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INVESTIGATION OF THERMOMECHANICAL BEHAVIORS OF THE AGED ALLOYS $Ti_{55.68}Ni_{44.32}$

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ABSTRACT

TiNi alloys are used in places requiring precision jobs for the last few decades. Thermally induced shape memory alloys such as TiNi are exposed to temperature cycle during the implementation, and the temperature causes an artificial aging effect on the alloy. In this study, we aimed at investigating whether the aging effects depend on time and temperatures for TiNi alloys. Seven waiting periods with three different temperature values were applied. Totally 22 experiments were conducted, and the results of the transformation temperatures were obtained for each experiment. Time depended results, especially for 200 °C samples exhibited more stable state than 300 and 400 °C. When the temperature values are considered, a remarkable increase is observed after 200 °C.

Keywords: Shape memory alloy, TiNi, Aging, Martensitic transformation

1. INTRODUCTION

The shape memory alloys (SMAs) take place in our daily life, whether we are aware or not. They are used in many sectors for descends. Due to the factors such as long life cycle, biocompatibility and precise transformation temperatures etc., TiNi alloys are still the most commonly used SMA types compared with many different alternative alloy materials which perform shape memory effect (SME). Ti and Ni elements exhibit good matrix features in alloys. Also, they have different crystalline structures and are found fcc and hcp structure for Ni and Ti respectively at room temperature [1]. Ni and Ti-based alternative shape memory alloys were studied and they performed extremely distinctive features like ferromagnetic and high temperature martensitic transformations [2-6]. However, when they are combined in alloy, they exhibit ultimate features as SMA. Furthermore, TiNi SMA has been studied with many alternative alloy- combinations and different addition elements with different fractions, and they make remarkable changes in the mechanics and thermomechanical behaviours [7-10]. As seen in other SMAs, diffusionless in a first-order reversible solid state phase transformation is observed in TiNi SMAs alloys [11]. TiNi alloys undergo the transformation in two and three step transformations between phases. The B2 phase is consisted of CsCl structure and called as parent phase (austenite). Intermediate R-phase (R) which is rhombohedral and B19′phase which is monoclinic can be shown as martensite phase [12-15]. Three phases perform several transformations in various sequences between the B2↔R, B2↔B19′and R↔B19′ transformations [16, 17].

The SMAs used in different sectors require diversity in material characters. Hence, considering the different operating scenario, the widespread problem is related to the thermal conditions. SMAs are affected firstly by the thermal conditions because SMA's mechanical cycles generally depend on the thermal changes. Moreover, the thermal operations are directly used in SMA manufacturing operations and training. So, the effect of the exposure on heat is of great importance. The aging treatment is an artificial process on material for faster material reactions without waiting. However, it can generate

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different phenomenon like a big amount of precipitates unlike the real state. Also, the aging process may be realized in use in different conditions by the end user. If the SMA part encounters the unplanned medium conditions, the systems can be a fault and that causes serious problems. The stability of the martensite transformation temperatures makes sense, otherwise its use will be limited. High temperature in the medium can be heat treatment for SMA. Because the fundamentality of the SMA is the relationship between atoms, some displacements between atoms disrupt the neighbourhood of atoms and stacking orders by the high temperature relatively to transformation temperature. The temperature under normal conditions also creates an aging effect, but it depends on the type of the material. For displacement of the atoms, it needs a big amount of endothermic process considering the material. Otherwise, the material will not react at all. In our study, we aimed at finding out the martensitic transformation temperature changes under the different aging conditions on $Ti_{55.68}Ni_{44.32}$ (at.%) alloy. We used different aging temperatures and durations for aging process. The transformation temperature results of the alloys were presented and discussed.

2. MATERIAL AND METHOD

A commercial polycrystalline wire TiNi alloy which is 0.7 mm in diameter was used in the experiments. The wire was cut into 22 equal pieces to apply different aging conditions in the experiments. 21 different tests were formed using 3 different temperature grades and 3 different waiting times. The sample which is not aged, was homogenised at 900 °C. To compare the aged results with just homogenous sample, additionally one piece was used as received. The samples were aged in an atmospheric environment by an electric resistance furnace and then cooled down to the room temperature. The aged samples martensitic transformation temperatures were measured by using differential scanning calorimetry (DSC) with the heating-cooling rate of 25°C/min. As well as, the samples were applied fine polishing and etched with 10%HF-60%HNO3-30%CH3COOH solutions for observation of microstructure of alloys by optical microscopy. The alloy chemical compositions were analysed by energy dispersive X-ray microanalyzer (EDX), and the results were presented at Table 1.

Table 1. Specimen chemical composition results

Element	Weight%	Atomic%
Ti	50.62	55.68
Ni	49.38	44.32

3. RESULTS

22 pieces TiNi SMA was measured by DSC to define the martensitic transformation temperature changes under the different aging conditions. The martensitic start temperature (Ms) and the martensitic finish temperature (Mf) values were obtained from the peak curve on the exothermic process line at the DSC plots and austenite start (As) with austenite finish (Af) temperatures from the peak curve on the endothermic process similarly. Also top peaks temperature values of austenite (Amax) and martensitic (Mmax) with thermal equilibrium (T0) was obtained. The peak zones indicate the energy transfer during the solid-state phase transition, and that proves the SME intensity. The all measured DSC data was depicted at Table 2, and a narrow transformations temperature hysteresis was observed.

In aging, the experiments were conducted under three different temperatures such as 200 °C, 300°C and 400 °C. In each temperature, samples were held in furnace at various waiting periods from 0.5h to 48h. In analysing, all samples exhibited characteristic austenite and martensite transformation. Individually, graphs for time depending are presented in Figure 1- Figure 3.

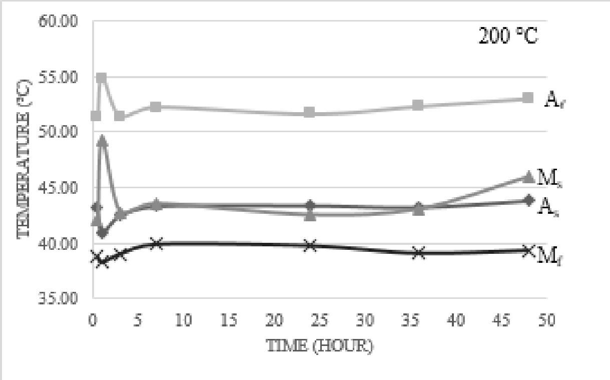


Figure 1. Comparison of transformation temperatures for aged samples at 200 °C

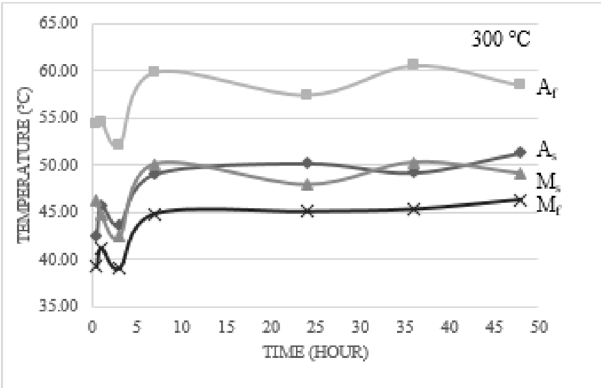


Figure 2. Comparison of transformation temperatures for aged samples at 300 °C.

Table 2. Aged TiNi samples martensite transformation analyze results

Item	As (C°)	Af (C°)	Amax (C°)	$\Delta H_{M\rightarrow A}$ (J.g-1)	T0 (C°)	Ms (C°)	Mf (C°)	Mmax (C°)	$\Delta H_{M\rightarrow A}$ (J.g-1)
Homogenized	43.94	52.26	48.32	-2.59	48.85	45.43	40.33	42.73	1.71
200 C° - 0.5h	43.23	51.39	47.12	-5.43	46.74	42.09	38.76	40.45	3.21
200 C° - 1h	40.93	54.86	47.08	-3.96	50.90	49.19	38.31	46.94	1.49
200 C° - 3h	42.5	51.42	46.84	-3.79	47.11	42.79	39.05	40.93	1.74
200 C° - 7h	43.36	52.26	47.43	-4.40	38.58	43.52	39.91	41.59	2.09
200 C° - 24h	43.42	51.64	47.08	-3.45	47.08	42.51	39.77	41.01	2.23
200 C° - 36h	43.26	52.31	47.55	-6.30	41.07	43.04	39.10	41.08	3.11
200 C° - 48h	43.87	52.99	48.05	-3.81	49.47	45.94	39.36	39.14	1.93
300 C° - 0.5h	42.54	54.36	47.92	-3.41	50.28	46.2	39.21	43.03	1.32
300 C° - 1h	45.73	54.60	49.94	-4.49	49.68	44.76	41.22	43.01	2.31
300 C° - 3h	43.63	52.04	47.59	-5.04	47.21	42.38	39.10	40.73	2.73
300 C° - 7h	49.02	59.84	53.69	-4.92	54.97	50.10	44.81	47.18	1.9
300 C° - 24h	50.17	57.38	53.59	-6.24	52.65	47.92	45.05	46.5	3.75
300 C° - 36h	49.16	60.55	53.97	-4.53	55.42	50.28	45.3	47.51	1.72
300 C° - 48h	51.3	58.42	54.58	-5.55	53.76	49.09	46.3	47.68	3.71
400 C° - 0.5h	47.64	55.46	51.25	-4.36	50.89	46.32	42.63	44.46	2.86
400 C° - 1h	48.06	55.5	51.35	-3.57	50.82	46.14	42.7	44.35	3.2
400 C° - 3h	46.29	57.41	51.36	-4.09	53.00	48.59	42.78	45.45	2.72
400 C° - 7h	49.33	56.51	51.8	-4.36	51.44	46.37	42.61	44.59	3.2
400 C° - 24h	47.78	55.58	51.72	-5.25	50.68	45.77	42.17	44.07	3.98
400 C° - 36h	49.3	56.93	52.88	-5.58	51.94	46.95	43.42	45.17	4.63
400 C° - 48h	49.14	58.59	53.97	-5.96	54.41	50.22	43.68	45.81	4.29

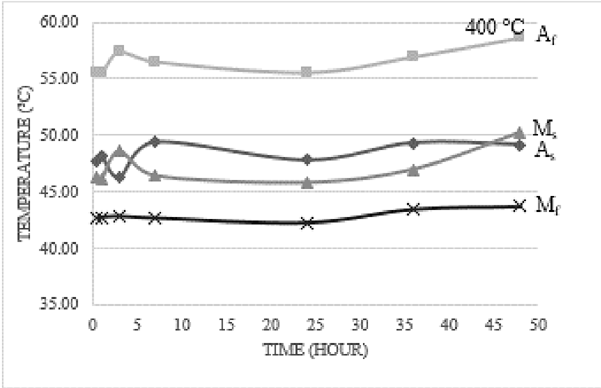


Figure 3. Comparison of transformation temperatures for aged samples at 400 °C.

In Figure 1, the curves for 200 °C show scarcely any temperature changes between the different waiting periods. However, between 0.5-3 h, a great activity due to the residual stress releases. That action is also observed in Figure 2 and Figure 3. When the time depended results were examined, it was reported that the first 3 hours has a great importance for the alloy to reach the stable state. After temperature changes finish at the end of three hours, the transformation temperatures did not exhibit massive amount-deviations except for after 36 hours. The precipitation replaces in more homogeneously in grain, and that provides more self-consistent structure for alloy use. When experiments are examined from the view-point of the temperature depend, the averages of the transition temperatures were calculated and presented in Figure4.

In Figure 4. Temperature depended curves in the graph tend to be similar in character. Homogenized sample values stand higher than 200 °C samples. 300 °C samples transformation temperatures increase around 5 °C and perform parallel values with 400 °C ones. The decrease of the temperatures in 200 °C compared with the homogenized sample can be ascribed to the residual stress release [18]. During the aging, internal stresses occurred on the precipitation dispersion, and that causes volume friction between the precipitates. Therefore, Ti content increases in the matrix, and that causes the increasing of the transformation temperatures [19]. That stress effects can also be seen easily in the enthalpy graph in Figure 5. A regular increase of the enthalpy was seen.

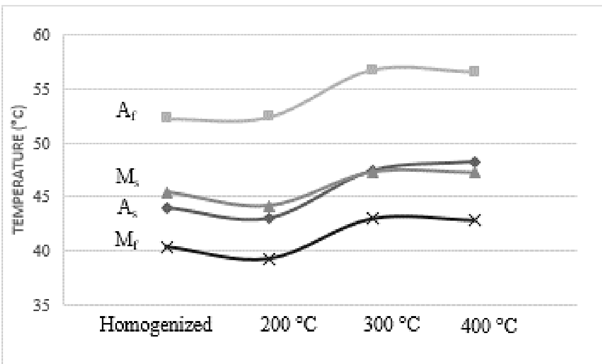


Figure 4. Comparison of mean values of the transformation temperatures.

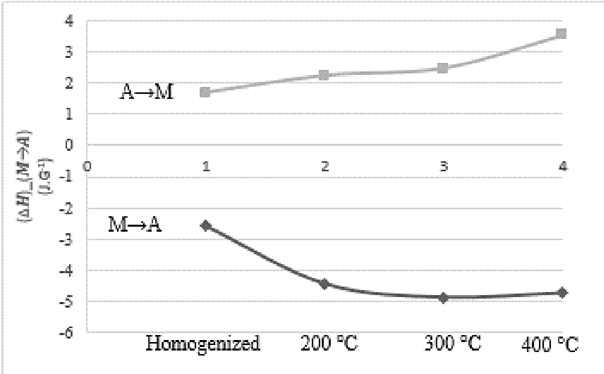
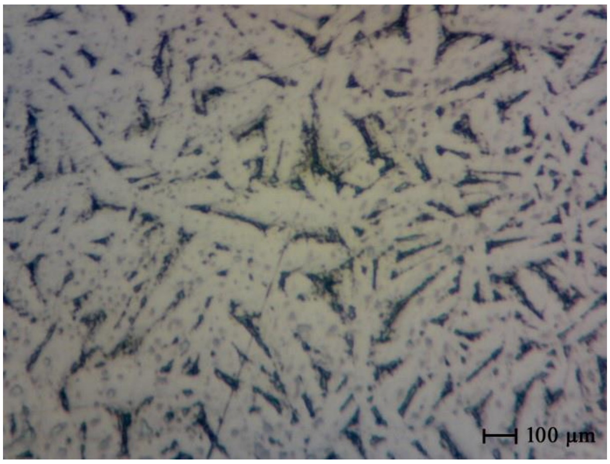


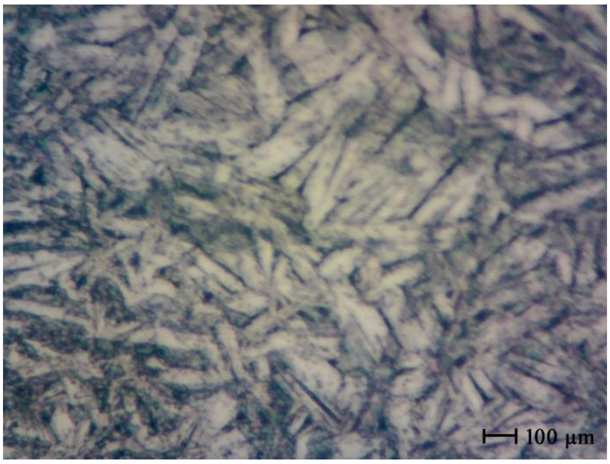
Figure 5. Comparison of mean values of the enthalpies.

That stress effects can also be seen easily in the enthalpy graph in Figure 2. It is seen that the increase of the enthalpy is regular. In ΔH, M→A curve shows the stable state at 300 - 400 °C range. However, it wasn't observed in ΔH A→M curve.

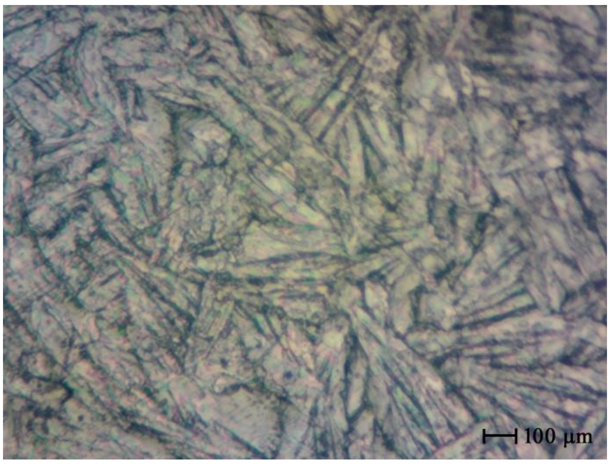
In Figure 6, the optic micrograph images were presented. In homogenized sample and 200 °C samples, the grains are apparently smaller than the others. The grains' size enlarges depending on the aging conditions. This aspect is also reported in the study of Wang et. Al [20].



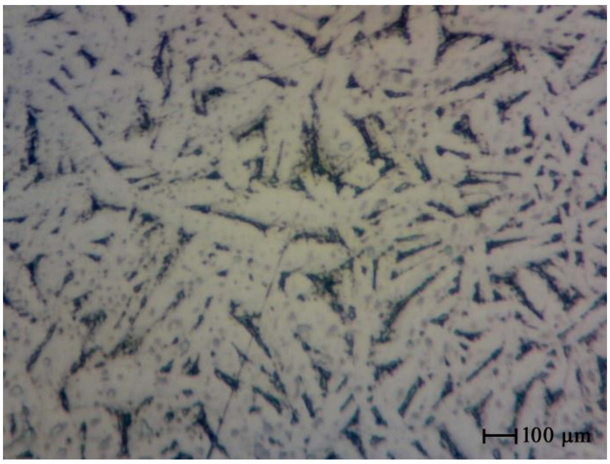
(a) Homogenized



(b) 200 °C – 36 Hours



(c) 300 °C – 36 Hours



(d) 400 °C – 36 Hours

Figure 6. Comparison of mean values of the transformation temperatures.

4. CONCLUSION

In this study, we studied the aging effects on $Ti_{55.68}Ni_{44.32}$ shape memory alloy wire. The experiments were made with 3 different temperatures and 7 different waiting periods. All samples exhibited martensite transformation. Results show us that just the homogenized samples have residual stress, and that makes structure unstable state. The temperatures 200 °C and above 200 °C with over than 3 hours release the existing stress and make the alloy more stable regarding the martensitic transformation temperatures in time depended conditions. When the results examined considering the aging temperature side, the aged samples at 300 °C after 200°C affected the sample transformation temperatures to upward. However, that tendency does not take long and the transformation temperature was thermodynamically stable. The aging with high temperature arranged the precipitations and increased Ti content fractions in the matrix, and that caused a regular increase in the transformation temperatures.

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