Research Article
Thermal Arrest Memory Effect in Ni-Mn-Ga Alloys

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Received 22 May 2008; Accepted 21 October 2008

Recommended by Paul Munroe

Dilatation characteristics were measured to investigate the thermal arrest memory effect in Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ and Ni$_{54.2}$Mn$_{29.4}$Ga$_{16.4}$ alloys. Interruption of the martensite-austenite phase transformation is connected with the reduction of the sample length after thermal cycle. If a total phase transformation took place in the complete thermal cycle following the interruption, then the sample length would return to its original length. Analysis of these results has shown that the thermal arrest memory effect is a consequence of a stress-focusing effect and shape memory effect. The stress-focusing effect occurs when the phase transformation propagates radially in a cylindrical sample from the surface, inward to the center. Evolution and release of the thermoelastic deformations in both alloys during heating and cooling are analyzed.

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1. Introduction

Johnson et al. [1] were the first to show the effect of interruption of phase transformations on transformations in subsequent cycles. They have shown that after arresting the M-P transformation in Ni-Ti alloy during the first thermal cycle, cooling causes the endothermic peak in the second thermal cycle to split into two. The M-P transformation in the second cycle remembers the arrest in the first thermal cycle. The authors of this study called this effect the “thermal arrest memory effect” (TAME) [2]. The authors of the cited work assume that the TAME is a consequence of the locked-in transformation strain energy in the self-accommodation martensitic structure. TAME effect has been the subject of intense investigation [3–8]. In contrast to Madangopal et al. [2], Airoldi et al. (they called this effect stepwise martensite to austenite reversible transformation (SMART)) suggest that the phenomenon TAME is related to the hysteresis associated with the martensitic transformation. Both hypotheses are based on DSC studies performed on Ti-Ni and Cu-Zn-Al shape memory alloys.

The TAME effect is undoubtedly a very interesting phenomenon that, with further investigation, can provide very important information about the behavior of shape memory alloys. Dilatometry is a method that measures all deformations occurring in a material. Dilatometry has not been used for the study of the TAME effect. The aim of this work is the dilatation investigation of the TAME effect in Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ and Ni$_{54.2}$Mn$_{29.4}$Ga$_{16.4}$ alloys in the temperature range of 20–380°C.

2. Experimental

The polycrystalline ingots of both Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ and Ni$_{54.2}$Mn$_{29.4}$Ga$_{16.4}$ alloys were prepared by arc melting in an argon atmosphere. The samples prepared from the ingots were annealed for 4 days at 850°C. The samples studied had structure with the columnar grains. The results obtained by studying the dilatation characteristics of Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ and the microstructure are presented in [9]. The linear thermal expansion of the samples was measured in a helium atmosphere using a Netzsch 402E dilatometer from room temperature to 380°C with a heating/cooling rate 2°C/min. During the interruption experiments, the interruption temperature was reached at a rate of 2°C/min followed by a 60-minute delay at the interruption temperature. The temperature was then decreased at a rate of 2°C/min. The samples were 6 mm in diameter and 25 mm in length. The accuracy of the measuring apparatus was checked by measuring the
coefficient of thermal expansion (CTE) of pure Mg and comparing it with the data available from literature. The agreement between the measured values and the values in literature is in the range of ±1%. Before investigation, the Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ alloy was predeformed by compression up to 1% using an Instron type deformation machine. The sample is placed in the center of the furnace, with a thermocouple located 1 mm above the sample. The front part of the sample is pushed on lock; the push rod is placed on the end part of the sample. We measured deformation changes only along the longitudinal axis (LA direction) of the sample. In this direction, the Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ alloy was predeformed in compression. The Ni$_{54.2}$Mn$_{29.4}$Ga$_{16.4}$ alloy was studied in the as-prepared and annealed state.

The total thermal cycle-up to 380°C was always made before and after the thermal cycle in which the interruption was performed. The dilatation characteristics were then compared. The dilatation characteristics of both materials before interruption are presented in Figures 1 and 2. The interruption temperatures are marked in these figures. Reproducibility of all experiments was perfect.

3. Results

Figure 3 reveals the temperature dependence of the relative elongation for the Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ alloy in the experiment where the temperature was increased up to 177°C, then stabilized for one hour, and cooled to room temperature. With this temperature sequence, the phase transformation takes place only partially. It can be seen that shortening of the sample occurs after this thermal cycle. The sample length was reduced by about 20 μm. The results presented in Figure 4 show the results after an additional total thermal cycle, after interruption. This figure reveals that permanent elongation of the sample occurs after this thermal cycle. Figure 5 displays the splitting of the peaks of the CTE during the phase transformation M→A. If additional complete (without interruption) thermal cycles were then made, the dilatation characteristics would be the same as before interruption. The Ni$_{54.2}$Mn$_{29.4}$Ga$_{16.4}$ alloy shows similar results; however, splitting of the CTE peaks is more visible than in the first alloy. Figure 6 shows the temperature dependence of the CTE after interruption when the interruption temperatures were...
The phase transformation starts to occur in the sample when its temperature reaches the transformation temperature $T_{tr}$. When the surface sample temperature reaches this temperature, the phase interface between martensite-austenite propagates from the surface towards the core of the sample during heating as well as cooling. The rate of the transient process ($u$) depends on the thermal conductivity of the both phases ($K_M, K_A$), the latent heat ($H$), density ($\rho$), heating rate, and time. For a given time, $u$ is given by following relation:

$$u = \frac{1}{\rho H} \left( K_M \left( \frac{\partial T}{\partial x} \right) - K_A \left( \frac{\partial T}{\partial x} \right) \right).$$

This relation was modulated from a relation that was originally derived for the propagation of a melting front in a conducting region [10]. In this relation, it was assumed that the density of both phases is the same. The rate of propagation of the phase interface, $u$, increases with an increasing/decreasing temperature rate during heating/cooling. The phase transformation in the Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ alloy (Figure 1) takes about 10 minutes for the given heating rate.

260°C, 261°C, and 265°C. The uninterrupted case is also shown in this figure.

4. Discussion

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of $2^\circ$C/min (the time between the start and end of the phase transformation). This time is reduced to 7 minutes for $5^\circ$C/min or 4 minutes for $7^\circ$C/min. On the other hand, it increases to 40 minutes for a heating rate of $0.5^\circ$C/min. It is necessary to note that the M\-A transformation is an athermal phase transformation that depends only on the temperature, and that it occurs practically immediately [11] after reaching the transient temperature. The relatively long duration of the phase transformation is a result of cooperation of phase transformation (the latent heat) and thermal conductivity.

It was mentioned in the experimental section that our samples have a cylindrical shape. If a cylindrical sample is suddenly subjected to an impact cooling or a phase transformation, thermal stress waves occur at the surface of the sample. Stress waves in a cylinder with a focusing point proceed radially inward to the center of the cylinder sample. The waves may accumulate at the focusing point and give rise to very large magnitude stresses. This phenomenon is known in the literature as the stress-focusing effect [12, 13]. Theoretical analysis of the stress-focusing effect induced by thermal expansion and phase transformation is presented in the work of Hata and Sumi [14]. These authors have shown that when a cylindrical metal sample is cooled instantaneously below the phase transformation temperature, the stress-focusing effect occurs via expansion due to phase transformation and thermal contraction.

When $T_{tr}$ is reached at the sample surface, the phase interface propagates into the sample and it divides the sample into two ranges that have different structures and sizes. During the phase transformation $M \rightarrow A$, the austenite layer occurs first on the surface of the cylinder. As the austenite volume increases in the cylindrical sample, the stress-focusing effect occurs at the center where the martensite exists. This martensite then experiences compressive stress. If we interrupt the phase transformation in a certain state, the sample will stay in this state as long as the temperature does not change (Figure 3). Decreasing temperature causes the austenite to transform to martensite (only the outside part of sample). As the martensite in the center of the sample is deformed by compression by the focusing effect, at the end of the interrupted thermal cycle, the sample length is reduced (Figure 3). The sample returns to the initial size when total thermal cycle including phase transformation is applied (Figure 4).

It can be seen that the influence of interruption on CTE is higher in the nondeformed Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ alloy than in the predeformed Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ alloy. Figure 6 shows the influence of the interruption temperature on the splitting of the CTE. The interruption temperatures were $260^\circ$C, $261^\circ$C, and $265^\circ$C. Splitting of the transformation peak occurs only in the case when the interruption was applied in the first cycle of transformation. It can be seen from Figure 6 that the second peak shifts to higher temperature with increasing interruption temperature. A higher interruption temperature corresponds to a higher compression stress in the center of the sample. Releasing of the compression deformation is a thermally activated process. We assume that the compression deformed center of the sample transforms at a higher temperature than the nondeformed center outside of the sample. The difference of these temperatures is $2^\circ$C for an interruption temperature of $260^\circ$C, and $2.5^\circ$C for an interruption temperature of $261^\circ$C. This shift of the transient temperature results in a splitting of the CTE transient peak. The splitting of the CTE does not occur when the phase transformation is interrupted before its end ($264^\circ$C) because nearly the whole sample is transformed.

Evolution of the thermoelastic deformations during the phase transformation is schematically shown in Figure 7. In this schematic, we consider only heating because all deformation changes occur during heating. The schematic of the phase transformation $M \rightarrow A$ without interruption is shown in the first part of Figure 7. In this schematic, we divide the duration of the phase transformation into two parts. First, the transformation occurs in the external part of the cylinder. This transformation is connected with the compression of the internal part of the sample due to the focusing stress effect. In the second cycle of transformation, the central part of the sample transforms and stresses what occurred in the first cycle of transformation release. If we interrupt the $M \rightarrow A$ phase transformation, then the sample stays deformed in compression (the second part of Figure 7).

The sample is then comprised of two parts: the center of the sample, which is the deformed martensite, and the outside of the sample, which is the austenite. During the following $A \rightarrow M$ transformation, only the austenite part of the sample transforms and the martensite center of the sample stays unchanged. After this thermal cycle, the sample stays macroscopically deformed in compression at room temperature, resulting in a shortening of the sample. The compression deformation is released only after the total $M \rightarrow A$ transformation, resulting in elongation of the sample.

The results, which are for both alloys, are summarized as follows.

1. Part of the compression deformation is released during heating of the martensite below the transient temperature. The second part of the deformation is released during the phase transformation.
(2) If the interruption is applied in the first transformation cycle, then splitting of the CTE is found in the transformation cycle when the sample center transforms.

During cooling, no changes occur in the alloy.

In our previous work [15], we have studied the dilatation characteristics of a compression predeformed Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ alloy up to 1% with a maximum thermal cycle temperature of 380°C. Relaxation of two sorts of strains took place in the thermal cycle after predeformation. First, the memory strain could not be removed from the sample because it is released during heating and occurs once more during cooling. Second, the residual strain is released only during heating as a thermally activated process. The residual strain is released in two temperature regions, during heating of the martensite below the transformation temperature and during the phase transformation. Release of compression deformation after interruption takes place in a similar manner. A chief difference between both types of relaxation is that in the first case, the entire sample was deformed and in the second case only a part was deformed. We assume that the deformed part of the sample (center) has a higher transient temperature than the nondeformed part. This difference was determined to be 2°C (from the temperature difference of the peak maximum) for an interruption temperature of 260°C and 2.5°C for an interruption temperature of 261°C. The first peak in the temperature dependence of the CTE in Figure 6 belongs to the phase transformation of the outside of the sample and the second lower peak in the temperature dependence of the CTE is connected with the phase transformation of the deformed sample center. This shift of the transient temperatures results in splitting of the CTE transient peak. The same results are presented in the DSC investigations. The transformation temperature of the second (third) peak is shifted to higher temperatures (see, e.g., [4]).

5. Conclusion

The dilatation measurements and their analyses show the evolution and release of thermoelastic deformations in Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ and Ni$_{54.2}$Mn$_{29.4}$Ga$_{16.4}$ shape memory alloys. If a cylindrical sample of the shape memory alloy is heated or cooled from the outside, the martensitic phase transformation starts on the surface and it propagates radially into the center of the sample. As a consequence of this process, the stress-focusing effect occurs in the sample center. During the M → A phase transformation, this effect causes a compression deformation of the martensitic center of the sample. Interruption of the M → A phase transformation results in a macroscopic compression deformation of the sample. The shortening of the sample length is a consequence of this process. Release of this compression deformation can be realized only with a total thermal cycle where the phase transformation M → A is completed. The compression deformation due to the focusing effect is released in two steps: during heating of the martensite and during the phase transformation of the sample center. These investigations show that TAME effect is a consequence of the stress-focusing effect and the shape memory effect.

Acknowledgment

This work is a part of the Research Program MSM 0021620834 that is financed by the Ministry of Education of the Czech Republic.

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