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EFFECT OF COOLING RATE ON THE SHAPE MEMORY BEHAVIOR OF Ti-54at.%Ni ALLOYS

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ABSTRACT

The effects of cooling rate after aging at 550 °C for 3 h on the shape memory behavior and mechanical properties of Ti-54at.%Ni alloys are investigated in compression. It was found that it is possible to tailor the transformation temperatures of Ti-54at.%Ni alloys with cooling rate where multiple step transformation can also be observed. Shape memory behavior with transformation strain of 1 % is observed under ultra high stress level of 1500 MPa. It is also found that shape memory effect is highly stress dependent.

Keywords: Ni-rich NiTi shape memory alloy, Cooling rate effect, Thermomechanical loading, Multiple step transformation, R-Phase transformation

1. INTRODUCTION

Nickel rich NiTi alloys are considered to be the most widely used shape memory alloys (SMAs) in many industries including aerospace, automotive, bio-medical, and construction due to their distinct shape memory and superelasticity properties [1-4]. The martensitic transformation of NiTi SMAs has been discussed in many studies [5, 6]. The high temperature phase of NiTi is austenite with the B2 structure, and the low temperature phase is martensite with the B19' structure [7, 8]. The single step martensite transformation can be changed to multiple step transformation by the heat treatment due to the precipitates formation. In multiple step transformation, the first transformation is B2 to R-phase; further cooling then transforms the resulting R-phase to B19' [9, 10]. R-phase transformation temperatures are very stable and independent of thermomechanical treatments [11].

Nishida and Kainuma reported that the precipitation properties depend on cooling rate, aging time and aging temperature [12-14]. The decrease of cooling rate leads to the formation of Ni4Ti3 and Ni3Ti precipitates, which decrease the Ni concentration of the matrix. The transformation temperatures of NiTi alloy decrease with increasing Ni content of matrix [2]. The presence of precipitates provides R-phase formation in NiTi SMAs. Ni-rich NiTi alloys show multiple step martensitic transformations associated with this intermediate R-phase [15, 16].

In this study, cooling rate effect on the shape memory properties of Ti-54at.%Ni alloys were studied. Systematic shape memory effect tests as a function of stress and superelasticity tests as a function of temperature were conducted under compressive stress. The effects of cooling rate after aging at 550 °C on the strain and hysteresis, the transformation temperatures, and R-phase formation were investigated.

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2. MATERIALS AND METHODS

The Ti-54at.%Ni ingots were homogenized at 1000 °C for 4 h in argon atmosphere in evacuated quartz tubes, followed by quenching into water. After homogenization, they were aged at 550 °C for 3 h which were selected to produce precipitates in the material to alter shape memory properties. Aged SMAs were cooled down by three methods; water quenching (WQ), air cooling (AC), and furnace cooling (FC) where 2 °C min^{-1} cooling rate was applied for furnace cool.

Transformation temperatures (TT) of the transformation were determined by Perkin Elmer 1 differential scanning calorimetry (DSC). The specimens of about 30 mg in weight were cut from the aged samples, and put in Al pans. The DSC measurements were made with a cooling and heating rate of 10 °C min^{-1} in helium atmosphere. The microstructure was investigated by transmission electron microscopy (TEM, JEOL JEM-2100HR). The thin foil specimens for TEM were prepared by a twin-jet electropolishing device in a solution consisting of (all vol%) 8% perchloric acid, 72% acetic acid, 12% methanol and 8% ethylene glycol at room temperature. TEM observations were carried out by TEM operated at an acceleration voltage of 200 kV. Compression testing of Ti-54at.%Ni was done on 4x4x8mm^3 samples that were cut by electro discharge machine. The compression tests were performed at the MTS Landmark servo-hydraulic load frame with 100 kN MTS load cell. Strain was measured using MTS high temperature extensometer with a 12 mm gage length. The temperature of sample was measured by K-type thermocouple attached on the center of the sample and also compression grips. Strain rate was 10^{-4} /s and heating rate was 10 °C min^{-1} while cooling rate was 5 °C min^{-1}. An Omega CN8200 series temperature controller was used to control the temperature rate.

3. RESULTS AND DISCUSSION

3.1 DSC and TEM

Figure 1a shows the DSC results of homogenized and aged Ti-54at.%Ni samples. In order to determine the effects of cooling rate, the samples were aged at 550 °C for 3 h and then cooled down by WQ, AC and FC methods. In Figure 1a, no peaks were observed for the homogenized sample. Austenite finish temperature (A_f) and martensite finish temperature (M_f) obtained from Figure 1a are given in Table 1. The decrease in cooling rate after 550 °C aging increased the TTs. TEM results were shown in Figure 1b and 1c for 550°C-WQ sample and 550°C-FC sample respectively. The obvious difference in microstructure was the only size of precipitate observed by TEM images. The FC sample had larger precipitates than WQ sample. It can be argued that the decrease in cooling rate promoted the formation of Ni-rich Ni4Ti3 precipitates, which in turn decreased the Ni concentration of the matrix [12]. Since the TTs of Ni-rich NiTi alloys decrease with increasing Ni content of matrix, lower nickel content of the matrix after 550°C-FC samples resulted in an increase in TTs [17]. In 550°C-FC, the first peak during cooling at about 40 °C was attributed to the R-phase formation. The other two peaks during cooling can be attributed to the B19’ martensite formation due to inhomogeneity in microstructure [18].

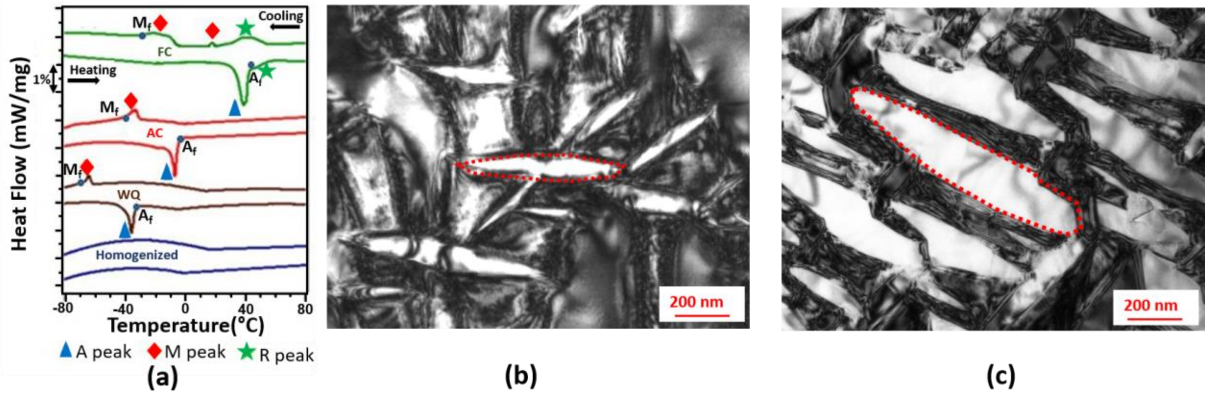

Figure 1. a) DSC curves of the Ti-54at.%Ni alloy aged 550°C. The chart shows the cooling effect on the martensitic transformation. **b)** TEM micrograph of WQ sample and **c)** TEM micrograph of FC sample

The A_f of FC, AC and WQ samples were 57 °C, -4 °C and -33 °C, respectively. The cooling rate affects the thermal hysteresis. It was seen that hysteresis (A_f - M_f) increased with decreased cooling rate (Table 1). The highest hysteresis of 86 °C (A_f -M_f) was observed with the lowest cooling rate that is the FC sample.

Table 1. Phase transformation temperatures of 550 °C aged samples

Sample	A_f (°C)	M_f (°C)	A_f - M_f (°C)
WQ	-33	-66	33
AC	-4	-38	34
FC	57	-29	86

3.2 Compression Test

Figure 2 shows the thermal cycling under stress curves of 550°C-WQ and 550°C-FC samples. Selected compressive stresses were applied in austenite and the specimens were cooled down below M_f. Then, it was heated above the A_f to complete the cycle under the applied constant compressive stress. In Figure 2, the transformation strain increased with stress. While transformation strain was 0.29 % under 200 MPa, it increased to 0.86 % under 1000 MPa for 550°C-WQ. Although very close transformation strains were detected at low stress levels, lower transformation strain (0.78 %) was obtained at high stress level (under 1000 MPa) for 550°C-FC [19]. The TTs increased with stress in both cases. M_s (martensite start temperature) and A_f were -37 °C and -22 °C under 400 MPa while they increased to 20 °C and 35 °C under 1000 MPa for 550°C-WQ sample. M_s and A_f were 51 °C and 58 °C under 400 MPa while they increased to 89 °C and 94 °C under 1000 MPa for 550°C-FC sample. The thermal hysteresis was determined as the midpoint of the transformation strain between the cooling and heating curves. The thermal hysteresis was substantially decreased with stress. For 550°C-WQ, the thermal hysteresis was 25 °C under 200 MPa and 18 °C under 1000 MPa. Thermal hysteresis of 550°C-WQ was higher than the thermal hysteresis of 550°C-FC under all stress levels but 1500 MPa. The high irrecoverable strain of 550°C-FC sample under 1500 MPa is responsible for the high temperature hysteresis.

Irrecoverable strain was found to be higher for the FC sample at 1500 MPa stress level. The irrecoverable strain of FC and WQ samples were 0.32 % and 0.23 %, respectively, at 1500 MPa. Additionally, increasing stress from 1000 MPa to 1500MPa elevated the irrecoverable strain from 0.08 % to 0.23 % for 550°C-WQ and from 0.09 % to 0.32 % for 550°C-FC samples.

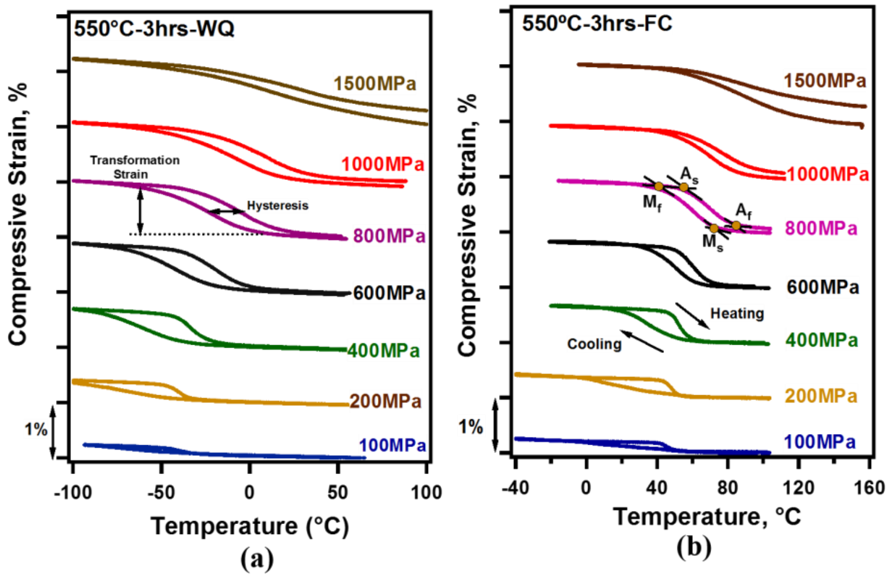

Figure 2. Thermal cycling under compressive stress results of **a)** 550°C-WQ and **b)** 550°C-FC samples after 3 h aging

Figure 3 shows the stress-strain results of 550°C-WQ [20] and 550°C-FC samples. 550°C-WQ sample was loaded to a transformation strain of 2 % at -90 °C (below M_f), and retained strain of 0.5 % was observed upon unloading. After heating the sample above A_f, the retained strain was fully recovered which is called shape memory effect. Superelasticity was observed with applying stress above A_f followed by unloading. The 550°C-WQ sample showed recoverable superelasticity at -30 °C while it had only 0.22 % irrecoverable strain upon loading to 4 % strain till 2000 MPa at 40 °C. Figure 3 demonstrates that Ti-54at.%Ni alloys have very high strength without being subjected to thermomechanical treatments.

Figure 3b shows the superelastic curves of 550°C-FC sample at selected temperatures (50, 70 and 140 °C). While the critical stress which is the stress level for the onset of transformation into martensite was 1030 MPa at 40 °C for 550°C-WQ sample, it was 408 MPa at 50 °C for 550°C-FC sample. When the operating temperature was increased to 70 °C, the critical stress was increased to 669 MPa for 550°C-FC sample. It should also be noted that 550°C-FC sample shows almost full recovery with loading up to 2 % strain at 70 °C. Figure 3 also shows that the temperature influences the critical stress. When the test temperature increases, high critical stress is acquired. The critical stress was 485 MPa at -30 °C while it was 1029 MPa at 40 °C for 550°C-WQ sample.

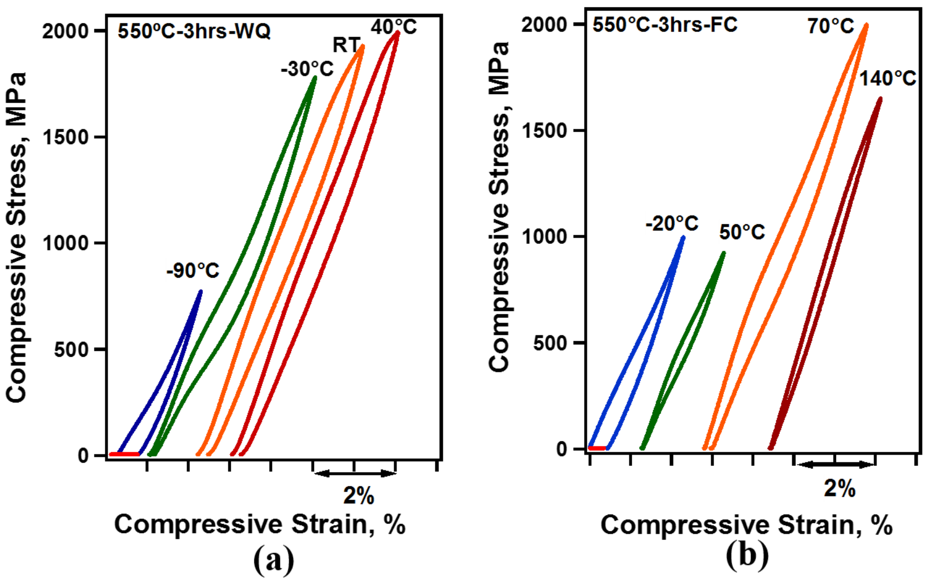

Figure 3. Stress - strain responses of Ti-54at.%Ni for **a)** 550°C-WQ and **b)** 550°C-FC samples

Figure 4a shows the transformation strains as a function of compressive stress obtained from thermal cycling under stress responses for aged samples (Figure 2). Upon application of stress, favored martensite variants can be formed [21]. Initially, the transformation strains increased with stress due to the formation of increased volume fraction of favored martensite variants and then they saturated. In the 550°C-WQ sample, the transformation strain initially increased with stress up to 1000 MPa, and then saturated. The maximum transformation strain of 1.08 % was obtained under 1000 MPa in the 550°C-WQ sample while it was 0.82 % for 550°C-FC sample. During furnace cooling, the specimen was subjected to lower temperature for a long time, resulting in the growth of the precipitates. It should be noted that according to the TEM results shown in Figure 1, the density of precipitates was higher in the 550°C-FC sample compared to 550°C-WQ sample. Due to the high density of precipitates, the distance between the particles was small and could prevent the transformation. Consequently, less transformation strain was observed for FC sample.

Figure 4b shows the effect of cooling rate on thermal hysteresis and irrecoverable strain responses as a function of applied compressive stress of Ti-54at.%Ni alloys. For 550°C-WQ sample, the thermal hysteresis did not change much initially and then decreased rapidly after 400 MPa stress level. After high stress level of 800 MPa, the thermal hysteresis saturated. For 550°C-FC sample, the thermal hysteresis decreased drastically at low stress region, and then saturated till 1000 MPa stress level. After this stress level, hysteresis rapidly increased due to the increased irrecoverable strain.

In Figure 4c, M_s of 550°C-WQ and 550°C-FC samples as a function of applied stress that were obtained from thermal cycling under stress responses shown in Figure 2. The relation between temperature and stress parameters has been expressed in a Clausius-Clapeyron (Cs-Cl) equation that is formulated as [22]

$$\frac{\Delta\sigma}{\Delta T} = -\frac{\Delta H}{T_0 \varepsilon_t} \tag{1}$$

where $\Delta\sigma$ is the difference between critical stresses, ε_t is the transformation strain, ΔH is the transformation enthalpy, ΔT is the temperature difference, and T_0 is the equilibrium temperature. The M_s temperature increases linearly with stress following the Clausius-Clapeyron (Cs-Cl) relationship. Cs-Cl slopes were 13.2 MPa/°C and 16.9 MPa/°C for WQ and FC samples, respectively. The FC sample has higher Cs-Cl slope that can be attributed to the lower transformation strain. In this study, the Cs-Cl slope for martensite was also high when compared to the Cs-Cl slope of near equiatomic NiTi alloys. For comparison, the Cs-Cl slope was 12 MPa/°C in compression for Ni50Ti50 polycrystalline alloys [23]. The increase in M_s temperatures with decreased cooling rate could clearly be seen in the Figure 4c. The M_s temperatures were -41 °C and 55 °C for the WQ and FC samples, respectively under 200 MPa stress. Figure 4c also shows that TTs can be tailored by applying different cooling rates in Ti-54at.%Ni alloys.

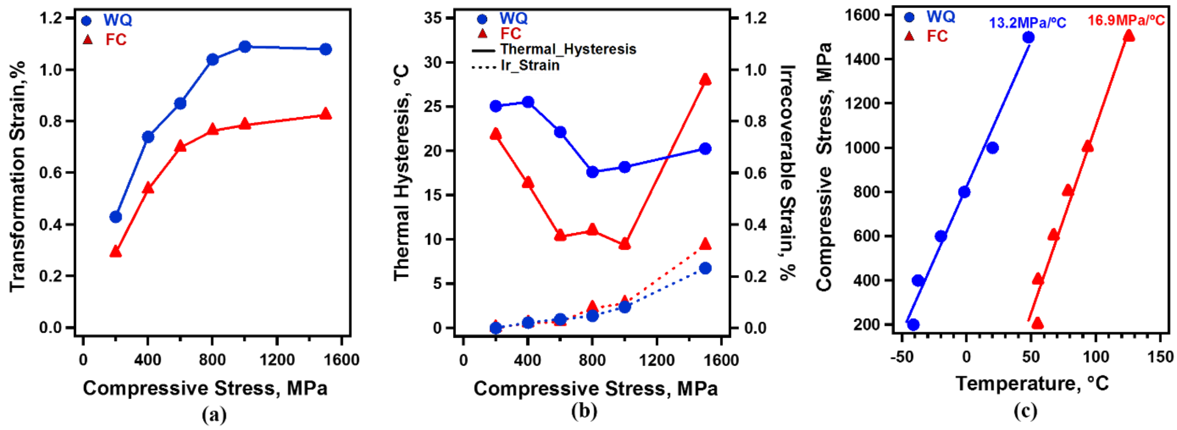

Figure 4. a) Transformation strain, **b)** thermal hysteresis and irrecoverable strain, **c)** M_s values as a function of applied stress.

4. CONCLUSION

This paper investigates the cooling rate effects on the shape memory behavior of Ti-54at.%Ni alloys. It is shown that mechanical and shape memory properties of Ti-54at.%Ni alloys were highly cooling rate and applied stress dependent. A_s transformation temperatures were increased from -39 °C to 32 °C with a decrease in cooling rate after aging at 550 °C. The shape memory behavior of Ti-54at.%Ni alloys were investigated under compression and it has been shown that they have low transformation strain but very high strength, very narrow temperature hysteresis and dramatic change in shape memory behavior with stress. The maximum transformation strain of 1.08 % was obtained under 1000 MPa in the WQ sample while it was 0.82 % for FC sample. Cs-Cl slopes were 13.2 MPa/°C and 16.9 MPa/°C for WQ and FC samples, respectively.

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