# DAVID HOLEC

**Diploma thesis:** 

# On the precipitation in NiTi based shape memory alloys



I declare that I have elaborated this work on my own and that I have used only bibliography resources listed on pages 66–67.

David Holec

Brno, April 2005

# Foreword

This diploma work has been elaborated as a part of my Master degree in Physics. It was advertised by the Department of Condensed Matter Physics of Masaryk University in Brno, Czech Republic, in a cooperation with the Institute of Physics of Materials, the Academy of Sciences of the Czech Republic.

The subject of this thesis is:

#### On the precipitation in NiTi based shape memory alloys.

Although this discourse is a theoretical work it has a very strong experimental background and the problems addressed here arose from need of better technological understanding of the microstructural development and the improvement of NiTi shape memory technology. Results known prior to this work and the objectives of the present thesis are summarized in the first introductory chapter. The following three chapters focuses on known theoretical results relevant to this work (chapter 2), design of microstructural models (chapter 3) and analytical and numerical methods (chapter 4).

Chapters 5 and 6 constitute the main part of this work as they present results of the stress state analysis under diverse conditions (chapter 5) and the influence of stress redistributions on the preferential precipitation (chapter 6). The obtained results are discussed and compared to recently published experimental data in chapter 7.

The results of this work were partially presented at the international conference *Applied mechanics 2005* held in Marh 2005 in Hrotovice, Czech Republic.

The present work should progress currently studied issues by introducing a new methodology used in numerical studies of the microstructural development in shape memory alloys. However, the suggested mechanisms of the stress redistribution could be important for a much wider class of problems associated with polycrystalline materials. Nevertheless, much more effort would be needed in the future to achieve a more complete quantitative agreement between the numerical results and the experimental data. I hope that some of my colleagues or I myself will continue in these studies.

# Acknowledgement

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David Holec

## Annotation

The present work deals with stress redistributions and their subsequent influence on the precipitation in NiTi based shape memory alloys. Two mechanisms which may result into the stress redistribution are selected. The calculations based on the linear elasticity theory are performed upon three simple models of microstructures with increasing complexity.

The obtained results clearly show that the selected mechanisms give a rise to the stress redistribution over the microstructures. The interaction energy between redistributed stress and the precipitate-matrix misfit strain is calculated. The selection of crystallographic precipitate variants as a result of the minimum interaction energy criterion is demonstrated. The obtained results are compared to the experimental data. The results suggest that it is possible to explain qualitatively the selective precipitation by the mechanisms of stress redistributions but for a quantitative agreement with experimental data the more detailed description of microstructures and the inclusion of other relevant processes is needed.

# Anotace

Předkládaná práce se zabývá vznikem redistribuce napětí a jejím následným vlivem na přednostní precipitaci krystalografických variant ve slitinách s tvarovou pamětí na bázi NiTi. Byly navrženy dva mechanismy vzniku redistribuce napětí. Výpočty vychází z lineární teorie elasticity a jsou provedeny na třech mikrostrukturních modelech se vzrůstající složitostí.

Dosažené výsledky jasně ukazují, že zvolené mechanismy vedou k redistribuci napětí v mikrostruktuře. Je napočítána interakční energie mezi redistribuovaným napětím a deformací spojenou s misfitem krystalové struktury precipitátu a matrice. Dále je ukázano, že výběrové kritérium založené na minimální interakční energii vede k selektivní precipitaci krystalografických variant. Na závěr jsou dosažené výsledky diskutovány ve vztahu ke známých experimentálním datům. Ukazuje se, že přednostní precipitaci lze kvalitativně vysvětlit pomocí redistribuovaných elastických polí, avšak pro kvantitativní porovnání by bylo třeba uvážit detailnější popis mikrostruktury a zahrnout i další relevantní vlivy.

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# List of symbols and abbreviations

symbol	meaning	definition
a	side length of a hexagonal grain (3D model) or	Section 3.3 or
	height of FEM elements (2D models)	Chapter 4
$A_f$	temperature at which transformation martensite $\rightarrow$ austenite finishes	Section 1.2
$A_s$	temperature at which transformation martensite $\rightarrow$ austenite starts	Section 1.2
α	mutual misorientation between type 1 grain and global coordinate system	Section 3.1
$\boldsymbol{\alpha}, \alpha_1, \alpha_2$	thermal expansion coefficients	Section 3.1
$b_1, b_2$	widths of FEM elements (2D models)	Subsection 4.3.3
B19'	martensite phase in NiTi alloys	Section 1.3
B2	austenite phase in NiTi alloys	Section 1.3
$\beta$	mutual misorientation between type 2 grain and global coordinate system	Section 3.1
$\boldsymbol{c}, c_{ijkl}$	elastic constants	Section 2.1
$\Delta G$	Gibbs free energy change associated with coherent precipitation	Section 2.4
$\Delta G_{\rm chem}$	part of $\Delta G$ representing the energy drop due to formation of more stable precipitate phase	Section 2.4
$\Delta G_{\text{elast}}$	part of $\Delta G$ representing the energy increment due to elastic strain field created by the precipitate	Section 2.4
$\Delta \boldsymbol{\sigma}, \Delta \sigma_{ij}$	deviation from the average stress $\overline{\sigma}$ over the surfaces $S_{ m top}$ and $S_{ m bottom}$	Eq.(7.4)
$\Delta \boldsymbol{u}, \Delta u_i$	deviation from the average displacement $\overline{u}$ over the surfaces $S_{\mathrm{top}}$ and $S_{\mathrm{bottom}}$	Eq.(7.6)
$E_{\rm int}$	interaction energy between a precipiate and a parent matrix	Eq. (2.29)
$\boldsymbol{\varepsilon}, \varepsilon_{ij}$	strain tensor	Eq. (2.2)
$oldsymbol{arepsilon}^T$	precipitate-matrix misfit strain	Eq. (1.3)
$\varphi(\mathbf{r})$	harmonic potential	Eq. (2.12)
$\mathcal{G}_1,\mathcal{G}_2$	groups of crystallographic variants with the same IED distribution (2D models)	Eq. (6.3)
$h_0$	half-height of a layer of grains	Chapter 3
$h_a, h_1, h_2$	heights of grains after cooling	Section 4.2
l	cutting distance for a model with semi-infinite grains	Subsection 4.3.3
$\lambda$	length of a periodic pattern of the model II	Section 3.2
$M_f$	temperature at which transformation austenite $\rightarrow$ martensite finishes	Section 1.2
$M_s$	temperature at which transformation austenite $\rightarrow$ martensite starts	Section 1.2
$n_1, n_2, n_h$	parameters describing the 2D FEM meshes	Subsection 4.3.2
<b>n</b> , n <sub>i</sub>	outer normal to the surface of the precipitate	Section 2.2
$\boldsymbol{\nu}, \nu_i$	outer normal to the surface of the specimen	Section 2.1

$\mathcal{P}_1, \mathcal{P}_2, \mathcal{P}_3, \mathcal{P}_4$	groups of crystallographic variants with the same IED distribution (3D model)	Eq. (6.4)
П	elastic potential energy	Eq. (2.6)
r	volume ratio of grains type 1 within one period $\lambda$	Section 3.2
R	soft martensite phase in NiTi allovs	Section 1.3
$R_1, R_2$	transformation matrices from local grain coordinate systems into the	Eq. (3.1)
	global coordinate system	24. (011)
ρ	linear size of an inclusion	Section 7.3
$s, s_{iikl}$	elastic compliances	Section 2.1
S	surface of the specimen	Section 2.1
$S_p$	surface of the precipitate	Section 2.2
$\tilde{S}_{top}, S_{bottom}, \tilde{S}$	planar surfaces of the grain layer perpendicular to the y-axis	Section 7.1.1
$\boldsymbol{\sigma}, \sigma_{ij}$	stress tensor	Eq. (2.3)
$\overline{\sigma}, \overline{\sigma}_{ij}$	average stress over the surfaces $S_{top}$ and $S_{bottom}$	Eq. (7.4)
$\boldsymbol{\sigma}^{A}, \sigma_{ij}^{A}$	extrenaly applied stress	Section 4.3
$\boldsymbol{\sigma}^{C}, \sigma_{ij}^{\check{C}}$	stress tensor connected with relaxation of the layer of body force	Section 2.2
· <b>J</b>	after insertion of an inclusion	
$\boldsymbol{\sigma}^{T}, \sigma_{ij}^{T}$	precipitate – matrix misfit stress tensor	Eq. (2.9)
$T_a$	annealing temperature	Section 3.1
$T_r$	room temperature	Section 5.1
$\boldsymbol{T}, T_i$	surface tractions	Eq. (2.8)
<b>u</b> , <i>u</i> <sub><i>i</i></sub>	displacement field	Eq. (2.1)
$\overline{u}, \overline{u}_i$	average displacement over the surfaces $S_{ m top}$ and $S_{ m bottom}$	Eq. (7.6)
$\boldsymbol{u}^A, u_i^A$	displacement of non-interacting grains subjected to the externally ap- plied stress are mutually independent	Section 4.1
$\boldsymbol{u}^{C}, u_{i}^{C}$	displacement field connected with relaxation of the body force layer	Section 2.2
	after insertion of an inclusion	
$oldsymbol{u}^M, u_i^M$	minimizing displacement field, second part in decomposition of the displacement $\boldsymbol{u}$ (the first term is $\boldsymbol{u}^A$ )	Eq. (4.1)
$\boldsymbol{u}^{\mathrm{tr}},u_i^{\mathrm{tr}}$	displacement representing a macroscopic translation of the specimen	Subsection 7.1.2
$v_{i,j}$	x-components of $\boldsymbol{u}^M$ for 2D models when FEM is used	Subsection 4.3.3
V	volume of the specimen	Section 2.1
$V_p$	volume of the precipitate	Section 2.3
$w_{i,j}$	y-components of $\boldsymbol{u}^M$ for 2D models when FEM is used	Subsection 4.3.3
$W(oldsymbol{arepsilon})$	strain energy density	Eq. (2.7)
$X_{i,j}$	nodes representing FEM discretization mesh for 2D models	Subsection 4.3.3
$\psi(\mathbf{r})$	biharmonic potential	Eq. (2.13)
abbreviation	meaning	definition

DSC	differential scanning calorimetry	Section 1.4
FDM	finite difference method	Subsection 4.3.2
FEM	finite element method	Subsection 4.3.3
GB	Graing boundary	Subsection 7.2.2
IED	interacion energy density	Section 6.1
MT	martensitic transformation	Section 1.2
SMA	shape memory alloy	Section 1.1
SME	shape memory effect	Section 1.2
TEM	transmission electron microscopy	Section 1.3

# **1** Introduction

#### 1.1 General background and history of shape memory alloys

The exciting field of smart materials is expanding rapidly with one of the most interesting areas being that of shape memory alloys. The term *shape memory alloys* (SMAs) is applied to that group of metallic materials that demonstrate the ability to return to some previously defined shape or size when subjected to appropriate thermal procedure during the preparation of the material. In general, these materials can undergo a significant plastic deformation. After exposing them to some higher temperature they are returning to their original shape.

HODGSON *et al.* (on-line) introduce further definition of a SMA as one that yields a thermoelastic martensite. In this case, the alloy undergoes a martensitic transformation of a type that allows the alloy to be deformed by a twinning mechanism below the transformation temperature. The deformation is then reversed when the twinned structure reverts upon heating to the parent phase.

The first recorded observation of the shape memory transformation was by CHANG and READ (1951) in 1932. They noted the reversibility of the transformation in AuCd by the metallographic observations and resistivity changes, and in 1951 the shape memory effect was observed in a bent bar of AuCd. In 1938, the transformation was seen in brass (CuZn). However, the serious research in both the metallurgy and potential practical uses began in 1962, when BUEHLER *et al.* (1963) discovered the effect in equiatomic nickel-titanium (NiTi). Since then the SMAs are intensively studied and the number of practical applications coming to the market is rapidly increasing each year.

As the shape memory transformation became better understood, a number of other SMAs were investigated. Table 1.1 lists some of them with their basic characterisation. Of all these systems, only the NiTi alloy and a few of the copper-base alloys have received the most development effort and commercial exploitation.

The area of commercial use of SMAs is very wide and it varies from aeronautical applications (flap/clap adjusters) to medicine tools (orthodontic archwires, arterial clips, bone plates) and everyday-use applications (kettle switchers, mobile phone antennas). One of the most often used materials for manufacturing "smart parts" of these devices is NiTi. This is the reason why we are interested in a more detailed understanding of NiTi properties. This work focuses on some aspects related to the processing and associated to microstructures of NiTi shape memory alloys that modify the shape memory behaviour.

#### 1.2 Shape memory effect

The shape memory transformation is a phase transformation in a solid state. Common name for the low- and high-temperature phases are *martensite* and *austenite*, respectively. The transformation is often referred to as *martensitic transformation* (MT). The typical temperature–transformation curve obtained in one cooling–heating cycle is shown in Fig. 1.1. This figure introduces characteristic phase transition temperatures. When heating the specimen up from the low-temperature martensitic domain, the transformation martensite  $\rightarrow$  austenite starts at the temperature  $A_s$  (austenite start) and the transformation is finished at the temperature  $A_f$  (austenite finish). At this temperature austenite domain the phase transformation austenite  $\rightarrow$  martensite starts at the temperature  $M_s$  (martensite start) and finishes at  $M_f$  (martensite finish).

alloy	composition	transformation temperature range
Ag - Cd	44/49 at%Cd	$-190^{\circ}\mathrm{C}$ to $-50^{\circ}\mathrm{C}$
$\mathrm{Au}-\mathrm{Cd}$	46.5/50  at%Cd	$30^{\circ}\mathrm{C}$ to $100^{\circ}\mathrm{C}$
Cu - Al - Ni	$14/14.5 \ \mathrm{wt}\%\mathrm{Al},  3/4.5 \ \mathrm{wt}\%\mathrm{Ni}$	$-140^{\circ}\mathrm{C}$ to $100^{\circ}\mathrm{C}$
$\mathrm{Cu}-\mathrm{Sn}$	approx. $15 \text{ at}\% \text{Sn}$	$-120^{\circ}\mathrm{C}$ to $30^{\circ}\mathrm{C}$
$\mathrm{Cu}-\mathrm{Zn}$	38.5/41.5  wt%Zn	$-180^{\circ}\mathrm{C}$ to $-10^{\circ}\mathrm{C}$
Cu - Zn - X (X = Si, Sn, Al)	a few $wt\%$ of X	$-180^{\circ}\mathrm{C}$ to $200^{\circ}\mathrm{C}$
In - Ti	18/23 at%Ti	$60^{\circ}\mathrm{C}$ to $100^{\circ}\mathrm{C}$
Ni – Al	$36/38 \mathrm{at}\%\mathrm{Al}$	$-180^{\circ}\mathrm{C}$ to $100^{\circ}\mathrm{C}$
Ni - Ti	49/51 at%Ni	$-50^{\circ}\mathrm{C}$ to $110^{\circ}\mathrm{C}$
Fe - Pt	approx. $25 \text{ at}\% \text{Pt}$	approx. $-130^{\circ}$ C
$\mathrm{Mn}-\mathrm{Cu}$	5/35 at%Cu	$-250^\circ\mathrm{C}$ to $180^\circ\mathrm{C}$
$\rm Fe-Mn-Si$	$32 \mathrm{~wt\%Cu}, 6 \mathrm{~wt\%Si}$	$-200^{\circ}\mathrm{C}$ to $150^{\circ}\mathrm{C}$

TABLE 1.1: View of some most important SMAs (passed from (SHIMIZU and TADAKI, 1987)).



FIGURE 1.1: Typical temperature-transformation curve for a specimen subjected to one coolingheating cycle. The four characteristic temperatures  $A_s$ ,  $A_f$ ,  $M_s$  and  $M_f$  of the phase transition process are also shown.

The temperatures  $A_s$ ,  $A_f$ ,  $M_s$  and  $M_f$  are generally all different and thus the transformation may exhibit hysteresis  $T_h$ .

The shape memory effect (SME) requires a certain succession of steps. First, the temperature of the alloy temperature is lowered below the temperature  $M_f$ . At this stage the piece of the alloy is completely composed of martensite which can be easily deformed <sup>1</sup>). After distorting the shape of the piece the original shape can be recovered simply by heating the specimen above the temperature  $A_f$ . The heat transferred to the specimen initiates the martensite  $\rightarrow$  austenite transition and contributes thus to the rearrangement of the alloy at an atomic scale. The deformed martensite is now transformed to the austenite which has the microscopic as well as macroscopic configuration of the initial undeformed state. The succession of SME events is schematically illustrated in Fig. 1.2.

<sup>&</sup>lt;sup>1)</sup> Martensite phase is softer than austenite phase.



FIGURE 1.2: Schematic illustration of how the martensite  $\rightarrow$  austenite transformation recovers the original shape. A shape of a specimen in martensitic phase is deformed. After heating it transforms to the autenite phase where the atoms are rearranged into their original positions. When the specimen is cooled it still keeps its original shape.

#### 1.3 NiTi based alloys

The SME in near-equiatomic NiTi based alloys is controlled by the concentration of Ni (SABURI, 1998) in the range between  $49 \div 51$  at%. The austenite phase in NiTi alloys has the cubic B2 structure with the lattice parametr a = 0.3007 nm. The arrangement of atoms in one unit cell is shown in Fig. 1.3(a). The crystal lattice of the martensite phase B19' is monoclinic and it belongs to  $P_{21/m}$  space group. The unit cell of the B19' phase in Ti – 49.2 at%Ni alloy is described by lattice parameters a = 0.2898 nm, b = 0.4108 nm, c = 0.4646 nm and  $\beta = 97.78^{\circ}$  (SABURI, 1998). The arrangement of atoms forming one unit cell is shown in Fig. 1.3(b). There are cases of a more complex B2 – B19' transformation path (so called two, three or generally multiple step MTs) when the "soft" martensite R phase forms as the intermediate transformation product (B2 – R – B19'). The R-phase has a trigonal lattice with lattice parameters a = 0.738 nm, c = 0.532 nm and belongs to the space group P3 (SABURI, 1998). The atomic setup of this phase is illustrated in Fig. 1.3(c). We note that the lattice parameters depend on temperature and precise composition.

During processing, Ni-rich NiTi alloys are generally subjected to solution annealing and subsequent aging (SABURI, 1998) where metastable coherent Ni<sub>4</sub>Ti<sub>3</sub> precipitates form (TADAKI *et al.*, 1986). This is illustrated in Fig. 1.4(a) where a transmission electron microscopy (TEM) micrograph is presented that documents a state of Ti – 50.7 at% Ni alloy after stress free aging at 530°C for 11 hours. The Ni<sub>4</sub>Ti<sub>3</sub> particles have lenticular shape and their atomic structure is rhombohedral (SABURI, 1998) (see Fig. 1.4(b)). The unit cell parameters are a = 0.6704 nm and  $\alpha = 113.83^{\circ}$ .

The space group of the B2 phase of the NiTi matrix is  $P_{m3m}$  with 48 operations of symmetry while the space group of the Ni<sub>4</sub>Ti<sub>3</sub> precipitate is  $R_3^-$  with only 6 symmetry operations (SABURI, 1998). The number of coherent Ni<sub>4</sub>Ti<sub>3</sub> variants coherent with the NiTi B2 matrix may be determined by decomposing the space group of the parent phase into the coset of the precipitate (PORTIER and GRATIAS, 1982). LI and



FIGURE 1.3: Unit cells of different phases in NiTi alloy: (a) cubic lattice of B2 austenite, (b) monoclinic lattice of B19' martensite and (c) trigonal lattice of R-phase (soft martensite).



FIGURE 1.4:  $Ni_4Ti_3$  precipitates: (a) a TEM micrograph of NiTi B2 matrix with  $Ni_3Ti_4$  precipitates after stress free aging at 530°C for 11 hours; (b) the arrangement of atoms in one unit cell of the rhombohedral structure of the  $Ni_4Ti_3$  precipitate.

CHEN (1997) have shown that the decomposition exists

$$P_{m3m} = (h_1 + h_2 + h_3 + h_4 + h_{13} + h_{14} + h_{15} + h_{16})R_{3[111]}^-,$$
(1.1)

where  $h_1, h_2, \ldots, h_{16}$  are operations of symmetry given in Table 1.2.

Taking into account the results of PORTIER and GRATIAS (1982), LI and CHEN (1997) conclude that there are 8 possible crystallographic orientations of  $Ni_4Ti_3$  precipitates in the NiTi matrix. The experimental crystallographic relationship between the coherent precipitate  $Ni_4Ti_3$  and the crystal lattice of the parent phase of NiTi is (SABURI, 1998)

$$\begin{array}{c} [0\,1\,0]_{\mathrm{Ni}_{4}\mathrm{Ti}_{3}} \parallel [\overline{2}\,\overline{1}\,3]_{\mathrm{Ni}\mathrm{Ti}}\,, \\ (0\,0\,1)_{\mathrm{Ni}_{4}\mathrm{Ti}_{3}} \parallel (1\,1\,1)_{\mathrm{Ni}\mathrm{Ti}}\,. \end{array}$$

$$(1.2)$$

This means that the habit plane  $(001)_{Ni_4Ti_3}$  of lenticular-shaped precipitates matches with one from the set of eight equivalent planes  $\{111\}_{NiTi}$  in the parent B2 phase.

symmetry element	operation	axis	angle
$h_1$	identity transformation		
$h_2$	rotation	$[100]_{\rm B2}$	180°
$h_3$	rotation	$[010]_{\rm B2}$	180°
$h_4$	rotation	$[001]_{\rm B2}$	180°
$h_{13}$	rotation	$[\overline{1}10]_{B2}$	180°
$h_{14}$	rotation	$[001]_{\rm B2}$	90°
$h_{14}$	rotation	$[001]_{\rm B2}$	$270^{\circ}$
$h_{15}$	rotation	$[110]_{B2}$	180°

TABLE 1.2: Operations of symmetry in decomposition  $P_{m3m}$  space group into the coset of precipitate with  $R_3^-$  space group.

 $Ni_4Ti_3$  particles shrink 2.7% along  $[0\ 0\ 1]_{Ni_4Ti_3}$  direction and 0.3% along their perpendicular directions relative to the matrix (SABURI, 1998). The precipitate–matrix misfit strain matrix (later used in the section 2.2) thus takes a form

$$\boldsymbol{\varepsilon}^{T} = \begin{pmatrix} -0.003 & 0 & 0\\ 0 & -0.003 & 0\\ 0 & 0 & -0.027 \end{pmatrix} . \tag{1.3}$$

#### 1.4 Martensitic transformations in NiTi alloys

MTs in NiTi alloys proceed in single-step  $B2 \leftrightarrow B19'$  transitions on heating and cooling after solution annealing and water quenching; by single-step transition we mean that, as shown in the differential scanning calorimetry (DSC) chart in Fig. 1.5, there is one single distinct peak on cooling from the B2-regime (temperature range where the B2 phase is stable) and one distinct peak on heating from the B19'-regime.



FIGURE 1.5: DSC chart for single-step martensitic transformation in a NiTi alloy.

After thermo mechanical processing Ni-rich NiTi alloys can undergo two and three step transformations (LIU *et al.*, 2003, CARROL *et al.*, 2004). The change from a one-step to a two-step transformation in NiTi SMAs has often been considered as well understood because both R-phase and B19'-phase are potential martensite candidates (REN *et al.*, 2001). This is suggested by the observation of corresponding soft phonons in inelastic neutron scattering experiments (TIETZE *et al.*, 1984, MOINE *et al.*, 1984). The coherent Ni<sub>4</sub>Ti<sub>3</sub> precipitates resist large deformations associated with the formation of B19' habit plane variants. The growing R-phase produces a significantly smaller deformation and is much less affected by particles. Therefore the presence of precipitates favours the formation of R-phase (REN *et al.*, 2001) which results in the first transformation step B2  $\rightarrow$  R (first DSC peak in Fig. 1.6) and only later at lower temperature (stronger undercooling) the second transformation step R  $\rightarrow$  B19' (second DSC peak) is observed (KHALIL-ALLAFI *et al.*, 2002a).



FIGURE 1.6: DSC chart for multiple-step martensitic transformation in NiTi alloy with  $Ni_4Ti_3$  precipitates.

However, recent careful neutron diffraction experiments supported by TEM investigations revealed that already in the temperature range between the first and second DSC peaks the alloy microstructure consists of a mixture of R- and B19'-phases (SITEPU *et al.*, 2002). In this case the Ti - 50.7 at% Ni alloy was subjected to a standard annealing treatment ( $850^{\circ}C/900 \text{ s/water quench}$ ) and subsequently aged at  $400^{\circ}C$  for 20 hours. Also the role of Ni<sub>4</sub>Ti<sub>3</sub> precipitates in multiple step (more than two steps) MTs as observed using DSC (BATAILLARD *et al.*, 1998) has been discussed controversially in the literature. There presently are three different explanations for multiple step MTs in Ni-rich NiTi SMAs:

- (i) MORAWIEC *et al.* (1995, 2002) suggest that the first DSC peak on cooling in a three step transformation observed for a solution annealed, cold deformed and subsequently aged Ni-rich NiTi material corresponds to the formation of R-phase. There then follow two martensite peaks, which are associated with a heterogeneous dislocation substructure. Microstructural regions with low dislocation densities produce a second DSC peak on cooling. Dislocation obstacles like subgrain boundaries suppress the MT until stronger undercooling provides the driving force for a third transformation step. Microstructural evidence for subgrain boundaries representing obstacles for the growth of B19' was presented by EGGELER *et al.* (2000) and KHALIL-ALLAFI *et al.* (2001).
- (ii) BATAILLARD *et al.* (1998) tackled the problem of multiple step MTs in Ni-rich NiTi alloys using insitu TEM. They provided clear evidence for the microstructural details of the overall transformation

process. They found that both R-phase and B19' martensite nucleate near  $Ni_4Ti_3$  particles and then grow into the matrix. However, they reported a difference in the growth behaviour of R-phase and B19' martensite. The R-phase grows smoothly without apparent interruptions (first transformation step). In contrast, the B19' martensite nucleates in sudden bursts and grows rapidly to a significant size; it then requires further undercooling before consuming the rest of the matrix. BATAILLARD *et al.* (1998) explain the two-step transformation of R-phase to B19' (and thus the overall threestep transformation) by pointing out that the transformation temperatures in regions near particles (governed by high coherency stresses) are different than in regions far from particles (where coherency stresses are not important). These two regions therefore transform in two steps at a higher (near particles) and lower (far from particles) temperature.

(iii) KHALIL-ALLAFI *et al.* (2002a) used DSC for a systematic investigation of the evolution of transformation behaviour with aging temperature and time. They demonstrated that during aging of Ni-rich NiTi alloys, DSC curves exhibit two transformation peaks on cooling after short aging times, three after intermediate aging times and finally again two peaks after long aging times (2-3-2 transformation behaviour). They proposed a new explanation for the 2-3-2-transformation behaviour that consists of two basic elements: (i) the composition inhomogeneity that evolves diffusion controlled during aging as Ni<sub>4</sub>Ti<sub>3</sub> precipitates grow. (ii) The difference between nucleation barriers for R-phase (small) and B19' (large). This third explanation can in principle rationalize the evolution of DSC charts during aging including the number of distinct DSC peaks and their positions; however, it is based on a microstructure with a homogeneous distribution of Ni<sub>4</sub>Ti<sub>3</sub>-precipitates; and KHALIL-ALLAFI *et al.* (2002a) did not attempt to provide microstructural evidence to support their claim and they did not consider the back transformation from B19' to B2.

Particularly, the homogeneity of Ni<sub>4</sub>Ti<sub>3</sub> precipitation has become an issue. Short-term stress free aging in the temperature range between 400–600°C can result in heterogeneous precipitation (FILIP and MAZANEC, 2001, KHALIL-ALLAFI *et al.*, 2002b); this normally means that  $Ni_4Ti_3$  particles nucleate and grow preferentially near grain boundaries, oxide inclusions and carbides while precipitate free regions characterize the grain interior (KHALIL-ALLAFI et al., 2002b); in this case different microstructural regions are characterized by different particle volume densities. Superimposing an external stress enforces a homogeneous particle volume density throughout the microstructure (KHALIL-ALLAFI et al., 2002b). A microstructure of this type that formed after stress assisted 1 hour aging at  $500^{\circ}$ C and 8 MPa is shown in the montage of transmission electron microscopy micrographs of Figure 1.7. A closer look at higher magnification into the upper right corner in Figure 1.7 reveals that the precipitation process is by no means fully homogeneous. When looking at zoomed detail of Fig. 1.7 shown in Fig. 1.8 it must be kept in mind that different  $Ni_4Ti_3$ variant disks appear in different projections. It can be clearly seen that the variant which is projected in an ellipsoidal shape (wider dark ellipsoids are precipitate disks almost parallel to image plane) only appears in some distance from the grain boundary; near the grain boundary only thin traces of projected edge-on variant disks are observed. Since this type of heterogeneity of the precipitate population may well govern multiple step martensitic transformation behaviour as described in the literature (KHALIL-ALLAFI et al., 2002b, KHALIL-ALLAFI et al., 2002a, BATAILLARD et al., 1998, DLOUHÝ et al., 2003, CARROL et al., 2004) it is important to investigate this microstructural feature in a detail. A quantitative experimental study of the inhomogeneity of Ni<sub>4</sub>Ti<sub>3</sub> precipitate variants in specimens after stress assisted aging has been presented in (BOJDA et al., 2005).

#### 1.5 Objectives of the present work

The precipitates  $Ni_4Ti_3$  give rise to coherency stress fields and therefore external and/or internal stresses can favour or suppress the occurrence of certain  $Ni_4Ti_3$  variants (LI and CHEN, 1998). Coherency stress fields and/or Ni concentration gradients associated with the  $Ni_4Ti_3$  precipitation influence considerably the B2 – B19' transformation characteristics. This work should contribute to the understanding of how



FIGURE 1.7: A uniform distribution of  $Ni_4Ti_3$  precipitates (in terms of number of particles per unit volume) after stress assisted 1 hour aging at 500°C and 8 MPa. Grain boundary areas and grain interiors of grains 1–3 are shown in the montage of TEM micrographs.



FIGURE 1.8: The formation of different crystallographic  $Ni_4Ti_3$  variants near to and far from the grain boundary as documented in the upper grain (see also the grain 3 in Fig. 1.7).

heterogeneous  $Ni_4Ti_3$  microstructures arise. Modelling of microstructural processes that contribute to the heterogeneous precipitation will be the basic methodology. Therefore, the aims of the thesis are as follows:

- 1. to select relevant mechanisms that can result in local redistributions of stress over the microstructure,
- 2. to introduce models of microstructure suitable for numerical modelling,
- 3. to calculate the stress redistribution within the framework of presented models and
- 4. to estimate the energy and distribution of different crystallographic  $Ni_4Ti_3$  precipitate variants in the external stress field redistributed over the microstructure.

### 2 Linear theory of elasticity. Eshelby method

#### 2.1 Notation of linear elasticity theory

The computations of stress redistributions will be performed within a framework of linear elasticity theory (BRDIČKA *et al.*, 2000, NYE, 2001).

Let

$$\boldsymbol{u}(\boldsymbol{r}) = \begin{pmatrix} u_x(\boldsymbol{r}) \\ u_y(\boldsymbol{r}) \\ u_z(\boldsymbol{r}) \end{pmatrix} = \begin{pmatrix} u_x(x, y, z) \\ u_y(x, y, z) \\ u_z(x, y, z) \end{pmatrix}$$
(2.1)

denote a displacement vector field in Cartesian coordinate system 0xyz. Then the strain tensor  $\varepsilon$  has components

$$\varepsilon_{xx} = \frac{\partial u_x}{\partial x}, \qquad \varepsilon_{xy} = \varepsilon_{yx} = \frac{1}{2} \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right),$$
  

$$\varepsilon_{yy} = \frac{\partial u_y}{\partial y}, \qquad \varepsilon_{xz} = \varepsilon_{zx} = \frac{1}{2} \left( \frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right),$$
  

$$\varepsilon_{zz} = \frac{\partial u_z}{\partial z}, \qquad \varepsilon_{yz} = \varepsilon_{zy} = \frac{1}{2} \left( \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} \right).$$
  
(2.2)

The stress tensor  $\sigma$  is related to the strain tensor  $\varepsilon$  through a generalized Hook's law<sup>2)</sup>

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl}, \quad i, j, k, l \in \{x, y, z\},$$

$$(2.3)$$

where  $c_{ijkl}$  are components of fourth-rank tensor of elastic constants. The inverse relation

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}$$
 (2.4)

introduces a fourth-rank tensor called elastic compliances (NYE, 2001).

Six-indices notation often simplifies the numerical implementation: to every pair of indices ij we assign a single-value index according to following rules

 $11 \to 1$ ,  $22 \to 2$ ,  $33 \to 3$ ,  $23, 32 \to 4$ ,  $13, 31 \to 5$ ,  $12, 21 \to 6$ .

In this notation, the elastic constants tensor  $c_{ijkl}$  can be represented as a  $6 \times 6$  matrix. For media with cubic

<sup>&</sup>lt;sup>2)</sup> In all following formulas the sum rule over repeated indices is assumed. If the sum rule should not be applied it would be mentioned explicitly. In expressions like  $\varepsilon_{xx}$ ,  $\varepsilon_{yy}$ , ...,  $\sigma_{zz}$  the repeated indices x, y and z do not invoke the summation.

symmetry this matrix takes a form

$$c_{ijkl} \sim \begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix}.$$

$$(2.5)$$

A method based on the minimisation of the elastic potential energy  $\Pi$  (BRDIČKA *et al.*, 2000) is employed to obtain the stress distribution. The stable state of a system is determined by a minimum of the potential

$$\Pi = \int_{V} W(\boldsymbol{\varepsilon}) \,\mathrm{d}V - \int_{S} \boldsymbol{T} \cdot \boldsymbol{u} \,\mathrm{d}S$$
(2.6)

where  $W(\varepsilon)$  is a density of strain energy given by

$$W(\boldsymbol{\varepsilon}) = \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl}$$
(2.7)

and T represents surface tractions related to the components  $\sigma_{ij}$  of the stress-tensor at the surfaces by

$$T_i = \sigma_{ij}\nu_j. \tag{2.8}$$

In Eq. (2.8)  $\nu$  represents an outer normal vector to the surface of the specimen. The integration in Eq. (2.6) is performed over the specimen's volume V and the specimen's surface S, respectively.

#### 2.2 Eshelby method for elastic continuum

ESHELBY (1961) developed a method that enables evaluating of elastic fields and energies caused by elastic inclusions and inhomogeneities. The method is based on a sequence of cutting and welding operations. This process is schematically illustrated in Fig. 2.1.

To find a state of stress caused by a misfitting particle (inclusion) in an infinite elastic body we start with a virtual closed surface  $S_p$  (Fig. 2.1(a)). A cut is made around  $S_p$  and the inclusion is removed (Fig. 2.1(b)). After this operation, the inclusion undergoes a stress free change of shape (a transformation) outside the body (Fig. 2.1(c)). After the transformation the inclusion no longer fits the cavity defined by the surface  $S_p$  and it is necessary to apply surface forces  $-\sigma_{ij}^T n_j$  to the surface of the inclusion to produce a strain  $-\varepsilon_{ij}^T$  which restores the original shape of the inclusion (Fig. 2.1(d)). The relation between the applied stress and the produced strain is

$$\sigma_{ij}^T = c_{ijkl} \varepsilon_{kl}^T \,. \tag{2.9}$$

The inclusion is now put back to the cavity and welded with the matrix across the surface  $S_p$  (Fig. 2.1(e)). The matrix is still unstressed and this state differs from the final state only in the presence of the layer of body force

$$\mathrm{d}F_i = -\sigma_{ij}^T n_j \mathrm{d}S\,. \tag{2.10}$$

Let these tractions relax (Fig. 2.1(f)). The relaxation process introduces a displacement  $\boldsymbol{u}^{C}$  associated with the stress state  $\boldsymbol{\sigma}^{C}$ .



FIGURE 2.1: The Eshelby's method

After this virtual operation there is a stress described by stress tensor  $\sigma^{C}$  in the matrix and the state of stress in the inclusion is characterized by a tensor

$$\boldsymbol{\sigma}^{I} = \boldsymbol{\sigma}^{C} - \boldsymbol{\sigma}^{T} \,. \tag{2.11}$$

#### 2.2.1 Stress field generated by an elastic inclusion in elastic continuum

LOVE (1954) has shown that the Green's function method provides a relation between the displacement  $u^{C}$  and the stress state  $\sigma^{T}$ . Let

$$\varphi(\mathbf{r}) = \int_{V_p} \frac{\mathrm{d}V}{|\mathbf{r} - \mathbf{r}'|}$$
(2.12)

be an ordinary harmonic potential of attracting matter of unit density and the inclusion of the volume  $V_p$  is assumed to be bounded by the surface  $S_p$ . The corresponding biharmonic potential is

$$\psi(\mathbf{r}) = \int_{V_p} |\mathbf{r} - \mathbf{r}'| \,\mathrm{d}V.$$
(2.13)

Using these two potentials the relation between the displacement  $u^{C}$  and the stress  $\sigma^{T}$  is obtained as

$$u_i^C = \frac{1}{16\pi\mu(1-\nu)}\sigma_{jk}^T \frac{\partial^3 \psi}{\partial x_i \partial x_j \partial x_k} - \frac{1}{4\pi\mu}\sigma_{ik}^T \frac{\partial \varphi}{\partial x_k}.$$
(2.14)

Similar relation can be also obtained for the strain  $\varepsilon^T$ 

$$u_i^C = \frac{1}{8\pi(1-\nu)}\varepsilon_{jk}^T \frac{\partial^3 \psi}{\partial x_i \partial x_j \partial x_k} - \frac{1}{2\pi}\varepsilon_{ik}^T \frac{\partial \varphi}{\partial x_k} - \frac{\nu}{4\pi(1-\nu)}\varepsilon_{kk}^T \frac{\partial \varphi}{\partial x_i}.$$
(2.15)

In the special case when the inclusion is of an ellipsoidal shape, which is a reasonable approximation of the precipitate form, the analytical formulas for the potentials  $\varphi$  and  $\psi$  can be found. For the inclusion bounded by the ellipsoid

$$\frac{x_1^2}{a^2} + \frac{x_2^2}{b^2} + \frac{x_3^2}{c^2} = 1,$$
(2.16)

ESHELBY (1961) has derived

$$\frac{\partial^2 \psi}{\partial x_1 \partial x_2} = \frac{a^2}{a^2 - b^2} x_2 \frac{\partial \varphi}{\partial x_1} + \frac{b^2}{b^2 - a^2} x_1 \frac{\partial \varphi}{\partial x_2}, \qquad (2.17)$$

$$\frac{\partial^2 \psi}{\partial x_2 \partial x_3} = \frac{b^2}{b^2 - c^2} x_3 \frac{\partial \varphi}{\partial x_2} + \frac{c^2}{c^2 - b^2} x_2 \frac{\partial \varphi}{\partial x_3}, \qquad (2.18)$$

$$\frac{\partial^2 \psi}{\partial x_3 \partial x_1} = \frac{c^2}{c^2 - a^2} x_1 \frac{\partial \varphi}{\partial x_3} + \frac{a^2}{a^2 - c^2} x_3 \frac{\partial \varphi}{\partial x_1}.$$
(2.19)

Equation (2.15) requires further manipulation to cast it into a form suitable for further calculations. Particularly the third partial derivatives of the potential  $\psi$  are needed. For example, we can write

$$\frac{\partial^{3}\psi}{\partial x_{1}\partial x_{1}\partial x_{2}} = \frac{\partial}{\partial x_{1}} \left( \frac{\partial^{2}\psi}{\partial x_{1}\partial x_{2}} \right) ,$$

$$\frac{\partial^{3}\psi}{\partial x_{1}\partial x_{1}\partial x_{1}} = 2\frac{\partial\varphi}{\partial x_{1}} - \frac{\partial}{\partial x_{2}} \left( \frac{\partial^{2}\psi}{\partial x_{1}\partial x_{2}} \right) - \frac{\partial}{\partial x_{3}} \left( \frac{\partial^{2}\psi}{\partial x_{1}\partial x_{3}} \right) .$$
(2.20)

The first of these relations is obvious, the second follows from

$$\nabla^2 \psi = 2\varphi. \tag{2.21}$$

Substituting Eqs. (2.17)–(2.20) into Eq. (2.15) for i = 1 gives

$$8\pi(1-\nu)u_1^C = \frac{e_{22}^T - e_{11}^T}{a^2 - b^2} \frac{\partial}{\partial x_2} \left( a^2 x_2 \frac{\partial\varphi}{\partial x_1} - b^2 x_1 \frac{\partial\varphi}{\partial x_2} \right) + \frac{e_{33}^T - e_{11}^T}{c^2 - a^2} \frac{\partial}{\partial x_3} \left( c^2 x_1 \frac{\partial\varphi}{\partial x_3} - a^2 x_3 \frac{\partial\varphi}{\partial x_1} \right) - 2\left\{ (1-\nu)e_{11}^T + \nu(e_{22}^T + e_{33}^T) \right\} \frac{\partial\varphi}{\partial x_1} - 4(1-\nu) \left( e_{12}^T \frac{\partial\varphi}{\partial x_2} + e_{13}^T \frac{\partial\varphi}{\partial x_3} \right) + \frac{\partial}{\partial x_1} \overline{\beta}, \quad (2.22)$$

where

$$\overline{\beta} = \frac{2e_{12}^T}{a^2 - b^2} \left( a^2 x_2 \frac{\partial \varphi}{\partial x_1} - b^2 x_1 \frac{\partial \varphi}{\partial x_2} \right) + \frac{2e_{23}^T}{b^2 - c^2} \left( b^2 x_3 \frac{\partial \varphi}{\partial x_2} - c^2 x_2 \frac{\partial \varphi}{\partial x_3} \right) + \frac{2e_{31}^T}{c^2 - a^2} \left( c^2 x_1 \frac{\partial \varphi}{\partial x_3} - a^2 x_3 \frac{\partial \varphi}{\partial x_1} \right). \quad (2.23)$$

The potential inside the inclusion is given by

$$\varphi(\mathbf{r}) = \frac{1}{2}(a^2 - x_1^2)I_a + \frac{1}{2}(b^2 - x_2^2)I_b + \frac{1}{2}(c^2 - x_3^2)I_c, \qquad (2.24)$$

where  $I_a$ ,  $I_b$  and  $I_c$  are constants for the ellipsoidal inclusion<sup>3)</sup>. From Eqs. (2.22)–(2.24) it follows immediately that  $\boldsymbol{u}^C$  is a linear function of the coordinates  $x_1$ ,  $x_2$ ,  $x_3$  and thus the strain  $\boldsymbol{\varepsilon}^C$  is constant inside the inclusion.

KELLOG (1929) and MACMILLAN (1958) showed that outside the ellipsoid the potential takes the form

$$\varphi(\mathbf{r}) = \frac{2\pi abc}{l^3} \left[ \left( l^2 - \frac{x_1^2}{k^2} + \frac{x_2^2}{k^2} \right) F(\theta, k) + \left( \frac{x_1^2}{k^2} - \frac{x_2^2}{k^2 k'^2} + \frac{x_3^2}{k'^2} \right) E(\theta, k) + \frac{l}{k'^2} \left( \frac{C}{AB} x_2^2 - \frac{B}{AC} x_3^2 \right) \right]$$
(2.25)

where

$$A = \sqrt{a^2 + \chi}, \quad B = \sqrt{b^2 + \chi}, \quad C = \sqrt{c^2 + \chi},$$
  

$$l = \sqrt{a^2 - c^2}, \quad k^2 = 1 - k'^2 = \frac{a^2 - b^2}{a^2 - c^2},$$
  

$$a^2 > b^2 > c^2.$$
(2.26)

and F, E are elliptic integrals of modulus k and argument  $\theta$ , given by

$$\sin \theta = \frac{l}{A} \,. \tag{2.27}$$

 $\chi$  is the greatest (and in fact the only positive) root of

$$\frac{x^2}{A^2} + \frac{y^2}{B^2} + \frac{z^2}{C^2} = 1.$$
(2.28)

#### 2.3 Energetics of the inclusion – stress field interaction

Let us assume that the specimen is under externally applied stress  $\sigma$  that produces strain  $\varepsilon$ . ESHELBY (1961) in his work argues that the strains  $\varepsilon$  and  $\varepsilon^T$  are independent. The independence means that the strain generated due to the formation of an inclusion would be the same in the stressed as in the unstressed specimen. The interaction energy is then given by the work of body tractions  $\sigma_{ij}n_i$  during the formation of the inclusion,  $n_i$  being the outer normal to the body surface which encloses the considered inclusion.

The interaction energy term can be expressed in the form (for details see work by ESHELBY (1961))

$$E_{\rm int} = -\int_{V_p} \sigma_{ij} \varepsilon_{ij}^T \,\mathrm{d}V\,, \qquad (2.29)$$

where,  $V_p$  denotes the volume of the inclusion (precipitate).

<sup>3)</sup> The factors  $I_a$ ,  $I_b$  and  $I_c$  can be expressed in terms of elliptic integrals  $F(\theta, k)$  and  $E(\theta, k)$  as

$$I_{a} = \frac{4\pi abc}{(a^{2} - b^{2})(a^{2} - c^{2})^{1/2}} [F(\theta, k) - E(\theta, k)],$$
  

$$I_{b} = 4\pi - I_{a} - I_{c},$$
  

$$I_{c} = \frac{4\pi abc}{(b^{2} - c^{2})(a^{2} - c^{2})^{1/2}} \left[ \frac{b(b^{2} - c^{2})^{1/2}}{ac} - E(\theta, k) \right],$$

where

$$k^{2} = \frac{a^{2} - b^{2}}{a^{2} - c^{2}}, \qquad \sin \theta = \left(1 - \frac{c^{2}}{a^{2}}\right)^{1/2}.$$

$$E_{\rm int} = -V_p \sigma_{ij} \varepsilon_{ij}^T \,. \tag{2.30}$$

As it was described in the literature (SABURI, 1998), the transformation strain  $\varepsilon^T$  can be associated with the misfit strain for coherent precipitates, and for the case of NiTi matrix and Ni<sub>4</sub>Ti<sub>3</sub> precipitates is given by Eq. (1.3). Consequently the distribution of the external stress (independent of the presence of an inclusion in the specimen) is a key factor that controls the selection of a particular crystallographic variant precipitating in a given location in the microstructure.

#### 2.4 Energy of precipitates

Due to the lower symmetry of the precipitate crystal lattice and given the crystallographic relationship, the precipitation may result in a number of crystallographic variants that can be unambiguously distinguished using, e.g. transmission electron microscopy (HIRSCH *et al.*, 1977). It is well known (see e.g. the monograph by PORTER and EASTERLING (1977)) that the Gibbs free energy change  $\Delta G$  associated with the coherent precipitation can be separated into two terms

$$\Delta G = \Delta G_{\rm chem} + \Delta G_{\rm elast} \,, \tag{2.31}$$

where  $\Delta G_{\text{chem}}$  represents a free energy drop due to the formation of a more stable precipitate phase and the term  $\Delta G_{\text{elast}}$  is a free energy increment accounting for the energy of the elastic strain field created by the coherent precipitate. According to Eq. (2.31), the amount of the free energy change may be different for different crystallographic variants of coherent precipitates in cases when the parent phase carries a distributed stress  $\sigma$  already before the precipitation.

Equation (2.29) gives the expression for the energy change resulting from the interaction between the stress field  $\sigma$  distributed in the parent phase before the precipitation and a strain field  $\varepsilon^T$  of the new misfitting particle. Since the interaction energy  $E_{int}$  is generally different for different crystallographic variants of coherent particles inserted into a given location of the parent crystal and since the interaction energy  $E_{int}$  represents an important contribution to the second term in Eq. (2.31), a selective precipitation of coherent particles can occur in the stress field  $\sigma$ .

The contribution of  $E_{\rm int}$  to the total Gibbs free energy change associated with the precipitation is used as criteria for the selection of different crystallographic precipitate variants. In each position inside the specimen interaction energies of all eight different crystallographic variants of precipitates are evaluated and the variant with the minimum value of  $E_{\rm int}$  is selected to be the preferred one in the considered position.

### 3 Models

#### 3.1 Model *I* – two semi-infinite grains

The simplest 2D model considered here deals with two semi-infinite grains. As it is shown in Fig. 3.1, the grain 1 occupies the half-space x < 0 and the grain 2 fills the half-space x > 0. The selected global coordinate system 0xy is also drawn in Fig. 3.1. When the z coordinate is needed, it is assumed that the specimen's state is constant along the z-axis (i.e. it does not depend on the z coordinate).



FIGURE 3.1: Geometry and global coordinate system 0xy of the model I.

Both grains are unstressed in the initial state. The size of the grains in the unstressed state is  $2h_0$  in the *y*-direction. The grains 1 and 2 differ in their properties when different mechanisms responsible for the stress generation are taken into account:

- (a) In the first case, a stress state builds up during cooling of the specimen from the annealing temperature due to different coefficients of thermal expansion in the grains 1 and 2. For simplicity the thermal expansion is allowed only along the y-direction and no other external load is applied to the specimen. This means that the thermal expansion tensor  $\alpha$  is replaced by a scalar parameter  $\alpha$  which is constant over each grain but different in the left and in the right grain. During cooling each grain shrinks at different rate. The requirement that the grains are "welded" at x = 0 results in a deformation (and a stress related to this deformation) in a region near to the grain boundary (see Fig. 3.2).
- (b) The second case deals with a stress state in the specimen subjected to an applied external load at constant temperature. Here it is assumed that the two grains have mutually rotated crystal lattices. The anisotropy of elastic constants and the external load are sources of a stress distribution in the system. The investigated grains have a cubic crystal structure so the most convenient coordinate system in both grains is Cartesian orthonormal system oriented parallel to the corresponding  $\langle 1 0 0 \rangle$  crystal axes.

Transformations from the coordinate systems  $0x_1y_1$  and  $0x_2y_2$  into the global coordinate frame 0xy (see Figs. 3.1 and 3.3) are linear transformations and thus can be described by matrices  $\mathbf{R}_i$  (i = 1, 2),



FIGURE 3.2: Variables and parameters describing model I in the case when the stress state builds up during cooling of a specimen from the annealing temperature  $T_a$ . The situation shown in the figure corresponds to a temperature  $T < T_a$ .



FIGURE 3.3: Local coordinate systems in both grains and their relation to the global coordinate system 0xy defined in Fig. 3.1. This geometry represents the specimen subjected to the applied external stress at constant temperature.

that take forms

$$\boldsymbol{R}_{1} = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0\\ \sin \alpha & \cos \alpha & 0\\ 0 & 0 & 1 \end{pmatrix}, \qquad \boldsymbol{R}_{2} = \begin{pmatrix} \cos \beta & -\sin \beta & 0\\ \sin \beta & \cos \beta & 0\\ 0 & 0 & 1 \end{pmatrix}$$
(3.1)

where  $z \equiv z_1 \equiv z_2$  is assumed as an axis of rotation and  $\alpha$  and  $\beta$  are the angles of rotation between the coordinate system 0xy and the corresponding systems in the individual grains.

Although the above described models I (a) and I (b) seem to be oversimplified when compared to real microstructures, they satisfactorily catch the process of stress redistribution and their simplicity facilitates calculations. This geometry thus provides a reasonable background for a qualitative assessment.

#### 3.2 Model II – 2D periodic model of two grains

This model is a periodic boundary conditions based generalization of the model *I* introduced in the previous section. The basic building pattern of two grains is the same as in the model *I* except that the two grains are constrained to lengths  $r\lambda$  and  $(1-r)\lambda$  in the *x*-direction – see Figs. 3.4 and 3.5. Here,  $\lambda$  is the length of the periodic two-grain pattern and  $r \in (0, 1)$  is a volume ratio of the grain 1 within one period (and thus within the whole specimen)<sup>4</sup>. The neighbouring grains are "welded" along all boundaries at position

 $x = k\lambda$  and  $x = (k - r)\lambda$ , where  $k \in \mathbb{Z}$ .

<sup>&</sup>lt;sup>4)</sup> A volume ratio of the grain 2 is 1 - r.

The nature of the studied stress redistribution requires the continuity of displacement throughout the specimen. The periodicity of the two-grain pattern allows to solve the problem over just one period  $\lambda$ . In that case the periodic boundary condition

$$\Phi(x,y) = \Phi(x+\lambda,y)$$

must be fulfilled for all  $y \in \langle -h_0, h_0 \rangle$ , all  $-\infty < x < \infty$  and an arbitrary quantity  $\Phi$ .

The geometry adopted for the case of thermal expansion is drawn in Fig. 3.4 and for the anisotropy of elastic constants in Fig. 3.5.



FIGURE 3.4: Parameters describing the model II in the case when the stress state originates due to the anisotropy of thermal expansion coefficients. The situation is drawn for  $r = \frac{1}{2}$ . The bottom part of the specimen (y < 0) can be obtained via a mirror operation on the upper part ( $y \ge 0$ ) with the xz mirror plane.



FIGURE 3.5: Periodic two-grain pattern (model II) in which misorientated crystal lattices of both grain types are shown. The volume fraction of the type 2 grain dominates the microstructure  $(r < \frac{1}{2})$ .

#### 3.3 Model III – 3D microstructure with periodic planar pattern

The third model is a further extension of the models I and II into three dimensions and serves calculations in which the stress redistribution originates due to the anisotropy of elastic constants in systems loaded by external stress at constant temperature. The specimen has a finite height  $2h_0$  along the y-axis and extends to infinity in the xz-plane. In this plane a periodic hexagonal pattern was chosen, see Fig. 3.6. The hexagonal shape of grains approximates closer the real grain microstructures as compared to, e.g. the grains of a rectangular cross-section, but it is still simple enough to avoid complex calculations. The entire specimen consists of grains of two types marked as "grain type 1" and "grain type 2". These two types differ in mutually misorientated crystal lattices. The coordinate systems connected with grains 1 and 2 are Cartesian and thus the transformations to the global coordinate system 0xyz (see Fig. 3.7) are orthogonal and described by orthogonal matrices  $\mathbf{R}_1$  and  $\mathbf{R}_2$ , respectively. The grains of each type form rows through the specimen shown in Fig. 3.6(b). The smallest grain set that repeats periodically consists of four grains – two grains of each type delimited by a bold boundary in Fig. 3.6(b). Any arbitrary quantity  $\Phi$  must exhibit the same behaviour at boundaries marked with the same number in Fig. 3.6(c) – this ensures the periodicity of this model. A 3D view of one periodic motive is shown in Fig. 3.7.

The model III is rather complex and demanding as far as the complexity of calculations is concerned. Therefore, this model will be used only to demonstrate the relevant differences that the 3D geometry brings about in comparison to the 2D models I and II.



FIGURE 3.6: Hexagonal periodic four-grain pattern of the model III . (a) The *xy*-plane projection. (b) The *xz*-plane projection. The *xy*-plane cut shown in (a) is marked by a broken line. Bold solid line delimits one cell of the periodic structure. (c) Four different grains of two types form the basic cell of the microstructure. Encircled numbers indicate pairs of related boundaries that fit together snugly and establish thus proper periodic boundary conditions.



FIGURE 3.7: 3D view of a periodic cell used in the model III. Grains are hexagons of a side a in the xz-plane. The height of the layer of grains is  $2h_0$ . The global coordinate system 0xyz is also shown.

# 4 Stress redistribution in the microstructure – modelling methodologies

#### 4.1 Decomposition of the displacement field

The displacement field  $\boldsymbol{u}$  (Eq. (2.1)) is an additive quantity within the linear elasticity theory. Consequently, we can employ a following concept. Let us first assume that one grain can be represented by homogeneous elastic continuum in an initial stress-free state. The grain then shrinks in the case of the specimen cooling or deforms in the case when the grain is subjected to an externally applied load. In the case of cooling, the state of the isolated grain after the shrinkage is still the stress-free continuum. For a model of misorientated grains subjected to the applied external load, the displacement is described by a vector field  $\boldsymbol{u}^A$ . The set of isolated grains forming the specimen can be regarded as if virtual cuts were made along all grain boundaries – that would interrupt all mutual interactions between grains.

To restore the mutual interactions among grains and establish a continuity of the resulting displacement, the second displacement field  $u^M$  must be introduced. The total displacement u in the specimen can thus be decomposed as

$$\boldsymbol{u} = \boldsymbol{u}^A + \boldsymbol{u}^M \,. \tag{4.1}$$

The displacement  $\boldsymbol{u}^M$  must fulfil following conditions:

- 1. the total displacement  $\boldsymbol{u} = \boldsymbol{u}^A + \boldsymbol{u}^M$  must be continuous over the whole specimen<sup>5)</sup> and
- 2. elastic potential energy  $\Pi$  given by Eq. (2.6) must reach its minimum with respect to all conceivable displacements  $u^M$ .

#### 4.2 Thermal expansion anisotropy models

#### 4.2.1 Cooling of two semi-infite grains

The basic geometry of the model I and the characteristics of the thermal expansion process were described in the section 3.1. Let us first investigate the case of two semi-infinite grains (see Fig. 3.1 on page 18). The thermal expansion coefficients  $\alpha_1$  and  $\alpha_2$ , respectively, describe the expansion along the y-axis in the left and right grain. The specimen is thought to be rigid along the x-axis. Thus the only non-zero component of the displacement vector **u** is the y-component

$$u_y(x,y) = y \frac{h(x) - h_a}{h_a}$$

$$\tag{4.2}$$

where a = 1 for x < 0 and a = 2 for x > 0. This form of the displacement provides a uniform deformation of the specimen along the y-axis. According to Eq. (2.2), the non-zero components of the strain tensor are

$$\varepsilon_{yy}(x,y) = \frac{h(x) - h_a}{h_a}$$
 and  $\varepsilon_{xy}(x,y) = \frac{1}{2}y\frac{h'(x)}{h_a}$ . (4.3)

<sup>&</sup>lt;sup>5)</sup> If the displacement  $u^A$  connected with the grain deformation has discontinuities over grain boundaries, the "minimizing" displacement  $u^M$  has the same discontinuities of the opposite sign in the same locations to ensure continuity of the total displacement u.

Substituting Eq. (4.3) into Eq. (2.7) yields the strain energy density in the form

$$W(x,y) = c_{11} \left(\frac{h(x) - h_a}{h_a}\right)^2 + \frac{1}{4} c_{44} \left(y\frac{h'(x)}{h_a}\right)^2 \,. \tag{4.4}$$

There are no external tractions over the specimen surface and thus the minimisation of elastic potential energy  $\Pi$  (Eq. (2.6)) is equivalent to minimisation of the strain energy  $\mathcal{U}$ 

$$\mathcal{U} = \int_{V}^{\infty} W(x, y) \, \mathrm{d}V$$
  
=  $\int_{-\infty}^{\infty} \mathrm{d}x \int_{-h_a}^{h_a} \mathrm{d}y \left[ c_{11} \left( \frac{h(x) - h_a}{h_a} \right)^2 + \frac{1}{4} c_{44} \left( y \frac{h'(x)}{h_a} \right)^2 \right]$   
=  $\int_{-\infty}^{\infty} \mathrm{d}x \left[ 2h_a c_{11} \left( \frac{h(x) - h_a}{h_a} \right)^2 + \frac{1}{6} h_a^3 c_{44} \left( \frac{h'(x)}{h_a} \right)^2 \right].$  (4.5)

The strain energy  $\mathcal{U}$  is now, in fact, a functional  $\mathcal{U}[h]$  of an unknown function h(x). This functional has to be minimised. According to the concept described in the section 4.1, the total energy  $\mathcal{U}$  is divided into two parts that correspond to the left and right grain

$$\mathcal{U}_{1}[h_{1}] = \int_{-\infty}^{0} \mathrm{d}x \left[ 2h_{1}c_{11} \left( \frac{h_{1}(x) - h_{1}}{h_{1}} \right)^{2} + \frac{1}{6}h_{1}^{3}c_{44} \left( \frac{h_{1}'(x)}{h_{1}} \right)^{2} \right] \to \min,$$
(4.6)

$$\mathcal{U}_{2}[h_{2}] = \int_{0}^{\infty} \mathrm{d}x \left[ 2h_{2}c_{11} \left( \frac{h_{2}(x) - h_{2}}{h_{2}} \right)^{2} + \frac{1}{6}h_{2}^{3}c_{44} \left( \frac{h_{2}'(x)}{h_{2}} \right)^{2} \right] \to \min,$$
(4.7)

that are minimized separately with the boundary condition

$$h_1(0) = h_2(0) \,. \tag{4.8}$$

The extremities at  $x = -\infty$  and  $x = \infty$  are assumed to behave as free, that means

$$h_1(-\infty) = h_1 = h_0(1 + \alpha_1 \Delta T),$$
(4.9)

$$h_2(+\infty) = h_2 = h_0(1 + \alpha_2 \Delta T).$$
(4.10)

The above equations constitute two minimization problems with fixed values of minimizing functions at boundaries.

A function with given endpoints that minimizes the functional

$$\mathcal{U}[h] = \int_{a}^{b} F(x, h(x), h'(x)) \, \mathrm{d}x \,, \quad h(a) = A \,, \quad h(b) = B \,, \tag{4.11}$$

is a solution of the Euler differential equation (POSPÍŠIL, 2000, GELFAND and FOMIN, 2000)

$$\frac{\partial F}{\partial h} - \frac{\partial^2 F}{\partial h' \partial x} - \frac{\partial^2 F}{\partial h' \partial h} h' - \frac{\partial^2 F}{\partial h'^2} h'' = 0, \quad h(a) = A, \quad h(b) = B.$$
(4.12)

The Euler equation for the problem described by Eq. (4.6) with boundary conditions given by Eqs. (4.8) and (4.9) is

$$4c_{11}\left(\frac{h_1(x)}{h_1}-1\right) - \frac{1}{3}c_{44}h_1h_1''(x) = 0, \quad \lim_{x \to -\infty} h_1(x) = h_1, \quad h(0) = \xi.$$
(4.13)

The general solution to the homogeneous part of differential equation (4.13) is a linear combination of two exponential functions. A requirement of convergency at  $x \to -\infty$  excludes the exponential function that diverges as  $x \to -\infty$ . The function  $h_1(x)$  thus takes form

$$h_1(x) = h_1 + (\xi - h_1) \exp\left(\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_1}\right).$$
(4.14)

In a similar way we obtain the solution  $h_2(x)$  for the second grain

$$h_2(x) = h_2 + (\xi - h_2) \exp\left(-\sqrt{\frac{12c_{11}}{c_{44}}}\frac{x}{h_2}\right).$$
(4.15)

The complete solution requires the determination of the parameter  $\xi$ . In fact, the function

$$h(x,\xi) = \begin{cases} h_1 + (\xi - h_1) \exp\left(\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_1}\right), & \text{if } x \le 0, \\ h_2 + (\xi - h_2) \exp\left(-\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_2}\right), & \text{if } x > 0. \end{cases}$$
(4.16)

now depends also on the parameter  $\xi$ . Introducing the function  $h(x,\xi)$  into Eq. (4.5) give the elastic potential energy as a function of the parameter  $\xi$ . The parameter  $\xi$  must attain a value that minimizes the elastic potential energy of the complete two-grain structure. The minimum of the function  $\mathcal{U}(\xi)$  occurs when

$$\xi = \frac{h_1 + h_2}{2} \,. \tag{4.17}$$

The Eq. (4.3) then yields the non-zero components of the strain tensor as

$$\varepsilon_{yy}(x,y) = \begin{cases} \frac{h_2 - h_1}{2h_1} \exp\left(\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_1}\right), & \text{if } x \le 0, \\ \frac{h_1 - h_2}{2h_2} \exp\left(-\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_2}\right), & \text{if } x > 0; \end{cases}$$
(4.18)

$$\varepsilon_{xy}(x,y) = \begin{cases} \frac{h_2 - h_1}{4h_1} \exp\left(\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_1}\right) \sqrt{\frac{12c_{11}}{c_{44}}} \frac{y}{h_1}, & \text{if } x \le 0, \\ \frac{h_2 - h_1}{4h_2} \exp\left(-\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_2}\right) \sqrt{\frac{12c_{11}}{c_{44}}} \frac{y}{h_2}, & \text{if } x > 0. \end{cases}$$
(4.19)

Finally, according to the relation (2.3) the components of stress tensor are

$$\sigma_{xx}(x,y) = \sigma_{zz}(x,y) = c_{12}\varepsilon_{yy}(x,y),$$
  

$$\sigma_{yy}(x,y) = c_{11}\varepsilon_{yy}(x,y),$$
  

$$\sigma_{xy}(x,y) = c_{44}\varepsilon_{xy}(x,y).$$
  
(4.20)

#### 4.2.2 Periodic two-grain pattern

The model *II* describes a non-uniform thermal expansion in a periodic microstructure (see Fig. 3.4 on page 20). The solution procedure is almost the same as in case of two semi-infinite grains. The minimization of the elastic potential energy over the complete specimen is equivalent to the minimization of the energy over one period  $\lambda$ . The functional  $\mathcal{U}[h]$  is again divided into two parts each of them corresponding to one grain of the periodic pattern. The boundary conditions of the model *I* at the extremities  $x = -\infty$  and  $x = \infty$  are replaced by periodic boundary condition

$$h_1(-r\lambda) = h_2((1-r)\lambda) = \zeta.$$
 (4.21)

Minimization of the functional  $\mathcal{U}[h]$  leads to the Euler equations for unknown functions  $h_1(x)$  in the grain of type 1 and  $h_2(x)$  in the grain of type 2. The general solution takes a form

$$h_1(x) = h_1 + k_1 \exp\left(\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_1}\right) + k_2 \exp\left(-\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_1}\right), \qquad (4.22)$$

$$h_2(x) = h_2 + \kappa_1 \exp\left(\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_2}\right) + \kappa_2 \exp\left(-\sqrt{\frac{12c_{11}}{c_{44}}} \frac{x}{h_2}\right).$$
(4.23)

The boundary conditions are described by the system of equations

$$h_1 + k_1 + k_2 = \xi \,, \tag{4.24}$$

$$h_2 + \kappa_1 + \kappa_2 = \xi \,, \tag{4.25}$$

$$h_1 + k_1 \exp\left(\sqrt{\frac{12c_{11}}{c_{44}}} \frac{-r\lambda}{h_1}\right) + k_2 \exp\left(-\sqrt{\frac{12c_{11}}{c_{44}}} \frac{-r\lambda}{h_1}\right) = \zeta,$$
(4.26)

$$h_2 + \kappa_1 \exp\left(\sqrt{\frac{12c_{11}}{c_{44}}} \frac{(1-r)\lambda}{h_2}\right) + \kappa_2 \exp\left(-\sqrt{\frac{12c_{11}}{c_{44}}} \frac{(1-r)\lambda}{h_2}\right) = \zeta, \qquad (4.27)$$

and the surface profile h(x) is given by

$$h(x) = \begin{cases} h_1(x), & \text{if } -r\lambda \le x < 0, \\ h_2(x), & \text{if } 0 \le x < (1-r)\lambda, \\ h(x-\lambda), & \text{if } x \ge (1-r)\lambda, \\ h(x+\lambda), & \text{otherwise}. \end{cases}$$
(4.28)

Solution of the system of Eqs. (4.24)–(4.27) for the unknown coefficients  $k_1$ ,  $k_2$ ,  $\kappa_1$  and  $\kappa_2$  and substitution of  $h_1(x)$  and  $h_2(x)$  into the elastic potential energy

$$\mathcal{U} = \int_{\text{one period}} W(x, y) \, \mathrm{d}V$$
  
= 
$$\int_{-r\lambda}^{(1-r)\lambda} \mathrm{d}x \int_{-h_a}^{h_a} \mathrm{d}y \left[ c_{11} \left( \frac{h(x) - h_a}{h_a} \right)^2 + \frac{1}{4} c_{44} \left( y \frac{h'(x)}{h_a} \right)^2 \right]$$
(4.29)

yields  $\mathcal{U}$  as function of two parameters,  $\xi$  and  $\zeta$ . Their values are determined by the minimization of the potential  $\mathcal{U}(\xi, \zeta)$ . In view of the complexity associated with the solution in the analytical form, the minimizing parameters  $\xi$  and  $\zeta$  were found numerically.

#### 4.3 Elastic constants anisotropy models

#### 4.3.1 Analytical solution for the specimen under the external load

When the crystal lattices in different grains are misorientated, no preliminary assumption about the minimizing displacement can be made. Thus the displacement field  $\boldsymbol{u}^M$  must be composed of two general functions  $u_x^M(x,y)$  and  $u_y^M(x,y)$  of two variables x and y.

In line with the general concept described in section 4.1, it is possible to rewrite the expression for the density of strain energy (Eq. (2.7)) as

$$\int_{V} W(\boldsymbol{\varepsilon}) \, \mathrm{d}V = \frac{1}{2} \int_{V} c_{ijkl} (\varepsilon_{ij}^{A} + \varepsilon_{ij}^{M}) (\varepsilon_{kl}^{A} + \varepsilon_{kl}^{M}) \, \mathrm{d}V =$$

$$= \underbrace{\frac{1}{2} \int_{V} c_{ijkl} \varepsilon_{ij}^{A} \varepsilon_{kl}^{A} \, \mathrm{d}V}_{\text{constant term}} + \underbrace{\int_{V} c_{ijkl} \varepsilon_{kl}^{A} \varepsilon_{kl}^{M} \, \mathrm{d}V}_{\text{mixed term}} + \underbrace{\frac{1}{2} \int_{V} c_{ijkl} \varepsilon_{ij}^{M} \varepsilon_{kl}^{M} \, \mathrm{d}V}_{\text{minimizing term}} \quad (4.30)$$

where the symmetry  $c_{ijkl} = c_{klij}$  of elastic constants was employed. The mixed term can be further simplified to

$$\int_{V} c_{ijkl} \varepsilon_{ij}^{A} \varepsilon_{kl}^{M} \, \mathrm{d}V = \int_{V} \sigma_{ij}^{A} \varepsilon_{ij}^{M} \, \mathrm{d}V \tag{4.31}$$

and similarly

$$\frac{1}{2} \int_{V} c_{ijkl} \varepsilon_{ij}^{A} \varepsilon_{kl}^{A} \, \mathrm{d}V = \frac{1}{2} \int_{V} \sigma_{ij}^{A} \varepsilon_{ij}^{A} \, \mathrm{d}V.$$
(4.32)

Let us assume that the applied load  $\sigma^A$  is constant over the whole specimen. Using the Gauss theorem for the second term in Eq. (2.6) yields

$$\int_{S} \mathbf{T} \cdot \mathbf{u} \, \mathrm{d}S = \int_{S} \sigma_{ij}^{A} \nu_{i} u_{j} \, \mathrm{d}S = \int_{S} (\sigma_{ij}^{A} u_{j}) \nu_{i} \, \mathrm{d}S = \int_{V} \frac{\partial}{\partial x_{i}} (\sigma_{ij}^{A} u_{j}) \, \mathrm{d}V =$$
$$= \int_{V} \sigma_{ij}^{A} \frac{1}{2} \left( \frac{\partial u_{j}}{\partial x_{i}} + \frac{\partial u_{i}}{\partial x_{j}} \right) \, \mathrm{d}V = \int_{V} \sigma_{ij}^{A} \varepsilon_{ij} \, \mathrm{d}V = \int_{V} \sigma_{ij}^{A} (\varepsilon_{ij}^{A} + \varepsilon_{ij}^{M}) \, \mathrm{d}V. \quad (4.33)$$

Substituting expressions Eqs. (4.31)–(4.33) into Eq. (2.6), the final formula for elastic potential energy is obtained in the form  $^{6)}$ 

$$\Pi = -\frac{V}{2}\sigma_{ij}^{A}\varepsilon_{ij}^{A} + \frac{1}{2}\int_{V}c_{ijkl}\varepsilon_{ij}^{M}\varepsilon_{kl}^{M}\,\mathrm{d}V\,.$$
(4.35)

The dependence of strain tensor  $\varepsilon^M$  on unknown displacements  $u_x^M$  and  $u_y^M$  is given by Eq (2.2). Therefore, the energy functional depends only on partial derivatives of the displacements  $u_x^M$  and  $u_y^M$ 

$$\Pi = \int_{V} F(u_{x,x}^{M}, u_{x,y}^{M}, u_{y,x}^{M}, u_{y,y}^{M}) \,\mathrm{d}V, \qquad (4.36)$$

where

$$u_{x,x}^{M} \equiv \frac{\partial u_{x}^{M}}{\partial x}, \quad u_{x,y}^{M} \equiv \frac{\partial u_{x}^{M}}{\partial y}, \quad u_{y,x}^{M} \equiv \frac{\partial u_{y}^{M}}{\partial x} \quad \text{and} \quad u_{y,y}^{M} \equiv \frac{\partial u_{y}^{M}}{\partial y}.$$
 (4.37)

The region, over which the integration indicated in Eq. (4.36) is performed, is  $(-\infty, \infty) \times \langle -h_0, h_0 \rangle$ . Similarly to the minimization problem described by Eq. (4.11), the minimisation of the functional in Eq. (4.36) translates to the system of Euler equations

$$\frac{\mathrm{d}}{\mathrm{d}x}F_{u_{x,x}^{M}}(u_{x,x}^{M}, u_{x,y}^{M}, u_{y,x}^{M}, u_{y,y}^{M}) + \frac{\mathrm{d}}{\mathrm{d}y}F_{u_{x,y}^{M}}(u_{x,x}^{M}, u_{x,y}^{M}, u_{y,x}^{M}, u_{y,y}^{M}) = 0,$$

$$\frac{\mathrm{d}}{\mathrm{d}x}F_{u_{y,x}^{M}}(u_{x,x}^{M}, u_{x,y}^{M}, u_{y,x}^{M}, u_{y,y}^{M}) + \frac{\mathrm{d}}{\mathrm{d}y}F_{u_{y,y}^{M}}(u_{x,x}^{M}, u_{x,y}^{M}, u_{y,x}^{M}, u_{y,y}^{M}) = 0.$$
(4.38)

The boundary conditions for the case of two semi-infinite grains require that the minimizing displacement  $u^M$  vanishes at  $x = -\infty$  and  $x = \infty$ 

$$\lim_{x \to \pm \infty} u_x^M(x, y) = 0, \quad \lim_{x \to \pm \infty} u_y^M(x, y) = 0 \quad \text{for all } y \in \langle -h_0, h_0 \rangle.$$
(4.39)

The surfaces at  $y = h_0$  and  $y = -h_0$  constitute free boundaries to the minimization problem. The so called transversality conditions take, in this case, a form

$$\begin{split} F_{u_{x,y}^{M}}(u_{x,x}^{M}, u_{x,y}^{M}, u_{y,x}^{M}, u_{y,y}^{M})\Big|_{y=\pm h_{0}} &= 0, \\ F_{u_{y,y}^{M}}(u_{x,x}^{M}, u_{x,y}^{M}, u_{y,x}^{M}, u_{y,y}^{M})\Big|_{y=\pm h_{0}} &= 0. \end{split}$$

$$\end{split}$$

$$(4.40)$$

$$c_{ijkl} = R_{i\alpha} R_{j\beta} R_{k\gamma} R_{l\delta} \tilde{c}_{\alpha\beta\gamma\delta} , \qquad (4.34)$$

where  $\tilde{c}_{\alpha\beta\gamma\delta}$  is a component of the tensor *c* in the grain coordinate frame.

<sup>&</sup>lt;sup>6)</sup> We note, that the difference between the two types of grains considered in the model rests in the misorientations of their crystal lattices. This affects coordinate representation of the tensor c which has to be projected into the global coordinate system 0xy. When the transformation from the grain coordinate system into the global coordinate frame is described by a matrix R, then the component  $c_{ijkl}$  of the tensor c takes in the coordinate frame 0xy a form

The last condition, which must be satisfied by the minimizing displacement  $\boldsymbol{u}^M$ , is the continuity of the total displacement  $\boldsymbol{u} = \boldsymbol{u}^A + \boldsymbol{u}^M$ . If the displacement due to the uniformly distributed load  $\boldsymbol{\sigma}^A$  is respectively described by  $\boldsymbol{u}_1^A$  and  $\boldsymbol{u}_2^A$  in the left and in the right grain, then the continuity condition

$$\lim_{x \to 0^{-}} u_x^M(x, y) + (\boldsymbol{u}_1^A)_x(0, y) = \lim_{x \to 0^{+}} u_x^M(x, y) + (\boldsymbol{u}_2^A)_x(0, y) ,$$

$$\lim_{x \to 0^{-}} u_y^M(x, y) + (\boldsymbol{u}_1^A)_y(0, y) = \lim_{x \to 0^{+}} u_y^M(x, y) + (\boldsymbol{u}_2^A)_y(0, y)$$
(4.41)

must hold along the whole boundary where the grains meet each other, i.e. for all  $y \in \langle -h_0, h_0 \rangle^{7}$ .

The system (4.38) with boundary conditions given by Eqs. (4.39)–(4.41) is rather complicated. Therefore, one can hardly expect any analytical solutions in a closed form. Thus the models based on the elastic constants anisotropy were further solved by numerical methods.

#### 4.3.2 Finite difference method

Finite difference method (FDM) is often used for numerical solution of differential equations. The method replaces differentials by finite differences. Since the problem of stress redistribution is represented by the system of partial differential equations (4.38), this method seems to be a first choice to find a solution.

Instead of continuous function, the FDM uses a set of function values in a system of nodes. The set of nodes covers an area of interest. It is clear that the denser node networks in the investigated region provide better approximations of the solution. However, calculations based on the denser network are also more CPU demanding. It is important to choose a suitable compromise between these two factors.

Discretization of the two-grain region is described by parameters  $a, b_1$  and  $b_2$  and indicies  $n_1, n_2$  and  $n_h$  as it is illustrated in Fig. 4.1. The nodes  $X_{i,j}$  corresponding to the discretization are numbered  $j = 1, 2, \ldots, n_i n_h$  for each grain i = 1, 2. There are two unknown variables  $v_{i,j}$  and  $w_{i,j}$  for each pair  $(i, j), i \in \{1, 2\}, 1 \le j \le n_i n_h$ . These variables represent values of unknown functions  $u_x^M$  and  $u_y^M$  at the node  $X_{i,j}$ .



FIGURE 4.1: A network of FDM nodes which discretizes a two-grain region. The index ranges that determine the disretization are in this example given by  $n_1 = 3$ ,  $n_2 = 6$  and  $n_h = 4$ . The number of elements in the grain 1 is 6, the number of nodes in the grain 1 is 12. The grain 2 consists of 24 nodes and 15 elements. The parameters a,  $b_1$  and  $b_2$  determine the size of individual elements.

<sup>&</sup>lt;sup>7)</sup> The above described concept is quite general. For the assumptions  $\sigma^A = 0$ ,  $u_x \equiv 0$  and  $u_y(x,y) = y\tilde{h}(x)$  the system of equations (4.38) simplifies to the equation of the type of Eq. (4.13).

In this notation, the approximations to the derivatives (in the volume of the grain 1) are

$$\frac{\partial u_x^M}{\partial x}(X_{i,j}) \approx \frac{v_{i+1,j} - v_{i-1,j}}{2b_1}, \quad \frac{\partial u_x^M}{\partial y}(X_{i,j}) \approx \frac{v_{i,j+1} - v_{i,j-1}}{2a},$$

$$\frac{\partial u_y^M}{\partial x}(X_{i,j}) \approx \frac{w_{i+1,j} - w_{i-1,j}}{2b_1}, \quad \frac{\partial u_y^M}{\partial y}(X_{i,j}) \approx \frac{w_{i,j+1} - w_{i,j-1}}{2a}.$$
(4.42)

and the differences for the boundary nodes are replaced by corresponding "one-side" differences.

Applying the FDM to the system of partial differential equations (4.38) with boundary conditions Eqs. (4.39)–(4.41) results in a system of linear algebraic equations. Although the above sketched procedure is, in principle, applicable, it does not yield satisfactory results. The system of linear equations is usually ill conditioned which makes the solution unreliable.

#### 4.3.3 Finite element method

Finite element method (FEM) is a robust numerical tool suitable for solving of variational problems. It is again based on a discretization of the investigated region similar to the case of FDM (see the subsection 4.3.2 and Fig. 4.1).

Let  $X_{i,j}$  be a *j*-th node in the grain *i*. Let  $v_{i,j}$  and  $w_{i,j}$  be components of unknown displacement  $\boldsymbol{u}^M$  in the node  $X_{i,j}$ . The elements are delimited by four nodes  $X_{i,j}$ ,  $X_{i,j+1}$ ,  $X_{i,j+n_i}$ ,  $X_{i,j+n_i+1}$  (i = 1, 2 and  $j = 1, 2, \ldots, n_i - 1, n_i + 1, \ldots, n_i n_h - 1$ ).



FIGURE 4.2: Linear approximation of the function f(x, y) defined by Eq. (4.43). Element size is given by a = 6, b = 7 and functional values in the element nodes are  $f_1 = 2$ ,  $f_2 = 5$ ,  $f_3 = 4$  and  $f_4 = 1$ .

The functions  $u_x^M$  and  $u_y^M$  are approximated over the area of each element. Let *a* denote the height of element  $(a = 2h_0/(n_h - 1))$  and  $b_i$  the length of element in the grain *i*. The linear approximation of any function *f* over a rectangular element given by the functional values  $f_1$ ,  $f_2$ ,  $f_3$  and  $f_4$  at element nodes is

$$f(x,y) = f_1 \frac{b-x}{b} \frac{a-y}{a} + f_2 \frac{x}{b} \frac{a-y}{a} + f_3 \frac{b-x}{b} \frac{y}{a} + f_4 \frac{x}{b} \frac{y}{a} .$$
(4.43)

Using this type of approximation for functions  $u_x^M$  and  $u_y^M$ , the strain tensor, the stress tensor and finally the elastic potential energy related to each element can be obtained as a function of eight variables  $v_{i,j}$ ,  $v_{i,j+1}$ ,  $v_{i,j+n_i}$ ,  $v_{i,j+n_i+1}$ ,  $w_{i,j}$ ,  $w_{i,j+1}$ ,  $w_{i,j+n_i+1}$ .

The total elastic potential is a sum of elastic potential terms over the number of elements. The total energy is thus a function of  $2(n_1 + n_2)n_h$  variables  $v_{1,1}, \ldots, w_{2,n_2n_h}$ .

In the next step, the boundary conditions are applied. The continuity condition at x = 0 requires

$$\begin{bmatrix} \mathbf{u}_{1}^{A}(X_{1,jn_{1}}) \end{bmatrix}_{x} + v_{1,jn_{1}} = \begin{bmatrix} \mathbf{u}_{2}^{A}(X_{2,(j-1)n_{2}+1}) \end{bmatrix}_{x} + v_{2,(j-1)n_{2}+1}, \\ \begin{bmatrix} \mathbf{u}_{1}^{A}(X_{1,jn_{1}}) \end{bmatrix}_{y} + w_{1,jn_{1}} = \begin{bmatrix} \mathbf{u}_{2}^{A}(X_{2,(j-1)n_{2}+1}) \end{bmatrix}_{y} + w_{2,(j-1)n_{2}+1}, \end{bmatrix} \qquad j = 1, \dots, n_{h}.$$
(4.44)

When the specimen extends to infinity along the x-axis, a cutting distance  $\ell$  from the grain boundary must be chosen, at which the displacements are given by their values at infinity. This stems from the fact that a numerical approach could not treat the infinite dimension of the investigated domain. Thus at  $x = \pm \ell$  the displacement  $\mathbf{u}^M$  is negligibly small and the boundary conditions take a form

$$v_{1,(j-1)n_1+1} = 0, \quad w_{1,(j-1)n_1+1} = 0,$$
  
 $v_{2,jn_2} = 0, \quad w_{2,jn_2} = 0,$   
 $j = 1, \dots, n_h.$ 
(4.45)

This approximation thus contributes to the error associated with the applied numerical method. Results of the numerical solution suggest that they are insensible to the choice of the value  $\ell$  provided that  $\ell$  takes on reasonably high values ( $\ell \gtrsim 4h_0$ ).

Sets of equations (4.44) and (4.45) reduce the number of independent variables by the number  $6n_h$ .

Now the elastic potential energy is constructed and, after the application of the boundary conditions, the function of  $2(n_1 + n_2 - 3)n_h$  independent variables is obtained. This function is minimized with respect to the vector of unknown variables.

#### 4.3.4 Modification of FEM for models with periodic structures

The models based on a periodic grain pattern were introduced in sections 3.2 and 3.3. We assume that the sizes of the periodic motive along x- and z-direction remain constant during the specimen loading. Additional stress components  $\sigma_{xx}^A$  (and in a 3D case also  $\sigma_{zz}^A$ ) are needed to keep the dimensions of the periodic pattern constant. However, values of these stress components are not known prior to loading – they depend on the value of the applied load  $\sigma_{uy}^A$  and result from the calculations.

The fact that the components  $\sigma_{xx}^A$  and  $\sigma_{zz}^A$  remain unknown during the computation precludes the determination of the displacement field  $\boldsymbol{u}^A$ . Consequently, the periodic boundary conditions cannot be written in a form

$$\begin{bmatrix} \mathbf{u}_{1}^{A}(X_{1,(j-1)n_{1}+1}) \end{bmatrix}_{x} + v_{1,(j-1)n_{1}+1}^{M} = \begin{bmatrix} \mathbf{u}_{2}^{A}(X_{2,jn_{2}}) \end{bmatrix}_{x} + v_{2,jn_{2}}^{M}, \qquad j = 1, \dots, n_{h}.$$

$$\begin{bmatrix} \mathbf{u}_{1}^{A}(X_{1,(j-1)n_{1}+1}) \end{bmatrix}_{y} + w_{1,(j-1)n_{1}+1}^{M} = \begin{bmatrix} \mathbf{u}_{2}^{A}(X_{2,jn_{2}}) \end{bmatrix}_{y} + w_{2,jn_{2}}^{M}, \qquad j = 1, \dots, n_{h}.$$

$$(4.46)$$

To overcome these difficulties we must abandon the concept of decomposition of the total displacement  $\boldsymbol{u}$  into  $\boldsymbol{u}^A + \boldsymbol{u}^M$ . The elastic potential, the minimum of which characterizes a stable state,

$$\Pi = \int_{V} W(\boldsymbol{\varepsilon}) \,\mathrm{d}V - \int_{S} \boldsymbol{T} \cdot \boldsymbol{u} \,\mathrm{d}S \tag{4.47}$$

consists now of two terms which are both non-constant.

Let us first concentrate on the 2D model (model II). The strain energy U (the first term in Eq. (4.47)) is calculated using FEM and the same rectangular elements as in the case of model of two semi-infinite grains
(see Fig. 4.1 on page 28). The only difference is that instead of the displacement field  $\boldsymbol{u}^M$  we now consider the total displacement  $\boldsymbol{u}$ .

The boundary conditions at x = 0 (Eq. (4.44)) take a form

$$v_{1,jn_1} = v_{2,(j-1)n_2+1}, \quad w_{1,jn_1} = w_{2,(j-1)n_2+1}, \qquad j = 1, \dots, n_h,$$

$$(4.48)$$

and at the periodic boundary conditions at points  $x = -\lambda r$  in grain 1 and  $x = (1 - r)\lambda$  in grain 2 (Eq. (4.46)) take a form

$$v_{1,(j-1)n_1+1} = v_{2,jn_2}, \quad w_{1,(j-1)n_1+1} = w_{2,jn_2}, \qquad j = 1, \dots, n_h.$$
 (4.49)

The complete potential for minimization requires the enumeration of the integral  $\int_S \mathbf{T} \cdot \mathbf{u} \, dS$ . Because the integration has to be performed over the surface of one two-grain period we employ one dimensional elements. The surface element is represented by an abscissa connecting two neighbouring surface nodes. The displacement over the surface element is approximated by a linear dependence, which is fully determined by values in the two nodes forming endpoints of the element.

The surface integral can be decomposed into two parts: the integral over the part of the surface which is parallel to the xz-plane and the integral over the rest of the surface. Due to the periodicity of the model for each planar part<sup>8</sup> of the surface with the outer normal  $\nu$ , which is perpendicular to the y-axis, there exists a corresponding planar part of the surface with the outer normal  $-\nu$ . Since the corresponding surface tensions represent pairs of reaction forces and regarding the boundary conditions Eqs. (4.49), the integrals  $\int \mathbf{T} \cdot \mathbf{u} \, dS$  over these parts of the surface cancel each other. Therefore, the second term in Eq. (4.47) simplifies to

$$\int_{S} \mathbf{T} \cdot \mathbf{u} \, \mathrm{d}S = \int_{S} \sigma_{ij} \nu_{i} u_{j} \, \mathrm{d}S \approx \sigma_{yy}^{A} \int_{S'} u_{y} \, \mathrm{d}S \,, \tag{4.50}$$

where S' is the part of the surface of one period which is perpendicular to the y-axis.

The component  $\sigma_{yy}^A$  of the applied stress is known and thus the second term of potential (Eq. (4.47)) can be expressed in terms of known constants and unknown displacements  $u_y$  in the surface nodes.

In the 3D case (model III) a planar mesh is generated to cover the area of four grains – the periodic pattern. The mesh is illustrated in Fig. 4.3(a). This mesh takes into account the fact that the grain boundary regions are expected to carry a considerable stress redistribution. The planar mesh is copied  $n_h$ -times along the *y*-axis and a 3D mesh of the periodic pattern is thus obtained (Fig. 4.3(b)).

The 3D mesh consists of the prismatic elements with triangular bases in the xz-plane. Each element is fully characterized by the set of six forming nodes. The approximation of any function f over an element is linear, i.e. the three nodes in each base determine a linear approximation of the function f in a form

$$f_{\text{base}}(x,z) = ax + bz + c, \qquad (4.51)$$

where constants *a*, *b* and *c* are uniquely determined by the values of the function *f* in the nodes. The linear approximations within each base are linearly changing one into the other along the *y*-axis (the bottom- and the upper-base approximations are multiplied by the factors (h - y)/h and y/h, respectively). Here, *h* is the height of the element. The 3D elements and the linear approximations of the displacement field over each element allow to determine the first term of the elastic potential given by Eq. (4.47) as a function of unknown displacements in each node <sup>9</sup>.

The surface elements are in fact of two kinds: the surface elements in the xz-plane are triangles while the surface elements in the planes perpendicular to the xz-plane are rectangles. A similar type of argument as

<sup>&</sup>lt;sup>8)</sup> By planar part of the surface in the 2D case we mean a straight line.

<sup>&</sup>lt;sup>9)</sup> We note that, since the model deals with a 3D structure, all three components of the displacement vector are non-zero in each node.



FIGURE 4.3: An example of the FEM mesh of the model III. (a) Discretization in the xz-plane, nodes and planar elements. The number of elements that cover one side of the hexagonal grain (which has an edge length a) is 8. (b) The complete 3D mesh with three layers along the y-direction ( $n_h = 3$ ) and thinner discretization in xz-plane as compared to the case (a).

in the 2D case permits to simplify the second term in Eq. (4.47) into the form of Eq. (4.50). This term can be directly rewritten into the expression that is a function of unknown displacements and thus is applicable for numerical minimization.

The last condition needed for correct formulation of the minimization problem within the framework of FEM concerns the periodic boundary conditions. These are applied in the same way as in the case of 2D models and, similarly to 2D models, reduce the number of independent variables that minimize the objective function. The sides of the four-grain cell related due to periodicity are marked in Fig. 3.6(c) on page 21.

# 5 Calculated stress distributions

# 5.1 Thermal expansion models

Analytical formulas for the functions representing surfaces in microstructures described by models I (Eqs. (4.16), (4.17)) and II (Eqs. (4.22)–(4.29)) were derived in the section 4.2. Parameter values obtained experimentally were used to investigate the behaviour of the analytical solutions. The elastic constants for NiTi alloy at the annealing temperature  $T_a = 773$ K, when the microstructure is stress-free, are summarized in Tab. 5.1 (REN *et al.*, 2001).

$c_{11}$ [GPa]	$c_{12}$ [GPa]	$c_{44}$ [GPa]	$\alpha_1  [\mathrm{K}^{-1}]$	$\alpha_2  [\mathrm{K}^{-1}]$
190	140	40	$14 \times 10^{-6}$	$8 \times 10^{-6}$

TABLE 5.1: The input parameters for thermal expansion models.

In view of the other model inaccuracies, these values are assumed to be independent of temperature during cooling from the annealing temperature  $T_a$  to the room temperature  $T_r = 300$  K. Since the main objective of this work is to qualitatively account for the effects associated with stress redistributions, the above approximation is fully sufficient. We note that on cooling the differences of elastic constants are more than one order of magnitude smaller as compared to their actual values (REN *et al.*, 2001).

The thermal expansion coefficients  $\alpha_1$  and  $\alpha_2$  are chosen such that they slightly differ from the tabulated value for NiTi (J. MATTEY, INC., on-line) ( $\alpha_{\text{NiTi}} = 11 \times 10^{-6} \text{ K}^{-1}$ ). Their values are also included in Tab. 5.1.

# 5.1.1 Stress distributions for the model I

The upper surface of two-grain structure after cooling from 773 K to 300 K is shown in Fig. 5.1. The scale of both axes is chosen so that the distance 1 corresponds to  $h_0$ .

In accord with the assumptions of the model, there is no displacement along the x-axis. The displacement exhibits its maximum at the surface of the specimen, i.e. at  $y = -h_0$  and  $y = h_0$ . Therefore, the stress component  $\sigma_{xy}$  also attains its maximum value at the specimen surface. The other components of the stress tensor do not depend on the y-coordinate. In agreement with Eq. (4.20), the xx- and zz-components of the stress tensor are identical. The spatial distribution of the stress components  $\sigma_{xx}$ ,  $\sigma_{yy}$  and  $\sigma_{xy}$  over the specimen are plotted in Fig. 5.2. The results presented in Fig. 5.2 suggest that the affected area (the area where stresses differ significantly from zero) extends only in the region between  $-\frac{h_0}{2}$  and  $\frac{h_0}{2}$  along the x-axis. Consequently, only in this region one can expect any effects associated with the stress redistribution.

# 5.1.2 Stress redistributions for the model *II*

As in the model I, also the numerical calculations based on the model II were performed with the same set of elastic constants and thermal expansion coefficients given in Tab. 5.1. The length of one two-grain period is  $\lambda = 4h_0$  and the volume fraction of grain 1 within one period is either r = 0.5 or r = 0.05. Coordinates



FIGURE 5.1: The upper surface of the specimen after cooling from the annealing temperature 773 K to the room temperature. The profile results from calculations based on the model I of two semi-infinite grains.



FIGURE 5.2: The distribution of the stress components  $\sigma_{xx}$ ,  $\sigma_{yy}$  and  $\sigma_{xy}$  along the x-direction in the two-grain structure after cooling. The calculation corresponds to the model I.

normalized by the parameter  $h_0$  are used to plot the surface profiles at the end of cooling.

The specimen surface is drawn in Fig. 5.3. It is worth noticing that in the equi-volume fraction case (r = 0.5) there are regions within the grains 1 and 2 that are essentially unaffected by the minimizing displacement  $u^M$ . The surface in the interiors of both grains is very close to the position where it would be if the grains were not welded. On the contrary, in the case of r = 0.05 the smaller grain (grain 1) is too small and the redistribution of deformation is significant over its entire volume.



FIGURE 5.3: The surface of the periodic two-grain system after cooling. Two surface profiles are plotted for (a) r = 0.5 and (b) r = 0.05. Calculations cover the cooling from the annealing temperature  $T_a = 773$  K down to the room temperature  $T_r = 300$  K.

The non-zero components of the strain tensor can be calculated based on Eq. (4.3). The non-zero stress components are then related to the strain components through Eq. (4.20). The resulting stress distributions for r = 0.5 and r = 0.05 are plotted in Fig. 5.4(a) and 5.4(b), respectively. The *zz*-component  $\sigma_{zz}$  and the *xx*-component  $\sigma_{xx}$  are identical.

### 5.1.3 Concluding remarks

The NiTi alloy crystallizes in a cubic type B2 lattice. NYE (2001) poited out that the tensor of thermal expansion coefficients is always isotropic for cubic lattices. Therefore, the models *I* and *II* calculating stress redistributions due to the anisotropy of thermal expansion are not applicable to the case of NiTi B2 alloys. Nevertheless, these models can be applied to other systems with the lattice symmetry lower than cubic. The results clearly support the idea that for non-cubic systems the stress state generated due to the anisotropy of thermal expansion can possess features characteristic for the stress redistribution in a polycrystalline sample.

The anisotropy of thermal expansion is directly connected with the misorientation of crystal lattices in neighbouring grains. Therefore, for the non-cubic systems subjected to an externally applied load, the



FIGURE 5.4: Spatial distribution of the stress over the specimen consisting of two-grain periodic pattern in the x-direction. The grains of different types have different coefficients of thermal expansion. The specimen was cooled from the annealing temperature  $T_a = 773$  K to the room temperature  $T_r = 300$  K. The stress distributions were calculated for positions at the upper surface  $(y = h_0)$ . The geometry is given by the parameter  $\lambda = 4h_0$  (length of one period) and by the volume ratio r of the grain 1: (a) r = 0.5 and (b) r = 0.05.

non-uniform strains due to the thermal expansion anisotropy and due to the external load may superimpose provided the crystal lattices of individual grains are misorientated. Fortunately, in the case of NiTi the thermal expansion strain is isotropic and thus does not contribute to the stress redistribution. Therefore, results obtained for misorientated crystal lattices of NiTi alloys subjected to the externally applied load and presented in next sections of this work do not include the thermal expansion effects. In passing we note that, whatever the crystal lattice, the thermal expansion effects do not contribute to the stress redistribution during isothermal heat treatments.

The stress generated during cooling the microstructure due to thermal expansion would cause just a constant contribution to the total stress state and thus this part of the total stress is not interesting from the point of view of the local stress redistribution.

# 5.2 External loading models

The analytical solution presented in the subsections 5.1.1 and 5.1.2 shown that a special class of problems can be solved under the assumption that components of the displacement vector are linear functions of the coordinate y. However, this form of the function  $\mathbf{u}^M(x, y)$  does not fulfil the system of Eqs. (4.38)–(4.41) and thus does not minimize the elastic potential in more general cases. These more general formulations require the components of the displacement vector being general functions of variables x and y and the system of Eqs. (4.38)–(4.41) then becomes to complicated for analytical solutions. The finite element method described in the subsection 4.3.3 is the most suitable numerical tool to solve these general problems when the energy minimisation principle is applied.

# 5.2.1 Stress distribution for the model I

As depicted in Fig. 3.3, the system of two semi-infinite misorientated grains is loaded by the applied stress  $\sigma_{yy}^A$  and the grains are welded at x = 0. General steps of the solution were discussed in the subsection 4.3.3. The discretization of the microstructure is shown in Fig. 4.1. The semi-infinite grain does not fit the concept of the FEM and it is thus important to select an appropriate cut-off distance  $\ell$  that limits the region of the solution with respect to the x-coordinate. The analytical solution presented for the case of thermal expansion in the subsection 5.1.1 suggested that there is a distance  $\ell$  from the grain boundary at x = 0 where the minimizing displacement is negligibly small and where the stress redistribution ceases. It has been found that the results are not affected when the cut-off distance  $\ell$  fulfils  $\ell \gtrsim 4h_0$ .

The results of the numerical solution presented below were obtained for material constants of NiTi alloy at the temperature 773 K, see work of REN *et al.* (2001). The grain misorientations are described by the angles  $\alpha$  and  $\beta$  (see Fig. 3.3). The applied load is characterized by the tensor  $\sigma^A$ . The only non-zero component of  $\sigma^A$  is  $\sigma_{yy}^A$ . All these parameters are summarized in Tab. 5.2. The value of  $\sigma_{yy}^A$  corresponds to the loads used experimentally during the stress assisted aging of NiTi alloys (BOJDA *et al.*, 2005).

$c_{11}$ [GPa]	$c_{12}$ [GPa]	$c_{44}$ [GPa]	$\alpha [\mathrm{rad}]$	$\beta  [\mathrm{rad}]$	$\sigma_{yy}^A$ [MPa]
190	140	40	0	$\pi/6$	8

TABLE 5.2: The basic input parameters for external loading models.

The geometry of the loaded specimen is fully characterized by the parameter  $h_0$ ;  $2h_0$  is the *y*-size of the grains. For purposes of the computation, both coordinates were normalized by  $h_0$  and, in what follows, the results are plotted in these dimensionless coordinates. The adopted value of the cut-off parameter  $\ell$  is  $5h_0$ .

The discretization (see Fig. 4.1) of the investigated region is given by a rectangular element mesh described by the parameters  $n_1 = 30$ ,  $n_2 = 30$  and  $n_h = 10$ . The number of nodes in each grain is 300 and the



FIGURE 5.5: The upper surface of the specimen composed of two semi-infinite grains with mutually misorientated crystal lattices. The top surface is a horizontal line at  $y = h_0$  before loading. When the load (8 MPa) is applied and the grains are treated independently, the upper surface of each grain moves and its new position is drawn by the blue line. A subsequent welding operation restores the continuity of the surface and, at the same time, minimizes the strain energy. The final surface profile after these operations is represented by the red line.

number of elements is 261. Considering the boundary conditions at x = 0 (continuity of the displacement) and at  $x = \pm \ell$  (where the minimizing displacement vanishes), the total number of independent variables reduces to 1160 for the designed mesh. Consequently, the energy term (Eq. (4.35)) to be minimized is a function of these 1160 variables. A build-in function of the system Mathematica (WOLFRAM, 1999) was used to minimize the objective energy function.

Figure 5.5 shows the calculated profile of the upper specimen surface after loading and the energy minimisation. Prior to loading, the upper surface of the specimen was at  $y = h_0$ . The blue line represents the upper surface of loaded grains when they are not welded together (each grain deforms as a free homogeneous continuum and corresponding surfaces of one grain are parallel to each other). The minimisation displacement  $u^M$  is computed so that it restores the continuity of the displacement over the microstructure and, at the same time, it minimizes the total strain energy. Finally, the total displacement u is obtained by adding the two vector fields  $u^A$  and  $u^M$  and its values at the specimen surface are represented by the red line in Fig. 5.5.

Corresponding stress components are plotted in Fig. 5.6. We note that, far away from the grain boundary, the only non-zero component of the stress tensor is  $\sigma_{yy}$  and its value converges to the externally applied stress of 8 MPa. The component  $\sigma_{zz}$  and its spatial distribution is similar to the component  $\sigma_{xx}$ . The components  $\sigma_{xz}$  and  $\sigma_{yz}$  of the stress tensor are identically zero which follows the fact that the model is 2D.

#### 5.2.2 Stress distributions for the model II

The FEM discussed in the subsection 4.3.4 can be also easily implemented to calculate stress redistribution for the model II of the periodic two-grain pattern of mutually misorientated crystal lattices. The periodic pattern is described by two parameters: the length of one period  $\lambda$  which was selected as  $\lambda = 4h_0$  and the volume ratio r of grain 1 within one period r = 0.5. In addition to the boundary conditions at x = 0, the periodic boundary conditions at  $x = -r\lambda$  and  $x = (1 - r)\lambda$  are now applied. The the material constants,



FIGURE 5.6: The distribution of the individual stress components over the entire specimen composed of two semi-infinite grains with mutually misorientated crystal lattices. The cut-off parameter is  $\ell = 5h_0$ .

misorientation of the lattices and the applied stress are listed in Tab. 5.2.

The upper surface of the specimen after loading is plotted in Fig. 5.7 over two  $\lambda$  periods. The blue lines represent the top surface of each grain in a situation when the grains were independently loaded by external stress  $\sigma_{yy}^A = 8$  MPa. The red line shows the upper surface profile for the grains welded together and after the minimisation of the strain energy.

The red line is shifted towards smaller displacements as compared to the blue line. This effect is associated with the boundary conditions set at the grain boundaries. If free, the individual grains subjected to the applied load would shrink such that gaps between each pair of neighbouring grains would appear (note the drastically different scales on both axes due to which the gap cannot be directly observed in Fig. 5.7). When the grains are welded, these gaps must be refilled with the material which leads (under the assumption of a constant volume) to the shrinkage of each grain along the *y*-direction and to the widening along the *x*-direction. This strain component is associated with the components  $\sigma_{xx}^A$  of the applied stress discussed in the subsection 4.3.4.



FIGURE 5.7: The upper surface of a periodic two-grain pattern. One period of length  $\lambda = 4h_0$  consists of two grains with mutually misorientated crystal lattices ( $\alpha = 0, \beta = \frac{\pi}{6}$ ). The red line represents the final top surface.

All the non-zero components of the stress tensor are plotted in Fig. 5.8 over one two-grain period. The stress distributions correspond to the displacement field shown in Fig. 5.7. Contour plots of the stress component profiles are plotted next to the corresponding surface plots.

The experimental results mentioned in the chapter 1 were obtained for three different values of the externally applied stress: 2 MPa, 8 MPa and 20 MPa. Therefore, simulations based on the model *II* were performed for the same set of three external loads  $\sigma_{yy}^A$  and the results are presented in Fig. 5.9. There is no qualitative difference between the stress distributions obtained for different  $\sigma_{yy}^A$  loads. The quantitative difference relates to the scaling factor for the stress coordinate that increases with the increasing external stress. This result reflects the linearity anticipated for the elastic continuum within a framework of the linear elasticity theory. Since the deformation is proportional to the applied load, higher applied load results in larger deformation. Therefore, the vector fields  $u^M$  computed for the same type but increasing loads are mutually proportional. This fact translates also into the shape of stress surface which is self-similar as it is demonstrated in Fig. 5.9.



FIGURE 5.8: The distributions of stresses over one period composed of the two-grain pattern. The grains have mutually misorientated crystal lattices. The length of one period is  $\lambda = 4h_0$  and the externally applied load is  $\sigma_{yy}^A = 8$  MPa.



FIGURE 5.9: Distributions of the stress components  $\sigma_{yy}$  for the periodic pattern of two-grains loaded by the external stress  $\sigma_{yy}^A$  of: (a) 2 MPa, (b) 8 MPa and (c) 20 MPa.



FIGURE 5.10: Distributions of stress components  $\sigma_{xx}$ ,  $\sigma_{yy}$ ,  $\sigma_{zz}$  and  $\sigma_{xy}$  over one period of the two-grain pattern. The grains have mutually misorientated crystal lattices. The length of one period is  $\lambda = 4h_0$  and the externally applied load is  $\sigma_{yy}^A = 8$  MPa. (a)  $\alpha = -\pi/6$ ,  $\beta = \pi/6$ , r = 0.5, (b)  $\alpha = 0$ ,  $\beta = \pi/6$ , r = 0.25.

The results presented so far in this subsection have been obtained for constant values of the parameters  $\alpha$ ,  $\beta$  and r given in Tab. 5.2. We are now interested in changes in the stress distribution due to the variations of parameters  $\alpha$ ,  $\beta$  and r. The results obtained for  $\alpha = -\pi/6$ ,  $\beta = \pi/6$  and r = 0.5 are shown in Fig. 5.10(a) whereas the stress redistributions for  $\alpha = 0$ ,  $\beta = \pi/6$  and r = 0.25 are shown in Fig. 5.10(b).

The decomposition of the displacement vector field  $\mathbf{u} = \mathbf{u}^A + \mathbf{u}^M$  used in calculations within a framework of the model *I* is not always a proper approach. A related erroneous result is demostrated in Fig. 5.11. Here displacement field  $\mathbf{u}^A$  associated with the applied load was calculated under the assumption that the only non-zero component of the applied stress is  $\sigma_{yy}^A$ . This is, in fact, not correct as it was discussed in the subjcction 4.3.4. As an evidence of the incorrect result we note that the average value of the redistributed stress component  $\sigma_{yy}$  is significantly higher than the expected value of 8 MPa equal to the applied stress.



FIGURE 5.11: Distribution of the component  $\sigma_{yy}$  over one two-grain period when the contribution of the component  $\sigma_{xx}^A$  is neglected. This simplification results in a redistribution of  $\sigma_{yy}$  with average value about 13 MPa which is much higher than the expected value equal to the applied stress  $\sigma_{yy}^A = 8$  MPa.

#### 5.2.3 Stress distributions for the model III

The FEM mesh generated for the 3D model of the misorientated grains was introduced in the subsection 4.3.4. The mesh consisted of eight elements along each side of the hexagonal grain (see Fig. 4.3(b)) and contained 2780 nodes that delimit 3648 elements. The basic motive of the periodic pattern consists of four grains (see Fig. 3.6 on page 21). These four grains can be sorted further into two classes where each class represents grains with the same orientation with respect to the global coordinate system. However, the grains from different classes exhibit different crystallographic orientation as far as the relation to the global coordinate system is concerned.

TEM micrographs of NiTi alloy were presented in the chapter 1. The evaluation of the corresponding electron diffraction patterns provides information on how the crystal lattices in different grains are orientated with respect to the global coordinate system. The orientation of each grain can be described by the transformation matrix  $\mathbf{R}$  from the global coordinate system 0xyz into the local coordinate system  $0x_iy_iz_i$  of the *i*-type grain. The transformation matrices were obtained from the TEM micrograph in Fig. 1.7 and

from corresponding diffraction patterns for the grain 1 and the grain 2 as

$$\boldsymbol{R}_{1} = \begin{pmatrix} 0.9505 & -0.1901 & -0.2458 \\ -0.2791 & -0.2072 & -0.9377 \\ 0.1254 & 0.9612 & -0.2456 \end{pmatrix}, \qquad \boldsymbol{R}_{2} = \begin{pmatrix} 0.6694 & 0.1116 & -0.7345 \\ -0.1570 & -0.9368 & -0.3126 \\ -0.72012 & 0.3444 & -0.6023 \end{pmatrix}. \quad (5.1)$$

These matrices were used in the calculations. The model geometry is further described by the undefined parameter  $h_0$  ( $2h_0$  is the thickness of the investigated layer of grains) and by the side length of the hexagonal grain  $a = h_0$ .

All other material constants remain the same as in previous calculations (NiTi alloy at 773 K), see Tab. 5.2 and the layer is subjected to the stress  $\sigma_{yy}^A = 8 \text{ MPa}$  applied externally.

When the periodic boundary conditions are correctly tied up (see Fig. 3.6(c) on page 21) the number of independent unknown variables is reduced. In the situation investigated here, the final elastic energy potential is a function of 6840 independent variables.

The upper surface of the 3D specimen, which was initially a plane at  $y = h_0$  before loading, is drawn in Fig. 5.12. The discontinuous surface shown in Fig. 5.12(a) represents a situations after loading the mutually independent grains by the applied stress  $\sigma_{yy}^A = 8$  MPa. The continuous surface in Fig. 5.12(b) results from the energy minimisation that introduces the smoothing displacement  $u^M$  and restores the continuity of the displacement field. The four grains that make up an elementary cell of the periodic pattern are highlighted and are plotted together with all surrounding grains. The surrounding grains are included in Fig. 5.12 to demonstrate the proper application of the boundary conditions.

Figure 5.13 illustrates all components of the stress tensor that correspond to the displacement shown in Fig. 5.12(b). These graphs suggest that the hydrostatic components are generally larger than the shear components. It is also evident that the stress redistribution affects preliminary grain boundary regions. Therefore, near grain boundaries one can expect the most pronounced effect as far as the selection of crystallographic precipitate variants is concerned.



FIGURE 5.12: The upper surface of the periodic 3D specimen after loading by  $\sigma_{yy}^A = 8$  MPa. The figure demonstrates how the total displacement **u** (b) recovers the continuity of the surface after application of the external stress when compared to the set of individual grains (a) subjected to the applied load.



FIGURE 5.13: Distributions of the individual stress tensor components over one cell of the periodic pattern calculated for the positions at the upper surface  $(y = h_0)$ . The microstructure is subjected to the applied load of  $\sigma_{yy}^A = 8$  MPa. The stress components vary significantly especially in grain boundary regions. The hydrostatic components are larger than the shear components.

# 6 Crystallographic variants and their preferential precipitation

All calculations summarized in following section focus on the interaction energy that contributes to the total energy of the crystal when a particle is placed in a preloaded (stress field  $\sigma$ ) elastic continuum. The equation for the interaction energy was derived by ESHELBY (1961)

$$E_{\rm int} = -\int_{V_p} \sigma_{ij} \varepsilon_{ij}^T \,\mathrm{d}V\,. \tag{6.1}$$

The meaning of the strain tensor  $\varepsilon^T$  and the crystallographic relationship between the Ti<sub>3</sub>Ni<sub>4</sub> precipitates and the NiTi matrix were discussed in the chapter 1.

The selection principle that specifies which crystallographic variant most probably precipitates in a given location of the microstructure is based on the interaction energy given by Eq. (6.1). Each crystallographic variant is placed into a position in the matrix where a particular stress state  $\sigma$  is present and the interaction energy is computed. The variant associated with the lowest interaction energy  $E_{int}$  is then identified as the selected variant. In the present approximation, we do not consider contributions to the stress state  $\sigma$  that might be associated with the presence of other particles in the vicinity of the given location.

# 6.1 Approximation of constant stress inside the precipitate

In the first step, it is convenient to simplify the evaluation of the interaction energy and to assume that the precipitate is so small that the stress field  $\sigma$  does not vary too much in the precipitate volume. This approximation yields qualitatively correct results without any special computational effort.

Within the approximation of the constant stress field inside the precipitate, the equation (6.1) simplifies to

$$E_{\rm int} = -V_p \sigma_{ij} \varepsilon_{ij}^T \,. \tag{6.2}$$

In what follows, the variable chosen for the comparison of different crystallographic variants is the interaction energy density (IED)  $E_{\text{int}}/V_p$ .

#### 6.1.1 Precipitates in two semi-infinite grains

The calculated stress distributions over the two semi-infinite grains loaded by the external stress  $\sigma_{yy}^A = 8 \text{ MPa}$  were presented in the subsection 5.2.1. The eight different crystallographic variants are divided into two groups  $\mathcal{G}_1$  and  $\mathcal{G}_2$  according to the orientation of their habit plane normal parallel to one of eight  $\{111\}_{NiTi,B2}$ -plane normals

$$\mathcal{G}_{1} = \left\{ [1\,1\,1], \ [\overline{1}\,\overline{1}\,\overline{1}], \ [1\,1\,\overline{1}], \ [\overline{1}\,\overline{1}\,1] \right\}, \qquad \mathcal{G}_{2} = \left\{ [\overline{1}\,1\,\overline{1}], \ [1\,\overline{1}\,1], \ [\overline{1}\,\overline{1}\,1] \right\}.$$
(6.3)

The numerical results show that variants within each group yield the same interaction energy in a given location of the system. It is worth noticing that so called "complementary variants" (variants with a parallel (but opposite) axis of the disk, e.q.  $[1 \ 1 \ 1]$  and  $[\overline{1 \ 1 \ 1}]$ ), are always in the same group.

The spatial distributions of IED for the precipitates from the group  $G_1$  and group  $G_2$  are plotted in Fig. 6.1(a) and (b), respectively. Since all precipitates belonging to one variant group (e.g. group  $G_1$ ) are equivalent



FIGURE 6.1: Spatial distribution of the interaction energy density associated with the  $Ti_3Ni_4$  precipitation. Precipitates are treated as elastic inclusions in the NiTi matrix. The parent NiTi B2 phase consists of two semi-infinite grains subjected to the externally applied stress 8 MPa. (a) Energy distribution for crystallographic variants [111],  $[\overline{111}]$ ,  $[11\overline{1}]$ ,  $[\overline{111}]$  (group  $G_1$ ), (b) energy distribution for crystallographic variants  $[\overline{111}]$ ,  $[1\overline{11}]$ ,  $[\overline{111}]$  (group  $G_2$ ).

as far as the IED is concerned, it is now sufficient to investigate the IED differences for only one variant type from the group  $\mathcal{G}_1$  and one from the group  $\mathcal{G}_2$ . This comparison of the IED yields the energetically more convenient group of variants for a given location in the microstructure. The corresponding IED map is plotted in Fig. 6.2.



FIGURE 6.2: Energy map showing the preferential precipitation of variants from either the group  $G_1$  or  $G_2$ . The underlying stress distribution  $\sigma$  was calculated using the 2D model of two semiinfinite grains subjected to the applied stress of 8 MPa. The preferential precipitation of variants from group  $G_1$  can be expected in red regions, the precipitates from the group  $G_2$  are beneficial in green regions. Dashed line represents the grain boundary.

More intensive colour in the map means a larger bias in favour of precipitates from a either group. The energy map in Fig. 6.2 suggests that the preferential selection of variants is expected in regions near the grain boundary. The results suggest that when the variant selection is mainly based on the interaction energy between the precipitate strain field and the external stress distributed over the matrix, then only four out of eight variants would be observed in the vicinity of the grain boundary. Taking into account the fact that it is very difficult to distinguish the complementary variants experimentally, the modelling results show that in some regions near to the grain boundary only two out of four distinguishable variants would grow. This result is in a qualitative agreement with the experimental observation in the Introduction and published in the literature (BOJDA *et al.*, 2005).

#### 6.1.2 Precipitates in 2D periodic two-grain pattern

The calculated stress distribution resulting from the model II (2D periodic two-grain pattern) was presented in the subsection 5.2.2. The estimate of the interaction energy is again based on Eq. (6.2). Similarly to the case of two semi-infinite grains, the set of eight variants is divided into two subsets  $\mathcal{G}_1$  and  $\mathcal{G}_2$  given by Eq. (6.3). The variants within each group exhibit the same probability of growth in a particular position as assessed based on the interaction energy of the precipitate. The applied load is  $\sigma_{yy}^A = 8$  MPa.

Figure 6.3 presents the energy distribution for variants from group  $\mathcal{G}_1$  (part (a)) and from group  $\mathcal{G}_2$  (part (b)). The IED is grater then zero everywhere in the microstructure and thus makes the precipitation less favourable (when the elastic part of the overall energy is taken into account). The situation may change when the chemical energy associated with the precipitate formation is considered. Since the chemical energy term is the same for all crystallographic variants, the IED determines the most favourable crystallographic variant that will form in a given location. The energy map for the most favourable variants is shown in Fig. 6.4.



FIGURE 6.3: Spatial distribution of the interaction energy density associated with the  $Ti_3Ni_4$  precipitation. Precipitates are treated as elastic inclusions in the NiTi matrix. The parrent NiTi B2 phase consists of two-grain periodic pattern subjected to the externally applied stress 8 MPa. (a) Energy distribution for crystallographic variants [111],  $[\overline{111}]$ ,  $[11\overline{1}]$ ,  $[\overline{111}]$  (group  $\mathcal{G}_1$ ), (b) energy distribution for crystallographic variants  $[\overline{111}]$ ,  $[\overline{111}]$ ,  $[\overline{111}]$  (group  $\mathcal{G}_2$ ).



FIGURE 6.4: Energy map for the 2D model of periodic two-grain pattern. Grains are subjected to the applied stress of 8 MPa. Variants from the group  $G_1$  are favourable in red regions, the precipitates from the group  $G_2$  are preferred in green regions. Dashed lines represent the grain boundaries.



FIGURE 6.5: Spatial distribution of interaction energies for variant groups  $G_1$  and  $G_2$ . Results are plotted for the 2D model of periodic two-grain pattern. Grains are loaded by 2 MPa (left column) and 20 MPa (right column).

The stress distributions for different values of the applied load were presented in the subsection 5.2.2. According to the arguments mentioned in the subsection 5.2.2 and based on Eq. (6.2), the different loads cause only a scaling in IED for the two variant groups  $\mathcal{G}_1$  and  $\mathcal{G}_2$  but the energy map in Fig. 6.4 is not affected. Each contour on this map connects positions with a constant value of the IED that a given fraction of the difference between the global minimal and the global maximal value of the IED over the entire microstructure). The energy distributions for both groups  $\mathcal{G}_1$  and  $\mathcal{G}_2$  and for different applied loads are plotted in Fig. 6.5.

#### 6.1.3 Four-grain periodic pattern – 3D model

The concept of the favourable precipitate variant selection is now demonstrated for a 3D specimen composed of a four-grain periodic pattern. The corresponding stress redistribution was investigated in the subsection 5.2.3.



FIGURE 6.6: Interaction energy distributions calculated for four pairs of complementary precipitate variants  $\mathcal{P}_1 - \mathcal{P}_4$  in one periodic cell that represents a NiTi microstructure in the model III. The energies were evaluated for positions at the upper surface of the specimen  $(y = h_0)$ .

The assessment of the interaction energy was again based on Eq. (6.2). The IED of all variants are almost identical in the interiors of the grains. On the contrary, in the grain boundary regions the IEDs of individual

variants differ significantly. Therefore, the preferential precipitation of crystallographic variants due to their different interaction energies can be expected mainly near the grain boundaries. Similarly to the results obtained for the 2D two-grain periodic model, the IED of each variant is positive everywhere. For a final decision whether a particular position is energetically favourable or not, the chemical term contributing to the change  $\Delta G$  of the Gibbs free energy must be taken into account.

The IEDs were calculated and compared for all eight variants and it was found that the energy distribution for complementary variants are identically the same. The corresponding IED distributions obtained for pairs  $\mathcal{P}_1 - \mathcal{P}_4$  are shown in Fig. 6.6.

$$\mathcal{P}_{1} = \left\{ [1\,1\,1], \ [\overline{1}\,\overline{1}\,\overline{1}] \right\}, \qquad \mathcal{P}_{2} = \left\{ [1\,1\,\overline{1}], \ [\overline{1}\,\overline{1}\,1] \right\},$$

$$\mathcal{P}_{3} = \left\{ [1\,\overline{1}\,1], \ [\overline{1}\,1\,\overline{1}] \right\}, \qquad \mathcal{P}_{4} = \left\{ [\overline{1}\,1\,1], \ [1\,\overline{1}\,\overline{1}] \right\}.$$

$$(6.4)$$

However, the IED differs when different pairs of the complementary variants are investigated. The IED calculations were performed for each node of the FEM mesh and this made it possible to estimate the energy of crystallographic variants in each node. The colour map that indicates variant with the lowest IED in a given location of the 3D specimen is shown in Fig. 6.7.

#### 6.2 Approximation of variable stress inside the precipitate

More accurate values of the interaction energy are obtained when the actual stress distribution inside the precipitate is taken into account and calculations are performed in accord with Eq. (6.1). The calculations are CPU demanding and thus they were performed only for the 2D model I of two semi-infinite grains. Results are representative enough to demonstrate changes with respect to the approximation of constant stress inside the precipitate volume. The shape of the precipitate was approximated by an ellipsoid of rotation with a diameter d and a thickness h. The particular d and h values used for the calculation were

$$d = \frac{h_0}{10}, \qquad h = \frac{d}{5}, \tag{6.5}$$

see Fig. 6.8.

The distribution of crystallographic variants that exhibit the lowest interaction energy in a given location near the grain boundary is drawn in Fig. 6.9. The four pairs of complementary variants  $\mathcal{P}_1 - \mathcal{P}_4$  (Eq. (6.4)) are distinguished by four colours (red, blue, green and yellow) and the two complementary variants within each pair are represented by the same colour but different shades. This figure clearly shows that in some locations only one of the two complementary variants reaches the energy minimum.

A preliminary conclusion supported by the more precise calculations is that there always are two regions in the microstructure where the variants with the lowest energy are either from the group  $\mathcal{G}_1$  or  $\mathcal{G}_2$  (the basic division into two groups is described in the subsection 6.1.1). These variants never precipitate simultaneously in the same location. Moreover, the more exact computations allowed distinguishing the energies of complementary variants. The minimum interaction energy is often reached by two of four experimentally distinguishable variants ( $\mathcal{P}_1 - \mathcal{P}_4$ ) but each distinguishable variant is then (sometimes) represented by only one of the two complementary particles.

It is worth noticing that there are also some locations where the lowest interaction energy is associated with only one of the eight crystallographic variants of Ni<sub>4</sub>Ti<sub>3</sub> precipitates. However, these results are strongly burden by the numerical part of the calculations and thus are debatable. The differences between energies of different variants are of the order of  $h_0^3 \cdot 10^{-5}$  J m<sup>-3</sup> and smaller whereas the total interaction energies are found in the  $h_0^3 \cdot 10^{-4}$  J m<sup>-3</sup> range.



FIGURE 6.7: Node positions in which the IED was calculated within a framework of the 3D model. The precipitation of the most favourable variant pair in the individual node is indicated by a corresponding colour dot. Layer 1 and layer 5 refer to the bottom and top surfaces of the specimen, respectively, while layers 2, 3 and 4 are located at  $y = -h_0/2$ , y = 0 and  $y = h_0/2$ , respectively. The stress redistribution which causes the preferential precipitation results from the externally applied stress of 8 MPa.



FIGURE 6.8: The precipitate shape is approximated by an ellipsoid of rotation. (a) 3D view, (b) projection parallel to and (c) perpendicular to the rotation axis.



FIGURE 6.9: The distribution of crystallographic variants near the grain boundary calculated for the non-uniform stress state inside the particle volume. The stress distribution  $\sigma$  in the matrix prior to precipitation results from the 2D model of two semi-infinite grains loaded by the externally applied stress of 8 MPa. This map can be compared with the energy map in Fig. 6.2.

# 7 Discussion of the results

# 7.1 Numerical techniques

#### 7.1.1 Surface term of elastic potential

Solutions to the problems in the present work were found by minimisation of the elastic potential given by Eq. (2.6). The second term of this potential

$$\int_{S} \mathbf{T} \cdot \mathbf{u} \, \mathrm{d}S \tag{7.1}$$

deals with virtual works done by surface tensions. The surface tension are given by

$$T_i = \sigma_{ij} \nu_j \,. \tag{7.2}$$

It was discussed in the subsection 4.3.4 that, for models considered in this investigation, a value of the work in Eq. (7.1) is given by the surface tensions acting over the parts of the surface that were originally planes perpendicular to the *y*-axis. These parts are two – the top surface  $S_{top}$  and bottom surface  $S_{bottom}$  of the grains, see Figs. 3.3, 3.5 and 3.6. In what follows, we refer to either  $S_{top}$  or  $S_{bottom}$  as  $\tilde{S}$ .

Let us decompose the stress field

$$\boldsymbol{\sigma} = \overline{\boldsymbol{\sigma}} + \Delta \boldsymbol{\sigma} \,, \tag{7.3}$$

where

$$\overline{\sigma}_{ij} = \frac{1}{\tilde{S}} \int_{\tilde{S}} \sigma_{ij} \,\mathrm{d}S \quad \text{and} \quad 0 = \frac{1}{\tilde{S}} \int_{\tilde{S}} \Delta \sigma_{ij} \,\mathrm{d}S \,. \tag{7.4}$$

Let us similarly decompose the displacement field

$$\boldsymbol{u} = \overline{\boldsymbol{u}} + \Delta \boldsymbol{u} \,, \tag{7.5}$$

where

$$\overline{u}_i = \frac{1}{\tilde{S}} \int_{\tilde{S}} u_i \, \mathrm{d}S \quad \text{and} \quad 0 = \frac{1}{\tilde{S}} \int_{\tilde{S}} \Delta u_i \, \mathrm{d}S \,.$$
(7.6)

Substituting these expressions into the surface term (7.1) yields

$$\int_{\tilde{S}} \mathbf{T} \cdot \mathbf{u} \, \mathrm{d}S = \int_{\tilde{S}} \overline{\sigma}_{ij} u_j \nu_i \, \mathrm{d}S + \int_{\tilde{S}} \Delta \sigma_{ij} \overline{u}_j \nu_i \, \mathrm{d}S + \int_{\tilde{S}} \Delta \sigma_{ij} \Delta u_j \nu_i \, \mathrm{d}S \,.$$
(7.7)

The average displacement  $\overline{u}_j$  and the outer  $\tilde{S}$  normals  $\nu_i$  in the second term of Eq. (7.7) are constant variables over the integration range. Following the second condition in Eq. (7.4), we found out that the second term in Eq. (7.7) is zero. The third term in Eq. (7.7) constitutes a second order corrections that we neglect. To support the omission of the last term in Eq. (7.7) we propose these two arguments: (i) corrections  $\Delta f$  of a quantity f are usually small when compared to  $\overline{f}$  (for both stress field  $\sigma$  and displacement field  $\boldsymbol{u}$ ) and (ii) considering the geometry of models used in this work, namely the periodic boundary conditions, and the continuity of all quantities this term presents a very small contribution. By these arguments we finally obtain the following approximation of the surface tension work

$$\int_{\tilde{S}} \boldsymbol{T} \cdot \boldsymbol{u} \, \mathrm{d}S \approx \int_{\tilde{S}} \overline{\sigma}_{ij} u_j \nu_i \, \mathrm{d}S \,. \tag{7.8}$$

In standard elasticity problems the boundary conditions prescribe either stress distribution or displacement field in each position over the surface. In our problems we consider a little bit different boundary condition in a form

$$\overline{\sigma} = \sigma^A \tag{7.9}$$

on both surfaces  $S_{\text{top}}$  and  $S_{\text{bottom}}$ . By summing approximations of the form of Eq. (7.8) for  $S_{\text{top}}$  and  $S_{\text{bottom}}$  we obtain the final expression for the potential surface term as

$$\int_{S} \mathbf{T} \cdot \mathbf{u} \, \mathrm{d}S \approx \int_{S} \sigma_{ij}^{A} u_{j} \nu_{i} \, \mathrm{d}S \,. \tag{7.10}$$

This form was used in the calculations.

#### 7.1.2 Search for a global minimum

All the numerical calculations were performed using the FEM. This technique aims at the minimization of a function of many-variables with the objective to find a global minimum of the investigated function in the region of interest. Naturally, a question arises whether a search for the global minimum could always be successful. The FEM approximates any function in the volume of one element by a polynomial with coefficients that consist of constants and powers of the unknown function values in the element nodes. The integral of this function over the element volume remains polynomial in the unknown function values in nodes. Solutions obtained in this work were all based on linear approximations of the unknown functions (displacements). Therefore, obtained coefficients were proportional either to zero or to the first power of the function values in nodes. Since the objective function (the elastic potential) is composed of sums of such integrals it remains a polynomial in unknown values of the displacements in nodes.

The build-in function Minimize of the system Mathematica 5.0 that was employed in the minimization process guarantees, see WOLFRAM (1999), that, for objective functions of a polynomial form, the procedure always reaches a global minimum of the objective function in the investigated region. Therefore the obtained minimum constitutes a true global minimum for the considered problem.

It is worth noticing that displacement field that minimizes the objective function is not, in general, a unique solution. Let us assume that u is a displacement field that minimizes the elastic potential, i.e. that the potential

$$\int_{V} W(\boldsymbol{\varepsilon}(\boldsymbol{u})) \,\mathrm{d}V - \int_{S} \boldsymbol{T} \cdot \boldsymbol{u} \,\mathrm{d}S \tag{7.11}$$

reaches its minimum possible value. Let us now assume another (constant) displacement field  $u^{tr}$ . The first term in Eq. (7.11) depends only on strain associated with the displacement field. Strain is given by partial derivatives of individual components of the displacement field and thus an additional constant term does not effect the resulting strain field

$$\boldsymbol{\varepsilon}(\boldsymbol{u}) \equiv \boldsymbol{\varepsilon}(\boldsymbol{u} + \boldsymbol{u}^{\mathrm{tr}}) \longrightarrow \int_{V} W(\boldsymbol{\varepsilon}(\boldsymbol{u})) \, \mathrm{d}V = \int_{V} W(\boldsymbol{\varepsilon}(\boldsymbol{u} + \boldsymbol{u}^{\mathrm{tr}})) \, \mathrm{d}V.$$
(7.12)

When the applied stress is uniform over the volume of a specimen, the second term in Eq. (7.11) can be converted to

$$\int_{S} \boldsymbol{T} \cdot (\boldsymbol{u} + \boldsymbol{u}^{\mathrm{tr}}) \,\mathrm{d}S = \int_{S} \boldsymbol{T} \cdot \boldsymbol{u} \,\mathrm{d}S + \int_{S} \boldsymbol{T} \cdot \boldsymbol{u}^{\mathrm{tr}} \,\mathrm{d}S \,.$$
(7.13)

Recalling the relation between stress  $\sigma$  and surface tractions T, the second term in Eq. (7.13) further simplifies to

$$\int_{S} \boldsymbol{T} \cdot \boldsymbol{u}^{\mathrm{tr}} \,\mathrm{d}S = \int_{S} \sigma_{ij} u_{j}^{\mathrm{tr}} \nu_{i} \,\mathrm{d}S = u_{j}^{\mathrm{tr}} \int_{S} \sigma_{ij} \nu_{i} \,\mathrm{d}S = 0\,,$$
(7.14)

where  $\nu$  represents the outer normal to the surface. The last integral in Eq. (7.14) is zero due to the equilibrium conditions.

Altogether we obtain

$$\int_{V} W(\boldsymbol{\varepsilon}(\boldsymbol{u})) \, \mathrm{d}V - \int_{S} \boldsymbol{T} \cdot \boldsymbol{u} \, \mathrm{d}S = \int_{V} W(\boldsymbol{\varepsilon}(\boldsymbol{u} + \boldsymbol{u}^{\mathrm{tr}})) \, \mathrm{d}V - \int_{S} \boldsymbol{T} \cdot (\boldsymbol{u} + \boldsymbol{u}^{\mathrm{tr}}) \, \mathrm{d}S.$$
(7.15)

The last equation means that a displacement field composed of a superimposed constant displacement and the displacement field that minimizes the elastic potential results in the same (minimum) value of the potential. Therefore, the global minimum of the elastic potential in terms of displacement is unique except for adding a constant displacement field. The constant displacement field  $u^{tr}$  constitutes a macroscopic translation of the whole specimen in the direction given by  $u^{tr}$  and thus does not contribute to the deformation of the elastic body. We are interested in stress redistributions that are proportional to strain and thus they are not affected by a possible additional displacement term connected with the translation of the entire specimen.

# 7.2 Comparision of calculated and experimental data

Although the microstructural models presented in preceding sections are oversimplified with respect to real microstructures, it is interesting to compare the numerical results with TEM observations. The contribution  $E_{\rm int}$  to the total Gibbs free energy was described by Eq. (2.31). This contribution is related to the interaction of the precipitate coherency strain and the stress distributed in the microstructure prior to precipitation. The part  $\Delta G_{\rm chem}$  of the Gibbs free energy change related to the nucleation and growth of the precipitate was not addressed. Therefore, the numerical results are not decisive with respect to whether the presence of a precipitate in a particular location decreases or increases the overall energy of the system. The  $E_{\rm int}$  contribution only indicates which crystallographic variant would precipitate in the position assuming that  $\Delta G_{\rm chem}$  provides enough driving force for precipitation. The distribution of precipitates will appear but rather on which crystallographic variant would be preferred.

#### 7.2.1 Stress-free aging

The models based on the anisotropy of thermal expansion may have a potential to explain the distribution of precipitates in specimens aged without applied stress. The obtained results (Figs. 5.2 and 5.4) suggest that the relevant stress redistribution exists only in grain boundary regions. Therefore, the preferential precipitation of crystallographic variants can be expected in the vicinity of grain boundaries. However, systems (like NiTi) with cubic crystal lattice have always isotropic tensor of thermal expansion coefficients and thus there is no stress redistribution associated with the thermal expansion.

The TEM micrograph in Fig. 7.1 documents a grain boundary region in the specimen which was aged without external stress. Since the precipitates are only observed near to the grain boundary one can argue that this heterogeneous precipitation results due to the stress redistribution. Nevertheless, this interpretation suffers from several weaknesses: (i) The results of the stress redistribution analysis do not suggest that the precipitates would occur only in grain boundary regions instead they predict a selection of crystallographic variants there. (ii) A closer examination of the TEM micrograph does not confirm any variant selection. All variants observed near to the grain boundary in Fig. 7.1 are distributed with a similar volume fraction. (iii) As it has already been pointed out, the models of thermal expansion are not applicable for the NiTi system.



FIGURE 7.1: A TEM micrograph of NiTi microstructure after stress-free aging. The precipitates are observed only in grain boundary regions but no variant preferential precipitation can be deduced – all crystallographic variants are distributed with similar volume fraction.

A more plausible reason for the documented heterogeneous precipitation has been suggested recently by KHALIL-ALLAFI *et al.* (2002b) and FILIP and MAZANEC (2001). It is now well established fact that the specimens aged without applied stress exhibit heterogeneous  $Ni_4Ti_3$  precipitation when particles nucleate and grow preferentially near grain boundaries, at  $Ti_4Ni_2O$  oxide inclusions and at TiC carbide particles while there are regions in the grain interior that are free of precipitates. The new explanation of this phenomenon suggested by NISHIDA *et al.* (2003) underlines the importance of the furnace atmosphere used during the heat treatment of the alloy. Questions related to the precise determination of microstructural parameters resulting from different heat treatment procedures are currently addressed.

# 7.2.2 Stress assisted aging

Microstructures that were subjected to the externally applied stress during the aging treatment match more closely situations modelled in this work, namely cases analyzed in terms of the anisotropy of elastic constants. The microstructural models considered here, the 2D model of two semi-infinite grains, the 2D model of periodic two-grain pattern and the 3D model of periodic four-grain structure, yield a stress redistribution when subjected to an externally applied stress. These models unanimously predict the identical behaviour of the complementary crystallographic variants (variants with parallel but opposite orientation of the main particle disk axis). This conclusion cannot be directly proved by existing TEM data because the experimental separation of the complementary variants would require more sophisticated TEM techniques. However, this prediction seems quite reasonable for both opposite variants have, in fact, identical atomic structure and habit plane orientation in the B2 matrix. There is thus no reason why these variants should interact with the parent matrix differently.

The other conclusion supported by all models is that the grain interiors do not exhibit any strong bias as far as the interaction energy  $E_{int}$  is concerned. However, the 3D model *III* predicts almost the same distribution of the IED for all crystallographic variants inside the grains. Closer to the grain boundary the preference of some variants is observed. Depending on the model and on the position in the grain boundary region, one or two variants reach the lowest interaction energy. The grain boundaries themselves separate regions with a preference for one particular variant on one side that rapidly changes into the preference for another variant on the other side of the boudary. Therefore, the interaction energy right at the grain boundary is almost the same for all variants.

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The strength of the preference precipitation not only depends on the position in the microstructure but it also depends on the grain orientation with respect to the direction of the applied load. In the case of two semi-infinite grains, there is much smaller difference between energies of variants from groups  $G_1$  and  $G_2$  in the grain 1, which has a rather special orientation ( $\alpha = 0$ ) with respect to the applied load ( $\sigma^A \sim \sigma^A_{yy}$ ), as compared to the difference of the energies of precipitates from these two groups computed for the grain 2.

Figure 7.2 shows a part of grain boundary (GB) and adjacent regions in the specimen after aging for 1 hour under the applied stress of 8 MPa at temperature 500°C. The TEM micrograph illustrates clearly that the grain interiors do not exhibit any strong selection of varinats – all crystallographic variants are present with almost the same volume fraction. This result was discussed by BOJDA *et al.* (2005). These authors estimate a distance of about  $2 \mu m$  from the GB above which no pronounced selection of varinats is observed. In the region closer to the grain boundary in Fig. 7.2, two out of four possible pairs of complementary variants are strongly preferred. This experimental feature is in qualitative agreement with the results of calculations where mainly the regions close to the grain boundary are affected by the preferential precipitation of variants. Moreover, the TEM micrograph in Fig. 7.2 reveals a region of thickness about  $0.2 \,\mu$ m next to the GB where no precipitation occurs. This denuded zone cannot be predicted from our calculations. Here the "chemical term"  $\Delta G_{chem}$  of Gibbs free energy starts to play a significant role that was not included in the present modelling approach.



FIGURE 7.2: Detail of a TEM micrograph of NiTi microstructure after aging for 1 hour under the applied stress of 8 MPa at temperature 500°C. A preferential precipitation of two out of four complementary variant pairs is clearly seen in the grain boundary region. On the contrary, the grain interiors do not exhibit any strong selection of variants.

All the calculation were performed within the framework of the linear elasticity theory. It is thus no surprise that higher applied stress results in the self-similar but boosted redistribution of the stress. Therefore, the energy distribution is also boosted for higher applied stress. In the shape memory technology there is an interest related to the width of the grain boundary region affected by the selective precipitation of  $Ni_4Ti_3$  variants. The extent of the selective precipitation influences the B2 - R - B'19 transformation path and may thus well govern the characteristics of the shape memory effects. In this respect, results of the calculations provide an important information on the size of grain boundary regions in which selective variant precipitation occurs. When we set a criterion requiring that a particular crystallographic variant nucleates and grows in a particular location only when  $E_{int}$  is lower then a threshold  $E_{min}$ , then the higher applied stress

causes widening of the region where the selection takes place. This result is again in qualitative agreement with the experimental data presented by BOJDA *et al.* (2005). According to the data tabulated by BOJDA *et al.* (2005) the affected region for the 20 MPa aging is approximately  $4.5 \,\mu\text{m}$  which is about 2.25-times bigger then for the case when the aging was assisted by the applied stress of 8 MPa. Our calculations within the framework of the linear elasticity theory predict that for 20 MPa the affected area should be about 2.5-times bigger then for 8 MPa. This is in a surprisingly good agreement with the experimental data.

In passing we can conclude, that the results obtained in the present work qualitatively agree with the TEM observations of real microstructres performed after the stress-assisted aging of the NiTi shape memory alloy. Therefore, the suggested mechanisms of stress redistribution and the subsequent precipitate–stress field interactions seem to describe the processes in microstructure in a rather satisfactory way.

# 7.3 Self-stress of precipitates

Results obtained by ESHELBY (1961), LOVE (1954), KELLOG (1929) and MACMILLAN (1958) were presented in the theoretical overview in the chapter 2. These authors derived an explicit formulas for deformation due to an elastic inclusion inserted into the elastic matrix. There are at least two reasons why the analytical formulas are not convenient for our calculations. First, the expression in Eq. (2.25) is truly complicated to investigate the stress field outside the precipitate. Second, Eq. (2.25) assumes that all the three axes of the ellipsoidal inclusion possess different lengths. In our case, we have a lenticular shaped precipitate with a = b > c and this considerably complicates the evaluation of the potential according to Eq. (2.25).

Fortunately, far from the inclusion the potentials  $\varphi(\mathbf{r})$  and  $\psi(\mathbf{r})$  can be approximated by  $V_p/r$  and  $V_pr$ , respectively. Here,  $V_p$  is the volume of precipitate. Inserting these potentials into Eq. (2.22) yields the displacement field. A standard procedure then provides all components of the stress field. Using the "far-from-inclusion" approximation of the potentials we found out that all stress components are negligibly small from the distance of about  $5\rho$  where  $\rho$  is the linear size of the inclusion. This means that the self-stress of precipitates is important only in a relatively small region near the precipitate. However, just a brief examination of the TEM micrograph in Fig. 7.2 suggests that even so small region close to a precipitate still contains neighbouring particles. Therefore, a more precise examination of the variant precipitation would give an account of the stress fields associated with the particles distributed in a vicinity of the investigated location. In this sense, the precipitate–precipitate interactions could play an important role in the variant selection.

# 7.4 Minimal interaction energy versus maximum/minimum normal stress

An interesting outcome of the numerical analysis performed in this work is an explicit prediction which variant yields the minimum interaction energy for a given location in the microstructure. The interaction energy term can be expressed in the coordinate frame of a precipitate. Equation (6.2) reveals that the interaction energy is composed of three terms and it has a form

$$E_{\rm int} = -V_p (\sigma_{xx} \varepsilon_{xx}^T + \sigma_{yy} \varepsilon_{yy}^T + \sigma_{zz} \varepsilon_{zz}^T) \,. \tag{7.16}$$

The first two terms are products of the stress and particle misfit strain components acting in the habit plane of the precipitate. The third term has a similar structure except it is constructed of components normal to the precipitate habit plane. Since all the stress components are of the same order and because the normal component of the misfit strain  $\varepsilon^T$  is about ten-times bigger than the two in-plane components, the interaction between the normal component of the stress and the normal component of the misfit strain  $\varepsilon^T$  represents the main contribution to the interaction energy.

Due to the fact that the normal component of misfit strain is negative and due to the structure of the interaction energy term (see Eq. (7.16)), the minimum of the total interaction energy is attained either for the lowest normal tensile stress or the highest normal compression stress. In principle, all the models considered in this work showed a tendency to follow this criterion. As an example we can discuss the results obtained with the 3D model of a planar four-grain periodic microstructure (model *III*). Figure 7.3(a) shows the distribution of variants based on the criterion of the lowest IED as calculated for positions at the upper surface of the specimen. Figure 7.3(b) shows the similar distribution of variants now based on the criterion of the lowest value of a normal tensile stress component. We can conclude that in most investigated locations these two variant distributions correspond to each other. In regions where the energy-based and normal stress-based distributions differ, the habit plane components of the stress tensor dominate the particle–stress field interaction and their contributions to the interaction energy outnumber the contribution due to the normal stress.



FIGURE 7.3: Comparison of particle distributions of precipitates calculated for locations at the upper surface of one four-grain cell (model III) using the criterion of (a) the lowest interaction energy and (b) the lowest stress component normal to the habit plane of the precipitate.

Therefore, the selection according to the lowest normal stress component can be only used as a rough criterion. Moreover, the estimate of the normal stress components needs the same computational effort as the evaluation of the interaction energies for all particle variants.

# 8 Summary and conclusions

Shape memory alloys are rapidly developing perspective materials. The wide range of applications requires precise knowledge of microstructures and processes governing microstructural changes of SMAs. The most often used SMAs are those based on the NiTi intermetallic system and thus the input in the calculations relies on the NiTi material data. The presented work has focused on the origin of inhomogeneous distributions of precipitates  $Ni_4Ti_3$  in NiTi microstructures since this feature essentially influences the martensitic transformations and shape memory characteristics.

Two mechanisms that can give a rise to stress redistributions throughout the microstructures were selected. The first mechanism deals with the anisotropy of thermal expansion coefficients. This type of anisotropy results in different rate of shrinkage between mutually misorientated neighbouring grains when the alloy is cooled from the annealing temperature to the room temperature. The second mechanism addresses the anisotropy of elastic constants and operates when a specimen is aged under the assistance of the externally applied stress. Because the parent NiTi B2 phase has cubic crystal lattice the second mechanism is particularly relevant.

The microstructure was described by three models with increasing complexity but simultaneously with increasing similarity to the real systems. The simplest model is 2D and consists of two semi-infinite grains. The next model is also 2D and represents infinite layer composed of a two-grain periodic pattern of a finite height. The most complex model is 3D and considers a layer with periodic pattern of four hexagonal grains.

The methods used to calculate stress redistributions are based on the linear elasticity theory, a minimisation of the elastic potential energy and Eshleby's concept of elastic inclusions within an elastic continuum. The finite element method was employed for the numerical minimisation of the elastic potential.

All models considered in this work predicted in stress redistributions. The numerical results support the conclusion that the stress is redistributed namely in the grain boundary regions whereas the interiors of grains are influenced only little. The numerical results also suggest that the hydrostatic components of the stress tensor are about one order of magnitude larger than the shear components. The models further predict that the higher applied stress results in larger displacement and that the stress redistributions for the same model of microstructure but subjected to different external stresses are self-similar.

The interaction energy between precipitate misfit strain and the stress state in the parent matrix prior to the precipitate formation was calculated. Generally, the grain boundary regions show a tendency for the preferential precipitation of  $Ni_4Ti_3$  crystallographic variants. In both 2D models the eight different crystallographic variants divide into two groups. The precipitate variants within each group exhibit the same interaction energy in a given location in the microstructure. For the 3D model the eight crystallographic variants form four equi-energy pairs each composed of two complementary variants. These results are in a qualitative agreement with the published experimental observations. The grain boundary regions are the locations where pronounced changes in the preferential precipitation of variants occur. The interaction energy calculations in combination with the energy threshold criterion show that higher applied stress causes widening of the region along the grain boundary affected by the heterogeneous precipitation. This result is in a good qualitative agreement with the experimental data.

The results obtained in this work support the suggested mechanisms of a heterogeneous variant precipitation in specimens during the stress assisted aging. Although the used models of microstructures are oversimplified when compared to the real systems they yield qualitative results that are in agreement with experimental findings. Objectives of this work have been fully reached. A further work should deepen the qualitative predictions and their correspondence to TEM experimental observations. The extensions should namely concentrate on (i) large scale models that better correspond to real microstructures, (ii) the self-stress of precipitates that may result in some autocatalytic precipitation processes and (iii) the nucleation and growth of the precipitate (the term  $\Delta G_{\text{chem}}$  of the Gibbs free energy).

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