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The Mechanical and Thermal Behaviors of Heat-Treated Ni-Rich NiTi Orthodontic Archwires

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The near equiatomic nickel-titanium alloy is an outstanding intermetallic compound exhibiting distinctive properties associated with characteristic thermal and stress-induced martensitic transformations. The process of producing orthodontic wires has been modified to obtain the optimal shape memory behaviors. Phase transformation temperatures and load-deflection characteristics of this binary alloy are very significant variables in the performance of this alloy and can be manipulated by different thermomechanical treatments via inducing precipitation or dislocation networks in the matrix. In this study, one brand of commercial heat-activated nickel-titanium archwire (3 M Unitek) was selected and solution treated. Then, the wires annealed at 400 °C for 10, 30, and 60 min. Thermal transformation temperatures were determined using differential scanning calorimeter. It was showed that these temperatures increased with increasing the time of heat treatment and multistage transformation occurred as the result of inhomogeneities. In order to evaluate mechanical parameters of heat-treated archwires, they were placed on an archform fixture simulating maxillary dentition and load-deflection curves were obtained by three-point bending test at 37 °C. The results compared to as-received archwires and the best superelasticity was observed after 30 min aging.

Keywords biomaterials, heat treating, mechanical testing

1. Introduction

The shape memory nickel-titanium alloys (Nitinol) have been used in wide applications in medical fields due to their unique blend of mechanical properties and biocompatibility. Application of this alloy in orthodontics has been initiated from early 1970s (Ref 1, 2).

When a superelastic NiTi wire is deflected over a long distance, it eventually springs back to nearly its original position by reverse transformation from monoclinic to B2 structure while exerting light continuous forces (Ref 3-6).

Recently, a new generation of NiTi wires, i.e., shape memory wires (heat-activated NiTi wires) have been employed which exhibits clinically useful shape memory as well as superelasticity and higher transition temperature range (TTR) (Ref 7).

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Nickel amount, oxygen content, heat treatment, the amount of cold working, and deformation temperature are important factors that can have influence on the mechanical properties and superelasticity of NiTi alloy (Ref 1, 8). Since NiTi orthodontic wires generally contain over 50% Ni in their composition (Ni-rich), aging treatment will strongly influence thermal transformation behavior and stress deformation.

Many researchers have studied transformation behavior of Ni-rich NiTi alloys aged at various temperatures for different times (Ref 9-21). It has been confirmed that aging treatment introduces Ti_3Ni_4 metastable precipitates which change the transformation path to B2 $\rightarrow$ R $\rightarrow$ B19′. Age hardening of the alloy by such a precipitation also affects shape memory effect and superelasticity greatly (Ref 8, 22). Ni-rich NiTi alloys exhibit superelasticity in a wide temperature range as the critical stress for slip increases when high density of small precipitates is available in the B2 matrix.

In recent years, the effect of aging of this alloy on thermal multistage transformations observed in DSC curves has been a controversial topic. Three different explanations including local stress inhomogeneity, local composition inhomogeneity, and the most important theory based on grain boundary effect have been exhibited. TEM observations have explained sequential peaks of DSC curves of low nickel supersaturated Ni-rich alloys by heterogeneous precipitation between grain boundaries and grain interiors.

The purpose of this work was to study the effect of aging treatment at 400 °C for short times without cold work on the force-deflection characteristics and thermal transformation behaviors of solution-treated nickel-titanium orthodontic archwires. In the research, force-deflection characteristics of the aged archwires were compared to as-received archwires using a special three-point bending fixture.

2. Experimental Procedures

In this study, shape memory NiTi orthodontic archwires (Nitinol Heat-Activated, 3 M Unitek, Monrovia, CA, USA) with diameter of 0.41 mm were used as the Ni-rich alloy material.

In order to investigate the effect of heat treatments, the wires were first enclosed in evacuated quartz capsule and solution treated at 1000 °C for 90 min followed by water quenching. Then aging of solution-treated wires were performed at 400 °C for different times of 10, 30, and 60 min in air atmosphere.

The thermal transformation characteristics were determined using differential scanning calorimeter (Mettler-822^e DSC instrument). The samples were cut from the end part of heat-treated wires and cleaned in acetone containing ultrasonic cleaner. The complete cooling and heating cycles were done as follows.

The samples were quickly heated to 120 °C and held for 3 min following by cooling to −140 at a rate of 10 °C/min and held for 3 min before heating to 120 °C at the same rate. The transformation temperatures were specified by extrapolated tangential method. In the case of multistage overlapped peaks, only sharper peaks were considered. The characteristic temperatures were R_s, R_f, M_s, M_f and R'_s, R'_f, A_s, A_f as R phase, martensite and reverse R phase, austenite start and finish transformation temperatures, respectively. Some of the characteristic temperatures were missed due to overlapping of the peaks.

The force-deflection properties of as-received and heat-treated wires were studied by three-point bending (TPB) test (loading-unloading) in the simulated clinical conditions with a Zwick universal testing machine fitted with a 2.5 kN compression load cell and a crosshead speed of 1.0 mm/min in a dentition simulated fixture (Ref 23, 24) (Fig. 1).

Fig. 1 Arch-form fixture simulating maxillary dentition for TPB tests (Ref 23, 24)

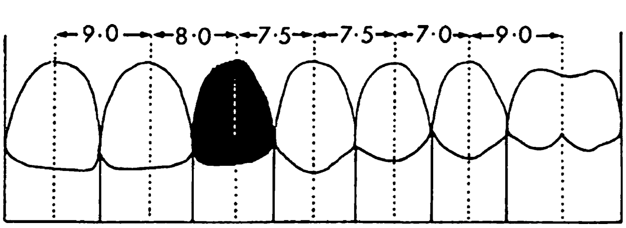

Fig. 2 Used Interbracket distance (mm) on fixture and location of irregular tooth (black tooth) (Ref 6)

By means of this fixture, the three-point bending test simulates wire force on the teeth in the oral configuration. The rods representing teeth No. 2 & 5 (left) and No. 3 & 5 (right) removed for dynamic three-point bending test. The wires were placed on the fixture through the brackets. The used inter-bracket distance on the fixture was selected according to Wilkinson et al.'s work (Fig. 2) (Ref 6). The tests were carried out on tooth No. 3 as irregular tooth to 4 mm deflection. The wires were tested in a water bath at 37 °C. The temperature control was done during each test with a K-type thermocouple in the range of accuracy of ±2 °C. Each bending test was repeated three times with the same new wire.

3. Results and Discussion

3.1 DSC and TPB Curves of As-Received Wires

Figure 3 shows the DSC curve of as-received orthodontic wire. As shown in the cooling cycle, two completely separated and distinct peaks can be seen. The peaks attributed to A → R and R → M transformations occur at 10 and −55 °C, respectively. In heating, only one sharp peak can be observed with the latent heat of −18 J/g, implying one stage transformation of M → A. The start and final transformation temperatures of the wires are shown in Table 1.

According to literature (Ref 22), two microscopic factors affect on the R phase formation prior to martensitic transformation: (1) introduction of dislocation network, (2) formation of Ti_3Ni_4 precipitates. In as much as combined cold work and aging treatments are a part of the process of orthodontic wire production, it is expected that the both factors induce internal stresses which consequently result in R phase transformation in DSC curve of NiTi wire.

TPB test of the wire at 37 °C in Fig. 4 demonstrates pseudoelastic behavior of the orthodontic wire with very limited residual strain. It should be noted the force level around 3 mm deflection in the unloading plateau drops due to slippage of wire through the brackets during loading as supported by Parvizi et al. (Ref 25).

According to Table 1, the A_f temperature of the as-received wire is about 19 °C. Thus, the deformation of wire has been done at about 20° above A_f temperature. So, the stress transformation behavior is reversible by unloading due to the higher critical stress for slip against the stress required to induce martensite.

Regarding the TPB curve of as-received wire (Fig. 4), the necessary force to move the austenite/martensite interface

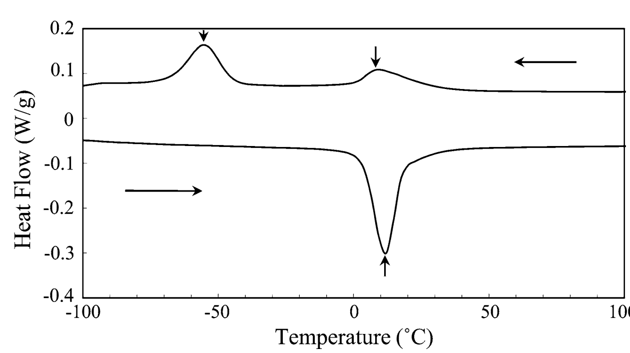

Fig. 3 DSC curve of as-received wire

Table 1 Transformation temperatures of as-received and heat-treated wires

Condition	Temperature							
	R_s	R_f	M_s	M_f	R'_s	R'_f	A_s	A_f
As-received wire	29	0	−44	−68	···	···	3	19
Solution-treated wire	···	···	−19	−26	···	···	−16	0
Aged wire at 400 °C/10 min	34	−20	−29	−60	−25	8	···	36
Aged wire at 400 °C/30 min	35	−14	−28	−54	−47	···	···	40
Aged wire at 400 °C/60 min	46	···	···	−13	−3	···	···	46

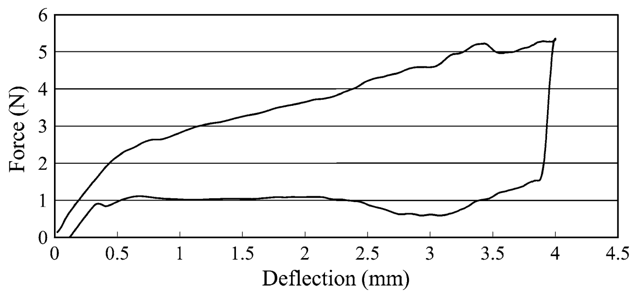

Fig. 4 TPB curve of as-received wire

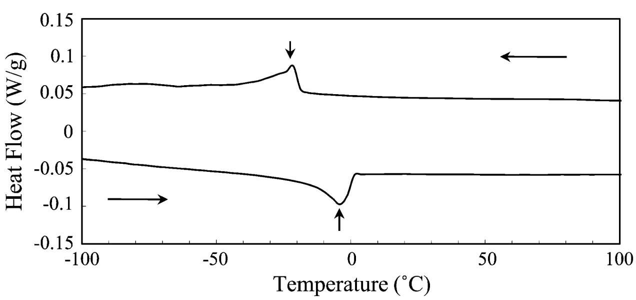

Fig. 5 DSC curve of solution-treated wire

during loading increases progressively as the deflection increases. However, unloading force level is almost constant at about 1 N during a wide range of deflection. This characteristic is a clinical advantage so as to accomplish optimal tooth movement (Ref 1).

3.2 DSC Curves of Heat-Treated Wires

DSC results of solution-treated and subsequent aged wires at 400 °C for 10, 30, and 60 min have been depicted in Fig. 5-8.

The solution-treated wire exhibits direct A↔M transformation upon both cooling and heating cycles with thermal hysteresis of 18 °C, suggesting recovery of defects in the microstructure and solution of precipitates in the matrix.

It can be possible to clarify the composition of NiTi alloy in solution-treated state by the following relation (Ref 26):

$$M_s = (60 - (\text{at.\%Ni} - 50.0) \times 180)\,^\circ\text{C}$$

So the approximate composition of this orthodontic wire is about 50.5 at.% Ni. Considering the excess nickel content in composition, nucleation of metastable Ti_3Ni_4 particles can be expected during aging at appropriate temperatures.

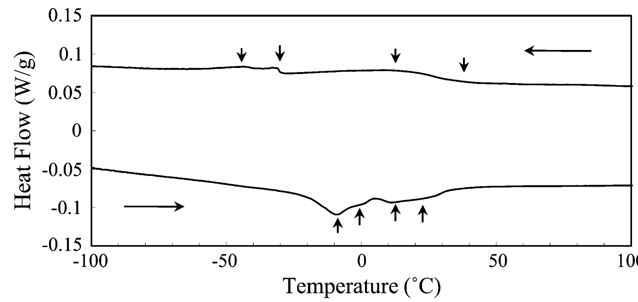

Fig. 6 DSC curve of solution treated and aged wire at 400 °C for 10 min

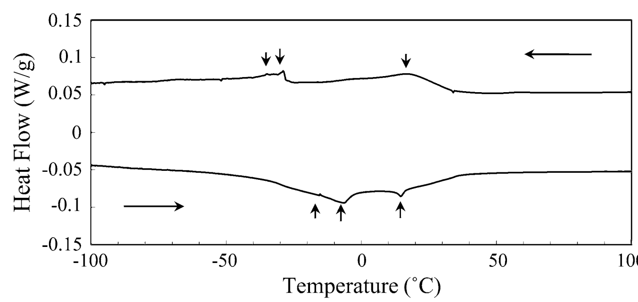

Fig. 7 DSC curve of solution treated and aged wire at 400 °C for 30 min

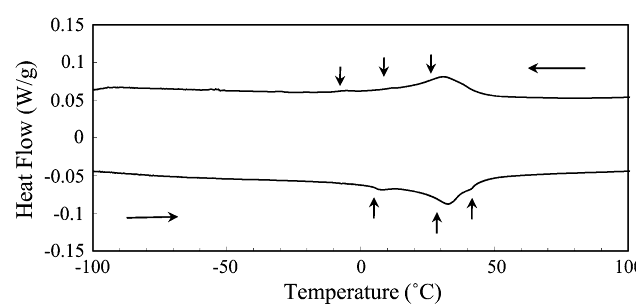

Fig. 8 DSC curve of solution treated and aged wire at 400 °C for 60 min

Figures 6-8 show that after aging treatment, A↔R and R↔M transformations take place as multistage transformations with determined transformation temperatures in Table 1.

The results indicate that transformation temperatures shift to higher temperatures with aging time. In addition, one-stage martensitic transformation in solution-treated wire turns to multistage transformation in a wide range of temperatures. It can be expected that due to dissolution of matrix and formation of coherent particles of Ti_3Ni_4, R phase transformation takes place in the way that its peak have partially overlapped on forward and reverse martensitic transformations.

Two points should be considered by comparing the DSC curves of aged wires: (1) The transformation temperatures particularly R↔M transformation increases with increasing aging time, (2) the number of R↔M transformation peaks reduces during both cooling and heating cycles with increasing aging time.

The changes in transformation temperatures with longer aging time can be related to increasing the density and size of Ni-rich Ti_3Ni_4 precipitates which result in depletion of Ni content of matrix. Therefore, the transformation temperatures move toward higher amounts. However, conversely A↔R transformation peaks are not greatly affected by the evolution of precipitates due to low transformation strain.

As a clinical point of view, since the reverse martensitic transformation should be completed about 37 °C to have superelastic properties, it could be seen in Fig. 7 and 8 that 30 min aging has risen A_f temperature a little higher than 37 °C while 60 min aging has increased the transformation temperatures inappropriately, so that 60 min aged wire has a partial martensitic structure at 37 °C.

On the number of transformation peaks, some studies have expressed various stress fields around the Ti_3Ni_4 particles (Ref 9-13). On the other hand, many previous studies have reported that heterogeneous precipitation reaction happens preferentially around the grain boundaries and the grain interior regions are free of precipitates (Ref 13-21). These inhomogeneities bring about multistage transformations in DSC curves of aged samples in the present study. However, it seems that the inhomogeneties decrease as aging period increases and the precipitation is developed in more regions. It is well understood in the DSC curves that transformation features have changed from four stages in aged wires at 400 °C for 10 min to three stages after 30 and 60 min aging. In general, formation of sharp peaks of transformation under 37 °C with lower inhomogeneities is an advantage for engineering design of orthodontic wires which result in lessening residual martensite.

3.3 TPB Curves of Heat-Treated Wires

In Fig. 9-12, stress-induced transformation loop of heat-treated wires at different conditions can be observed.

It is obvious from the results that after unloading, only a small amount of deformation of solution-treated wire is reversible. This phenomenon reveals the low resistance of matrix to slip. Therefore, the plastic deformation of austenite by slip occurs in advance of the formation of stress-induced martensite by twinning mechanism.

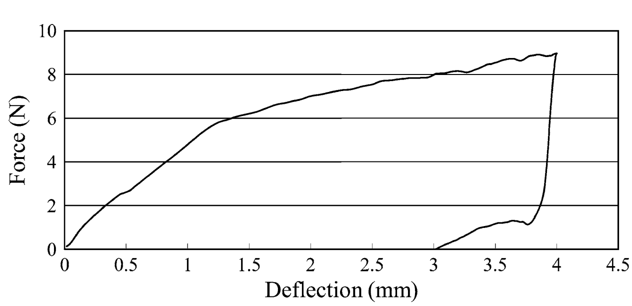

Fig. 9 TPB curve of solution-treated wire

It seems that after 10 min aging, localized precipitation leads to increase in magnitude of transformation strain recovery. After 30 min, more coherent particles precipitate and disperse in such a way that the strength of the matrix increases. According to DSC data in Table 1, although A_f temperature is about 40 °C, the superelasticity of the wire is revealed completely probably due to dynamic mechanical effects. The resistance of particles to the reverse martensitic transformation causes a considerable hysteresis, about 5.5 N, between loading and unloading plateaus.

The size of Ti_3Ni_4 precipitates is supposed to increase with increasing aging time up to 60 min (Ref 22). This increase may result in a decrease in the strength of the austenite matrix and the plastic deformation of the austenite may probably cause residual deformation in the matrix. Thus, the stress level of the unloading plateau shifts to a higher level and the stress hysteresis is reduced considerably. In addition, by increasing the size of precipitates and depletion of Ni content of the

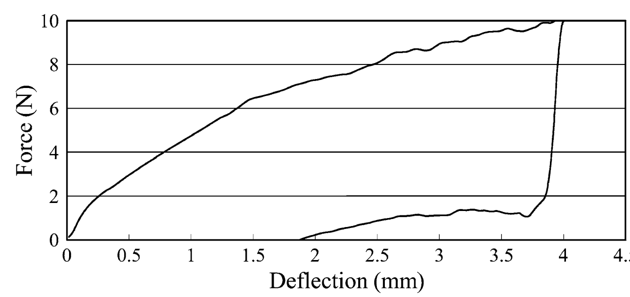

Fig. 10 TPB curve of solution treated and aged wire at 400 °C for 10 min

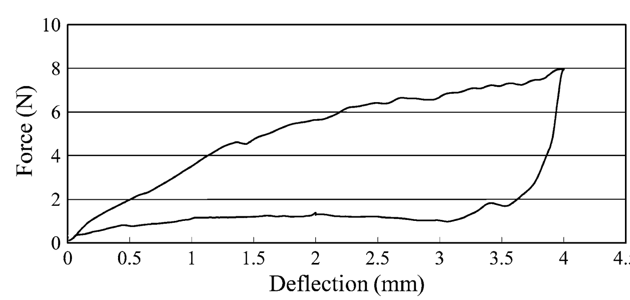

Fig. 11 TPB curve of solution treated and aged wire at 400 °C for 30 min

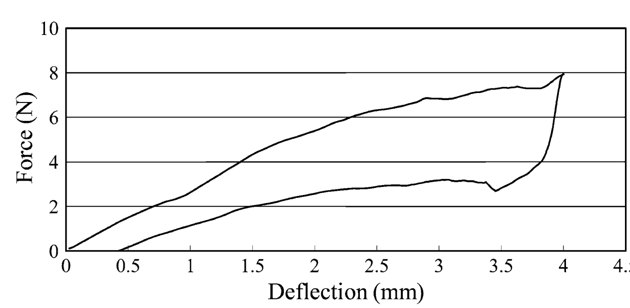

Fig. 12 TPB curve of solution treated and aged wire at 400 °C for 60 min

matrix, according to Table 1, the transformation temperatures have risen up and some remaining martensite in the matrix has caused residual deformation of the wire during TPB test.

4. Conclusions

1. Multistage martensitic transformations can be observed in DSC peaks for 10, 30, and 60 min aging of wires at 400 °C while there are quite sharp peaks in as-received wires.
2. Transformation temperatures shift to higher temperatures with increasing time of aging.
3. Strain recovery improved with increasing time of aging up to 30 min and TPB curve showed complete superelasticity after 30 min aging, but after 60 min aging, strain recovery decreased.
4. The superelasticity of the wire after 30 min aging was similar to as-received wire although the stress hysteresis of the aged wire is higher than for the others.
5. In terms of unloading plateau and residual deformation, 30 min aged wire shows the best result among heat-treated wires for orthodontic application but with quietly high loading plateau in comparison to as-received wire.

References

1. R. Sachdeva and S. Miyazaki, Superelastic Ni-Ti Alloys in Orthodontics, *Engineering Aspects of Shape Memory Alloys*, T.W. Duering, K.N. Melton, D. Stöckel, and C.M. Wayman, Ed., Butterworth-Heinemann, London, 1990, p 452-457
2. V.G. Dorodeiko, V.V. Rubanik, V.V. Rubanik Jr., and S.N. Miliukina, Heat Treatment of TiNi Wire Used for Interauterine Contraceptives, *Mater. Sci. Eng. A*, 2007, **481-482**, p 616–619
3. C. Gioka and T. Eliades, Superelasticity of Nickel-Titanium Orthodontic Archwires: Metallurgical Structure and Clinical Importance, *Hell. Orthod. Rev.*, 2002, **5**, p 111–127
4. D.C. Mallory, J.D. English, J.M. Powers, W.M. Brantley, and H.I. Bussa, Force-Deflection Comparison of Superelastic Nickel-Titanium Archwires, *Am. J. Orthod. Dentofacial. Orthop.*, 2004, **126**, p 110–112
5. B.K. Ruckerand and R.P. Kusy, Elastic Properties of Alternative Versus Single Stranded Leveling Archwires, *Am. J. Orthod. Dentofacial. Orthop.*, 2002, **122**(5), p 28–41
6. P.D. Wilkinson, P.S. Dysart, J.A.A. Hood, and G.P. Herbison, Load-Deflection Characteristics of Superelastic Nickel-Titanium Orthodontic Wires, *Am. J. Orthod. Dentofacial. Orthop.*, 2002, **121**, p 483–495
7. M. Iijima, H. Ohno, I. Kawashima, K. Endo, and I. Mizoguchi, Mechanical Behavior at Different Temperatures and Stresses for Superelastic Nickel-Titanium Orthodontic Wires Having Different Transformation Temperatures, *Dent. Mater.*, 2002, **18**, p 88–93
8. A.R. Pelton, J. DiCello, and S. Miyazaki, Optimisation of Processing and Properties of Medical Grade Nitinol Wire, *Min. Invas. Ther. Allied. Technol.*, 2000, **9**(1), p 107–118
9. L. Bataillard, J.-E. Bidaux, and R. Gotthardt, Interaction Between Microstructure and Multiple-Step Transformation in Binary NiTi Alloys Using In Situ Transmission Electron Microscopy Observations, *Phil. Mag. A*, 1998, **78**(2), p 327–344
10. J.I. Kim, Y. Liu, and S. Miyazaki, Ageing-Induced Two-Stage R-Phase Transformation in Ti-50.9 at.% Ni, *Acta. Mater.*, 2004, **52**, p 487–499
11. M. Peltonen, T. Lindroos, and M. Kallio, Effect of Ageing on Transformation Kinetics and Internal Friction of Ni-rich Ni-Ti Alloys, *J. Alloys Comp.*, 2007, **460**(1–2), p 237–245
12. J. Michutta, Ch. Somsen, A. Yawny, A. Dlouhy, and G. Eggeler, Elementary Martensitic Transformation Processes in Ni-Rich NiTi Single Crystals with Ni_4Ti_3 Precipitates, *Acta. Mater.*, 2006, **54**, p 3525–3542
13. L.J. Chiang, C.H. Li, Y.F. Hsu, and W.H. Wang, Age-Induced Four-Stage Transformation in Ni-Rich NiTi Shape Memory Alloys, *J. Alloys Comp.*, 2008, **458**, p 231–237
14. Z.G. Wang, X.T. Zu, X.D. Feng, H.Q. Mo, and J.M. Zhou, Calorimetric Study of Multiple-Step Transformation in TiNi Shape Memory Alloy with Partial Transformation Cycle, *Mater. Lett.*, 2004, **58**, p 3141–3144
15. Y. Zheng, F. Jiang, L. Li, H. Yang, and Y. Liu, Effect of Ageing Treatment on the Transformation Behaviour of Ti-509 at% Ni alloy, *Acta. Mater.*, 2008, **58**, p 736–745
16. P. Filip and K. Mazanec, On Precipitation Kinetics in TiNi Shape Memory Alloys, *Scri. Metall.*, 2001, **45**, p 701–707
17. Y. Zhou, J. Zhang, G. Fan, X. Ding, J. Sun, X. Ren, and K. Otsuka, Origin of 2-Stage R-Phase Transformation in Low-Temperature Aged Ni-rich Ti-Ni Alloys, *Acta. Mater.*, 2005, **53**, p 5365–5377
18. G. Fan, W. Chen, S. Yang, J. Zhu, X. Ren, and K. Otsuka, Origin of Abnormal Multi-Stage Martensitic Transformation Behavior in Aged Ni-Rich Ti-Ni Shape Memory Alloys, *Acta. Mater.*, 2004, **52**, p 4351–4362
19. G. Fan, Y. Zhou, W. Chen, S. Yang, X. Ren, and K. Otsuka, Precipitation Kinetics of Ti_3Ni_4 in Polycrystalline Ni-Rich TiNi Alloys and Its Relation to Abnormal Multi-Stage Transformation Behavior, *Mater. Sci. Eng. A*, 2006, **438-440**, p 622–626
20. O. Bojda, G. Eggeler, and A. Dlouhy, Precipitation of Ni_4Ti_3-Variants in a polycrystalline Ni-Rich NiTi shape memory alloy, *Scri. Mater.*, 2005, **53**, p 99–104
21. J.K. Allafi, G. Eggeler, W.W. Schmahl, and D. Sheptyakov, Quantitative Phase Analysis in Microstructures Which Display Multiple Step Martensitic Transformations in Ni-Rich NiTi Shape Memory Alloys, *Mater. Sci. Eng. A*, 2006, **438-440**, p 593–596
22. K. Otsuka and X. Ren, Physical metallurgy of Ti-Ni-Based Shape Memory Alloys, *Prog. Mater. Sci.*, 2005, **50**, p 511–678
23. M. Nili-Ahmadabadi, T. Shahhoseini, M. Haj-Fathalian, M.H. Parsa, H. Ghadirian, T. Hoseinzadeh-Nik, Cyclic Load-Deflection Characteristics of NiTi Orthodontic Archwires at Different Temperatures, *Proceedings of the 8th Asia-Pacific Conference on Materials Processing*, Guilin-Guanzhan, 2008
24. H. Ghadirian, "The Evaluation of Superealasticity of Nickel-Titanium Orthodontic Archwires in the Simulated Oral Environment," Ph.D. Thesis, Tehran University of Medical Sciences, 2008
25. F. Parvizi and W.P. Rock, The Load/Deflection Characteristics of Thermally Activated Orthodontic Archwires, *Eur. J. Orthod.*, 2003, **25**, p 417–421
26. W. Tang, Thermodynamic Study of the Low-Temperature Phase B19′ and the Martensitic Transformation in Near-Equiatomic Ti-Ni Shape Memory Alloys, *Metall. Trans. A*, 1997, **28**, p 537–544