Thermal and deformation-induced phase transformation behavior of Fe–15Cr–3Mn–3Ni–0.1N–(0.05–0.25)C austenitic and austenitic–martensitic cast stainless steels

M. Wendler, M. Hauser, O. Fabrichnaya, L. Krüger, A. Weiβ, J. Mola

A T R I C L E  I N F O

Article history:
Received 21 April 2015
Received in revised form 27 July 2015
Accepted 28 July 2015
Available online 1 August 2015

Keywords:
Martensitic transformation
Austenite stability
As-cast austenitic and austenitic–martensitic stainless steel
TRIP effect

A B S T R A C T

The austenite-stabilizing effect of carbon on the martensitic transformation behavior and the temperature dependent tensile properties of five Fe–15Cr–3Mn–3Ni–0.1N–(0.05–0.25)C cast stainless steels with austenitic and austenitic-martensitic microstructures was studied. As the carbon concentration increased in 500 ppm increments from 0.05 mass-% to 0.25 mass-%, the as-quenched martensite fraction as well as $M_s$, $A_s$, and $A_f$ phase transformation temperatures decreased. Increased carbon content was also found to increase the austenite stability against the deformation-induced α′-martensite formation. During tensile tests in the temperature range of $-40$–$200 \, ^\circ \text{C}$, stress- and strain-induced martensite formation occurred in the investigated steels. Due to the low room temperature stability of austenite in the examined steels, more favorable combinations of tensile properties were obtained at high tensile test temperatures where the deformation-induced martensite transformation of the austenite phase was postponed to high strains or completely suppressed.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In conventional fully austenitic stainless steels such as the AISI 316L, high demands are placed on the microstructure stability. Such steels require a high resistance against martensitic transformation during quenching and cold working operations in the temperature range of application in order to maintain their excellent properties in terms of ductility, toughness, para-magnetism and corrosion resistance. In order to fulfil the above-mentioned conditions, a high austenite stability is needed. To achieve this, the Gibbs free energy of austenite must be lower than that of the martensite at the temperature of interest. At temperatures below $T_0$ which denotes the temperature at which the Gibbs energies of austenite and martensite are equal, however, austenite becomes metastable and from a thermodynamic perspective, the deformation-induced martensitic transformation becomes possible [1–4]. In practice, however, the martensitic transformation starts at temperatures well below $T_0$ where the chemical driving force suffices to supply the interfacial energy between the martensite nuclei and the fcc matrix as well as the elastic strain energy associated with the transformation [3,5]. Depending on the chemical composition and temperature which both influence the stacking fault energy (SFE), various deformation mechanisms such as $\gamma \rightarrow \alpha'$, $\gamma \rightarrow \varepsilon$, and $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ martensitic transformations and the mechanical twinning can occur under external loading [3,5–12]. These plasticity mechanisms which are responsible for the TRIP (Transformation Induced Plasticity) and TWIP (Twinning Induced Plasticity) effects can result in impressive mechanical properties e.g. an extraordinary increase of strength [8,9,13–15] and ductility [2] in comparison to the highly stable austenitic steels. To trigger strain-induced $\varepsilon$-martensite formation or twinning, low SFEs are required. In the case of high-manganese TWIP steels, SFEs below 15–20 mJ/m² are known to favor the $\gamma \rightarrow \varepsilon$ phase transformation, higher values the twinning of austenite [16–20]. Investigations on FeCrMnNi TRIP/TWIP steels indicated that twinning in the austenitic stainless steels occurs in the SFE range of 20–40 mJ/m² [14]. The temperature dependent deformation mechanisms (TRIP/TWIP) in the austenite can therefore be adjusted by the variation of the chemical composition which in turn influences the SFE [18,19,21–23]. Accordingly, with the adjustment of common alloying elements in stainless steels such as Cr, C, N, Mn and Ni, a metastable austenite capable of TRIP and/or TWIP effects can be achieved in the required temperature range.
For the description of martensitic transformation, temperatures such as \( M_d \), \( M_{cm} \), \( M_s \), and \( M_f \) are commonly used. \( M_d \) is defined as the highest temperature at which strain-induced martensitic transformation can be triggered in the plastic deformation range \([1,3]\). Martensitic transformation in the elastic deformation range, referred to as the stress-induced martensite formation, can occur below the \( M_{cm} \)-temperature. This mechanism takes place without any recognizable increase in the elongation but it has a significant strengthening effect \([2]\). Between \( M_{cm} \) and \( M_s \)-temperatures, the strain-induced formation of martensite which is responsible for the TRIP effect can take place. Below the \( M_s \) temperature, the formation of as-quenched martensite without external loading is enabled. Under favorable conditions, full transformation of austenite to as-quenched martensite might be achieved at the \( M_f \) temperature.

The aim of this study is to investigate the impact of carbon content on the austenite stability in Fe–15Cr–3Ni–3Mn–0.5Si–0.1 cast stainless steels. The possibility of obtaining different as-quenched martensite fractions in the steels also enabled the study of the associated phase hardening effect. The main focus is placed on the microstructure formation processes and variation with the temperature of tensile properties as a result of the activation of stress- and strain-induced \( \alpha \)-martensite formation mechanisms. Furthermore, a detailed overview of the phase transformation behavior caused by deformation and cryogenic treatment of the experimental high-strength steels is provided.

### 2. Experimental procedure

#### 2.1. Fabrication of cast steels

The steels used in this study were produced in a vacuum induction furnace. Initially, an argon partial pressure of 350 mbar was used to melt down the feedstock. After the complete formation of the molten bath, nitrogen gas with a partial pressure of 250 mbar was applied for nitriding. Finally, the steels were cast into a water-cooled copper mold placed in the furnace chamber. From each melt, two ingots with the dimensions of \( 220 \times 35 \times 95 \) mm\(^3\) were cast and then machined to round tensile specimens. To eliminate the possible machining-induced martensite in the manufactured tensile specimens, the heat treatment step was performed just prior to tensile tests. Chemical compositions of the five cast steels produced in this manner and their respective SFEs at RT according to the empirical relationship proposed by Dai et al. \([24]\) are given in Table 1.

#### 2.2. Constitutional diagram and heat treatment

In order to determine optimal heat treatment conditions for the five as-cast steels, thermodynamic calculations using Thermo-Calc were carried out. The pseudo-binary phase diagram for Fe–15Cr–3Mn–3Ni–0.5Si–0.1N alloys containing up to 0.3 mass-%C is shown in Fig. 1. For the complete dissolution of carbides and carbonitrides as well as the reduction of segregation originating from the solidification, the as-cast microstructure was homogenized in the single-phase austenitic phase field (fcc) under an argon atmosphere. The carbon dependent heat treatment temperatures were chosen in the upper area of the thermodynamic stability range of the fcc phase. It is clearly shown in the constitutional diagram that a higher carbon content increases the dissolution temperature of \( M_{23}C_6 \) (M denotes Fe and substitutional alloying elements notably Cr) carbides. Accordingly, the solution annealing temperature of alloys was adjusted based on their carbon content as listed in Table 2. All the steels were water quenched to ensure the suppression of precipitation formation processes during cooling from the annealing temperature.

#### 2.3. Dilatometry measurements

A BÄHR 80A/D quenching and deformation dilatometer was used to determine the austenite start (\( A_s \)), austenite finish (\( A_f \)), and martensite start (\( M_s \)) temperatures. For dilatometry, 10 mm-long hollow cylindrical specimens with an inner diameter of 2 mm and an outer diameter of 4 mm, were taken from ingots in the as-cast condition. The specimens were heated up with a heating rate of 10 °C s\(^{-1}\) to the austenitization temperature and held for 3 min followed by cooling to −130 °C at a cooling rate of 50 °C s\(^{-1}\). In dilatometry cycles, austenitization temperature of all alloys except the NC25 was chosen according to Table 2. For the steel NC25, austenitization temperature was set to 1180 °C which was the highest operation temperature of the dilatometer used. To obtain a

### Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Fe + others</th>
<th>SFE at RT [m J m(^{-2})]</th>
<th>[24]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC05</td>
<td>0.052</td>
<td>0.103</td>
<td>14.90</td>
<td>2.86</td>
<td>3.11</td>
<td>0.51</td>
<td>bal.</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>NC10</td>
<td>0.100</td>
<td>0.107</td>
<td>15.20</td>
<td>2.89</td>
<td>3.20</td>
<td>0.48</td>
<td>bal.</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>NC15</td>
<td>0.155</td>
<td>0.122</td>
<td>14.90</td>
<td>2.91</td>
<td>2.97</td>
<td>0.53</td>
<td>bal.</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>NC20</td>
<td>0.200</td>
<td>0.106</td>
<td>15.10</td>
<td>3.23</td>
<td>2.99</td>
<td>0.49</td>
<td>bal.</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>NC25</td>
<td>0.250</td>
<td>0.132</td>
<td>14.90</td>
<td>3.03</td>
<td>3.02</td>
<td>0.57</td>
<td>bal.</td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solution annealing T [°C]</th>
<th>Quenching t [min]</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC05</td>
<td>1050</td>
<td>30</td>
<td>Water</td>
</tr>
<tr>
<td>NC10</td>
<td>1050</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>NC15</td>
<td>1150</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>NC20</td>
<td>1150</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>NC25</td>
<td>1200</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>
more pronounced contraction during the $\alpha' \rightarrow \gamma$ reversion in the heating step, all specimens were quenched into liquid nitrogen ($-196 \degree C$) prior to dilatometry cycles. This measure was taken to increase the fraction of as-quenched $\alpha'$-martensite in the metastable steels.

2.4. Tensile tests and magnetic measurements

The heat treated specimens were tensile-tested in a Zwick 1476 universal testing machine. The crosshead velocity was set to 1 mm s$^{-1}$ corresponding to an initial strain rate of $4 \times 10^{-4}$ s$^{-1}$. The strain was measured by means of a clip-on extensometer. With the aid of a thermal-chamber which surrounded the tensile specimen and its fixtures, different temperatures in the range of $-40$ to $200 \degree C$ could be adjusted. For tensile testing round specimens with a gauge diameter of 6 mm and a gauge length of 30 mm were prepared in accordance with the DIN 50125 standard.

For the quantification of the ferromagnetic phase constituents, a Metis MSAT magnetic saturation device equipped with a Lake Shore 480 model fluxmeter was used. The equipment measures the magnetic flux density of samples magnetized until saturation in an external magnetic field with an intensity of over 300 kA m$^{-1}$. The ferromagnetic phase content was quantified based on the measured magnetic flux density after corrections for the effect of alloying elements on the magnetic moment of pure iron.

2.5. XRD and hardness measurements

To quantify the microstructural constituents, X-ray diffraction (XRD) measurements with CuK$_\alpha$ radiation were conducted using a Seifert-PM RD7 diffractometer. Sample preparation for XRD consisted of hot grinding to minimize the transformation of austenite during sample preparation followed by electro-polishing.

The occurrence of decarburization and denitriding on the surface was confirmed by Vickers micro-hardness profile measurements in the radial direction of tensile-tested NC20 and NC25 steels. Hardness measurements were done using a SHIMADZU HMV-2000 indenter. To reduce the spacing between the consecutive indentation points to 15 $\mu$m, a small indentation load of 0.049 N (HV0.005) was used.

3. Results and discussion

3.1. Microstructure of cast Steels after solution annealing

The initial microstructure at ambient temperature of steels after solution heat treatments was martensitic-austenitic for all steels except the NC25 alloy which had a fully austenitic microstructure. Light optical microscopy examination confirmed the absence of delta ferrite in the microstructure of steels.

For a simple assessment of the resistance against the $\gamma \rightarrow \alpha'$ formation of stainless steels, the well-known Schaeffler diagram was consulted. This constitutional diagram was originally developed for the microstructure prediction subsequent to the welding of high-alloy steels [25]. Nevertheless, it may as well be used for the prediction of cast microstructures [26,27]. By means of the following Ni- and Cr-equivalent equations by Weiss et al. [28], the austenite stability was calculated.

$$\text{Ni}_{\text{eq}} = \%\text{Ni} + 30\%\text{C} + 18\%\text{N} + 0.5\%\text{Mn} + 0.3\%\text{Co} + 0.2\%\text{Cu} - 0.2\%\text{Al}$$

$$\text{Cr}_{\text{eq}} = \%\text{Cr} + \%\text{Mo} + 4\%\text{Ti} + 4\%\text{Al} + 1.5\%\text{Si} + 1.5\%\text{V} + 0.9\%\text{Nb} + 0.9\%\text{Ta} + 0.5\%\text{W}$$

The calculated Cr- and Ni-equivalent values for the alloys are listed in Table 3. The Schaeffler diagram with the position of cast steels is presented in Fig. 2. Numbers next to the symbols in Fig. 2 denote the as-quenched $\alpha'$-martensite content according to MSAT measurements in the solution annealed condition of alloys. The occurrence of as-quenched martensite which was also predicted by the Schaeffler diagram indicates the low austenite stability of the alloys.

Fig. 3 shows the evolution with the temperature of equilibrium phase fractions in alloys. The solidification of all alloys was predicted to begin with the formation of primary ferrite and proceed with the second-phase austenite formation in the later stages of solidification (FA mode of solidification). Because of the austenite-stabilizing effect of carbon, the fraction of primary ferrite decreases from the alloy NC05 to NC25. Changes in the primary ferrite content have important consequences for the segregation and nitrogen solubility of the alloys. On the one hand, a high primary ferrite fraction leads to an enhanced compositional homogeneity of steels. This is due to the higher diffusivity of the main alloying elements in the ferrite which is almost 100 times that in the austenite. On the other hand, the lower solubility of nitrogen in the ferrite compared to that in the austenite facilitates the pore formation during casting of the high-N ingots.

According to thermodynamic calculations, increasing carbon content from NC05 to NC25 displaces the stability range of single-phase austenite to higher temperatures, enabling austenitization at higher temperatures which is beneficial for the purpose of homogenization. Furthermore, the stability of precipitates increases with increasing carbon content. For instance, as the carbon concentration increases, the calculated full dissolution temperature of M$_2$3C$_6$ carbides increases from 860 °C (NC05) to 1025 °C (NC25).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Creq [-]</th>
<th>Nieq [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC05</td>
<td>15.67</td>
<td>7.83</td>
</tr>
<tr>
<td>NC10</td>
<td>15.92</td>
<td>9.52</td>
</tr>
<tr>
<td>NC15</td>
<td>15.70</td>
<td>11.24</td>
</tr>
<tr>
<td>NC20</td>
<td>15.84</td>
<td>12.63</td>
</tr>
<tr>
<td>NC25</td>
<td>15.76</td>
<td>14.42</td>
</tr>
</tbody>
</table>

Fig. 2. Positions of the cast steels in the Schaeffler diagram adapted from Ref. [28]. Numbers next to each symbol denote the as-quenched martensite fractions based on MSAT measurements.
Fig. 3. Equilibrium phase fraction diagrams calculated with Thermo-Calc: (a) NC05 steel; (b) NC10 steel; (c) NC15 steel; (d) NC20 steel and (e) NC25 steel.
functions of the sum of C and N. The derived linear relationships
dictative of an increased austenite stability. Due to the comparable
decrease with increasing C content from 0.05 to 0.25 mass-% in-
measurements.
fraction of

tensite formation after dilatometry cooling to
metry specimens cooled to
°C0

expansion was detected during dilatometry cooling to room tem-
perature. Since no
temperatures were below room temperature was enabled by a

3.2. Dilatometry analysis of the \( \gamma \rightarrow \alpha' \) transformation behavior

The \( M_s, A_s, \) and \( A_f \) temperatures obtained from subzero dilato-
metries are given in Table 4. All alloys exhibited as-quenched mar-
tensite formation after dilatometry cooling to \(-130^\circ\text{C}\). The \( M_s \) temperatures were determined using the strain offset method [29]
at an offset strain corresponding to 1 vol.% \( \alpha' \). The quantification of
\( A_s \) and \( A_f \) temperatures for steels NC15, NC20 and NC25 whose \( M_s \) temperatures were below room temperature was enabled by a
prior liquid nitrogen treatment of dilatometry specimens. Since no
expansion was detected during dilatometry cooling to room tem-
perature of NC15 and NC20 alloys, the low martensite fractions
after solution annealing of these alloys (Fig. 2) are likely due to the
martensite formation near the surface as discussed later. Table 4
also includes the as-quenched \( \alpha' \)-martensite fractions in dilatol-
metry specimens cooled to \(-130^\circ\text{C}\) determined by MSAT
measurements.

Obviously, the phase transformation temperatures in Table 4
decrease with increasing C content from 0.05 to 0.25 mass-% indi-
cative of an increased austenite stability. Due to the comparable
concentration of alloying elements other than C and N in all alloys,
the phase transformation temperatures were expressed as linear
functions of the sum of C and N. The derived linear relationships
for \( M_s, A_s, \) and \( A_f \) temperatures are given in Eqs. (3)–(5) and also
plotted in Fig. 4.

\[
M_s = -680.59\%C + 220.16^\circ\text{C}
\]

(3)

\[
A_s = -150.09\%C + 694.98^\circ\text{C}
\]

(4)

\[
A_f = -104.57\%C + 870.11^\circ\text{C}
\]

(5)

In Fig. 4, the dependence on the interstitial content of the \( M_s, \)
temperature is compared with the calculated values based on the
empirical relationships by Eichelmann and Hull (Eq. (6)) [30] and
Pickering (Eq. (7)) [31] as listed below.

\[
M_s = 1350 - 1665\%C + 28\%Si - 33\%Mn - 42\%Cr - 61\%
N\]

\[
Ni^\circ\text{C}
\]

(6)

\[
M_s = 502 - 810\%C - 1230\%N - 13\%Mn - 30\%Ni - 12\%
Cr - 54\%Cu - 46\%Mo^\circ\text{C}
\]

(7)

Compared to the experimental results, the above equations
which have been derived for interstitially-alloyed stainless steels
predict a larger dependence on the (C+N) concentration of the \( M_s \)
temperature.

It is worth mentioning that none of the investigated steels
exhibited full \( \gamma \rightarrow \alpha' \) transformation. This could be associated with
a decrease in the chemical driving force for the spontaneous \( \alpha' \)-
martensite formation \((\Delta G' - \alpha')\) after passing through a maximum
at cryogenic temperatures. Reduction in the chemical driving force
for the \( \gamma \rightarrow \alpha' \) transformation likely originates from changes in the
magnetic state of austenite for instance a transition from parama-
agnetism to antiferromagnetism at Néel temperature \((T_N)\). This
transition is associated with changes in the physical properties of
austenite such as a decrease in the shear modulus \((G)\), Young’s
modulus \((E)\), thermal conductivity \((\lambda)\), and thermal expansion
\((\alpha_{th})\), and an increase in the Poisson’s ratio \((\nu)\) [32,33]. Because of the
magnetic ordering during the paramagnetic to anti-
ferromagnetic transition which reduces the entropy \((S)\) of the
austenite, the temperature dependence of the Gibbs free energy
for the austenite phase \((G^0)\) is decreased below the \( T_N \) [34]. As a
consequence of a change in the slope of the \( G^0 \) curve, the
thermodynamic driving force of the martensitic transformation \((\Delta G' -
\alpha')\) may increase at a lower rate or even decrease at temperatures
below \( T_N \). This implies that the maximum as-quenched mar-
tensite fraction might be generated in the vicinity of the \( T_N \)
without further martensite formation upon continued cooling. In
other words, the as-quenched \( \gamma \rightarrow \alpha' \) martensite transformation
may come to a standstill below the \( T_N \). With the aid of the CAL-
PHAD method [35] using Thermo-Calc version S [36], the \( T_N \) of
alloys was calculated after the extrapolation of the available
thermodynamic database to temperatures below RT. Due to the
low sensitivity of the \( T_N \) to the carbon content of alloys, the
calculated Néel temperatures of alloys remained between \(-132^\circ\text{C}\)
and \(-128^\circ\text{C}\).

To examine the low-temperature evolution of as-quenched \( \alpha' \)-
martensite fraction, solution annealed cylindrical specimens 6 mm
in diameter and 3.5 mm in length were isothermally held at var-
ious temperatures between RT and \(-196^\circ\text{C}\). The holding time at
each temperature was 10 min. The ferromagnetic phase fraction
was subsequently determined by MSAT measurements. Fig. 5
presents the \( \gamma \rightarrow \alpha' \) transformation behavior below RT of the in-
vestedigated as-cast steels. The curves confirm the incomplete
transformation to \( \alpha' \)-martensite at temperatures as low as
\(-196^\circ\text{C}\). Moreover, a diffuse maximum in the martensite fraction
of all alloys (marked by symbol * in Fig. 5) was noticed in the
examined temperature range. The less obvious decrease in the \( \alpha' \)-
martensite fraction of NC05, NC15, and NC25 alloys at tempera-
tures below the marked maxima in Fig. 5 might be related to the
use of only one specimen per temperature in the subzero cooling
treatments. After all, compositional inhomogeneities originating
from the casting step may not be fully eliminated in the sub-
sequent heat treatment step. Although specimens quenched to
temperatures below the maximum martensite fraction were
shortly exposed to the temperature associated with the maximum
martensite fraction, they do not contain as much martensite.

### Table 4

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( M_s ) [°C]</th>
<th>( A_s ) [°C]</th>
<th>( A_f ) [°C]</th>
<th>As-quenched martensite after dilatometry cooling to (-130^\circ\text{C} ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC05</td>
<td>134</td>
<td>671</td>
<td>856</td>
<td>82</td>
</tr>
<tr>
<td>NC10</td>
<td>72</td>
<td>663</td>
<td>848</td>
<td>67</td>
</tr>
<tr>
<td>NC15</td>
<td>13</td>
<td>657</td>
<td>840</td>
<td>58</td>
</tr>
<tr>
<td>NC20</td>
<td>0</td>
<td>649</td>
<td>835</td>
<td>18</td>
</tr>
<tr>
<td>NC25</td>
<td>(-20)</td>
<td>636</td>
<td>833</td>
<td>15</td>
</tr>
</tbody>
</table>

![Fig. 4](image-url)
Therefore, a small contribution of isothermal martensite to the total martensite fractions in Fig. 5 is quite likely. Isothermal martensite can occur in steels with low SFEs due to an increasing dissociation width of partial dislocations during holding at cryogenic temperatures [37,38]. The growing stacking faults are then able to intersect and form martensite. Lower martensite fractions at temperatures below the maximum can be explained by the absence or a lower rate of isothermal martensite formation. Since the temperatures associated with the maximum $\alpha'$-martensite formation in Fig. 5 are reasonably close to the calculated Néel temperatures of the alloys (−128 °C to −132 °C), the absence or the lower rate of martensitic transformation at very low temperatures might originate from a change in the magnetic state of austenite and a decrease in the thermodynamic driving force for the $\gamma \rightarrow \alpha'$ transformation.

3.3. Mechanical properties and microstructure evolution

Fig. 6 shows the stress–strain curves, the strain-hardening behavior, and the evolution of $\alpha'$-martensite phase fractions for tensile tests at RT. According to the $M_s$ temperatures in Table 4, the microstructure prior to tensile tests at room temperature must be austenitic–martensitic for the NC05 and NC10 alloys and fully austenitic for the remainder of alloys with higher interstitial contents. Small fractions of as-quenched $\alpha'$-martensite were however quantified by the MSAT measurements of solution
annealed NC15, NC20, and NC25 alloys (Fig. 2). This might be related to a more pronounced surface decarburization and denitriding during furnace heat treatments compared to the dilatometry. Moreover, some additional α' martensite might have been induced during the cutting of specimens used for MSAT measurements in the solution annealed condition. The quantification of the α'-martensite induced by tensile deformation was done by the subtraction of as-quenched martensite fractions from the values determined in the uniformly-elongated gauge section of tensile specimens strained until fracture. Due to the low mechanical stability of austenite, deformation-induced α'-martensite occurred during tensile testing of all alloys. The low mechanical stability of austenite is thought to be responsible for the low RT tensile ductilities. Due to the presence of a high fraction of as-quenched martensite, the fraction of deformation-induced α'-martensite in NC05 and NC10 alloys was very small. The strain-hardening rate of the NC05 alloy resembles that of martensitic steels with an initially high rate of strain-hardening which rapidly decreases at higher strains [8]. The rapid decrease in the strain-hardening rate of the NC05 alloy resembles that of martensitic steels with an initially high rate of strain-hardening which rapidly decreases at higher strains [8].

The deformation-induced formation of α'-martensite in NC10 and NC15 alloys with higher fractions of austenite, on the other hand, was reflected in the form of an inflection point in their stress–strain curves or an increase in their strain-hardening rates. The inflection point in both alloys occurred at very small strains. The occurrence of an inflection point in the stress–strain curve is a characteristic of metastable austenitic steels undergoing deformation-induced α'-martensite formation [9,39–41]. Inflection points in stress–strain curves were similarly observed for the NC20 and NC25 alloys. Nevertheless, due to the increased stability of austenite in the latter alloys with higher concentrations of interstitial alloying elements, the inflection points appeared at higher strain levels.

According to the Considère criterion for the onset of plastic instability, the true strain-hardening rate at the point of necking must be equal to the true stress. This criterion may be represented by the superimposition of true stress–strain curves on true strain-hardening curves. The intersection point of these curves will then mark necking. As shown in Fig. 6b, the Considère criterion is not satisfied for the RT-tested tensile specimens. The deviation between these two curves at the maximum stress level is marked by vertical arrows. The premature fracture of RT tensile specimens is attributed to the presence of as-quenched α'-martensite and/or the early deformation-induced transformation of the austenitic constituent with a low mechanical stability at RT. The presence of untempered α'-martensite with high interstitial contents can facilitate the crack formation and lead to brittle fracture without post-uniform elongation [42]. Although fracture in alloys with higher interstitial contents was postponed to higher strains, they exhibited a higher sensitivity to the embrittlement caused by α'-martensite formation. Accordingly, fracture in the presence of higher interstitial contents occurred after the formation of smaller amounts of deformation-induced α'-martensite.

In addition to magnetic saturation measurements, XRD was used for the phase analysis of the examined steels. In particular, XRD allows to evaluate the possibility of ε-martensite formation, Fig. 7 shows the XRD patterns in the solution annealed and tensile strained conditions of the NC05 and NC25 steels with the lowest and highest carbon contents, respectively. The heat treated
The microstructure of the NC05 steel (Fig. 7a) was found by quantitative XRD analysis to consist of 87 vol% $\alpha'$-martensite, 12 vol% austenite, and 1 vol% $\varepsilon$-martensite. The higher fraction of $\alpha'$-martensite compared to the MSAT estimation of 79 vol% might be due to the partial transformation of austenite during sample preparation for XRD. After tensile straining at RT, XRD results indicated a fully $\alpha'$-martensitic microstructure for the NC05 steel. This result suggests that the deformation-induced transformation of austenite in the NC05 alloy might have occurred according to the $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ sequence which is also a common observation in low SFE Fe-Cr-Ni [39,43,44] and Fe-Cr-Mn-Ni [14,45-47] stainless steels.

The study of the evolution of austenite in the NC25 steel was facilitated by the increased stability of austenite which led to the presence of a higher fraction of untransformed austenite prior to the tensile test. The XRD pattern in the solution annealed condition of the NC25 steel (Fig. 7b) confirmed that the microstructure was fully austenitic, which is in a good agreement with the MSAT quantification. The extra low-intensity peaks visible in the XRD pattern of the solution annealed NC25 steel and some other patterns in Fig. 7, denoted by arrows, are the parasitic diffraction peaks due to the tungsten deposition on the X-ray anode (tungsten $L_\alpha$ radiation with a wavelength of 0.147639 nm) and may be therefore neglected. The quantitative XRD analysis after tensile straining at RT of the NC25 alloy confirmed the presence of 12 vol% $\varepsilon$-martensite in coexistence with 56 vol% austenite and 32 vol% $\alpha'$-martensite. The results suggest that although the alloys might be free of $\varepsilon$-martensite in the solution annealed condition, the formation of strain-induced $\varepsilon$-martensite during tensile straining cannot be excluded. The XRD results in Fig. 7 also include the lattice parameters of austenite in the NC05 and NC25 alloys. The larger lattice parameter of austenite in the NC25 alloy is in accord with the well-known effect of C on the lattice dilatation of austenite.

Examination of the cross section in the gauge length of tensile strained specimens confirmed the presence of cracks near the surface. Cracks on the surface of the NC25 alloy are typified in Fig. 8. The presence of cracks near the surface layer is thought to originate from decarburization and/or denitriding processes during heat treatments particularly in the case of heat treatments at 1150 °C (NC15 and NC20) and 1200 °C (NC25). The reduced C and N content of austenite then resulted in a lower stability of austenite in such regions compared to the bulk material. The consequence was a ready formation of deformation-induced martensite near the surface leading to an earlier onset of surface crack formation and propagation.

Fig. 9 shows the microstructure near the surface of tensile specimens of NC20 and NC25 alloys after tensile straining until fracture at RT. The outer surface layer consists almost entirely of martensite. At farther distances from the surface, the microstructure becomes martensitic–austenitic and the fraction of austenite increases. Martensitic transformation and crack formation in the alloys is therefore triggered near the surface and then propagates to the inner sections of the material. The cracks in the micrographs of Fig. 9 appear to have grown along the prior austenite grain boundaries. This suggests that the intergranular oxidation during heat treatments might have facilitated the crack formation in the outermost martensitic layer of tensile specimens.

To confirm the occurrence of decarburization and denitriding, hardness profiles were measured in the radial direction of tensile-tested NC20 and NC25 steels. The hardness profiles are presented in Fig. 10. The decrease in hardness upon approaching the center of the material could be confirmed for both steels. The highest hardness numbers were measured near the surface which implies the presence of martensite and further verifies the loss of carbon and/or nitrogen. Below the outer martensitic layer, the microstructure consisted of martensite and austenite with high and low hardness values, respectively, which caused fluctuations in the hardness profile. The segregation of alloying elements during solidification, which could not be eliminated by solution annealing, is responsible for the observed distribution of deformation-induced martensite in the microstructure as shown in Fig. 9b and the associated hardness fluctuations in Fig. 10. In this respect, the
formation of martensite preferentially occurs in regions containing a lower concentration of alloying elements which are usually near the dendritic cores [48]. As a result of a more pronounced surface decarburization and/or denitriding in the NC25 steel which was heat treated at a higher temperature than the NC20 alloy (1200 °C vs 1150 °C), the martensitic layer at the surface of the NC25 alloy was thicker and had a lower hardness compared to the NC20 alloy. The former statement could be understood from the fact that the hardness fluctuations associated with the presence of austenite begin at a smaller depth from the surface in the case of the NC20 alloy.

Fig. 11 shows the stress–strain curves, the strain-hardening behavior, and the evolution of α’-martensite phase fraction for the tensile tests at 200 °C. According to Fig. 11c, the fraction of deformation-induced α’-martensite remains negligible for almost all alloys. The small fractions of deformation-induced α’-martensite in NC15, NC20, and NC25 alloys are expected to have formed near the surface due to the local loss of C and N. The absence of deformation-induced α’-martensite in NC05 and NC10 alloys with an already high fraction of as-quenched martensite might then have been caused by a process similar to that occurring during the quenching and partitioning (Q&P) processing [42,49,50]. Nevertheless, due to the short diffusion distance of interstitial atoms within the timeframe of tensile tests at 200 °C (approximately 20 min), a uniform interstitial concentration profile in the austenite may not be achieved. Accordingly, the calculated diffusion distance of carbon in the austenite containing 0.1 mass-%C remains in the range of 4–20 nm after a diffusion time of 20 min at 200 °C [51–53]. More precisely, the escape of interstitial atoms from the supersaturated martensitic plates to the martensite nucleation sites near the γ-α’ boundaries, which is the most likely mechanism for the low-temperature thermal stabilization of austenite [38] and has been demonstrated in numerous atom probe tomography studies of as-quenched austenitic–martensitic steels [54–56], accelerates upon exposure to 200 °C of tensile specimens. The enhanced stability of austenite with respect to the α’-martensite formation in the subsequent liquid nitrogen treatment step was further studied using a solution annealed specimen of the NC10 alloy containing 46 vol% α’-martensite at room temperature (Fig. 5b) which was additionally soaked for 20 min at 200 °C. Liquid nitrogen treatment of the latter specimen did not increase the α’-martensite fraction. As shown in Fig. 5b, a solution annealed specimen of the NC10 alloy without exposure to 200 °C will form an additional α’-martensite fraction of approximately 17 vol% after liquid nitrogen treatment. Therefore, the modification of the interstitial concentration profile in the vicinity of the γ-α’ boundaries must have contributed to an increased stability of austenite in the NC05 and NC10 alloys with a high α’-martensite fraction. Regardless of the presence or the absence of as-quenched α’-martensite in the microstructure, the decrease in the ΔG°γ-α’ is assumed to be the main reason behind the absence or the low fractions of deformation-induced α’-martensite after tensile tests at 200 °C.

As the interstitial content of alloys increased, the stress–strain...
behavior of alloys transitioned from that characteristic of martensitic steels namely an initially high but rapidly decreasing rate of strain-hardening to that of stable austenitic steels characterized by near-linear strain-hardening. The low rate of decrease in the strain-hardening rate of alloys with higher interstitial contents is thought to be responsible for the enhanced elongations, namely 54% and 61% for the NC20 and NC25 alloys, respectively.

The improved tensile elongation of austenitic steels at raised tensile deformation temperatures where the deformation-induced $\alpha'$-martensite formation is suppressed is a characteristic of many metastable austenitic steels and fcc metals [8,9,11,13,41,57–62]. In the absence of martensitic transformation, strain in the austenite is accommodated by the glide of dislocations. The temperature dependence of the SFE which controls the dissociation distance of partial dislocations and therefore the ease of the cross slip then decides the extent of glide planarity [63–65]. The latter parameter in turn influences the strain-hardening rate and therefore the uniform tensile elongation of austenitic steels [48].

The temperature dependence of the stress-strain behavior and the strain-hardening rate for the NC25 alloy is shown in Fig. 12. Before tensile straining at $-40^\circ$C, an as-quenched martensite fraction of almost 9 vol% formed in the microstructure. Due to the

---

**Fig. 11.** Mechanical properties and phase evolution during deformation at $200^\circ$C: (a) engineering stress–strain-curve; (b) strain-hardening behavior and (c) evolution of $\alpha'$-martensite phase fractions.

**Fig. 12.** Temperature dependence of stress–strain behavior (a) and corresponding strain-hardening rates (b) for the NC25 alloy. Numbers next to the curves in (a) denote the total $\alpha'$-martensite content in the gauge section of tensile specimens after straining until fracture.
low mechanical stability at –40 °C of the austenite, a further α'-martensite fraction of 34 vol% was induced by tensile straining until fracture. The occurrence of deformation-induced α'-martensite caused an increase in the strain-hardening rate. At RT, the increase in the work-hardening rate which is proportional to the rate of α'-martensite formation was smaller. The delayed formation of α'-martensite in turn resulted in a higher tensile elongation. At 100 °C, a total α'-martensite fraction of only 2 vol% was quantified after a uniform tensile elongation of 27%. This martensite was formed near the surface and facilitated the formation of surface cracks. The high ductility of the austenite at inner sections of the tensile specimen, however, inhibited immediate rupture of tensile specimen after the maximum stress level was reached. The premature fracture at 100 °C of tensile specimen was reflected in the fact that the Considère criterion was not satisfied (Fig. 12b). Eventually at 200 °C, the suppression of deformation-induced α'-martensite formation and the enhanced toughness of the α'-martensite at surface, which could at least temper by forming transition carbides/carbo nitrides [42], are thought to be responsible for the enhanced ductility.

4. Conclusions

The spontaneous and deformation-induced formation of α'-martensite was investigated in five interstitial-containing Fe–15Cr–3Ni–3Mn–0.5Si–0.1N–(0.05–0.25)C as-cast steels with austenitic and austenitic–martensitic microstructures at RT. The contribution of deformation-induced α'-martensite formation to the strain-hardening behavior was studied by tensile tests at temperatures between –40 °C and 200 °C. The main conclusions are as follows:

1. Increase in the carbon content raised the austenite stability with respect to both deformation-induced and thermally-induced α'-martensite formation. Furthermore, the phase transformation temperatures $M_s$, $A_s$, and $A_f$ decreased with increasing carbon content.

2. Full martensitic transformation of austenite could not be achieved at temperatures as low as –196 °C. This might be related to the constancy or reduction of the chemical driving force for the γ→α' transformation at temperatures below the Néel temperature.

3. As a result of the low mechanical stability of austenite in alloys with lower interstitial contents, the deformation-induced α'-martensite formed more readily during RT tensile tests. This led to the premature fracture of tensile specimens, namely fracture at strains short of that predicted by the Considère criterion. The premature fracture of tensile specimens was assisted by the presence of surface decarburization and denitriding which facilitated the formation of surface cracks.

4. The increased stability of austenite during tensile deformation at 200 °C resulted in the suppression of deformation-induced α'-martensite formation. As a consequence, a tensile elongation of 61%, comparable to typical values for conventional austenitic stainless steels deformed at RT, was achieved in the NC25 alloy.

Acknowledgment

The authors gratefully acknowledge Mr. Schreiber from the Institute of Material Science for performing the XRD measurements and the financial support of this research by the German Research Foundation (DFG) within the framework of the Collaborative Research Center 799 (CRC 799).

References