In Situ Investigation of the Evolution of Lattice Strain and Stresses in Austenite and Martensite During Quenching and Tempering of Steel

Villa, M.; Niessen, F.; Somers, M. A. J.

Published in:
Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science

Link to article, DOI:
[10.1007/s11661-017-4387-0](https://doi.org/10.1007/s11661-017-4387-0)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Villa, M., Niessen, F., & Somers, M. A. J. (2018). In Situ Investigation of the Evolution of Lattice Strain and Stresses in Austenite and Martensite During Quenching and Tempering of Steel. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, 49(1), 28–40. <https://doi.org/10.1007/s11661-017-4387-0>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

In situ investigation of the evolution of lattice strain and stresses in austenite and martensite during quenching and tempering of steel

M. Villa^{1,a}, F. Niessen^{2,b}, M.A.J. Somers^{1,c}

¹Technical University of Denmark, Department of Mechanical Engineering, 2800 Kgs. Lyngby, Denmark

²Technical University of Denmark, Danish Hydrocarbon Research and Technology Centre, 2800 Kgs. Lyngby, Denmark

[a](mailto:matv@mek.dtu.dk)matv@mek.dtu.dk; * [b](mailto:frannie@dtu.dk)frannie@dtu.dk; [c](mailto:somers@mek.dtu.dk)somers@mek.dtu.dk

Abstract

Energy dispersive synchrotron X-ray diffraction was applied to investigate in situ the evolution of lattice strains and stresses in austenite and martensite during quenching and tempering of a soft martensitic stainless steel. In one experiment, lattice strains in austenite and martensite were measured *in situ* in the direction perpendicular to the sample surface during an austenitization, quenching and tempering cycle. In a second experiment, the $\sin^2\psi$ method was applied in situ during the austenite-to-martensite transformation to distinguish between macro- and phase specific micro-stresses and to follow the evolution of these stresses during transformation. Martensite formation evokes compressive stress in austenite that is balanced by tensile stress in martensite. Tempering to 748 K (475 °C) leads to partial relaxation of these stresses. Additionally, data reveals that (elastic) lattice strain in austenite is not hydrostatic but *hkl* dependent, which is ascribed to plastic deformation of this phase during martensite formation and is considered responsible for anomalous behavior of the 200_γ reflection.

Keywords: Martensite; Synchrotron X-ray diffraction (XRD); Residual stresses; Tempering; Steel

* corresponding author

1. Introduction

Modern steels are multi-phase materials. The response of a multi-phase material to an applied load is a function of the volume fraction, distribution, orientation and shape of the phases present [1,2], as well as of the presence and magnitude of internal stresses, which remain after processing [3]. On loading, the applied external forces are superimposed on the internal stresses [1,2].

Internal stresses can be classified by the length scale over which they equilibrate [1,4,5]. Macro-stresses (type I) act over large distances and are an average over all phases and grains present; micro-stresses vary from grain to grain and from phase to phase (type II) or within a single grain/phase (type III). Internal stress can arise as a consequence of inhomogeneous elastic and thermal properties [2,3], inhomogeneous plastic strain [2], or a phase transition occurring in association with a shape change [5].

The austenite (γ)-to-martensite (α') transformation in steel is associated with a shape change, the so called transformation strain, which consists of a volume expansion of approx. 3% and a shear [6-9]. Additionally, austenite and martensite have different thermal and elastic properties. Thus, martensite formation is associated with the development of residual stress in the material, with contributions from the transformation itself as well as thermal mismatch [3,9].

The development of macro-stresses during quenching of steel parts is a well described subject [3-5,9,10]. Similarly, the generation of lattice defects (micro-stresses of type III) in austenite during martensite formation has been investigated in details [6-8]. On the other hand, the evolution of micro-stresses of type II is controversial: martensite formation has been reported to invoke compressive stress [11-22], tensile stress [22,23], or no stress [24-27] in austenite, while information about the stress state in the developing martensite is incomplete. The evolution of micro-stresses of type II during martensite formation is of fundamental interest because these stresses affect the transformation kinetics [28].

In the absence of macro-stresses (type I), the grain- or phase-specific micro-stresses (type II) can be evaluated from the lattice strain as experimentally determined by X-ray diffraction (XRD) [1,4] by measuring in the direction i the lattice spacing, $d_i^{hkl\varphi}$, for a given family of lattice planes, $\{hkl\}$, in the crystalline phase φ . Comparison of the measured lattice spacing with a reference lattice spacing, $d_{ref}^{hkl\varphi}$, provides the lattice strain, $\varepsilon_i^{hkl\varphi}$:

$$\varepsilon_i^{hkl\varphi} = \frac{d_i^{hkl\varphi} - d_{ref}^{hkl\varphi}}{d_{ref}^{hkl\varphi}} \quad (1)$$

55 The hkl -specific strain $\varepsilon_i^{hkl\varphi}$ represents the average lattice strain, $\langle \varepsilon^{hkl\varphi} \rangle$, for a given
 56 family of lattice planes $\{hkl\}$ in the probed volume and can be converted into an average
 57 (hydrostatic) stress, $\langle \sigma^\varphi \rangle$, applying the appropriate X-ray elastic constants, XECs [4]:

$$58 \quad \langle \varepsilon^{hkl\varphi} \rangle = \left(3 \cdot S_1^{hkl\varphi} + \frac{1}{2} S_2^{hkl\varphi} \right) \cdot \langle \sigma^\varphi \rangle \quad (2)$$

59 where $S_1^{hkl\varphi}$ and $\frac{1}{2} S_2^{hkl\varphi}$ are the XECs of phase φ for probing the family of lattice planes $\{hkl\}$.

60 Experimental XRD work on the evolution of lattice strain and phase-specific stresses in steel during
 61 martensite formation was firstly reported in 1957 [11]. It was suggested that a low content of
 62 retained austenite is in a state of compressive stress. In the same year, comparison of the lattice
 63 parameter of Fe-30%Ni austenite in as-received condition and after approx. 80 % transformation by
 64 sub-zero Celsius treatment did not show a significant change [24]. Therefore, it was concluded that
 65 martensite formation did not evoke micro-stresses of type II in austenite.

66 More than 10 years later [12], Ridley et al. reproduced the results in Ref. [11] and suggested that
 67 data could be interpreted in terms of a state of compression in austenite caused by martensite
 68 formation. Alternatively, data could indicate depletion of austenite in C during quenching and room
 69 temperature storage of the material. Nevertheless, in a study published 1 year earlier, Yeshov and
 70 Oslon followed a^γ during quenching of several steel samples by probing $\{200\}_\gamma$ lattice planes and
 71 showed the build-up of a tensile state of stress in austenite at the beginning of the transformation,
 72 followed by relaxation of these stresses at a later stage [23]. Remarkably, later work by the same
 73 authors [22] showed that martensite formation evokes a state of tensile lattice strain in austenite for
 74 probing $\{200\}_\gamma$, while probing $\{111\}_\gamma$ showed compression. These results seem irreconcilable.

75 However, it should be realized that for f.c.c. metals lattice strains depend non-linearly on the
 76 applied load if strained into the plastic region [29-32]. This non-linear behavior is hkl dependent
 77 and yields anisotropic strains that are retained upon unloading. The $[200]_\gamma$ direction is elastically
 78 the most compliant and plastically the softest and therefore has the most pronounced non-linear
 79 behavior. Consequently, the 200_γ reflection is inappropriate for the evaluation of the average state
 80 of residual stress in f.c.c. metals subjected to plastic deformation. According to Refs. [29-31],
 81 probing 311_γ , or averaging lattice strains over several reflections, is most appropriate. Later,
 82 reconsidering the results in Ref. [30], it was suggested that 111_γ or 422_γ are the most appropriate
 83 reflections [32]. Evidently, an incorrect choice of the reflections probed for the evaluation of the
 84 state of stress in austenite may have played a role in the discrepancy between data.

85 The first serious attempt to solve the controversy appeared in 1974, when Golovchiner determined
 86 *in situ* the evolution of lattice strain in austenite versus the fraction transformed in a large number of

ferrous alloys [13]. These alloys were fully austenitic at room temperature and largely transformed to martensite during cooling to 93 K (-180 °C). Determination of a^γ was performed based on the 311_γ reflection. In all investigated samples, compression was observed in austenite after martensite formation for transformed fractions beyond 10-60 %, depending on the chemical composition of the alloy.

In 1980, the focus firstly included the state of stress in martensite [14]. It was claimed that martensite formation evoked compressive stresses in both austenite and martensite. Nevertheless, this claim violates the condition that, in absence of external forces, balancing of forces should be obtained for a finite matrix [3-5]:

$$\sum_{\varphi} f^{\varphi} \cdot \langle \sigma^{\varphi} \rangle = 0 \quad (3)$$

with f^{φ} volume fraction of phase φ . Hence:

$$f^{\alpha'} \cdot \langle \sigma^{\alpha'} \rangle = -f^{\gamma} \cdot \langle \sigma^{\gamma} \rangle \quad (4)$$

with $f^{\alpha'}$ and f^{γ} the volume fraction of martensite and austenite, respectively. Thus, compression in austenite should be balanced by tension in martensite. It is important to realize that the lattice strains determined in Ref. [14], departed from the assumption that stresses were null at the beginning of the transformation. This is unlikely for the minority phase, martensite (cf. Eq. 4), suggesting that the analysis may have been faulty. Additionally, data may have been affected by the presence of macro-stresses, implying that Eq. 2 could not be used. Unfortunately, similar arguments apply for all references cited above.

The need for more thorough stress analysis was firstly recognized in 1990 [15]. XRD was applied at room temperature to determine a_{γ} (based on 220_γ) in Fe-C and Fe-N thin foils. Data indicated that retained austenite experienced compressive strain in the direction perpendicular to the sample surface. To convert strain into stress, measurements were performed in various directions. Because of the shallow penetration depth of laboratory X-rays, all components of stress in martensite in the direction perpendicular to the sample surface, $\sigma_{\perp}^{\alpha'}$, were assumed equal to zero. The principal stress component parallel to the sample surface, $\sigma_{\parallel}^{\alpha'}$ was evaluated applying the $\sin^2\psi$ method (cf. Ref. [4]). Data revealed that stresses in martensite were negligible within the probed volume. Since a negligible state of stress in the majority phase (i.e. martensite) does not imply that the balancing stress in the minority phase (i.e. austenite) is negligible, (cf. Eq.4) compressive strain in austenite was interpreted in terms of a state of compressive stress in this phase.

The limitations associated with the shallow penetration/information depth of laboratory X-rays could be overcome by applying Neutron diffraction [25,26] or synchrotron XRD [16-20,27].

119 In Refs. [25,26], a^γ was measured in homogeneous Fe-Ni-C austenite as well as after partial
 120 transformation of the austenite into martensite. Data indicated that martensite formation did not
 121 affect a^γ . Similarly, San. Martin et al. followed the formation of martensite in Fe-Cr-Ni-Mo
 122 maraging steel up to 40 % fraction transformed and showed that the averaged value of a^γ does not
 123 change with $f^{\alpha'}$ [27]. Conversely, Villa et al. showed that martensite formation during sub-zero
 124 Celsius treatment of steel induces compressive lattice strain in austenite [16-18]. The application of
 125 the $\sin^2\psi$ method ex situ indicated that lattice strain was caused by compressive stress in austenite,
 126 which was hydrostatic within the probed volume. Similarly, Epp showed that compressive
 127 hydrostatic stress build up in austenite during quenching of high C steel [19,20]. Evidently,
 128 diffraction experiments at large scale facilities did not provide a unanimous answer.

129 A last attempt to clarify the picture was presented in Ref. [21]. Laboratory XRD was applied to
 130 measure a^γ before and after martensite formation in a Fe-Ni alloy and data was complemented with
 131 measurement of a^γ after tempering to 523 K (250°C). Tempering is expected, at least partially, to
 132 lead to relaxation of internal stresses. Data showed that compressive lattice strain develops in
 133 austenite during martensite formation for $f^{\alpha'} > 75\%$, and that this strain is largely annihilated during
 134 tempering. No strain was observed in martensite. Compressive strain in austenite was interpreted in
 135 terms of hydrostatic compressive stress in this phase.

136 Summarizing, no consistent picture exists of the evolution of stress in austenite and martensite
 137 during martensite formation in steel. Careful evaluation of the discussed literature reveals that
 138 during martensite formation a state of compressive stress builds-up in austenite. The compression is
 139 observed by XRD only after a threshold fraction of austenite has transformed to martensite and
 140 appears hydrostatic when averaged over the probed volume. The internal stress in austenite is
 141 interpreted as micro-stress of type II, but this hypothesis has never been verified with the
 142 simultaneous observation of balancing tensile micro-stress of type II in martensite. Tempering may
 143 promote relaxation of stresses and give indication on their actual presence. In the present work,
 144 experiments were designed to investigate the evolution of phase specific stresses in both austenite
 145 and martensite during quenching and tempering of steel.

146 **2. Material and methods**

147 The material selected for investigation was commercial EN 1.4418 steel (Table 1), which is a soft
 148 martensitic stainless steel grade, with a low fraction of interstitials. Martensite in this alloy is body
 149 centered cubic b.c.c. and has lath morphology [33,34]. The martensite start temperature, M_s , equals
 150 408 K (135 °C) [34] and the Curie temperature, T_C , of martensite equals 898 K (625 °C) [34].

Two Ø10 mm x 0.15 mm disks, labelled sample 1 and sample 2, respectively, were prepared for synchrotron XRD investigation. Preparation comprised austenitization at 1223 K (950 °C) for 10 min in a continuous flow of Ar gas, followed by cooling to room temperature at an average rate of approx. 1 K s⁻¹. Thereafter, samples were ground and electro-polished for 5 s at 40 V in Struers A-2 electrolyte. The condition of the material after preparation is labelled “as normalized”.

Energy-dispersive XRD investigation was performed in situ at the EDDI beamline of the BESSY II synchrotron facility [35]. In Energy dispersive XRD, the investigation is carried out using a beam of white X-rays at a fixed diffraction angle, 2θ , and diffraction for crystallographic planes, $\{hkl\}$, will occur at a photon energy, E^{hkl} . The energy position, E^{hkl} , of the diffraction lines in the energy spectrum is inversely proportional to the interplanar spacing, d^{hkl} [36]:

$$E^{hkl} = \frac{hc}{2 \sin \theta} \cdot \frac{1}{d^{hkl}} : \quad (5)$$

with h Planck’s constant and c the speed of light. The average information depth for each diffraction line is a function of its energy, and of the diffraction geometry applied [37].

In the present investigation, the acquisition time was set to 60 s per spectrogram (i.e. diffractogram) and the experiments were conducted with a 0.5 x 0.5 mm² slit configuration on the primary side applying the diffraction geometry $\theta - 2\theta = 7^\circ - 14^\circ$. The equatorial slit aperture was set to 0.03 mm. Two configurations were applied: in the first, the scattering vector was kept perpendicular to the sample surface; in the second, the angle between the scattering vector and the surface normal, ψ , was varied by tilting the sample around an axis parallel to the plane through incident and diffracted beam ($\sin^2\psi$ method). The experimental setup is presented in Fig. 1.

Diffraction lines were fitted with pseudo-Voigt profile functions. Each reflection was analyzed independently to account for anisotropic lattice strain. A gold reference standard was used for calibration of the absolute value of the lattice parameter. The quantification of f^γ and $f^{\alpha'}$ was based on a direct comparison of the integrated intensity of the diffraction peaks of austenite and martensite [38]. Additional details were given in Ref. [33]. The analysis included the 200_γ , 220_γ , 311_γ and 222_γ reflections of austenite and the $200_{\alpha'}$, $211_{\alpha'}$, $220_{\alpha'}$ and $321_{\alpha'}$ reflections of martensite. The $111_\gamma/110_{\alpha'}$ couple was excluded because these reflections largely overlap and because these line profiles correspond to the lowest information depth among all reflections and, thus, are most sensitive for surface effects.

steps of 15 K maintaining an overall average cooling rate of 0.017 K s^{-1} and ψ , was varied from 0° to 72° in steps of 8° at each investigation temperature (in situ $\sin^2\psi$ method); sample 2 was continuously cooled at a rate of 0.017 K s^{-1} and ψ was maintained equal to 0° . Additionally, the $\sin^2\psi$ method was applied ex situ at the beginning of the thermal cycle and at the end of the investigation.

3. Results and interpretation

3.1. Evaluation of lattice strains and stress analysis

The calculation of lattice strains in austenite, $\varepsilon_{\psi}^{hkl\gamma}$, and martensite, $\varepsilon_{\psi}^{hkl\alpha'}$, from Eq.1 requires that the strain-free lattice parameter of austenite, a_{ref}^{γ} , and of martensite, $a_{ref}^{\alpha'}$, are known as a function of temperature.

The value of a_{ref}^{γ} was obtained by extrapolating a second order polynomial fitted through $a_{\perp}^{\gamma}$ (averaged over all hkl) as measured during cooling in the temperature interval 418-1193 K (145-920 $^\circ\text{C}$), where austenite is the only phase present because $T > M_s$. In particular, $\lambda^{\gamma} = 1.285 \cdot 10^{-5} + 1.052 \cdot 10^{-8} T - 4.677 \cdot 10^{-12} T^2$, with T temperature expressed in K, which is consistent with literature data for austenitic stainless steels in the same temperature interval [45].

A similar experimental condition for $a_{ref}^{\alpha'}$, where martensite is the only phase present in the sample, is not available. Therefore, the value of $a_{ref}^{\alpha'}$ at 298 K (25 $^\circ\text{C}$) was calculated under the condition of balancing micro-stresses of type II (cf. Eq.4) at the beginning of investigation. The value of $a_{ref}^{\alpha'}$ for the temperature interval 298-898 K (25-625 $^\circ\text{C}$) was calculated from $a_{ref}^{\alpha'}$ at 298 K (25 $^\circ\text{C}$) and the coefficient of thermal expansion of strain-free martensite, $\lambda^{\alpha'} = 1.266 \cdot 10^{-5} \text{ K}^{-1}$, as evaluated by fitting $a_{\perp}^{\alpha'}$ as measured during cooling tempered martensite from 748 K (475 $^\circ\text{C}$) to room temperature. This is consistent with literature data for martensitic stainless steel in the same temperature interval [45]. For $T > 898 \text{ K}$ (625 $^\circ\text{C}$), martensite is paramagnetic and $\lambda^{\alpha'}$ evaluated for ferromagnetic martensite does no longer apply [45]. This is beyond the scope of the present work.

Lattice strains were converted into stresses. During all thermal steps where $\psi = 0$, the average stresses in the phases, $\langle \sigma^{\varphi} \rangle$, could be determined only under the assumption that the samples are free from macro-stresses (cf. Eq. 2). Unfortunately, this assumption does not apply in the present case, as will be shown in section 3.3.

In a thin sample, macro-stresses can be considered relaxed, and thus equal to zero, in the direction normal to the sample surface, $\perp$. In the direction parallel to the sample surface, $\parallel$, macro-stresses

balance over the sample cross section, but are not necessarily balanced within the volume of material probed by XRD, and can thus deviate from zero.

To account for the possible presence of macro-stresses, lattice strains were measured in sample 1 at several ψ angles at fixed temperature. This procedure was applied only to the part of the thermal cycle of most interest for the current investigation. Stresses were determined under the assumption of rotational symmetry within the plane of the sample and the stress components $\sigma_{\parallel}^{\varphi} - \sigma_{\perp}^{\varphi}$ and $\sigma_{\perp}^{\varphi}$ were calculated applying the $\sin^2\psi$ method. Assuming that the stress is rotationally symmetric, the lattice strain is given by [4]:

$$\varepsilon_{\psi}^{hkl\varphi} = S_1^{hkl\varphi} [2 \cdot \sigma_{\parallel}^{\varphi} + \sigma_{\perp}^{\varphi}] + \frac{1}{2} S_2^{hkl\varphi} \cdot \sigma_{\perp}^{\varphi} + \frac{1}{2} S_2^{hkl\varphi} [\sigma_{\parallel}^{\varphi} - \sigma_{\perp}^{\varphi}] \cdot \sin^2\psi \quad (6)$$

The XEC $S_1^{hkl\varphi}$ and $\frac{1}{2} S_2^{hkl\varphi}$ (Table 2) were calculated from the single crystal elastic constants for ferrite [39] and austenite [40][†] applying the Eshelby/Kröner model for elastic grain interaction [41,42][‡] and the material is assumed free of texture.

For Energy Dispersive XRD, and under the assumption that macro-stresses in the $\perp$ direction are null, the slope of the dependence of lattice strain, $\varepsilon_{\psi}^{hkl\varphi}$, on $\sin^2\psi$ provides $\sigma_{\parallel}^{\varphi} - \sigma_{\perp}^{\varphi}$ while the intercept equals $S_1^{hkl\varphi} [2 \cdot \sigma_{\parallel}^{\varphi} + \sigma_{\perp}^{\varphi}] + \frac{1}{2} S_2^{hkl\varphi} \cdot \sigma_{\perp}^{\varphi}$. The equations for slope and intercept provide the set of equations to assess the individual values of $\sigma_{\parallel}^{\varphi}$ and $\sigma_{\perp}^{\varphi}$, provided that the XECs are known. The macro-stress $\sigma_{\parallel}^{\varphi} - \sigma_{\perp}^{\varphi}$ (of type I) in phase φ corresponds to an hkl -dependent depth, ζ^{hkl} , and $\sigma_{\perp}^{\varphi}$ represents the average micro-stresses of type II in φ . From Eq.3 it is obtained:

$$\sum_{\phi} f^{\varphi} \cdot \langle \sigma_{\perp}^{\varphi} \rangle = 0 \quad (7)$$

where $\langle \sigma_{\perp}^{\varphi} \rangle$ represents the stress averaged over all investigated hkl for phase φ .[§]

In the present case, ζ^{hkl} can be estimated using the absorption coefficient of Fe for the appropriate energy and equals to approx. 4 μm , 5 μm , 14 μm , 22 μm and 25 μm for the 111_{γ} , 200_{γ} , 220_{γ} , 311_{γ} and 222_{γ} reflections of austenite, respectively, and approx. 4 μm , 10 μm , 18 μm , 27 μm and 55 μm for the $110_{\alpha'}$, $200_{\alpha'}$, $211_{\alpha'}$, $220_{\alpha'}$ and $321_{\alpha'}$ reflections of martensite, respectively.

[†] The bulk elastic modulus of austenite, B^{γ} , and of martensite, B^{α} calculated from Refs. [51,52] are 184 GPa and 167 GPa, respectively. From Ref. [56], for Fe-15%Cr-5%Ni $B^{\gamma} = 164$ GPa and is not significantly affected by the presence of interstitials.[57] This indicates that Ref. [52] most likely overestimated the stiffness of austenite. No accurate information is available to evaluate the value of B^{α} from Ref. [51].

[‡] It should be noted that the Eshelby/Kröner model for the present case is an approximation, as it assumes elastic interaction of crystals with identical elastic constants, while the present material is two phase with different elastic constants for the two phases.

[§] The multiplicity of the various hkl was not taken into account, implying that all reflections was equally weighted.

3.2. Evolution of phase fraction and lattice strain during thermal cycling

3.2.1. Phase fraction

The evolution of the fraction of martensite as measured for diffraction vector perpendicular to the surface, $f_{\perp}^{\alpha'}$, is shown in Fig. 3a versus temperature, T. Data plotted in Fig. 3a represents the average value over the two investigated samples and is only representative of the fraction of martensite in the material, $f^{\alpha'}$, for the (unlikely) assumption of random grain orientation [46].

At the beginning of the investigation $f_{\perp}^{\alpha'}$ is 0.93 (Fig. 3a). During heating, reverse austenite formation starts at about 823-848 K (550-575 °C). Austenitization proceeds in two steps and is completed just below 1193 K (920 °C). Two-step kinetics of reverse austenite formation in soft martensitic stainless steel is discussed in detail elsewhere [33,34,47]

On cooling from the austenitization temperature, martensite is firstly observed at 703 K (330 °C), approx. 200 K above M_s , by appearance of the $110_{\alpha'}$ line profile, which is probed at the lowest average information depth of all hkl s. On continued cooling, the intensity of $110_{\alpha'}$ increases and is accompanied by $200_{\alpha'}$, $211_{\alpha'}$, $220_{\alpha'}$ and $321_{\alpha'}$ in the order of mentioning, consistent with a gradual increase of the information depth ζ^{hkl} . Evidently, martensite formation starts at 703 K (330 °C) in the near surface region and progresses in the depth direction on continued cooling. It has repeatedly been reported that the formation of lath martensite starts at the free surface at a temperature significantly higher than M_s [47-52]. The present results are fully consistent with these observations.

The martensite content $f_{\perp}^{\alpha'}$ exceeded 0.03 at about 403 K (130 °C), which is below M_s . Thereafter, on continued cooling, a large fraction of martensite formed within the temperature range 383-353 K (115-85 °C) followed by martensite formation at a progressively reduced rate. At 298 K (25 °C), about 93 % of the austenite had transformed into martensite, consistent with the starting condition.

Upon quenching, the material was tempered to 748 K (475 °C) without affecting the fraction of martensite in the sample.

Figure 3. a) Fraction of martensite evaluated in the direction normal to the sample surface $f_{\perp}^{\alpha'}$ plotted versus temperature T (values represent average values for sample 1 and sample 2; the error bars are the standard deviation); b) lattice parameter of austenite measured in the direction normal to the sample surface $a_{\perp}^{\gamma'}$ plotted versus temperature T ; c) lattice parameter of martensite measured in the direction normal to the sample surface $a_{\perp}^{\alpha'}$ plotted versus temperature T . The blue continuous lines in b) and c) represent the strain free lattice parameter of the phases a_{ref}^{ϕ} . The black continuous lines in b) and c) show the value of the lattice parameter of the phases a_{ref}^{ϕ} averaged over the probed reflections, not including $200_{\alpha'}$. In order to compare between the two data sets, 1 data point every 15 K is considered for sample 2 when cooled within the temperature range $298 \text{ K} < T < 448 \text{ K}$ ($25^{\circ}\text{C} < T < 175^{\circ}\text{C}$).

3.2.2. Lattice strains

The lattice parameters calculated from the lattice spacing for $\{hkl\}$ are given for austenite in Fig. 3b and for martensite in Fig. 3c. The evolutions of lattice strains in these phases are described separately below.

Austenite

At the beginning of the quenching cycle, a^γ was significantly smaller than a_{ref}^γ (given by the drawn blue line) and varies with the hkl probed, which indicates that austenite experiences anisotropic compressive lattice strain in the direction $\perp$.

On heating, a^γ expands at a (hkl -dependent) rate which deviates from the value expected from the thermal expansion coefficient λ_γ , indicating changes in lattice strain, $\varepsilon_\perp^{hkl\gamma}$. Compressive lattice strains $\varepsilon_\perp^{hkl\gamma}$ increase up to 523 K (250 °C), decrease in the temperature range 523-748 K (250-475 °C), where after they increase again up to 798 K (525 °C), and eventually are annihilated at about 848 K (575 °C), when the reverse austenite formation commences.

On cooling, $a^\gamma = a_{ref}^\gamma$ for $T \geq 418$ K (145 °C) (by definition), implying that $\varepsilon_\perp^{hkl\gamma} = 0$. Thereafter, for temperatures below M_s , $a^\gamma < a_{ref}^\gamma$, which indicates that martensite formation is accompanied by compressive lattice strain in austenite in the direction perpendicular to the surface. The observed lattice strain is largest at 298 K (25 °C) and depends on hkl : the largest $\varepsilon_\perp^{hkl\gamma}$ is observed for 220_γ and 222_γ , while $\varepsilon_\perp^{hkl\gamma}$ is negligible for 200_γ and for 311_γ it shows a value close to the average over hkl . This behaviour for the various hkl is analogous to the dependence on hkl for the starting condition.

On tempering, the evolution of $\varepsilon_\perp^{hkl\gamma}$ during heating to 748 K (475 °C) reflects the same trends as on heating the “as normalized” condition. On reaching 748 K (475 °C), about half the compressive lattice strain evoked in austenite during quenching has relaxed, assuming that no change in composition occurred. On cooling to 298 K (25 °C), no additional changes of $\varepsilon_\perp^{hkl\gamma}$ are observed. Data is largely consistent with recent work in the literature [53], and indicates that residual stresses in austenite are partially relaxed during tempering of martensitic stainless steel to 748 K (475 °C).

Martensite

At the beginning of the investigation, $a^{\alpha'} \approx a_{ref}^{\alpha'}$, which implies that $\varepsilon_\perp^{\alpha'} \approx 0$.

On heating, the measurement of $a^{\alpha'}$ shows four distinct regimes:

- for $T < 423$ K (150 °C), the rate of expansion of the unit cell of martensite is consistent with $\lambda_{\alpha'}$;
- for the temperature range 423-748 K (150-475 °C), $a^{\alpha'}$ expands at a rate that varies with hkl and in general is smaller than $\lambda_{\alpha'}$;
- for temperatures in the range 748-898 K (475-625 °C) a significant difference between $a^{\alpha'}$ and $a_{ref}^{\alpha'}$ yields a large deviation between the observed and predicted lattice parameter at 898 K (625 °C);
- at 898 K (625 °C), martensite becomes paramagnetic and $\lambda_{\alpha'}$ increases significantly.

On cooling, martensite reflections have sufficient intensity for a temperature of 403 K (130 °C), when approx. 5 % of the austenite has transformed. For fractions up to $f_{\perp}^{\alpha} \approx 0.2$, data scatters significantly. For martensite fractions beyond 0.2, the lattice strain in martensite varies significantly depending on the probed hkl . On average, $a_{\perp}^{hkl\alpha'} < a_{ref}^{\alpha'}$ and about constant over the whole transformation process.

During tempering, the evolution of $a_{\perp}^{\alpha'}$ on heating to 748 K (475 °C) is consistent with the data obtained on heating the sample “as normalized” and the lattice of martensite expands less than predicted based on $\lambda_{\alpha'}$ in the temperature interval 448-748 K (175-475 °C). This deviation is retained on subsequent cooling to 298 K (25 °C).

Data acquired during the two heating steps indicates that tempering of martensite proceeds in two stages in this alloy: the first stage extends from 423 K (150 °C) to 623 K (350 °C); the second stage from 748 K (475 °C) to 898 K (625 °C). Data is consistent with previous work in the literature [53] and could either be interpreted in terms of the introduction of compressive lattice strains, $\varepsilon_{\perp}^{hkl\alpha'}$, in martensite or as the rejection of C and N from solid solution. Applying the unit cell volumes for Fe-C and Fe-N martensite from Ref. [15],** and assuming that $\varepsilon_{\perp}^{hkl\alpha'}$ is not affected by tempering, the observed differences between the variation of $a_{\perp}^{\alpha'}$ with temperature and $\lambda_{\alpha'}$ would correspond to the rejection of approx. 0.03 wt% C+N during the first stage of tempering and 0.04 wt% C+N during the second stage. These values are considered realistic taking into account the alloy composition (cf. Table 1), and imply that the effect of tempering on $a_{\perp}^{\alpha'}$ can mainly have its origin in a change of the content of interstitials in solid solution in martensite.

3.3.State of stress – sample 1

** Note that the relative difference between the effects of C and N (in wt%) on the unit cell volume of martensite is <3 %, and can be neglected within the experimental accuracy indicated in Ref. [15].

3.3.1. “as normalized” condition

Figure 4. Lattice parameter of austenite a^γ evaluated from 200_γ , 311_γ , 220_γ and 222_γ and plotted versus $\sin^2\psi$. Data acquired: (a) at the beginning of the investigation; (b) at 403 K (130 °C) during quenching; (c) at 373 K (100 °C) during quenching; (d) at 328 K (55 °C) during quenching; (e) at the end of the quenching cycle; (f) at room temperature after tempering to 748 K (475 °C). The blue continuous lines represent the strain-free lattice parameter of austenite a^γ_{ref} . The black dashed lines were obtained by linear regression among a^γ values averaged over the probed hkl .

Figure 5. Lattice parameter of martensite $a^{\alpha'}$ evaluated from $200_{\alpha'}$, $211_{\alpha'}$, $220_{\alpha'}$ and $321_{\alpha'}$ and plotted versus $\sin^2\psi$. Data acquired: (a) at the beginning of the investigation; (b) at 403 K (130 °C) during quenching; (c) at 373 K (100 °C) during quenching; (d) at 328 K (55 °C) during quenching; (e) at the end of the quenching cycle; (f) after tempering to 748 K (475 °C). The blue continuous lines represent the strain free lattice parameter of martensite $a^{\alpha'}_{ref}$. The black dashed lines were obtained by linear regression among $a^{\alpha'}$ values averaged over the probed hkl , excluding $200_{\alpha'}$.

363

364 In the normalized condition the steel contains a martensite fraction $f^{\alpha'} = 0.95$; the rest is retained
 365 austenite. Representative values of a^{γ} and $a^{\alpha'}$, determined from various hkl are presented as a
 366 function of ψ in Figs. 4a and 5a, respectively. Some data points at high ψ angles were excluded
 367 because the diffracted intensity was insufficient for accurate peak fitting.

368 Fig. 4a shows that, within experimental accuracy, a^{γ} is independent of ψ , indicating that the state
 369 of stress is effectively hydrostatic (or, trivially, nil), but depends on hkl . Comparing a^{γ} with a_{ref}^{γ}
 370 (the latter as represented by the solid blue line in Fig. 4a) reveals that austenite experiences a hkl
 371 dependent compressive lattice strain. Compressive strain is largest for 220_{γ} and 222_{γ} , very small
 372 for 200_{γ} , while compression for 311_{γ} is close to the value obtained from averaging over all
 373 measured hkl . Stress analysis yields $\sigma_{\parallel}^{\gamma} - \sigma_{\perp}^{\gamma} \approx 0$ and $\sigma_{\perp}^{\gamma}$ equal to -0.21 GPa, -1.22 GPa,
 374 -0.85 GPa and -1.29 GPa for probing 200_{γ} , 220_{γ} , 311_{γ} and 222_{γ} , respectively, giving an
 375 average stress value $\langle \sigma^{\gamma} \rangle = -0.89$ GPa. It is noted that the order of increasing lattice strain (and
 376 associated elastic residual stress), coincides with an increase of the orientation parameter $3\Gamma = 3 \cdot$
 377 $\frac{h^2k^2+k^2l^2+l^2h^2}{(h^2+k^2+l^2)^2}$, which varies from 0 for 200_{γ} to 1 for 222_{γ} and for 311_{γ} is about half-way the range
 378 ($3\Gamma = 0.47$), consistent with 311_{γ} representing the average over all hkl . This would suggest that
 379 the observed differences for the probed hkl s are a consequence of elastic anisotropy in austenite.
 380 This contrasts with the zero slope in Fig. 4a., because for a hydrostatic state of stress no dependence
 381 of (elastic) lattice strain over hkl would be expected. In fact, $\left[3 \cdot s_1^{hkl\phi} + \frac{1}{2}s_2^{hkl\phi} \right]$, cf. Eq.1, is
 382 independent of hkl , as can be verified for the data in Table 2. Evidently, the state of stress in
 383 austenite is hydrostatic within the probed volume, but not necessarily hydrostatic over the length
 384 scale of a single austenite grain (cf. Refs. [19,20]).

385 Fig. 5a shows that $a^{\alpha'}$ evaluated from $211_{\alpha'}$, $220_{\alpha'}$ and $321_{\alpha'}$ neither varies with ψ nor with hkl
 386 within experimental accuracy. In contrast, the $\sin^2\psi$ dependence of $a^{\alpha'}$ derived from $200_{\alpha'}$ is
 387 characterized by oscillations (cf. Ref. [4]) and therefore excluded from the analysis. Stress analysis
 388 based on $211_{\alpha'}$, $220_{\alpha'}$ and $321_{\alpha'}$ showed that $\sigma_{\parallel}^{\alpha'} - \sigma_{\perp}^{\alpha'} \approx 0$. The average phase specific
 389 (hydrostatic) stress in martensite calculated with Eq.4 is $\langle \sigma^{\alpha'} \rangle = 0.04$ GPa.

390 3.3.2. Stress developing on martensite formation

391 Representative examples of lattice parameter a_{ψ}^{ϕ} versus $\sin^2\psi$ data, as obtained with in situ
 392 application of the $\sin^2\psi$ method, are reported in Figs. 4b-e and Figs. 5b-e. Stress values were
 393 derived from such a_{ψ}^{ϕ} versus $\sin^2\psi$ relations, applying the XECs from Table 2. The stress values

394 obtained are given in Figs. 6 and 7 as a function of $f^{\alpha'}$. The fraction of transformed austenite was
 395 determined by averaging the values of $f_{\psi}^{\alpha'}$ measured at all the applied tilting angles, ψ . This
 396 procedure reduces significantly the uncertainty caused by crystallographic texture [46]. Figures 6a
 397 and 7a show the stresses in austenite and martensite as determined in the $\perp$ direction. These stresses
 398 are interpreted as phase specific micro-stresses of type II. Figures 6b and 7b illustrate the difference
 399 between the stress components in the $\parallel$ and $\perp$ directions versus $f^{\alpha'}$. These stresses are interpreted as
 400 macro-stresses of type I, for austenite (Fig. 6a) and martensite (Fig. 7a), respectively.
 401 From Fig. 4, it follows that as long as martensite is the minority phase in the sample, i.e. for $T \geq$
 402 388 K ($115\text{ }^{\circ}\text{C}$), the lattice parameter for austenite is about the reference value, $a_{\psi}^{\gamma} \approx a_{ref}^{\gamma}$,
 403 implying that $\varepsilon_{\psi}^{hkl\gamma} \approx 0$ (Fig. 4b). At 373 K ($100\text{ }^{\circ}\text{C}$), a small compressive lattice strain develops in
 404 austenite (Fig. 4c). This lattice strain increases on further cooling (Figs. 4c-e) and is most
 405 pronounced at 298 K ($25\text{ }^{\circ}\text{C}$) (Fig. 4e). The lattice strain does not depend significantly on ψ , but it
 406 does vary with hkl . The variation among the various $\varepsilon_{\psi}^{hkl\gamma}$ increases during continuous cooling and,
 407 analogously, is most pronounced at 298 K ($25\text{ }^{\circ}\text{C}$) (Fig. 4e). Stress analysis reveals that
 408 compressive stress of type II builds up in austenite for $f^{\alpha'} > 0.2$ (Fig. 6a). Compressive stress
 409 increases steadily with a reduction of the austenite fraction and depends on the $\varepsilon_{\psi}^{hkl\gamma}$ from which it
 410 is evaluated.

411

412

413 **Figure 6. State of stress in austenite evaluated from lattice strains obtained for 200_{γ} , 220_{γ} , 311_{γ} and 222_{γ} and plotted**
 414 **versus the fraction of martensite formed $f^{\alpha'}$: a) stress component in the direction perpendicular to the sample surface $\sigma_{\perp}^{\gamma}$; b)**
 415 **difference between the stress components parallel and perpendicular to the sample surface $\sigma_{\parallel}^{\gamma} - \sigma_{\perp}^{\gamma}$. The black lines and**
 416 **symbols represent the state of stress averaged over all probed reflections. Error bars indicate the standard error of the**
 417 **estimate for linear regression of data in Fig. 2. An additional experimental error related to the alignment of the**
 418 **diffractometer is estimated in the order of $\pm 30\text{ MPa}$.**

419

Figure 7. State of stress in martensite evaluated from lattice strains obtained for 200 $_{\alpha'}$, 211 $_{\alpha'}$, 220 $_{\alpha'}$ and 321 $_{\alpha'}$ and plotted versus the fraction transformed $f^{\alpha'}$: a) stress component in the direction perpendicular to the sample surface $\sigma_{\perp}^{\alpha'}$. b) difference between the stress components parallel and perpendicular to the sample surface $\sigma_{\parallel}^{\alpha'} - \sigma_{\perp}^{\alpha'}$. The black lines and symbols represent the state of stress averaged over all probed reflections apart from 200 $_{\alpha'}$. Error bars indicates the standard error of the estimate for linear regression of data in Fig. 2. An additional experimental error related to the alignment of the diffractometer is estimated in the order of ± 30 MPa.

After quenching, $\sigma_{\perp}^{\gamma}$ equals +0.23 GPa, -0.86 GPa, -0.54 GPa and -0.86 GPa when evaluated from 200 $_{\gamma}$, 220 $_{\gamma}$, 311 $_{\gamma}$ and 222 $_{\gamma}$, respectively, and $\langle \sigma_{\perp}^{\gamma} \rangle = -0.51$ GPa. The atypical behaviour of 200 $_{\gamma}$ cannot be explained solely in terms of elastic anisotropy in austenite (see previous paragraph). This behavior is consistent with observations in the literature on the influence of plastic accommodation of the volume changes on the suitability of hkl for the determination of residual stresses in f.c.c. metals [29-32] and strongly suggests that plastic deformation has occurred in austenite during martensite formation.

During the transformation, the state of stress in (untransformed) austenite is close to hydrostatic within the probed volume (i.e. $\sigma_{\parallel}^{\gamma} - \sigma_{\perp}^{\gamma} \ll \sigma_{\perp}^{\gamma}$). However, measurable macro-stress is present, as reflected by $\sigma_{\parallel}^{\gamma} \neq \sigma_{\perp}^{\gamma}$ (Fig. 6b). At the beginning of the transformation, $\sigma_{\parallel}^{\gamma} > \sigma_{\perp}^{\gamma}$ as evaluated from $\varepsilon_{\psi}^{222\gamma}$, which, among the probed γ reflections, offers the largest information depth. Probing the other hkl at shallower information depths it is found that $\sigma_{\parallel}^{\gamma} \leq \sigma_{\perp}^{\gamma}$. Along with an increase of the fraction of martensite, a small tensile macro-stresses, i.e. ($\sigma_{\parallel}^{\gamma} > \sigma_{\perp}^{\gamma}$), builds up for $f^{\alpha'} > 0.2$.

Fig. 5 shows that $a_{\psi}^{\alpha'}$ was linearly dependent on $\sin^2\psi$ at $T = 403$ K (130 °C), i.e. just below M_s (Fig. 5b). The slope of $a_{\psi}^{\alpha'}$ versus $\sin^2\psi$ is negative. Upon cooling to $T=373$ K (100 °C), the slope of $a_{\psi}^{\alpha'}$ versus $\sin^2\psi$ reverts to positive (Fig. 5c) and a non-linear dependence of $a_{\psi}^{\alpha'}$ on $\sin^2\psi$ is observed for 200 $_{\alpha'}$, reflecting the oscillations in the $a_{\psi}^{\alpha'}$ vs. $\sin^2\psi$ distribution in the “as normalized” condition (Fig. 5a). On continuous cooling to 298 K (25 °C), $a_{\psi}^{\alpha'}$ shrinks at a rate

446 commensurate with the thermal expansion coefficient $\lambda_{\alpha'}$ and $\varepsilon_{\psi}^{hkl\alpha'}$ does not vary significantly
 447 with hkl (Figs. 5c-e).

448 Stress evaluation reveals that martensite experiences an average compressive stress at the beginning
 449 of the transformation, which reverts into an average tensile stress for $f^{\alpha'} > 0.5$ (Fig. 7a). The state
 450 of stress is not particularly sensitive to the hkl used for probing the lattice strain. Finally, after
 451 quenching, $\langle \sigma_{\perp}^{\alpha'} \rangle = +0.08 \text{ GPa}$.

452 Fig. 7b also indicates the presence of macro-stresses. At the beginning of the process, macro-
 453 stresses are compressive and significant, approx. -0.25 GPa . With increasing martensite content,
 454 compression decreases and is reversed into tensile macro-stress for $f^{\alpha'} > 0.2$.

455 3.3.3. The tempered condition

456 The values of $a_{\psi}^{hkl\gamma}$ and $a_{\psi}^{hkl\alpha'}$ are shown as a function of $\sin^2\psi$ in Figs. 4f and 5f, respectively.

457 The fraction of martensite in the sample is $f^{\alpha'} = 0.95$, consistent with the “as normalized” and “as
 458 quenched” conditions. The result in Fig. 4f shows that $a_{\psi}^{hkl\gamma}$ varies with hkl , but not with ψ .

459 Comparison of a^{γ} with a_{ref}^{γ} reveals that lattice strain evaluated from 200_{γ} and 311_{γ} is negligibly
 460 small, whereas $\varepsilon^{222\gamma} \ll 0$. Stress analysis shows that $\sigma_{\perp}^{\gamma}$ is -0.07 GPa , -0.23 GPa , -0.08 GPa and
 461 -0.86 GPa when evaluated based on 200_{γ} , 220_{γ} , 311_{γ} and 222_{γ} , respectively. The stress is
 462 approximately hydrostatic within the probed volume, with $\langle \sigma_{\perp}^{\gamma} \rangle = -0.31 \text{ GPa}$ and $\sigma_{\parallel}^{\gamma} - \sigma_{\perp}^{\gamma} =$
 463 $+0.04 \text{ GPa}$. The hkl -dependent lattice strain suggests that a hydrostatic state of stress does not
 464 apply at the length scale of a single austenite grain.

465 Fig. 5f shows that $a_{\psi}^{hkl\alpha'}$ evaluated from $211_{\alpha'}$, $220_{\alpha'}$ and $321_{\alpha'}$ is a linear function of $\sin^2\psi$ but
 466 does not vary with hkl ; $a_{\psi}^{200\alpha'}$, instead, shows a $\sin^2\psi$ dependence characterized by oscillations as
 467 earlier reported for the material in “as normalized” and “as quenched” conditions. Stress analysis
 468 was based on $211_{\alpha'}$, $220_{\alpha'}$ and $321_{\alpha'}$. Under the assumption that the chemical composition of the
 469 martensite has not changed during tempering it is obtained $\langle \sigma_{\perp}^{\alpha'} \rangle = -0.09 \text{ GPa}$ and $\sigma_{\parallel}^{\alpha'} - \sigma_{\perp}^{\alpha'} =$
 470 $+0.08 \text{ GPa}$.

471 Nevertheless, the material is almost fully martensitic during tempering. A significant variation of
 472 $\langle \sigma_{\perp}^{\alpha'} \rangle$ from $\langle \sigma_{\perp}^{\alpha'} \rangle = 0.08 \text{ GPa}$ before to tempering to $\langle \sigma_{\perp}^{\alpha'} \rangle = -0.09 \text{ GPa}$ after tempering would
 473 imply an enormous (about 3 GPa) balancing variation in $\langle \sigma_{\perp}^{\gamma} \rangle$, (cf. Eq.7), which is not confirmed by
 474 the experimental data. Evidently, the shrinkage of the martensite lattice from the “as quenched” to
 475 the “tempered” condition is not due to a change of $\langle \sigma_{\perp}^{\alpha'} \rangle$, but has its origin in a change in chemical

composition. The measured change in the lattice parameter corresponds to expelling approx. 0.03 wt% C+N from solid solution in martensite during tempering to 748 K (475 °C).

4. Discussion

4.1. Partitioning of stresses in austenite and martensite during martensite formation

Historically, the evolution of the phase specific stresses, $\langle \sigma^\varphi \rangle$, in austenite and martensite during the austenite-to-martensite transformation has been investigated by measuring the evolution of the phase specific strain, ε^φ , as a function of the corresponding phase fraction, f^φ , either in a single direction [14,16-18,22,23], or in a set of directions (approx.) normal to the incident beam [19,20,27]. These investigations departed from the hypothesis that macro-stresses are negligible within the volume probed by XRD.

Figure 8. Calculated phase-specific stresses $\langle \sigma^\varphi \rangle$ for a) sample 1 and b) sample 2. Data re plotted versus fraction transformed $f^{\alpha'}$ (averaged over all ψ) and fraction transformed evaluated in the direction normal to the sample surface $f_{\perp}^{\alpha'}$, for sample 1 and sample 2, respectively. Error bars indicates minimum and maximum values based on data in Figs. 6a and 7a. An additional experimental error related to the alignment of the diffractometer is estimated in the order of ± 30 MPa. Error analysis do not consider uncertainty in the determination of $f^{\alpha'}$ and $f_{\perp}^{\alpha'}$.

In the present work, the evolution of stress in the material during martensite formation including the separation of macro- and micro-stresses was investigated in situ for the first time (sample 1). To verify whether the measured lattice strains in austenite can be ascribed to (micro-)stresses of type II, a balancing of average stress values in the phases in the sample (cf. Eq. 7) with $f^{\alpha'}$ was considered. The results of this verification for the stress values presented in Fig. 6a and 7a are shown in Fig. 8a. Fig. 8a shows that, within experimental accuracy, internal balance of average stresses is satisfied from the onset of the transformation to its completion. At the beginning of the transformation martensite is the minority phase and experiences significant phase specific compressive (micro-

502)stress of type II, which is balanced by very small tensile (micro-)stress of type II in the dominating
503 austenite. During martensite formation, the state of stress in the phases reverses. For $f^\alpha > 0.2$,
504 tension builds up in martensite and compression develops in austenite. At the end of the
505 transformation, significant compressive (micro-)stress of type II in austenite is balanced by small
506 tensile (micro-)stress of type II in martensite. Data does not provide a reason for the observed
507 reversion of the state of stress in the phases during transformation.

508 The importance of performing in situ stress analysis to evaluate the state of stress in the phases is
509 clarified from comparing Fig. 8a and Fig. 8b. The stress values presented in Fig. 8b (sample 2) were
510 obtained applying Eq. 2, under the assumption that the state of stress in both phases is hydrostatic.
511 Fig.8b indicates that martensite formation leads to compressive stresses in both martensite and
512 austenite, in agreement with a previous claim in Ref. [14]. The in situ stress analysis as determined
513 for sample 1 demonstrates that this conclusion is incorrect. Evidently, Eq.2 can be applied only if
514 the assumption that macro-stresses are negligible is validated.

515 Macro-stresses can be introduced as a consequence of a variation in the degree of transformation
516 over the sample thickness. It is well accepted that martensite formation starts at the surface and is
517 associated with a volume expansion. This expansion is partially relaxed in the $\perp$ direction and
518 partially accommodated within the sample. Martensite, which is concentrated at the sample surface,
519 experiences compressive macro-stresses (Fig. 7b, left), which are balanced by tensile macro-stresses
520 in the bulk austenite, as reflected in Fig. 6b (left) by probing the 222_γ reflection. Thereafter,
521 continuous cooling promotes continuation of the transformation (from left to right in Figs. 6 and 7),
522 including transformation of the bulk. Transformation of the bulk, is similarly associated with a
523 volume expansion. However, the expansion of the bulk is fully counteracted by the martensitic case,
524 which surrounds it. As a result, macro-stress in the near surface region changes from compressive to
525 tensile during continued transformation, as evidenced in Figs. 6 and 7 at $f^{\alpha'} > 0.2$.

526 Additionally, hkl dependent lattice strain in austenite should be addressed. Historically, the lattice
527 strain in austenite, ε^γ , developing during martensite formation was obtained from either a^γ
528 evaluated from the position of a single reflection [11-15,23,24], or from an average a^γ value
529 obtained from the simultaneous evaluation of the position of all probed reflections [19,20,27]. In a
530 few studies [16,17,22], hkl -specific ε^{hkl_γ} relying on an independent evaluation of corresponding
531 a^{hkl_γ} were presented. These latter studies revealed that the lattice strain is compressive ($\varepsilon^{hkl_\gamma} < 0$)
532 and largest for $111_\gamma/222_\gamma$ [16,17,22], moderately negative and close to the average value for 311_γ
533 [16,17] and negligible [16,17] or positive, for 200_γ [22]. These observations are confirmed by the
534 results obtained in the present investigation. The hkl -dependence of lattice strain in austenite can

535 partly be explained from the anisotropic elastic properties of austenite (see section 3.3.). However,
 536 lattice strains of opposite sign for different hkl , as observed for the material as quenched and as
 537 tempered, cannot be reconciled with elastic anisotropy only. Plastic accommodation of the
 538 transformation strain is considered responsible for this behavior. When a unit of martensite forms,
 539 the transformation evokes tension in the surrounding austenite, which yields heterogeneously.
 540 Crystal plasticity in f.c.c. crystals yields hkl dependent non-linear stress-strain behaviour in addition
 541 to elastic anisotropy and consequently, a change of the apparent elastic constants. As a result,
 542 anisotropic residual stress remains after unloading. Unloading of the state of tension in austenite
 543 takes place during continued martensite formation, as revealed by the development of an average
 544 compressive state of stress in this phase.

545 Unfortunately, controversy exists as to which hkl s should be chosen to prevent these anisotropy
 546 effects (cf. Ref. [29-31] vs. Ref. [32]). If only elastic anisotropy is responsible for hkl dependence,
 547 averaging is effectively obtained by choosing the 311_γ reflection, as the corresponding orientation
 548 parameter 3Γ for this reflection is close to 0.5, i.e. half way the range from 0 to 1. In the present
 549 work, $\langle \sigma^V \rangle$ was taken as the average value for stress obtained from lattice strain over ε^{200_γ} , ε^{220_γ} ,
 550 ε^{311_γ} and ε^{222_γ} . This procedure yielded the conclusion that Eq. 3 was satisfied throughout the
 551 whole transformation process. It is explicitly mentioned that choosing the 311_γ reflection would
 552 have given a comparable result.

553 Further insight in the elasto-plastic interaction between the phases during transformation is provided
 554 by data collected for the ψ -dependent lattice parameter $a_\psi^{200_{\alpha'}}$. A rigorous treatment to interpret a d
 555 vs. $\sin^2\psi$ distribution characterized by oscillations is missing [4]. However, in a cubic phase,
 556 oscillations in the d -vs. $\sin^2\psi$ distribution can be caused by texture and/or plastic strain. In textured
 557 elastically strained cubic materials, no oscillation of $a_\psi^{\alpha'}$ versus $\sin^2\psi$ is expected for the $h00_{\alpha'}$
 558 reflections [4,54]. On the other hand, oscillations will arise in plastically strained crystals, and will
 559 be most significant for $200_{\alpha'}$ [4,55]. Hence, the present data indicates that both austenite and
 560 martensite are plastically strained during the transformation.

561 Finally, we suggest that a consistent description of the evolution of strain and phase-specific
 562 stresses in the material during the austenite-to-martensite transformation requires that the elasto-
 563 plastic interaction of the two phases and the elasto-plastic anisotropy of the two crystal lattices is
 564 taken into account. Developing such description is beyond the scope of the present work.

565 5. Conclusion

566 Stress analysis was applied to investigate in situ stresses of type II evoked by the austenite-to-
567 martensite transformation in steel. The analysis shows indeed that such stresses do build up.

568 Stresses of type II have a significant magnitude for the minority phases, *i.e.* for martensite at the
569 beginning of the transformation and for austenite at the end.

570 Stresses of type II in the minority phase are compressive and are balanced by small tensile stresses
571 of type II in the majority phase.

572 Strain in austenite is anisotropic: maximum compression is observed for spacings of the $(222)_\gamma$ and
573 $(220)_\gamma$ planes, while tension was revealed in the $[200]_\gamma$ direction. Anisotropic strain in austenite is
574 particularly significant in the latest stage of the transformation.

575 Strain anisotropy in austenite and a d-vs. $\sin^2\psi$ distribution characterized by oscillations in
576 martensite indicate that both phases are subjected to plastic deformation during quenching.

577 An in-depth evaluation of the state of stress in the phases requires further investigation in the effect
578 of plasticity on the determination of stresses in iron-based alloys.

579 Tempering of soft martensitic stainless steel to 748 K (475 °C) yields partial relaxation of stresses.

580 **Acknowledgements**

581 M. Klaus, D. Apel and Ch. Genzel from Helmholtz Zentrum für Materialien und Energie (HZME)
582 are acknowledged for their enthusiastic support during the activity at the HZB-BESSY II
583 synchrotron facility and during subsequent data analysis. The activity was supported by the
584 European Commission under the 7th Framework Program through the 'Research Infrastructure'
585 action of the 'Capacities' Programme, CALIPSO (Grant n: 312284) and by the Danish Natural
586 Science Research Council via Danscatt. The Danish Council for Independent Research (G.R. grant:
587 DFF-4005-00223) and the Danish Underground Consortium are gratefully acknowledged for
588 financial support.

589 **References**

- 590 [1] P. J. Withers, W.M. Stobbs, O.B. Pedersen: *Acta metal.*, 1989, vol. 37, pp. 3061-3084
- 591 [2] O.B. Pedersen: *Acta Metall.*, 1983, vol. 31, pp. 1795-1808
- 592 [3] P.J. Withers and H.K.D.H. Bhadeshia: *Mater. Sci. Tech.*, 2001, vol. 17, pp. 366-375
- 593 [4] V. Hauk: *Structural and Residual Stress Analysis by Non-Destructive Methods: Evaluation –*
594 *Application – Assessment*, Elsevier Science, 1997

- 595 [5] P.J. Withers and H.K.D.H. Bhadeshia: *Mater. Sci. Tech.*, 2001, vol. 17, pp. 355-365
- 596 [6] G.B. Olson and W.S. Owen: *Martensite*, ASM International, (OH) USA, 1992
- 597 [7] Z. Nishiyama, *Martensitic Transformation*, Academic Press, New York, USA, 1978
- 598 [8] J.W. Christian: *Proc. Int. Conf. on martensitic Transformation*, 1979, pp. 220-233
- 599 [9] H.K.D.H. Bhadeshia: *Mater. Sci. Eng. A*, 2004, vol. 378, pp. 34-39
- 600 [10] G.E. Totten, M. Howes, T. Inoue: *Handbook of Residual Stress and Deformation of Steel*,
601 ASM International, (OH) USA, 2002
- 602 [11] V.I. Gridnev, V.I. Trefilov: *Dokl. Akad. Nauk SSSR*, 1957, vol. 116, pp. 60-62
- 603 [12] N. Ridley, H. Stuart, L. Zwell: *Trans. AIME*, 1969, vol. 245, pp. 1834-1836
- 604 [13] K. Ya Golovchiner: *Fiz. Metal. Metalloved.*, 1974, vol. 37, pp. 363-368
- 605 [14] Y. Tanaka and K. Shimizu: *Trans. JIM*, 1980, vol. 21, pp. 42-50
- 606 [15] L. Cheng, A. Bottger, T.H. de Keijser, E.J. Mittemeijer: *Scripta Mater.*, 1990, vol. 24, pp. 509-
607 514
- 608 [16] M. Villa, F.B. Grumsen, K. Pantleon, M.A.J. Somers: *Scripta Mater.*, 2012, vol. 67, pp. 621-
609 624
- 610 [17] M. Villa, K. Pantleon, M.A.J. Somers: *J. Alloys Compd.*, 2013, vol. 577, pp. S543-S548
- 611 [18] M. Villa, K. Pantleon, M.A.J. Somers: *Acta mater.*, 2014, vol. 65, pp. 383-392
- 612 [19] J. Epp.: *Advanced Mater. Res.*, 2014, vol. 996, pp. 525-531
- 613 [20] J. Epp.: *Proc. IFHTSE 2016*, 2016, pp. 440-447
- 614 [21] N. Nakada, Y. Ishibashi, T. Tsuchiyama, S. Takaki: *Acta Mater.*, 2016, vol. 110, pp. 95-112
- 615 [22] V.M. Yeshov, M.L. Oslon: *Fiz. Metal. Metalloved.*, 1968, vol. 25, pp. 874-881
- 616 [23] V.M. Yeshov, M.L. Oslon: *Fiz. Metal. Metalloved.*, 1972, vol. 33, pp. 215-217
- 617 [24] E. Scheil, E. Saftig. *Arch. Eisenhüttenw.* 1957, vol. 28, pp. 49-51
- 618 [25] K. Ullakko and V.G. Gavriljuk: *Acta Metall. Mater.*, 1992, vol. 40, pp. 2471-2482
- 619 [26] K. Ullakko: *Aging of iron-based martensites at low-temperatures*, PhD thesis, Helsinki, 1992
- 620 [27] D. San Martin, E. Jimenez-Melero, J.A. Duffy, V. Honkimaki, S. van der Zwaag, N.H. van
621 Dijk: *J. Appl. Crystallogr.*, 2012, vol.45, pp. 748-757
- 622 [28] T. Kakeshita, T. Saburi, K. Kind, S. Endo: *Phase Transitions*, 1999, vol. 70, pp. 65-113.

- 623 [29] A.N. Ezeilo, G.A. Webster, P.J. Webster, X. Wang: *Physica B*, 1992, vol. 180-181, pp. 1044-
624 1046
- 625 [30] B. Clausen, T. Lorentzen, T. Leffers: *Acta. Mater.*, 1998, vol. 46, pp. 3087-3098
- 626 [31] E.C. Oliver: *The generation of internal stresses in single and two phase materials*, PhD Thesis,
627 Manchester, 2002
- 628 [32] B. Clausen, T. Leffers, T. Lorentzen: *Acta. Mater.*, 2003, vol. 51, pp. 6181-6188
- 629 [33] F. Niessen, M. Villa, D. Apel, O. Keßler, M. Reich, J. Hald, M.A.J. Somers: *Mater. Sci.*
630 *Forum*, 2016, vol. 879, pp. 1381–1386
- 631 [34] F. Niessen, M. Villa, J. Hald, M. AJ Somers: *Mater. and Design*, 2017, vol. 116, pp. 8–15.
- 632 [35] Ch. Genzel, I. A. Denks, M. Klaus, *Mater. Sci. Forum*, 2006, vol. 524-525, pp. 193-198
- 633 [36] B.C. Giessen, G.E. Gordon: *Science*, 1968, vol. 159, pp. 973–975
- 634 [37] Ch. Genzel, I.A. Denks, M. Klaus: *Residual Stress Analysis by X-Ray Diffraction Methods*, in
635 *Modern Diffraction Methods*, Wiley-VCH, 2013, pp. 127–154
- 636 [38] E.S.U. Laine: *J. Phys. F Met. Phys.*, 1978, vol. 8, pp. 1343-1348
- 637 [39] Landoldt-Börnstein, New Series, Group III Vol. 11, Springer, Berlin 1979
- 638 [40] H. Behnken: *Berechnung und Ermittlung der röntgenographischen Elastizitätskonstanten*
639 *sowie der Mikro- und Makro-Spannungen heterogener und texturierter Werkstoffe*, PhD thesis,
640 RWTH Aachen, 1992
- 641 [41] E. Kröner: *Z. Physik*, 1958, vol. 151, pp. 504-518
- 642 [42] J.D. Eshelby: *Proc. Roy. Soc. London A*, 1957, vol. 241, pp. 376-396
- 643 [43] A. Teklu, H. Ledbetter, S. Kim, L.A. Boatner, M. McGuire, V. Keppens: *Metall. Mater. Trans.*
644 *A*, 2004, vol. 35, pp. 3149-3154
- 645 [44] H.M. Ledbetter and M.W. Austin: *Mater Sci Eng*, 1985, vol. 70, pp. 143-149
- 646 [45] Y.S. Touloukian, *Thermophysical Properties of Matter. The TPRC Data Series 12: Thermal*
647 *Expansion Metallic Elements and alloys*, IFI/Plenum, 1975
- 648 [46] T. Gnaupel-Herold, A. Creuziger: *Mater. Sci. Eng. A*, 2011, vol. 528, pp. 3594-3600
- 649 [47] A. Bojack, L. Zhao, P.F. Morris, J. Sietsma: *Mater. Charact*, 2012, vol. 7, pp. 77-86
- 650 [48] C.M. Wayman: *Iron and Steel Inst. - Special Report*, 1965, pp. 153-163
- 651 [49] J. Pak, D.W. Suh, H.K.D.H. Bhadeshia: *Metall. Mater. Trans. A*, 2012, vol. 43, pp. 4520-4524

- 652 [50] J.A. Klostermann and W.G. Burgers: *Acta Metall.*, 1964, vol. 12, pp. 355-360
- 653 [51] J.A. Klostermann: *J. Less-Common Metals*, 1972, vol. 28, pp. 75-94
- 654 [52] G. Faria, J. Escobar, A.J. Ramirez: *Proc. Int. Conf. on Solid-solid Phase Transf. in Inorganic*
655 *Mater. 2015*, 2015, pp. 637-638
- 656 [53] A. Beneteau, E. Aeby-Gautier, G. Geandier, P. Weisbecker, A. Redjaimia, B. Appolaire: *Acta*
657 *Mater.*, 2014, vol. 81, pp. 30-40
- 658 [54] A.J.C. Wilson: *Acta Cryst.*, 1952, vol. 5, pp. 318-322
- 659 [55] J.W.L. Pang, T.M. Holden, T.E. Mason: *J. Strain Analysis Eng. Design*, 1998, vol. 33, pp. 373-
660 383