Effect of Ferroelastic Cycling via Martensite Reorientation on the Transformation Behaviour of Nickel–Titanium

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It has been observed that deformation stabilises martensite in a number of shape memory alloys, as evidenced by the increase of the critical temperature for the reverse transformation of the deformed martensite as compared to undeformed martensite. Some hypotheses have been proposed in the literature to explain this phenomenon, including the pinning effect of deformation-induced defects and the release of internal elastic energy stored in thermal martensite. This study continues the experimental work by studying the effect of ferroelastic cycling via martensite reorientation on the transformation behaviour of a binary near-equiatomic NiTi, with the aim to provide further experimental evidence for the clarification of the mechanisms responsible for this effect. It was observed that the critical temperature and the heat of the reverse transformation of oriented martensite increased progressively with deformation cycles, although the limits of the deformation cycles remained unchanged.

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1. Introduction

As functional materials, shape memory alloys are used in applications often involving repeated transformation or deformation cycles. For successful applications and reliable designs, understanding of the transformation behaviour and functional properties of the alloys subjected to various transformation/deformation cycling is important. Whereas there have been numerous investigations reported in the literature on the evolution of deformation behaviour during deformation cycling and the evolution of transformation behaviour during thermal transformation cycling, little is known of the effect of deformation cycling on the transformation behaviour of these alloys.

It has been reported in the literature that deformation results in the temperature for the reverse transformation of deformed martensite shifting to higher temperatures, indicating a stabilisation effect. This stabilisation effect has been observed after deformation via either martensite reorientation or stress-induced martensitic transformation, for shape memory alloys including NiTi, NiTiNb and CuZnAl.¹–⁵ In specimens of both single crystals and polycrystalline materials.² Deformation modes by which this effect has been observed include simple shear,³ uniaxial tension²,³ and cold rolling.¹,⁶ The stabilisation effect is generally observed to manifest in three aspects. (1) The critical temperature for the first reverse transformation after the deformation is increased relative to the undeformed martensite formed by cooling.¹–⁵ (2) The endothermic heat associated with the reverse transformation has been measured to have increased in the case of simple shear deformation by martensite reorientation⁴ or decreased in the case of cold rolling or tensile deformation via stress-induced martensitic transformation.³,⁶ (3) A two-way memory effect is developed after the deformation.⁷ The magnitude of the increase of the critical temperature of the first reverse transformation is observed to increase with increasing deformation.

Changes in the critical temperature and the heat effect of the reverse transformation, however, are largely restored in subsequent thermal transformation cycles after the first reversion, whereas the two-way memory effect prevails in subsequent transformation cycles.

A number of hypotheses have been suggested in the literature for mechanisms responsible for the stabilisation effect, as reviewed in.⁸ These hypotheses include the pinning effect of deformation-induced defects, which increase the resistance for the reverse transformation,¹ the release of internal elastic energy stored in the self-accommodating martensite, which causes a decrease in the driving force for the reverse transformation,² and interaction between martensite variants and polycrystalline matrix.⁵ In all these hypotheses the extent of stabilisation is related to the magnitude and mode of deformation, in accordance with experimental observations. This work continues the study by investigating the effect of repeated deformation via martensite reorientation within predetermined limits (ferroelastic cycling) on the transformation behaviour of NiTi, in an effort to provide further experimental evidences for the clarification of the mechanisms responsible for this stabilisation effect.

2. Experimental Procedure

The material used was a commercial polycrystalline Ti–50.15 at%Ni alloy supplied by Memometal (France) in plate form. The as-received material was solution treated at 1173 K for 1.8 ks and cold rolled for more than 40% thickness reduction, followed by a recrystallisation anneal at 978 K for 1.8 ks. After the treatment the alloy exhibited single-step transformation behaviour of austenite and martensite. The critical temperatures of the transformations were determined by differential scanning calorimetric measurement to be $M_f = 293$ K, $M_s = 305$ K, $A_s = 323$ K and $A_f = 336$ K. Plate specimens of $30 \text{ mm} \times 18 \text{ mm} \times 1 \text{ mm}$ in dimension...
were deformed in martensitic state in simple shear using an Adamel Lhomargy DY35 universal mechanical testing machine. The shear gauge section was 30 mm × 3 mm × 1 mm and the shear direction was along the length of the specimen. This deformation mode was effective in avoiding localised deformation behaviour. Testing temperature was controlled using a liquid bath at 283 K, which was 40 K below the $A_u$ temperature of the specimens. Prior to cycling, specimens were cooled in liquid nitrogen to ensure a martensitic structure. Deformation cycling was performed between ±6% shear strains in martensitic state by displacement control using an LVDT mounted on the grips near the specimen.

Transformation behaviour of the specimens after the cyclic deformation was studied by differential scanning calorimetry (DSC) using a NETZSCH STA-409 simultaneous thermal analyser. Specimens for DSC measurement were cut from the centre of each deformed plate using a low speed diamond cutoff wheel. All the cutting and specimen handling after the deformation were carried out at below 293 K to avoid any undesired phase change prior to DSC measurement. All DSC measurements started by heating from room temperature and followed through another complete thermal transformation cycle. DSC measurements were performed in Ar atmosphere with a cooling/heating rate of 10 K/min.

3. Results

Figure 1 shows a collection of stress-strain curves recorded during deformation cycling at 283 K, 10 K below the $M_f$ temperature of the specimen. Thus the deformation proceeded via martensite reorientation. The curves correspond to deformation cycles of 1, 2, 5, 20 and 100, as indicated in the figure. It is seen that the magnitude of the stresses at both strain limits of the cycle increased progressively during cycling whereas the stresses at zero strain decreased with cycling, resulting in a decrease in the stress hysteresis of the ferroelasticity.

Samples deformed for different number of cycles were produced for thermal analysis of transformation behaviour. For each analysis a new sample was used. All ferroelastic cycling tests started from the origin marked as point O in the figure and stopped by unloading to zero stress in the first quadrant to position A. The sample deformed to +6% strain is denoted as having been cycled for 0.5 cycle; the sample cycled by deforming to +6% → -6% → +6% is denoted as for 1.5 cycles, as indicated in the figure. For specimens deformed for more than 50 cycles, this decimal notation is omitted when the error thus caused becomes insignificant.

Figure 2 shows DSC measurements of transformation behaviour in the first cycle of three specimens: an undeformed specimen (a), a specimen deformed to 6% via martensite reorientation (b), and a specimen deformed between ±6% strains for 50 cycles (c). For each transformation the critical temperature at the maximum heat flow was determined. It is seen that deformation to 6% strain caused an increase in the temperature for the reverse transformation by 14 K. Cycling to the same strain limit for 50 cycles resulted in a further increase of this temperature by another 14 K. For the forward transformation on cooling, on the other hand, deformation to 6% resulted in a decrease in the transformation temperature, however by a smaller margin as compared to the change in the temperature for the reverse transformation. After 50 cycles a further decrease in transformation temperature on cooling was observed. Associated with the changes in transformation temperatures, the transformation sequence on cooling also changed, from a single step $A \rightarrow M$ transformation to a two step $A \rightarrow R \rightarrow M$ process.

Figure 3 shows the transformation behaviour of specimen (c) in the second thermal transformation cycle in comparison with that in the first transformation cycle. A remarkable difference in temperature for the reverse transformation was evident between the first heating and the second heating. For specimen (c), the reverse transformation in the first cycle occurred at a temperature 34 K above that in the second cycle. Comparing with specimen (a), it is seen that the reverse transformation in the second cycle occurred at a similar temperature with the reverse transformation of the undeformed specimen. The forward transformations on cooling, on the other hand, showed little difference between the first and second cycles. In subsequent cycles the transformation behaviour was found to be essentially the same as that observed in the second cycle, except for some moderate changes as expected for the effect of thermal cycling.
DSC measurements for all specimens are shown in Fig. 4. The reverse transformation on first heating was observed to increase continuously to higher temperatures with increasing number of cycles (Fig. 4(a)). For the forward transformation on cooling (Fig. 4(b)), it is seen that the R-phase transformation emerged after 1.5 cycles whilst the martensitic transformation shifted continuously to lower temperatures. The reverse transformation in the second cycle was affected only moderately by the ferroelastic cycling (Fig. 4(c)). The forward transformations in the second cycle were essentially the same as those in the first cycle; thus their DSC curves are omitted from presentation.

Transformation temperatures determined from the DSC measurements are shown in Fig. 5. The temperature for the reverse transformation on the first heating, $T_{\text{fA}}^1$, increased rapidly during initial cycles and saturated at $\sim 362$ K after 10 cycles, 30 K above the initial value prior to cycling. The temperature for the reverse transformation on the second heating ($T_{\text{fA}}^2$), on the other hand, decreased moderately in the initial cycles, and stabilised at $\sim 326$ K, 5 K below that of the undeformed specimen. For the forward transformations on cooling, the temperatures for the martensitic transformation decreased with cycling in initial cycles and saturated at $\sim 285$ K after 10 cycles. The temperature for the R-phase transformation remained unchanged once the transformation emerged, at $\sim 299$ K. Practically no systematic differences were observed between the transformation temperatures in the first and the second cycles for both the martensitic transformation and the R-phase transformation.

Figure 6 shows the measurement of temperature intervals for the reverse transformation, determined as $\Delta T = A_f - A_s$, on the first heating ($\Delta T_1$) and the second heating ($\Delta T_2$). The temperature intervals for the forward transformations on cooling were not measured because of the appearance of the R-phase transformation. It is seen that $\Delta T_1$ decreased with ferroelastic cycling, from 11 to $\sim 7$ K after 10 ferroelastic cycles. $\Delta T_2$, on the other hand, increased rapidly in the initial cycles to a maximum of 19 K after 10 cycles and then decreased continuously to below the initial value.

Measurements of transformation heat are shown in Fig. 7. The endothermic heat of the reverse transformation in an undeformed sample was measured to be 22 J/g. After a simple deformation to 6% shear strain, i.e., after 0.5 cycle of deformation, the heat was increased to 28 J/g. Continuation of the deformation cycling resulted in a further increase of $Q_{h}^1$. After 100 cycles, $Q_{h}^1$ reached 37 J/g, an increase of nearly 70% of that of the undeformed specimen or a further increase of 32% compared to the specimen after 0.5 cycle (simple defor-
The mechanical work dissipated in a ferroelastic cycle, as measured as the area enclosed inside a ferroelastic stress-strain loop, is shown in Fig. 9 as a function of the number of cycles. It is seen that the mechanical work dissipated in a ferroelastic cycle decreased during cycling. The initial value of the mechanical work dissipated in a ferroelastic cycle between ±6% was measured to be 3.54 J/g. After 200 cycles the value decreased to 2.74 J/g, corresponding to 77% of the original value. The rate of decrease of the mechanical work dissipation diminished with deformation cycling, as expected.

4. Discussion

4.1 Stabilisation of martensite due to ferroelastic cycling

The phenomenon of martensite stabilisation, as indicated by the increase of the transformation temperature for the reverse transformation, has been reported for a number of deformation conditions, including shear deformation of martensite, tensile deformation of martensite, tensile deformation of austenite and cold rolling. It has been suggested that reorientation of martensite variants and introduction and rearrangement of defects caused by the deformation are responsible for this effect. In a polycrystalline matrix, reori-
entation of martensite variants via deformation releases internal elastic energy stored in the self-accommodating thermal martensite and, on further deformation, creates an internal elastic stress filed in the direction of the reoriented martensite. The release of the internal elastic stresses in the thermal martensite reduces the driving force for the reverse transformation. The creation of the new internal elastic stress field in the direction of the oriented martensite imposes a resistance to the reverse transformation. Both changes contribute to the stabilisation effect. According to this hypothesis, the degree of stabilisation, i.e., the magnitude of the increase of $T_m^2$, is expected to be dependent on the state of internal elastic stresses, which is determined by the mode and degree of deformation. The experimental results of this study, however, demonstrated that deformation cycling to the same strain limits is effective in causing further stabilisation to the martensite, as evident in Fig. 5. This suggests that a second mechanism in addition to the release of internal elastic energy is also effective in causing the stabilisation effect. This is attributed to internal plastic deformation.

It has been suggested that internal plastic deformation is required for martensite variant reorientation in polycrystalline matrices as a mechanism to co-ordinate for the orientation mismatch among neighbouring grains during deformation. Xie et al. observed under transmission electron microscope that after ferroelastic cycling in tension and compression some local spots with highly concentrated dislocations were formed at junctions of martensite variants in NiTi. The occurrence of such an internal plastic deformation not only results in the establishment of a new internal elastic stress field but also leads to an increase in the resistance to displacive transformation boundary movement. Therefore, the reverse transformation of the oriented martensite has to overcome this additional internal resistance to proceed. This also contributes to the stabilisation effect.

4.2 Effect of ferroelastic cycling on transformation temperatures

In addition to the continuous increase of $T_m^2$ with ferroelastic cycling, transformation temperatures after the first reverse transformation, $T_m^2$ and $T_M$, were also affected. Both $T_m^2$ and $T_M$ decreased with increasing number of ferroelastic cycles. Decreases of $T_m^2$ and $T_M$ are consistent with the expectation for the effect of internal plastic deformation on transformation behaviour, such as in the case of thermal cycling. The appearance of the R-phase transformation after ferroelastic cycling is also indicative of internal plastic deformation. The temperature for the R-phase transformation remained unchanged during ferroelastic cycling. This phenomenon is commonly observed under other experimental conditions, such as thermal cycling. This is attributed to the small magnitude of lattice distortion associated with the R-phase transformation, which renders the transformation lower sensitivity to the influence of stress.

Significant changes in temperature interval of the transformations have been observed, as shown in Fig. 6. As discussed previously, temperature interval of a transformation is determined by two factors: spatial inhomogeneity of the matrix and shift of local thermodynamic equilibrium during the process of transformation. In a fully annealed matrix, when microstructural inhomogeneity is ignored, transformation interval (for the reverse transformation) is determined by:

$$
\Delta A = A_f - A_s = \frac{[\Delta E_{el}(0) - \Delta E_{el}(1)] + [\Delta E_{ir}(0) - \Delta E_{ir}(1)]}{\Delta S}
$$

where $\Delta E_{el}(f_m)$ is the change of mechanical elastic energy density associated with one infinitesimal step of transformation at $f_m$, $\Delta E_{ir}(f_m)$ is the density of irreversible energy dissipated during one infinitesimal step of transformation at $f_m$, $f_m$ is the volume fraction of martensite, and $\Delta S$ is the transformation entropy change. For the oriented martensite induced by deformation in a polycrystalline matrix, an internal stress field is created in the direction of the deformation.

Thus, the reverse transformation of the oriented martensite proceeds by overcoming this resistive stress, which is limited by the strength of the matrix. This implies that whilst the resistive force to the reverse transformation remains high, its variation during the course of the transformation is small, i.e., $[\Delta E_{el}(0) - \Delta E_{el}(1)]$ and $[\Delta E_{ir}(0) - \Delta E_{ir}(1)]$ are small. This is believed to be responsible for the reduced temperature interval. For the transformation in the second cycle, martensite is formed in response to residual internal stresses at the beginning of the transformation, causing a relaxation of internal elastic energy change, as evidenced by the occurrence of two-way memory after the deformation. The internal elastic stresses are quickly relaxed during the early stages of the martensitic transformation, due to the fact that transformation lattice distortion of martensite is much greater than the elastic strain of the matrix. Continuation of the transformation creates new internal stresses in the opposite direction to each martensite, causing a positive elastic energy change. Thus, $[\Delta E_{el}(0) - \Delta E_{el}(1)]$ and $[\Delta E_{ir}(0) - \Delta E_{ir}(1)]$ are expected to be much greater than in the case of reverse transformation of oriented martensite. This is believed to be responsible for the enlarged temperature interval of the reverse transformation in subsequent transformation cycles. The decrease of the temperature interval with further ferroelastic cycling may be attributed to increased mechanical regularity of the matrix.

![Diagram](https://via.placeholder.com/150)
due to repeated deformation.

4.3 Effect of ferroelastic cycling on transformation heat

The transformation heat, as measured by DSC, was increased as a result of the ferroelastic cycling. After a simple deformation to 6% shear strain, the heat of the reverse transformation increased by $\sim 6.1 \text{ J/g}$. Ferroelastic cycling resulted in a further increase by another 9 J/g, totalling 15 J/g. The instantaneous heat effect associated with an infinitesimal step of the (reverse) transformation at stage $f_{m}$, as measured by DSC, can be expressed as: $^{4}$

$$dq = [\Delta H + \Delta E_{el}(f_{m}) + \Delta E_{ir,w}(f_{m})] \cdot df_{m} \quad (2)$$

where $\Delta H$ is transformation enthalpy change and $\Delta E_{ir,w}$ is the irreversible energy dissipated in any form other than heat. The total heat effect (assuming a complete transformation), i.e., the total heat exchange between the transformation system and its surroundings (the DSC), of the reverse transformation is:

$$Q = \int_{f_{m}}^{0} dq = \Delta H + e_{el} + e_{ir,w} \quad (3)$$

where $e_{el} = \int_{f_{m}}^{0} [\Delta E_{el}(f_{m})] \cdot df_{m}$ is the total internal elastic energy change in the matrix and $e_{ir,w} = \int_{f_{m}}^{0} [\Delta E_{ir,w}(f_{m})] \cdot df_{m}$ is the total irreversible work other than heat dissipated during the reverse transformation. In this equation, $\Delta H$ is a material-constant. $\Delta E_{el}$, hence $e_{el}$, is regarded as a function of state and is dependent on the structure of martensite variants, thus the degree of deformation. Therefore, these two parameters cannot be responsible for the further increase of transformation heat caused by ferroelastic cycling to the same strain limits. $\Delta E_{ir,w}$, on the other hand, is dependent on the resistance the reverse transformation is experiencing. As discussed in the previous section, the reverse transformation of oriented martensite proceeds against consistent high resistive internal stresses. Repeated ferroelastic cycling is expected to further increase this resistance by accumulating internal plastic deformation, resulting in further increase of transformation heat.

4.4 Mechanical work dissipated during a ferroelastic cycle

A mechanical work is consumed during a ferroelastic cycle of deformation. It is interesting to notice that whereas the endothermic heat of the reverse transformation was increased with ferroelastic cycling, implying an increased resistance to the thermal transformation, the mechanical work dissipated in a deformation cycle was decreased, as shown in Fig. 9. A mechanical work may be either dissipated as heat, for example when a dislocation is moved, or stored in the structure as defects, such as dislocations. An increase in dislocation density in the matrix is expected to increase heat dissipation whereas a decrease in the rate of dislocation production will lead to a decrease in the storage of irreversible mechanical work in the matrix in each cycle. In light of this concept, the decrease of the mechanical work during ferroelastic cycling is attributed to the combined effect of both and is dominated by the decrease of the number of defects produced in each deformation cycle.

It is also interesting to compare the effects of ferroelastic cycling on the mechanical work dissipated in a ferroelastic cycle and the heat loss of a thermal transformation cycle. It is seen in Fig. 8 that the heat loss, $Q_{h} - Q_{c}$, increased slightly with cycling. The increase in the heat loss was clearly due to the increase in dislocation density, which increased the frictional resistance to transformation phase boundary movement.

5. Conclusions

(1) Deformation by martensite reorientation in a polycrystalline matrix causes stabilisation to martensite, as indicated by the increase of the first reverse transformation of the deformed martensite. Repeated deformation within the same deformation limit further stabilises the martensite. In addition to the increase of transformation temperature, transformation heat of the first reverse transformation was also increased by as much as 70% as a result of ferroelastic cycling.

(2) Whereas the stabilisation caused by martensite reorientation deformation can be attributed to variations in transformation elastic and irreversible energies, further stabilisation caused by ferroelastic cycling is largely attributed to an increase in the irreversible energy due to accumulated internal plastic deformation.

(3) The mechanical energy dissipated during a ferroelastic deformation cycle decreases with ferroelastic cycling. This is attributed to the decrease in the rate of dislocation production with cycling. The heat loss during a thermal transformation cycle, as measured by thermal analysis, increased with ferroelastic cycling. This is attributed to the increase in dislocation density caused by the cyclic deformation.

REFERENCES