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EFFECT OF HEAT TREATMENT ON THE MICROSTRUCTURAL AND SUPERELASTIC BEHAVIOR OF NiTi ALLOY WITH 58.5wt% Ni

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Abstract

The effect of aging process on hardness as well as the superelastic behavior of NiTi shape memory alloy with 58.5% wt.% Ni has been investigated in this paper. The aging process has been performed at different temperatures ranging from 400 to 800 °C and for various exposure times from 30 min to 8 hours. The results showed an increase in hardness in the temperature range from 400 to 500 °C and then a decrease occurs. At constant temperature with prolonged aging time a gradual increase of hardness occurs. SEM observations showed that there is some precipitation in specimens aged from 600 to 800 °C. The decrease of hardness can be due to an increase in precipitate size. The superelastisity investigation at 25 and 60 °C showed that the maximum superelastisity results are related to specimens aged at 400 °C. The superelastisity properties of NiTi were discussed in terms of hardness and microstructure.
Key words: shape memory alloy, nitinol, heat treatment, superelasticity, structural properties

Introduction

Superelastic shape memory NiTi alloys have wide commercial applications due to their considerable mechanical properties such as hardness and high corrosion resistance as well as their environmental compatibility. The commercially named alloy Nitinol is made of nickel and titanium and its mechanical properties are highly affected by its chemical composition. Mechanical properties of this alloy can be remarkably controlled by heat treatment and work hardening processes [1].

Shape memory and superelastic effects of this alloy are mostly obtained for a chemical composition of equivalent volume fraction of nickel and titanium. Due to

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phase stability of NiTi, various compositions of NixTix may exist in the matrix microstructure [2].

Superelastic effect is obtained through phase transformation of parent (austenite) phase to martensite phase under the applied deformation (stress induced transformation). The martensitic phase can be transformed back to the parent phase upon unloading (reverse transformation). The stresses at which the forward and reverse transformations occur are mostly constant and can be obtained from the stress-strain curve of these alloys [3].

In nickel rich alloys, three solid phases exist in equilibrium with each other, i.e. $TiNi_3$, Ti_2Ni_3, and Ti_3Ni_4 [4-10]. $TiNi_3$ [7] and Ti_2Ni_3 [5,8] are incoherent with the matrix, thus ineffective to the transformation behavior of the B2 matrix. In comparison Ti3Ni4 is more influential to the transformation behavior and thermomechanical properties of NiTi, including the R-phase transformation [11, 12], all-round shape memory effect [13] and multiple-stage transformation behavior [14].

Yeung [15] has shown that heat treatment affects austenite→martensite stress transformation and investigated the effect of various factors on the AP. AP is the temperature at which the peak of differential scanning calorimetry (DSC) curve is obtained.

Transformation temperature is a function of chemical composition and heat treatment and quenching processes done on these alloys. In heat treatment process, the rate of quenching, exposure time and heat treatment temperature, control the forward and reverse transformation temperatures of austenite to martensite and martensite to austenite [15].

The effect of different heat treatment parameters on microstructure and hardness of NiTi shape memory alloy composed of 58.5wt.% nickel has been investigated in this paper. Since the mechanical behavior of this alloy is highly affected by its microstructure, studying the effect of heat treatment process helps to obtain a good microstructure with desired mechanical properties.

Experimental procedure

In order to study the mechanical and microstructural properties of NiTi alloy, samples of NiTi alloy were prepared by melting nickel and titanium ingots using vacuum induction melting furnace (VIM), and cast into graphite mold coated with boron nitride. The as-cast specimens then were hot-rolled. Heat treatment was carried out in a tubular furnace under argon atmosphere. To investigate the microstructure of samples and the hardness variations, scanning electron microscopy (SEM) and Rockwell-C hardness test were used, respectively. Each hardness test was performed three times and the average value was taken as the final result. The superelastic behavior of the alloy was characterized by three point bending test conducted at 25 and 60 ^{o}C.

Results

A summary of the experimental conditions is listed in Table 1. Results of Table 1 show the hardness values of solution annealed and aged samples in the temperature range from 400 to 800 ^{o}C for 70 min. It is obvious that application of aging treatment in the above mentioned temperature range increases the hardness compared to the case of solution annealing condition. Furthermore, increasing the temperature from 400 to 600 °C slightly decreases the hardness. On the other hand, increasing the aging temperature from 600 to 700° C, the hardness drops abruptly. However, hardness increases again with further increase in temperature from 700 to 800 °C

Table 1: Different heat treatment processes applied on NiTi 58.5% Ni alloy

Heat treatment	Temperature (°C)	Time	Hardness (HRC)
Solution annealing	900	30(min)	53.8
Aging	400	70(min)	59.1
Aging	400	3(h)	57.2
Aging	400	5(h)	57.8
Aging	400	8(h)	60.2
Aging	400	70(min)	59.5
Aging	500	70(min)	58.5
Aging	600	70(min)	56.9
Aging	700	70(min)	42
Aging	800	70(min)	46.2

Fig. 1 shows variation of the alloy hardness as a function of aging time at a fixed temperature of 400 °C. It may be seen that with prolonged aging time a gradual increase of hardness occurs.

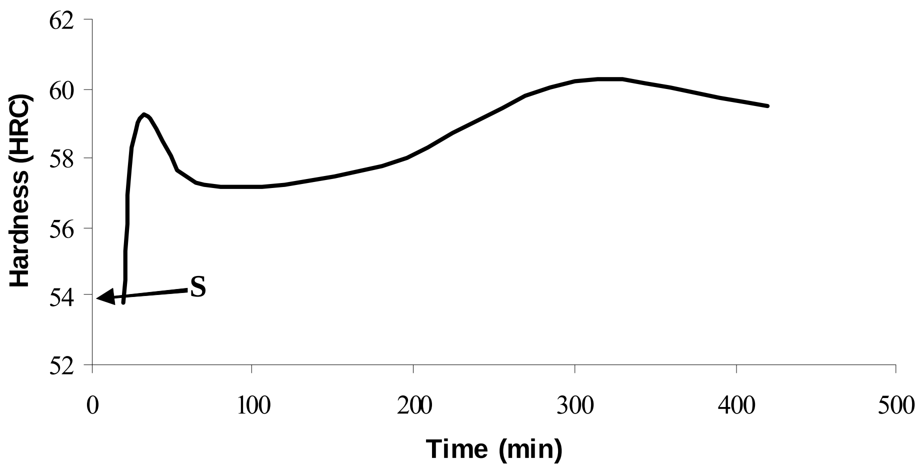

Fig. 1 Hardness vs. different aging time at fixed temperature of 400 °C

Variation of hardness of samples aged at different temperatures and fixed aging time of 70 min is shown in Fig. 2. Hardness of samples aged within the temperature range of 400 to 500 °C shows an increase as compared to the hardness of annealed samples. Increasing temperature from 500 to 600 °C causes a small drop in the hardness value. With further increase in temperature from 600 to 700 ˚C a small hardness drop of about 14 HRC occurs. Finally, increasing aging temperature from 700 to 800 ˚C causes an increase in the hardness.

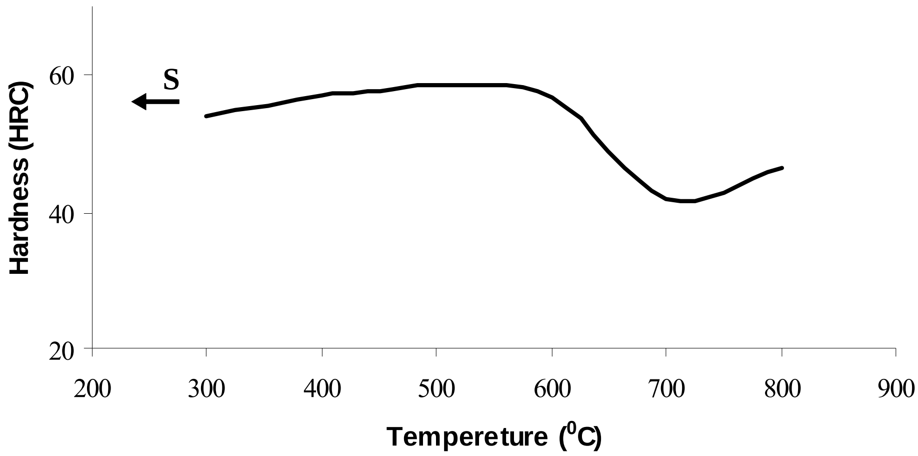

Fig. 2. The alloy hardness vs. different aging temperature at fixed time of 70 min

Fig. 3 shows the microstructure of the sample after 30 min of aging at 400 ˚C. Some oxide and carbide inclusions as well as porosity are shown in the microstructure. Ni-rich precipitates are not visible in the sample; however, their existence can be justified because of variation of hardness. With longer time of aging such precipitates becomes larger and incoherent.

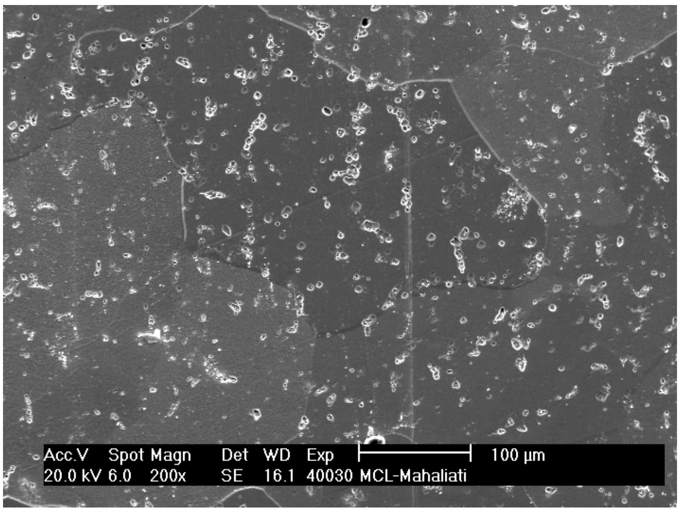

Fig. 3 SEM image of alloy aged at 400 °C for 30 min

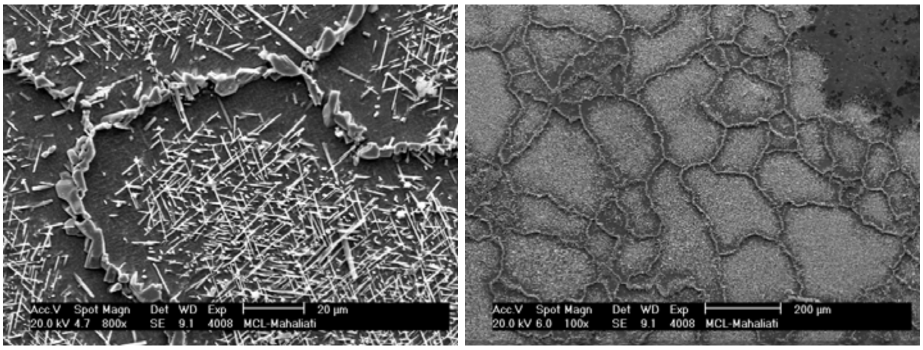

Fig. 4 a. SEM image of alloy aged at 400 ˚C and 8 h; b. magnified image

As shown in Fig. 4 precipitates in samples aged at 400 ˚C for 8 h are rather large. Oxide and carbide particles are also presented at the grain boundaries. These precipitates increase the hardness to some extent and affect the discrepancy of the measured data.

The increasing part of hardness curve in Fig. 2 is due to the formation of precipitates in the austenite matrix and the density of these precipitates increases with increasing temperature. Images taken by SEM show formation of precipitates at aging temperature 600 ^{o}C (Fig. 5).

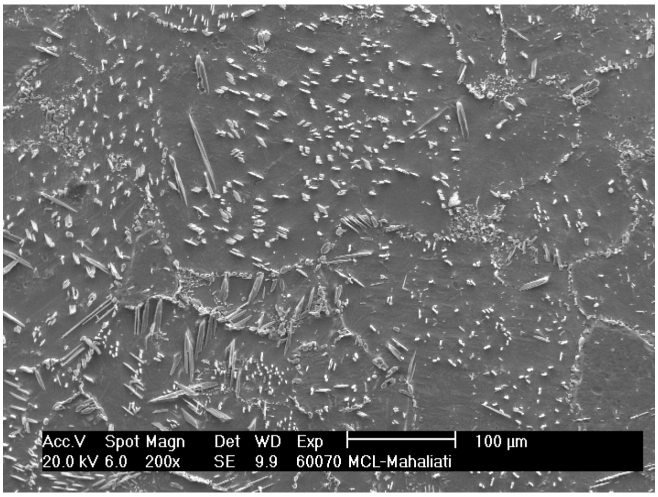

Fig. 5. SEM image of alloy aged at 600 ^{o}C and aging time of 70 min

As expected, by increasing the temperature at fixed aging time, the precipitates become coarser. At 700 and 800 ˚C these precipitates have specific orientation with respect to the austenitic matrix. Increasing the aging temperature to 700 ˚C the microstructure of the matrix remarkably changes and coarse precipitates of Ni_3Ti have been formed. In this case, the NiTi matrix has a martensitic microstructure (Fig. 6) which is due to the reduction of nickel volume fraction in the matrix and the martensite phase transformation occurs at the working temperature.

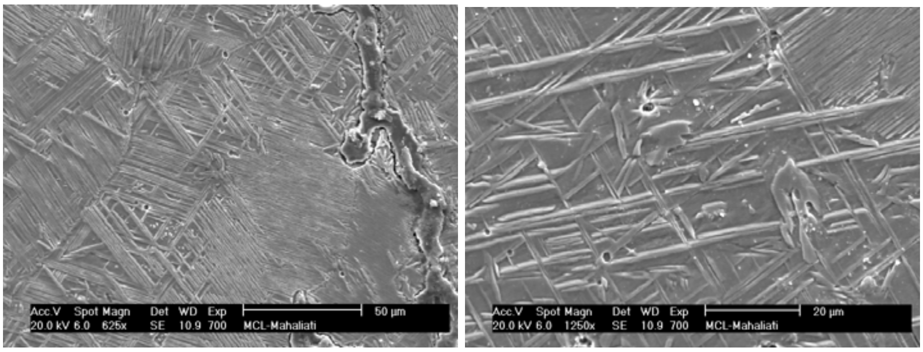

Fig. 6 a. SEM image of alloy aged at 700 °C for 70 min; b. magnified image

The superelastic behavior of the alloys is summarized in Table 2. The superelastic index, γ, is proportional to the inverse of residual strains upon unloading the 3-point bending specimen. The following equation is used for identifying the superelsticity index of the alloy:

$$\gamma = (\Delta\varepsilon/\varepsilon) \times 100 \quad (1)$$

where Δε is the recoverable part of the deformation and ε is the total amount of deformation applied to the specimens. The value of γ and the residual strains show that specimens aged at temperature 800 °C for 70 min exhibit less superelasticity and greater residual strain as compared to the other specimens. Furthermore, test at higher temperature (60 °C) shows that the superelasticity of specimens aged at 400 °C for 70 min, and those annealed and aged at 700 ˚C for 70 min reduces as compared to those specimens tested at room temperature (25 °C). However, the superelasticity index of specimens aged at 800 °C for 70 min increases at testing temperature of 60 °C as compared to the testing temperature of 25 ˚C.

Table 2 Residual strain upon unloading and superelasticity index for testing temperature of 25 and 60 °C.

	Temperature (˚C)	Specimen ID			
		400	S	700	800
Residual Strain	25	0.16	0.19	0.26	3.2
	60	0.54	0.45	0.3	0.96
γ Superelasticity index	25	96	94	94	20
	60	87	89	93	77

The force-deflection of the 3-point bending specimens tested at 25 and 60 °C temperature is shown in Figs. 7 and 8, respectively. The specimen aged at 400 °C exhibits the higher superelasticity index compared to the other specimens. The aged specimen at 700 ^oC, annealed specimen and specimen aged at 800 ^oC exhibit lower superelasticity index.

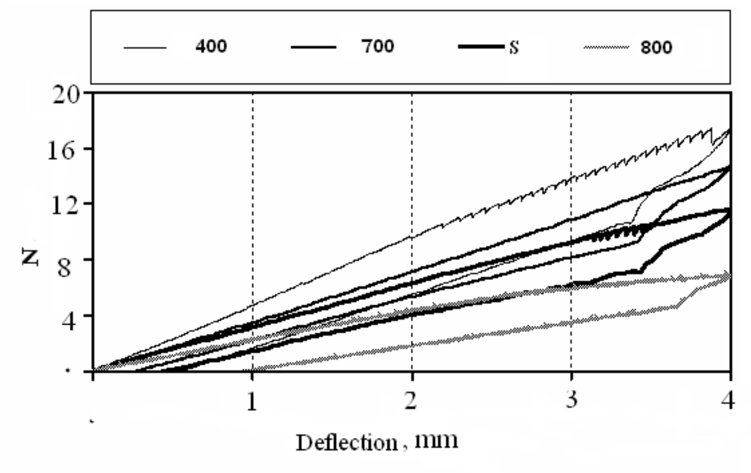

Fig. 7 Load-deflection curves of 3-point bending test performed at 25 ˚C

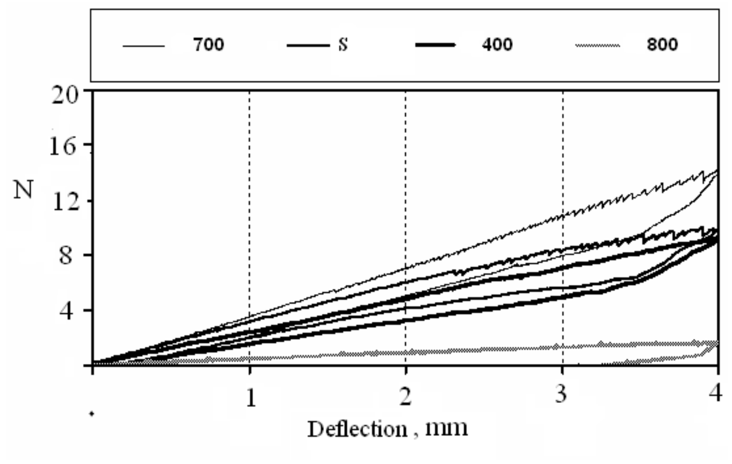

Fig. 8 Load-deflection curves of 3-point bending test performed at 60˚C

Discussion

Fig. 1 shows the variation of the alloy hardness with aging time in the range from 0.5 to 8 hours at the fixed temperature 400 ^oC. As shown in this figure, a gradual increase of hardness is reported as the aging time increases from 70 min to 5 hours. This is because of the presence of Ni_4Ti_3 and Ni_3Ti_2 particles in the austenitic matrix at the above mentioned temperature range at 400 ^oC [4-10]. Further aging (from 5 to 8 hours) causes a small drop in hardness which indicates that exposure to longer aging time causes more incoherency in the matrix due to formation of larger precipitated particles. This is well documented by the microphotographs shown in Fig 4. For the case when the specimens are aged for the longer aging time, less discrepancy in the measured data is obtained and hardness values are more uniform which may be ascribed to a more uniform microstructure.

Fig. 2 shows the variation of the aged samples at different temperatures for a fixed aging time of 70 min. In the temperature range from 400 to 500 ^oC, an increase of the hardness is obtained. As shown in Fig. 2 increasing the aging temperature from 500 to 600 ^oC, the hardness decreases. This may be due to formation of coarse precipitates at high temperature.

In the temperature range from 600 to 700 ^oC the hardness remarkably drops to the 42 RC which is due to the phase transformation of the matrix. If the matrix was fully martensite this drop may be expected to be bigger. Reports show that the austenite hardness is twice as that of martensite. At temperatures above 600 ˚C reaction close to the equilibrium diagram occurs and, as a result, hardness is slightly increased in the temperature range from 700 to 800 ^oC. In this case, at temperatures over 700 ^oC, Ni-rich precipitates are in equilibrium with the matrix. According to the equilibrium diagram [16], the solubility slope of nickel in NiTi stability region is positive and the solubility increases with increasing temperature. At 800 ^oC, Ni_3Ti precipitates are in equilibrium with a NiTi matrix which has 57 % Ni and this composition lowers M_S temperature compared to that at 700 ^oC. As a result, at room temperature austenite phase exists in the matrix. At this point M_S temperature is lower due to higher nickel amount in the matrix. Hardness at 800 ^oC is higher than that at 700 ^oC. In this case, a high percentage of the matrix microstructure is martensitic and the effect of non-equilibrium precipitates on hardness is not remarkable.

Considering conditions corresponding to specimens aged at 800 ^oC for 70 min (see Fig. 2), it is clear that these specimens at room temperature (which is below the austenite finish temperature A_F) may have austenitic-martensitic microstructure. Existence of high martensite content in the microstructure at room temperature (25 ^oC) causes higher residual strains (about 80%) after unloading in the 3-point bending test.

Increasing the 3-point bending test temperature to 60 ^oC (test temperature above A_F), microstructure of specimens is fully austenitic enabling higher superelasticity and lower residual strains upon unloading. For specimens having A_F lower than the room temperature, when the 3-point bending test is conducted at room temperature they are initially in their fully austenite phase and therefore possess high superelasticity and low residual strain upon unloading. The 3-point bending test at 60 ^oC shows higher residual strain and lower superelasticity of specimens. This is due to the fact that superelasticity exists in the temperature range from A_F to M_S. At 60 ^oC specimens are far from A_F and forward stress which induces austenite→martensite transformation causes lower superelasticity.

Conclusion

1- Presence of coherency strain around Ni_4Ti_3 and Ni_3Ti_2 at low aging temperature causes higher hardness and strength of matrix. These precipitates are very fine at low temperature and over a long period of time or high temperature become larger and lose their coherency with the matrix. As a result, it is expected that the temperature increase causes the hardness drop.

2- Austenite phase has a greater hardness value as compared to martensite phase. Any parameter which causes austenite→martensite transformation of the matrix initiates the hardness drop.

3- Increasing the temperature the NiTi matrix composition is in equilibrium with Ni_3Ti precipitates and has less nickel content. Therefore, at high temperatures, i.e. over 800 ^oC, the matrix is composed of NiTi with low nickel content**.**As a result a higher M_S temperature is obtained as compared to the matrix at 700 ^oC.

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