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Effect of heat treatment conditions on the phase transformation characteristics of nitinol

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ABSTRACT

Nitinol is the most widely used shape memory alloy in medical applications. In this study, the effect of different heat treatment conditions on the phase transformation characteristics of medical-grade nitinol was investigated. Nickel-rich nitinol wires containing 50.6% nickel with a diameter of 120 μm were used in the experimental studies. The nitinol wires were heat treated for 10 minutes at heat treatment temperatures between 540 and 570 °C. Then, nitinol wires were heat treated at a heat treatment temperature of 550 °C between 8 and 14 minutes. The austenitic and martensitic transition temperatures of these samples were measured using differential scanning calorimetry (DSC). In the experiments with 10 minutes of heat treatment time, transition temperatures decreased, and hysteresis increased with the increase in heat treatment temperature. This is related to the amount of precipitates in the structure. In the experiments carried out at 550 °C, transition temperatures decreased, and hysteresis increased with increasing heat treatment time. Experimental studies showed that the austenite finish (A_f) temperature of all nitinol wire samples was below 37 °C, and they will exhibit superelasticity in the human body.

I. INTRODUCTION

Conventional engineering materials are inadequate for some engineering applications due to their limitations. Their ability to be exposed to high elastic strain without undergoing plastic deformation and to achieve the desired design with temperature change make shape memory alloys (SMAs) a privileged class of materials. The unique properties of SMAs make it possible to create products that cannot be produced with conventional engineering materials.

Since the discovery of martensitic transformation in steels at the end of the nineteenth century, numerous studies have been carried out on this subject. While martensitic transformation is an irreversible process in steels, this process is reversible in SMAs [1]. This allows the emergence of products with innovative designs using SMAs. In 1963, the discovery of the shape memory effect in nitinol, a Ni-Ti alloy, marked a turning point for shape memory alloys [2]. Nitinol's good shape memory effect and remarkable mechanical properties have increased interest in shape memory alloys, leading to more studies in this field and the emergence of industrial applications [3-7]. As with every new material, there were technical problems with nitinol, and attempts were made to eliminate these problems until 1982. At this time, Miyazaki et al. explained the relationship between microstructure and mechanisms, including shape memory effect and superelasticity, at a fundamental level [8]. As a result of understanding these mechanisms, many technical problems of SMAs have been eliminated with the results obtained from various studies [9]. As a result, the use of SMAs in industrial applications has increased rapidly.

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There are three main classes of SMAs: NiTi-based, Fe-based, and Cu-based SMAs. Of these three classes of materials, the most commonly employed is NiTi-based SMAs. Nitinol's one-way and two-way shape memory effect capabilities are critical characteristics that make it stand out. Nitinol's superiority as a shape memory alloy can be attributed to several properties, including its high fatigue resistance, high corrosion resistance, high electrical resistance, high ductility, and very good biocompatibility [10]. The high price of nitinol has encouraged companies to use other shape memory alloys in some applications. Among the SMAs used as alternatives to nitinol, copper-based SMAs stand out [11]. High thermal and electrical conductivity are attractive properties of copper-based SMAs. Compared to nitinol, copper-based SMAs have a narrower temperature hysteresis. This results in phase transitions occurring in a lower temperature range.

Martensitic phase transformation is the phenomenon that enables the unique capabilities of SMAs, like shape memory effect and superelasticity, which have made SMAs a popular choice in various industries. Phase transformation in crystalline materials can occur in two ways; diffusional transformation and diffusionless transformation. The main difference between diffusionless transformation and diffusional transformation is that in diffusionless transformation, atoms do not leave their positions in the crystal structure due to an external factor. In diffusionless transformation crystal structure is altered by a cooperative movement. Also, in diffusional transformation, the transformation takes a longer time to complete [9]. Martensitic phase transformation is a diffusionless phase transformation. Martensitic phase transformation is also divided into two as thermoelastic and non-thermoelastic martensitic transformation. Non-thermoelastic martensitic transformation occurs in irons and steels, and thermoelastic martensitic transformation occurs in SMAs. During the thermoelastic martensitic transformation, the formation and development of martensite plates occur due to the temperature decrease, whereas the temperature increase leads to the shrinkage and disappearance of these plates. The formation, growth, shrinkage, and disappearance of martensite plates occur within a very small temperature range [12, 13].

SMAs have two phases - austenite at high temperatures and martensite at low temperatures. The high-temperature phase possesses high symmetry of crystallographic lattice, and the low-temperature phase possesses low symmetry of the crystallographic lattice. The austenite phase usually has a cubic crystal structure, whereas the martensite phase has an orthorhombic, tetragonal, or monoclinic crystal structure [1].

The distinct characteristics of SMAs are grounded on the reversible transformation between austenite and martensite. Austenite remains stable at high temperatures, while martensite remains stable at low temperatures. If nitinol is in the austenite phase, when cooled, an exothermic reaction will occur, and it will transform into the martensite phase. The process of converting from austenite phase to martensite phase is known as forward transformation. If the material is heated, the alloy undergoes an endothermic reaction to return to the austenite phase. This process is called the reverse transformation [14].

Forward and reverse transformations are completed within a particular temperature interval. These alloys have four distinct temperatures associated with their phase transformations. The initial temperature is known as M_s temperature (martensite start), which indicates the point at which the alloy begins to convert from austenite to martensite. The second temperature is called the M_f temperature (martensite finish), which is the temperature at which the conversion from austenite to martensite is fully accomplished. The third temperature is A_s temperature (austenite start), indicating the onset of the transformation from martensite to austenite. Finally, the fourth temperature is known as A_f temperature (austenite finish), and it marks the point at which the transformation from martensite to austenite reaches completion [1, 15].

SMAs are in the austenite phase above their A_f temperature. When a SMA in the austenite phase is subjected to stress, it undergoes stress-induced martensitic transformation. When stress is removed, it returns to its original shape and austenite phase. This phenomenon is called superelasticity. For the occurrence of shape memory effect in a SMA, it is necessary for the alloy to be in the twinned martensite phase. The material, which is below the A_s temperature, is heated over the A_f temperature. When the temperature of SMA is over the austenite finish temperature, it will be in the austenite phase completely. As a result of this transformation, it will regain its original shape [1, 16].

SMAs can display either shape memory effect, superelasticity, or a combination of both. Below the M_f temperature, the structure is in 100% martensite phase, and above the A_f temperature, the structure is in 100% austenite phase. The material structure contains both phases between the M_f temperature and the A_f temperature. Between M_f and A_f temperatures, both mechanisms are active. Only the shape memory effect occurs if the temperature is below the M_f temperature. If the temperature is over the A_f temperature, the only active mechanism will be superelasticity [16]. The shape memory effect occurs when an alloy deformed below its A_f temperature returns to its original shape upon heating above A_f. On the other hand, superelasticity occurs when an alloy deformed above A_f returns to its original shape upon removal of stress without the need for heating.

Calorimetric and electrical resistivity measurements are used to detect phase transformations in shape memory alloys. Among these methods, the most used method to detect phase changes is differential scanning calorimetry (DSC). DSC is a method used for thermal analysis that helps to determine how the heat capacity of a substance changes as its temperature changes. In this technique, a substance with a known mass is either heated or cooled. The changes in the material's heat capacity are monitored as changes in the heat flow. In the initial stage, the amount of heat energy required to increase the temperature of the reference material is determined. Subsequently, the quantity of heat energy needed to raise the temperature of the reference material is also calculated.

In this study, the effects of heat treatments applied to nitinol at different temperatures and at different times in order to provide shape memory effect and superelasticity, on its phase transition properties were examined using the DSC method.

II. EXPERIMENTAL METHOD

The focus of this research was to examine how nitinol's phase transformation characteristics are affected by various heat treatment conditions. Fort Wayne Metals supplied the nitinol used in the experiments. It is in wire form with a diameter of 120 μm and contains 50.59 nickel (at.%). The austenite finish (A_f) temperature of nitinol is 15 °C. The chemical composition of the wires used in experimental studies is given in Table 1.

Table 1. Chemical composition of the nitinol wires (at.%)

Ni	Ti	O	C	Fe	Cu	Co	Cr	H
50.59	Bal.	0.10	0.12	0.012	0.003	0.001	0.0005	<0.26

Heat treatment conditions

The nitinol wires underwent heat treatment using the Nabertherm N30/65 HA high-temperature oven. Initially, the wires were subjected to heat treatment for a duration of 10 minutes at temperatures of 540, 550, 560, and 570 °C. Subsequently, the wires were heat treated for a range of 8 to 14 minutes at 550 °C. Perkin Elmer DSC8000 was used in DSC analyses to determine the heat-treated samples' martensitic and austenitic transition temperatures. In analyses performed in a nitrogen environment, heating and cooling rates are 5 °C/minute. Each sample was initially heated to 100 °C, and analysis was commenced following 3-minute period of maintaining this temperature. The temperature of sample was brought down to -80 °C and maintained at this temperature for 3 minutes. Then, they were heated again to 100 °C, and the analysis was concluded by maintaining this temperature for 3 minutes. Leica ICC50 HD was employed for taking optical microscope micrographs.

III. RESULTS AND DISCUSSION

Differential scanning calorimetry is the most widely employed method used today to determine the phase transition characteristics of a material. In this study, DSC was employed to determine the phase transformation characteristics of nitinol material that comprises 50.6% nickel.

The DSC analysis result of the nitinol wire supplied by the manufacturer is given in Figure 1 and Table 2. When the calorimetric change is examined, it appears that the endothermic transformation begins at 4.27 °C, the peak is reached at 10.32 °C, and the transformation is completed at 17.13 °C. The endothermic enthalpy of the transformation is 2.5643 J/g. Upon evaluation of the acquired data, one can observe that the austenite start (A_s) temperature is 4.27 °C, where the endothermic behavior begins. Above this temperature, nitinol begins to transition into the austenite phase. 17.13 °C is the austenite finish (A_f) temperature at which endothermic behavior is completed. The NiTi alloy is in a 100% austenite phase at this temperature and above. 14.57 °C is the martensite start temperature (M_s), where exothermic behavior begins, and -5 °C, where exothermic behavior ends, is the martensite finish (M_f) temperature. Below M_f, the NiTi alloy is in the 100% martensite phase.

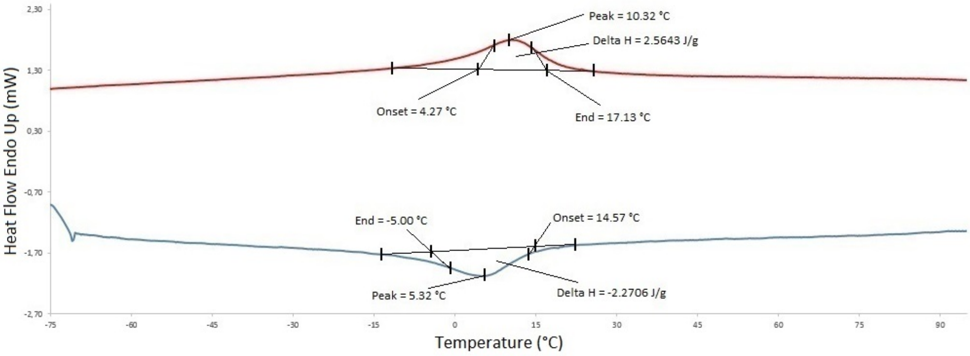

Figure 1. DSC analysis of nitinol wire supplied from the manufacturer

Figure 2 and Table 2 display the outcomes of DSC analyses of nitinol wires heat-treated at different temperatures for 10 minutes. Upon evaluation of the analysis results, it appears that the sample that underwent heat treatment at 540 °C had higher A_s, A_f, M_s, and M_f temperatures than those heat treated at 550, 560, and 570 °C. Furthermore, an increase in heat treatment temperature led to a decline in transition temperatures.

Figure 3 shows the microstructure of the nitinol sample subjected to heat treatment at 540 °C for 10 minutes. Upon inspection of the microstructure, it is evident that the quantity of precipitates present in the structure is high. As the amount of precipitates increase in the nickel-rich nitinol material, the amount of nickel in the matrix decreases, which causes the transition temperatures to increase [17]. Hysteresis increased with increasing heat treatment temperature, and endothermic and exothermic enthalpy showed irregular changes with increasing heat treatment temperature.

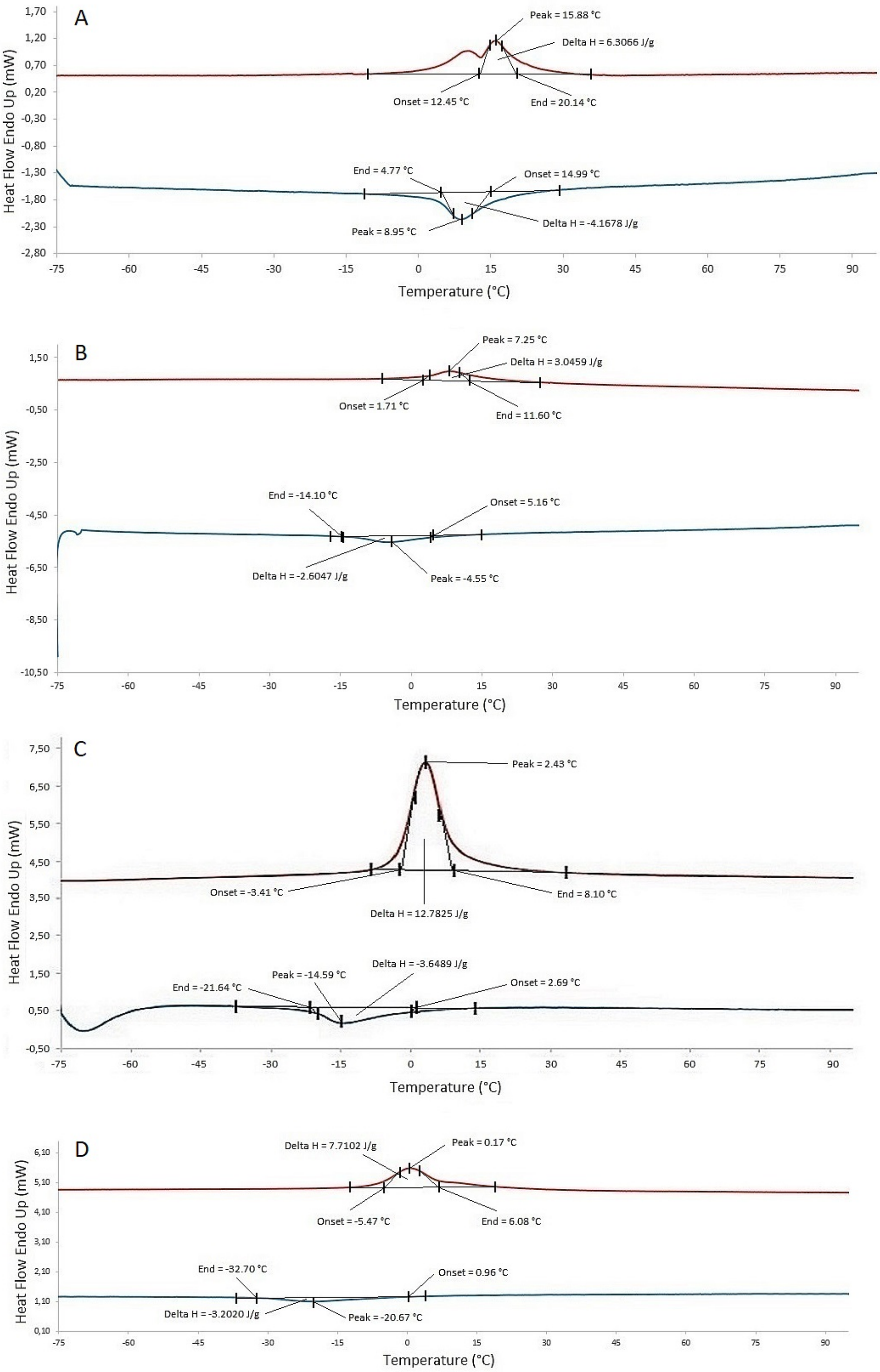

Figure 2. DSC analyzes of samples heat treated for 10 minutes **(a)** 540 °C **(b)** 550 °C **(c)** 560 °C **(d)** 570 °C

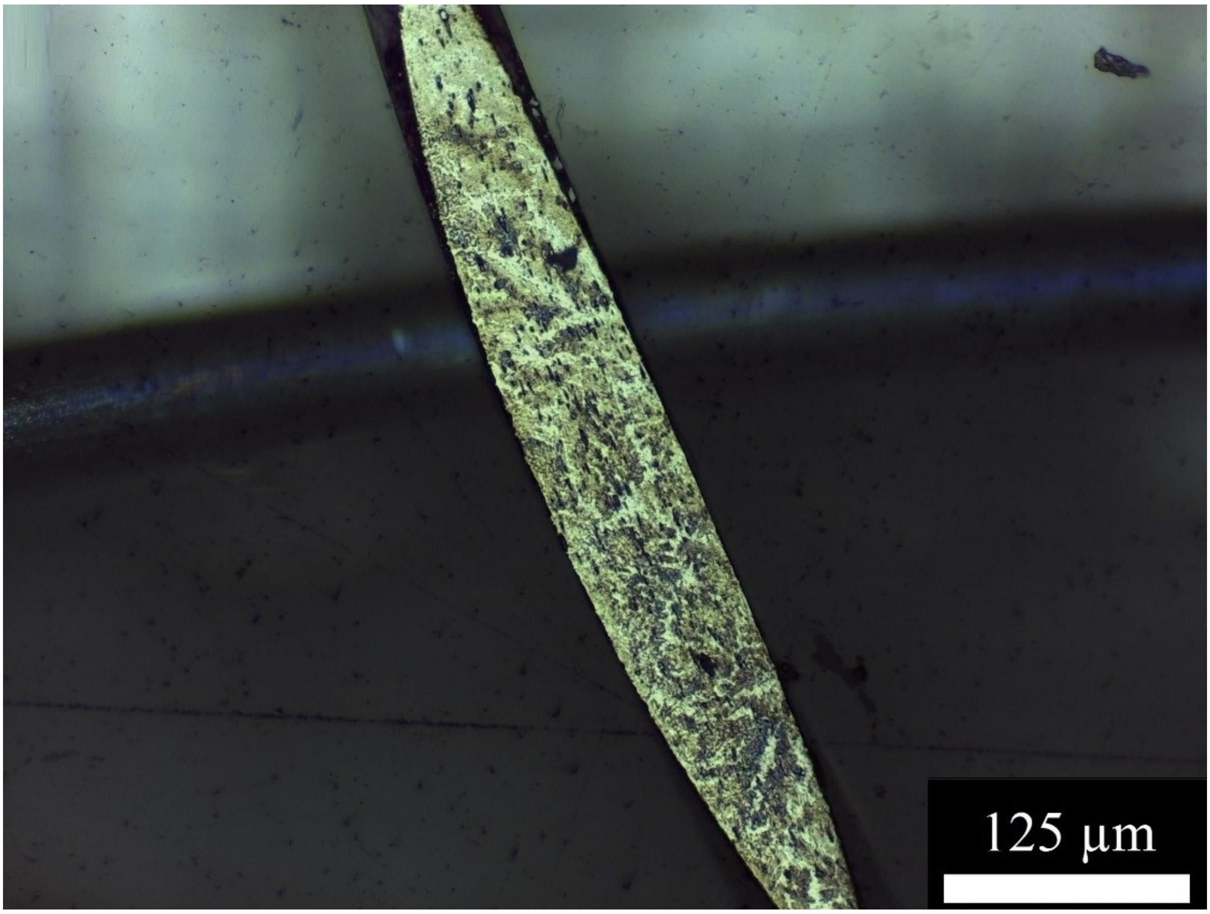

Figure 3. Optical micrograph of nitinol wire heat treated at 540 °C for 10 minutes

Figure 4 and Table 2 display the findings of DSC analyses of nitinol wires that were subjected to heat treatment at 550 °C for varying durations. Upon scrutiny of the analysis results, it was observed that the A_s, A_f, M_s, and M_f temperatures of the sample exposed to a heat treatment process lasting for 8 minutes are higher compared to the samples subjected to longer heat treatments. As the heat treatment time increased, it was noticed that the transition temperatures exhibited a decline. The reduction in transition temperatures as the heat treatment time increased was less rapid compared to the decline observed as a result of raising the temperature. This is because the decrease rate of precipitates occurring in the material structure with increasing heat treatment time is lower than the decrease rate of precipitates formed with increasing heat treatment temperature. As experienced with increasing heat treatment temperature, hysteresis also increased with increasing heat treatment time. Out of the seven distinct heat treatment times tested, the only anomaly was the reduction in hysteresis that occurred when the time was extended from 12 minutes to 13 minutes. When endothermic and exothermic enthalpies were examined, it was evident that increasing the heat treatment time caused irregular changes in the enthalpies.

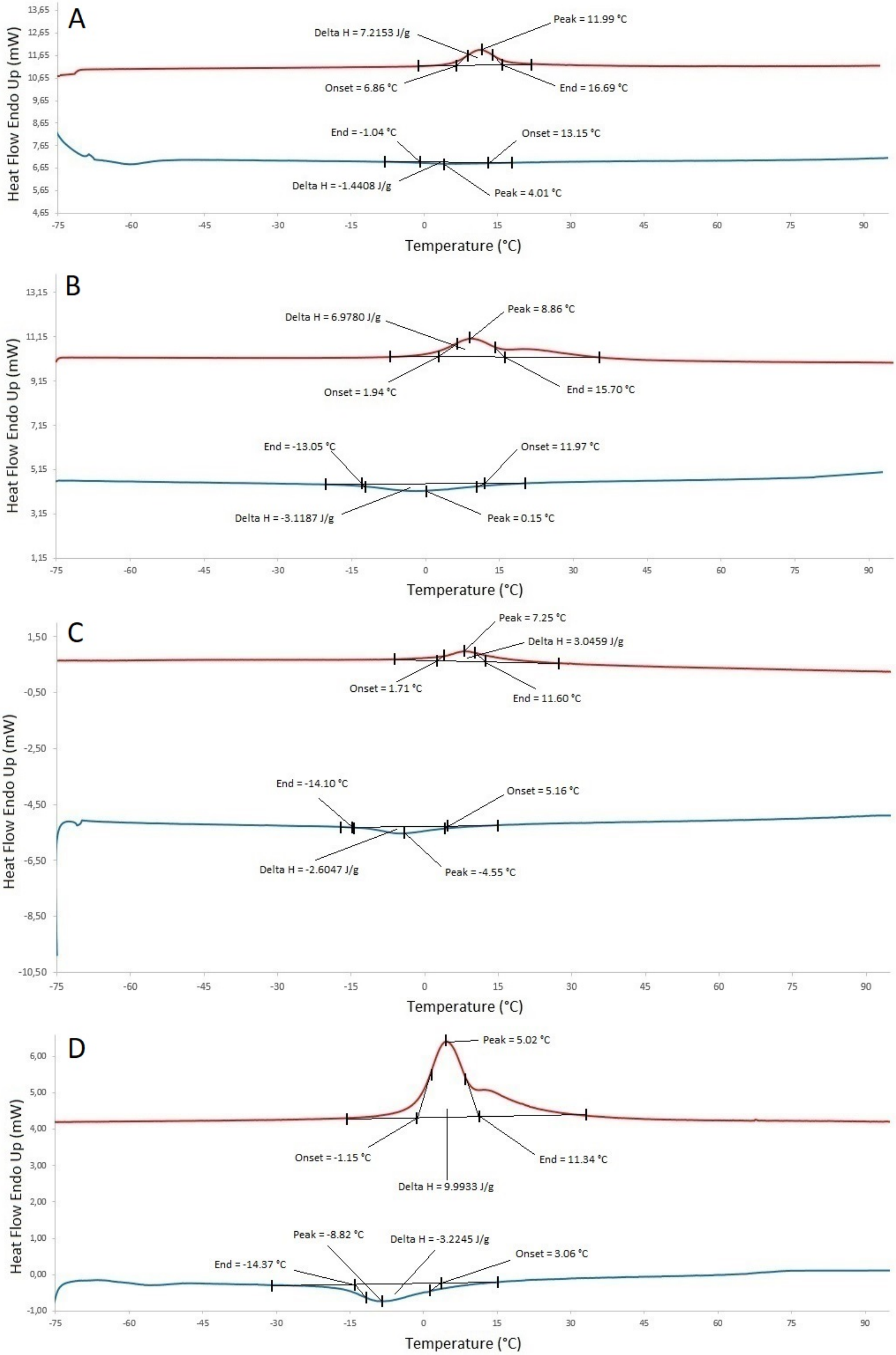

Figure 4. DSC analyzes of samples heat treated at 550 °C **(a)** 8 minutes **(b)** 9 minutes **(c)** 10 minutes **(d)**11 minutes

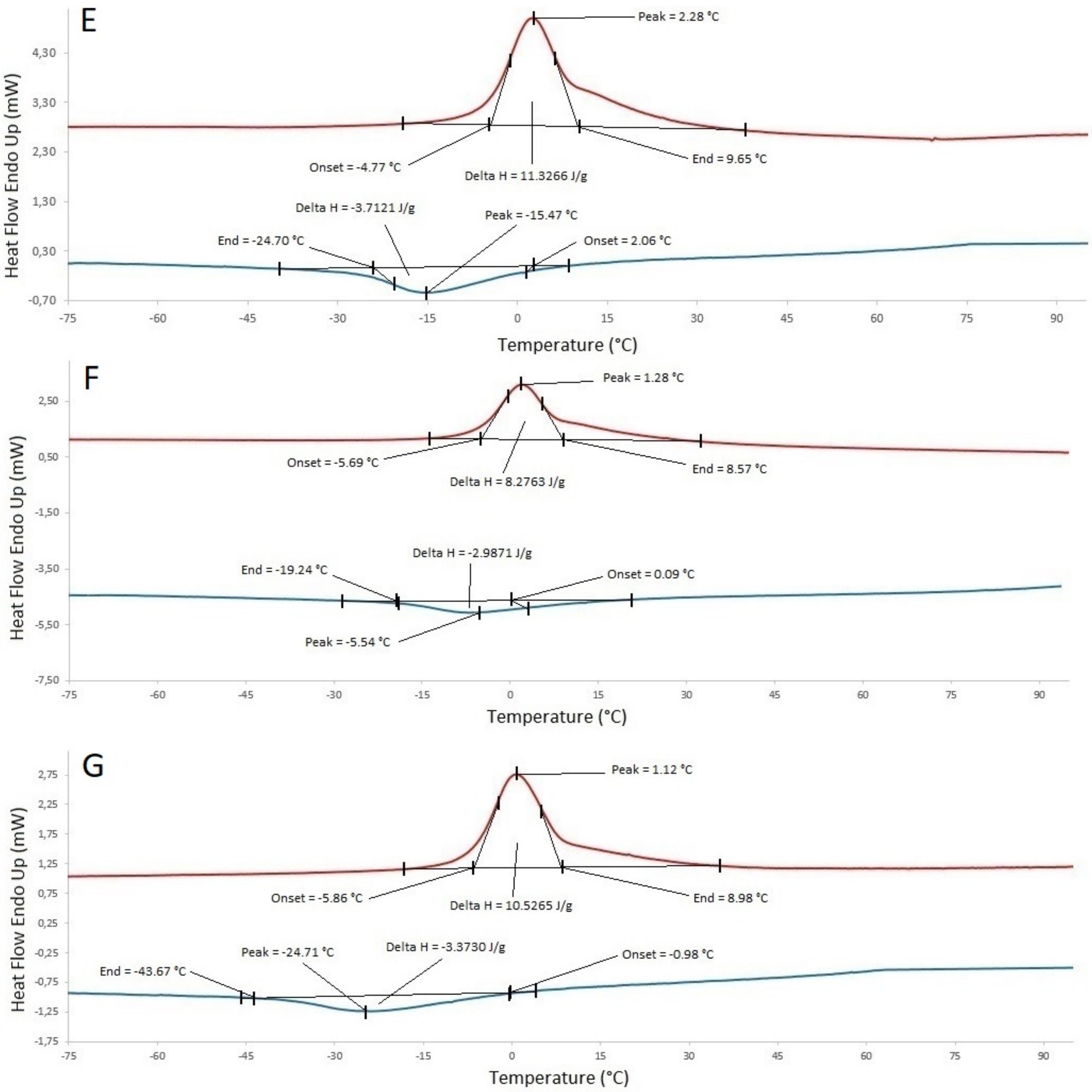

Figure 4. (Continuum) DSC analyzes of samples heat treated at 550 °C **(e)** 12 minutes **(f)** 13 minutes **(g)** 14 minutes

Table 2. DSC analysis results of nitinol wires subjected to heat treatment under different heat treatment conditions

Heat Tretament Condition	**A_f** *(° C)*	**A_s** *(° C)*	**Endo. Enthalpy** *(J/g)*	**M_s** *(° C)*	**M_f** *(° C)*	**Exo. Enthalpy** *(J/g)*	**Hysteresis A_{peak} - M_{peak}** *(° C)*
Non-heat treated	17.13	4.27	2.56	14.57	-5.00	-2.27	5.00
540 °C/10 min.	20.14	12.45	6.30	14.99	4.77	-4.16	6.93
550 °C/10 min.	11.60	1.71	3.04	5.16	-14.10	-2.60	11.80
560 °C/10 min.	8.10	-3.41	12.78	2.69	-21.64	-3.64	17.02
570 °C /10 min.	6.08	-5.47	7.71	0.96	-32.70	-3.20	20.84
550 °C / 8 min.	16.69	6.86	7.21	13.15	-1.04	-1.44	7.98
550 °C / 9 min.	15.70	1.94	6.97	11.97	-13.05	-3.11	8.71
550 °C / 10 min.	11.60	1.71	3.04	5.16	-14.10	-2.60	11.80
550 °C / 11 min.	11.34	-1.15	9.99	3.06	-14.37	-3.22	13.84
550 °C / 12 min.	9.65	-4.77	11.32	2.06	-24.70	-3.71	17.75
550 °C / 13 min.	8,57	-5,69	8,27	0,09	-19,24	-2,98	6,82
550 °C / 14 min.	8,98	-5,86	10,52	-0,98	-43,67	-3,37	25,83

IV. CONCLUSION

In this study, the effect of diffetent heat treatment conditions on the phase transition characteristics of nitinol, the most commonly employed SMA in medical applications, was investigated. Initially, nickel-rich nitinol wires containing 50.6% nickel were heat treated at 540, 550, 560 and 570 °C for 10 minutes. Then, the nitinol wires were subjected to heat treatments at a constant temperature of 550 °C, but for varying durations of 8, 9, 10, 11, 12, 13, and 14 minutes.

After analyzing the samples using DSC, it was found that the sample exposed to heat treatment at 540 °C for 10 minutes had higher transition temperatures compared to the samples heat treated at 550, 560, and 570 °C. As the heat treatment temperature increased, it was observed that the transition temperatures decreased while the hysteresis increased. The increase in hysteresis resulted from a reduction in the austenitic transition temperatures, and a greater decrease in the martensitic transition temperatures, both directly caused by the elevated heat treatment temperature.

In the DSC analysis of the samples obtained in the heat treatments using a constant temperature of 550 °C, the data revealed that the transition temperatures of the nitinol wire subjected to heat treatment for 8 minutes were comperatively higher than the samples that underwent heat treatment for a prolonged period. As the heat treatment time increased, there was a decline in the transition temperatures and an increase in hysteresis. Similar to the effect of temperature increase, hysteresis increased as the decrease in martensitic transition temperatures was greater than the decrease in austenitic transition temperatures with the increase in heat treatment time.

The experimental studies revealed that the A_f transition temperatures of all samples were below 37 °C as a result of all the heat treatments performed. This shows that the nitinol wire will be 100% austenite at body temperature and will exhibit superelasticity.

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