Aging-induced complex transformation behavior of martensite in Ni$_{57.5}$Mn$_{17.5}$Ga$_{25}$ shape memory alloy

V.V. Khovailo, R. Kainuma, T. Abe, K. Oikawa, and T. Takagi

1 National Institute of Advanced Industrial Science and Technology, Tohoku Center, Sendai 983-8551, Japan
2 Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
3 Institute of Fluid Science, Tohoku University, Sendai 980-8577, Japan

Ni$_{57.5}$Mn$_{17.5}$Ga$_{25}$ shape memory alloy exhibits a complex transformation behavior, appearing after aging. Aging in the austenitic state resulted in an ordinary decrease of the martensitic transformation temperature. Contrary to this, aging in the martensitic state brought about unusual features of the martensitic transformation observed so far only in Ni-Ti shape memory alloys.

I. INTRODUCTION

Early studies of ferromagnetic shape memory alloys Ni-Mn-Ga have already indicated that the martensitic transformation temperature is sensitive to composition and can be observed in a wide temperature range. Further systematic studies of composition dependencies of the martensitic transformation temperature $T_m$ showed that there is a relation between $T_m$ and the electron concentration $e/a$, and that $T_m$ increases with increasing $e/a$.\(^1\) These observations have provoked studies of Ni-Mn-Ga aimed at the development of new high-temperature shape memory alloys system\(^5\)...

Recent experimental investigations\(^6\) were devoted to the study of Ni-Mn-Ga alloys with deficiency in Ga, Ni$_{51.2}$Mn$_{31.1}$Ga$_{17.7}$ and Ni$_{54.1}$Mn$_{25.3}$Ga$_{21}$, which undergo a martensitic transformation at $M_s = 423$ K and 533 K, respectively. A high stability of martensitic transformation temperature during thermocycling and a well-defined shape memory effect\(^6\) were reported for the studied alloys. The influence of aging on martensitic transformation of Ni-Mn-Ga high-temperature shape memory alloys has not been studied so far. This aspect, however, is important for potential applications of these materials.

Besides Ni-Mn-Ga alloys with deficit in Ga, a martensitic transformation could occur at high temperatures in the alloys with Ni excess, because substitution of Mn or Ga for Ni results in an increase of electron concentration $e/a$. Our study of Ni$_{50+x}$Mn$_{25-x}$Ga$_{25}$ ($4 \leq x \leq 9.75$) has shown that this is indeed the case and in the alloys with $x \geq 7.5$ the martensitic transformation is observed at temperatures above 530 K\(^6\). In the present work we report on the influence of aging on martensitic transformation in a Ni$_{57.5}$Mn$_{17.5}$Ga$_{25}$ composition. The obtained experimental results indicated a drastic difference between aging performed in the martensitic and austenitic state and showed unusual aging-induced features of martensitic transformation, observed so far only in Ni-Ti shape memory alloys.

II. EXPERIMENTAL DETAILS

Ingots of the above mentioned nominal composition were prepared by a conventional arc-melting method. The ingots were annealed at 1100 K for 777.6 ks and quenched in water. Optical observation of annealed samples showed no trace of a secondary phase. EDX characterization confirmed that real composition of the samples was close to the nominal one. Samples for calorimetric measurements were cut from the middle part of the ingots. Characteristic temperatures of direct and reverse martensitic transformations were determined from the results of differential scanning calorimetry (DSC) measurements, performed with a heating/cooling rate 10 K/min.

An example of DSC scans performed on the samples before aging procedures is shown in Fig. 1. Typical feature of all the samples studied is the absence of a well-defined anomaly at the austenite start temperature $A_s$. The DSC heating curve smoothly deviates from the baseline, reaches a maximum at $A_p = 544$ K and exhibits a marked change in the slope at austenite finish temperature $A_f = 547$ K. Subsequent cooling from the austenitic state results in martensitic transformation with characteristic temperatures martensite start $M_s = 512$ K and martensite finish $M_f = 502$ K. It is worth noting that for the samples studied the exothermic peak has a complex character, which could be attributed to two (or more) martensitic phases forming upon cooling from the high-temperature state.

III. RESULTS AND DISCUSSION

A. Aging in the austenitic state

Aging in the austenitic state was performed at a temperature $T_{aging} = 560$ K. Since the aging did not affect significantly $M_s$ and $M_f$ temperatures, shown in Fig. 2 are DSC curves of the aged samples measured at heating immediately after each thermal treatments. These results evidence that aging in the austenitic state results in a marked decrease of the reverse martensitic transformation temperature (Fig. 3). As evident from Fig. 3, the $A_p$ temperature decreases with aging time approximately.
exponentially and for aging time $t \geq 432$ ks it is equal to 520 K, a 20 K lower than that observed in the samples before aging.

In our opinion there are several scenarios, which could explain the decrease of $A_p$ after aging in the austenitic state. Considering that the samples after water quenching have a high concentration of vacancies, which is enhanced by a significant deviation of the studied composition from stoichiometry, the high density of vacancies can actually produce a permanent strain in the samples. In this sense the high density of vacancies is equivalent to the deformation, leading to an increase in the reverse martensitic transformation temperature. In this case one can expect to observe a decrease in the direct martensitic transformation temperature as well. Our experimental results have shown, however, that the $M_s$ temperature is not affected by the aging.

Besides this possibility, the decrease of $A_p$ can be explained as caused by aging-induced changes in the thermodynamical properties of the martensitic phase in such a way that the crystal structure of martensite forming upon martensitic transformation in the aged samples differs from that in the as-quenched samples. Formation of the austenite-aging martensite having another crystal structure may result in the alteration of characteristic temperatures and the temperature hysteresis of the martensitic transformation, i.e. the features which indeed have been observed in the samples after aging.

B. Aging in the martensitic state

Aging of Ni$_{57.5}$Mn$_{17.5}$Ga$_{25}$ performed in the martensitic state at $T_{\text{aging}} = 528$ K revealed a typical influence of aging of a shape memory material in the martensitic state, i.e. an increase in the reverse martensitic transformation temperature (stabilization of martensite) (Fig. 4). The rate of martensite aging depends on the reduced martensitic transformation temperature $T_m = M_s/T_m$, where $M_s$ is martensite start temperature, $T_m$ is the melting temperature of an alloy. Assuming that Ni$_{57.5}$Mn$_{17.5}$Ga$_{25}$ has a melting temperature $T_m \sim 1400$ K, we obtain $T_m \sim 0.37$ which should results in a considerable aging rate. It is interesting to note that for Ni-Mn-Ga alloys the reduced martensitic transformation temperature is very similar to that for Au-Cd and, therefore, a strong aging effect could be expected even at room temperature. In fact, this has already been observed experimentally in stoichiometric and off-stoichiometric compositions of Ni-Mn-Ga alloys.

The most interesting and significant finding of our study is the appearance of an additional DSC peak on...
heating curves of the samples aged in the martensitic state at \( T_{\text{aging}} = 528 \text{ K} \) (Fig. 5). This well-defined two-step martensitic transformation has been observed only for the reverse martensitic transformation; neither martensite start temperature \( M_s \) nor the shape of the exothermic peak changed significantly after the aging procedure. As far as we are aware, such an unusual phenomenon, appearing after aging in the martensitic state, has been observed so far only in Ni-Ti shape memory alloys. This complex transformation behavior in Ni-Ti has attracted a considerable interest and its mechanism is still not understood clearly (see Refs. 16, 17, 18, 19 and references therein).

Our preliminary study of aging-induced two-step martensitic transformation in \( \text{Ni}_{57.5}\text{Mn}_{17.5}\text{Ga}_{25} \) revealed that this phenomenon depends both on aging time and aging temperature. The additional peak, appearing at \( T_I \approx 520 \text{ K} \) after aging in the martensitic state at \( T_{\text{aging}} = 528 \text{ K} \), is already clearly seen after aging time \( t = 18 \text{ ks} \), although it becomes the most pronounced in the sample aged for 36 ks. Further increase in the aging time leads to a progressive degradation of the peak, which transforms to a weak anomaly in the samples aged for \( t \geq 216 \text{ ks} \) (Fig. 5). In order to check whether the complex transformation behavior will appear after aging at a temperature below \( T_I \), a \( \text{Ni}_{57.5}\text{Mn}_{17.5}\text{Ga}_{25} \) sample was subjected to aging at \( T = 473 \text{ K} \) for 190.8 ks. DSC measurement of this sample showed that after this thermal treatment the behavior of the reverse martensitic transformation was essentially the same as before the aging procedure.

The observed phenomenon could be explained, in principle, by assumption that the martensitic transformation in \( \text{Ni}_{57.5}\text{Mn}_{17.5}\text{Ga}_{25} \) results in formation of a mixture of two martensitic phases, coexisting in a wide temperature interval. In such a case, aging at a particular temperature in the martensitic state would promote phase separation, favoring the martensitic phase, stable at the aging temperature. As a result of the phase separation, two endothermic peaks, corresponding to the martensite-martensite and martensite-austenite transformations, might appear on the heating curve. Such a scenario, however, seems to be inconsistent with the result of aging at \( T = 473 \text{ K} \), which showed no detectable influence on the transformation behavior of \( \text{Ni}_{57.5}\text{Mn}_{17.5}\text{Ga}_{25} \).

It seems to be more likely, therefore, that the origin of the observed phenomenon has to be looked for in austenite-aging-induced changes in the crystal structure of martensite in \( \text{Ni}_{57.5}\text{Mn}_{17.5}\text{Ga}_{25} \). We have suggested that such a mechanism could be responsible for the observed decrease of \( A_p \) temperature after aging in the austenitic state (Fig. 3). In the case of aging in the martensitic state at \( T_{\text{aging}} = 528 \text{ K} \), the appearance of the two-step martensitic transformation points to the formation of an inhomogeneous martensitic state consisting of two martensitic phases with different transformation temperatures. The fact that the temperature of the additional endothermic peak, \( T_I \approx 520 \text{ K} \) is essentially the same as the \( A_p \) temperature in the samples long-term aged in the austenitic state (Figs. 2, 3) supports this suggestion.

It is worth noting that, as evident from the DSC data (Fig. 1), the existence of a trace of the austenitic phase can be reasonably expected at the aging temperature \( T_{\text{aging}} = 528 \text{ K} \). Since aging at \( T = 473 \text{ K} \), far below austenite start temperature, did not result in a two-step martensitic transformation, the presence of a small amount of austenitic phase at \( T_{\text{aging}} = 528 \text{ K} \) is probably a crucial factor for the formation of inhomogeneous martensitic state. It can be suggested that after aging at \( T_{\text{aging}} = 528 \text{ K} \) the part of the austenitic phase stabilized by the aging transforms to the austenite-aging martensite upon cooling to room temperature. Thus, the martensitic state of the samples cooled to room temperature after thermal treatments consists of austenite-aging martensite phase embedded in the matrix of the as-quenched martensite. During subsequent heating, a transforma-

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**FIG. 4:** Change in \( A_p \) temperature after aging of \( \text{Ni}_{57.5}\text{Mn}_{17.5}\text{Ga}_{25} \) in the martensitic state as a function of aging time.

**FIG. 5:** Influence of aging performed in the martensitic state at \( T_{\text{aging}} = 528 \text{ K} \) on transformation behavior of \( \text{Ni}_{57.5}\text{Mn}_{17.5}\text{Ga}_{25} \).
tion from the austenite-aging martensite to the stabilized austenite takes place at $T_I \approx 520$ K; at further heating, reverse transformation of the matrix martensite occurs at $A_p \approx 545$ K.

As evident from Fig. 5, the complex transformation behavior in Ni$_{57.5}$Mn$_{17.5}$Ga$_{25}$ depends on aging time and become less pronounced in the samples aged for $t \geq 216$ ks. This can be presumably ascribed to the competition between thermodynamic stabilization of austenitic and martensitic phases coexisting at $T_{\text{aging}} = 528$ K; the latter process dominates in the case of a long-term aging.

IV. CONCLUSION

Differential scanning calorimetry study of the influence of aging on martensitic transformation in the Ni$_{57.5}$Mn$_{17.5}$Ga$_{25}$ shape memory alloy revealed complex and intriguing transformation behavior. Decrease in the reverse martensitic transformation temperature is observed after aging in the austenitic state. The main and most interesting finding of this work is the observation of a complex transformation behavior after aging in the martensitic state at $T_{\text{aging}} = 528$ K. As for now, we presume that both the decrease of $A_p$ temperature after aging in the austenitic state and the multi-step martensitic transformation appearing after aging in the martensitic state may be accounted for by the aging-induced formation of a different type of martensitic phase having a lower, as compared to the as-quenched martensite, transformation temperature. To give an unambiguous interpretation on the nature of this effect, further intensive studies of Ni-Mn-Ga alloys with this or similar composition are necessary.

Acknowledgements

This work was partially supported by the Industrial Technology Research Grant Program in 2002 from New Energy and Industrial Technology Development Organization (NEDO) and by the Grant-in-Aids for Scientific Research from the Ministry of Education, Culture, Science, Sports and Technology (MEXT), Japan. One of the authors (VVK) gratefully acknowledges the Japan Society for the Promotion of Science (JSPS) for a Postdoctoral Fellowship Award.

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