Martensite formation during incremental cooling of Fe-Cr-Ni alloys: An in-situ bulk X-ray study of the grain-averaged and single-grain behavior

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Abstract

The formation of martensite (ϵ and α') in metastable austenitic Fe-18Cr-(10-11.5)Ni alloys was investigated in-situ during cooling. High-energy X-rays were used to study the bulk of the alloys. Both grain-averaged and single-grain data was acquired. ϵ played an important role in the formation of α' with an indistinguishable difference in the martensite start temperature. The single-grain data indicated that stacking faults appear as precursors to ϵ . An analogy can be made with deformation-induced martensitic transformation, where the generation of nucleation sites would significantly lower the driving force required to overcome the energy barrier in low stacking fault energy Fe-Cr-Ni alloys.

Keywords: Martensitic phase transformation, Synchrotron radiation, Austenitic stainless steel, In-situ investigation, Three-dimensional X-ray diffraction (3DXRD).

Metastable austenitic stainless steels are of high technical interest due to their great formability where necking is delayed by the pronounced work-hardening behavior. Part of the work-hardening behavior is due to deformation-induced martensitic transformation (DIMIT), which has been the subject of extensive research in commercial steels [1–5]. The austenite (hereinafter referred to as γ) stability is critical in order to tailor the mechanical properties of these alloys, and it can be correlated to three fundamental factors: i) chemical driving force ($-\Delta G_{chem}^{fcc \rightarrow bcc/hcp}$), ii) mechanical driving force ($-\Delta G_{mech}^{fcc \rightarrow bcc/hcp}$), and iii) strain-induced generation of potent nucleation sites. The chemical effect can be evaluated by considering the thermal stability, e.g. the martensite start temperature (M_s), but the two other factors are interrelated and their individual contributions are hard to separate. The general mechanical stability towards DIMIT is conventionally evaluated by the M_{d30} temperature, which is the temperature at which 50% of bcc-martensite (hereinafter referred to as α') form at 30%

1 applied true tensile strain. M_s and M_{d30} are closely related for certain alloys, but not for others
2 [6]. The reason for these differences between alloys should be related to the three fundamental
3 factors and presumably to the difference in the formation of martensite, e.g. the difference in
4 nucleation between deformation-induced and athermal transformations. The discussion about
5 the role of hcp-martensite (hereinafter referred to as ϵ) on the formation of α' has been going
6 on for decades. Nowadays, the commonly accepted point of view is that ϵ can be a transient
7 phase [7,8], but it is not a necessary precursor for α' formation [9,10]. Experiments have
8 demonstrated the role of ϵ during deformation and it has been shown to be the favorable
9 nucleation site for α' [11,12]. In contrary, little is known about the influence of ϵ on the
10 formation of α' during cooling. In this case, carefully tailored alloys with close, but different,
11 thermodynamic conditions for α' and ϵ are required to explore the role of ϵ in the formation of
12 athermal α' , and it could also shed further light on the role of ϵ for the nucleation of α' during
13 deformation. The stability of γ is, furthermore, strongly influenced by microstructural factors
14 such as grain size, morphology, and crystallographic orientation [13,14]. Therefore, it is
15 necessary to employ methods that can accurately characterize the phase transformations, in
16 the bulk of alloys, at the level of individual grains, during cooling, in order to improve our
17 current understanding.

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19 In the present work, we have utilized a combination of in-situ grain-averaged (powder) X-
20 ray diffraction and single-grain X-ray diffraction (3D X-ray diffraction (3DXRD) [15]) to
21 investigate the athermal martensitic transformation in Fe-Cr-Ni alloys with different γ
22 stabilities. The γ stability was incrementally controlled by varying the nickel content in these
23 ternary model alloys with low stacking fault energy (SFE).

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25 The alloys were produced by lab-scale arc-melting [16] (grain size $\sim 20 \mu\text{m}$) and in
26 industrial-scale (grain size $\sim 50 \mu\text{m}$). The lab-scale samples were used for in-situ powder
27 diffraction experiments and the industrial-scale samples were used for 3DXRD experiments.
28 The chemical compositions, the calculated SFEs at room temperature [12], the measured M_s
29 (α' and ϵ) and the $\Delta G_{chem}^{fcc \rightarrow bcc/hcp}$ (calculated using Thermo-Calc [17] and database TCFE8
30 [18] at M_s) for the alloys are given in Table 1. The in-situ XRD experiments were performed
31 in the EH3 experimental station at the P07 High-Energy Materials Science (HEMS) beamline
32 at the PETRA III synchrotron source, DESY, Germany. A monochromatic X-ray beam of
33 energy 65 keV and a beam size of $0.4 \times 0.2 \text{ mm}^2$ (3DXRD)/ $0.8 \times 1 \text{ mm}^2$ (Powder diffraction)
34 was transmitted through the bar-shaped samples with the dimensions $1 \times 1 \times 15 \text{ mm}^3$. The
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diffraction patterns were recorded on a 2D PerkinElmer XRD 1621 xN detector placed at about 1108 mm behind the sample. The cooling device consisted of a reservoir of liquid nitrogen and resistivity heating which was controlled by a PID regulator. The experimental setup is schematically presented in Figure 1, where η is the azimuth angle on the area detector, θ is the Bragg angle and ω is the rotation angle of the sample. The cooling rate applied was about 1.5 °C/min. For the 3DXRD experiments, a full scan was carried out with a total angular rotation range from -90° to +50° around the vertical axis (ω) at each temperature step. The acquisition time per diffraction pattern was 0.1 s while continuously rotating the sample over an ω angle of 0.25°. The FABLE software package [15,19] was used to analyze the 3DXRD dataset to determine the position and orientation of specific individual grains [20–22].

Table 1. Chemical compositions (wt. %), SFEs (mJ m⁻²), M_s (°C), and $\Delta G_{chem}^{fcc \rightarrow bcc/hcp}$ (J mol⁻¹) of the investigated Fe-Cr-Ni alloys

Designation	Fe	Cr	Ni	C	N	W	Ti	SFE[12]	$M_s(\alpha', \epsilon)$	$\Delta G^{fcc \rightarrow hcp}$	$\Delta G^{fcc \rightarrow bcc}$	$\Delta G^{hcp \rightarrow bcc}$
L-18-10	Bal.	18.1	9.9	0.002	0.025	-	-	6.6	-20	-1382	-3280	-1898
L-18-10.5	Bal.	17.9	10.4	0.004	0.033	0.02	0.09	7.8	-60	-1467	-3457	-1990
L-18-11	Bal.	18.1	11.0	0.008	0.046	0.03	-	9.6	-110	-1605	-3626	-2021
L-18-11.5	Bal.	18.0	11.5	0.006	0.053	-	-	9.8	-130	-1644	-3669	-2025
I-18-10.5	Bal.	17.9	10.6	0.002	0.019	0.02	0.003	7.8	-60	-1536	-3487	-1951

L: produced in lab-scale I: produced in industrial-scale

Figure 2a shows an example of the 1D X-ray diffraction line profiles for the alloy L-18-10.5 during in-situ cooling. These powder diffraction patterns were obtained from 23 to -150 °C with temperature decrements of -5 °C. The volume fraction evolution of the different phases was evaluated using the direct comparison method [23] and the results are presented as a function of temperature in Figure 2b. The M_s for both α' and ϵ were evaluated using the common tangent method (Table 1). It was found that M_s of α' ($M_s(\alpha')$) was the same as M_s of ϵ ($M_s(\epsilon)$), whereas the driving forces, i.e. $\Delta G^{fcc \rightarrow bcc}$ and $\Delta G^{fcc \rightarrow hcp}$ differ, also between different alloy compositions. Even if the accuracy of the thermodynamic calculations at this low temperature is uncertain, they may assist the understanding of the clear experimental indications that ϵ can reduce the energy barrier for α' nucleation, also seen for DIMIT in [24]. According to the calculated driving forces, about 1500 J mol⁻¹ is required to initiate ϵ

1 formation, whereas larger than about 3200 J mol^{-1} is required to initiate α' formation. When ε
2 has formed, a driving force of less than 2100 J mol^{-1} seems to be sufficient to trigger the
3 transformation of α' , i.e. α' can form more easily at ε plates. It should be noticed, though, that
4 this may only be true for low SFE Fe-Cr-Ni alloys.
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7 By visual inspection of the 2D powder diffraction patterns it is possible to see a few weak
8 diffraction reflections corresponding to α' and ε phases, even above the M_s . Hence, it seems
9 like there are a few relatively unstable γ grains and these were further investigated using the
10 3DXRD data. Figure 3 shows the position and the orientation of these grains in alloy I-18-
11 10.5. Firstly, the position of the γ grain was determined and, for instance, it was found that the
12 position of γ -grain3 equals to ε -grain1 (their center positions are within $100 \mu\text{m}$) (Figure 3a,
13 b). Secondly, the orientation relationship between these two phases was investigated and they
14 followed the S-N (Shoji-Nishiyama) relationship (Figure 3c, d). According to a previous
15 microstructural investigation for the same set of alloys, the equivalent orientation relationship
16 was observed by EBSD [16]. Figure 3e-g illustrates this for alloy Fe-18Cr-12Ni with a
17 composition (wt. %) of 18.1%Cr, 12%Ni, 0.03%Ti, 0.008%C, 0.055%N, and the balance Fe
18 quenched to -196°C . Similar results have also been reported previously [6,25]. The
19 correspondence of both the spatial position and the orientation relationship thus proved that
20 the ε -grain1 formed within γ -grain3 during the in-situ cooling process. The same approach
21 was applied to other γ grains and similar agreements of both orientation and position were
22 found, two representative additional γ - ε pairs were analyzed. The α' units could not be
23 characterized using FABLE due to the small grain size. Instead, with the help of the
24 Kurdjumov–Sachs orientation relationship (Figure 3e, g and h), the position of the α'
25 reflections could be predicted. It is known that the γ plane ($2\bar{2}\bar{2}$) should be parallel to the
26 martensite α' (022), and from the S-N relationship $\gamma(2\bar{2}\bar{2})$ is parallel to $\varepsilon(0004)$. Thus the
27 diffraction vector of ($\gamma(2\bar{2}\bar{2})$, $\varepsilon(0004)$ and $\alpha'(022)$) must be parallel, i.e. at the same ω and η
28 (Figure 4a-1). This approach was used to track the formation of α' within the individual γ
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51 Figure 4 shows the results from the diffraction pattern analysis from the γ -grain3, ε -grain1
52 and the variants forming at the related habit plane, i.e. 6 α' variants. The reflections are
53 indicated in Figure 4a-1, and the integrated area is indicated in Figure 4a-2. It can be seen in
54 Figure 4a-2iii that the diffraction reflections are aligned along the radial direction (red dashed
55 line) which is indicative for their orientation relationships. However, the diffraction
56 reflections are quite different when investigating the peak breadth (2-Theta) as well as the
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angular spread in ω and η . The angular spread is clearly larger for the α' reflections as compared to γ and ε due to their larger misorientations (Figure 3h). The full peak intensity was integrated in both ω and η , and the XRD profiles were evaluated using Fit2D (Figure 4a-2 and 4b). Then, the direct comparison method was applied to evaluate the volume fraction of different phases within the specific γ grains for the specific habit plane (Figure 4c). Due to the large angular spread of the α' reflections, it is possible that some minor intensity was lost during integration. This is a compromise to avoid overlapping reflections, and it may cause a slight underestimation for the α' volume fraction. Figure 4c shows the volume fraction evolution of these phases corresponding to the habit plane ($2\bar{2}2$) within γ -grain3. The observation that $M_s(\alpha')$ is equal to $M_s(\varepsilon)$ is further confirmed here. A discontinuous change of the volume fraction of γ in individual grains was observed. Furthermore, except for the linearly decreasing lattice parameter with the lowered temperature, a sudden but minor decrease of the lattice plane spacing $d\{222\}$ was observed at the onset of the ε and α' formation, see red arrow in Figure 4c, d and e. The sudden decrease of the lattice plane spacing would be in agreement with the formation of stacking faults, especially intrinsic stacking faults [26–28]. As the phase transformation to ε and α' proceeds, the faulted γ is consumed and will not contribute to the peak shift anymore. Thus, the lattice plane spacing d of γ will return to the linearly decreasing behavior as soon as the faulted γ has transformed. It can also be observed that the larger the transformation rate, the larger the deviation of the lattice plane spacing d (Figure 4c-e). This can be interpreted as larger faulted areas of γ that are created when the phase transformation rate is larger. These observations lead us to hypothesize that in these low SFE materials the formation of stacking faults is a precursor for ε . The transformation behavior is schematically illustrated in Figure 4f. The bandlike structure that forms will occur in a sequence with stacking faults creating faulted area of γ , followed by ε , thus facilitating α' nucleation. The final bandlike microstructure is also seen in the EBSD micrograph in Figure 3e. It should, however, be mentioned that it cannot be ruled out that the sudden change of the lattice plane spacing d may be due to other effects such as e.g. internal stresses.

To summarize, the observations in the present work give a strong indication that the phase transformation in low SFE Fe-Cr-Ni alloys occurs via the following sequence $\gamma \rightarrow$ stacking faults $\rightarrow \varepsilon \rightarrow \alpha'$ during incremental cooling. The transient faulting was visualized when considering the individual grains and it could not be seen in the average polycrystalline data most likely due to the transient nature and the averaging of data. Furthermore, the nucleation

of α' is facilitated by the ε formation, which lowers the barrier for the α' nucleation. In the present alloys, the decisive factor for the formation of α' is the introduction of potent nucleation sites in the form of ε . This is the reason for the coincidence of the M_s for ε and α' . A parallel could also be drawn to the deformation-induced martensitic transformation in this alloy system where it is indicated that the formation of ε is very efficient for assisting the formation of α' . This work supports the notion that the generation of potent nucleation sites is critical for the accurate prediction of the deformation-induced α' -martensite formation.

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Figure 1. Schematic illustration of the high-energy X-ray diffraction setup employed for the in-situ cooling experiments. a) Sample and detector layout, b) Cooling device.

Figure 2. In-situ powder diffraction analysis of alloy L-18-10.5 upon cooling. (a) XRD profiles from 23 °C down to -150 °C. (b) Volume fraction evolution of γ , α' and ϵ as a function of temperature.

Figure 3. Tracking of specific grains with the help of 3DXRD and EBSD. (a-d) 3DXRD results for I-18-10.5 at $-65\text{ }^{\circ}\text{C}$, and (e-h) EBSD results for alloy Fe-18Cr-12Ni quenched to $-196\text{ }^{\circ}\text{C}$. (a) Grain positions of γ . (b) Grain positions of ϵ . (c) Pole figure of $\gamma\text{-grain3}$. (d) Pole figure of $\epsilon\text{-grain1}$. (e) IPF map. (f) Pole figure of ϵ . (g) Pole figure of γ . (h) Pole figure of α' .

Figure 4. X-ray diffraction pattern of alloy I-18-10.5 and related analysis. (a) The pattern at -65°C and (a-1) single diffraction peaks of $\gamma\text{-grain3}$, $\varepsilon\text{-grain1}$ and related α' . (a-2) integrated area for the single grain analysis. (b) XRD profile and fitting corresponding to the integrated area. (c) Volume fraction evolution based on integrated area for grain3. (d) Volume fraction evolution based on integrated area for grain11. (e) Volume fraction evolution based on integrated area for grain12. (f) Schematic illustration of the formation of athermal martensite.