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Effect of Heat Treatment Temperature and Heat Treatment Time on Properties and use of NiTi Shape Memory Implant Material

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Abstract: In this study, effect of heat treatment parameters, which is applied in order to achieve superelasticity and shape memory, on the nitinol microstructure was investigated. Nitinol is a commonly used material in cardiovascular and orthopedic implant production. Nitinol material used in this study has 50.59% Ni, 0.12% C, 0.0005% Cr, 0.003% Cu, 0.001% Co, 0.012% Fe, 0.1% O, <0.26% H andbalanceTi chemical composition (in at.%).Nitinol wires were heat treated at 540 °C, 550 °C, 560 °C and 570 °C for 10 minutes. Then, heat treatment was applied at 550 °C for 8, 9, 10, 11, 12, 13 and 14 minutes. Heat treated nitinol wires were characterized by optical microscope, Energy-dispersive X-ray Spectroscopy (EDS) and mechanical tests.Results show that Ni_4Ti_3 phase was formed as a result of heat treatment. Heat treatment time and temperature affected amount, distribution and shapes of NiTi and Ni_4Ti_3 phases. Among heat treatment conditions, suitable microstructures were obtained at 540 °C and 550 °C heat treatment temperature and heat treatment times not exceeding 10 minutes. This finding was verified with mechanical tests.

Keywords: Heat Treatment, Nitinol, Shape Memory Alloy, Super elasticity, Medical Device, Ni_4Ti_3.

I. INTRODUCTION

Major materials used in medical implant production are metals, ceramics, composites and polymers. Since there is continual progress in the medical area, performance features expected from implant materials are increasing and there are medical operations that traditional materials are inadequate [1].

One of the examples of this situation is an implant named occluder. Occluder is a device that is used to clog a defect in the walls of the heart. Occluder must fit into a delivery system with a very small diameter for its delivery to the heart. When occluder is delivered to target destination, it must recover to its original shape upon getting out of the delivery system. This procedure is not possible with traditional materials. Shape memory alloys must be used in these types of operations [2].

Superelasticity was first discovered in Au-Cd alloy in 1932. Although there were many studies on Au-Cd and Cu-Zn alloys, these alloys were not used in commercial applications. Shape memory effect in Ni-Ti alloy was discovered in 1963. After technical problems of this alloy were solved, nitinol has got a wide application area [3].

Nitinol is the most commonly used shape memory alloy nowadays. Some important features of the nitinol make it an ideal material for using in medical implant production. These features are; suitable transition temperatures for use in human body, good biocompatibility, high elastic strain ratio and high corrosion resistance. Stress-temperature relationship for shape memory effect and superelasticity behaviour is seen in Fig. 1. In nitinol, if critical stress for slip is high enough (Critical Stress for Slip: A), material exhibits shape memory effect below austenite start (A_s) temperature, superelasticity occurs above $A_s$temperature but full recovery of superelasticity shape change occurs above austenite finish (A_f) temperature. In nitinol, critical stress for slip is improved by precipitation hardening [4].

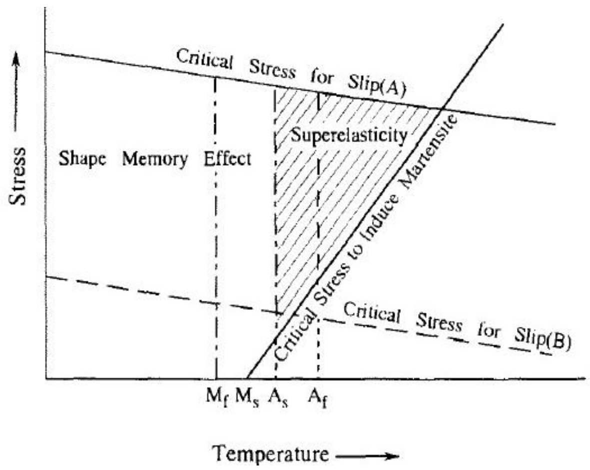

Fig. 1. Schematic representation of stress and temperature ranges for shape memory effect and superelasticity behaviour and critical stress for slip (A: high critical stress, B: low Critical Stress) [4]

Chemical composition of nitinol, heat treatment time and heat treatment temperature affect type, quantity and shape of precipitates. Aging heat treatments is an effective

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method to improve mechanical, superelastic and shape memory properties of Ni-rich nitinol alloys those were greater than 50.5 at. %nickel. Main reason of these improvements is the formation of coherent Ni_4Ti_3 precipitates because ofaging heat treatment. These precipitates cause coherency stress fields in the microstructure [5].

Precipitation sequence for Ti-52Ni (at.%) was revealed as $Ti_{11}Ni_{14}$-Ti_2Ni_3-$TiNi_3$ by Nishida et. al in 1986. TTT diagram of Ti-52Ni is seen in Fig. 2 [6]. $Ti_{11}Ni_{14}$ was correctly determined as Ni_4Ti_3 by further EDS analysis later [7].

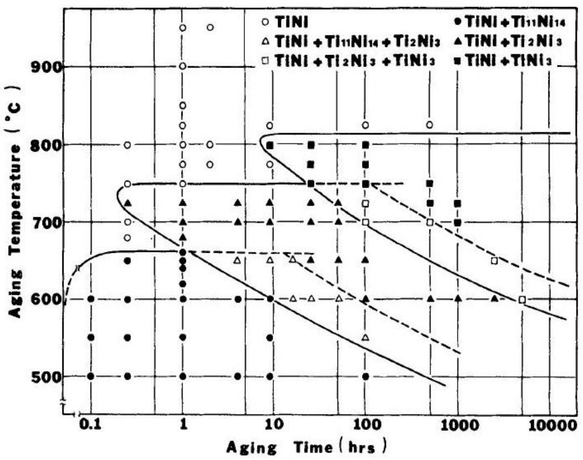

Fig. 2. TTT diagram describing aging behaviour for Ti-52Ni [6]

Heat treatment conditions affect precipitate type, precipitate volume fraction, precipitate distribution and interparticle distance between precipitates. These criteria about precipitates affect many properties including superelasticity behaviour, shape memory effect, transition temperatures, strain ratio and martensitic transformation [5,6,8 and 9].

II. EXPERIMENTAL

In this study, effect of heat treatment parameters (time and temperature), which was applied in order to achieve superelasticity and shape memory, on microstructure of Ti-50.6Ni (at.%) was investigated. Chemical composition of Ti-50.6Ni wires used in experimental studies is given in Table 1. Diameter of nitinol wires used was 120 µm and A_f (austenite finish) temperature was 15 °C.

TABLE I CHEMICAL COMPOSITION OF TI-50.6NI WIRE SAMPLE

Element	Chemical Composition (at.%)
Ni	50.59
Ti	Bal.
O	0.10
C	0.12
Fe	0.012
Cu	0.003
Co	0.001
Cr	0.0005
H	< 0.26

Heat treatment was applied to nitinol wires in Nabertherm N 30/65 HA heat treatment furnace. Nitinol wires were heat treated at 540 °C, 550 °C, 560 °C and 570 °C for 10 minutes. Then, heat treatment was applied at 550 °C for 8, 9, 10, 11, 12, 13 and 14 minutes.

Heat treated samples were cold mounted in resin. 1000 and 2500 grits were applied and 1 micron diamond paste was used in the polishing stage of the samples. Then, samples were etched for 1 minute using HF 4% and HNO_3 15.5% by volume. Optical microscope micrographs were taken with Leica ICC50 HD. EDS analyses were carried out by using Tracor attachment which was integrated to JEOL JMS 5410 SEM.

III. RESULTS AND DISCUSSION

Fig. 3 shows optical microscope micrograph of Ti-50.6Ni wires which were supplied from the manufacturer. Because of the standard wire production procedure, which includes cold drawing and subsequent annealing, its structure was composed of recrystallised grains [10].

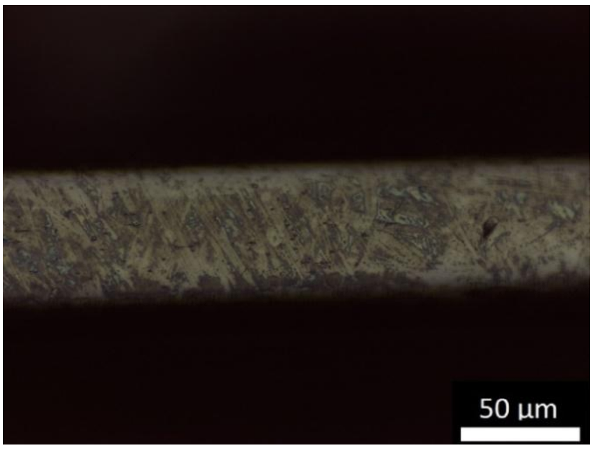

Fig. 3. Optical microscope micrograph of Ti-50.6Ni wire supplied from the manufacturer

Fig.4 shows optical microscope micrographs of nitinol wires heat treated for 10 minutes; (A) 540 °C, (B) 550 °C, (C) 560 °C and (D) 570 °C.

As it can be seen in Fig.4 (A), Ni_4Ti_3 precipitates were dominant in the structure after heat treatment applied at 540 °C. In addition, precipitates were spread uniformly in the structure. When compared to heat treatments applied at 550 °C, 560 °C and 570 °C, precipitate ratio was higher in heat treatment applied at 540 °C. It is well known that the Ni_4Ti_3 precipitation rate achieves a maximum at 400-450 °C and precipitates temporarily re-dissolve in B2 matrix at heat treatment temperatures above 500 °C [11]. Decrease of precipitate ratio above 540 °C is an expected result.

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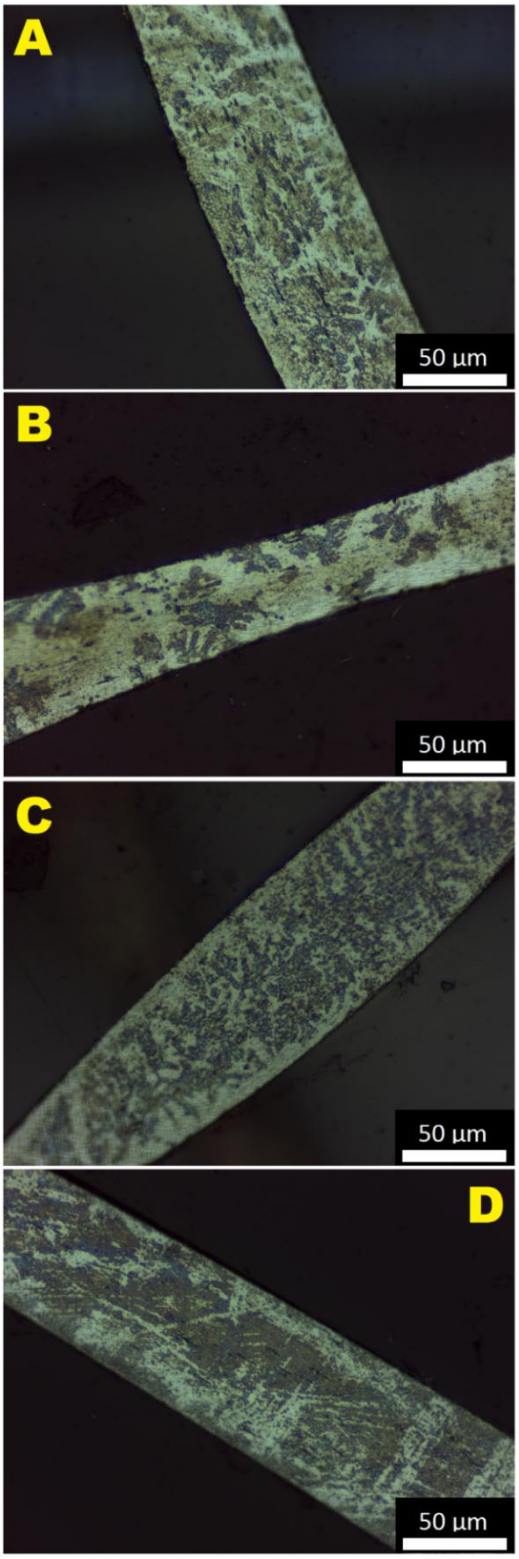

Fig. 4.Optical microscope micrographs of Ti-50.6Ni wires heat treated for 10 minutes; (A) 540 °C, (B) 550 °C, (C) 560 °C, (D) 570 °C

Fig. 4(B) shows that increasing of temperature to 550 °C resulted in smaller precipitate size and lower precipitate ratio. Columnar grains were appeared at 560 °C for 10 minutes. In addition, precipitates became smaller when compared to heat treatment at 550 °C [Fig. 4(C)]. In the sample heat treated at the highest heat treatment temperature (570 °C), form and distribution of Ni_4Ti_3 and NiTi phases in the microstructure were different from all of the samples subjected to heat treatment in scope of this study [Fig. 4(D)]. Size of Ni_4Ti_3 and NiTi phases became bigger. It was seen that volume fractions of Ni_4Ti_3 and NiTi phases were variable in different parts of the sample.

In these four heat treatment conditions, precipitates were determined as Ni_4Ti_3 by EDS analyses. In EDS analyses, it was seen that chemical composition of the precipitates were close to Ni_4Ti_3. Previous studies also indicated that precipitates which were formed in these heat treatment conditions were Ni_4Ti_3[6, 12]. Fig.5 shows EDS analysis of precipitates in the sample heat treated at 540 °C for 10 minutes.

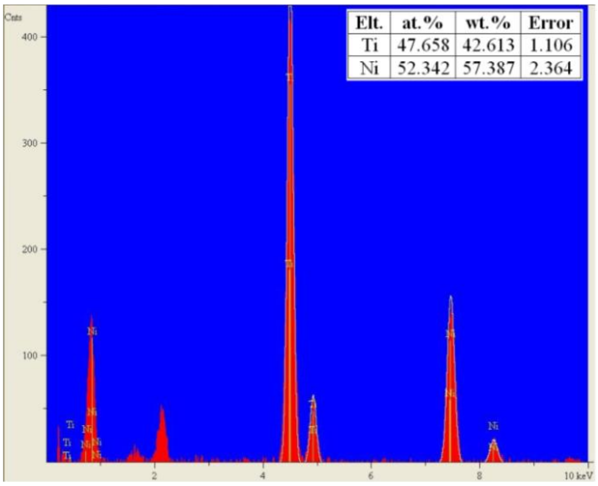

Fig. 5. EDS analysis of precipitates in the sample heat treated at 540 °C for 10 minutes

Fig. 6 shows optical microscope micrographs of heat treated Ti-50.6Ni wires at 550 °C; (A) 8 minutes, (B) 9 minutes, (C) 10 minutes, (D) 11 minutes, (E) 12 minutes, (F) 13 minutes and (G) 14 minutes.
Fig.6(A) illustrates that, Ni_4Ti_3 precipitates in the sample, which was subjected to heat treatment for 8 minutes, were small and in a large number. These precipitates were spread homogenously throughout the microstructure. As it can be seen from Fig.6(B), precipitates were still dominating the microstructure after heat treatment applied for 9 minutes. In addition, precipitates became bigger and number of precipitates were decreased.

When heat treatment time was increased to 10 minutes, precipitates became smaller and ratio of precipitates were decreased [Fig.6(C)]. Interparticle distance between precipitates increased when it wascompared to 8 and 9 minutes. It is known that interparticle distance between precipitates increases with increasing heat treatment time [5]. As it can be seen from Fig.6(D), heat treatment at 550 °C for 11 minutes caused precipitates to become partially smaller but microstructure was similar to the microstructure obtained at heat treatment applied for 10 minutes.

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Fig.6(E) shows that increasing heat treatment time to 12 minutes caused precipitates to become spherical similar to heat treatment applied for 8 minutes. In comparison, size of Ni_4Ti_3 precipitates obtained at 12 minutes heat treatment time were bigger than the precipitates obtained at 8 minutes.

Fig.6(F) illustrates that precipitate ratio was decreased significantly after heat treatment applied for 13 minutes. When compared to heat treatment applied for 12 minutes, precipitate size was smaller. In addition to these precipitates, there were also smaller precipitates around a few micrometers, which were spread throughout the material microstructure.

As it can be seen from Fig.6(G), these precipitates remained in the structure after heat treatment applied for 14 minutes. Relatively bigger precipitates were partially dissolved in the matrix and the number of smaller precipitates was increased when heat treatment time was increased from 13 to 14 minutes. It was detected that these smaller precipitates(not exceeding a few micrometers in size) had an effect of embrittlement on material because they were very finely dispersed.

In heat treatments applied at 550 °C between 8 and 14 minutes, precipitates were determined as Ni_4Ti_3 by EDS analyses. Chemical composition of the precipitates was close to Ni_4Ti_3 as in heat treatments applied between 540 °C and 570 °C. Previous studies also indicated that precipitates formed in these heat treatment conditions were Ni_4Ti_3 [6, 12].

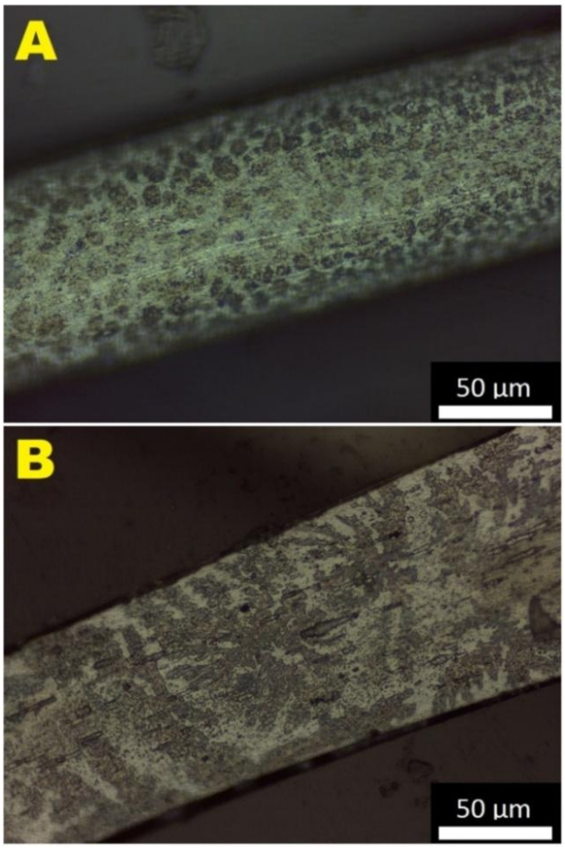

Fig. 6. Optical microscope micrographs of Ti-50.6Ni wires heat treated at 550 °C; (A) 8 minutes and (B) 9 minutes

Fig.7 shows EDS analysis of precipitates in the sample heat treated at 550 °C for 14 minutes.

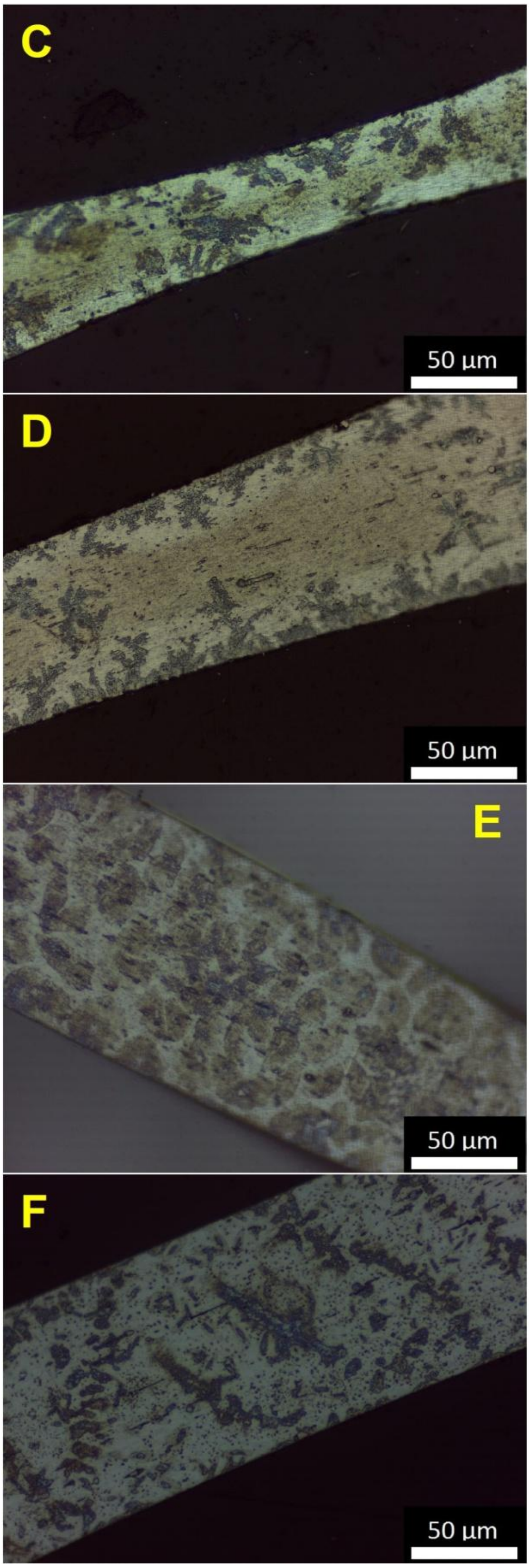

Fig. 6. (Continuum) Optical microscope micrographs of Ti-50.6Ni wires heat treated at 550 °C; (C) 10 minutes, (D) 11 minutes, (E) 12 minutes and (F) 13 minutes

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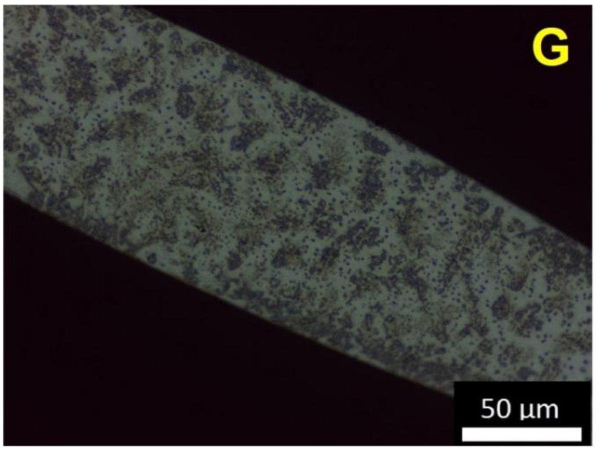

Fig. 6. (Continuum 2) Optical microscope micrographs of Ti-50.6Ni wires heat treated at 550 °C; (G) 14 minutes

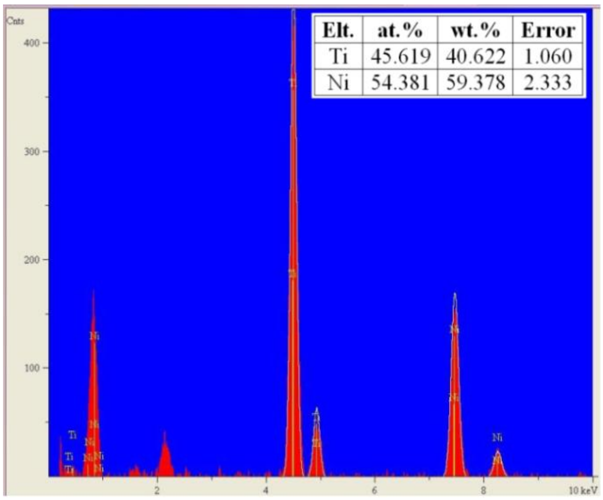

Fig. 7. EDS analysis of precipitates in the sample heat treated at 550 °C for 14 minutes

In scope of this study, mechanical tests were carried out for the use of nitinol in the medical field. These tests were fatigue test and retraction force test. In fatigue test, fatigue life of heat treated anterior cruciate ligament (ACL) prostheses were measured by a fatigue test machine which simulates motion of a knee. ACL prosthesis was produced by braiding of nitinol wires. In retraction force test, the force needed to pull the heat treated occluder inside the delivery system with a very small diameter was measured by a forcemeter. In this test, occluder becomes deformed when entering into the delivery channel. Retraction force test provides information about flexibility and mobility of occluder inside the delivery system. In this test, the upper limit that the force value should not exceed is 15 Newtons. Implants with higher retraction force isn't flexible enough and their movement in the delivery system is difficult.

Some critical mechanical test values of samples heat treated at constant time / different temperatures and constant temperature / different times are given in Table 2. As it can be seen from the table, at the heat treatments with constant time and different temperatures, retraction force increased with increasing heat treatment temperature, whereas fatigue life decreased. In the same table, it is also seen that at the heat treatments with constant temperature and different times, retraction force increased with increasing heat treatment time, whereas fatigue life decreased.

TABLE II MECHANICAL TEST RESULTS OF TI-50.6NI SAMPLES HEAT TREATED AT DIFFERENT TEMPERATURES AND TIMES

	540 °C / 10 min.	**550 °C / 10 min.**
Fatigue Life	23,209,000	21,448,000
Retraction Force	9.4 N	11.8 N
	560 °C / 10 min.	**570 °C / 10 min.**
Fatigue Life	16,103,000	11,907,000
Retraction Force	17.8 N	23.2 N
	550 °C / 8 min.	**550 °C / 10 min.**
Fatigue Life	24,102,000	21,448,000
Retraction Force	9.1 N	11.8 N
	550 °C / 12 min.	**550 °C / 14 min.**
Fatigue Life	19,098,000	13,605,000
Retraction Force	15.1 N	21.8 N

IV. CONCLUSION

This study shows that heat treatments applied at various temperatures and various times has an important effect on shape setting and mechanical properties of nitinol, which is a commonly used material in cardiovascular and orthopedic implant production.

Experiments proved that, in heat treatments with constant heat treatment time, increasing of heat treatment temperature caused change in shape and size of Ni_4Ti_3 precipitates. Experiments also proved that in heat treatments with constant heat treatment temperature, increasing of heat treatment time caused mechanism of shape change, dissolve in the structure and reappearing of Ni_4Ti_3 precipitates with fine grain size.

Only shape setting and mechanical specification in production of anterior cruciate ligament (ACL) prosthesis and occluder is the retraction force. Upper limit for retraction force is 15 Newtons (manufacturer information). Between the samples subjected to heat treatment at different heat treatment temperatures and heat treatment times, samples that satisfy the retraction force upper limit were obtained at heat treatment temperature of 540 °C and 550 °C and heat treatment times not exceeding 10 minutes. Coarse grained precipitates were dispersed in the microstructure of the samples, which were subjected to heat treatment under optimum conditions. It was seen that, these precipitates dominated the microstructure more homogenously with increasing heat treatment time and temperature. There were very finely dispersed Ni_4Ti_3 precipitates (micrometer scale) in the microstructure of the samples, which were heat treated other than optimum heat treatment conditions (higher heat treatment temperature and longer heat treatment time). These very fine precipitates caused embrittlement of the material and retraction force increased over 15 Newtons, so material became unusable. Decrease of the fatigue life with increasing heat treatment time and heat treatment temperature also verifies that detection.

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