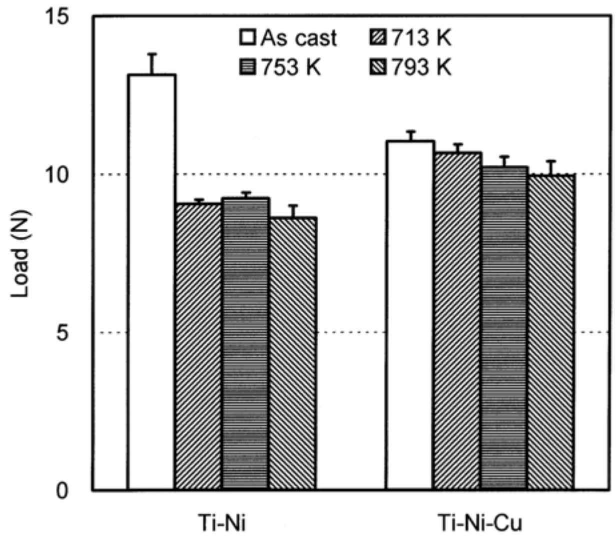

Figure 5 Load values at 1.0 mm deflection in the loading process. Cross-sectional configuration was round shape, 0.8 mm in diameter.

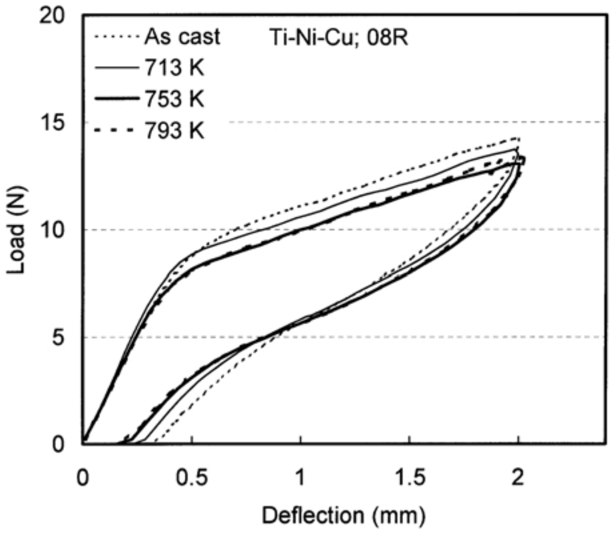

Figure 4 Typical load–deflection diagrams of Ti–Ni–Cu alloy castings with heat treatment. Cross-sectional configuration was round shape, 0.8 mm in diameter.

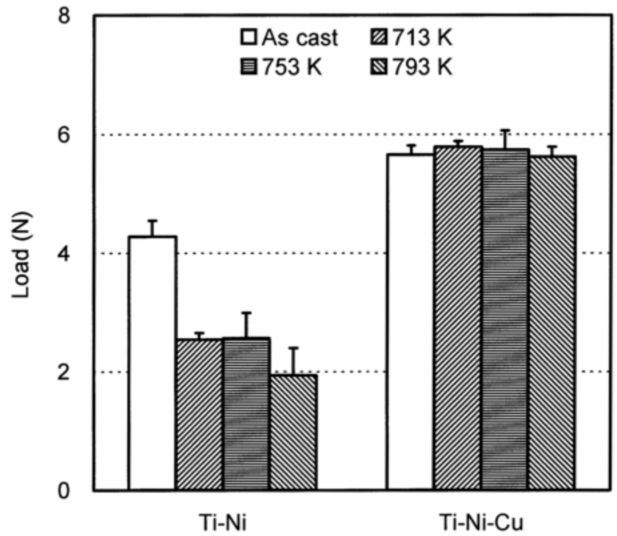

Figure 6 Load values at 1.0 mm deflection in the unloading process. Cross-sectional configuration was round shape, 0.8 mm in diameter.

3.2. Bending property

Figs 5 and 6 show the load values of the 0.8 mm round specimens at 1.0 mm deflection in the loading and the unloading processes, respectively. Within Ti–Ni alloy group, the load value with each heat treatment was statistically lower than that for as cast condition, while there were no significant differences among the heat-treated conditions. This tendency was observed both in the loading and the unloading processes.

The load value of Ti–Ni–Cu alloy decreased with heat treatment and increasing temperature of treatment. There were statistically significant differences between as cast and 753 or 793 as well as 713 and 793 K conditions in the loading process. However, there was no significant difference among those in the unloading process.

In the comparison between the alloys with the same treatment condition, the load values of Ti–Ni alloy were statistically lower than those of Ti–Ni–Cu alloy in every treatment condition except the as cast condition in the loading process.

The residual deflection values of the alloys are shown in Fig. 7. Although the values were considerably scattered, there were no significant differences among the Ti–Ni group. In the Ti–Ni–Cu group, the residual deflection decreased with heat treatment as well as increasing temperature of treatment. The value for the as cast condition was statistically higher than that for 753 or 793 K condition, and that for 713 K was higher than 793 K. There was no significant difference between the residual deflection values of Ti–Ni and Ti–Ni–Cu alloys with the same treatment.

3.3. Thermal behavior

Fig. 8 shows typical DSC curves of Ti–Ni binary alloy castings in as cast and 793 K treated conditions. The exothermic peaks indicate the exothermic reaction accompanying the martensitic transformation in the cooling process, while the endothermic ones are caused by the reverse transformation from martensitic phase to parent phase in the heating process. The thermal peak

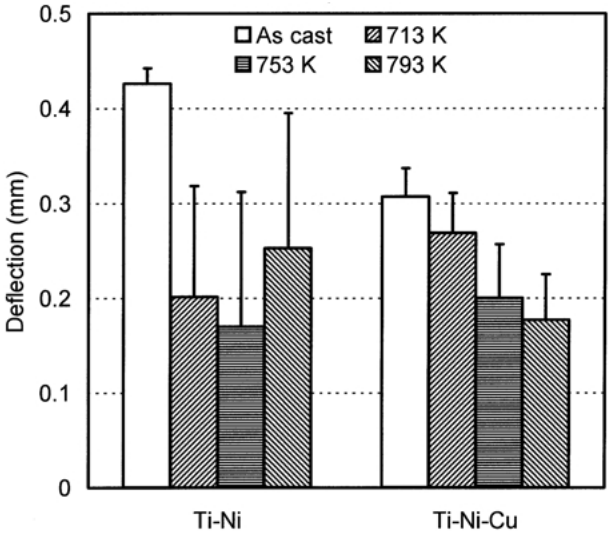

Figure 7 Residual deflection after being unloaded. Cross-sectional configuration was round shape, 0.8 mm in diameter.

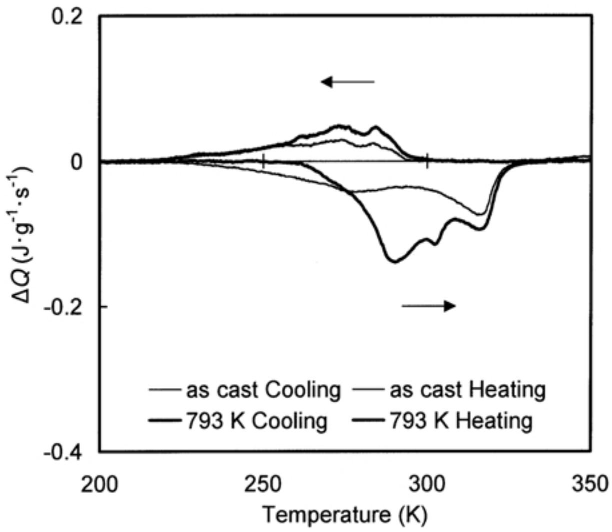

Figure 8 Typical DSC diagrams of Ti–Ni alloy castings.

height increased by the heat treatment, but the reverse transformation finishing (A_f) temperature was almost unchanged. In addition, three endothermic peaks were observed for the heat-treated specimens. On the other hand, simple and sharp thermal peaks were observed in the thermal behavior for Ti–Ni–Cu ternary alloy castings, in which there was no distinct change by the heat treatment, as shown in Fig. 9.

Transformation temperatures of Ti–Ni and Ti–Ni–Cu castings are shown in Table I. The martensitic transformation starting (M_s) temperature of Ti–Ni alloy

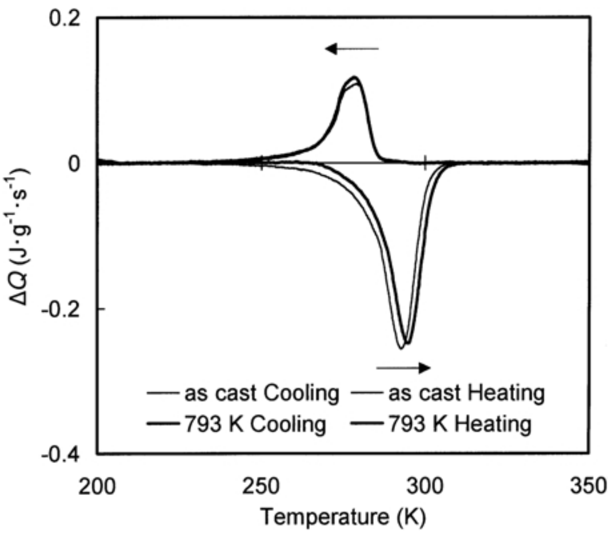

Figure 9 Typical DSC diagrams of Ti–Ni–Cu alloy castings.

increased by 713 or 753 K treatment, but the increase was not observed by 793 K treatment. The martensitic transformation finishing (M_f) and the reverse transformation starting (A_s) temperatures increased by every heat treatment condition. A_f temperature of the binary alloy and every transformation temperature of the ternary alloy were not changed by these heat treatments.

4. Discussion

The special properties of Ti–Ni alloy occur in association with the thermoelastic martensitic transformation, and super-elasticity is observed above the reverse transformation temperature range through the stress-induced martensitic transformation. This alloy is soft and easy to change in shape in martensitic phase, and the deformation recovers by being unloaded through the reverse transformation to parent phase. Therefore, the alloy exhibits high flexibility owing to wide recoverable strain range and rather constant and low stress level.

In the load–deflection diagrams with different cross-section of the specimens, the bending load changed by the cross-sectional size and shape. The main reason for this change was the difference in the moment of inertia of area, determined by the cross-section. However, the load–deflection relation did not differ proportionally in the unloading process, which was thought to be caused partly by the stress distribution.

With respect to the comparison between Ti–Ni and Ti–Ni–Cu alloys in the load–deflection diagrams, the load

TABLE I Transformation temperatures of Ti–Ni and Ti–Ni–Cu alloys castings

Alloy	Condition	M_s (K)	M_f (K)	A_s (K)	A_f (K)
Ti-Ni	As cast	295.3 ± 1.0	202.5 ± 21.4	234.7 ± 1.7	323.1 ± 2.2
	713 K	315.4 ± 1.7	232.2 ± 2.7	271.1 ± 1.2	324.8 ± 0.7
	753 K	308.0 ± 0.9	232.5 ± 12.2	269.1 ± 2.2	323.5 ± 1.3
	793 K	294.7 ± 0.6	235.6 ± 8.7	269.9 ± 2.5	324.1 ± 0.9
Ti-Ni-Cu	As cast	286.0 ± 1.4	266.0 ± 1.3	281.9 ± 1.3	301.2 ± 0.5
	713 K	286.8 ± 1.9	264.3 ± 1.1	280.7 ± 0.9	301.4 ± 0.9
	753 K	288.4 ± 1.4	265.2 ± 2.1	281.4 ± 1.4	302.8 ± 1.0
	793 K	286.9 ± 2.4	265.9 ± 0.7	281.0 ± 0.4	302.5 ± 0.6

Mean ± SD.

level for as cast condition in the loading process was higher for the binary alloy; however, that in the unloading process was higher for the Cu-added alloy. Therefore, the difference between the load values in the loading and the unloading processes was relatively small for Ti–Ni–Cu alloy. One of the main reasons for this difference was thought to be the difference between M_s and A_f temperatures, which were 27.8 K for the binary alloy and 15.2 K for the ternary alloy. It was reported that the apparent proof stress also decreased by Cu addition in tensile test [19, 20].

Considering the relation between the testing temperature ($T = 310$ K) and the transformation temperatures, it was $M_s < T < A_f$ for Ti–Ni alloy and $A_f < T$ for Ti–Ni–Cu alloy as shown in Table I. The former relation was characterized by the presence of residual strain, while the latter led to the transformation pseudoelasticity [23], i.e. super-elasticity. However, with respect to the residual deflection values in this study, there was no significant difference between Ti–Ni and Ti–Ni–Cu alloys with the same treatment condition. One of the possible reasons was the wide transformation temperature range of the binary alloy, in which considerable part of the endothermic reaction occurred below 310 K as shown in Fig. 8.

The load values in the loading and the unloading processes decreased by the heat treatment for Ti–Ni alloy. It is thought to be caused by the increase in M_s and A_s temperatures by the heat treatment, since these temperatures have an influence on the initial stress to induce martensitic and reverse transformations, respectively. On the other hand, the decrease in the load values for Ti–Ni–Cu alloy was not distinct as shown in Figs 5 and 6. One of the most probable reasons for this result could be the less change in the thermal behavior for Ti–Ni–Cu alloy by the heat treatment, which is shown in the DSC diagram as well as the transformation temperatures.

It was difficult to cast Ti–Ni alloy without losing its special properties. One of the major problems was thought to originate from the high reactivity of titanium with melting atmosphere and mold materials, which resulted in deteriorated mechanical property. However, dental casting technology, including machines and materials, has seen much progress for titanium, recently, which is also applicable to Ti–Ni alloy. Another problem exists, which is specific to Ti–Ni alloy. The property of this alloy is easily influenced by small changes in composition and impurities [24] in addition to heat treatment condition and the degree of machining.

In this study, Ti–Ni–Cu alloy castings were proved to produce effective orthodontic force as well as stable low residual deflection, which is likely to be caused by the high and sharp thermal peaks during phase transformation, though the heat treatment effect was not significant. This property is thought to be effective especially to the final stage in orthodontic treatment with three-dimensional tooth alignment and sufficient anchorage. This alloy is also believed to have the potential to develop new orthodontic cast appliances.

Acknowledgments

The authors would like to acknowledge Professor H. Hamanaka of Tokyo Medical and Dental University for his guidance and discussion throughout this research.

References

1. K. M. SPECK and A. C. FRAKER, *J. Dent. Res.* **59** (1980) 1590.
2. L. S. CASTLEMAN, S. M. MOTZKIN, F. P. ARICANDRI, V. L. BONAWIT and A. A. JOHNSON, *J. Biomed. Mater. Res.* **10** (1976) 695.
3. K. WATANABE, *J. Jpn. Soc. Dent. Appar. Mat.* **23** (1982) 47.
4. K. WATANABE, *J. Jpn. Dent. Mater.* **2** (1983) 594.
5. Y. OHURA, *J. Jpn. Orthodon. Soc.* **43** (1984) 71.
6. C. J. BURSTONE, B. QIN and J. Y. MORTON, *Am. J. Orthod.* **87** (1985) 445.
7. F. MIURA, M. MOGI, Y. OHURA and H. HAMANAKA, *Am. J. Orthod. Dentofac. Orthop.* **90** (1986) 1.
8. Y. OKAMOTO, *J. Stomatol. Soc. Jpn.* **54** (1987) 57.
9. F. MIURA, M. MOGI and Y. OHURA, *Eur. J. Orthod.* **10** (1988) 187.
10. F. MIURA, M. MOGI, Y. OHURA and M. KARIBE, *Am. J. Orthod. Dentofac. Orthop.* **94** (1988) 89.
11. J. H. LEE, J. B. PARK, G. F. ANDREASEN and R. S. LAKES, *J. Biomed. Mater. Res.* **22** (1988) 573.
12. T. YONEYAMA, H. DOI, H. HAMANAKA, Y. OKAMOTO, M. MOGI and F. MIURA, *Dent. Mater. J.* **11** (1992) 1.
13. M. THEIR, D. TREPPMANN, D. DRESCHER and C. BOUREAUL, *J. Mater. Sci. Mater. Med.* **3** (1992) 229.
14. Y. OKAMOTO, H. HAMANAKA, F. MIURA, H. TAMURA and H. HORIKAWA, *Scripta Metall.* **22** (1988) 517.
15. H. HAMANAKA, T. YONEYAMA, H. DOI, Y. OKAMOTO, M. MOGI and F. MIURA, *J. Jpn. Dent. Mater.* **8** (1989) 216.
16. S. CIVJAN, E. F. HUGET and L. B. DESIMON, *J. Dent. Res.* **54** (1975) 89.
17. J. TAKAHASHI, M. OKAZAKI, H. KIMURA and Y. FURUTA, *Dent. Mater. J.* **4** (1985) 146.
18. H. HAMANAKA, H. DOI, T. YONEYAMA and O. OKUNO, *J. Dent. Res.* **68** (1989) 1529.
19. K. KOHNO, *J. Stomatol. Soc. Jpn.* **54** (1987) 577.
20. H. DOI, E. KOBAYASHI, T. YONEYAMA and H. HAMANAKA, *J. Jpn. Dent. Mater.* **20** (2001) 48.
21. K. TSUJI and K. NOMURA, *J. Mater. Sci.* **27** (1992) 2199.
22. T. YONEYAMA, H. DOI, H. HAMANAKA, M. YAMAMOTO and T. KURODA, *J. Biomed. Mater. Res.* **27** (1993) 399.
23. S. MIYAZAKI, K. OTSUKA and Y. SUZUKI, *Scripta Metall.* **15** (1981) 287.
24. T. YONEYAMA, H. DOI and H. HAMANAKA, *Dent. Mater. J.* **11** (1992) 157.

Received 2 April
and accepted 19 July 2001