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The effect of aging time on at.%$Ti_{59.27}Ni_{40.73}$ shape memory alloy

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ABSTRACT

Shape memory alloys are frequently used in many areas. However, the working conditions affect material properties after a certain time. In this study, temperature-induced transformation on a TiNi shape memory alloy was investigated by aging experiments at 400 °C for different durations. The aged samples were examined by DSC, EDC, XRD and SEM methods. The results were compared and analyzed.

1. Introduction

Shape memory alloys (SMAs) have been widely studied because of their unusual properties. Engineering and medical applications of SMAs have attracted research efforts to reveal their mechanical responses [1,2]. SMAs are characterized by austenite (high temperature) and martensite (low temperature) phases. The characteristic transformation temperatures are austenite phase start and finish (A_s, A_f) and martensite phase start and finish (M_s, M_f) temperatures. These temperatures can be changed through heat, aging or stress treatments [3–6]. There is a range of transition temperatures over which temperature-induced phase transformation occurs. Heating an object that appears to be permanently deformed at low temperature in its martensitic phase above the transition temperature will cause it to return to its original shape in the austenite phase due to solid state phase transformation from martensitic back to austenite. In the literature, various SMAs have been produced, characterized, and used. Among these, nickel-titanium (TiNi)-based SMAs have been utilized in many different applications. First discovered in the 1960s, TiNi SMAs led to the growth of interest in the shape memory phenomenon [7]. Then, the properties of nitinol were documented by a series of extensive reports. TiNi SMAs are ordered, intermetallic compounds based on an equiatomic composition. A TiNi phase diagram shows that this compound exists in a stable phase at room temperature [7].

In TiNi SMAs that are in equilibrium with each other, three solid phases occur; $TiNi_3$, Ti_2Ni_3, and Ti_3Ni_4 [8–12]. $TiNi_3$ and Ti_2Ni_3 cannot transform the B2 matrix due to their incompatibility [5,11]. TiNi SMAs are commonly used in medical products, such as stents and orthodontic archwires. Generally, complex thermomechanical treatments are applied to their microstructures to attain suitable properties; e.g., thermal SMAs and superelasticity. Contrary to the general view, the Ni to Ti ratio does not change these properties. Heat treatment affects austenite → martensite stress transformation. Austenite and martensite peaks are the temperatures at which the peak of the differential scanning calorimetry (DSC) curve is obtained. In the heat treatment procedure, the reverse and forward temperatures of transforming austenite to martensite and martensite to austenite are controlled by the rate of quenching, exposure time, and heat treatment temperature to develop and produce SMAs with the desired character.

SMAs are one of the unusual materials we often encounter in our daily lives. These materials are utilized in areas that require precision in the design and use. Although SMAs can also be produced through magnetic field-, electricity- and stress-induced transformation, thermally induced transformation types are most widely used [13,14]. Such SMAs generally operate in hot environments. Although a high temperature is necessary for the operation of these alloys, this also causes the deterioration of the material. Thus, an operation temperature of less than 100 °C is usually chosen for TiNi SMAs but this limits applications requiring high temperatures [15]. Therefore, in this study, TiNi alloys were investigated at low transformation temperatures but under high temperature operation conditions. In the experiments, first, the samples were aged at a high temperature for different aging durations taking into consideration the transformation temperatures of TiNi SMAs; then, the variations in the material properties were examined using different methods.

2. Experimental

In the experiments, a binary titanium-rich commercial polycrystalline TiNi wire of 0.8 mm in diameter was used. The chemical composition of the wire was analyzed by an energy dispersive X-ray microanalyzer. The values obtained are given in Table 1.

In order to obtain the samples, the wire was sliced into six equal pieces. All pieces were cleaned by alcohol to remove organic or

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Table 1
Results of chemical analysis of the TiNi wire.

Element	wt. %	at. %	e/a
Ti	54.27	59.27	6.44
Ni	45.73	40.73	

inorganic particles which can affect experimental results. The experiments were undertaken at 400 °C using five different aging times, namely 1 h, 2 h, 3 h, 4 h and 5 h. The as-received sample was also analyzed before treatment for comparison purposes. Each sample was aged in a muffle furnace at 400 °C and cooled to room temperature on special on high heat-resistant refractory material plate. Then, the specimens calorimetric measurements were analyzed by DSC with a heating-cooling rate of 25 °C/min for each sample. An X-ray diffraction (XRD) analysis was carried out to determine the crystal structure using CuKα radiation at room temperature by a Rigaku device at a scanning speed of 5 deg/min. The samples were etched in a solution with the composition of 10%HF-60%HNO_3-30%CH_3COOH to observe the microstructure. Thereafter, the metallographic morphologies of the samples were examined and the SEM micrographs of the aged microstructures were obtained.

3. Results

The transformation temperatures of SMAs are key parameters in revealing their working conditions. The results of DSC help to observe the solid state transitions in samples. Endothermic and exothermic energy shifts indicate the austenite and martensite phases, respectively. The enthalpy, entropy and transformation temperature values of the aged and as-received samples were determined by DSC measurements (Table 2). The equilibrium temperature between the martensite and austenite phases was determined by the following relationship as described by Salzbrenner and Cohen [16];

$$T_0 = \frac{1}{2}(M_s + A_f) \quad (1)$$

In order to see the transition between austenite and martensite phases, the comparison graphs are presented in Figs. 1 and 2, respectively. In both graphs, hour "0″ indicates the as-received sample to reveal the exact changes in the transformation temperature compared to the samples aged over different durations. Both graphs for Figs. 1 and 2 have the notable variance for 1 h and that major shifts indicate a stress relief on the material [17]. The plot trends reache the regime after following first aging hours. It was observed that after 2 h of aging the samples austenite and martensite transformation temperatures increased with a low percentage. In general, the transformation temperature variance was found around 4%.

The hysteresis loop between the start and finish temperatures at hours 1 and 2 is observed to widen, and after hour 3, it gets closer to the curve. The enthalpy and entropy graphs in Figs. 3 and 4 also support this phenomenon. Generally, an R phase, which is the transition between the austenite and martensite phases, also occurs in TiNi alloys. This R phase is observed as a result of endothermic reactions between

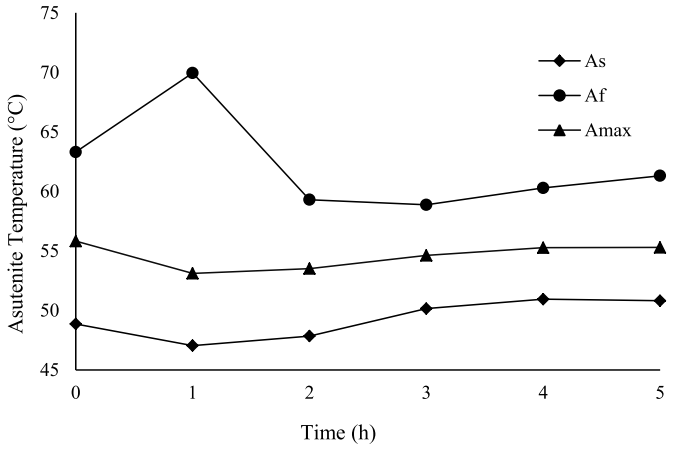

Fig. 1. Variations in austenite phase transformation temperatures due to aging.

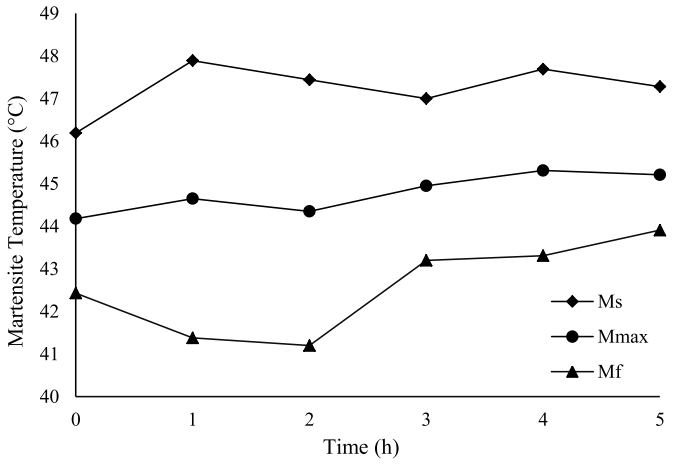

Fig. 2. Variations in martensite phase transformation temperatures due to aging.

the parent and product phases [18–20]. However, in the DSC curves obtained in this study, the R phase was not observed. The DSC plots for all the samples are presented in Fig. 5.

The XRD curves are presented as a single graph in Fig. 6. The diffraction peaks belonging to Ti_2Ni dominate the plots. B19′ and B2 phases also appear around 29° and 61° 2-theta degree. The phases are in good agreement with the reports in the literature [21,22]. The intensity of the peaks around 29.5° increases with the increased aging time. However, new peaks are not observed except for the intensity of peaks. This was also confirmed by surface morphological observations.

The microstructural characteristics of the samples were investigated by SEM, and the results are presented in Fig. 7. The martensitic plates covered the surface as expected. As reported in the literature, the acicular structure was found on the surface of an austenitic TiNi sample [23]. The plates had an acicular structure with inhomogeneous grain

Table 2
The kinematic parameters of the samples.

	A_s (°C)	A_f (°C)	*Amax* (°C)	T_0 (°C)	$\Delta H_{M\to A}$ (J/g)	$\Delta S_{M\to A}$ (J/g°C)	M_s (°C)	*Mmax* (°C)	M_f (°C)	$\Delta H_{A\to M}$ (J/g)	$\Delta S_{A\to M}$ (J/g°C)
As received	48.86	63.31	55.82	54.750	3.75	0.068	46.19	44.18	42.43	−0.91	−0.016
400 °C for 1 h	47.04	69.95	53.11	58.920	5.61	0.095	47.89	44.65	41.38	−2.67	−0.045
400 °C for 2 h	47.84	59.30	53.51	53.370	4.93	0.092	47.44	44.35	41.20	−3.36	−0.062
400 °C for 3 h	50.15	58.87	54.62	52.935	4.09	0.077	47.00	44.95	43.20	−3.75	−0.070
400 °C for 4 h	50.94	60.29	55.27	53.990	4.27	0.079	47.69	45.31	43.31	−3.30	−0.061
400 °C for 5 h	50.81	61.31	55.29	54.295	4.64	0.085	47.28	45.21	43.91	−3.39	−0.062