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Experimental Investigation on Effect of Different Heat Treatments on Phase Transformation and Superelasticity of NiTi Alloy

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***Abstract*—**NiTi alloys possess magnificent superelastic, shape memory, high strength and biocompatible properties. For improving mechanical properties, foremost, superelasticity behavior, heat treatment process is carried out. In this paper, two different heat treatment methods were undertaken: (1) solid solution, and (2) aging. The effect of each treatment in a constant time is investigated. Five samples were prepared to study the structure and optimize mechanical properties under different time and temperature. For measuring the upper plateau stress, lower plateau stress and residual strain, tensile test is carried out. The samples were aged at two different temperatures to see difference between aging temperatures. The sample aged at 500 °C has a bigger crystallite size and lower amount of Ni which causes the mentioned sample to possess poor pseudo elasticity behaviour than the other aged sample. The sample aged at 460 °C has shown remarkable superelastic properties. The mentioned sample's higher plateau is 580 MPa with the lowest residual strain (0.17%) while other samples have possessed higher residual strains. X-ray diffraction was used to investigate the produced phases.

***Keywords*—**Heat treatment, phase transformation, superelasticity, NiTi alloy.

I. Introduction

TECHNOLOGY and new era's necessities, pulls humans to use new materials and systems. Shape memory alloys are one of those mentioned systems to assign a big importance in the world of technology [1]. The "pseudo elasticity" behavior of shape memory alloys (SMAs), which is well known as "super elasticity", is the reversible reaction of these materials against the applied stress [2], [3]. Super elastic materials, recover their initial shape with or without a thermal process, which is named as shape memory effect (SME) [4]-[6]. The mentioned effect is related to the reversible transformation between two crystalline phases named austenite and detwinned martensite [7], [8] and it has been a real concern in different experiences [9], [10].

NiTi SMAs has attracted a lot of attention lately because of all its special applications in human body implants and joints, stents, sensors, elevators [11]-[13]. Also, the structure of NiTi alloys helps the body cells and tissues to grow [14]. Heat treatment of these alloys affects the mechanical properties by producing precipitations such as Ti_3Ni_4, $Ni_{14}Ti_{11}$, etc. [15]-[17]. These small sized and distributed precipitations in the main phase of NiTi make barriers against slipping of dislocations and achieving to super elastic properties. Also the mentioned precipitation could modify the phase deformation temperature which is an important factor on the mechanical properties [18]-[20]. Liu and McCromics [21] showed that NiTi samples were fractured at a strain of 8%. Also, ultimate tensile strength of the samples is 300 MPa. Sadrnezhad et al. study, on SME of Nitinol, has increased the Ms temperature which could be effective on fatigue life [22]-[24].

Due to biocompatibility, excellent mechanical properties such as high ultimate tensile strength and a long fatigue life, unique shape memory, effect and twinning mechanism [25], there is a wide range of NiTi and other SMA applications. So there is a necessity to enhance its mechanical properties, to grow them better than before, which could be obtained via heat-treatment techniques [26], [27]. Also, Paryab et al. showed that temperatures of selected treatment could even affect properties such as pseudo elasticity [35]. Using other cycles such as two step cycles or just annealing cycles may cause a shorter fatigue life or fraction of sample in tensile testing in a low strain amount [28]. As an example of thermal treatments to nitinol wires, shape setting operations also could be mentioned. Normally, shape setting operations occurs in a specific shape of the sample, for a specific temperature [29]. This paper reports an optimized heat treatment to improve the mechanical properties, such as martensitic transformation temperature which is directly in contact with super elasticity behavior [30]. Also, the effects of heat treatment on mechanical properties and shape memory behavior are investigated by scanning electron microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray Diffraction (XRD), tensile test and differential scanning calorimetry (DSC).

II. Experimental

The chemical composition of NiTi SMA was determined by EDS with an EDAX Element Silicon drift 2017 machine. Also, microstructure of the samples was studied by SEM, FEI Quanta 200 ESEM machine. Phase studies were conducted by XRD, PW1730 device. The crystallite size and lattice parameter were calculated via Williamson-Hall equations [31]. Quantity of the phases and lattice parameter were obtained by High Score software. Also, lattice parameter was calculated by

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Bragg's law through the following equations [32]:

$$b\cos\Theta = (0.9\,\lambda)/d + 2\eta\sin\Theta \text{ (Williamson-hall equation)}$$

$$n\lambda = 2d\sin\Theta \text{ (Bragg's law)}$$

$$a = d\sqrt{(h^2+k^2+l^2)}$$

In Williamson-hall equation, b is the width of a peak at its half intensity obtained from the Expert software, Θ is the angle of the peak at the pattern, **λ** is the wavelength of X-ray, η is the lattice strain and a is the lattice parameter [33]. Tensile test was carried at room temperature. In the first step, samples were elongated and when reached to 6% strain, after one second, the stress was removed and they returned to their initial state. In tensile test which was carried out by ETM-200/300KN High Speed universal tester, hysteresis diagrams were obtained. Also re-crystallization and transformation temperatures were analyzed by DSC under nitrogen atmosphere. NiTi alloy used in this process was a commercial alloy with nominal composition of 49%Ti-51%Ni. Effects of heat-treatment cycles and their parameters such as time and temperature of aging and annealing and cooling rate on the microstructure and mechanical properties were investigated. It is also necessary to remind that high amount of titanium could result a high risk of oxidation of NiTi samples at high temperatures [34]. To avoid this destructive issue, a controlled atmosphere furnace with a 200 ml/min argon flow was used. NiTi Specimen was purchased from G&H Orthodontics, Earlywood, Franklin, USA as an arch wire. The diameter of the specimen was 0.5 millimeter. For carrying out the tensile test, they were cut into samples with a length of 10 centimeters. The specifications of each cycle are presented in Table I.

TABLE I
PERFORMED HEAT TREATMENT (TIME AND TEMPERATURE)

cycle	Annealing Time (min)	Annealing temperature (◦C)	Aging Time (min)	Aging temperature (◦C)
1	60	850	-	-
2	60	850	30	500
3	-	-	60	500
4	-	-	17	460

In the cycle.1 the sample was just annealed to determine the effects of anneal treatment on the mechanical properties and also microstructure of sample. It is also necessary to say that the applied temperature of annealing is used for cycle.2 samples. In the cycle.2, after quenching of the sample in the water, aging treatment was performed. Among the multi-step cycles, cycle 2 was the optimum cycle which was selected after testing different temperatures. The cycle.3 is just a one-step cycle which has a bigger hysteresis diagram with better pseudo elasticity effect and SME. Cycle.4 is the optimum cycle. It has the biggest hysteresis diagram with the minimum amount of residual strain. After the tensile test, the samples were electro-polished to have a clear surface and then electro-etched to reveal their microstructure under optical microscope. Chemical etch solutions may solve the cold mount material, thus, electro-polishing is the best way to achieve a clear surface of the samples. Intended electro-polish solution contains 5% perchloric acid, 25% glycerin in the main phase of ethanol for 30 seconds and voltage of 20 volts with current of 0.7 A of electricity.

III. RESULTS AND DISCUSSION

A. Characterization

Figs. 1 and 2 indicate the SEM results of the materials in which (a) and (b) are related to the raw sample, (c) and (d) for sample aged at 460 ℃. Figs. 2 (a) and (b) are for sample aged at 500 ℃, (c) and (d) for samples solution treated at 850 ℃ and aged at 500 ℃, (e) and (f) for solution treated at 850 ℃. In these figures some oxide inclusions as well as porosity could be seen in the microstructure. In Figs. 1 (c), (d) and 2 (a) and (b) the precipitations are detected which can cause an incomparable super elasticity behaviour. As it can be seen in the mentioned figures, precipitations get larger by increasing the aging temperature. In Figs. 2 (a) and (b) precipitations are bigger than Figs. 1 (c) and (d), which is related to the time and temperature of aging treatments. Also, bigger size of precipitations could have a negative effect on mechanical properties. Samples aged at high temperatures, may have high amount of residual strain, which may cause a short fatigue life.

The precipitations consist of two kinds: Ni rich and Ti rich. Here, the formed precipitation is Ni_4Ti_3. Precipitations of aged samples which could be seen in SEM images are the reason of low residual strain and remarkable tensile stress. Oxide inclusions are detected in all images but at images related to annealed samples there are more oxide inclusions which may cause fraction even at low amount of loads. In Figs. 2 (c)-(f), grains have become so small. Small grains of NiTi samples affect the mechanical properties of the samples by decreasing tensile stress and increasing residual strain.

B. Phase Analysis and Chemical Compositions

EDS is carried out to measure the amount of the elements in each sample. Moreover, the composition of the samples is calculated via the atomic amount of the elements. These measurements are shown in Table II. Main phase in NiTi samples is austenite. However, by applying heat treatment cycles, the other unwanted phases, such as Ni_3Ti, could be removed. These phases cause a decrease in A_f (Austenite finish temperature). To utilize shape memory behavior of the alloy, A_f temperature has to be under 25 °C. So, if the mentioned phases are not removed, instead of detwinning mechanism, transfiguration of the samples will be affected from slip of boundaries and residual strain will not be returnable, therefore, the samples will not be able to return to their first state. It can be figured out by applying solution treatment that amount of "Ti" precipitations increases. The EDX spectra are indicated in Fig. 3. It can be concluded that the sample "aged at 460 °C" has the same amount of Ni and Ti.

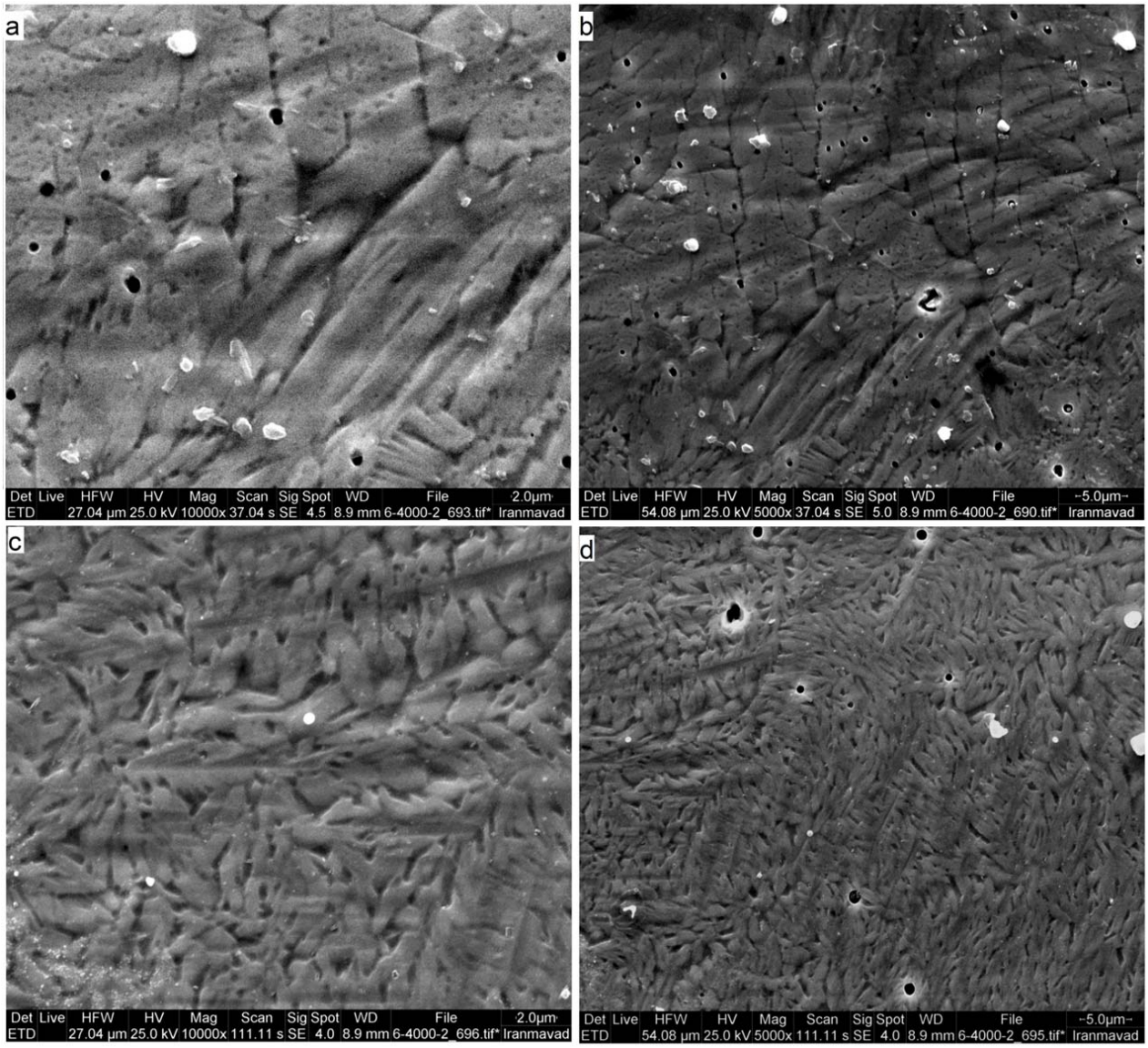


Fig. 1 SEM images of the etched samples in two magnifications: 5000X and 10000X (a) and (b) for raw sample, (c) and (d) for sample aged at 460 ℃

TABLE II
COMPOSITION, AND ATOMIC AND WEIGHT PERCENTAGES OF THE SAMPLES ACCORDING TO THE EDX SPECTRA

Sample	Atomic% of Ni	Atomic% of Ti	Weight% of Ni	Weight% of Ti	Element% of Ni in Map	Element% of Ti in Map	Composition
Raw	48.91	51.09	59.99	46.01	41	59	$Ni_{0.49}Ti_{0.51}$
Aged at 460	49.32	50.68	54.39	45.61	41	59	$Ni_{0.49}Ti_{0.51}$
Aged at 500	48.17	51.83	53.26	46.74	42	58	$Ni_{0.48}Ti_{0.52}$
Solution treated at 850 ℃	5.61	94.39	6.79	93.21	42	58	$Ni_{0.05}Ti_{0.95}$
Solution treated at 850 ℃ and aged at 500 ℃	65.19	34.81	69.65	30.35	41	59	$Ni_{0.65}Ti_{0.35}$

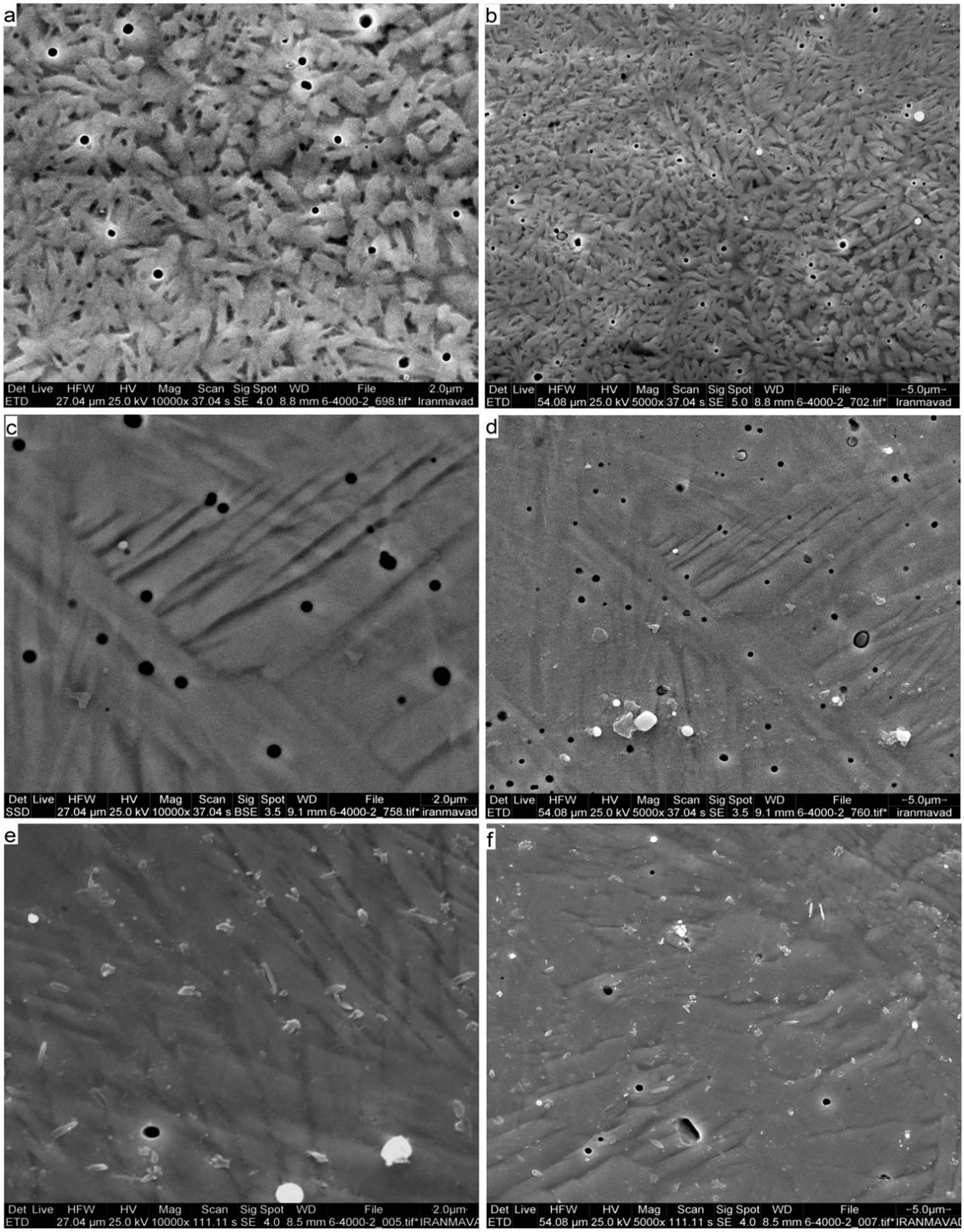
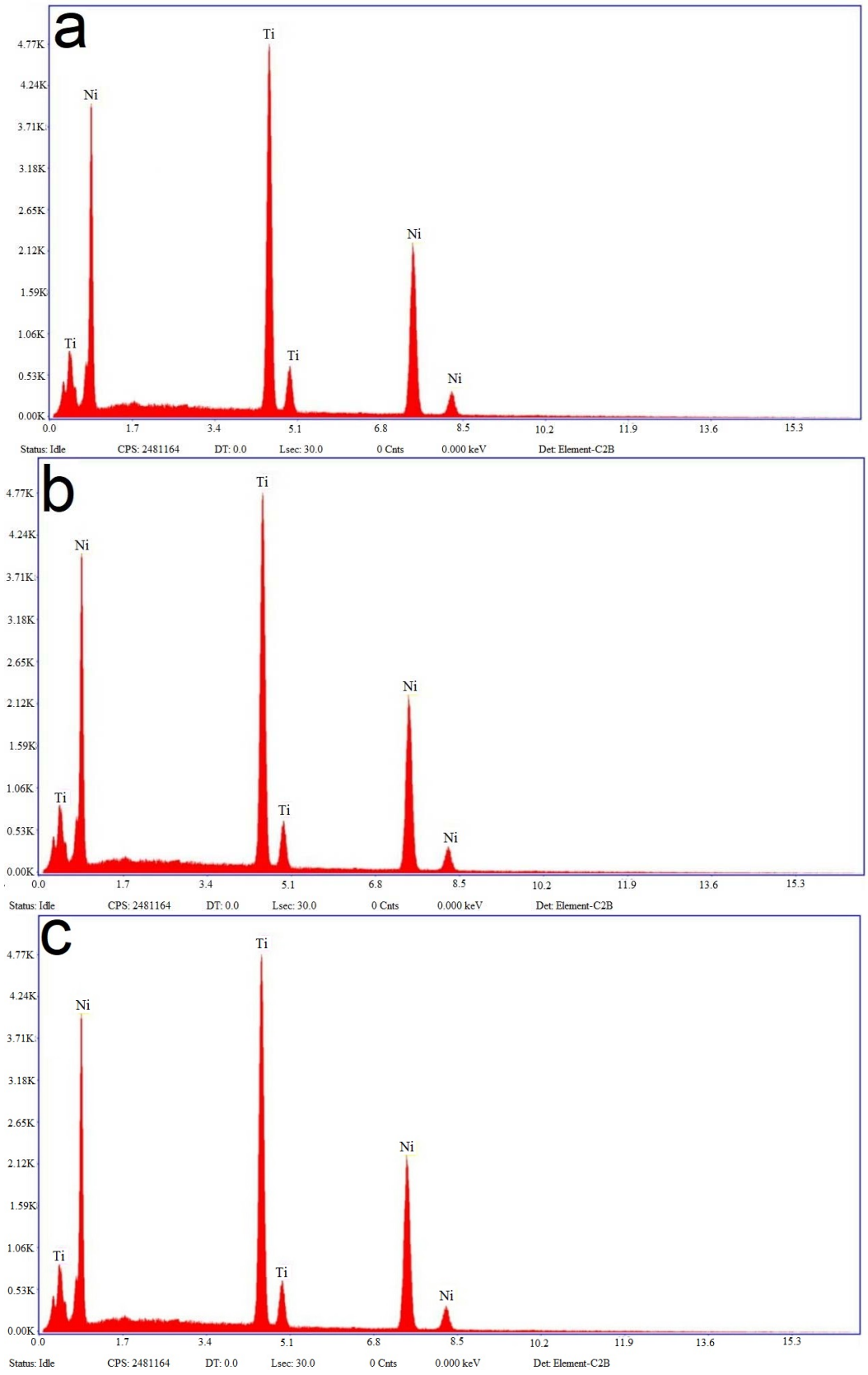


Fig. 2 FESEM images in two magnification of (a) and (b) sample aged at 500 ℃, (c) and (d) sample solution treated at 850 ℃, and (e) and (f) sample solution treated at 850 ℃ then aged at 500 ℃


a
b
c
Ti
Ni
4.77K
4.24K
3.71K
3.18K
2.65K
2.12K
1.59K
1.06K
0.53K
0.00K
0.0
1.7
3.4
5.1
6.8
8.5
10.2
11.9
13.6
15.3
Status: Idle
CPS: 2481164
DT: 0.0
Lsec: 30.0
0 Cnts
0.000 keV
Det: Element-C2B

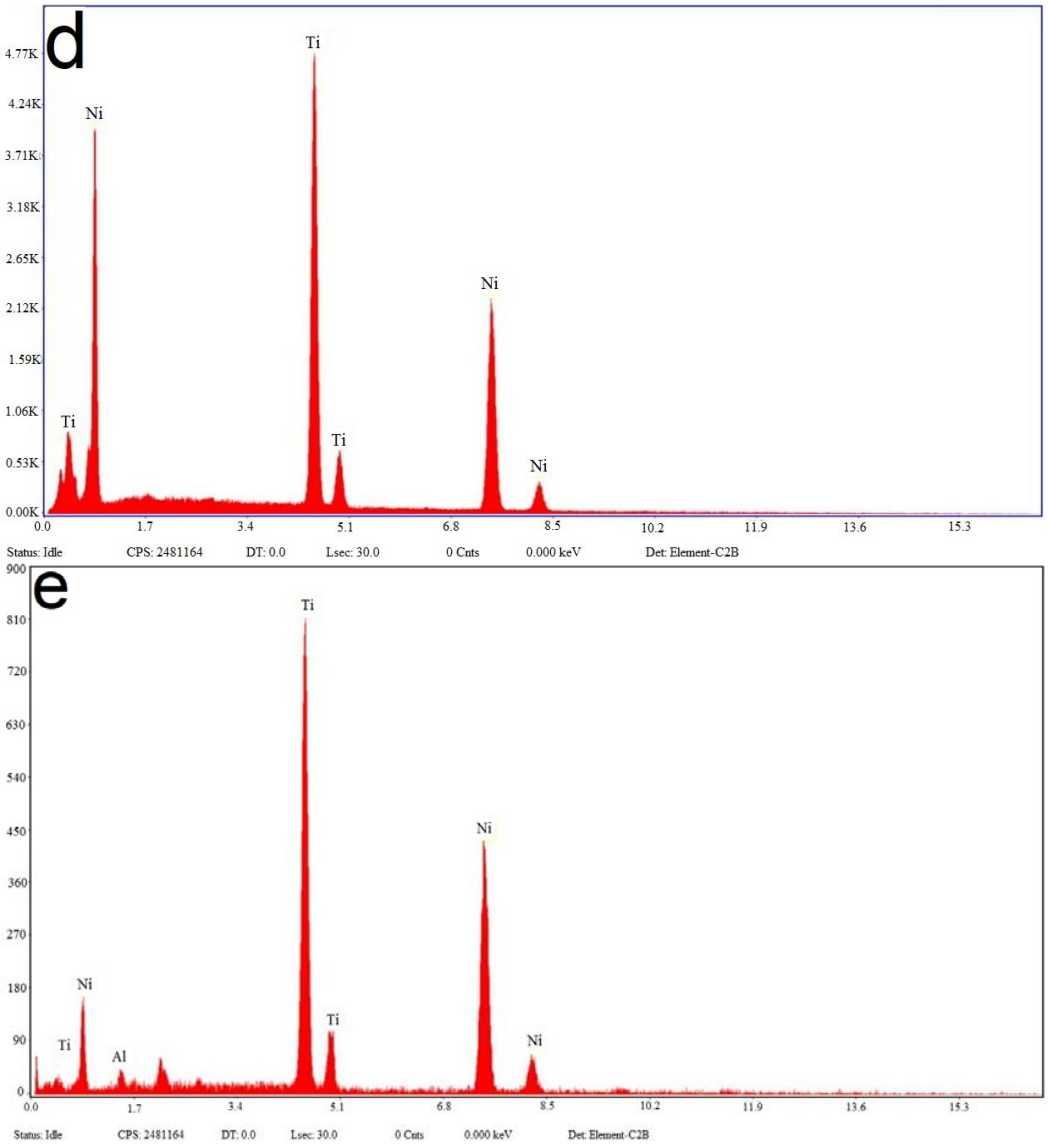


Fig. 3 EDX spectra of the samples: (a) raw, (b) aged at 460 ℃, (c) aged at 500 ℃, (d) solution treated at 850 ℃ and (e) solution treated at 850℃ then aged at 500 ℃

Fig. 4 illustrates the XRD analysis of the samples. Figs. 3 (a)-(e) refer to raw, aged at 460 °C, aged at 500°C, annealed at 850 °C and annealed at 850 then aged at 500 °C samples, respectively. Formed phases are analyzed using High Score software. The raw material (Fig. 3 (a)), as it was expected, consists of NiTi single phase. The peaks correspond with the reference code 03-065-7711. Figs. 3 (b) and (c) are the same as the raw material. It means that aging at 460 and 500 °C does not change the single phase. The sample that was solution treated at 850 °C (Fig. 3 (d)) consists of three phases: Ni, NiTi, and TiO_2. But in the sample that was solution treated at 850 °C and then aged at 500 °C (Fig. 3 (e)), beside mentioned phases, Ni_3Ti precipitation has been formed. The reference codes for these phases are 98-009-0603, 03-065-5537 and 01-076-0318, respectively [21].

Crystallite sizes of the samples are calculated via Williamson-Hall equation. These calculations are illustrated in Table III. It can be recognized that the minimum crystallite size is according to the sample aged at 460 °C.

TABLE III
CRYSTALLITE SIZE OF THE SAMPLES

Sample	Crystallite size (nm)
Raw	26.7
Aged at 460°c	18.573
Aged at 500°c	69.609
Solution treated at 850 ℃	40.527
Solution treated at 850 ℃ and aged at 500 ℃	73.384

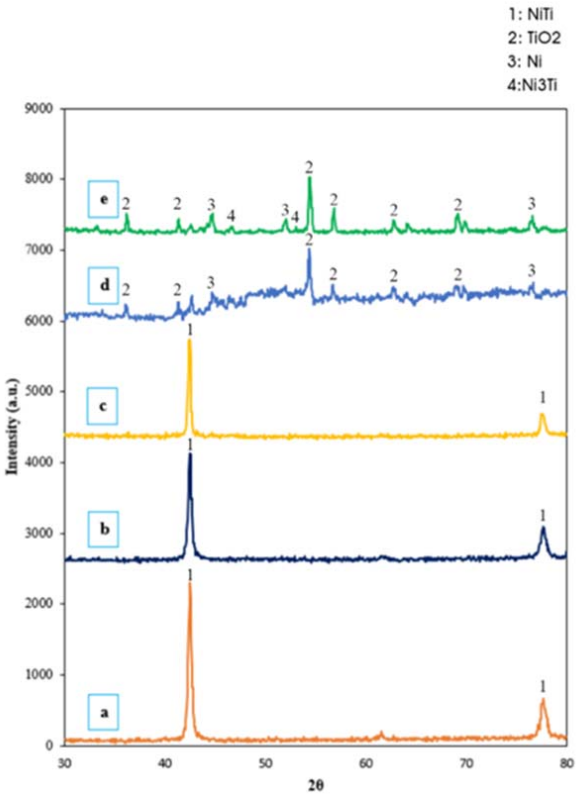


Fig. 4 XRD patterns of the samples: (a) raw, (b) aged at 460 ℃, (c) aged at 500 ℃, (d) solution treated at 850 ℃ and (e) solution treated at 850 ℃ then aged at 500 ℃

C. Thermal Analysis

Fig. 5 shows the DSC measurements of the samples. The number of developed peaks for all of the samples is the same. However, there is a little temperature difference. Three endothermic peaks can be seen in every sample which means there are three transformations. The transformation of martensite to austenite occurs due to heating the NiTi alloys. Ni_4Ti_3 precipitations preparation is between the austenite and martensitic transformation which develops another peak in the DSC curves. So, there should be three peaks. The third peak can be corresponding to the non-homogeneous precipitation of the Ni_4Ti_3 near the grain boundaries [36].

D. Mechanical Properties

Fig. 6 shows the stress-strain diagram of the samples. In this figure the ultimate strain is constant (6.5%). It can be determined from this figure that the sample aged at 460 °C has the highest upper plateau stress (580 MPa), the maximum curve area and the least residual strain (0.17%). So, the best heat treatment process for obtaining both the higher upper plateau stress and lower residual strain is aging at 460 °C (the optimum sample). The minimum of the lower plateau is for the raw sample. This sample has the least upper plateau. However, it has an acceptable residual strain (0.17%) in comparison with the sample solution treated at 850 °C. The highest plateau stress is due to the formation of the dislocations. These dislocations act as an obstacle to the austenite martensite interface which is the cause of the highest upper plateau stress [1].

TABLE IV
M_S AND A_S TEMPERATURES OF THE SAMPLES

Sample	M_s	A_s
Raw	-137.28°C	2.7°C
Aged at 460°c	-138.56°C	31.43°C
Aged at 500°c	-137.17°C	17.82°C
Solution treated at 850 ℃	-137.82°C	-6.82°C
Solution treated at 850 ℃ and aged at 500 ℃	-138.56°C	29.43°C

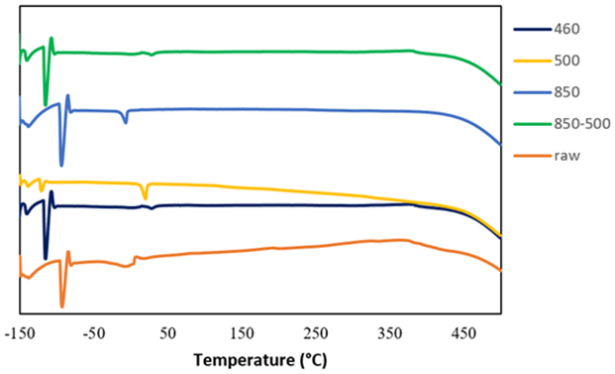


Fig. 5 DSC curves of the samples: raw, aged at 460 ℃, aged at 500 ℃, solution treated at 850 ℃ and solution treated at 850 ℃ then aged at 500 ℃ in the temperature range of -150 to 500 ℃

The sample which is just solution treated has the maximum amount of residual strain (3%). So it is clear that, annealing the samples would cause a decrease in mechanical properties of Nitinol. It may result in increasing residual strain and accordingly, a short fatigue life. The achieved data from stress-strain curves (Fig. 6) are given in Table V. The M_s temperature of the samples are close to each other but, the A_s temperature differs widely for each sample. These temperatures are reported in Table IV. It can be seen that the austenite temperature of the sample aged at 460 °C has the highest value of all. As much as M_s temperature grows bigger, yield stress increases. In other words, as much as M_s grows bigger, martensitic transformation occurs at high temperatures. Therefore, yield stress of samples will increase. Higher difference between M_s and A_s improves super-elasticity.

Martensitic transformation takes place via shear phenomena. If this transformation takes place with an external stress simultaneously, the superelasticity occurs. There are two kinds of martensitic transformation: thermal and athermal. If the temperature of the tensile test is around martensitic transformation, the thermal transformation helps its counterpart to improve the superelasticity [29].

According to Fig. 6, it can be seen that grade of each tension graph is different from other samples. This happens when Yang's modulus changes and it fluctuates when chemical composition is changed. After heat treatment of samples, new compounds such as Ni_3Ti, Ni_4Ti_3 form. The highest value of Yang's modulus is related to the aged sample at 460 ℃. Higher Yang's modulus helps mechanical properties

grow better. As it is known, Yang's modulus is directly connected with tensile stress. In other words, by increasing Yang's modulus, tensile stress of the samples would increase. Also, with a decreasing Yang's modulus at high temperatures, operations which cause an increase in Yang's modulus provide high temperature applications.

TABLE V
UPPER PLATEAU, LOWER PLATEAU AND RESIDUAL STRESS OF THE SAMPLES

Sample	Upper plateau (MPa)	Lower plateau (MPa)	Residual stress
Raw	100	22.5	0.61
Aged at 460°c	580	55	0.17
Aged at 500°c	388	32	0.7
Solution treated at 850 ℃	222	34	3
Solution treated at 850 ℃ and aged at 500 ℃	208	72	0.44

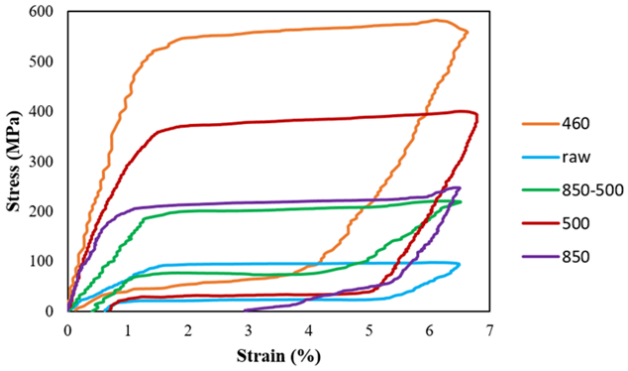


Fig. 6 Stress-strain curves of the samples: raw, aged at 460 ℃, aged at 500 ℃, solution treated at 850 ℃ and solution treated at 850 ℃ then aged at 460 ℃ in the constant strain of 6.5%

As it was mentioned, in addition to the phases which were formed in the solution treated sample at 850 ℃, Ni_3Ti precipitation was formed at the sample which was solution treated at 850 ℃ and aged at 500 ℃. According to Fig. 6, it could be seen that residual strain in solution treated sample is 3% while, in solution treated sample and aged sample, amount of residual strain is 0.3%. It is related to the formed precipitation which improves SME. However, it has not affected tensile strength.

IV. CONCLUSION

NiTi alloys have superelastic behavior that differs in various heat treatments. It is illustrated that the grain size of the samples gets larger when the aging temperature gets higher. For this alloy, solution treatment is not a helpful issue. The cause of the high super elasticity is the precipitation of the Ni_4Ti_3. Some porosity and oxidation can be seen due to SEM and XRD results, respectively. According to DSC curves, three transformations occur while heating the samples from -150 to 500 °C (Martensite, Austenite and Ni_4Ti_3 precipitation). Furthermore, the optimum aging temperature is 460 °C which is concluded from tensile test. The sample aged at 460 ℃ has the highest upper plateau (580 MPa) and the lowest residual strain (0.17%).

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