Erciyes University Journal of the Institute of Science and Technology
Erciyes Üniversitesi Fen Bilimleri Enstitüsü Dergisi
ISSN 1012-2354
Cilt (Volume): 31 , Sayı (Issue): 3,Kasım/November-2015
http://fbe.erciyes.edu.tr/

Isıl işlemin NiTi şekil hatırlamalı alaşımın (şha) mikroyapısı, dönüşüm sıcaklığı ve termal çevrimi üzerine etkisi

***Fethi DAGDELEN[1], Soner BUYTOZ[2], Mediha KOK[2], Ercan ERCAN[3]**
[1]Fırat Üniversitesi, Fen Fakültesi, Fizik Bölümü
[2]Fırat Üniversitesi, Teknoloji Fakültesi, Metalurji ve Malzeme Mühendisliği
[3]Bitlis Eren Üniversitesi, Fen Edebiyat Fakültesi, Fizik Bölümü

Anahtar Kelimeler: NiTi, Şekil hatlrlamalı alaşım, termal çevrim, ısıl işlem

ÖZET

Hava atmosferinde 400-700 ˚C aralığında ısıl işlem uygulanan, atomik konsantrasyonu Ni-45.16%Ti şekil hatırlamalı alaşımın termal stabilitesi (çevrim) ve aktivasyon enerjisi incelenmiştir. Thermal çevrim, düşük dönüşüm sıcaklığına meyilli ve R faz göstermemektedir. Ana numune ve ısıl işleme maruz bırakılmış numunelerin thermal stabilitesinin deneysel işlemlerle düştüğünü göstermiştir. Bu alaşımların aktivasyon enerjisi Diferansiyel taramalı kalorimetre (DSC) ile belirlenmiştir. Dönüşüm sıcaklıklarının (Ms, Mf, As ve Af) Kissinger ve Ozawa yöntemiyle ölçülen termal aktivasyon enerjilerinin, ısıl işlem ile arttığı görülmüştür. Bununla birlikte Vickers sertlik değerlerinin ise ısıl işlemle azaldığı görülmüştür.

Heat treatment effects on thermal cycle, transition temperature and microstructure of NiTi SMA

Key Words: NiTi, shape memory alloy, thermal cycle, heat treatment.

ABSTRACT

The thermal stability (cycle) and activation energies of NiTi shape memory alloy (SMA), in Ni-45.16%Ti atomic concentration exposed to heat treatment in air in the temperature range 400-800 ^{0}C, was investigated. The thermal cycles tend to low transformation temperature, and couldn't display R phase. Experimental results indicate that thermal stability of as-cast and heat treated samples were decreased. The thermal activation energies of these alloys were determined by Differential Scanning Calorimeter (DSC). It was seen that both transformation temperature of samples (M_s, M_f, A_s and A_f) and the thermal activation energies calculated by Ozowa and Kissinger *methods increased with the heat treatment.* However, it was determined that Vickers hardness values of these shape memory alloys were decreased with the heat treatment.

*Sorumlu Yazar (Corresponding author) e-posta: fdagdelen@firat.edu.tr

1. Introduction

Nickel-titanium shape memory alloys (NiTi SMAs) are widely use today in different fields of industry because of superior shape memory effect and its mechanical memory properties such as pseudo elasticity, thermal memory (one way effect) and corrosion resistance [1, 2]. The application of shape memory effect and superelasticity of NiTi SMA for engineering fields is considerably dependent on both the martensitic transformation from austenite to martensite on cooling (through the martensite start and finish temperatures, M_s and M_f) and the reverse transformation on heating (through the austenite start and finish temperatures, A_s and A_f). It is well known that Ni or Ti concent in NiTi SMA affects to the phase transition temperatures. It shows that increase of Ni content in NiTi shape memory alloys induce a decrease in M_s [3]. Thus, properties of shape memory alloys are strongly dependent on alloy composition. Also, the studies have been shown that transition properties of SMAs are strongly depend on heat treatment effects [4], cooling conditions [5], pressure effects [6], radiation effects [7], as well as alloys composition. The most desirable memory properties for NiTi SMAs are obtained with 49.5–57 at. % Ni because of the high-temperature shape memory effect [8].

In the present work, we investigated the effects of heat treatment temperatures (HTTs) on transformation behavior, thermal stability, microstructure, thermal activation energies and enthalpy change of treated alloys. According to the variation of HTTs, the microstructure and micro hardness values of NiTi SMA were also investigated.

2. Experimental

Ni-45.16%Ti (at %) was supported by Nimesis tecnology. Samples were cut into small pieces from NiTi alloy ingot and samples were subjected to heat treatment at 400˚C, 500˚C, 600˚C, 700˚C and 800˚C for 2 hours in an air atmosphere and quenched in ice brine. A slight polishing was made to remove the native oxide layer on the surface which occur heat treatment process. Then the experiments were carried out. Firstly, Differential Scanning Calorimetry (DSC) (Perkin Elmer Sapphire) was used for determining the number of cycle as an indicator of stability under zero pressure, the martensite-austenite transformation temperatures, thermodynamic parameters and activation energy of alloys. In order to investigate microstructures and micro hardness changes with heat treatment, optical microscope and vickers hardness measurements were done. After polishing of as-cast and treated alloys, they were etched in 40 ml HF, 60 ml HNO_3, 100 ml H_2O. The etched alloys were examined by using Nikon Eclipse MA200 optical microscope. Micro hardness measurements of alloys were done via Emco test Durascan testing machine. Surface characterization of specimens was performed using SEM (JEOL JSM 7001F) equipped with an energy dispersive X-ray spectroscope (EDX).

1. Results and Discussion

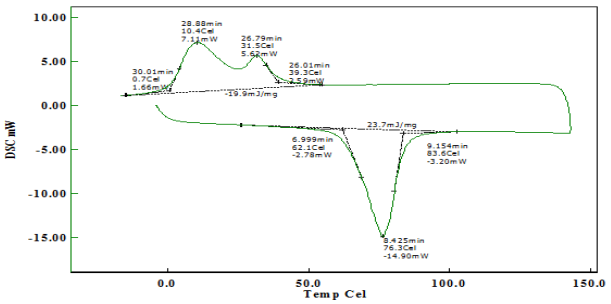
*Thermal Analysis*In order to investigate the effect of heat treatment temperatures (HTTs) on NiTi alloys, samples subjected to heat treatment at 400˚C, 500˚C, 600˚C, 700˚C and 800˚C for 2 hours in an air atmosphere. After treatment, DSC measurements were done. Heat flow curves of as-cast and heat treated samples at 800˚C was given in Fig. 1, and changes of transformation temperature of as-cast and heat treated samples were summarized in Table 1.

According to these results, the transformation temperatures increased with the rise of HTTs, and R (Rombohedral) phase, which is a formation prior to martensite, was disappeared when the samples heat treated at 600 ˚C, 700˚C and 800˚C. This result is in accordance with literature [9, 10]. The absorbed heat during heating and cooling is defined as enthalpy change *(ΔH)*. As a result of acustic emussion, enthalpy change of alloys shows little displacement during cooling. Consequently, calculating average enthalpy change (ΔH_{ave}) is made as $(\Delta H_{heat}+\Delta H_{cool})/2$. Benefiting from average enthalpy change, entropy change calculated as follow:

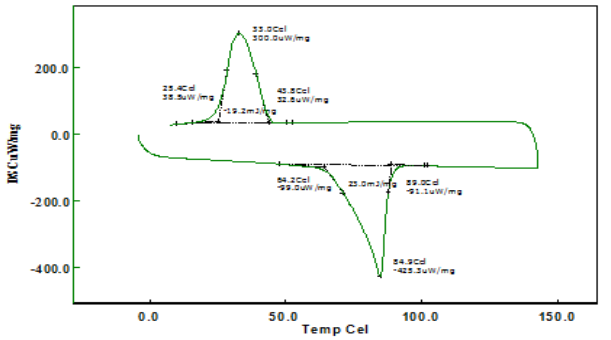
$$\Delta S=\Delta H_{ave}/T_o \qquad (1)$$

where T_o is equilibrium temperature $(A_s+M_s)/2$.

As seen in Table 1, variation of enthalpy change with HTTs shows linear trend with maximum ΔH_{ave} value at 600˚C which is in accordance with literature [11, 12]. After 600˚C HTT, ΔH_{ave} values decreased until 800˚C HHT.



(a)



(b)

Fig. 1. Schematic illustration of DSC result for a) as-cast and b) heat treated at 800 ºC sample.

The thermal activation energies of samples were carried out by DSC with different heating rates as 10, 15, 20, 25 ˚C /min (Fig. 2). The purpose of calculating the activation energy is to determine level of energy required by the sample as the martensite transformation takes place, which indicates how stable a structure is displayed by alloy. The Johnson–Mehl–Avrami (JMA) equation for solid state transformation can be used to determine activation energy of shape memory alloys when phase tranformations occur. The JMA equation can be applied non-isothermal case. Two methods, namely Ozawa and Kissinger are proposed for anlyzing non-isothermal activation energy of samples [13].

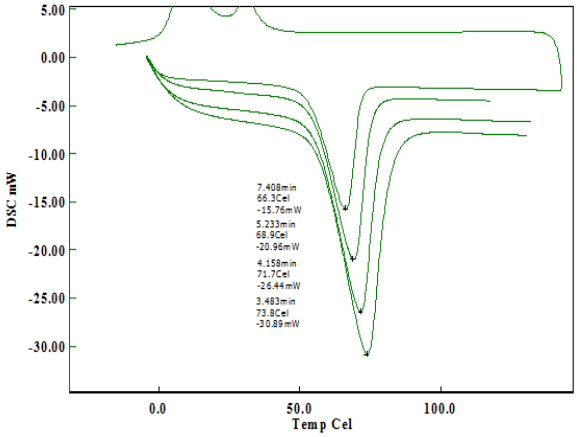


Fig.2. DSC curves of different heating rate for as-cast sample.

According to JMA the fraction X of the SMAs after a time t given by:

$$X=1-\exp[-(Kt)^n] \quad (1)$$

where n is the Avrami exponent and K is the effective reaction rate usually assigned Arrhenius temperature dependence:

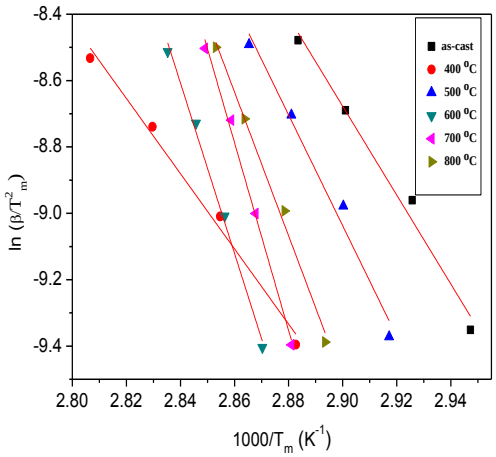
$$K=K_o exp(-E/RT) \quad (2)$$

Kissinger and Ozawa Methods is a solution of Arrhenius equation. Activation energy can be calculated by following equations according to Kissinger and Ozawa Methods, respectively.

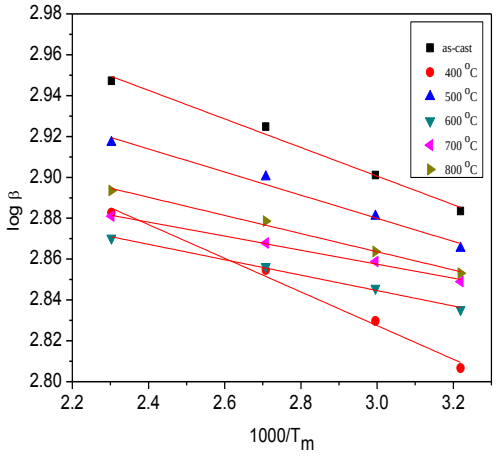
$$\ln(\beta/T)^2=A-E/RT \quad (3)$$

$$\log\beta = B - E/RT \quad (4)$$

where β is the heating rate, T is the maximum peak on the DSC curve, E is the thermal activation energy, R is the universal gas constant and A and B are integration constants. Using the T, the graphs of $ln\beta/T^2$ versus $1/T$ and log β versus $1/T$ respect to Kissinger and Ozawa method were plotted (Fig. 3). The activation energies for samples were calculated by two methods, the results were given in Table 2. It was determined that the thermal activation energies increased with the rising of heat treatment temperatures in both methods.



(a)



(b)

Fig. 3. a) Kissinger's plot and b) Ozawa's plot based on the DSC results obtained by using different heating rate.

Tab. 1. The thermal activation energies of Ni-45.16%Ti alloy before and after heat treated according to Kissinger and Ozawa methods.

Samples	E_{Ozowa} (kJ/mol)	$E_{Kissinger}$ (kJ/mol)	E_{ave} (kJ/mol)
as-cast	111.298	111.366	111.332
400	95.170	94.264	4.717
500	137.420	138.794	138.107
600	208.587	213.570	211.079
700	229.170	235.244	232.207
800	176.770	180.148	178.459

The thermal cycles are a good method to determine the thermal stability of a shape memory alloy, due to thermoelastic martensitic transformation is very sensitive to thermal cycle [11].

Also, the thermal cycling regulates martensitic transformation. At the first cycle, irreversible dislocation defects strengthen the matrix of alloys, then, reversible martensitic transformation tends to stable at the continuous cycles [14]. The thermal cycle's measurements were carried out using DSC. The changes of martensite-austenite transformation temperatures for as-cast and treated NiTi alloys at 400˚C, 500˚C, 600˚C, 700˚C and 800˚C were determined for two hours in an air atmosphere at the 10˚C/min. heating/cooling rate. After the first reverse martensitic transformation, martensitic stabilization disappears and transformation temperature is depressed by the permanent dislocations on following thermal cycles [15]. The minimum cycle numbers when alloys reached to thermal stability at the earliest were determined. The minimum cycle numbers for thermal stability were determined four times for as-cast, four times for 400 ºC, five times for 500˚C, five times for 600˚C, six times for 700˚C and nine times for 800˚C heat treatment temperatures (HTTs).

At the same time, it was seen that characteristic temperatures (Austenite, martensite start-A_s, M_s, Austenite martensite final temperature-A_f, M_f; Austenite martenstite peak temperature-A_p, M_p) of as-cast and treated alloys were decreased up to the minimum cycle number for thermal stability.This result is in accordance with the literature [11]. These observations indicated that transformation temperatures and thermal stability of NiTi alloys affected by thermal cycle. The result of the minimum thermal cycles for heat treated sample at 800˚C was given in Fig. 4. Also, when the effects of HTTs on thermal cycle number were investigated, the results showed that the minimum cycle numbers were decreased with the increasing of HTTs.

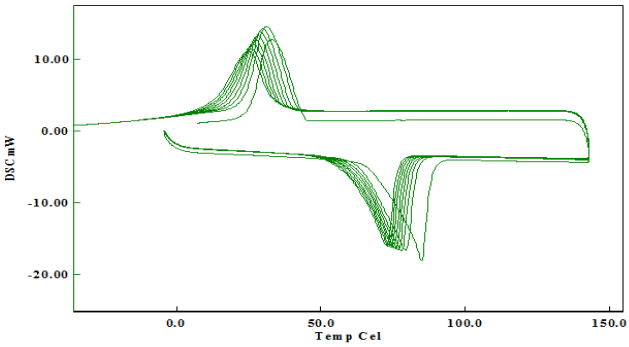


Fig. 4. The thermal cycles of DSC curves of heat treated sample at 800 C.

Tab. 1. Transformation temperature, some thermodynamic parameters and hardness results of Ni-45.16%Ti alloy before and after heat treatment.

samples	As (^{0}C)	Af (^{0}C)	Ap (^{0}C)	Ms (^{0}C)	Mf (^{0}C)	Mp (^{0}C)	Rp (^{0}C)	ΔH_A (J/g)	ΔH_M (J/g)	T_o	ΔH_{ave} (J/g)	ΔS (J/g^{o}C)	HV_1
as-cast	62.1	83.6	76.3	39.3	0.7	10.4	31.5	23.7	-19.9	50.70	21.80	0.43	262
400	58.8	74.9	70.2	37.8	14.8	22.2	32.7	24.4	-21.4	48.30	22.90	0.47	251
500	58.5	75.4	70.9	36.1	15.1	22.6	31.2	24.6	-21.1	47.30	22.85	0.52	219
600	64.5	84.5	81.0	40.7	25.2	30.4	-	26.4	-23.0	52.60	24.70	0.47	232
700	64.9	87.5	83.7	43.0	26.0	32.8	-	25.6	-22.0	53.95	23.80	0.44	223
800	64.2	89.0	84.9	43.8	25.4	33.0	-	23.8	-19.2	55.50	21.60	0.39	232

Microstructure Analysis

Figure 5 shows the optical microscopy microstructure of as-cast and treated NiTi shape memory alloys. Participates belongs to second phase were found in all figure. The size of participates grown with the rising HTTs. The former phase exhibits a heterogeneous microstructure because of transformation characteristics in terms of shape memory alloys. However, the grain could be seen at 700 and 800 ºC in microstructure during the heat treatment of NiTi shape memory alloys.

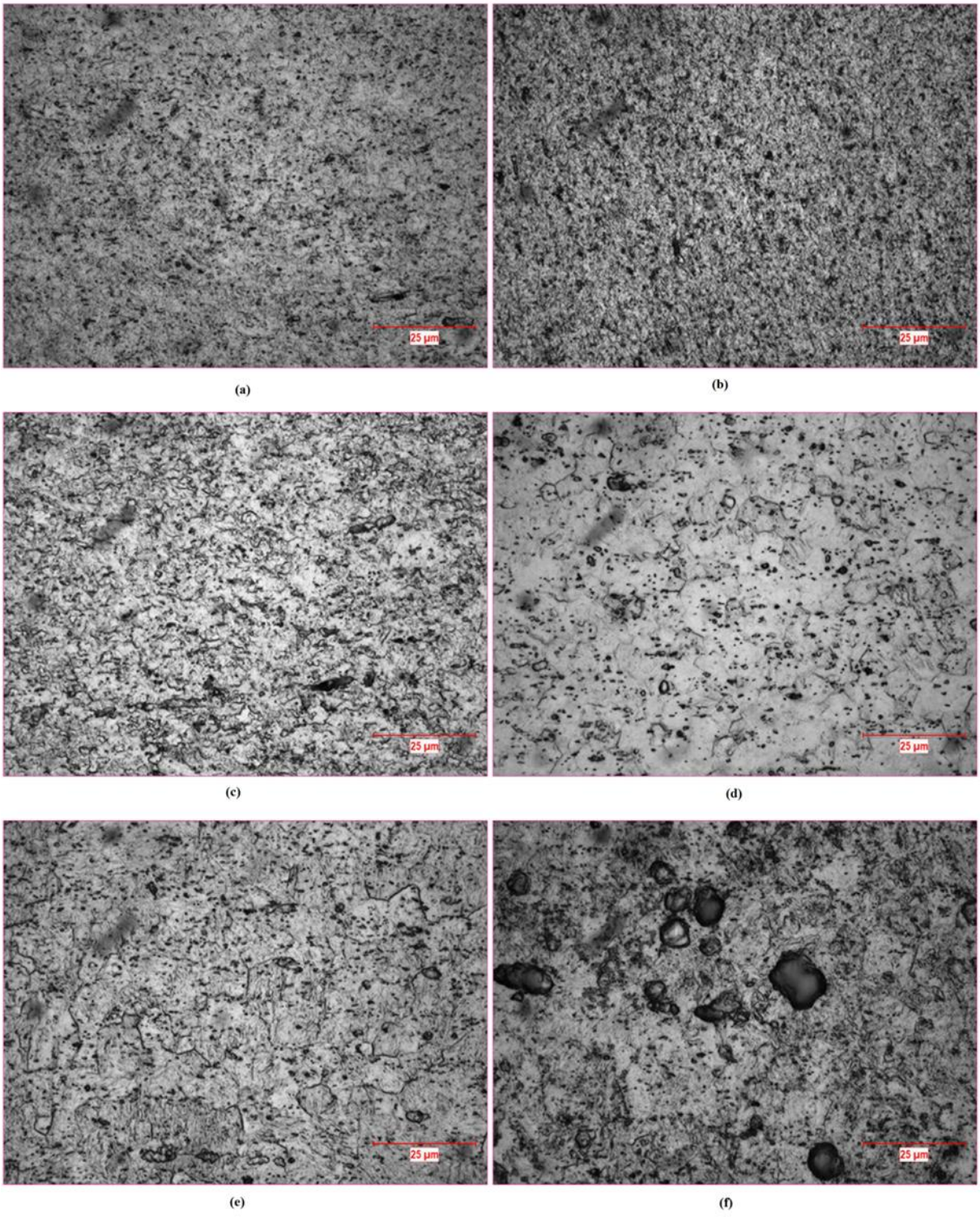
According to EDX measurement, increase of heat treating temperature increased the atomic percentage of Ti element. Table 1 shows micro hardness change of NiTi alloys with HTTs. Untreated and treated NiTi alloys where compared with each other, untreated alloys had maximum micro hardness value. Vickers hardness testing generally used to control strengthening of shape memory alloys on their

But this decrease was not regular. There were fluction among the microhardness value.

The most important conlusion is that, the micro hardness values of heat treated NiTi alloys was smaller than as-cast NiTi alloy which is in accordance with Brailovski and coworkers' study.

They observed that decreasing hardness value with the increasing heat treatment temperatures is resulted from dislocation [11]. At 500 ^{o}C HTT, the vickers hardness values reached minimum. This result can be explained as recrystallization and dissolution of participates [15].

HTTs and the martensitic plate occurred in grains, as indicated in Fig.6. These figures clearly show the changes termomechanical history [11]. When NiTi alloy subjected to heat treatment, micro hardness values decreased.



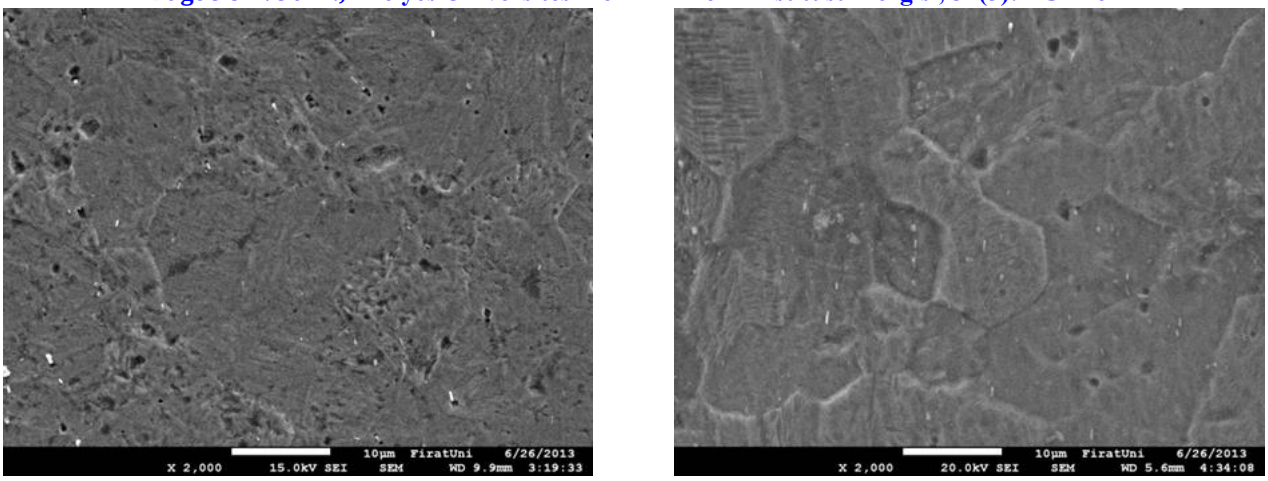


Fig. 5. Optical micrographs of NiTi SMAs; a) as-cast b) heat treated at 400 ˚C, c) 500 ˚C, d) 600 ˚C, e)700 ˚C, f)800 ˚C.

(a) (b)

Element	Weight(%)	Atomic (%)
Ti	42.66	47.69
Ni	57.34	52.31

(c)

Fig. 6. SEM micrographs of NiTi SMAs; a) heat treated at 700 ˚C, b) heat treated at 800 ˚C, c) EDS analysis of heat treated at 800 ˚C.

Conclusions

The effects of heat treatment on the properties of NiTi SMA can be outlined as follow:

According to DSC results, transformaiton temperatures increased by rising HTTs and R phase disappeared at 600, 700, 800 ˚C heat treated temperatures. Variation of enthalpy change with HTTs demostrated linear trend up to 600 ˚C.

There was increment in thermal cycle numbers, which is indicator of thermal stability of NiTi shape memory alloy.

It is seen that second phase particle (R phase) in all optical micrsocopy images were observed. The particle grown up by the increase of HTTs. Untreated alloys had maximum microhardness value within the untreated and treated NiTi alloys.

Kaynaklar

1. Kabiri, Y., Kermanpur, A., Foroozmehr, A., Vacuum, 86, 1073, 2012.
2. Frenzel, J., Zhang, Z., Neuking, K., Eggeler, G., J.Alloy. Compd. 385,214, 2004.
3. Frenzel, J., George, E.P., Dlouhy, A., Somsen, Ch., Wagner, M.F.-X., Eggeler, G., Acta Mater. 58, 3444, 2010.
4. Nayan Govind, N., Saikrishna C.N., Venkata, Ramaiah, K., Bhaumik, S.K., Suseelan, Nair, K., Mittal, M.C., Mater. Sci. Eng., 44, 465-515, 2007.
5. Chang, S.H., Wu, S.K., Mater. Charact. 59, 987, 2008.
6. Dagdelen, F., Gokhan, T., Aydogdu, A., Aydogdu, Y., Adigüzel, O., Mater. Lett. 57, 1079, 2003.
7. Zengin, R., Yakuphanoglu, F., Mater. Lett. 57, 3107, 2003.
8. Zengin, R., Thermochim. Acta, 61, 503–504, 2010.
9. Choi, J.Y., Nemat-Nasser, S., Mater. Sci. Eng. 432, 100, 2006.
10. Sadrnezhaad, S.K., Selahi, A.R., Mater. Manuf. Process., 1, 475, 2004.
11. Paula A.S., Mahesh, K.K., Dos Santos, C.M.L., Braz Fernandes, F. M., and Da Costa Viana, C.S., Mater. Sci. Eng. 146, 481-482, 2008.
12. Brailovski, V. P., Terriault, S., Prokoshkin, J., Mater. Eng. Perform. 11, 614, 2002.
13. Lafi, O.A., Imran, M.M.A., Abdullah, M.K., Al-Sakhel, S.A., Thermochim. Acta., 71, 560, 2013.
14. Zhirong, H.E., Wang, F., Zhou, J., J. Mater. Sci. Technol., 22, 634, 2006.
15. Gu, Q., Van Humbeeck, J., Delaey, L., Journal De Physique., C3-135, 111-114, 1994.
16. Treppmann, D., Hornbogen, E., Journal De Physique, C2-211, 4-5, 1995.