Thermally activated growth of lath martensite in Fe–Cr–Ni–Al stainless steel

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Thermally activated growth of lath martensite in Fe–Cr–Ni–Al precipitation hardenable stainless steel

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The austenite to martensite transformation in a semi-austenitic stainless steel containing 17 wt-%Cr, 7 wt-%Ni and 1 wt-%Al was investigated with vibrating sample magnetometry and electron backscatter diffraction. Magnetometry demonstrated that, within experimental accuracy, martensite formation can be suppressed on fast cooling to 77 K as well as on subsequent fast heating to 373 K. Surprisingly, martensite formation was observed during moderate heating from 77 K, instead. Electron backscatter diffraction demonstrated that the morphology of martensite is lath type. The kinetics of the transformation is interpreted in terms of athermal nucleation of lath martensite followed by thermally activated growth. It is anticipated that substantial autocatalytic martensite formation occurs during thermally activated growth. The observation of a retardation of the transformation followed by a new acceleration during slow isochronal (i.e. at constant rate) cooling is interpreted in terms of the combined effect of the strain energy introduced in the system during martensite formation, which thermodynamically and/or mechanically stabilises austenite, and autocatalytic nucleation of martensite.

Keywords: Isothermal martensite, Steels, Sub-zero Celsius treatment, Magnetometry

Introduction

Martensite in iron based alloys can appear as laths, characterised by an internal sub-structure with a high density of dislocations,1,2 or as plates, which are partially3,4 or fully5 internally twinned.6 Regardless of the morphology of martensite, the kinetics of martensite formation is historically described as nucleation-controlled,7 with the implicit assumption of instantaneous growth of martensite upon nucleation.

However, growth of lath martensite proceeds at a velocity in the range of $10^{-2}$ to $10^{-1}$ m s$^{-1}$ (Ref. 8) and is therefore not instantaneous, but time-dependent. In Refs. 9–10 a growth rate for lath martensite formation in the order of $10^{-3}$ mm s$^{-1}$ was reported9 and a martensite formation event was estimated to last $10^{-3}$ s.10 Although these observations are consistent with time-dependent martensite formation (Ref. 8), surprisingly they were considered to corroborate nucleation-controlled descriptions.7

Time-dependent growth of lath martensite was followed in-situ by microscopical investigations in Refs. 11–15 and it was observed to induce time-dependent (autocatalytic) nucleation of lath martensite.12,13,15 After initial nucleation and growth, autocatalytic nucleation is responsible for an acceleration of the rate of the transformation.7,16 Autocatalytic nucleation of martensite can result in the abrupt transformation of a part of the material in an instantaneous event, a so-called burst.17 A burst takes place within a millisecond,18 implying that it cannot rely on substantial growth of martensite nuclei.

Autocatalytic nucleation can occur within the same austenite grain wherein martensite has already formed and/or in neighbouring austenite grains.19,20 According to Ref. 21, martensite formation occurs in a limited number of austenite grains and extends throughout the entire material by autocatalysis. Autocatalysis consists of the activation of pre-existing nucleation sites in austenite and in the formation of new martensite embryos during the transformation process. Following Ref. 22, these nucleation processes are of stress assisted and strain induced type, respectively.

Clearly, suppressing autocatalytic nucleation may result in suppressing a major part of the transformation. Suppression of martensite formation by fast cooling was demonstrated in Ref. 23 and was rationalised as an intrinsic characteristic of steels.24 Upon suppressing martensite formation by fast cooling, subsequent martensite formation can occur on controlled (slow) heating.23 Furthermore, continuous martensite formation can be inhibited by the transformation process itself.

The formation of martensite introduces both elastic and plastic strains in the remaining austenite (and in
martensite as well). Hydrostatic (elastic) stress opposes the volume expansion associated with martensite formation and thus counters the continuation of martensite development. On the other side, shear stress components promote the transformation of austenite into martensite (both nucleation, i.e. stress assisted, and growth). Plastic deformation by dislocation production in austenite stabilises austenite against movement of an existing martensite/austenite interface in austenite, often referred to as mechanical stabilisation of austenite. Conversely, dislocations in austenite have been considered as martensite nucleation sites and hence can promote martensite formation.

The total strain energy, i.e. all elastic and all plastic contributions, together with the interfacial energy stored in the created austenite/martensite interfaces counteract the (chemical) driving force for martensite formation. When the total strain and interfacial energy that accompany the transformation outweigh the energy gain provided by the driving force, further martensite formation is not possible.

Omitting the energy stored at newly created interfaces (A similar omission was made for considering the energy balance involved in the massive fcc to bcc transformation (Refs. 59–61). It is noted that even though the total interfacial energy is anticipated to be small as compared to the absolute values of driving force and total strain energy, it may have a substantial value as compared to the difference between driving force and total strain energy.), the kinetics of fcc to bcc transformation in steel is macroscopically controlled by the balance of the total strain energy introduced in the system and the driving force for martensite formation that is governed by the undercooling. According to Refs. 39 and 40, this balance is essential for the observation of athermal martensite transformation kinetics in steel.

Regarding the microstructure, for lath martensite, austenite grains are subdivided by martensite formation at four length scales. Firstly austenite grains are divided into groups of laths with the same habit plane, so-called packets. Each packet contains several blocks, which are groups of laths with one or two variants of the orientation relationship with parent austenite. Block boundaries are high-angle boundaries. The individual laths represent the smallest level of subdivision.

In Ref. 15, continuous growth of lath martensite was observed to promote autocatalytic nucleation (mainly) within a single block of laths. In Refs. 12 and 13, continuous growth of lath martensite was observed to promote the generation of new martensite variants, leading to the formation of new blocks and packets. Finally, in-situ (synchrotron) X-ray diffraction investigations in Ref. 25 suggested that autocatalytic nucleation of lath martensite spreads the transformation over neighboring austenite grains.

Accordingly, the applicability of fully nucleation-controlled kinetics can be questioned. In Refs. 44–46 time-dependent formation of lath martensite was interpreted in terms of thermally-activated nucleation, while in Refs. 47 time-dependent lath martensite formation was described in terms of thermally activated growth of athermally formed nuclei.

The purpose of the present work is to contribute to understanding the kinetics of lath martensite formation. For this purpose, a Fe–17Cr–7Ni–1Al (wt-%) stainless steel was chosen with $M_T$ close to room temperature. In this steel grade isothermal martensite formation at sub-zero Celsius temperature is industrially exploited.

Martensite formation was investigated by magnetometry, which has been demonstrated to be an accurate technique to study the martensitic transformation in iron-based alloys. Magnetometry was supplemented by electron backscatter diffraction, which was applied to evaluate the morphology of martensite.

### Experimental methods

#### Material and heat treatments

The material used in the present work is a 0.15 mm thick foil AISI 631 stainless steel, which essentially is a Fe–17Cr–7Ni–1Al (wt-%) alloy, supplied by Goodfellow Cambridge Ltd in rolled condition with the chemical composition reported in Table 1.

Two sets of samples, 0.15 mm thick disks 3 mm in diameter, were prepared from the rolled condition for magnetometry investigation: a first set of three samples I, II and III; a second set of three samples A, B and C. An additional plate shaped sample $10 \times 10 \times 0.15$ mm was prepared for microstructure investigation.

Austenitisation of samples was performed in argon at $1127 \pm 10$ K for 0.6 ks and cooled to 423 K at an approximate average rate of 20 K min$^{-1}$ in an argon flow. Hereafter the flow was interrupted and the samples were slowly cooled to room temperature in the sealed furnace. The carbon content was measured in separate samples before and after austenitisation and remained constant within experimental accuracy (i.e. $\pm 0.01\%$).

The as-quenched material was stored at 295 ± 2 K for about 10 Ms (4 months) before magnetometry investigation; this is the controlled temperature in the room where magnetometry was performed. The additional sample, which was used for microstructure investigation, was stored at room temperature for about 30 Ms (12 months).

The two sets of samples prepared for magnetometry investigation were considered for two sets of experiments. In the first set of experiments, after storage, samples I, II and III were heat treated as follows. On installing the sample in the magnetometer the samples were cooled to 290 K for 60 s and thereafter kept at room temperature, 295 K, for 180 s. Then, samples (one at a time) were immersed in boiling nitrogen and kept at 77 K for 60 s. From this temperature, the samples were isochronically (i.e. at a constant rate) heated to 290 K at 10 K min$^{-1}$ (sample I), 3 K min$^{-1}$ (sample II) and 0.15 K min$^{-1}$ (sample III). The temperature history is shown in Fig. 1a for the first 6 ks. The first set of experiments aims to demonstrate that martensite formation in the present system is not athermal but thermally activated and can occur during heating. In the second set

### Table 1 Chemical composition (wt-%) of 17-7 PH steel as determined with energy dispersive spectroscopy (EDAX SD Apollo 10 Pegasus System)*

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Cu</th>
<th>Ti</th>
</tr>
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<tbody>
<tr>
<td>Bal.</td>
<td>0.08</td>
<td>0.5</td>
<td>0.6</td>
<td>17.3</td>
<td>7.1</td>
<td>1.1</td>
<td>0.3</td>
<td>0.1</td>
<td></td>
</tr>
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*The carbon content was measured with a LECO-CS230 Carbon analyser.
of experiments, after room temperature storage and pre-treatment for 60 s at 290 K (identical to samples I, II and III) samples A, B and C were treated as follows:

(i) sample A: immersion in boiling nitrogen (77 K) for 60 s followed by immersion in boiling water (373 K). Thereafter, isochronal cooling from 373 to 80 K (at 0.1 K min\(^{-1}\)) and heating to 290 K (at 10 K min\(^{-1}\)) was followed with magnetometry.

(ii) sample B: immersion in boiling water (373 K), followed by magnetometry investigation on isochronal cooling from 373 to 80 K (at 0.1 K min\(^{-1}\)) and heating to 290 K (at 10 K min\(^{-1}\)) (The quenching steps for samples A and B were performed outside the cryostat chamber. Consequently, the content of martensite in sample A after quenching in boiling nitrogen was not measured.)

(iii) sample C: magnetometry investigation of isochronal cooling from 290 to 80 K (at 0.1 K min\(^{-1}\)) and heating to 290 K (at 10 K min\(^{-1}\)).

The second set of experiments aims to investigate the identity of the thermally activated step, i.e. nucleation or growth, and is based on the following reasoning.

Provided that martensite formation is completely suppressed on fast cooling, followed by fast (re)heating above the threshold temperature where martensite formation is inhibited by thermodynamics, the martensite formation in a second (slower) cooling step is:

(i) not influenced by the initial cooling/heating cycle, if the kinetics of the transformation is (largely) controlled by time-dependent nucleation

(ii) strongly influenced by the initial cooling/heating cycle if the kinetics of the transformation is controlled by time-dependent growth of nuclei that have developed a-thermally upon the initial cooling.

Samples A, B and C were heat treated consistently.

**Vibrating sample magnetometry**

Magnetometry was performed with a Lake Shore Cryotronics 7407 vibrating sample magnetometer equipped with a Janis SuperTran-VP continuous flow cryostat. Samples were mounted onto a rigid fibre pole using non-magnetic Kapton tape. The degree of transformation was followed by recording the magnetic moment of the samples at saturation. A magnetic field of 1 Tesla was applied to bring the samples to magnetic saturation.

The absolute temperature was verified and validated at the boiling point of liquid nitrogen (i.e. 77 K) and at room temperature (i.e. 295 ± 2 K). During thermal cycling, the temperature relative to the set point was accurate within ±0.5 K.

The molar fraction of martensite \(f_a(t,T)\) in the material, as measured versus time, \(t\), and temperature, \(T\), was determined on the basis of the following assumptions:

(i) the as received (i.e. as rolled) material is fully martensitic, as was validated by transmission X-ray diffraction\(^{54}\)

(ii) the molar fraction of martensite is proportional to the magnetic moment at magnetic saturation (Note that Refs. 44, 45, 51 and 52 refer to the volume fraction of martensite as determined by magnetometry. This is incorrect; magnetometry provides a measure for the molar fraction of the martensite formed, corrected for its dependence on temperature\(^{54,55}\))

(iii) the as rolled sample remains stable in the temperature interval under investigation.
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With these assumptions, $f_a(t,T)$ is given by

$$f_a(t,T) = M(t,T)/M_a(t,T)$$  \(1\)

where $M(t,T)$ is the magnetic moment at saturation measured in the sample and $M_a(t,T)$ is the magnetic moment at saturation measured in the as rolled material (fully martensitic). It is noted that a value of $136 \pm 4$ emu g$^{-1}$ is identical with the value of $135$ emu g$^{-1}$ calculated for ferrite in the present system. Since, for the present case, ferrite and martensite are crystallographically identical, it is concluded that $M_a(t,T) = 136 \pm 4$ emu g$^{-1}$ is representative for martensite in this system.

**Electron backscatter diffraction (EBSD)**

Electron backscatter diffraction was performed in a dual beam FEG-SEM FEI Helios Nanolab 600 SEM equipped with an EBSD system from EDAX-TSL and a Hikari camera. The measurements were performed with an electron probe current of 11 nA at an acceleration voltage of 18 kV, with a step size of 80 nm; data were collected at four different sample locations on an overall surface area of 0-025 mm$^2$ (i.e. 4 million points).

The OIM TSL 6 software was used for analysis of the EBSD results. Only data with confidence index, CI>$0-1$ were taken into account; only data points referring to martensite were considered. These represent about 90% of the totally acquired data points.

**Results and discussion**

**Thermally activated martensite formation**

The microstructure of the material after room temperature storage is shown in Fig. 2. The material is dual phase, containing austenite and a small fraction of martensite.

The units of martensite phase are agglomerated in clusters (Fig. 2a). It is observed that a large part of the austenite grains do not contain martensite (Fig. 2b). In Fig. 1b the molar fraction of martensite, $f_a$, measured by magnetometry is shown as a function of temperature, $T$, for samples I, II and III.

The initial content of martensite measured in the samples just before immersion in boiling nitrogen is $15 \pm 3\%$ (point 1 in Fig. 1b). Apparently, within experimental accuracy, fast cooling to 77 K does not lead to a measurable formation of martensite (point 2 in Fig. 1b – $16 \pm 3\%$). Martensite formation is first observed during subsequent isochronal heating from 77 K, which is counterintuitive and irreconcilable with athermal nucleation and instantaneous growth of martensite nuclei. A heating-rate dependent transformation curve implies that the development of martensite during heating from 77 K is thermally activated.

The present set of experiments does not give an indication whether this thermally activated martensite formation concerns thermally activated nucleation and/or thermally activated growth. A kinetic analysis of the data in Fig. 1b for 50% transformation (cf. Ref. 58) yielded a low activation energy of about 15 kJ mol$^{-1}$.

**Thermally activated growth of martensite**

This section presents the results of the second set of magnetometry experiments. The fractions of martensite measured during the different controlled thermal cycles are collected in Fig. 3a. The transformation rate on controlled cooling at 0·1 K min$^{-1}$ in the temperature interval 330 to 240 K is shown in Fig. 3b.

Martensite formation appears suppressed on fast (re)heating to 373 K, both from 290 and 77 K. The slightly higher fraction of martensite at 373 K, (i.e. 19% ± 3%) as compared to points 1 and 2 (i.e. 15% ± 3%) is not significant within experimental error.

On isochronal cooling from 373 K, neither sample A nor sample B showed a measurable transformation until reaching 310 K (Fig. 3b). The criterion for a measurable transformation is taken as $df_a/dT > 2 \times 10^{-8}$ s$^{-1}$, which is a value safely larger than the noise level (see arrow in Fig. 1b) and larger than the average transformation rate as calculated for room temperature storage ($=0·15f_a/10^{3}$ s$^{-1}$ $=1·5 \times 10^{-8}$ s$^{-1}$).

At 310 K, martensite formation is observed to start slowly in sample A, while martensite formation in sample B is firstly observed at 304 K. The onset of the transformation in samples A and B at temperatures well-above the long-term storage and stabilisation temperature of 295 ± 2 K after austenitisation, cannot be reconciled with athermal nucleation; neither can it be a consequence of thermally activated nucleation of martensite. These results strongly suggest that both the pre-treatment from 295 to 290 K (sample B) and the
additional cooling to 77 K (sample A) have led to the development of martensite nuclei, and that these nuclei are thermally activated to grow during the isochronal cooling from 373 K at a temperature higher than the storage temperature. The instantaneous martensite formation as observed in sample C on cooling from 290 K corroborates that cooling from 295 to 290 K could indeed have led to the development of martensite nuclei.

It is mentioned that the differences reported between samples that have undergone different thermal cycles cannot be explained from the initial martensite content, which is a constant factor in all experiments. The observation that significant martensite formation commences at a higher temperature in sample A than in sample B (Fig. 3), could be explained from a larger number of nuclei formed on cooling to 77 K (sample A) as compared to cooling to 290 K (sample B). During continuous cooling, the transformation rate reaches a maximum at 293, 289 and 287 K for samples A, B and C, respectively. After this maximum, the transformation in samples A and C shows deceleration followed by acceleration, while for sample B the transformation rate decelerates monotonically. It is anticipated that transformation characterised by more than one rate maximum is the result of autocatalytic nucleation promoted by thermally activated growth of martensite nuclei (cf. the section on ‘Multiple transformation rate maxima’). In this respect, it is suggested that the activation energy for thermally-activated martensite formation during heating (see the section on ‘Thermally activated martensite formation’), reflects the activation energy for moving the martensite/austenite boundary into (strengthened) austenite.

Effect of thermal cycle on microstructure
The results of orientation image microscopy of samples A and B are shown in Fig. 4. A quantitative evaluation of the EBSD results (Fig. 5) was obtained for the areas separated by high angle grain boundaries, i.e. for a misorientation angle larger than 15°. Areas separated by high angle grain boundaries are considered to represent blocks in the lath martensite microstructure.

Evidently, the quantitative size distributions of martensite blocks in samples A and B are identical within experimental accuracy (Fig. 5). Hence, if the number of nuclei in samples A and B were identical (as suggested in Fig. 3b; see above) this is not reflected in the microstructure at the block scale after completed transformation. Thus, it is concluded that additional nucleation has occurred in sample B during isochronal cooling. In principle, such nucleation could have taken place purely athermally. However, since a major part of the transformation is accomplished within a very narrow temperature range for all investigated samples (cf. Fig. 3b), EBSD investigation supports a substantial contribution of autocatalytic nucleation to the transformation process. The effect of the thermal cycle on the scale of the single martensite laths is beyond the scope of this work.

Multiple transformation rate maxima
In this section, the observation of two transformation rate maxima (i.e. a new acceleration of the transformation after deceleration in samples A and C) is discussed in relation to the abnormal massive transformation of austenite into ferrite, as described in Refs. 59–62. The latter is introduced first.

At the beginning of the massive transformation, nucleation of ferrite at several locations in the sample is followed by thermally activated growth. The strain energy which is introduced locally in the system as a consequence of the volume misfit between ferrite and austenite (i.e. the introduction of shear stresses), promotes autocatalytic nucleation of ferrite in front of the ferrite/austenite interface.59 Autocatalytic nucleation yields a strong acceleration of the transformation, which comes to a halt when the total strain energy, i.e. both elastic and plastic, introduced in the system by the transformation itself, averaged over the entire sample (i.e. the sum of interfacial energies, introduction of crystal defects and buildup of hydrostatic pressure in
austenite), equals the chemical driving force. Thereafter, an increment of the driving force upon continuous cooling is necessary to initiate a new (autocatalytic) nucleation event.

In the present case, at 310 K, several (infinitely small) nuclei of lath martensite are present in the material as a consequence of athermal nucleation in the first cooling step. The number of nuclei differs for samples A and B and is largest in sample A, because of the significantly lower temperature reached in sample A during cooling (i.e. 77 K versus 290 K).

On cooling below 310 K, martensite starts to grow. Evidently, the driving force at 310 K is sufficient to compensate for the interfacial energy and the elastic and plastic strain energy terms associated with martensite formation, including the frictional work accompanying the movement of the austenite/martensite interface into strengthened austenite. For a relatively small transformed fraction, martensite formation introduces shear and tensile dilatational stresses in the surrounding austenite matrix, which exceeds the other energy terms in austenite accompanying martensite formation and promotes the driving force for (autocatalytic) martensite formation.

For a relatively large transformed fraction, (retained) austenite regions become encaged by martensite. Then additional martensite formation induces compressive strain energy terms in austenite, which counteract the driving force for martensite formation. The compressive strain energy in austenite suppresses martensite nucleation and results in a deceleration of the transformation.

Additionally, strengthening of the austenite, as promoted by plastic accommodation of the transformation strain in the austenite during martensite formation, contributes the strain energy term suppressing the transformation process. However, martensite formation does not completely stop, because growth of pre-existing nuclei can still occur to a limited extend.

A new acceleration of the martensite formation occurs when additional undercooling leads to a further increase in the driving force for martensite formation. At this point, provided that there is enough austenite to transform, the formation of new martensite nuclei yields a new acceleration of the transformation, as it is observed at 280 K in sample A (and C). The reason that this acceleration is not observed for sample B, could be the lower fraction of untransformed austenite as compared to sample A (and C) at this point.

To summarise, autocatalytic nucleation of martensite can provide a consistent interpretation of the results and is promoted by thermally activated growth of martensite nuclei. The combined effect of autocatalytic nucleation and self-induced stabilisation of austenite yields martensitic transformation characterised by repeated acceleration and deceleration. It is stressed that this phenomenon substantially differs from the occurrence of multiple bursts, which take place at a time scale not compatible with autocatalytic nucleation of martensite as promoted by thermally activated growth.

Conclusions
Martensite formation in a steel containing 17 wt-%Cr, 7 wt-%Ni and 1 wt-%Al was investigated with magnetometry and electron backscatter diffraction. It was observed that fast cooling to 77 K, which is well below , did not lead to a measurable formation of martensite. Similarly, fast heating from well below to a temperature well above can suppress the martensite formation.

Instead, martensite developed during controlled heating from a temperature well below to a temperature well above . Surprisingly, and shown for the first time, the application of an initial fast cooling step followed by fast heating influences the kinetics of martensite formation during a second, slower, cooling, in spite of suppression of the transformation during both fast cooling and fast heating.
The results are interpreted as the outcome of athermal nucleation of martensite, followed by thermally activated growth of the nuclei and growth induced autocatalytic nucleation. The activation energy for thermally activated growth of martensite was experimentally assessed at about 15 kJ mol$^{-1}$, which is suggested to be the energy necessary for the movement of the martensite/austenite interface into (strengthened) austenite.

On slow continuous cooling more than one transformation rate maximum was observed. This peculiar phenomenon is interpreted as the outcome of an interplay between strain (and interfacial) energy and autocatalytic nucleation of martensite as induced by thermally activated growth of martensite nuclei.

References


