Two-Step Martensitic Transformation in an Aged $\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}$ High Temperature Shape Memory Alloys

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Multi-step martensitic transformation in an aged Ni-rich binary NiTi shape memory alloy is considered as usual behavior during transformation from austenite to martensite phase; from (austenite) $B2$ to R -phase and then R -phase to $B19'$ (monoclinic). However, for equi-atomic NiTi-based quaternary high temperature shape memory alloy, two-step martensitic transformation was detected for the first time. The $\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}$ high temperature shape memory alloys were investigated for the evolution of transformation temperatures at aging temperature of 550°C and 700°C . Aging at 550°C for 6 h resulted in significant reduction of phase transformation temperatures. During forward transformation from austenite to martensite, two-step martensitic transformation $B2 \rightarrow R$ and $R \rightarrow B19'$ (orthorhombic) was observed. By aging the alloy at 700°C for 6 h, no significant effect was found on phase transition behavior and transformation temperatures.

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1. Introduction

The most commercialized shape memory alloy (SMA) till date is considered to be NiTi due to its excellent functional and mechanical properties. The solubility of Ni increases in the intermetallic NiTi phase by increasing the temperature. The phase diagram for Ni-rich NiTi alloys suggests a two phase region below 600°C ; NiTi and Ni_3Ti . Upon solution annealing followed by water quenching, the two-phase region transforms to a single phase microstructure, intermetallic NiTi. By aging the single phase NiTi, precipitates of type Ni_4Ti_3 are observed [1].

In Ni-rich NiTi, the phase transition in martensitic transformation is different, depending on its composition and thermomechanical treatments. On cooling, the solution treated Ni-rich NiTi alloys transform from $B2$ austenite phase to $B19'$ monoclinic martensite phase. By aging the Ni-rich NiTi alloys, precipitates of type Ni_4Ti_3 are made in the $B2$ matrix, which change the transformation behavior from one step into two steps. In two-step transformation, the transformation takes place from $B2$ to R -phase and then from R -phase to $B19'$ martensite phase [2]. The change in transition behavior from one-step to two-step in NiTi SMAs can be explained by the fact that both the R -phase and $B19'$ are martensite phases. Further, the presence of coherent precipitates produces enough resistance to larger lattice deformations corresponding to the formation

of $B19'$ martensite phase. On the other hand, the R -phase yields a considerably smaller lattice deformation and it is not affected by the formation of precipitates [3]. Consequently, the formation of precipitates enhances the formation of R -phase in the matrix and changes the transformation behavior from $B2 \rightarrow B19'$ into $B2 \rightarrow R \rightarrow B19'$. This behavior for Ni-rich NiTi binary alloys are quite usual and researched extensively [4, 5].

However, the two-step martensitic transformation behavior in the equi-atomic NiTi-based quaternary high temperature SMAs was studied for the first time. In the present research, $\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}$ high temperature SMA was aged at temperature of 550°C and 700°C to investigate the effect of precipitation on phase transition behavior and transformation temperatures.

2. Material processing and characterization

An alloy in which composition of $\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}$ (at.%) is nominal was prepared by vacuum arc melting process. The cast button was homogenized at 950°C for 2 h in a sealed quartz tube to avoid oxidation and then quenched in cold water. Using wire electrical discharge machine (EDM), the homogenized button was sliced into 0.4 mm thick strips and then the strips were cold rolled to a thickness of 0.3 mm. Samples of dimensions $2 \times 2 \times 0.3 \text{ mm}^3$ for evolution of transformation temperatures were machined by wire EDM. All the samples were solution treated at 900°C for 1 h followed by quenching in cold water. The resulting samples were then subjected to aging process at 550°C and 700°C for 6 h. Differential scanning calorimetry (DSC) was carried out to investigate the transformation temperatures of the aged samples under stress-free conditions at a heating/cooling rate of $5^\circ\text{C}/\text{min}$.

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3. Results and discussion. Effect of aging on phase transition behavior and transformation temperatures

To investigate the phase transition behavior and transformation temperatures, DSC analysis was carried out. Figure 1 demonstrates the DSC heating and cooling cycles of the samples aged at 550 °C and 700 °C for 6 h. Phase transformation temperatures (M_s — martensite start, M_p — martensite peak, M_f — martensite finish, R_p — R -phase peak, A_s — austenite start, A_p — austenite peak, and A_f — austenite finish) of both samples were found by the tangent intersection method as shown in the same figure.

Fig. 1. DSC curves showing the transformation behavior of the samples aged at 550 °C and 700 °C for 6 h.

The transformation temperatures calculated from Fig. 1 were summarized in Table to compare their transformation temperatures. The transformation peaks resulting from the DSC analysis of 700 °C-aged sample were properly developed and easy to calculate exactly their transformation temperatures. On the other hand, the transformation peaks of 550 °C-aged sample were broadened and difficult to calculate M_f and A_s and hence not given in Table. Moreover, the transformation temperatures given for 550 °C-aged sample is significantly lower than the corresponding transformation temperature resulted by 700 °C-aged sample.

TABLE

Transformation temperatures for the samples aged at 550 °C and 700 °C for 6 h under stress free condition.

Aging temp. [°C]	Transformation temp. [°C]						
	M_s	M_p	M_f	A_s	A_p	A_f	R_p
550	136	127			154	162	154
700	183	176	169	189	195	202	

From the above observations it was noticed that aging at 550 °C resulted in significant decrease of transformation temperatures. The decrease in transformation temperatures was attributed to the formation of Ni-lean Ti_2Pd and TiPdCu precipitates as discussed in our previous work [6, 7]. Due to formation of these precipitates,

the Ni concentration in the matrix increased and resulted in decrease of transformation temperature [8].

From Fig. 1 it was also observed for the 700 °C-aged sample that during cooling, the transformation was completed in one step; from austenite $B2$ to martensite $B19$, whereas in case of 550 °C-aged sample, transformation completed in two steps. Here it is difficult to identify the exact nature of each martensite peak. However this phenomenon can be explained possibly by three processes: (1) different stress states near and away from the precipitates [4], (2) two-step transformation from $B2$ to R -phase and then R -phase to $B19$ or some other intermediate martensitic phase [9] and (3) chemical inhomogeneity near the precipitates as compared to the bulk matrix [2].

Now we consider the existence of different stress states near and away from the precipitates. In this case, upon cooling the transformation starts in the stressed region near the precipitates when the temperature comes closer to the alloy martensitic transformation. According to the Clausius–Clapeyron equation, presence of stresses in the alloy always enhance the martensitic transformation temperature [10]. When martensite forms, the stress field is relaxed near the precipitates and further martensite transformation stops temporarily. Upon further cooling, when the temperature drops to stress-free martensite start temperature, the martensitic transformation again starts. In such type of transformation, the initial martensite peak appears with greater transformation heat released as compared to the final martensite peak [9]. However the two-step martensitic transformation observed in Fig. 1 cannot be explained by the first process, because the transformation heat released during first peak is lower than the following peak. Now we consider the second process to explain the two-step martensitic transformation by $B2 \rightarrow R$ and then $R \rightarrow B19$. In this transformation, the transformation heat corresponding to $B2 \rightarrow R$ peak is always smaller than the following $R \rightarrow B19$ peak [11]. Here the morphology of the DSC scans given in Fig. 1 is consistent with the explanation given by Ren et al. [11], thus it may be suggested that the two-step martensitic transformation was attributed to the formation of intermediate R -phase.

4. Conclusion

From the above results and discussion, the following key results were concluded:

1. Formation of precipitates at aging temperature of 550 °C for 6 h resulted in reduction of transformation temperatures; M_s and A_f decreased by 34 °C and 30 °C, respectively.

2. Aging at 550 °C for 6 h, also caused to change the transformation behavior from one step ($B2 \rightarrow B19$) to two steps ($B2 \rightarrow R \rightarrow B19$).

3. No significant effect was found when the same alloy was aged at 700 °C for 6 h.

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