The Effect of Heat Treatment Conditions on the Mechanical Behavior of Ni-Ti Shape Memory Alloys

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Abstract: Ni-Ti shape memory alloy (SMA), and its alloys have been widely used for medical, mechanical and electrical applications. In this study, a (Nitinol) Ni-Ti alloy medical plate was prepared and cut using a wire cut machine. Eight samples were heat treated at 800°C and used for heating samples for 30 min and 60 min at this temperature, then cooled in four media: furnace, water, air, and ice bath. Micro-hardness and microstructure measurements were taken, as characterization techniques, to investigate the effect of cooling rate on mechanical properties. Micro-hardness results showed the HV is 316.36 HV at ice cooling rate for 800°C and 60 min heating time, and 275.5 HV for 800°C heating for 30 min and ice cooling media. The results show the correlation between cooling rate and properties of the alloy.

Key words: SMA, Ni-Ti, Nitinol, microstructure, Micro-hardness

1. Introduction

The Nickel–Titanium alloy was first developed in the 1960s. It was named Nitinol, an acronym for the elements from which the material was composed, (Ni for Nickel and Ti for Titanium) and the location for these investigations, (nol, from the Naval Ordnance Laboratory).

Based on the equiatomic, intermetallic compound Ni-Ti, the alloy composition used for the manufacture of Ni-Ti instruments is about 55% nickel and 45% titanium (wt.%) [1]. Shape memory alloys (SMAs), have been widely utilized for their excellent functional properties and high magnitude of actuation energy density. Of the various SMAs, nickel–titanium (Ni-Ti) has the optimal combination of properties including a high percentage of shape recovery, recovery stress and super-elastic strain. However, the limitations of traditional manufacturing technologies and the poor machinability of Ni-Ti have critically restricted the application of its full potential [2].

The SMAs have been found useful in many areas due to their high power density, solid state actuation, high damping capacity, durability and fatigue resistance when integrated with civil structures [3]. It is well known that the Ni or Ti content in a Ni-Ti SMA affects the phase transition temperatures, and that increase of Ni content in Ni-Ti shape memory alloys induces a decrease in Ms [4]. Chemical composition and heat treatment temperature and the time for annealing will influence the super-elasticity and the shape effect of the Ni-Ti shape memory alloy, so their use may enhance the shape memory alloy’s attributes [5].

In light of this, the present study was conducted to impose multiple heat treatments upon a Ni-Ti alloy at different heating rates and for different cooling media. Hardness and microstructure were examined to assess the extent of heat treatment effects and results were gathered concerning heat time, value and cooling rate.

2. Experimental procedures

The experimental procedures comprised the following steps:

1. The plate of Ni-Ti was prepared by wire cut machine.
2. The plate studied had a thickness of 1 mm.
3. Chemical composition of the Ni-Ti plate is given in Table 1.
4. Samples were heat treated using a CARBOLITE SWF 1200 Chamber Furnace.
5. DSC testing was conducted to find the transformation temperature at conditions of heating range from -100 to 500 of the plate.

The repertoire of comparative results will be Ni-Ti plate as-received, with heat treated samples, to examine the microstructure and micro-hardness outcomes from heat treatment and time of heating, with cooling patterns.

The heat treatment commenced with the preheating of samples at 800 °C for a period of 30 mins or 1 hour, then it was cooled using four cooling media (ice bath, water, air and furnace). Following water, ice bath, air and furnace cooling, another heat treatment was given at 450 °C for 16 min, to permit study of the heat treatment effect on the micro-hardness and microstructure of Ni-Ti alloy and predict the austenite and martensite phases that occur in the presence of stress or heat treatment [6].

Table 1: Chemical composition of Ni-Ti shape memory alloy plate as certificated

| Wt.% | Ti     | Ni | Co | Cu  | Cr | Fe | Nb | N   | C   | O   |
|------|--------|----|----|-----|----|----|----|-----|-----|-----|
| reminder | 55.75  | 0.01 | 0.005 | 0.005 | 0.012 | 0.01 | 0.001 | 0.04 | 0.03 |

The wire cut specimens were etched using a chemical solution for etching that contained HNO₃ 15.5% and HF 4% by volume balance with H₂O [7]. Microstructure was investigated after etching of the plate, using optical microscopy. The Vickers micro-hardness was measured by digital micro-hardness test apparatus. Micro-hardness values were determined using three indents in each test point taken on the prepared surface (2.0 N load held for 10 seconds), the average diagonal of the indentation was approximately 35–38 μm for all samples.

3. Results and discussion
Samples were heated to 800°C and then 450 °C, for periods of approximately 30 min or 1 h, and 16 min respectively. For cooling the heated samples we employed ice bath, water, air and furnace media. Findings include the appearance of multiple craggy precipitates. The craggy precipitates appeared with heat treatment and increased in roughness with increasing heat treatment temperature, as can be seen in Figures 1, 2 and 3 [8]. The (Ni₃Ti) precipitations can be seen in all alloys that have a high content of Ni, which is to say higher than 50%. The studied plate had 55.75% Ni.

Heat treatment time and temperature form an effective method for improving the mechanical properties of Ni-rich alloys with this content and the formation of Ni₃Ti precipitates generates a coherency field of stress in the microstructure. The phase diagram shows these alloys at this content of TiNi₃ and TiNi [7-9]. Precipitates are as shown in Figures 2 and 3, and represent the Ni₃Ti precipitates (as concluded from the phase diagram of the Ni-Ti shape memory alloy plate studied). Figure 4 shows the the Ni-Ti plate very clearly with the phase diagram that shows the precipitates of NiTi and Ti Ni₃ at Ni 55.75% (the studied plate), and at temperature heat treatment at 800°C and 450°C . The occurrence of a martensitic structure can be understood in Figure 2d, which has a homogeneous distribution of precipitates.

The application of heat treatment will create new structures that differ with each cooling media according to the shape, count and distribution of the precipitates, which will in turn generate the new roughness of structure. The scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) for ice- and furnace-cooled samples show that the matrix of Ni-Ti consists of near-equiaatomic phase in a distributed particles and the structure is coarse and scattered (Figure 5).
Figure 1: SEM microstructure of Ni-Ti sample 800°C heat treated and ice bath cooling rate used to quench NiTi2, matrix formed, a) at 1mm and 100X magnification b) at 200 X magnification 500 µm.

The austenite phase (with small and dot-shaped precipitates) arises more frequently with heat treatment of 450°C at 16 min than at the heat treatment of 800°C, whereby there is little genesis of austenite, as Figure 2 shows [8].

Figure 2: Ni-Ti sample structure a) as-received and b) heat treated (450 °C) time of heating was 16 min, c) 800°C /30 min, and d) at 800°C /1 h (ice cooled)
Figure (3): (a-b-c-d-e-and f) optical microscopic results to study the microstructure changes during heat treatment at different cooling rates
Figure (3 a) shows clearly the austenite and martensite phases, where M1 shows the austenite phase that it is the sample heat treated at 800°C for 30 min and cooled using water. In Figure 3 d, M3 (which was cooled by air cooling), M5 and M6 the austenite clearly appears with 800°C/60 min and ice-furnace cooling, respectively. In Figures 3b and 3c, M2–M4 reveal the martensite phase that used ice and furnace cooling rates, respectively. These results verify that the heat treatment of SMAs will affect the microstructure and the appearance of the phases, which are the most important properties of shape memory alloys and determine the suitable applications for the studied alloy.

Figure 5: EDS of Ni-Ti sample heat treated at 800 °C/30 min, ice bath quenched, showing the Ni-rich alloy

An indentation mark of the micro-hardness load is shown in Figure 6.
The micro-hardness Vickers HV results are presented in Figure 7, and indicate that the hardness of the ice bath will give micro-hardness results higher than other cooling rates (317.36 HV) that is to say, higher than water, air and furnace. Also the results show that lower values are associated with use of furnace cooling. However, the increase of the annealing temperature to 800 °C/1h promoted an increment in hardness values (ice cooling rate, 317.36 HV), possibly due to precipitation of Ti3Ni4, a decrease (275.5 HV), for the same cooling rate media in further annealing treatment at 800°C/1h. Another cooling medium, water, corresponds to decreasing hardness values attained from the cooling rate used at (450 °C/16) min.

The average results of HV micro-hardness are in Figure 5. The results of the heat-treated samples with the base metal more appreciably dropping in micro-hardness at 800°C /30min than at 800°C/1h; that is due to the fine precipitates composed at high temperatures over an extended period, at the lower temperatures rough precipitates will form at the same phase. These results will be different with air than in water and
different still in ice and furnace where the values of micro-hardness of an ice bath cooling rate will be much better than for furnace, and with heat treatment for 30 min will be much smaller than at 1 h heat treatment at the same temperature. Subsequently, this increase in micro-hardness results with the heat treatment will be useful to create mutations in the Ni-Ti structure. But when the hardness increases, the ductility will decrease [10].

One of the reasons for martensite subsisting in the structure will be the presence of the precipitates, but this retards its germination [11]. In this study, the precipitates’ size and amount varied with the heat treatment applied to the plate; heat will rearrange and resize precipitates. The micro hardness variation is mainly due to grain size, so we see the multiple values of hardness when these grains are affected by the heat treatment [12] Hardness increases as the grain size decreases, so the decrease in microhardness was due to the discrepancy of the grains as shown in the microstructure [13]. Finally, there is a proportional increase in hardness for the 800°C/1 h from the values of 800°C/30 min.

Increasing Ni content (the studied plate is rich in Ni) reduces the ductility that will decrease the recoverable strain that can be attained, so for that heat treatment will help to maintain the strain recoverability of this plate [14,15,16]. It is optimal to heat treat Ni-Ti alloy with around 460°C for drip periods of about 16 min, to ameliorates the mechanical properties of the alloy. Elevating this temperature to 485°C reduces the quality of these properties [17], so for that context the furnace-cooled sample shows the highest values in terms of shape effect and strain recovery. Annealing at temperatures below 450°C/16 min produced the desired thermo-mechanical properties for the alloy in applications that exploit the shape memory effect. The 450°C heat-treated specimen, presented in Figure 6b, contains much larger coherent precipitates than the 800°C heat treated specimen [18].

Additionally, the phase diagram shows the samples as measured in hardness measurements indicate increasing hardness values with increasing cooling rate (i.e. use of water, ice rather than furnace/air). The hardness increased with increasing the cooling rate, but increasing shape effect (SE) by using 450°C/16 min attained better hardness and better shape effect than use of 800°C, which decreased the shape effect compared with 450°C. The porosity percentage for the samples quenched in water or ice bath is lower than those cooled in the furnace because of the rapid cooling rate; elimination of porosity will increase the SME by increasing the cooling rate [19].

The pores of various sizes are irregular for the differently heat-treated and cooled samples but have been rounded. Pore size is small for samples after heat treatment. So, it is likely that further heat treatments cause the coarsening of the precipitates, rather than an increase in phase amount [20] and that for heat treatment of range 550–600°C this coarsening will disappear when increasing temperature for 800°C, but strain recovery (SE) will decrease.

As mentioned it is assessed that the best heat treatment for Ti –55.8 % Ni is on the limit heat treatment of 450°C. The transformation plasticity and shape memory effects are observed in the Ni-Ti alloys in cooling and heating under a constant stress. Any increase in dislocation yield limit should result in a decrease in plastic strain accumulation, however it may be achieved by an increasing in Ni concentration [21, 22]. Diferential scanning colorimeter DSC results are shown in Figures 8, 9, 10 and11.
Figure 8: DSC response of the Ni 55.87-Ti remainder as-received plate, exhibiting multi-stage transformation.

Figure 9: DSC responses of the furnace-cooled of heat treatment 800 °C /60 min exhibiting stage transformation.
The DSC test was implemented with the given conditions, to investigate the austenitic and martensitic transformation phases. Multiple peaks appeared for each condition at cooling and heating, the as-received DSC curve shows the martensite peak at values 62.34°C and 50.76°C Mf and Ms respectively, and 65.8°C and 110.65°C As and Af respectively. The peaks show no intermediate phases, i.e. that it is a one-way shape memory alloy used in staple medical applications and others that need to transform the material.
without return. The transformation temperatures identified were high compared with human body temperature, which is relevant since this plate may be used for medical applications, thus transformation phase should be around 37 °C. So the best heat treatment (which gives a transformation temperature of 35.81 °C) is 450 °C. Also, as expected the R phase did not appear in this plate’s DSC which shows it to have one stage transformation (one-way); this property is needed for the specified application and was studied to be improved for this purpose.

4. Future work

In this work, we studied the micro-hardness and microstructural properties and the effects of heat treatment on the shape effect of Ni-Ti alloy. It is recommended that future investigations study the super-elastic properties in light of these heat treatments and cooling rates, by studying the X-ray diffraction and SEM for nano examination. It would also be helpful for future scholars to examine the fatigue properties.

5. Conclusions

1. The plate used in this study is Ni-rich that decreasing the ductility thereby decreasing the shape effect, which is needed in many shape memory alloys. To adjust that, heat treatments at different rates of heating and cooling were used to moderate ductility that decreased with increasing Ni content in the alloy.
2. Micro-hardness results in water and ice cooling rate were higher than for cooling in furnace and air, because fast cooling rate increases the hardness.
3. Prior annealing treatments are useful, to adjust the recoverable strain in the shape effect.
4. Heat treatment affected the Ni-Ti shape memory alloy’s thermo-mechanical properties.
5. Nickel content reduces ductility and to attain the shape effect heat treatment was used at 800-450°C, respectively.
6. Heat treatment at 800°C will conduct the shape effect less than 450°C, and then it is better to use the second to maintain or increase the shape effect of (55.75%) Ni-Ti alloy.
7. Mutations in micro-hardness through heat treatment will subjoin the microstructure.
8. The optimal heat treatment to give a transformation temperature the same or approximate to the human body temperature is 450 °C.

6. References

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