In situ transmission electron microscopy of stress-induced martensite with focus on martensite twinning

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Abstract

At the proper composition and after receiving the appropriate thermomechanical treatment, NiTi shape memory alloys show shape memory and superelastic behaviour. These effects are due to the martensitic transformation, and a proper understanding of the microstructural aspects of this transformation is essential to develop accurate models describing the macroscopical behaviour. In this work, transmission electron microscopy combined with in situ straining is used to investigate microstructural features of the stress-induced transformation. Two kinds of samples are investigated: a superelastic polycrystalline NiTi sheet and a single crystal of NiTi, both overstoichiometric in Ni. Regarding the superelastic material, the martensite plates induced by straining are reversible upon relaxing and do not seem to consist of more than one variant. In the single-crystal sample, the induced martensite plates are not reversible and contrasts possibly due to twinning are observed.

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1. Introduction

Near equiatomic NiTi alloys show good shape memory behaviour and/or superelastic properties, normally after having been received an appropriate thermomechanical treatment [1,2]. These properties find their origin in the martensitic transformation, in this case a transformation from the cubic B2 phase (austenite) to the monoclinic B19' phase (martensite), and a possible intermediate R-phase. This transformation can be induced by temperature change and/or applying a stress. In the second case this might yield strains of 10% that are almost fully recoverable, better known as super- or pseudoelasticity. The stress–strain curve of the material has a plateau where continuous straining can be performed at a constant stress. Models have been produced [3–6] in order to be capable of predicting these stress–strain curves as accurately as possible, eventually for being used in simulations to predict the response of industrial components. Knowledge concerning the microstructure of this transformation is a necessity to develop such accurate models. Using in situ optical microscopy of a stress-induced martensite transformation, Brinson et al. [7] were able to study polycrystalline samples concluding that different orientation variants are induced and that the transformation occurs throughout the entire specimen during straining and not only in macroscopically observed transformation bands. However, optical microscopy is not able to resolve the possible microtwins that are expected to occur in martensite plates. In the present work in situ transmission electron microscopy (TEM) straining experiments are used to study the stress-induced martensitic transformation. Similar experiments were done previously [8–10] and although in Ref. [9] the presence of twins is used to explain the reversibility of martensite it is still unclear whether the observed contrasts are due to twinning or stacking faults. In the present experiments the relation between reversibility and microstructure of the stress-induced plates is investigated. Bright-field (BF) imaging in combination with diffraction patterns (DP) and DP simulations are used to determine whether twinning is present or not. Since the microstructure has such a large influence on the properties of NiTi, two different kind of samples were investigated; treated polycrystalline NiTi exhibiting superelasticity...
and non-superselastic single crystal material without a particular thermomechanical history.

2. Experimental setup

Samples are made from the two different kinds of Ni-rich NiTi, a sheet of superelastic polycrystalline NiTi with a thickness of 120 µm containing multiple dislocations and nanosized Ni₃Ti₃ precipitates and single crystals of Ni₅₀.₂Ti₄₉.₈ (at.%) grown by the Bridgman technique. All samples were prepared to have a dog-bone shape by sawing a basic rectangular shape, spark cutting to drill the mounting holes and dimpling from the side for the (circular) intrusions that yield the typical dog-bone shape. A final electropolishing step was used to create a thin part in the middle of the sample and a centred hole surrounded by an electron transparent area. The latter was done in a twin-jet electropolishing unit using a mixture of 20% sulphuric acid and 80% methanol with a potential of 21 kV at a temperature of 9 °C. In some cases a pre-thinning was done in the middle of the specimen by dimpling in order to assure the electropolishing results in a hole centred in the middle of the rod. The holder is used in a CM20 microscope operated at 200 kV but has only one tilt axis available, which is coinciding with the direction of specimen elongation. A consequence of this single tilt axis is that specific crystal zone orientations could not always be obtained or at least not in exact conditions. The strain-holder only allows controlling the strain and no information concerning the magnitude of the applied stress is available.

3. Results

3.1. Superelastic polycrystalline NiTi

The first strain induced martensite plates appear in the electron transparent area of the polycrystalline sample after 1% of elongation, which incorporates a possible accommodation of the specimen versus the holder. These first platelets grow in areas that accommodate to higher stresses like at crack tips, grain boundaries and small inclusions as carbide or oxide particles. Upon further straining martensite plates also appear in areas located in the interior of grains Fig. 1. These plates start out very thin with a 2D aspect ratio of about 1/20 and have the same growth direction and orientation in one given area of approximately 20 µm². In different areas, which might be localized in one single grain, the plates may have different growth directions, which meet and intersect when the separated martensite areas get larger upon continued straining. These different growth directions might be related with different orientation variants of martensite, although this could not be confirmed by diffraction measurements. During straining the plates continue to grow in a discontinuous manner and in addition new plates nucleate and keep growing upon straining. The arrow in (b) points towards a newly nucleated plate.

![Fig. 1. Growing of martensite plates during straining of the sample, with a sample elongation of (a) 1.06%, (b) 1.08%, (c) 1.10% and (d) 1.16%; new plates nucleate and keep growing upon straining. The arrow in (b) points towards a newly nucleated plate.](image-url)
in between the already present ones, as seen at the arrow in Fig. 1b. The reversibility of the transformation was examined by subsequently straining and relaxing (with the remark that the specimen was relaxed up to a point where the area of interest was retransformed into austenite which is not necessarily a complete relaxation of the specimen as such). From the observations it is seen that the martensite plates completely disappear after relaxation and always nucleate and grow at the same positions and in the same direction, even after the fifth cycle. This suggests a possible pinning of the martensite plates at certain nucleation sites.

As mentioned before, only one tilt axis is available, but nevertheless the transformation from austenite to martensite could in some cases be observed in diffraction mode. From the obtained patterns it is seen that the (1 1 1)_{B2} zone transforms into the [1, −1, 0]_{B19'} zone, which confirms the transformation from B2 to

Table 1
Most common twinning modes in NiTi B19' martensite [1]

<table>
<thead>
<tr>
<th>Twinning mode</th>
<th>$\kappa_1$</th>
<th>$\eta_1$</th>
<th>$\kappa_2$</th>
<th>$\eta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I {−1, −1, 1}</td>
<td>(−1, −1, 1)</td>
<td>[0.540430, 0.45957, 1]</td>
<td>(0.246950, 0.50611, 1)</td>
<td>[−2, −1, 1]</td>
</tr>
<tr>
<td></td>
<td>(−1, 1, 1)</td>
<td>[0.540430, −0.45957, 1]</td>
<td>(0.246950, −0.50611, 1)</td>
<td>[−2, 1, 1]</td>
</tr>
<tr>
<td>Type I {1 1 1}</td>
<td>(1 1 1)</td>
<td>[−1.51172, 0.51172, 1]</td>
<td>(−0.66875, 0.33750, 1)</td>
<td>[2 1 1]</td>
</tr>
<tr>
<td></td>
<td>(1, −1, 1)</td>
<td>[−1.51172, −0.51172, 1]</td>
<td>(−0.66875, −0.33750, 1)</td>
<td>[2, −1, 1]</td>
</tr>
<tr>
<td>Type I {0 1 1}</td>
<td>(0 1 1)</td>
<td>[1.57271, 1, −1]</td>
<td>(0.72053, 1, −1)</td>
<td>[0 1 1]</td>
</tr>
<tr>
<td></td>
<td>(0, −1, 1)</td>
<td>[−1.57271, 1, −1]</td>
<td>(−0.72053, 1, 1)</td>
<td>[0, 1, −1]</td>
</tr>
<tr>
<td>Type II {0 1 1}</td>
<td>(0.72053, 1, −1)</td>
<td>[0 1 1]</td>
<td>(0 1 1)</td>
<td>[1.57271, 1, −1]</td>
</tr>
<tr>
<td></td>
<td>(0.72053, 1, −1)</td>
<td>[0, 1, −1]</td>
<td>(0, 1, −1)</td>
<td>[−1.57271, 1, 1]</td>
</tr>
</tbody>
</table>
B19′. Note that there is no indication of the occurrence of the R-phase. A series of diffraction patterns during straining is shown in Fig. 2, and allows to determine the orientation relationship between austenite and martensite which is in this case [1, −1, 0]B19′//[1, 1, −1]B2 with an angle of 4.2° between (0 0 1)B19′ and (1 0 1)B2 which is coinciding well with the known one for B2 and B19′, except that the angle between (0 0 1)B19′ and (1 0 1)B2 is somewhat smaller than what is expected (around 6.5°) [11].

Neither the BF images nor the DP’s show any contrast or spot splitting that can be immediately related to twinning. In order to find out whether this effectively implies the definite lack of twinning a comparison with simulated diffraction patterns in case of twinning was performed.

Most observations were close to the [1 1 1]B2//[1, −1, 0]B19′ zone, probably due to texture of the material, so diffraction patterns for different types of possible twinning are simulated in this zone orientation and compared to the experimental ones. This was done with a standard kinematical DP simulation in which both B19′ variants are given a 50/50 ratio in the considered twin band structure. The different twin relations checked for being present are given in Table 1, for which the parameters $K_1$ and $\eta_1$ are used to create the correct orientation relationship between the two variants. Four of the eight resulting diffraction patterns are given in Fig. 3, in which the black spots are belonging to the variant in the [1, −1, 0]B19′ orientation and the grey ones to the twin variant. These illustrations show that if twinning occurs there should be well-separated spots present, originating from the second variant, which should show up in the experimental diffraction pattern. In case of two of the simulated relations: Type I {001} with $K_1$: (0, 1, −1) and Type II ⟨001⟩ with $\eta_1$: [0, 1, −1] (which is the one most observed [1]) there is only a fine splitting of spots present, but nevertheless this should be noticeable in the observed diffraction patterns. Regarding the obtained patterns it is concluded that if one of the twinning modes of Table 1 is present it should be detectable in the [1, −1, 0]B19′ zone orientation. Investigating the diffraction recordings made for stress-induced martensite plates these kinds of patterns or spot splitting were never observed. This is illustrated in Fig. 2c in which indeed only spots from [1, −1, 0]B19′ appear and the vague spot splitting which is present is due to remnants of the B2 structure. Also compound twins are expected to yield extra diffraction spots. However, this was not explicitly checked, since they are not allowed according to the crystallographic theory of martensite [1].

3.2. Single crystal

Lesser observations were made in the single crystal material since after preparing the TEM specimen a high amount of martensite appeared to be already present [the ($M_S$) temperature around 10°C was close to the electropolishing temperature] and it can not be regarded anymore as being a perfect austenite single crystal. Nevertheless, the untransformed regions of austenite do not show the dense dislocation/precipitation structure as in the case of the polycrystalline sample but only a few more widely dispersed carbide/oxide inclusions are found. In this case martensite is nucleating at less numerous sites and the plates grow larger having a different geometry compared to those in the superelastic material. A recording of the growing martensite plates is given in Fig. 4, a magnification of the inset in Fig. 4(d) shows possible twinning contrast, but insufficient diffraction data could be obtained to confirm this. Still,
4. Discussion

Regarding the observations obtained from the superelastic material, the strain induced martensite plates seem to consist of one variant since most common types of twinning, normally occurring in temperature induced martensite, are not present nor was there any other indication of twinning in these reversible martensite plates. This possibly relates to experiments and simulations for polycrystalline material performed by Lexcellent and Blanc which show that when twinning is incorporated in the model of simulation the phase transformation yield surface is not well coinciding with the results of biaxial loading experiments. When simulations are performed assuming an untwinned interface between martensite and austenite there is a far better agreement with the experimental results [6]. The modeled material in their simulations can be identified with the superelastic material used in present experiments, and the current observations seem indeed to confirm the hypotheses of an untwinned martensite–austenite interface. On the other hand, twins or corresponding-variant pairs are normally considered necessary to have a compatible interface between austenite and martensite satisfying the invariant plane strain condition. However, the crystallographic theory of martensite [12–14] does allow the possibility of an interface between austenite and untwinned martensite for special cases of the martensite monoclinic lattice constants, but these conditions are not fulfilled in the actual case of near-equiatomic NiTi as pointed out by Lexcellent and
Blanc [6]. However, as we are dealing with strained material it could be conceived that the lattice constants of the structures involved are different from those of the listed thermoelastic structures and thus might fit the conditions for an untwinned martensite–austenite interface. When taking this reasoning one step further one could realize that, due to the straining, also the austenite could deviate from the perfect cube before transforming so that in fact more complicated equations should be developed for describing the actual rules for twinning at the martensite–austenite interface.

The experimental findings in the superelastic material are in contradiction to what is observed in the non-superelastic NiTi single crystals for which twinning or at least defect structures seems to be present in the stress-induced martensite plates. Moreover, in this case the martensite plates are not reversible upon relaxing, and they are larger in size. A reason for larger plate size could be found in the fact that there are less nucleation sites for the martensite, since the investigated areas are single crystalline with a very low density of lattice defects, so a single plate can grow larger whereas in the first case more small plates merge with each other to form larger martensite areas. Normally first twinning is expected followed by detwinning upon further straining.

5. Conclusion

Strain-induced martensite plates in the polycrystalline superelastic material are reversible in nature and this during several straining and relaxing cycles. Moreover, a diffraction study points out that no twinning seems to be present in these martensite plates, which is supporting a hypotheses made by Lexcellent and Blanc [6]. When a same experiment is repeated with a single crystal of austenite the strain-induced plates are not reversible, they are larger in size and twinning of the plates seems to be present. Thus, the morphology of martensite plates yielding superelasticity seems to be different compared to those that do not transform in a reversible way.

Acknowledgments

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