Investigation of martensite formation in Fe based alloys during heating from boiling nitrogen temperature

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The austenite-to-martensite transformation at temperatures below room temperature was investigated in situ by magnetometry in Fe-N, Fe-Cr-C and Fe-Cr-Ni based alloys. After quenching to room temperature, samples were immersed in boiling nitrogen and martensite formation was followed during subsequent heating to room temperature. Different tests were performed with heating rates ranging from 0.5 K/min to 10 K/min. For comparison a sample was up-quenched in water to verify whether martensite formation can be suppressed at high heating rates. Thermally activated formation of martensite during heating was convincingly demonstrated for all investigated materials by showing heating rate dependent transformation kinetics. Moreover, magnetometry showed that the heating rate influences the fraction of martensite formed during the thermal treatment. The activation energy for thermally activated martensite formation as quantified by a Kissinger-like method lies in the range 11-18 kJ/mol and increases with the total fraction of interstitials in the alloy.

KEYWORDS: MARTENSITE - STEEL - CRYOGENIC TREATMENT - KINETICS OF TRANSFORMATIONS - MAGNETOMETRY

INTRODUCTION

Martensite formation is generally believed independent of time (i.e. athermal) and is modelled according to such behaviour [1]. This approach is clearly visible in Time-Temperature-Transformation, TTT [2], diagrams, where the temperature at which martensite formation is observed upon cooling is represented by a horizontal line at the martensite start temperature, M_s. Also the temperature where martensite formation is completed upon further cooling, the martensite finish temperature, M_f, is represented by a horizontal line. Consequently, the transformation is presumed not to depend on time and the martensite fraction to be governed by the undercooling reached [3].

However, time-dependent, so-called isothermal, martensite formation was reported as early as 1948 [4]. Several observations followed and are listed in Ref. [5]. At temperatures above room temperature, time-dependent martensite formation is generally too fast to be measurable, while the phenomenon may be easily observable at sub-zero Celsius temperatures [6].

At sub-zero Celsius temperatures, time-dependent martensite formation can display C-shape transformation curves in TTT diagrams (analogous to the classical diffusional transformations)

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[7-11]. C-shaped transformation curves in TTT diagrams arise from the counteracting effects of (i) driving force for transformation, which increases with undercooling, and (ii) thermal activation, which is favored by a higher temperature [12].

Time-dependent martensite formation was reported for several iron-based systems, among which Fe-C [13], Fe-N [14] and Fe-Ni-Cr [15,16] model alloys as well as several steels [4,8,10,11,17-29]. In steel, time-dependent martensite formation was documented for high carbon steels [4,17-21], low carbon steels [22] and stainless steels [8,10,11,23-29]. Despite the poor understanding of the thermally activated mechanism responsible for time-dependent martensite formation, the phenomenon has for many years been industrially exploited in sub-zero Celsius treating (cryogenic treatment) of, in particular, tool steels (see Ref. [30]) but also stainless steel components [31,32].

Interestingly, time-dependence was rationalized as an intrinsic characteristic of martensitic transformations in steel [3]. According to Ref. [3], the representation of martensite formation in terms of horizontal lines in TTT diagrams is not correct and martensite formation should always be represented in terms of C-shaped transformation curves. Specifically, in Ref. [3] it was suggested that two distinct transformation curves should be reported, associated with the formation (i.e. nucleation and growth) of slipped and twinned martensite.

The internal sub-structure of martensite in steel is characterized by a high density of defects, i.e. dislocations (slipped martensite) or twins (twinned martensite). The martensite substructure plays a fundamental role in the kinetics of the transformation:

slip is thermally activated [33,34], whereas twinning proceeds athermally [33]. The martensite sub-structure is associated with the morphology of martensite, which is classified as either lath type or plate type [35,36]. Plate martensite is partially or fully internally twinned [33,37-40], while lath martensite is fully internally slipped [26,41,42]. Consistently, in plate martensite, the twinned areas form instantaneously upon nucleation, while the formation of the slipped regions is time dependent [43-45]. According to the theory of martensite nucleation in Ref. [46,47], spontaneous nucleation of martensite firstly occurs either athermally, when the critical driving force for transformation is reached at the martensite start temperature, M_s, for the most potent nucleation sites in the material, or after an incubation time defined by the presence of an energy barrier, when the critical driving force for transformation is not reached (i.e. above M_s) [46,47]. The theory for martensite nucleation in Ref. [46,47] applies to all nucleation sites (i.e., to all nucleation events after the first one) and does not distinguish between martensites with different sub-structures.

After the first nucleation event, martensite formation is characterized by a strong form of autocatalysis, which consists of the stress-assisted activation of pre-existing nucleation sites as well as of the strain-induced formation of new nucleation sites during the transformation process [48]. Autocatalytic nucleation has a strong influence on the kinetics of transformation and can yield the abrupt transformation of a part of the material in an instantaneous event, a so-called burst [49]. Burst kinetics is observed in systems characterized by the formation of plate martensite.

The major implication of the rationalization in Ref. [3], which indicates time-dependent martensite formation as an intrinsic characteristic of steel, is the theoretical possibility to (at least partially) suppress martensite formation during very fast cooling so that the C-curve describing martensite formation is not crossed. Subsequently, martensite formation can be promoted upon isothermal holding at temperatures below M_s [30,45,51,52] as well as upon (re)heating [13,24,26,30,45]. Consequently, time-dependent martensite formation may have noteworthy, hitherto unexploited, applications in heat treatment practice.

For example, in Refs. [22,51,52], it is shown that time-dependent martensite formation may result in the possibility to tailor the mechanical properties of steel products via thermal treatment engineering. Also, time-dependent martensite formation may facilitate improved performance of high carbon steel and stainless steel parts by the development of tailored sub-zero Celsius treatments (see Refs. [30,45]).

Furthermore, by following martensite formation during heating, it is possible to measure the activation energy for time-dependent martensite formation [24,26,53]. The activation energy for martensite formation reflects the mechanism that governs the transformation rate and its measurement may contribute further to the understanding and, eventually, modelling of the phenomenon.

Ref. [6] is a particularly extensive study of the activation energy for isothermal martensite formation in iron based alloys and is based on a comprehensive review of experimental data. According to Ref. [6], two thermally activated mechanisms exist that can control the rate of isothermal martensite formation. The first mechanism yields an activation energy of about 7 kJ/mol and governs austenite-to-martensite transformation in high alloy steels forming martensite at sub-zero Celsius temperatures; the second mechanism yields an activation energy of about 80 kJ/mol and governs martensite formation in Fe-Ni and Fe-C systems transforming well above room temperature.

According to Ref. [6], the first mechanism is associated with the thermally activated movement of dislocations. This interpretation is in agreement with previous works on the kinetics of isothermal martensite formation reviewed in Ref. [5]. On the other hand, the mechanism yielding an activation energy of about 80 kJ/mol remained unrevealed. Ref. [6] suggests that martensite formation in Fe-C and Fe-Ni systems may be triggered by the time-dependent formation of bainite.

The aim of the present work is to further investigate the generalities of thermally activated martensite formation in iron-based alloys at sub-zero Celsius temperatures and to investigate the influence of the chemical composition on the activation energy for isothermal martensite formation. Moreover, the work aims to identify the optimal temperature interval wherein sub-zero Celsius treatment of steel components is performed.

MATERIALS AND METHOD

The investigation was performed for a series of alloys and conditions. Table 1 reports the chemical compositions of the chosen model alloys and steels. Starting conditions, austenitization treatments and sample geometries are described in Table 2, which also lists the morphology of the developing martensite. Alloys were chosen to be representative of a large number of commercial steels and ferrous-based systems. Austenitization conditions were chosen such that the formation of phases other than austenite and martensite is avoided; this is necessary for a correct quantification of the martensite and austenite fractions by magnetometry investigation.

After austenitization and quenching to room temperature, samples were stored at room temperature and thereafter subjected to the sub-zero Celsius investigation. Sub-zero Celsius investigation was performed with a Lake Shore Cryotronics 7407 vibrating sample magnetometer equipped with a Janis superTran-VP cryostat and consisted in the following:

1. the magnetization of the material after austenitization and storage is measured at 20°C applying a magnetic field of 0.3 Tesla; thereafter the sample is removed from the cryostat;
2. the cryostat chamber is partially filled with boiling nitrogen; thereafter the sample is reinserted and quenched in boiling nitrogen;
3. the magnetization of the material is measured at -190±5°C applying a magnetic field of 0.3 Tesla after complete evaporation of the nitrogen;
4. the magnetization of the material is monitored during controlled isochronal (constant rate) heating from -190±5°C to 20°C applying a magnetic field of 0.3 Tesla.

For each alloy, a series of tests was performed (on distinct samples) with heating rates ranging from 0.5 K/min to 10 K/min. An additional test consisted in fast (re)heating of the material to 20°C in water outside the cryostat chamber.

Tab. 1 - Chemical composition (in wt-%) of the materials as determined with Energy Dispersive Spectroscopy.
The carbon content was measured with a LECO-CS230 Carbon analyser.
The nitrogen content was determined by X-Ray Diffraction [54].
Dashes indicate values that cannot be measured with the applied methods.
Alloys A and B are essentially Fe-N. Alloys C and D are Fe-Cr-C based. Alloys E and F are Fe-Cr-Ni based.

Alloy	Fe	N	C	Cr	Ni	Mn	Si	Mo	Cu	Al
A	Bal.	2.2	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
B	Bal.	1.8	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
C	Bal.	-	0.96	1.6	0.1	0.3	0.1	<0.1	0.2	<0.1
D	Bal.	-	0.38	17.0	2.1	0.5	0.5	0.1	0.4	0.2
E	Bal.	-	0.09	15.5	7.1	0.8	0.6	2.1	0.4	1.2
F	Bal.	-	0.08	17.2	7.0	0.6	0.5	<0.1	0.3	1.1

Tab. 2 - Starting conditions, sample geometries and austenitization treatments.
For the geometry: "D" and "SP" refer to disc and square plate, respectively; "Ø", "d" and "t" refer to diameter,
diagonal of the square and thickness, respectively. For the austenitization: Ar refers to cooling in argon at an average cooling rate
of 20 K/min; alloys A and B were synthetized and austenitized in a single treatment applying controlled NH_3 and H_2 atmosphere.
All samples were cut in the starting condition (prior to austenitization).
Plate martensites (i.e. alloys A-D) are all of lenticular type (i.e. partially twinned - see Refs. [33,35]).

Alloy	Starting condition	Geometry [mm]	Austenitization / synthesis	Morphology
A	Armco® Fe	SP: d=3, t=0.025	650°C, 30min, Water	Plate + Lath
B	Armco® Fe	SP: d=3, t=0.025	650°C, 30min, Water	Plate + Lath
C	AISI 52100, as rolled	D: Ø=3, t=0.7	1080°C, 3min; Oil (80 °C), Air	Plate
D	AISI 431, carburized, homogenized	D: Ø=3, t=0.7	1180°C, 5min, Ar	Plate + Lath
E	AISI 632, as rolled	SP: d=3, t=0.25	980°C, 5min, Ar	Lath
F	AISI 631, annealed	SP: d=3, t=0.15	980°C, 5min, Ar	Lath

The (molar) fraction of martensite in the samples, $f_{a'}$, was quantified versus temperature, T, and time, t, according to:

$$(1) \qquad f_{a'} = \frac{M(T,t)}{M_{sa'}} \cdot \frac{M_{1.5b}}{M_{sb}(T)}$$

where M is the magnetization of the sample under investigation, $M_{sa'}$ is the magnetization at saturation of a fully transformed specimen calculated according to Ref. [55], M_{sb} is the magnetization at saturation (measured at 0.3Tesla) of a reference sample consisting of 100% martensite during measuring of the baseline and $M_{1.5b}$ is the magnetization of the same reference sample measured at room temperature applying a magnetic field of 1.5 Tesla.

The following materials were used as references: Armco® Fe for 0.025 thick foils, AISI 431 as quenched for 0.7 mm thick samples, AISI 631 as rolled for 0.15 mm and 0.25 mm thick samples. Reference materials correspond to the starting condition for alloys A, B, D and F - see Table 2.

Quantitative phase analysis presupposes that martensite is the only ferromagnetic phase in the material (which is true for the temperature interval of investigation in absence of phases other than martensite and austenite [45]) and that a magnetic field of 0.3 Tesla is sufficient to approach magnetic saturation in the material. This was verified to be the case by recording hysteresis curves. At magnetic saturation and in the presence of martensite as the only ferromagnetic phase in the material, the magnetization of the material is proportional to the fraction of martensite [56,57]. For a magnetic field of 0.3 Tesla, rather than 1.5 Tesla, the contribution of the magnetic field to the driving force for martensite formation is negligible [33,47,58].

The activation energy for martensite formation is measured from the temperatures, $T_{f'}$, corresponding to a fixed stage of transformation, f', measured for for a series of heating rates [53]. The fixed stage of transformation was chosen on the basis of the following criterion:

$$(2) \qquad f' = \frac{f_{a'\,BN} + f_{a'\,RT-10K/min}}{2}$$

were $f_{a'\,BN}$ is the fraction of martensite measured at -190±5°C upon quenching the material in boiling nitrogen and $f_{a'\,RT-10K/min}$ is the fraction of martensite measured in the material upon reheating to room temperature at a rate of 10 K/min.

RESULTS AND INTERPRETATION

The condition of the materials prior to sub-zero Celsius investigation is presented in Fig. 1 and Table 3. Fig. 1 reports $f_{a'}$ as measured by magnetometry during thermal treatment as a function of temperature, T, for a heating rate of 3 K/min.

By means of example the influence of the heating rate on the transformation curve is given for Alloy E only. Table 3 lists $f_{a'}$ at different thermal steps and versus the most significant thermal treatments.

Tab. 3 - Molar fraction of martensite, $f_{a'}$, measured by magnetometry versus thermal step / thermal treatment. A-F refers to the alloy of investigation.

Thermal step / treatment	A	B	C	D	E	F
Prior to sub-zero Celsius	1%	32%	59%	3%	13%	7%
At -190°C	35%	53%	79%	46%	13%	7%
After up-quenching in water	38%	62%	80%	50%	15%	12%
f'	41%	63%	82%	57%	53%	47%
After heating 0.5K/min	52%	77%	86%	73%	100%	93%

Table 3 and Fig. 1 show that magnetometry revealed the presence of a certain fraction of martensite in all investigated materials prior to sub-zero Celsius treatment. Consequently, none of the sub-zero Celsius treatments deal with virgin austenite. This condition appears representative of a large number of alloyed commercial steels, where a certain fraction of austenite is retained after cooling to room temperature.
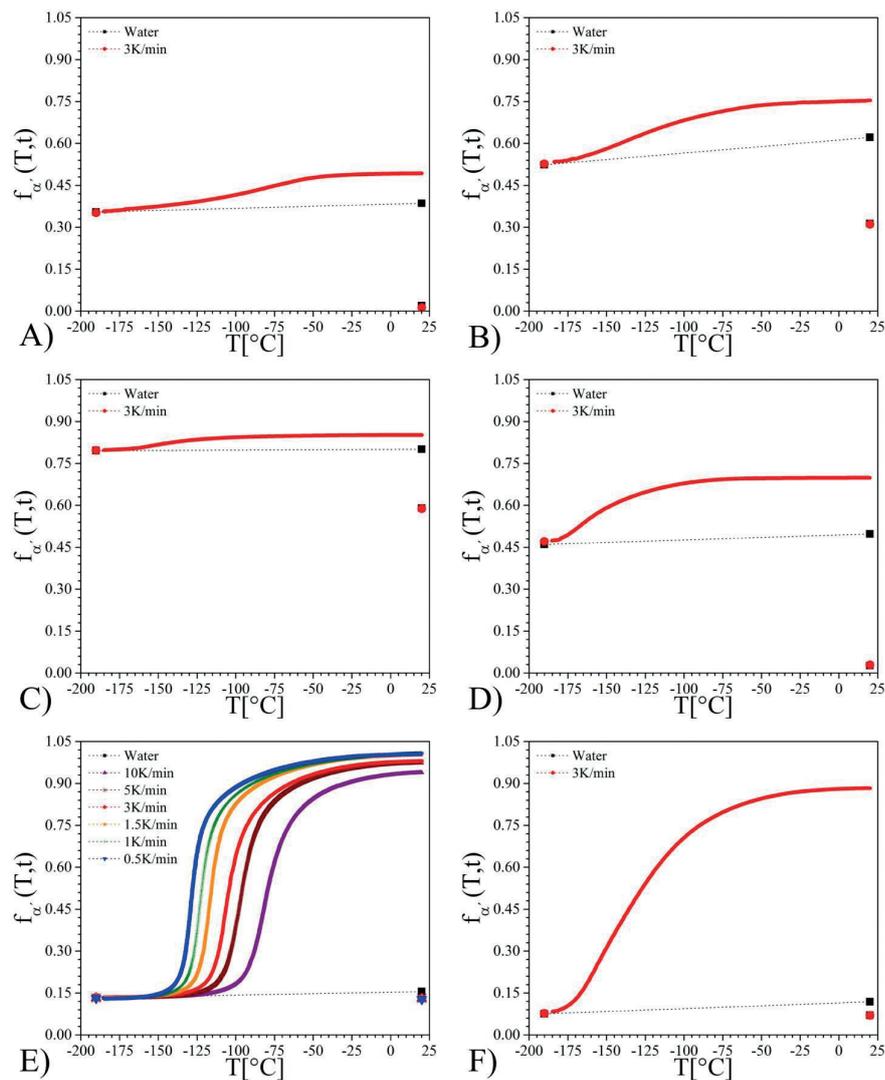

Fig.1 - Molar fraction of martensite $f_{a'}$ versus temperature T plotted as a function of the heating rate Θ; labelling A to F refer to the alloy of investigation. Dotted lines indicate unmonitored heating performed by up-quenching in water.

Fig.1 shows that during sub-zero Celsius treatment, the austenite-to-martensite transformation continues in all the investigated alloys. Martensite formation is observed both during cooling and during heating. Specifically, measurable martensite formation upon quenching in boiling nitrogen occurs for the alloys A-D, where plate martensite with lenticular morphology forms. Martensite formation during subsequent (re)heating from boiling nitrogen temperature is reported in all materials. Evidently, in spite of differences in chemical composition, thermal history and martensite morphology, martensite formation is (at least partially) suppressed in all investigated systems upon fast cooling to boiling nitrogen temperature.

On heating from boiling nitrogen temperature to room temperature martensite formation occurs, irrespective of whether lath or lenticular martensite formation is expected. This is irreconcilable with an athermal mechanism and proves that thermally activated martensite formation occurs in all investigated alloys. As revealed for alloy E in Fig.1, and confirmed for the other alloys (data not shown), the slower the heating rate the lower is the temperature where the maximum rate for martensite formation occurs during heating. Furthermore, the slower the heating the higher is the martensite content reached at 20°C. Clearly, data in Fig. 1 is consistent with the claim in Ref. [3] that martensite formation is steel is always time-dependent. The activation energy for thermally activated martensite formation was investigated with a Kissinger-like analysis for a fixed stage of transformation as defined by Eq.(2). For the theory on kinetics analysis of phase transformations the reader is referred to Ref. [53]. In Fig. 2a the activation energy for martensite formation is determined from the slope ($=E_A/R$ where R is the gas constant) of the straight line through the data in Fig. 2a [53].

The values of the activation energy measured for the investigated alloys are presented versus the total interstitial (N or C) content in the alloy in Fig. 2b.
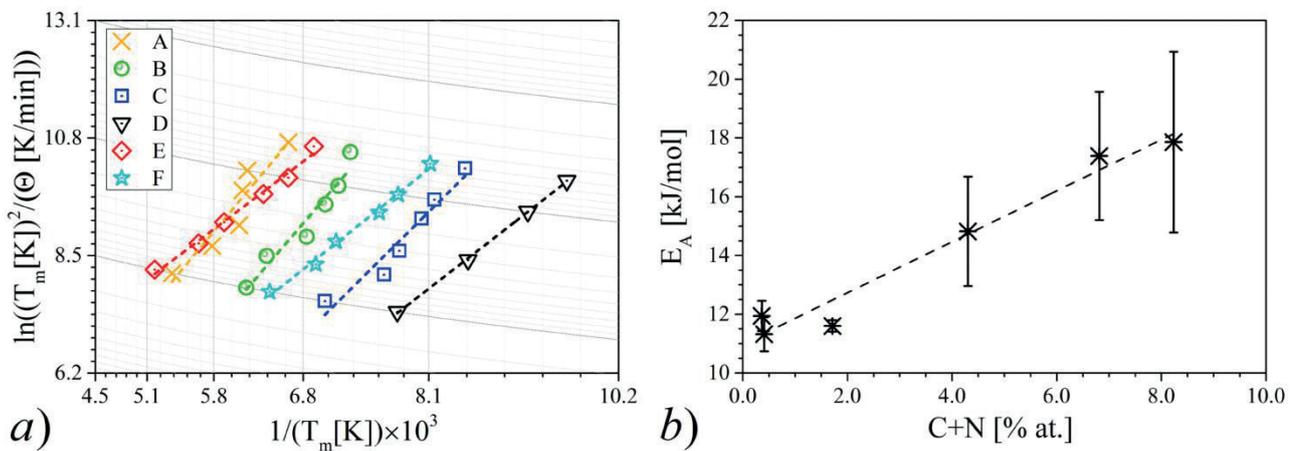

Fig.2 - a) Kissinger-like plot for different materials and austenitization conditions. T_m (i.e. T_f, see above) is the temperature corresponding to the fraction transformed $f_{\alpha'}$; Θ is the heating rate. Axes include the temperature interval -175°C to -50°C and the cooling rate interval 0.1K/min to 100 K/min; b) Activation energy for martensite formation E_A plotted versus the total content of interstitials in the alloy C+N (% at.).

Fig. 2 shows that the activation energy for martensite formation in the investigated systems ranges between 11 kJ/mol and 18 kJ/mol. As reflected by Fig. 2b a linear correlation exists between the interstitial content in the alloy and the activation energy for thermally activated martensite formation. It is noted that this conclusion presupposes that other factors, like the presence of substitutional elements, the transformed fraction at the point of measurement and the austenite grain size have a minor influence on the measured value. This is not always the case (see for example Refs. [26,28] for the influence of the fraction transformed). Therefore, a more systematic analysis, which decouples the influence of the different factors, will be the focus of future activity. At present, it is anticipated that an increase of the activation energy with increased interstitial content reflects an interaction between the movement of dislocations and the presence of interstitials, which can be anticipated considering the displacement fields associated with line and point defects.

DISCUSSION
In the following, the transformation process is discussed in the light of the theory for martensitic transformations in steel. The data in Fig.1 is interpreted in connection with the morphology of martensite (see Table 2), and more specifically with the martensite sub-structure.

In the light of Refs. [35,37-42], martensite is partially internally twinned in alloys A-D while it is fully internally slipped in alloys E and F.

During quenching in boiling nitrogen, the increment in driving force for martensite formation promotes spontaneous athermal nucleation of martensite [46,47], which occurs in several locations in the samples as determined by the potency distribution of the nucleation sites [48]. After nucleation, the martensite units start to grow. Growth is either athermal or time dependent, as determined by the martensite sub-structure - see above.

Athermal growth of the twinned areas, induces autocatalytic nucleation of several martensite units in the surrounding austenite, which are also internally twinned and which also grow (at least partially) athermally, yielding instantaneous transformation of a large part of material. On the other hand, thermally activated growth of the slipped areas cannot occur upon fast cooling to a temperature where the thermal energy is insufficient for thermal activation, i.e., upon quenching the material to boiling nitrogen

temperature. Consequently, autocatalytic nucleation is inhibited and the reaction is frozen (see Refs. [24,25]).

It follows that spontaneous athermal nucleation of martensite upon quenching in boiling nitrogen yields a measurable increase of $f_{a'}$ when the martensite has plate morphology (alloys A-D), while athermal nucleation of lath martensite upon quenching in boiling nitrogen remains unrevealed by magnetometry (alloys E, F). It is remarked that this interpretation implies that martensite formation in alloys A-D cannot be fully suppressed upon cooling to very low temperatures, irrespective of how fast the cooling step is performed and the twinned martensite indeed forms athermally.

During heating, the martensite with slipped sub-structure grows by thermal activation. This applies for both lath martensite as well as for lenticular martensite. As a matter of fact, it has been demonstrated that for lenticular martensite the inner structure, close to the midrib, is twinned, while slip becomes dominant towards the rim [34]. Then it is suggested that the twinned structure develops athermally on cooling while the actual lens shape develops thermally activated by slip.

Martensite growth induces the autocatalytic formation of new martensite nuclei, both laths (with internal slip) and plates (with internal twins). The temperature where martensite formation is firstly observed on heating depends on the heating rate and of the chemical composition of the material. As a general trend, martensite formation occurring during heating appears more prominent in the temperature interval -180°C to -50°C.

Upon approaching room temperature, martensite formation stops. Evidently, thermal energy alone cannot promote martensite formation until completion, as a certain level of undercooling, i.e. an additional driving force, is required for continued transformation. More specifically, a sufficient undercooling is required for continued growth-induced/assisted autocatalytic nucleation of martensite [46,47]. Consequently, the slower the heating, the more martensite forms in the material during the thermal treatment.

The simultaneous interplay of thermal energy and driving force for transformation implies that an optimal temperature exists, wherein sub-zero Celsius treatments are optimally performed. The optimal temperature for sub-zero Celsius treatment is a function of chemical composition, which determines the driving force for transformation and which has an influence on the activation energy for thermally activated martensite formation, thus on transformed fraction.

At present, a general prescription for optimal sub-zero Celsius treatment of steel components is highly non-trivial. On the other hand, it appears clear that long isothermal treating at boiling nitrogen temperature is ineffective to promote martensite formation in steel, independently of the chemical composition. Higher temperatures, in the range -180°C to -50°C should be applied.

CONCLUSIONS

A series of iron-based alloys has been investigated during heating from boiling nitrogen temperature. In all materials, martensite formation during heating is demonstrated by magnetometry. Martensite formation during heating is thermally activated, as demonstrated by a heating rate dependent transformation curve.

The activation energy for martensite formation is measured in the range 11-18 kJ/mol and it is observed to be linearly dependent on the fraction of interstitial atoms in the material.

Martensite formation is interpreted in terms of athermal nucleation of martensite followed by growth. Growth is athermal or thermally activated as determined by the martensite sub-structure and promotes the autocatalytic nucleation of martensite.

A general prescription for sub-zero Celsius treatment of steel parts was not obtained, but it is assessed that boiling nitrogen temperature is likely to be too low for effective formation of martensite isothermally. An effective temperature interval is suggested to be -180°C to -50°C for the present alloys.

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