Microstructural and mechanical challenges in biomedical NiTi

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Abstract. The mechanical behaviour of NiTi shape memory alloys superficially resembles that of certain biomaterials, such as bones or tissues: By virtue of a reversible martensitic phase transformation, NiTi alloys can recover relatively large strains; uniaxial stress-strain curves exhibit constant stress-plateaus (at several hundreds of MPa, depending on alloy composition and testing temperature) associated with the phase transition. These novel functional properties, in combination with high mechanical strength in ultra-fine grained NiTi and good biocompatibility, are utilized in various implants and medical devices. Yet – and quite similar to hierarchically structured biomaterials – the deformation behaviour of NiTi is intricately linked to distinct deformation processes on several length scales, and there remain significant gaps in our understanding of the microstructure-property relations. In the present paper, recent experimental and theoretical results from first-principles calculations, micromechanical modelling and nanoindentation are discussed with a focus on the role of inelastic deformation processes, twin boundaries and the interaction of plastic deformation and stress-induced phase transformations. These novel findings challenge our understanding of the fundamental mechanical properties of NiTi. They highlight the importance of inelastic deformation mechanisms for the overall mechanical properties and strength of NiTi.

1. Introduction
NiTi shape memory alloys are the most important shape memory alloys today, mostly because their superior mechanical properties have led to the development and successful market launch of products and devices in the field of biomedical applications [1-4]. In particular implants such as stents are in direct contact with biological materials (tissues, bones), and therefore biocompatibility is an important topic in NiTi research in the chemistry and medical communities. It has been noted before [4] that shape memory alloys phenomenologically share some characteristic features in terms of mechanical behaviour, in particular non-linear behaviour associated with extended constant stress-plateaus in uniaxial tensile testing, thermo-mechanical hysteresis and the ability to recover substantial amounts of strain (in pseudoelastic NiTi, of the order of 10%). One may argue that there is also a microstructural analogy that extends beyond a merely superficial resemblance in mechanical behaviour: Biomaterials are characterized by highly hierarchical microstructures, where different elements and substructures on various length scales fulfil several functions [5-7]. At least to some extent, the stress-induced martensitic transformation (which is fully reversible during unloading and thus gives rise to the shape memory effect) results in the formation of similarly complex substructures. Martensite nucleating in the austenitic matrix forms twins in order to minimize strain energy related to the accompanying shape change (transformation strain), and the resulting martensitic microstructures consist of increasingly finer martensite plates and needles which are often internally twinned [1]. In ultrafine grained NiTi,
twin variants with widths as small as a few nanometers are observed [8,9]. Research on the mechanical properties of pseudoelastic NiTi shape memory alloys is challenging because the deformation behaviour is not only directly affected by the stress-induced phase transformation. Additional deformation mechanisms encompass several length scales and also need to be considered in detail to obtain a better understanding of the pseudoelastic deformation of NiTi.

![Figure 1](image)

**Figure 1.** Schematic representation of some of the relevant length scales associated with various deformation mechanisms in pseudoelastic NiTi. This paper is focused on transformation-induced, elastic and plastic deformation at the atomistic and microstructural length scale.

Figure 1 provides a schematic overview of those length scales that are typically important for the mechanical behaviour of materials. The macroscopic mechanical properties of NiTi (pseudoelastic stress-strain curve on the upper right; the beginning and end of the forward and reverse phase transformations is highlighted by arrows) are typically investigated by conventional tensile testing. However, localized deformation (formation and propagation of Lüders-like transformation bands) occurs in thin tensile NiTi specimens, and the distinct stress- and strain-states, as well as the distribution of volume fractions of the different phases, in the transition regions between fully martensitic and fully austenitic regions play a key role in stabilizing this mode of deformation [10-14]. Direct experimental investigations of micro-scale mechanical properties and transformation processes can for instance be performed by nanoindentation, micro-pillar testing and in-situ transmission electron microscopy (TEM) studies [15-18]. On the atomistic length scale, the fundamental thermoelastic properties of the crystal lattices are directly related to the electronic structure and lattice dynamics of the different phases [19-21].
Despite a vast body of literature on NiTi shape memory alloys, the aforementioned aspects of their mechanical behaviour are not yet understood completely. They are subject of intensive ongoing research activities. In this paper, several results from recent theoretical and experimental studies on different length scales will be briefly reviewed and discussed. Special emphasis is placed in (1) the elastic anisotropy of B19’ martensite, (2) the contribution of inelastic (but reversible) deformation mechanisms to the macroscopic mechanical behaviour, (3) elastic compatibility stresses at martensitic twin boundaries, and (4) the interaction of stress-induced phase transformation and conventional plastic deformation during nanoindentation of NiTi.

2. Elastic anisotropy in twinned NiTi martensites

Following a (rather idealized) bottom-up approach, one would like to completely capture the mechanical properties of an individual martensite variant, then study the mechanics of twinned microstructures, the properties of austenite/martensite interfaces, the interaction of distinct deformation processes with microstructural elements like grain boundaries and precipitates, and finally derive an accurate model for the resulting macroscopic mechanical behaviour, properly taking localized deformation of macro-scale specimens into account (see also figure 1). One most simple and first step is to study the elastic properties of the individual phases in NiTi. The anisotropic elastic behaviour of a crystal is fully determined by Hooke’s law

\[ \sigma_{ij} = c_{ij} \varepsilon_{j} \]

where the elastic constants \( c_{ij} \) relate stresses \( \sigma \) and strains \( \varepsilon \). Resonant ultrasound spectroscopy (RUS) has been used to experimentally determine the elastic constants of B2 NiTi austenite (cubic structure: 3 independent \( c_{ij} \), [23], and also for single variant specimens of 2H martensite (orthorhombic symmetry: 9 independent \( c_{ij} \)) in a CuAlNi shape memory alloy [24]. Unfortunately, this experimental approach is not feasible for B19’ NiTi martensite because of the very fine twins that are present even after the application of high stresses (which generally favour the formation of fewer martensite variants and which have been used in [24] to obtain single variant RUS specimens of CuAlNi). The full set of 13 independent elastic constants of monoclinic B19’ NiTi has, however, been recently estimated by a theoretical approach [22]. Ab-initio quantum-mechanical calculations allow the application of arbitrary strain states to a crystal lattice, and from the changes of free energy (and from the Hellmann-Feynman forces), the corresponding stress states and all elastic constants can be determined. The results are strictly valid only at zero K (i.e., finite temperature effects are neglected), and the high computational effort typically restricts such calculations to the simulation of perfect
crystal lattices (i.e., important microstructural features like dislocations, phase or grain boundaries, cannot be easily incorporated in these calculations). Moreover, when studying the elastic properties of the different phases of NiTi, additional difficulties arise (further details, both technical and on the interpretation of the results, are presented in [22,25]): As B2 austenite is only stabilized by entropical contributions at higher temperatures, the corresponding crystal structure is mechanically unstable at zero K, and while they qualitatively agree with those measured by RUS at higher temperatures, the elastic constants of B2 NiTi determined from ab initio calculations reflect this instability. Furthermore, in the calculations special shear stresses are needed to stabilize B19’ martensite which in their absence reverts into an orthorhombic B33 structure that has not been observed in experiment [21]. But despite these issues, the ab initio simulations were found to be useful in determining the elastic constants of B19’ NiTi, and several interesting conclusions can be drawn.

The ab initio calculations indicate that the NiTi martensites (B19’ as well as the theoretical B33 structure) are elastically anisotropic. To compare the anisotropic elastic properties of austenite and martensite, it is instructive to study the elastic modulus that would be measured if a single crystal specimen were subjected to uniaxial loading in a certain crystallographic direction. Figure 2 represents the direction-dependent elastic moduli for B2 austenite (determined from experimental elastic specimen were subjected to uniaxial loading in a certain crystallographic direction. Figure 2 represents the direction-dependent elastic moduli for B2 austenite (determined from experimental elastic constants after [23]) and B19’ martensite for the case where B2 and B19’ share one (001)-plane and the direction of loading is contained in that plane (see also the schematic representation of the cubic and monoclinic unit cells in the upper half of figure 2; the monoclinic unit cell of B19’ is uniquely characterized by the lattice constants/ monoclinic angle $a = 0.4108 \text{ nm}$, $b = 0.4646 \text{ nm}$, $c = 2.898 \text{ nm}$, $\beta = 97.8^\circ$, [26]). The distance of each curve from the origin is proportional to elastic modulus in that crystallographic direction. Figure 2 clearly demonstrates that B19’ martensite is elastically stiffer than austenite. In the case of purely elastic deformation of twinned B19’ martensite, Voigt-Reuss-Hill averaging predicts a macroscopic Young’s modulus of ~120 GPa [22], which is considerably larger than that of austenite (~60-80 GPa). This finding apparently contradicts most experimental data, where the macroscopic Young’s modulus of martensite is usually reported in the range of ~20-50 GPa (i.e., smaller than the theoretical value by a factor of three, and, more importantly, much smaller than that of austenite). Yet, the ‘true’ elastic modulus determined from ab initio calculations is in good agreement with recent neutron diffraction studies [27]; a high modulus confirms some long-held predictions [28] that additional deformation mechanisms play an important role in softening the macroscopic stress-strain response of martensitic NiTi. In fact, when the elastic constants of B19’ are used as input for an advanced micro-mechanical model, an analysis of the evolution of the volume fractions of different martensite variants clearly shows that detwinning (growth of one favoured variant that consumes a less favoured twin variant), reorientation (growth of entirely new variants from an already twinned martensitic structure), or additional transformation of residual austenite can occur during uni- and biaxial loading [29]. In particular at higher stresses, these inelastic (but reversible) deformation mechanisms contribute by more than 50% to macroscopic strains. Therefore, despite the high elastic stiffness introduced in the micromechanical model, the macroscopic stress-strain behaviour is in excellent agreement with experimental data [30].

Further mechanical analysis of B19’ martensite requires consideration of the special mechanical properties of twinned structures. While such analyses have been performed to a great level of detail and in excellent agreement with experimental observations before [31], the effect of the elastic anisotropy of B19’ on the stress-states at twin boundaries has not been studied before simply because the elastic constants were unknown. In a first (and strongly simplified) attempt to study B19’ twin boundaries, consider a stack of thin martensite twins as shown schematically in figure 3. When such a twinned structure is subjected to external loading, individual variants will deform differently because of elastic anisotropy and because of their different orientation (shown schematically by the monoclinic unit cells in figure 3) with respect to the external loads. As the thin twin variants are coherently joined at the twin boundaries, additional stresses (so-called compatibility stresses) arise at each twin boundary. A simple analytical model of these purely elastic compatibility stresses in (infinitely large) bicrystals has been presented by Gemperlova et al [32]. The special symmetry of twin boundaries can
be used to further simplify their expressions for the compatibility stresses at the interface. The most important twins in coarse grained NiTi, <110> type II twins, are characterized by an irrational habit plane \( K_1 = (-1,1,0.72053) \) and by a shearing direction \( \eta_1 = [1,1,0] \). \[33\]. When the matrix of elastic constants is rotated so that \( \eta_1 \) points in the 1-direction indicated in figure 3, and \( K_1 \) is parallel to the 2-direction, the compatibility stresses \( \sigma^C \) in the first variant (e.g., the blue variant in figure 3) according to the model of Gemperlova et al. (and using Voigt's notation, \[34\]) for an arbitrary applied load case \( \sigma^A \) are given by

\[
\begin{align*}
\sigma_{1C}^C &= -0.156 \cdot \sigma_{1}^{A} - 0.1804 \cdot \sigma_{6}^{A} \\
\sigma_{5}^{C} &= -0.679 \cdot \sigma_{5}^{A} - 1.187 \cdot \sigma_{6}^{A} \\
\sigma_{5}^{C} &= -0.054 \cdot \sigma_{1}^{A} - 0.304 \cdot \sigma_{6}^{A} + 0.297 \cdot \sigma_{5}^{A} - 0.209 \cdot \sigma_{4}^{A}
\end{align*}
\]

\[2\] \[3\] \[4\]

Figure 3. Compatibility stresses arise at twin boundaries between individual variants (blue or green; different crystal orientations are indicated by the orange unit cells) because of the anisotropic deformation of individual variants. In the simple scenario shown schematically here, stresses and elastic constants are defined in the Cartesian coordinate system with the 2-direction perpendicular to the twin boundaries.

The stresses in the second variant (green in figure 3) have the same magnitude, but an opposite sign. In polycrystalline NiTi, the interaction with an adjacent austenitic or partly martensitic matrix does obviously impose more complicated boundary conditions than those considered in the simple toy scenario depicted in figure 3. Moreover, the approach of Gemperlova et al. is strictly only valid at the twin boundary and in infinite bodies. While further work is required to develop these considerations into a more realistic model of twin boundary compatibility stress in martensitic NiTi, it is noteworthy that equations (2)-(4) demonstrate that the elastic compatibility stresses in B19\(^\prime\) type II twins are of a similar order of magnitude as the applied stresses. Because this scenario is purely elastic, the compatibility stresses are superimposed to the applied stresses. The resulting stress state may therefore well affect dislocation nucleation at twin boundaries or provide an additional driving force for reorientation or detwinning.

3. Nanoindentation and plastic deformation

Given the many different deformation mechanisms that can be activated in NiTi as well as the excellent shape recovery of pseudoelastic alloys, it is perhaps not too surprising that plastic deformation by conventional dislocation slip has not been studied in detail by the shape memory community. Instead, the focus of research has been mainly placed on crystallographic and thermodynamic aspects of the reversible phase transformation. However, dislocations do indeed play an important role in determining the mechanical properties of NiTi in several respects: During cyclic mechanical or thermal loading, the gradual accumulation of dislocations and stabilized martensite results in functional fatigue (changing phase transformation temperatures, decreasing plateau stresses). This degradation of functional properties limits the service life of NiTi applications and is not fully understood today \[35,36\]. Moreover, nanoindentation experiments indicate that, while pseudoelastic recovery during unloading can clearly be observed, strain gradients related with this micro-scale testing method also result in a more pronounced plastic deformation below the indenter tip. During nanoindentation, the applied force and the indentation depth are continuously recorded. As a measure
of pseudoelastic recovery, one can define the ratio of residual indentation depth and maximum indentation depth at maximum load (remnant depth ratio: $\rho$). $\rho$-values near zero indicate perfect shape recovery during unloading (i.e., no residual indent remains after indentation), and large $\rho$-values are related to plastic deformation, [37].

![Figure 4. Remnant depth ratio during nanoindentation of pseudoelastic NiTi as a function of representative strain. Spherical indentation data [37] exhibit increasing $\rho$-values with increasing strain. Some residual deformation is observed even at small strains.](image)

In figure 4, typical remnant depth data from experiments with different spherical indenter tips and maximum loads are summarized as a function of representative strain below the indenter tip. The representative strain, $0.2 \ a/R$, where $a$ is the contact radius and $R$ is the radius of the indenter tip, provides a simple yet effective estimate of the complex strain state below the indenter. It increases with increasing indentation depth in the case of spherical indentation. Indentation with sharp (Berkovich) tips is associated with a constant representative strain of $\sim 7.2\%$ for all indentation depths/maximum loads because of the self-similar shape of the pyramidal indenter tip. Figure 4 demonstrates that the large representative strain associated with sharp indentation cannot be provided by the stress-induced phase transformation alone. Instead, dislocation-mediated plasticity must occur, and this is reflected by large $\rho$-values of $\sim 65\%$ which are consistently observed for a wide range of indentation depths. An increased dislocation density has been reported below a Berkovich indent in a pseudoelastic NiTiFe alloy [38].

Spherical indentation allows to systematically vary the ratio between pseudoelastic and plastic deformation, figure 4. An increasing dislocation density below spherical indents with increasing indentation depth has also been documented [39]. But, most interestingly, even under optimum conditions (large indenter radii, small indentation depths and therefore small residual strains), some plastic deformation is evident from the corresponding $\rho$-values (which are typically $\sim 5-10\%$, figure 4). It is well known that nanoindentation is associated with large strain gradients [40]. Obviously, these strain gradients can only be accommodated by the formation of (geometrically necessary) dislocations even when the material can in principle accommodate large strains by a stress-induced phase transformation. The nanoindentation results presented here show that there is an intimate interaction between plastic deformation and transformation when pseudoelastic NiTi is deformed, in particular when strain gradients are present. As a closing thought, it is noted that future research on shape memory alloys may therefore allow extending conventional strain gradient plasticity models to more general classes of materials.
4. Summary and conclusions
The mechanical behaviour of NiTi shape memory alloys is affected by processes on various length scales. The present paper summarizes some aspects of the deformation mechanisms on the nano- and micro-scales. Recent ab initio simulations have demonstrated that B19’ NiTi martensite is elastically anisotropic, and that – in contrast to macroscopic observations – the ‘true’ elastic modulus of B19’ does exceed that of B2 austenite. While theoretically stiffer than austenite, martensitic NiTi is characterized by a considerably lower modulus of elasticity during macroscopic testing because additional deformation mechanisms occur when twinned NiTi martensite is subjected to external loading. The most important inelastic (but reversible) deformation processes include additional transformation, detwinning, or reorientation of twinned martensite. The effect of these deformation mechanisms has been demonstrated and analyzed by using the ab initio-derived elastic constants of B19’ NiTi in a micromechanical model. These simulations of uni- and biaxial load cases indicate that inelastic deformation processes considerably contribute to the macroscopic stress-strain behaviour in polycrystalline NiTi. Elastic anisotropy moreover results in compatibility stresses at twin boundaries of B19’ martensite. These stresses may well affect the twin boundary movement and/or dislocation nucleation at stresses beyond the pseudoelastic plateau. Finally, dislocation-mediated plastic deformation does not only affect the cyclic behaviour of NiTi – it becomes evident (and, in some cases, dominant) during nanoindentation of NiTi. While indentation with spherical indenters (where representative strains depend on the indentation depth and on the tip radius) allows studying the pseudoelastic behaviour of NiTi in small testing volumes, plastic deformation cannot be prevented completely because the strain gradients inherent in nanoindentation testing can only be accommodated by dislocation slip. Sharp (Berkovich) indenters are associated with a characteristic strain that requires considerable plastic deformation irrespective of indentation depth. One of the key challenges for future micromechanical/ microstructural studies lies in a detailed analysis of the complex interactions between dislocations (in both austenite and martensite) and the stress-induced, twinned martensite. Nanoindentation, in combination with in-situ or post-mortem microstructural analysis techniques, may represent a pathway for future systematic studies that address this need.

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