The influence of twinning in B19' martensitic structure of NiTi alloy on mechanical properties from first principles

P. Šesták[1, a], M. Černý[1,b] and J. Pokluda[1,c]

[1]Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2, 616 69, Brno, Czech Republic

[a]sestak@kn.vutbr.cz, [b]mcerny@fme.vutbr.cz, [c]pokluda@fme.vutbr.cz

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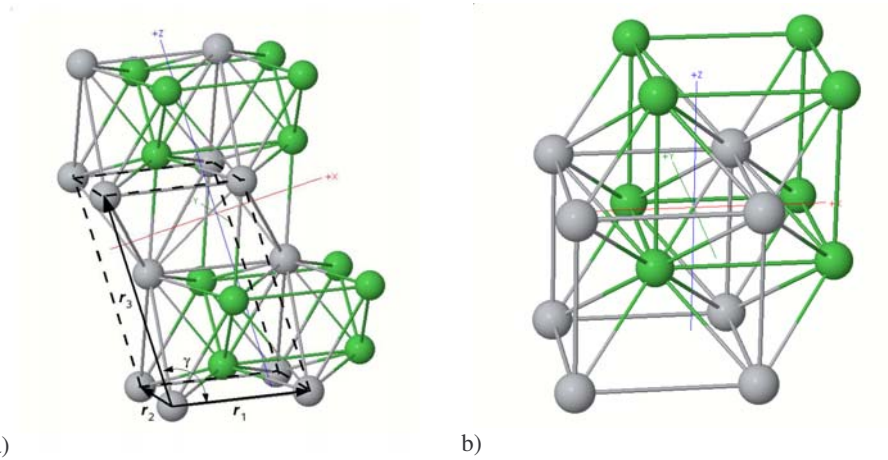
Abstract. The NiTi alloy (Nitinol) has become very important material in last years mainly owing to its shape memory effect which is connected with martensitic transformation from martensitic B19' to austenitic B2 structure and vice versa. The aim of this work is the study of (100) compound twinning mode in B19' martensitic structure of NiTi alloy and its influence on elastic moduli C_{ij}. The computed results show that the studied twinning mode does not have a significant influence to the elastic constants C_{ij}. Only a slight decrease of C_{44} and C_{66} constants was observed in a system containing twins.

Introduction

The NiTi alloys are important materials used in many industrial (actuators) and medicine (stents, bone implants, etc.) applications due to their shape memory effect. This effect is caused by transformation from martensitic (Fig. 1 on the left) to austenitic (Fig. 1 on the right) phase and vice versa and can be started by an external pressure or a temperature change. There are several types of the transformations, depending on a particular alloy composition. An extensive overview of current state of the art can be found in the paper by Otsuka and Ren [1]. There are also some papers investigating this alloy using the first principles calculations [2],[3] including twinning in martensite [4], but no data have been found from theoretical computations of the elastic constants C_{ij}.



a) b)

Figure 1. Two stable structures of NiTi alloy: a) martensite of monoclinic symmetry (with translational vectors $\boldsymbol{r_1}$, $\boldsymbol{r_2}$ and $\boldsymbol{r_3}$) and b) cubic austenite.

Our previous first principles calculations [5] show that the Young`s moduli of B19` martensitic structure of NiTi alloy are approximately three times higher than those measured experimentally. It can be expected that the difference is caused by the fact that the experimental results were measured on the polycrystals containing twins whereas the first principles results were obtained on the monocrystal. In the present first principles study, the elastic constants C_{ij} are computed for monocrystals as well as the crystal structure containing twins at the twinning plane {100}. The results obtained for both models are compared to determine the influence of selected twins on elastic response of the martensitic structure.

The first principles calculations

The total energies of the studied system have been computed by the Abinit program code [6], [7]. Abinit is a large tool for electronic structure calculations developed at the *Université Catholique de Louvain* and is distributed under GNU General Public License. Another additional package including pseudopotentials [8] together with its generators, manuals, tutorials, examples, etc. is available at [9].

The calculations were performed using GGA utrasoft pseudopotentials and the cutoff energy was set to 270 eV. The solution was considered to be self-consistent when the energy difference of three consequent iterations became smaller than 1.0 μeV.

Computation of elastic constants

The elastic constants C_{ij} (i,j = 1..6 according to Voight notation) can be computed from the dependence of either the total energy E_{tot} or stress tensor σ_i on an appropriate deformation. In the present work, the stress tensor σ_i was used to determine the elastic constants and the procedure using the total energy calculations was used only as a benchmark. The elastic constant C_{ij} can be computed according to the relation

$$C_{ij} = \frac{\partial \sigma_i}{\partial e_j},$$

where σ_i and e_j correspond to applied stresses and strains, respectively.

Structural data of B19` NiTi martensite

Table 1. The values of the experimental [1] and the theoretical lattice parameters.

	r_1 [Å]	r_2 [Å]	r_3 [Å]	γ [°]	V_0 [Å ^{3}]
experimental	2.89	4.12	4.62	96.8	54.62
theoretical (first principles)	2.95	4.02	4.77	102.2	55.34
difference	2.1 %	-2.4 %	3.2 %	5.6 %	1.3 %

Table 2. The experimental [1] and the theoretical values of the ionic positions. The values are relative according to the translation vectors $\boldsymbol{r}$.

	X (expt./comp./diff.)	Y (expt./comp./diff.)	Z (expt./comp./diff.)
Ti	0 / 0 / 0	0 / 0 / 0	0 / 0 / 0
Ti	0.165 / 0.195 / 18 %	½ / ½ / 0	0.567 / 0.568 / 0.1 %
Ni	0.620 / 0.646 / -4.3 %	0 / 0 / 0	0.459 / 0.455 / -0.8 %
Ni	0.545 / 0.519 / -4.8 %	½ / ½ / 0	0.108 / 0.112 / 3.3 %

In the first step of calculation, the simulated structure was fully relaxed to obtain a stress-free state (absolute values of the stress tensor and inter-atomic forces must be negligible). Table 1 contains experimental and the computed lengths of the primitive cell edges and values of γ angle. Table 2 contains ionic positions relative to translation vectors. As can be seen, the theoretical data are in a good agreement with those obtained experimentally. Thus, the theoretical data can be used as a basis for further computations.

Created twins in martensitic structure

According to Ref. [1], there are several types of the twinning modes in NiTi martensite. In the present study, {100} plane was chosen as the twinning plane.

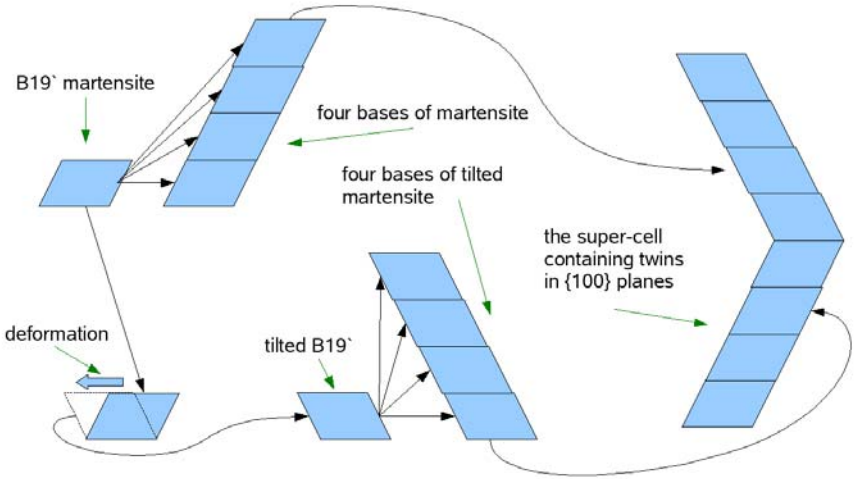


Figure 2: The process of building the computational super-cell containing {100} twins.

The simulation cell was build as a supper-cell which is composed of eight primitive cells (of two different bases). The first base corresponds to a standard B19` martensite and the second one represents a tilted base of B19` martensite. The tilted base was created by giving the translation vector $\boldsymbol{r_3}$ a tilt that leads to an increase of the γ angle. Fig. 3 displays a dependence of E_{tot} on a normalized tilt n that was scaled so that its values 0 and 1 correspond to the optimized B19' and the tilted structures, respectively. At each step of the tilting process, the ionic positions were optimized. As can be seen from Fig. 3, the energies of both structures are almost equal and their difference $\Delta E_{\text{tot}} = 11.7$ μeV is negligible with respect to the energy barrier of 0.11 eV.

The simulation cell is shown in Fig. 4 on the left. However, this cell cannot be used for computations of elastic constant C_{ij} yet, because the values of stress tensor and forces acting to individual atoms at the twin interface are still too high. For this reason, the translation vectors describing the primitive cell and the ionic positions at the twins interface have been optimized using a relaxation procedure that guarantees the stress values lower than 500 MPa and the atomic forces below 10^{-1} eV/Å. It is very difficult to relax the stresses and forces to lower values because the cell contains an interface between two different variants of B19' martensite and the optimization process must be partially constrained to preserve the twinned structure.

The optimized simulation cell is displayed on the right side of Fig. 4. As can be seen, the optimized atomic positions in the vicinity of the interface are arranged along the {100} plane,

making the interface almost flat in agreement with data available in Ref. [4]. The optimized cell was used for computation of elastic constants for twinned structure.

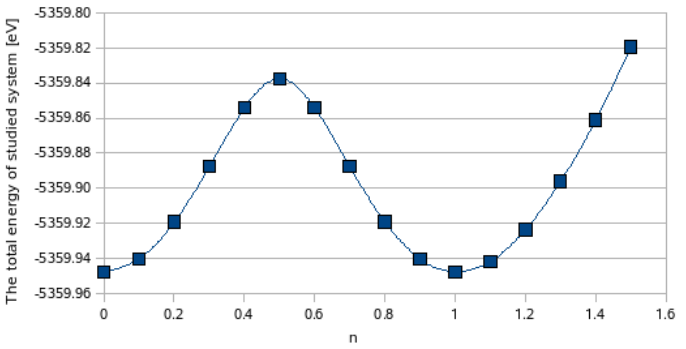


Figure 3: The total energy E_{tot} as a function of normalized tilt n where $n = 0$ for B19` martensite and $n = 1$ at the state corresponding to the tilted B19` martensite.

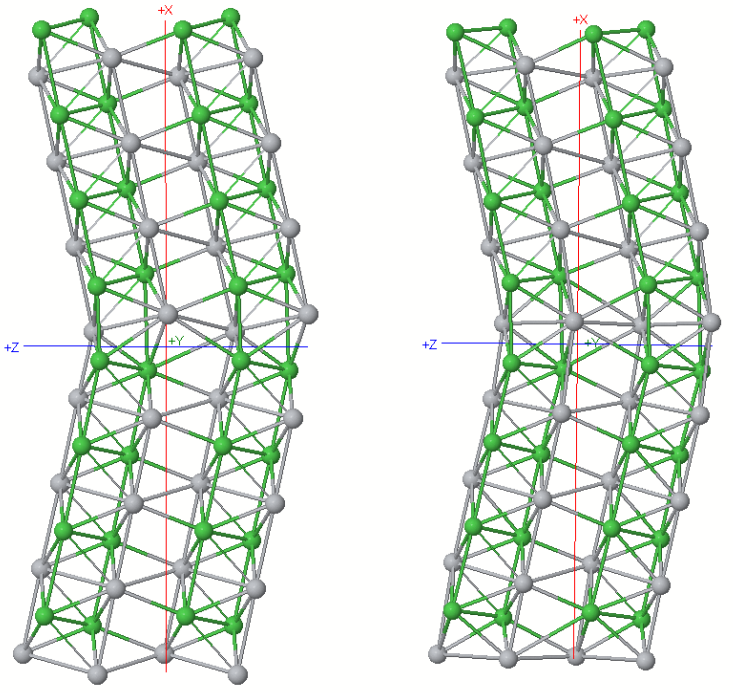


Figure 4: The super-cell containing twins in {100} planes before optimization of ionic position at the interface (on the left) and after the optimization (on the right).

The computed elastic constants

There is no complete experimental review of all elastic constants of B19` NiTi martensite. However, three experimental elastic constants C_{11}, C_{12} and C_{44} can be found in Ref. [10]. The comparison of these experimental data with the computed theoretical results (Table 4) shows their good mutual correspondence with the exception of the elastic constant C_{44} which is four times higher than the experimental one. Due to the impossibility to exactly determine the crystal orientation during experimental measurement on polycrystals, the C_{44} in Table 3 might be equivalent to C_{55} or C_{66}. The computed C_{55} is only one half of any of the other two but still twice of the experimental value. This can be explained by the presence of other twins (not considered in the computation) in the experimental sample.

Table 4 contains the computed elastic constants for both structures, the original B19` martensite and the martensite with twins in {100} plane. As can be seen, the investigated twins do not exhibit any significant influence on the elastic constants C_{ij}. One can see only a small decrease of the shear constants C_{44} and C_{66}. The negligible influence of (100) compound twinning mode can be explained by the fact that the energy of the twinning interface for the compound twinning mode is ten times lower than that for the twinning modes type-I or type-II [4]. Considering these facts the other twinning modes can have a higher influence to the elastic constants C_{ij}.

Because there is no significant difference between untwined and twinned martensite, the high values of the Young's moduli published in [5] remain still unexplained.

Table 3: The available experimental elastic constant C_{ij} for martensite [10].

struct. \ C_{ij} [GPa]	C_{11}	C_{12}	C_{44}
exp. B19'	170	135	22

Table 4: The computed elastic constant C_{ij} (in GPa) for B19` martensite and B19` martensite with twins in {100} plane.

Structure	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}
B19`	184	236	236	133	118	130	87	44	80
B19` with twins	201	228	224	126	109	127	74	45	72
difference	9 %	-3 %	-5 %	-5 %	-8 %	-2 %	-15 %	2 %	-10 %

Results and discussion

The comparison of the elastic constant C_{ij} of B19` martensite with and without twins in {100} plane didn't show any significant influence of the studied twinning mode on the elastic response of the crystal. The relevant decrease of C_{ij} between studied structures was observed only for two constants, C_{44} and C_{66}. These two constants show a small decrease when the system contains twins in {100} plane. Other constants for twinned martesite have similar values as those for untwined martensite.

The difference between experimental and theoretical value of the shear constant C_{44} can be explained by the fact that the experimental results were measured on the polycrystals while the theoretical data stem from calculations on the monocrystal. Also, the experimental data were measured slightly below a room temperature, whereas the present calculation assumed an absolute zero temperature.

Acknowledgement

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