The change of transformation temperature on NiTi shape memory alloy by pressure and thermal ageing

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Abstract. We have investigated the effect of pressure and thermal ageing on transformation behavior of Ni-%45.16Ti shape memory alloy. 70-320 MPa pressure was applied and annealed at 500 °C for 2 hour to see the effect of applied pressure on transformation temperature. It was observed that the starting and final temperature of austenite increased, the martensite start temperature almost remain constant and final temperature decreased with the increase of pressure. The interval stress value of NiTi alloy was determined as 13.77 MPa/°C during austenite transformation. The transformation temperature of Ni-%45.16Ti alloys after thermal ageing was also investigated. No significant variation in these parameters was obtained. According to XRD measurements, there are two phases namely R (rhombohedral) and B19 (monoclinic) martensite were obtained. We did not see any change on the peaks after ageing.

1. Introduction
NiTi alloy with near-equiatomic composition is the most useful shape memory alloy (SMA) among many shape memory alloys. The application fields of these alloys are production of various medical devices such as orthopedic surgical implant, artificial prosthesis [1]. There are three different phases that have been observed throughout the martensitic transformation of NiTi: B2 (cubic), R (rhombohedral) and B19' (monoclinic). The high temperature austenitic B2 phase (CsCl) undergoes a displacive structure transformation to intermediate R phase about 293 K and transforms to the low temperature martensite B19’ phase. It is not clear in which condition this unusual behavior occurs. This can be explained as another formation of martensitic behavior [2,3]. In summary, there are two series of phase transitions in NiTi:

B2→B19 and B2→R→B19’.

The first series of transformations is observed in NiTi samples containing less than 50 %at Ni; the second occurs in samples with higher Ni concentration [4]. The shape memory behavior of NiTi alloys is influenced by their chemical composition, heat treatment (annealing and ageing) and mechanical deformation [5]. Effect of ageing treatment on the transformation behavior of NiTi alloy was studied by Y. Zheng and co-workers [6]. They chose various ageing temperature for 1.8 ks (30 min.) and investigated variation on martensitic transformation temperature and crystal structure. It was seen that the multistage phase appeared or disappeared by variable temperatures. Lin et al. were focused on
ageing effect on V doped NiTi alloy. They aged this alloy at 400 °C for 1-10 h and examined martensitic transformation temperature and crystal structure changes. It was found that R phase appeared with residual ageing time [7]. K. Allafi and co-workers investigated the mechanism of multistage martensitic transformations in aged NiTi shape memory alloys. According to their study, annealed NiTi alloys at 850 °C for 15 minutes showed one step on both heating and cooling. When alloys exposed ageing at 400 and 500 °C for different times, multistage transformation was seen [8]. Chu et al. were focused on DSC study of aged porous Ni-rich NiTi shape memory alloy which fabricated by combustion synthesis. Their experimental study indicated that shape memory properties of porous NiTi alloy could be improved by optimizing the ageing technology [9]. The understanding of strain and phase transformation behavior under constant applied pressure is essential, because of improving recent application of NiTi shape memory alloys, including smart structures, intelligent controllers and memory device [10]. There is few study about effect of constant pressure on shape memory alloys. Kröger et al. studied pressure-induced martensitic transformation in Ni rich NiTi alloys [11]. They measured DSC pressure-free and pressure-assisted aging for 4 ks (almost an hour) at 550 °C. It was seen that martensitic transformation temperature of NiTi alloys increased after pressure. The aim of this study is to investigate the effect of pressure and thermal aging on the martensitic transformation of Ni-%45.16Ti shape memory alloys.

2. Experimental
NiTi shape memory alloy with nominal composition of Ni-%45.16Ti (atomic) was supplied by Nimesis technology. All samples were annealed for 2 hour at 500 °C and rapidly quenched in ice brined. DSC measurements were done in order to investigate the effect of pressure and thermal ageing on transformation temperature. These temperatures namely Martensite finish-$M_f$, Martensite start-$M_s$, Austenite start-$A_s$ and Austenite finish-$A_f$ of alloys were measured by Perkin Elmer Sapphire differential scanning calorimetry with 10 °C/min heating and cooling rate at the temperature range of 0 and 150 °C in Nitrogen atmosphere. X-ray analysis system (Bruker D8 Advance) using Cu K$_\alpha$ radiation was used to determine crystal structure of thermal aged alloys. The X-ray diffraction (XRD) measurements were carried out in the range of 20-80° at the rate of 2°.

3. Result and discussion
The DSC charts on heating and cooling of the NiTi shape memory alloy annealed at 500 °C were shown in Figure 1. According to Figure 1, two phase transformation occur during cooling. One of these phase is martensite other is rhombohedral (R) phase.

![Figure 1. DSC thermogram of NiTi alloy annealed at 500 °C](image)
It is known fact that the phase transformation steps of NiTi alloy depends on heat treatment temperature: $A \leftrightarrow R$ at annealing temperatures below 400 °C, $A \leftrightarrow R \leftrightarrow M$ at temperatures 400-600 °C and $A \leftrightarrow M$ at temperatures above 600 °C [12,13]. R phase transformation is related to formation of Ti$_3$Ni$_4$ precipitates [7].

### 3.1. Pressure ageing

Figure 2 show the DSC thermogram of unloaded and loaded NiTi shape memory alloy during heating and cooling. Transformation temperatures of the material are summarized in Table 1. Phase transformation temperatures ($A_s$, $A_f$, $M_s$, $M_f$), Temperature Transition Region (TTR) which is equal to $A_f - M_f$ and the variation of thermodynamics parameter (enthalpy and entropy) are given together.

### Table 1. Transformation temperatures and thermodynamic parameters list of pressure aged NiTi.

| No-Pressure | 78 MPa | 156 MPa | 243 MPa | 312 MPa |
|-------------|--------|---------|---------|---------|
| $A_s$ (°C)  | 58.0   | 61.7    | 75.5    | 74.4    | 80.4    |
| $A_p$ (°C)  | 66.4   | 80.2    | 88.3    | 89.6    | 92.3    |
| $A_f$ (°C)  | 70.0   | 88.3    | 94.8    | 95.2    | 99.0    |
| $M_s$ (°C)  | 37.8   | 34.7    | 39      | 38.1    | 40.3    |
| $M_p$ (°C)  | 34.0   | 28.2    | 30.8    | 30.7    | 30.9    |
| $M_f$ (°C)  | 26.1   | 14.7    | 12      | 11.9    | 10      |
| $T_{tr}$ (°C) | 21.0  | 3.7     | 4.1     | 2.7     | 1.8     |
| $T_{tr}$ (°C) | 47.9  | 48.2    | 57.2    | 56.2    | 60.3    |
| TTR         | 49.0   | 84.6    | 90.7    | 92.5    | 97.2    |
| $\Delta H_{heating}$ (Jg$^{-1}$) | 27.6  | 24.1    | 25.4    | 24.8    | 22.4    |
| $\Delta H_{cooling}$ (Jg$^{-1}$) | -23.6 | -19.2   | -19.8   | -19.4   | -17.4   |
| $\Delta S$ (Jg$^{-1}$1°C$^{-1}$) | 0.53  | 0.45    | 0.39    | 0.39    | 0.33    |
Transformation temperatures generally increase with the rising amount of pressure. Besides, decomposition occurred at transformation temperature. The electron distribution rises with the shrinkage of the atomic distance by the pressure; hence a significant change occurs at transformation temperature. Evaluation of critical temperatures is presented in the Figure 3. The austenite start and final temperature increase, the martensitic start temperature remains almost constant and martensitic final temperature decrease with the rising pressure. The reason of decreasing in martensite final temperature may be the increasing of Ni concentration in NiTi matrix or the growth of the Ti-rich phase by applied pressure [14].

It was seen by evaluating the thermodynamic parameters given in Table 1 that the average enthalpy values obtained for the alloys subjected to pressure ($\Delta H_{\text{average}} = (\Delta H_{\text{heating}} + \Delta H_{\text{cooling}})/2$) increases than that of not to subject pressure. Besides a reduction were determined in entropy variation with the pressure. These indicate that reduction in entropy variation can induce a reduction in unsteady structure of NiTi alloy. Clausius-Clapeyron equation for austenite transformation can be written as

$$\frac{d\sigma}{dT} = -\rho \frac{\Delta H}{\varepsilon T_o}$$

(1)

where $\rho$ is density of NiTi alloys and equal 6500 kg/m$^3$, $\Delta H$ is enthalpy change, $T_o = (A_s + M_s)/2$ is equilibrium temperature, $\sigma$ is the pressure and $\varepsilon$ is the strain associated with transformation. The strain values are proportional to transformation temperature and especially to $T_o$ temperature at which martensite and austenite transformation are equal to Gibbs free energy according to Clausius-Clapeyron equation [15]. The $T_o$ value increases with the pressure as seen in Table 1. The strain values also increase with the pressure. Clausius-Clapeyron equation can be used another form for the previous equation:

$$\frac{d\sigma}{dT} = -\rho \frac{\Delta S}{\varepsilon}$$

(2)

$\Delta S$ is entropy change and equal to $\Delta H/T_o$. DSC measurements give enthalpy change of NiTi alloys during heating or cooling [14]. The define Stress rate described at the left side of the equation for the stress induced transformation was determined as 13.77 MPa$^o$C during austenite transformation. For NiTi alloys the stress range is between 3 and 20 MPa $^o$C$^{-1}$ [16]. The results are in accordance with the literature.

Figure 3. The change of transformation temperature with applied pressure
Table 2. Transformation temperatures and thermodynamics parameters list of thermal aged NiTi Alloys.

| Ageing Time at 200 °C | 0h | 1h | 2h | 3h | 4h | 5h | 6h | 7h |
|-----------------------|----|----|----|----|----|----|----|----|
| \( A_s (°C) \)       | 58.0 | 58.2 | 58.0 | 58.6 | 58.7 | 59.3 | 59.0 | 59.1 |
| \( A_f (°C) \)       | 66.4 | 65.6 | 64.5 | 65.6 | 65.6 | 69.0 | 66.1 | 67.3 |
| \( A_t (°C) \)       | 70.0 | 68.3 | 67.4 | 68.9 | 68.7 | 72.5 | 68.7 | 70.3 |
| \( M_s (°C) \)       | 37.8 | 37.6 | 38.2 | 38.4 | 38.0 | 37.6 | 38.2 | 38.5 |
| \( R_p (°C) \)       | 34.0 | 34.5 | 35.6 | 35.1 | 35.1 | 33.2 | 35.2 | 34.3 |
| \( M_p (°C) \)       | 26.1 | 26.7 | 28.5 | 28.1 | 28.1 | 24.9 | 28.3 | 26.6 |
| \( M_f (°C) \)       | 21.0 | 22.4 | 24.3 | 22.9 | 23.1 | 18.6 | 23.7 | 21.1 |
| \( T_o (°C) \)       | 47.9 | 47.9 | 48.1 | 48.5 | 48.5 | 48.4 | 48.6 | 48.8 |
| \( \Delta H_{\text{heating}} (\text{Jg}^{-1}) \) | 27.6 | 26.6 | 27.0 | 26.6 | 27.0 | 24.9 | 26.8 | 25.4 |
| \( \Delta H_{\text{cooling}} (\text{Jg}^{-1}) \) | -23.6 | -22.6 | -22.9 | -22.7 | -23.2 | -22.3 | -22.8 | -22.2 |
| \( \Delta S (\text{Jg}^{-1}\text{o}^{-1}\text{C}^{-1}) \) | 0.53 | 0.51 | 0.52 | 0.51 | 0.52 | 0.49 | 0.51 | 0.49 |

3.2. Thermal ageing

The DSC measurements for investigating the effect of thermal ageing depending on time are summarized in Table 2. The austenite start temperatures \( A_s \) of Ni-Ti alloy are almost same with the changed ageing time but there is an increase in austenite final temperatures \( A_f \) of Ni-Ti alloy at 5 hour ageing (Figure 4). This increase in thermal transformation temperature can be explained as the instantaneous change in entropy of the aged alloy or this feature is believed to be related to the variation of Ni/Ti ratio in the NiTi matrix [7]. If, Ni/Ti ratio decreases in matrix, the transformation temperatures increase. So, transformation temperatures are very sensitive to the composition of the NiTi alloy and increase with decrease of Ni concentration [7, 17].

The martensitic start temperature \( M_s \) of alloy remains almost constant as well austenite transformation. The opposite of \( A_s \), the martensitic final temperature \( M_f \) of alloy fall down at 5h ageing time (Figure 4). As seen Table 2, presence of R phase, there was difference at austenite and martensitic final temperature and enthalpy change, for the 5h aged time. The biggest \( A_s \) and enthalpy change were seen in this ageing time. The calculated \( \Delta S \) and \( T_o \) values were given in Table 2. \( \Delta S \) and \( T_o \) values were almost constant with rising ageing time.

![Figure 4. The change of transformation temperature with ageing time](image-url)
Fig. 3 and Fig. 4 represent the effect of pressure and thermal ageing on transformation temperature respectively. It is seen from the figures that an observable change in transformation temperature occurs by the applied pressure. There is no significant variation at 200 °C temperature and 0-7 hour interval. X-ray patterns of thermal aged NiTi alloys at room temperature were given in Figure 5. The X-ray pattern of unaged alloy demonstrates the main peak occurred at about 42.5° (-101) with minor peaks at about 41° (-111), 42° (110), 43.5° (002) and 44.5° (111). These are the characteristic peaks and in agreement with the peaks observed by Czeppe et al. [18]. It is seen that there are two phase in crystal structure of unaged NiTi shape memory alloy. The main peak (-101) and at 42°(110) belong to rhombohedral (R) phase, other peaks belong to monoclinic (B19) phase. All XRD pattern exhibited similar characteristics according to investigation of the changes in peak characteristics of XRD patterns with ageing duration [19]. However, for one hour ageing time, some peaks such as 43.5° (002)B19 and 44.5° (111)B19 disappeared.

Figure 5. XRD diffractograms of thermal aged NiTi alloy
4. Conclusion
The results obtained from this study can be outlined as follows:

- It was determined that while the transformation temperature increased the entropy change decreased by the pressure ageing. The stress interval value was determined as 13.77 MPa/°C during the austenite transformation temperature.

- When ageing time effect on transformation examined at 500°C annealing temperature, the stable position was seen for 200°C ageing temperature. The X-ray analyses showed that there was two phase as R (rhombohedral) and B19 (monoclinic) martensite. There was not important change in characteristics peaks by ageing process.

In conclusion it was observed by comparing the pressure and thermal ageing that while there is a significant variation in transformation temperature with the pressure, there is not an observable change with the chosen ageing temperature.

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