Research Article

Influence of the Texture and Strain on the Behaviour of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ and $Ni_{54.2}Mn_{29.4}Ga_{16.4}$ Shape Memory Alloys

Alexandra Rudajevova and Jiří Pospíšil

Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5,
121 16 Praha 2, Czech Republic

Correspondence should be addressed to Alexandra Rudajevova; rud@mag.mff.cuni.cz

Polycrystalline samples of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ and $Ni_{54.2}Mn_{29.4}Ga_{16.4}$ shape memory alloys were investigated using dilatometry. The longitudinal axes of the samples were perpendicular to the columnar grains. Both alloys showed positive shape memory effects. The martensitic phase transformation occurred without hysteresis in both alloys with transformation temperatures of 174°C for the $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy and 253°C for the $Ni_{54.2}Mn_{29.4}Ga_{16.4}$ alloy. The dilatation characteristics for both alloys were determined in three perpendicular directions. The strain associated with the internal stress at the interface between the two martensitic structures and the two grains affected the dilatation characteristics in the y and z directions (perpendicular to the longitudinal axis of the sample). The microstructure was determined for all the directions investigated. To investigate the mechanical history, a round cross-section of the $Ni_{54.2}Mn_{29.4}Ga_{16.4}$ sample was machined using a milling machine along the longitudinal axis so that both sides of the sample were symmetrical. This sample treatment changed the dilatation characteristics of the martensite and austenite. The study and analysis of the dilatation characteristics of the thermal cycle showed the relaxation of internal stresses and the reorientation of the martensitic variants.

1. Introduction

Ni-Mn-Ga-based shape memory alloys (SMAs) exhibit excellent shape memory behaviour and high thermal stability; therefore, the materials are promising high-temperature SMAs with a wide variety of possible future applications [1]. Although single crystals have been reported to yield substantial magnetic field-induced strains [2, 3], economic and engineering demands led to an interest in the development of polycrystals, which are easier and cheaper to produce. However, polycrystals usually exhibit lower shape memory effect because of the presence of grain boundaries, which act as pinning centres and impede twin boundary motion. A possible approach to improve the properties of polycrystalline materials is to use coarse-grained and highly textured samples because the properties resemble the properties of single crystals. Anisotropy in detwinning enables the potential of the polycrystalline SMAs to be maximised [4].

The martensitic transformation is a strain transformation. The lattice strain is a transformation parameter that determines the physical state of the initial and product phases as well as the local intermediate states of the alloy during the phase transformation. The low-temperature martensitic Ni-Mn-Ga phase usually has a tetragonal lattice. Anisotropy of the thermal properties (e.g., thermal expansion and thermal conductivity) is present in the system. Thermal stresses in polycrystalline materials are a natural consequence of anisotropy. The coefficient of expansion is the immediate cause of the thermal stresses, and the thermal conductivity determines the temperature gradient. For example, the thermal conductivity of a Ni_3Ta single crystal along the a-axis was more than twofold higher than the thermal conductivity along the b-axis [5]. Thermal stresses can even exist in single grains because several martensitic domains (orientations) exist in a grain of the polycrystalline material.

At the microstructure scale, the reversible deformation of martensite is proceeded by detwinning and/or reorientation,
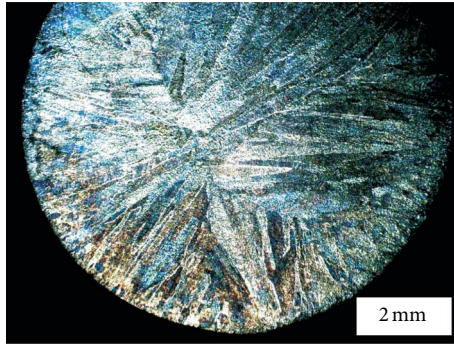
FIGURE 1: Cross-section of the structure of the $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ ingot.

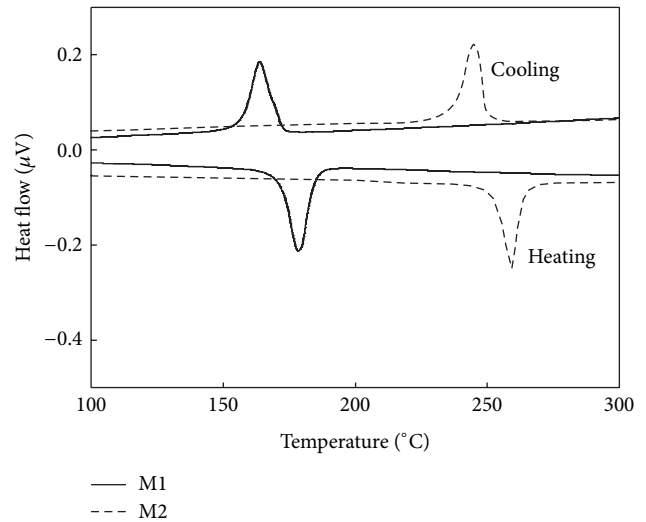FIGURE 2: Cross-section of the structure of the $Ni_{54.2}Mn_{29.4}Ga_{16.4}$ ingot ($23 \times 48 \times 85$ mm).

FIGURE 3: Temperature dependence of the heat flow for the M1 and M2 alloys.

which are of primary importance for the one-way shape memory effect (OWSME) and two-way shape memory effect (TWSME) [4, 6] and can be accompanied by plastic deformation [6]. The texture, which causes direction-dependent enhancement and reduction for the detwinning process, is crucial to obtain optimal deformation behaviour of the polycrystalline SMAs [7–12]. In practice, SMAs, especially nitinol, are prepared in a variety of forms (e.g., bars, tubes, rods, wires, sheets, ribbons, or thin films). All of these polycrystalline materials have a texture that is preparation dependent. The cooling rate during preparation of the alloy and the machining process can determine the properties of the shape memory product. Stebner et al. [13] investigated the development of textures using neutron diffraction and multivariate simulations. The authors observed that if a pre-textured sample was loaded in an orientation perpendicular to the texture, then the reorientation plateau widened (i.e., greater strain was achieved).

Dilatometry provides important information regarding the relaxation of all the strains that occur during thermal changes. The relative changes of the sample lengths are the sum of all the strains that occur in the sample. The martensitic transformation is a strain transformation; therefore, dilatometry is an important method used to study shape memory materials. This work investigated the dilatation behaviour of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ and $Ni_{54.2}Mn_{29.4}Ga_{16.4}$ alloys over a temperature range of 25 to 500°C. The dilatation characteristics of the alloys were measured and analysed according to the texture and mechanical history dependence of the samples.

2. Experimental Part

Polycrystalline ingots of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ (M1) and $Ni_{54.2}Mn_{29.4}Ga_{16.4}$ (M2) were prepared by arc melting the elements under an argon atmosphere. The samples of the $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy were prepared from a 1 cm-diameter rod. The microstructure of the cross-section of a sample is shown in Figure 1. The $Ni_{54.2}Mn_{29.4}Ga_{16.4}$ samples were prepared from ingot with dimensions of $23 \times 48 \times 85$ mm, which is shown in Figure 2. The longitudinal axes of the samples were perpendicular to the planes shown in Figures

1 and 2. The alloys were annealed at 850°C. Long columnar grains were observed that were oriented along the direction of the temperature gradient as the ingots solidified.

The EBSD analysis was performed on Scanning Electron Microscope FEI Quanta 200 FEG using Digi View EBSD detector. The analysis of the data was carried out using TSL software (detector software). The EBSD patterns were recorded from two locations of all three planes of the sample. The EBSD study was carried out on the same sample which was used for dilatation study.

The temperature dependences for the heat flow of the M1 and M2 alloys were obtained using DSC Setaram Setsys. The heating/cooling rate was 10 K min^{-1}. The results are shown in Figure 3. The transient temperatures for the M1 alloy were determined to be 176°C for heating and 172°C for cooling. The martensitic transient in the M2 alloy occurred at 253°C during heating and 252°C for the reverse transformation. The reported temperatures were determined as onset temperatures for the temperature dependences of heat flow. The linear thermal expansion of the samples was measured in a helium atmosphere using a Netzsch 402 dilatometer from room temperature to 500°C. The temperature dependence of the
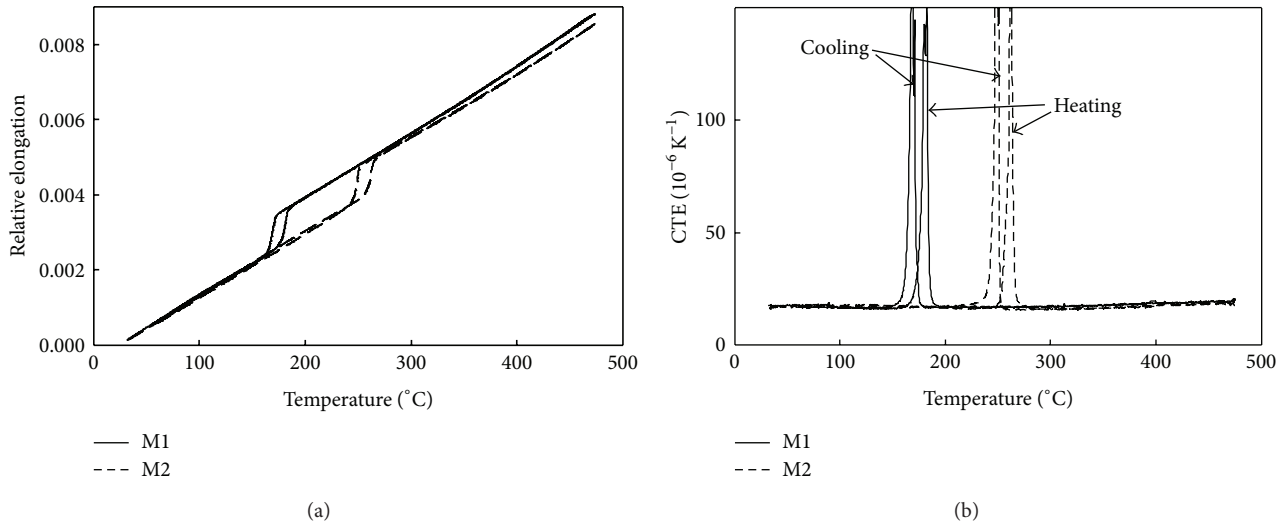
FIGURE 4: Dilatation characteristics for the M1 and M2: (a) temperature dependence of the relative elongation and (b) temperature dependence of the CTE.

relative elongation was measured, and the coefficient of thermal expansion (CTE) was calculated as a derivation of relative elongation against the temperature. The heating/cooling rates were 2 K min^{-1}. The transformation temperatures were determined from the onset of the transformation peaks, which were obtained from the temperature dependence of the CTE. The martensite-austenite transformation temperature determined using this method for the M1 alloy was 175°C, while the reverse transient temperature was 173°C. The transformation temperatures for the M2 alloy were 252 and 254°C, respectively. The enthalpies for the M1 and M2 alloys were 9.0 and 8.5 Jg^{-1}.

3. Results and Discussion

The temperature dependences of the dilatation characteristics for the M1 and M2 alloys are shown in Figure 4. The martensitic transformation can be observed to occur without hysteresis in both alloys. In addition, the DSC results shown in Figure 3 show no hysteresis. The martensitic transformation temperature was higher for the M2 alloy than the M1 alloy. The dilatation characteristics of the austenite phases were similar for both alloy types. The CTE in the M1 alloy increased up to 150°C and then decreased until the martensitic transformation began to occur. Shape memory effects in both of the polycrystalline alloys were a consequence of the existence of preferential structural variants for a given sample direction. We reported on the shape memory effect in Ni$_3$Ta single crystals [5]. Positive shape strain was identified for two directions, while a negative shape strain was identified for the third dimension; however, the sample volume remained the same. Shape memory effects are often studied in cold-rolled or hot-rolled Ti-Ni alloys. In these materials, anisotropy of the shape memory effect was previously demonstrated to be a consequence of the material texture [14, 15]. The shape memory effect was studied using dilatometry in both reports.

Positive and negative shape strain was determined to be dependent on the direction of the rolling process. Changes in the transformation temperatures due to the rolling process were elucidated by the high density of dislocations and the inhomogeneous internal stress fields introduced by the rolling process.

The influence of the texture on the behaviour of the martensite and on the shape memory effect on the M1 as well as M2 samples was studied. The samples for this measurement was prepared on a wire saw to minimize any pressure on the sample during preparation. The longitudinal sample axis (i.e., the x-axis) was the same as in the original cylinder sample; the dilatation characteristics are shown in Figure 4. The dilatation characteristics were determined for the y and z directions, which were perpendicular to the longitudinal axis (it was selected randomly). The results are shown in Figures 5 and 6, where a large difference in the dilatation characteristics of the martensite can be observed between directions investigated. Relative elongation of the martensite increases more rapidly in the y and the z directions than in the x direction in both alloys. This result indicates that the sample was under compressive stress in the y and z directions before heating. During heating, compressive strains were released, and the relative elongation increased because strains are additive. During cooling, compressive stresses (strains) were reintroduced, and the sample length decreased to reach length before application of the thermal cycle. The temperature dependences of the released strain are shown for M1 alloy in Figure 7. These strains were obtained by subtraction of the relative elongation in the x direction from the relative elongation in the y and z directions. We can see that strains decrease during heating not only in the martensitic temperature range but also in the phase transformation temperature range where the rate of releasing is the highest. Substantial difference between the y and z directions can be seen on the cooling branches in the temperature range of the phase transformation. While in the
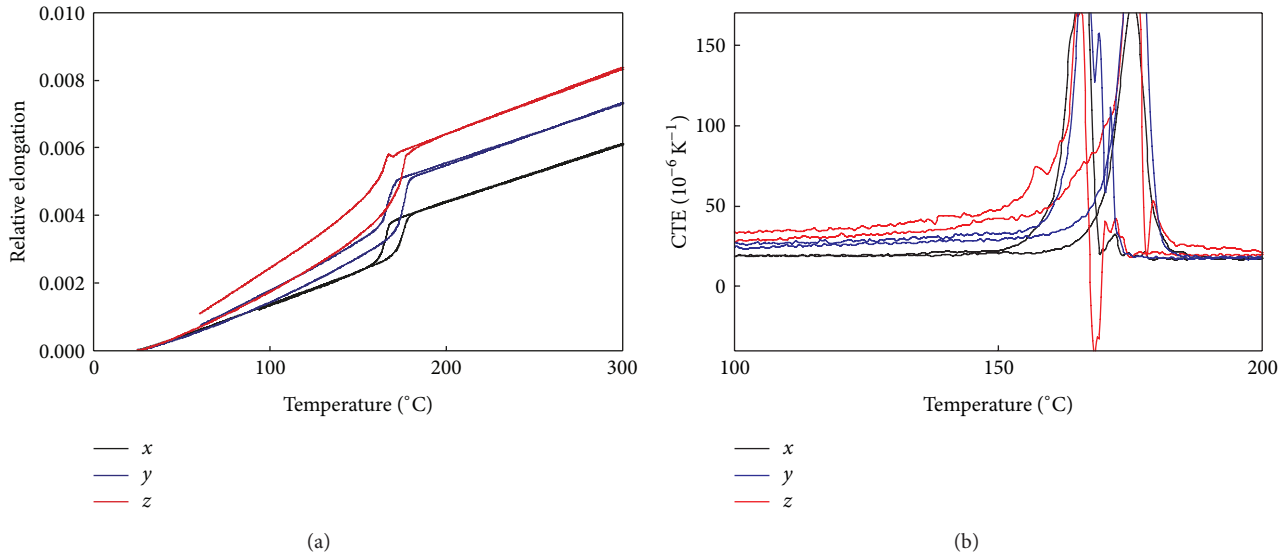
(a)

(b)

FIGURE 5: Anisotropy of the dilatation characteristics in M1 alloy: (a) temperature dependence of the relative elongation and (b) temperature dependence of the CTE.
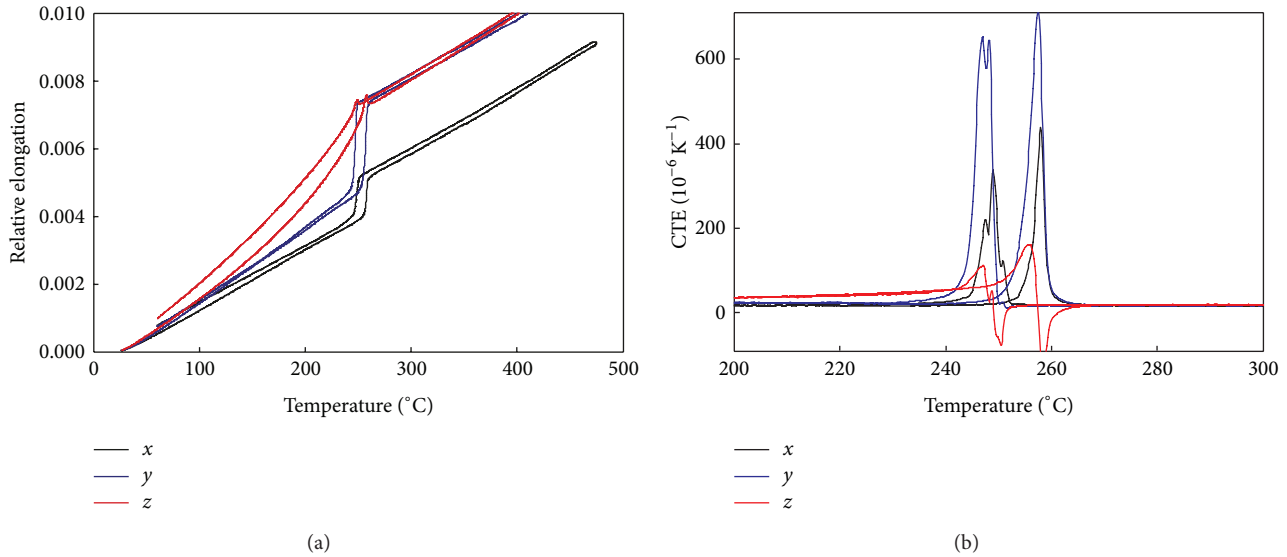

(a)

(b)

FIGURE 6: Anisotropy of the dilatation characteristics in M2 alloy: (a) temperature dependence of the relative elongation and (b) temperature dependence of the CTE.

y direction strain firstly decreases, in the z direction firstly increases. In our polycrystalline M1 and M2 alloys, we have found negative shape strain only in z direction (negative peak on the temperature dependence of the CTE). This negative shape strain, however, occurs only in a part of the sample. It can be seen in Figures 5 and 6 where negative peak occurs in the first phase of the cooling; however, it is immediately followed by positive peak. The martensitic transformation in this direction is evidently influenced by the internal stresses which occur as a consequence of different memory strain in neighbouring variants or grains. No internal stresses

influenced the dilatation characteristics in the single crystals of Ni$_3$Ta shape memory alloy [5].

If two crystallographic orientations are connected, for example, by a coherent interface in martensite, then compatibility between the phases can be obtained by the elastic adjustment of the phases. Those coherent interfaces are then the source of internal stresses [16]. These stresses will be the largest in cases when variants with positive and negative transformation strains are connected. Figure 7 shows that stresses and with them connected strains revealed anisotropy that is a natural consequence of the texture in
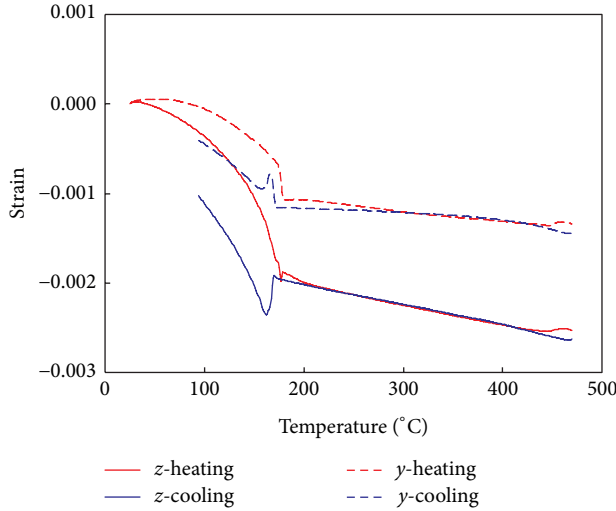
FIGURE 7: Temperature dependence of strain for M1 alloy in the y and z directions, which were obtained as the difference of the relative elongations $(\Delta l/l_o)_y - (\Delta l/l_o)_x$ and $(\Delta l/l_o)_z - (\Delta l/l_o)_x$.

(a)

(b)

(c)

FIGURE 8: Microstructure of the M1 alloy in the x, y, and z directions.

the polycrystalline sample (i.e., the martensitic strains varied with crystal directions). Stresses (strains) that occur during the martensitic transformation are dependent on temperature (i.e., the strain increased as the temperature decreased and the strain decreased as the temperature increased).

Microstructure of the samples whose dilatation characteristics are revealed in Figure 5 is shown in Figure 8. Long large grains are perceptible in the x direction, which is the direction with the lowest internal stresses. The microstructure in this direction is nearly without defect lines (dark lines), which are only perceptible at the grain boundaries (e.g., the dark line in the top section of Figure 8(c)). In the perpendicular directions, y and z, dark lines can be observed in all the planes shown in Figures 8(a) and 8(c). The dark lines are located in the grain boundaries and at the interfaces between martensitic planes. The dark lines were assumed to be associated with high values of internal stresses that formed during the martensitic transformation. The microstructure and dilatation investigations indicate that the polycrystalline alloy, which had columnar grains in a certain direction that are necessary for shape memory effect, was subjected to internal stresses associated with the anisotropy of the shape memory effect in the tetragonal lattice of the Ni-Mn-Ga alloy. The internal stresses occurred during the austenite-martensite phase transformation and disappeared during the martensite-austenite phase transformation. The CTE of austenite was the same in all directions. Srivastava and Chatterjee [17] demonstrate that, due to large internal friction energy in the off-stoichiometric polycrystalline $Ni_{52}Mn_{26}Al_{22}$ alloy, the use of this alloy for ferromagnetic shape memory alloy is limited.

The results of the EBSD analysis are shown in Figure 9—two integrated patterns from two places to polar diagrams. These results are bound only on the surface plane locations of the sample. They show strong local texture in the given place but they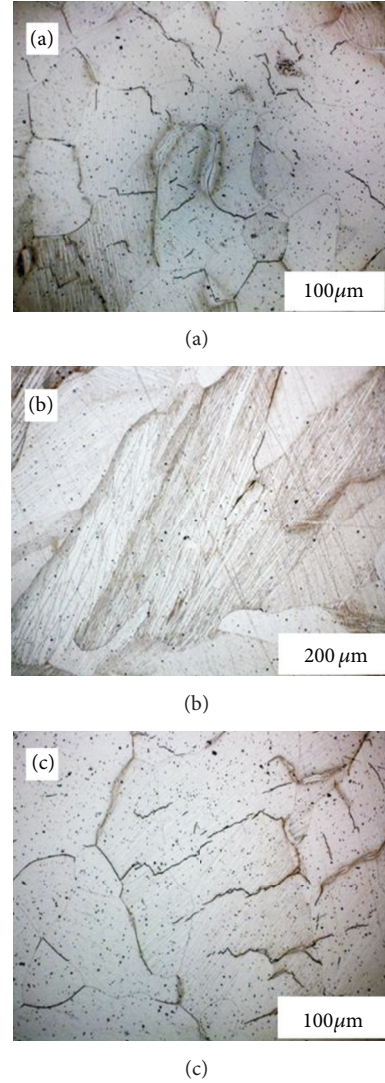 do not give information about preferential crystallographic orientation in whole sample. Volume texture analysis is complicated by the existence of the martensitic variants in one grain. Analysis complexity can be perceptible from Figure 10 where the microstructure of the plane perpendicular to x-axis is displayed in colored EBSD pattern. Dilatation results give information about the whole volume of the sample in comparison to the EBSD.

Thermal and mechanical history is retained by shape memory alloys. The CTE of the martensite of the M2 alloy was higher for a maximum thermal cycle temperature of 500°C than 700°C. The transient temperatures did not change. The influence of the maximum temperature cycle is different for alloys with hysteresis. For example, a Ni_3Ta shape memory alloy [5] has a transient temperature for the austenite-martensite transformation that decreases as the maximum temperature cycle increases, while the transformation temperature for martensite-austenite transition remains the same.
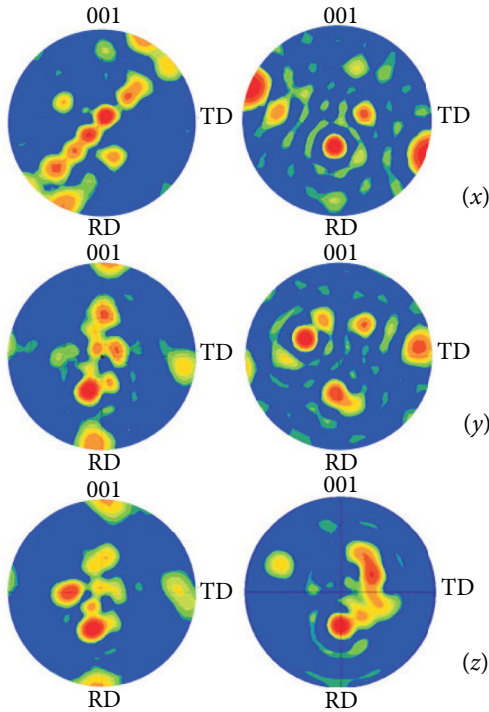
FIGURE 9: Couples of polar diagrams from two various places of each studied M1 sample plane. The *x*, *y*, and *z* correspond to the directions as described within the text.

FIGURE 10: EBSD pattern of the surface in the *x* direction of the M1 alloy.

The influence of the mechanical history on the M2 alloy was investigated. The dilatation characteristics shown in Figure 4 were obtained from a sample with a round cross-section that had a 6 mm diameter and 20 mm length. The sample was symmetrically machined on both sides using a milling machine along the longitudinal axis. The relative
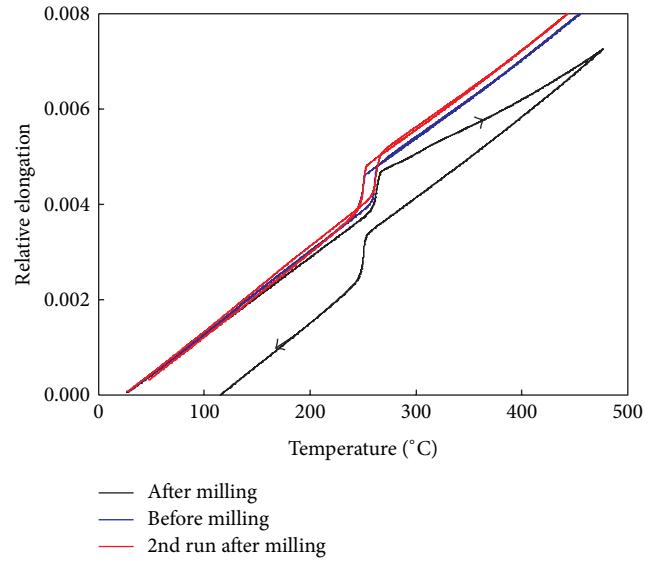

FIGURE 11: Temperature dependence of the relative elongation of the M2 alloy in the first run after milling, before milling and in the second run after milling.
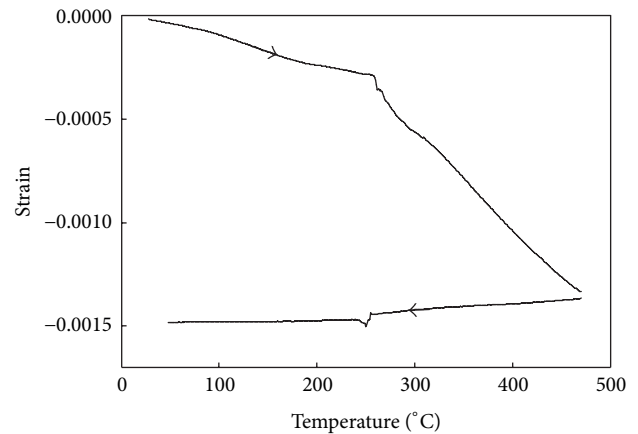

FIGURE 12: Temperature dependence of strain obtained as the difference between the relative elongation in the first and second runs after milling.

elongation was measured, and the results are shown in Figure 11. The figure clearly shows that after milling, relaxation of the strain occurs only during heating. Permanent reduction of the sample length after the completion of a temperature cycle is a consequence of the relaxation of plastic strain. The temperature dependence of the strain relaxation is shown in Figure 12. This dependence was obtained by subtracting the relative elongation of the second run after milling from the first run after milling (strains are additive). The strain relaxation occurred in the martensitic temperature range; however, a major portion of the strain relaxed in the austenite. The following thermal cycle showed nearly the same temperature dependence of the relative elongation as before the sample was milled. Jones and Dye [18] studied the microstructural evolution of a hot-rolled sheet of a
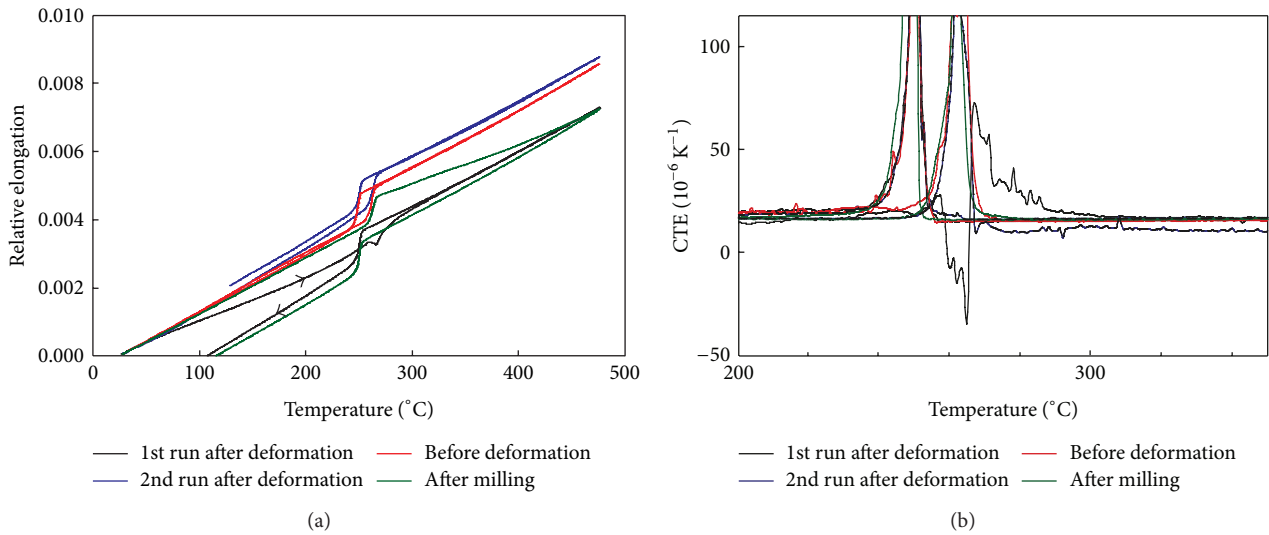
(a)

(b)

FIGURE 13: Temperature dependence of the dilatation characteristics of the milled M2 sample after compression deformation occurred perpendicular to the longitudinal sample axis: (a) temperature dependence of the relative elongation and (b) temperature dependence of the CTE.

nearly equiatomic Ni-Ti shape memory alloy, in situ, using synchrotron diffraction under thermal cycling and an applied stress. As martensite formed upon cooling under an applied stress, significant elongation of the sample was observed. This result was in contrast to the results obtained under stress-free conditions. The elongation was associated with a change in the martensitic texture, where the preferential martensitic variants were oriented along the tensile axis to accommodate for the applied stress. This result demonstrated that dislocations are generated and accumulated during each thermal cycle, which increased as the applied stress increased. A comparison of the shape memory effect before milling and the second run after milling indicates that milling increased the martensitic strain. Therefore, some reorientations that occurred in the martensitic domains were a consequence of the mechanical manipulation.

The M2 sample that was milled and measured twice was subsequently deformed by compression of up to 30 MPa using a laboratory press machine in a direction perpendicular to the longitudinal axis. The dilatation characteristics obtained from the thermal cycle are shown in Figure 13, where the data are compared with the dilatation characteristics of the milled sample. Relaxation of strain occurred in both cases during the heating of the samples, while the cooling of the samples remained the same. In both cases, permanent reduction of the sample length was discovered after the first thermal cycle. Different behaviour was observed during the martensite-austenite transformation and throughout the austenite temperature range. The negative peak that can be observed in Figure 13 indicates that compression deformation leads to reorientation of certain martensitic variants with positive memory strain on the martensitic variants with negative strain (measured in the longitudinal direction). This reorientation process was reversible because no negative peak was observed in the next thermal cycle, and the memory

strain remained nearly the same as it was observed in the sample before deformation. Figure 13(b) also shows broadening of the transformation peak between martensite and austenite after deformation. This effect indicates that part of the sample was under pressure. The transformation temperature of the deformed martensite was higher than that of the martensite without deformation. Böhm et al. [19] analysed structural and functional properties of $Ni_{50}Mn_{30}Ga_{20}$ after plastic deformation. Microstructural studies demonstrated that the destruction of the as-cast state was dependent on the deformation and hot-rolling processes.

4. Conclusion

Our results indicate that the austenite-martensite transformations in polycrystalline Ni-Mn-Ga alloys were associated with the development of internal stresses, which were strongly dependent on the anisotropy of the structure of the material. The relative elongations and CTEs of the martensite phases were higher along the longitudinal axes of the long grains than in directions perpendicular to the longitudinal axes. This result indicates that the alloys were in compression stress in the nonlongitudinal directions. This stress and the associated strain were dependent on the temperature. Areas with high stresses were observed as dark lines in the microstructure. The dark lines were only observed in the y and z directions and were localised at the grain/grain and martensitic plane/plane interfaces. This result is in agreement with the dilatation measurements.

The mechanical manipulation of the sample was dependent on the machining technique and the direction relative to the texture. The use of milling or compression deformation of the sample perpendicular to the long grains led to the formation of dislocations and other structural changes that

increased the sample length in the longitudinal direction. Relaxation that occurred following the heating of the alloy was associated with a permanent reduction in the length of the sample in the longitudinal direction. When the milled sample was heated, relaxation processes occurred in the martensite and austenite phases. Compression deformation in a given direction can lead to reversible reorientation of the martensitic variants.

Acknowledgments

References

[1] O. Söderberg, I. Aaltio, Y. Ge, O. Heczko, and S. P. Hannula, "Ni-Mn-Ga multifunctional compounds," *Materials Science and Engineering A*, vol. 481-482, no. 1-2, pp. 80–85, 2008.

[2] R. C. O'Handley, S. J. Murray, M. Marioni, H. Nembach, and S. M. Allen, "Phenomenology of giant magnetic-field-induced strain in ferromagnetic shape-memory materials (invited)," *Journal of Applied Physics*, vol. 87, no. 9, pp. 4712–4717, 2000.

[3] S. J. Murray, M. Marioni, P. G. Tello, S. M. Allen, and R. C. O'Handley, "Giant magnetic-field-induced strain in Ni-Mn-Ga crystals: experimental results and modeling," *Journal of Magnetism and Magnetic Materials*, vol. 226, pp. 945–947, 2001.

[4] Y. Liu, "Detwinning process and its anisotropy in shape memory alloys," in *Smart Materials*, vol. 4234 of *Proceedings of SPIE*, pp. 82–93, December 2000.

[5] A. Rudajevova and J. Pospisil, "Influence of anisotropy, the latent heat and the thermal history of alloy on martensitic transformation strain in Ni3Ta single crystal," *Journal of Alloys and Compounds*, vol. 509, no. 18, pp. 5500–5505, 2011.

[6] Y. Liu, Z. Xie, J. Van Humbeeck, and L. Delaey, "Asymmetry of stress-strain curves under tension and compression for NiTi shape memory alloys," *Acta Materialia*, vol. 46, no. 12, pp. 4325–4338, 1998.

[7] Y. Ma, C. Jiang, Y. Li, H. Xu, C. Wang, and X. Liu, "Study of $Ni_{50-x}Mn_{25}Ga_{25}$ ($x = 2 − 11$) as high-temperature shape-memory alloys," *Acta Materialia*, vol. 55, no. 5, pp. 1533–1541, 2007.

[8] Y. Liu, Z. Xie, J. Van Humbeeck, and L. Delaey, "Deformation of shape memory alloys associated with twinned domain reconfigurations," *Materials Science and Engineering A*, vol. 273–275, pp. 679–684, 1999.

[9] Y. C. Shu and K. Bhattacharya, "The influence of texture on the shape-memory effect in polycrystals," *Acta Materialia*, vol. 46, no. 15, pp. 5457–5473, 1998.

[10] A. Rudajevova, M. Frost, and A. Jäger, "Thermal expansion characteristic of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy with columnar structure," *Materials Science and Technology*, vol. 23, no. 5, pp. 542–546, 2007.

[11] J. Wang, P. Li, and Ch. Jiang, "Phase stability and magnetic properties of $Ni_{50-x}CuxMn_{31}Ga_{19}$ alloys," *Intermetallics*, vol. 34, pp. 14–17, 2013.

[12] D. Sing, R. S. Tiwari, and O. N. Srivastava, " Structural and magnetic properties of $Cu_{50}Mn_{25}Al_{25-x}Gax$ Heusler alloys," *Journal of Magnetism and Magnetic Materials*, vol. 328, pp. 72–79, 2013.

[13] A. Stebner, X. Gao, D. W. Brown, and L. C. Brinson, "Neutron diffraction studies and multivariant simulations of shape memory alloys: empirical texture development-mechanical response relations of martensitic nickel-titanium," *Acta Materialia*, vol. 59, no. 7, pp. 2841–2849, 2011.

[14] J. J. Wang, T. Omori, Y. Sutou, R. Kainuma, and K. Ishida, "Two-way shape memory effect induced by cold-rolling in Ti-Ni and Ti-Ni-Fe alloys," *Scripta Materialia*, vol. 52, no. 4, pp. 311–316, 2005.

[15] R. I. Babicheva, I. Z. Sharipov, Ya. Mulyukov et al., "Dilatation anisotropy upon the phase transition in the rolled Ti- 49.8% Ni alloy," *Physics of the Solid State*, vol. 53, no. 9, pp. 1947–1958, 2011.

[16] A. I. Roytburd, "Kurdjumov and his school in martensite of the 20th century," *Materials Science and Engineering*, vol. 273–275, pp. 1–10, 1999.

[17] V. K. Srivastava and R. Chatterjee, "Physical properties of polycrystalline $Ni_{52}Mn_{26}Al_{22}$ around martensitic transformation," *Solid State Communications*, vol. 149, no. 5-6, pp. 247–251, 2009.

[18] N. G. Jones and D. Dye, "Martensite evolution in a NiTi shape memory alloy when thermal cycling under an applied load," *Intermetallics*, vol. 19, no. 10, pp. 1348–1358, 2011.

[19] A. Böhm, S. Roth, G. Naumann, W. G. Drossel, and R. Neugebauer, "Analysis of structural and functional properties of $Ni_{50}Mn_{30}Ga_{20}$ after plastic deformation," *Materials Science and Engineering A*, vol. 481-482, no. 1-2, pp. 266–270, 2008.