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# IN-SITU INVESTIGATION OF MARTENSITE FORMATION IN AISI 52100 BEARING STEEL AT SUB-ZERO CELSIUS TEMPERATURE

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## ABSTRACT

Martensite formation in AISI 52100 bearing steel at sub-zero Celsius temperature was investigated with Vibrating Sample Magnetometry. The investigation reports the stabilization of retained austenite in quenched samples during storage at room temperature and reveals the thermally activated nature of the martensitic transformation.
The kinetics of the transformation is interpreted in terms of a-thermal nucleation and thermally activated growth of lenticular martensite.

## KEYWORDS

## 1. INTRODUCTION

The literature reports beneficial effects of sub-zero Celsius treatments on the mechanical properties of high carbon steel products such as tools, dies and bearings. A complete list of observations and interpretations is reviewed in [1−5].
The transformation of retained austenite into martensite is among the metallurgical reasons for the beneficial effects of sub-zero Celsius treating. High carbon steels may present a partially austenitic, partially martensitic structure upon austenitization and quenching to room temperature. Additional sub-zero Celsius treatment promotes a reduction of the content of retained austenite due to an enhanced driving force for martensite formation.
Retained austenite is generally unwanted in tools, dies and bearings, since its presence reduces the homogeneity of the hardness and, owing to a potential stress- or strain induced transformation of austenite into martensite, the dimensional stability of products in an application. Sub-zero Celsius martensite formation is suggested to modify the tempering

response of high carbon steels [6] and has a particularly beneficial effect on the wear performance.

Martensite formation is generally considered to proceed *a-thermally*, i.e., independent on time, implying that the degree of martensite formed is only determined by lowest temperature reached during cooling and develops instantaneously. However, at sub-zero Celsius temperature *thermally activated* martensite formation is a general feature observed in iron-based alloys [7−8]. For AISI 52100 bearing steel, thermally activated martensite formation was previously reported in [6,9−12].

So far, the mechanism behind thermal activation of the martensite formation is unrevealed. Traditionally, thermal activation is interpreted as thermally activated nucleation of martensite [7,13], presuming instantaneous growth of the developing nuclei to their final size. Recently, the potential role of thermally activated growth was recognized [6,11].

Martensite formation at sub-zero Celsius temperature in carbon steels also depends on the storage time at room temperature before sub-zero treatment. On storage retained austenite is stabilized [14] and martensite formation is (partially) suppressed on subsequent cooling.

The purpose of the present investigation is to study thermally activated martensite formation and achieve insight in the mechanism associated with the stabilization of retained austenite.

## 2. METHODS

### 2.1. Material and treatments

The alloy investigated is a commercial 100Cr6 steel extruded to a 10mm rod with the composition given in Table 1. Samples were 0.2mm thick disks, 3mm in diameter.

Table 1: Chemical composition (in wt-%) of AISI 52100 as determined by Glow Discharge Optical Emission Spectrometry (GDOES)

| Fe | C | Cr | Ni | Mn | Si | Mo | Cu |
|---|---|---|---|---|---|---|---|
| Bal. | 0.96 ±0.02 | 1.60 ±0.05 | 0.10 ±0.01 | 0.28 ±0.04 | 0.13 ±0.04 | 0.05 ±0.01 | 0.15 ±0.01 |

Austenitization was performed at 1353 K for 60s, followed by quenching in oil at 413 K; the material was kept in the oil bath (martempered) for 20 s and air cooled before storing at room temperature. Protection from oxidation during austenitization was ensured through embedding the samples in 4 layers of 30 µm thick foils of stainless steel Fe-18%Cr-12%Ni-2%Mo. Different sets of samples, S1 to S6, were prepared in independent austenitization batches.

Samples in set 1 were exposed to storage times at room temperature varying from 3 h to 1500 h (10 ks to 3.6 Ms) before the samples were cooled to 123 K at a constant rate (isochronally) of 1.5 K/min.

Samples in sets S2- S6 were stored at room temperature for a minimum of 600 hours (2 Ms), before sub-zero treatment. Samples S2 were isochronally cooled to 123 K applying cooling rates ranging from 0.015 K/min to 40 K/min.

Samples S3 were cooled isochronally applying cooling rates ranging from 0.15 K/min to 75 K/min and subsequently held at 123 K for 16 hours (58ks).

Sample sets S4 and S5 were quenched to 123 K in a nitrogen flow within 30 s. Thereafter, set S4 was isochronally (re)heated to room temperature at heating rates varying from 0.05K/min and

50K/min; set S5 was held at 123 K for 16 hours (58 ks) before (re)heating at 15K/min to room temperature.
Set S6 was quenched to 93 K in nitrogen flow within 35s. Thereafter, the samples were isochronally (re)heated to room temperature applying heating rates ranging from 0.05K/min to 50K/min.

### 2.2. Vibrating Sample Magnetometry, VSM

The samples were subjected to different sub-zero Celsius thermal cycles in a Lake Shore Cryotronics 7407 Vibrating Sample Magnetometer (VSM) equipped with a cryostat. Magnetometry was applied to follow the martensitic transformation in-situ. A magnetic field of 1 Tesla was applied to bring the sample to saturation. The temperature was measured in the cryostat close to the sample.
Details on the experimental method and the procedure applied for the quantification of the fractions of austenite and martensite are reported in [11]. As the reference state for the quantification of the fraction transformed the material prior to the sub-zero treatment was taken. In this condition, the sample is dual phase containing lenticular martensite and 29.6% retained austenite as determined with (synchrotron) transmission X-Ray Diffraction; a negligible fraction of primary carbides is also present [6].
The baseline to correct for temperature dependence of the signal was measured using a reference sample cooled 1.5 K/min.

## 3. RESULTS AND INTERPRETATION

### 3.1. Thermal stabilization of austenite, set S1

The formation of martensite during isochronal sub-zero Celsius cooling at 1.5 K/min is reported after storage for various times is shown in Fig.1. Data is presented as the transformation rate $\frac{\Delta f_{\alpha'}}{\Delta T}$ and the fraction of retained austenite $f_\gamma$ versus absolute temperature T; the inset shows the actual transformation curves.
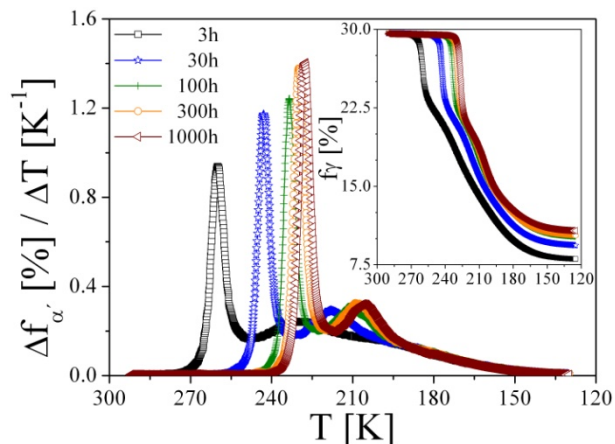


Figure 1 Set S1: transformation rate $\frac{\Delta f_{\alpha'}}{\Delta T}$ as a function of initial storage time at room temperature versus temperature T. Differentiation was done on $4K$ temperature interval. Inset: fraction of retained austenite $f_\gamma$ versus temperature T.

As Fig.1 shows austenite is stabilized during storage and a certain undercooling below room temperature is required to continue the transformation. The undercooling necessary for the regaining martensite formation is the larger the longer the storage times.

This austenite stabilization phenomenon is particularly relevant in the first 100 h. The time scale of the stabilization appears compatible with room temperature relaxation of the tetragonal unit cell of previously formed martensite. This relaxation is promoted by the diffusion of carbon atoms to lattice defects [15]. The nature of the stabilization is consequently thermally activated (see [13]).

From the inset in Fig.1 it is observed that the total reduction of retained austenite content during sub-zero Celsius treatment is larger for shorter storage times.

Clearly, the transformation rate in Fig.1 shows two distinct peaks. The peaks appear sharper and closer to each other for the longer storage times at room temperature.

The multi-peak transformation process is defined as ab-normal martensite formation, following [11]. In [11], ab-normal martensite formation was explained assuming that the kinetics of the transformation as described in terms of a-thermal nucleation and thermally activated growth of lenticular martensite and taking into account the austenite-stabilizing effect of the compressive transformation strain, evoked by the volume expansion on transformation of austenite into martensite.

### 3.2. Transformation during isochronal cooling to 123 K and subsequent isothermal holding, sets S2 and S3.

For sets S2 and S3 a minimum storage time of 600 h (2 Ms) was applied to introduce a comparable stabilization of retained austenite among the different samples.

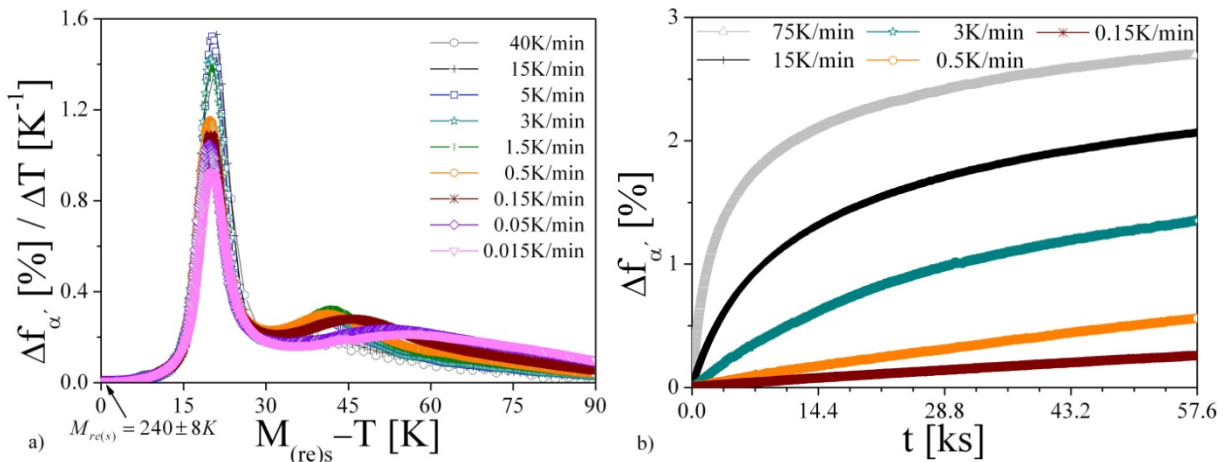Fig.2 reports martensite formation as a function of cooling rate.



**Figure 2 a) Set S2: transformation rate $\frac{\Delta f_{\alpha'}}{\Delta T}$ as a function of cooling rate versus temperature T. Differentiation was done on data averaged over a 4K temperature interval. b) Set S3: isothermal martensite formation at 123 K: $\Delta f_{\alpha'}$ versus time t after isochronal cooling at the indicated rates.**

In Fig. 2, isochronal data are plotted in terms of transformation rate, on a logarithmic scale, versus undercooling below the martensite (re)start temperature $M_{(re)s}$=240±8 K. Scattering of $M_{(re)s}$ is appointed to: (i) differences in the stabilization of retained austenite; (ii) experimental error; (iii) a possible effect of the cooling rate on $M_{(re)s}$. The experimental method does not allow concluding on the effect of the cooling rate on $M_{(re)s.}$

The data in Fig.2a show that the martensite formation depends on the undercooling below $M_{(re)s}$ and on the cooling rate. This observation suggests that martensite formation is not a-thermal, but rather thermally activated.

In Fig.2, ab-normal behavior is reported (cf. Fig.1). A first transformation peak is observed at about 20 K undercooling independently on the cooling rate; the maximum transformation rate reflected by the first peak appears higher for faster cooling. A second transformation rate maximum is smaller and is closer to $M_{(re)s}$ for faster cooling. The second peak was not observed for the highest cooling rates, i.e. 15 K/min and 40K/min.

Fig.2b shows that martensite formation continues on interrupting the cooling and holding the sample isothermally at 123 K. Evidently, the extent of isothermal transformation depends on the cooling rate applied to reach 123 K and is the larger the faster the cooling rate. Obviously, isothermal martensite formation indicates a thermally activated process.

### 3.3. Thermally activated martensite formation, sets S4, S5 and S6

For sets S4, S5 and S6, the sub-zero Celsius treatment was started with a quenching step in nitrogen flow. The experimental setup does not allow following in-situ martensite formation during quenching. Sets S4 and S5 were quenched to 123 K; set S6 was quenched to 93 K. The retained austenite content in the sub-zero Celsius quenched material amounts to 15.7±1.0% and 16.0±1.0% for quenching temperatures of 123 K and 93 K, respectively. The content of retained austenite, being 29.6% before sub-zero Celsius treating (Fig 1), is reduced during quenching in nitrogen flow, but it is significantly larger than the content measured in the material subjected to controlled cooling at 1.5 K/min to 123 K (10.5±0.2%, Fig 1). Consequently, the results clearly show that the transformation is (partially) suppressed by the fast cooling in nitrogen flow and that the martensite content is not merely determined by the lowest temperature reached during cooling. Therefore, the observation that the transformation is (partially) suppressed upon fast cooling, or, equivalently that austenite is stabilized during fast cooling, indicates that martensite formation requires thermal activation. On the other hand, the observations do not exclude the presence of an a-thermal component in the transformation process.

In Fig.3 the in-situ investigation that followed the quenching step to 123 K (sets S4 and S5) is given. Martensite formation occurs during isochronal (re)heating from 123 K (Figs. 3a and 3b) as well as during isothermal holding (Fig.3b). The development of martensite from austenite during heating is clearly irreconcilable with the classical interpretation of martensite formation as a-thermal and (again) indicates a thermally activated process (either nucleation or growth). Summarizing, the following observations support thermal activation: (i) time dependent martensite formation on cooling; (ii) suppression of the transformation upon quenching to sub-zero Celsius temperatures; (iii) isothermal transformation; (iv) formation of martensite during heating.

Interestingly, in Fig.3 the possibility to suppress martensite formation upon fast (re)heating is reported. As a matter of fact, if (re)heating is sufficiently slow (<0.5 K/min), the fraction of martensite formed on (re)heating is almost independent on the heating rate and is about 3.6±0.2%. On the other hand, a progressively reduced fraction of martensite forms when the heating rate is increased to 1.5 K/min, 5 K/min, 15 K/min and 50 K/min (Fig. 3a). Similarly, about 3.6±0.2% is the total fraction transformed upon a sufficiently long (>2 hours) isothermal holding at 123 K followed by (re)heating with 15 K/min (Fig. 3b). The total fraction transformed is reduced upon shorter isothermal treatment.
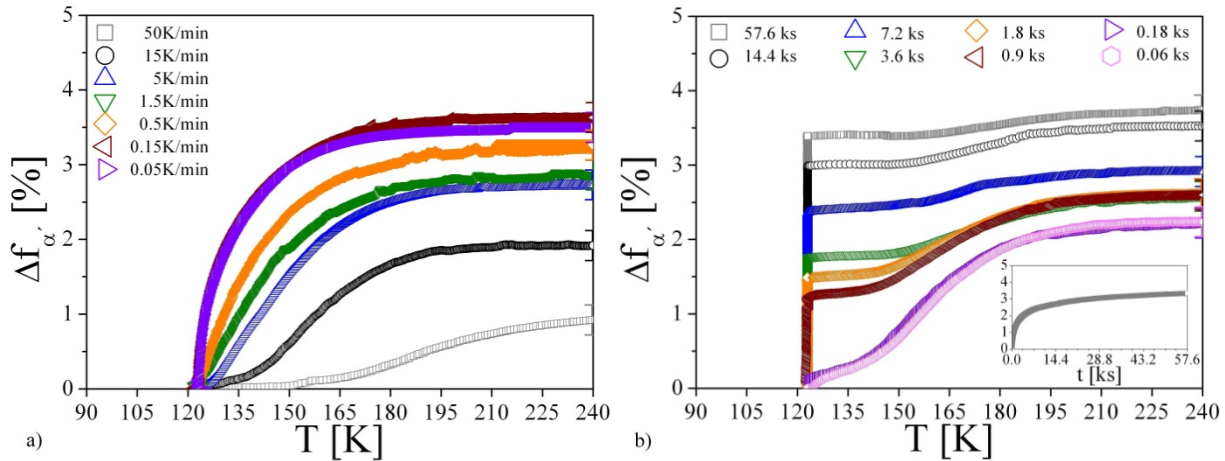


**Figure 3 Martensite formation $\Delta f_{\alpha'}$ versus temperature T and time t. a) S4: after quenching to 123 K, as a function of heating rate. b) S5: after quenching to 123 K, as a function of time of isothermal holding at 123K for fixed heating rate of 15K/min. Inset: reports isothermal martensite formation in the sample held for 57.6ks.**

In-situ investigation following the quenching step to 93 K is reported in Fig.4a. Data for heating rates in the range 0.05 K/min to 1.5 K/min were selected for determination of the activation energy of the rate determining step(s) for martensite formation during heating [16].
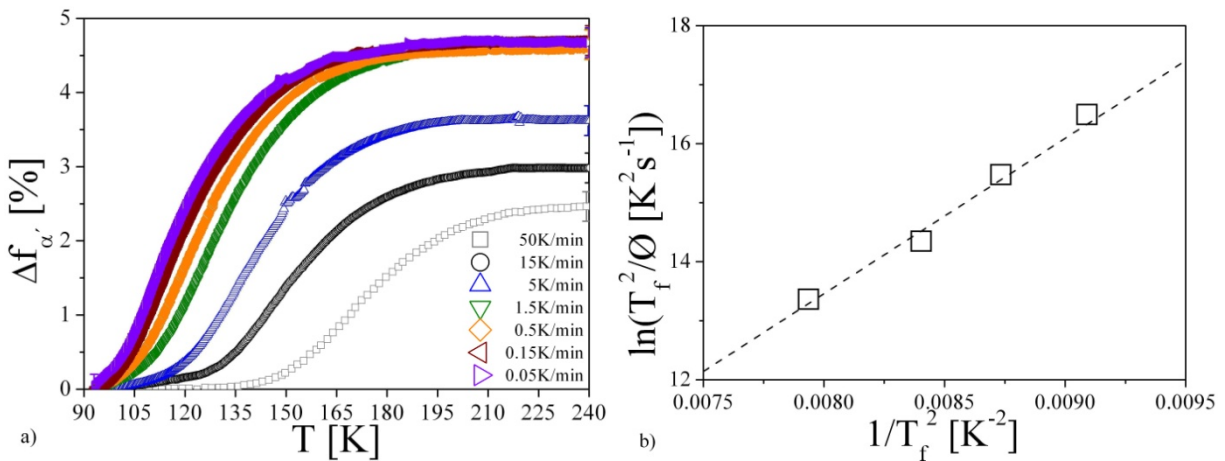


**Figure 4. a) Martensite formation versus temperature during isochronal (re)heating; data are collected after quench to 93 K and as a function of the heating rate. b) Plot to obtain the activation energy for the transformation according to the method in [16].**

Data in Fig.4 are consistent with data in Fig.3. The martensite formation reaches a saturation level for a sufficiently slow heating rate (<5 K/min), but is reduced for heating rates larger than 1.5 K/min. The maximum fraction transformed upon (re)heating is 4.8±0.2%.
Summarizing, the following observations are reported in Fig.3 and Fig.4 with respect to martensite formation on heating from a sub-zero temperature: (i) partial suppression of martensite formation is possible; (ii) martensite formation is limited to a maximum amount; (iii) the maximum amount appears larger for lower quenching temperatures (cf. fig.3a and 4a). The activation energy determined for thermally activated martensite formation is 22 kJ/mol. This value is consistent with data reviewed in [7] and may indicate thermally activated dislocation movement as the rate limiting mechanism for the martensitic transformation.

### 3.4. Kinetics of thermally activated martensite formation

In [11], the kinetics of martensite formation is interpreted in terms of a-thermal nucleation followed by thermally activated growth of plate nuclei into lenticular martensite. Moreover, it is assumed that the driving force at $M_{(re)s}$ is the minimum value necessary to form martensite. As a consequence of these assumptions: (i) nucleation is possible only on cooling; (ii) growth is allowed both during cooling and during (re)heating; (iii) the transformation is never allowed at temperatures above $M_{(re)s}$. This description is consistent with the data in Figs.2b, 3 and 4. During sub-zero Celsius cooling, a certain number of nuclei forms; the number of formed nuclei depends on the maximum undercooling below $M_{(re)s}$ reached during the thermal cycle and is larger for larger undercooling. Upon cooling, growth is the more suppressed the lower the temperature; hence, suppression is more pronounced for faster cooling. The suppressed transformation reconvenes on isothermal holding or (re)heating, provided enough time is spent at a temperature below $M_{(re)s}$. No transformation can occur at temperatures higher than $M_{(re)s}$. For the data reported in Fig. 2, the isothermal martensite formation is more pronounced for increased cooling rates, since faster cooling suppresses a larger part of the transformation. For Figs. 3 and 4, the minimum content of retained austenite in the material is fixed by the quenching temperature (the number of nuclei). The suppressed part of the transformation is defined by the cooling rate, which is also determined by the quenching temperature. Consequently, the quenching temperature fixes the maximum fraction of martensite that can form during isothermal holding and (re)heating. The maximum value is reached only if enough time is spent at temperatures below $M_{(re)s}$ during either a long isothermal holding or a slow isochronal (re)heating. A fast (re)heating hinders growth and the completion of the transformation process.
In connection with the above interpretation, thermally activated martensite formation is controlled by either the movement of dislocation that leads to plastic accommodation of the transformation strain arising upon growth into lenticular morphology, or a not conservative movement of the martensite to austenite interface during growth.

### 4. CONCLUSIONS

During sub-zero Celsius treatment, a reduction of the content of retained austenite is observed; this reduction is the consequence of a continuation of martensite formation during the thermal cycle at sub-zero Celsius temperature.

After austenitization and standard quenching, retained austenite is stabilized upon room temperature storage. A sub-zero Celsius treatment performed directly after quenching is more effective in reducing the content of retained austenite in the material.

Martensite formation in AISI 52100 at sub-zero Celsius temperature is thermally activated. Martensite can form on cooling, isothermal holding and (re)heating. Martensite formation can be (partially) suppressed upon fast cooling and fast (re)heating.

The kinetics of the transformation is described in terms of a-thermal nucleation and thermally activated growth of lenticular martensite in agreement with previous studies. Nucleation can occur during cooling; growth is allowed at temperatures below the martensite (re)start temperature both on cooling, on isothermal holding and on (re)heating.

The activation energy for thermally activated martensite formation was determined from heating at various heating rates starting at 93 K, and amounts to 22 kJ/mol. This value is compatible with thermally activated dislocation movement.

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