Exploiting heat treatment effects on SMAs macro and microscopic properties in developing fire protection devices

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Abstract. Ni-Ti shape memory alloys (SMAs) are intelligent alloys which demonstrate unique properties, such as shape memory effect, two-way shape memory effect, super-elasticity and vibration damping which, accompanied by good processability, excellent corrosion resistance and biocompatibility as well as fair wear resistance and cyclic stability, enabled the development of important industrial applications (such as sensors, actuators, fasteners, couplings and valves), medical applications (such as stents, bone implants, orthodontic archwires, minimal invasive surgical equipment) as well as environmental health and safety devices (anti-seismic dampers, fire safety devices). The phase transitions in Ni-Ti SMAs are strongly influenced by processing methods, chemical compositions and thermomechanical history. This paper presents a study of the effects of heat treatment on the mechanical and thermal properties of commercial Ni-Ti shape memory alloy (SMA). The experimental work involved subjecting a SMA rod to heat-treatment consisting in heating up to 500°C, 10 minutes-maintaining and water quenching. Mechanical properties were highlighted by micro-hardness tests while thermal characteristics were emphasized by differential scanning calorimetry (DSC). The presence of chemical composition fluctuations was checked by X-ray energy dispersive spectroscopy performed with an EDAX Bruker analyzer.

1. Introduction
SMAs are a group of alloys with unique properties to return to their predefined form after heating or unloading [1, 2]. This behavior is associated with a thermoelastic martensitic phase transformation from a parent phase called austenite (A) to a phase called martensite (M). Commercial SMAs can be classified into: NiTi-based [3], Cu-based (ternary CuZnAl, CuAlNi and CuAlMn) [4], Fe-based [5] and NiMn based [6]. Although NiTi alloys have many common properties with other SMAs: one-way shape memory effect (OWSME), superelasticity (SE) [7], two-way shape memory effect memory effect (TWSME) or temperature memory effect (TME) [8], they also show many other good properties that are unique, when compared to other SMAs. Among these properties we mention low elastic anisotropy [3], very good biocompatibility and corrosion resistance [9, 10]. Due to these special properties, NiTi SMAs have been used in a wide range of applications in various fields such as medicine, aerospace industry, industrial application and, recently, architecture application (NiTi honeycomb or cellular structures) [10, 11, 12]. In NiTi SMAs the reverse martensitic transformation results between monoclinic B19' type crystal structure -M and cubic B2 type crystal structure - A [13, 14]. In some cases, after NiTi cooling, it is possible to observe the formation of an intermediate rhombohedral phase, between A and M, called R phase. The occurrence of the R phase was associated with the presence of Ti₃Ni₄ precipitates [3]. The unique behavior of NiTi alloys with near equiatomic compositions has made this material to be used for safety and security as well as for electronic applications [4]. Thermal and electrical actuators are successfully used for various engineering applications [15] due to their potential for detection and / or actuation. Special interest was given to applications for fire protection that materialized in fire alarms or fire sprinklers [16].
Martensitic transformation and shape memory effect in NiTi alloys are strongly influenced by chemical composition, thermal treatment temperatures and their thermomechanical history [17, 18]. In the case of heat treatments, the temperature of the treatment is very important. Studies have shown that annealing above 600 °C reduces the maximum recovery stress while annealing below 400 °C significantly enhances superelasticity [17]. The present paper aims to experimentally investigate the influence of heat treatment on the critical temperatures of reverse martensitic transformation ($A_s$ – austenite start temperature, $A_{50}$ – temperature corresponding to the formation of 50% transformed phase and $A_f$ – austenite finish temperature) and direct martensitic transformation ($M_s$ – martensite start temperature, $M_{50}$ - temperature corresponding to the formation of 50% transformed phase and $M_f$ – martensite finish temperature) as well as the influence of heat treatment on the mechanical properties of the studied NiTi alloy.

2. Materials and methods

A Ti-rich SMA with the chemical composition Ni$_{40.35}$Ti$_{30.65}$ (at %), 4 mm-diameter rods was purchased from Saes Getters. Some samples were subjected to a heat-treatment consisting of heating up to 500°C, 10 minutes-maintaining, immediately followed by water quenching. Fragments from heat treated and untreated samples were cut, weighing typically 30 mg, for differential scanning calorimetry (DSC). The preparation of the specimens complies with the ASTM F2004-05 standard. The calorimetric measurement were made using a DSC F3 Maia provided by NETZSCH, with sensitivity: <1 W, temperature accuracy: 0.1 K and enthalpy accuracy—generally <1%, calibrated with Bi, In, Sn, and Zn standards. The temperature program comprised: a heating from room temperature (RT) to 150°C, with a heating rate = 20 °C/min; cooling to RT with a cooling rate = 10 °C /min. With Proteus software the reverse and direct martensitic transformation temperatures were identified ($A_s$, $A_{50}$, $A_f$, $M_s$, $M_{50}$ and $M_f$), using tangent method. The amount of dissipated/ absorbed heat ($\Delta H$) was determined using a sigmoidal baseline.

Vickers micro-hardness values were determined by using a CV 400 DM CV Instruments Namicon equipment. Micro-hardness tests were performed with a 100 gf force and 10 s dwell time. Each hardness test was repeated three times and the average value was taken as the final result.

The presence of chemical composition fluctuations on the heat treated and untreated specimen was checked by X-ray energy dispersive spectroscopy with a scanning electron microscopy (SEM – VegaTescan LMH II) equipped with an EDAX Bruker analyzer.

3. Results

3.1. DSC results

The heat flow variation during a heating-cooling cycle, of the NiTi SMA in untreated and heat treated condition, are illustrated in Figure 1. It is obvious that the thermodynamic response of heat treated specimen is very much larger than that of the specimen in initial condition. It can be seen that heat treatment caused a shift to higher temperatures of the endothermic peak ascribed to reverse martensitic transformation during heating with approx. 30°C. On the other hand, the exothermic peak attributed to direct martensitic transformation shows a decrease of the transformation temperature, with approximately 2°C. Such increases in the direct martensitic transformation temperatures can be caused by the precipitate coarsening and (or) grain growth [19]. In Ti-rich SMAs, Ti$_2$Ni$_2$O and Ti$_2$Ni phase precipitates can be present [3, 20]. It is known that heat treatment can stimulate the nucleation and growth of Ti$_2$Ni precipitates [21].
Figure 1. DSC thermogram recorded during a heating-cooling cycle of the untreated and heat treated NiTi SMA specimens.

Figure 2. Evaluation of the DSC thermograms recorded during a heating-cooling cycle of the (a) untreated and (b) heat treated NiTi SMA specimens.
Figure 2 presents the DSC thermograms recorded during a heating-cooling cycle of the (a) untreated and (b) heat treated specimen, evaluated with Proteus software. It can be observed that not only the temperature of the exothermic and endothermic peaks have shifted, but also the quantity of absorbed or dissipated heat for the treated specimen is significantly higher. Therefore, during heating, the amount of the absorbed heat during the reverse martensitic transformation for the treated specimen is approx. 5.5 times higher than for untreated specimen. On the other hand, during cooling, the amount of the dissipated heat is about 18 times higher, according to the data shown in Table 1. It can be concluded that the annealing treatment followed by water cooling in enhanced the martensitic transformation.

| Specimen | $A_s$ °C | $A_{S0}$ °C | $A_t$ °C | $\Delta H$ kJ/kg | $M_s$ °C | $M_{S0}$ °C | $M_t$ °C | $\Delta H$ kJ/kg |
|----------|----------|-------------|----------|-------------------|---------|-------------|---------|------------------|
| untreated | 55,5     | 79,1        | 98,4     | -5,510            | 67,5    | 56,5        | 34,6    | 1,68             |
| heat treated | 91,5     | 109,1       | 117,6    | -29,28            | 65,9    | 57,1        | 48,4    | 29,69            |

### 3.2 Micro-hardness results

In order to highlight the effect of thermal treatment on the mechanical properties, micro-hardness tests were performed on the untreated and heat treated specimens, the results being summarized in Table 2. It is known that in Ni-rich SMAs heat treatments cause the occurrence of Ti$_2$Ni$_4$, Ti$_2$Ni$_3$ and TiNi$_3$ precipitates, resulting in the change of micro-hardness value [22, 23]. For the Ti-rich SMA studied, it can be noticed that heat treatment caused a decrease of the micro-hardness with about 73 Vickers units. The decrease of the hardness can be attributed to decreased volume fraction of precipitates or the overaging and coarsening of precipitates [22].

| Specimen | Test 1 | Test 2 | Test 3 | Average |
|----------|--------|--------|--------|---------|
| NiTi untreated | 325,3  | 328,7  | 324,2  | 326,1   |
| NiTi treated  | 255,2  | 253,4  | 255,5  | 253,7   |

From the above DSC results, it is obvious that a less amount of martensite retransformed to parent phase (austenite) during the heating of untreated specimen, Figure 2(a) as compared to heat treated one, Figure 2(b). It follows that heat treated specimen contained an almost five time larger amount of martensite that retransformed to austenite during heating. Since thermoelastic martensite is softer than austenite [1] it is obvious that untreated specimen, containing less martensite and more austenite, must have a larger hardness than untreated one. So, the average hardness values can be associated with DSC response during heating.

### 3.3 EDS mapping

The flatness of DSC maxima can be caused by stabilization phenomena, enhanced by precipitation [14, 24]. In NiTi SMAs, precipitation phenomena usually change the chemical composition of the matrix, causing a decrease of critical transformation temperatures with the increase of Ni content [25]. Consequently, the increase of $M_s$ critical temperature with several degrees can be associated with a decrease of Ni content, in the matrix. In order to verify this assumption, EDS mappings were recorded on the two specimens under study. The results are illustrated in Figure 3.

In Figure 3(a) Ti is the predominant element, justifying the Ti-rich character of the alloy under study. Yet, there are no large areas that can be ascribed to a single element, since Ni and Ti dissolved each other in order to form a single solid solution.
Figure 3. EDS elemental mappings of (a) untreated and (b) heat treated specimens.

After heat treatment, the formation of Ni-rich precipitates is noticeable since this element obviously occupies larger areas in Figure 3 (b) than in Figure 3(a). The formation of Ni-rich precipitates depletes the nickel amount of the matrix, thus justifying the increase of $M_s$, critical transformation temperature.

4. Summary and conclusions
A commercial Ni$_{49.35}$Ti$_{50.65}$ (at%) alloy, under the form of 4 mm-diameter rods, was studied in untreated and heat treated condition. The heat treatment consisted heating up to 500°C, 10 minutes-maintaining followed by water quenching. The untreated and heat treated specimen were analyzed using DSC, micro-hardness tests and EDS elemental mapping.

After heat treatment, the transformation temperatures for the direct ($M_s$, $M_{50}$ and $M_f$) and reverse martensitic transformation ($A_s$, $A_{50}$ and $A_f$), were shifted to higher values. The amounts of absorbed and dissipated heat were significantly higher, as a consequence of heat treatment. Micro-hardness tests highlighted the decrease of Vickers value, the cause being the higher amount of martensite in heat treated specimen. EDS mapping revealed the formation of Ni-rich precipitates, after heat treatment. This Ni-depletion of the matrix represents the cause of the increase of $M_s$, critical transformation temperature, at heat treated specimen. These results proved that, by means of a simple heat treatment, one can increase both critical transformation temperatures and the amount of heat exchange. These both features can be fructified in the development of high-temperature executive elements of fire protection devices with fast operative response.

5. References
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