



## Regular article

***In-situ* analysis of redistribution of carbon and nitrogen during tempering of low interstitial martensitic stainless steel**F. Niessen <sup>a,b,\*</sup>, M. Villa <sup>b</sup>, F. Danoix <sup>c</sup>, J. Hald <sup>b</sup>, M.A.J. Somers <sup>b</sup><sup>a</sup> Technical University of Denmark, Danish Hydrocarbon Research and Technology Centre, 2800 Kgs. Lyngby, Denmark<sup>b</sup> Technical University of Denmark, Department of Mechanical Engineering, 2800 Kgs. Lyngby, Denmark<sup>c</sup> Normandie Univ, UNIROUEN, INSA Rouen, CNRS, Groupe de Physique des Matériaux, F-76000 Rouen, France

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## ABSTRACT

The redistribution of C and N during tempering of X4CrNiMo16-5-1 martensitic stainless steel containing 0.034 wt% C and 0.032 wt% N was studied using *in-situ* synchrotron X-ray diffraction (XRD) and atom probe tomography (APT). The unit cell volume of martensite decreased continuously during tempering. APT showed that this volume decrease is accounted entirely for by segregation of the interstitial atoms, implying that in low interstitial martensitic stainless steel stress relaxation only contributes negligibly to changes in the martensite unit cell volume.

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Martensitic steels with lath microstructure stand out by an exceptional combination of high strength, good ductility and low cost for numerous structural applications. These properties are conventionally obtained through a hardening and tempering heat treatment cycle. Hardening consists of high temperature austenitization followed by martensite formation during fast cooling to room temperature. With a dislocation density comparable to that of heavily cold rolled ferrite, martensite is brittle and thus unsuitable for practical use [1]. Tempering of the hardened material below  $A_{c1}$  promotes optimization of the mechanical properties through redistribution of the interstitial atoms and relaxation of internal stresses [2]. In martensitic stainless steels, annealing in the inter-critical region between  $A_1$  and  $A_3$  leads to formation and stabilization of reverted austenite at lath boundaries [3–5]. Such dual phase microstructure significantly enhances toughness and ductility, and reduces yield strength, hardness and ultimate tensile strength [6–8].

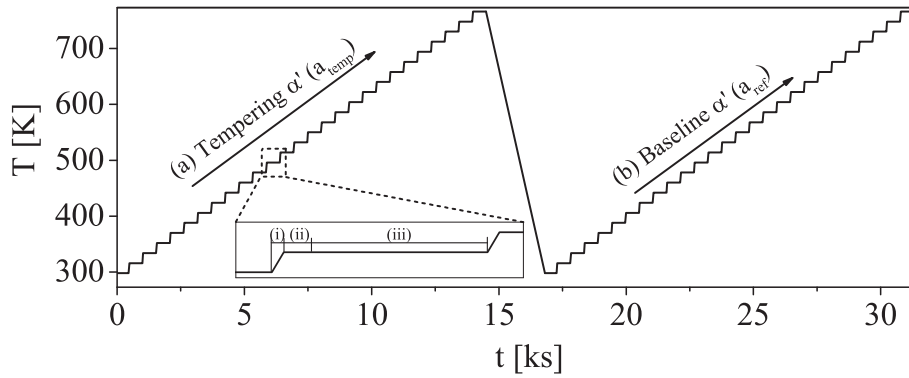
A few *in-situ* studies focused on tempering of martensitic stainless steels with >0.6 wt% interstitial content below  $A_{c1}$  [9, 10], or on inter-critical annealing of martensitic stainless steels with <0.08 wt% interstitial content [4, 11–13]. These *in-situ* studies were based on measurement of the planar spacings of the present phases as a function of temperature with synchrotron X-ray diffraction (XRD). Tempering

below  $A_{c1}$  in low interstitial martensitic stainless steels appears still uninvestigated. Generally, it is not possible to distinguish unequivocally between the contributions of changes in interstitial content in solid solution and changes in internal stresses on the evolution of the austenite and martensite unit cell volumes. In martensite, the change in tetragonality of the unit cell with C and N content [14] is a widely applied relation to determine the interstitial content [9, 15, 16]. In the present system, the martensite unit cell must be regarded as cubic, because of the low total interstitial (C + N) content [14]. Hence, the unit cell volume is represented by a single lattice parameter. For cubic martensite, as well as for austenite, XRD studies which involve both changes in chemistry and stresses are either limited to semi-quantitative conclusions based on assumptions [10, 15, 17–20], or rely on additional results from numerical modeling [9, 21, 22]. The present study aims to elucidate the interpretation of changes in the unit cell volume of martensite during tempering by correlating *in-situ* energy-dispersive synchrotron X-Ray diffraction (XRD) with atom probe tomography (APT) results.

The steel investigated has the metallic composition Fe-15wt%Cr-5.8wt%Ni-1.0wt%Mo-0.86wt%Mn-0.4wt%Si (EN 1.4418) measured by optical emission spectroscopy as well as  $0.034 \pm 0.005$  wt% C and  $0.032 \pm 0.001$  wt% N as interstitials, measured by LECO CS230 and LECO TC500 instruments, respectively. Samples from an extruded rod of  $\varnothing 10$  mm were austenitized at 1223 K for 0.6 ks in an Ar flow, where the average heating and cooling rate were  $0.75$  and  $1.15 \text{ K} \cdot \text{s}^{-1}$ , respectively. The martensite start temperature ( $M_s$ ) of the material is 408 K, and the amount of retained austenite at room temperature is  $3.5 \pm 0.5$  vol% [23]. Microstructure characterization revealed that retained

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**Fig. 1.** Thermal cycles applied for measurement of the lattice parameter during (a) tempering of virgin martensite ( $a_{temp}$ ) and (b) reheating of tempered martensite ( $a_{ref}$ ). The average heating and cooling with  $0.033 \text{ K} \cdot \text{s}^{-1}$  was discretized into isothermal plateaus of 540 s consisting of (i) rapid heating ( $0.6 \text{ K} \cdot \text{s}^{-1}$ ), (ii) 80 s equilibration and (iii) 430 s of  $\sin^2\psi$ -analysis at stationary thermal conditions (see inset).

austenite is present as bulky retained austenite, mostly in the corners of martensite packets.

*In-situ* XRD was carried out on the EDDI-beamline of the synchrotron facility HZB-BESSY II [24] and consisted of high temperature measurement of the evolution of the unit cell volumes of the phases. Sample preparation, experimental setup and measuring conditions are described in Ref. [23].

Residual stresses can be categorized according to the length scale over which they equilibrate. Macro-stresses (type I) occur over large distances within a sample, micro-stresses of type II equilibrate at the grain or phase scale, and micro-stresses of type III are stresses which occur at a level considerably smaller than the grain size [25, 26]. Stresses are manifested as lattice strains and, for polycrystalline mono-phase materials with random grain orientation, lead to line profile shifts (type I) or line profile broadening (type II and III) in XRD. For dual-phase polycrystalline materials, as under consideration in the present work, stresses of type I are partitioned into phase specific stresses of type II, which lead to phase specific line profile shifts, while broadening of the line profiles reflects the variation in phase specific stresses of type II and stresses of type III.

The austenite-to-martensite transformation in steel is associated with a shape change, a so-called transformation strain, which, on average, invokes a state of phase-specific hydrostatic residual stress of type II in the material with contributions from the transformation itself and thermal mismatch [23]. In a thin sample, as under consideration in the present study, macro-stresses (type I) are considered biaxial, *i.e.* relaxed in the direction normal to the sample surface, and can be separated from hydrostatic type II stresses by measuring over several  $\psi$  angles [26, 27]. Stresses were determined from the arithmetic average of the lattice parameters from the  $211_{\alpha'}$ ,  $220_{\alpha'}$  and  $321_{\alpha'}$  reflections, weighted by their multiplicity. Further details on the applied methodology and the X-ray elastic constants are given in Ref. [23].

The lattice parameter of martensite was acquired during the thermal cycles depicted in Fig. 1. Virgin martensite was heated at  $0.033 \text{ K} \cdot \text{s}^{-1}$  and heating was interrupted at 766 K to prevent nucleation of austenite (Fig. 1(a)). A second heating cycle was applied to obtain the reference lattice parameter of tempered martensite (Fig. 1(b)). For the accurate determination of lattice strains with the  $\sin^2\psi$  method stationary conditions are required. For this reason, the average heating rate of  $0.033 \text{ K} \cdot \text{s}^{-1}$  was realized by rapid heating by 18 K at  $0.6 \text{ K} \cdot \text{s}^{-1}$ , 80 s of temperature equilibration and 430 s measurement for a range of  $\psi$  angles (see inset in Fig. 1, intervals (i), (ii) and (iii), respectively). It was found for martensite that phase specific macro stresses, *i.e.* biaxial stresses determined by the  $\sin^2\psi$  method, were in the range of  $-30$  to  $30 \text{ MPa}$  for the entire thermal cycle and thus can be neglected.

The change in the lattice parameter of martensite during tempering of virgin martensite ( $a_{temp}$ , cycle (a) in Fig. 1) relative to the lattice parameter of tempered martensite ( $a_{ref}$ , cycle (b) in Fig. 1) is represented

by the green dots and the green dashed line in Fig. 2. Since no biaxial stresses are present, this relative change in lattice parameter can be conceived as the lattice strain under an average value of the phase specific hydrostatic lattice stresses of type II [26]. Evidently, on tempering the volume of the martensite unit cell is reduced relative to the reference condition. The volume fraction of retained austenite was too small to allow accurate lattice strain determination.

The change in lattice parameter of martensite may be an effect of partitioning of mechanical stress, but may also be the result of a redistribution of interstitials. Interpreting the contraction in terms of a change in total interstitial content, the well-established relationships for Fe-C and Fe-N martensite from Ref. [14] could be applied. Recognizing that both N and C are present, the arithmetic average of the dependence of unit cell volume on interstitial (N or C) content can be used to estimate the change in total interstitial content<sup>1</sup>:

$$V_{Me} = 1.1776 \cdot 10^{-2} + 8.1 \cdot 10^{-5} y_{N+C} [\text{nm}^3] \quad (1)$$

where  $V_{Me}$  is the volume per metal atom and  $y_{N+C}$  is the total number of interstitials per 100 metal atoms. This conversion of relative contraction of the unit cell volume into the change of total interstitial content from the initially average alloy interstitial content is given on the right-hand vertical axis in Fig. 2.

Assuming a pure effect of rejection of C and N on the relative change in the martensite lattice parameter, the measured change in lattice parameter corresponds to a progressive rejection of C and N from solid solution in martensite (green dashed line in Fig. 2). Altogether  $y_{C+N} = 0.18$  is rejected, while  $y_{C+N} = 0.10$  remains in solid solution.

In order to verify the validity of the hypothesis of a mere rejection of interstitials, local composition measurements with atom probe tomography (APT) were conducted for specimens in the hardened condition and specimens tempered by heating to 568 K and 703 K at the same heating rate as in the XRD investigations. Needle-shaped specimens for APT were prepared by electrolytic polishing [28] and subsequently field-evaporated in a CAMECA LEAP 4000 HR® in voltage mode. The analysis was conducted at 50 K, 20% pulse fraction, 200 kHz pulse rate and 0.3% detection rate in legacy mode. In mass spectra, carbon was detected as  $\text{C}^+$ ,  $\text{C}^{2+}$ ,  $(^2\text{C})^{2+}$ ,  $(^3\text{C})^{2+}$  and  $\text{C}^{3+}$  ions and compositions were determined following the peak assignment proposed by Sha et al. [29]. Singly charged nitrogen overlaps with doubly charged Si, but as no characteristic shoulder for the  $\text{Si}^{2+}$  was observed, and nitrogen has a strong tendency to form molecular ions with Mo [30], virtually all N was detected as  $(\text{MoN})^{2+}$ . Grain boundaries were identified by qualitative structural analysis of the desorption pattern [31]. The method consisted of analyzing the shift of crystallographic poles across grain boundaries,

<sup>1</sup> Adopting the average of the lattice expansions caused by C and N an error of maximally 1% is introduced, which is within experimental accuracy.

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