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Abstract

© 2020 Acta Materialia Inc. Electron diffraction coupled with aberration-corrected (AC) scanning transmission electron microscopy (STEM) is used to image, identify and confirm the structure producing double diffracted spots seen in electron diffraction patterns in twinned high-carbon steels. The experimental and simulated data show that regions comprising: (i) overlaps between a twin and the matrix or, (ii) overlapping twins, create projected structures that are similar to the ω phase observed in other metastable bcc systems. Thus, AC STEM is proficient in the definitive identification of twins in bcc high carbon steels or nanoscale phases in metastable bcc systems.

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Twins or the omega phase: Which is it in high carbon steels?

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Abstract

Electron diffraction coupled with aberration-corrected (AC) scanning transmission electron microscopy (STEM) is used to image, identify and confirm the structure producing double diffracted spots seen in electron diffraction patterns in twinned high-carbon steels. The experimental and simulated data show that regions comprising: (i) overlaps between a twin and the matrix or, (ii) overlapping twins, create projected structures that are similar to the ω phase observed in other metastable bcc systems. Thus, AC STEM is proficient in the definitive identification of twins in bcc high carbon steels or nanoscale phases in metastable bcc systems.

Keywords: omega; twinning; steel; scanning-transmission electron microscopy (STEM)

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Since the publication of Ref. [1], the idea that a metastable hexagonal omega (ω) phase exists in body-centred-cubic (bcc) high carbon steel has entered into popular scientific discourse. Several papers were subsequently published that notionally confirm the existence of this ω phase as: (i) particles that form at nano-twin boundaries of high carbon martensitic steels and return low ductility by impeding the motion of said twins [2], (ii) a transitional phase that leads to the formation of (112) $\langle$ 111 $\rangle$ nanotwins [2] or, (iii) carbides ascribed as ω particles at twin boundaries of high carbon steels [3].

Following the first reports, a common investigative trend emerged. To confirm the existence of the ω particles as shown in Refs. [1-10], electron diffraction, dark field imaging (diffraction contrast) and/or conventional high-resolution transmission electron microscopy (HRTEM) was employed to first identify and confirm the ω phase. The problem with electron diffraction is that different crystallographic conditions can lead to nearly identical electron diffraction patterns as shown by Cayron [11]. The interpretation of dark field images can be problematic due to its sensitivity to the Bragg angle of the crystals in the specimen; with fractions of a degree causing large changes in intensities [12]. Cases of misinterpretation of dark field images are Refs. [1-4, 6, 7, 10] where granularity in the dark field images is assigned to particles in the electron transparent specimen without further confirmation. Conventional HRTEM as seen in Refs. [2, 8] is never straight forward to interpret due to contrast reversal. Moreover, its limited spatial resolution due to spherical aberration provides a restricted view of the crystal structure; which in turn leads to the misidentification of structures or phases in a specimen [12].

In this work, electron diffraction in conjunction with aberration-corrected (AC) scanning transmission electron microscopy (STEM) is used to unequivocally image, identify and confirm the structure producing the double diffracted spots seen in all electron diffraction patterns in twinned high carbon steels. From the data, regions comprising: (i) overlaps between a twin and the matrix or, (ii) overlapping twins, create structures similar to the ω phase observed in other metastable bcc systems, e.g. β Ti alloys [13].

The nominal chemical composition of the investigated A100Cr6 grade martensitic bearing steel is Fe-1.38Cr-0.97C-0.28Mn-0.28Si-0.21Cu-0.18Ni-0.06Mo-0.04Al wt.%. The material was cast and industrially forged at ~ 1100 °C. After hot forging, the material was subject to soft annealing at 800 °C for 7200 s, followed by slow cooling to form a spheroidised microstructure. $1 \times 4 \times 7$ mm³ sized specimens were then austenitised at 850 °C for 300 s followed by quenching to room temperature in Ar in a Bähr 805A dilatometer. On account of the fast cooling rates during quenching, the undercooled austenite in high carbon steel is transformed to twinned martensite. In the literature under debate in this short communication, austenite is purported to have transformed to the ω phase at this processing step. The specimens were polished to mirror finish

following which 15 μm wide, ≤ 50 nm thick lamellae were prepared in an FEI Helios Nanolab G3 CX FIB-SEM. The lamellae were analysed in a probe corrected JEOL ARM200F cold FEG equipped with a Quantum Gatan Imaging Filter.

Figures 1a and 1b show a grain with multiple edge-on twins and a diffraction pattern from the region marked by the white circle in 1b. Double diffracted spots (or ω spots) clearly appear in the latter. The diffraction pattern is indexed as bcc Fe observed down the $[011]$ zone axis (yellow unit cell), with a twin (green unit cell) and two extra spots (red circles) within the unit cells of the matrix and twin. These spots can either be formed by the double diffraction effect as described by Cayron [11] or by the ω phase as seen in β -metastable Ti alloys [13, 14].

In subsequent paragraphs, we will unequivocally show that it is the former case. By selecting a (011) diffracted spot from the twin (Figure 1c) and the double diffracted spot close to the transmitted beam (Figure 1d), we generated dark field images and combined them into an RGB composite (Figure 1e) such that the image formed by the twins is shown using the green channel and the image formed by the double diffracted spot is shown using the red channel. As seen in the intensity profile in Figure 1f, the regions generating double diffracted spots always overlap with the twinned region. Refer to Figure S1 showing the individual red, green and yellow micrographs. While this result is by no means conclusive, it does provide supporting evidence that the spots are generated by double diffraction.

If the ω phase was real, it is reasonable to expect the formation of more than one variant during quenching. Generally speaking, this expectation is in line with published literature on phase transforming and/or shape memory alloys. For instance, in metastable β Ti alloys [13], the well-known orientation relationship $(111)_{\beta}|| (0001)_{\omega}$ and $[1\bar{1}0]_{\beta}|| [11\bar{2}0]_{\omega}$ between the parent β matrix and the daughter ω phase results in 24 possible variants (including symmetric equivalents) of which 4 are crystallographically unique¹ [15]. However, all the recent articles that claim to identify and confirm the ω phase in high carbon steels always show only one variant in their results. This indicates that the double diffraction spots form on account of the unique crystallographic twinning relationship between the matrix and twins and not the orientation relationship between the parent α -Fe matrix and daughter variants of the ω phase. Regardless of this logic, we undertook atomic resolution imaging to unequivocally identify the structures responsible for these spots.

Figure 2a shows a high resolution HAADF-STEM image of a heavily twinned region as confirmed by the inset fast Fourier transformation (FFT). Figure 2b is an atomic resolution image showing

¹ The misorientation angle/axis between these 4 crystallographically unique hcp variants is $V_1-V_1 = 0^\circ/[2\bar{1}\bar{1}0]$, $V_1-V_2 = 70.5288^\circ/[\bar{1}\bar{1}20]$, $V_1-V_3 = 70.5288^\circ/[\bar{1}2\bar{1}0]$ and $V_1-V_4 = 70.5288^\circ/[2\bar{1}\bar{1}0]$.

a matrix region at the top right, a twinned region at the bottom left and an overlapped region between them in the middle. In the literature, the latter overlapped region is identified and confirmed as the ω phase using electron diffraction, dark field imaging and/or HRTEM. Figures 2c and 2d show atomistic models of how perfect and overlapped (112) $\langle$ 111 $\rangle$ twins appear in an edge-on condition, respectively. Based on Figures 2b and 2d, we conclude that the twins in Figure 2b are not perfect and that an overlapped region exists. The magnified image in Figure 2e underscores the good match between the experimental and simulated atomic structures comprising an overlapped twin-matrix region. When Figure 2d is rotated 90° into the screen or rotated around the local horizontal (or x) axis to a cross-sectional edge-on condition, Figure 2f appears with the atoms in red and blue showing the twin and matrix areas, respectively. The good match between the red and blue atoms indicates that the energy of formation of these interfaces is low and that this could be the prevalent situation whenever twins are formed in high carbon steels. The good match in the atomic planes of the matrix and twins could also be a factor behind α -Fe forming large twin-matrix boundary segments with the same crystallographic twinning relationship. While this aspect is worthy of further study, it is beyond the scope of the present short communication.

Figures 3a shows a HAADF-STEM image of overlapped twins in the present high carbon steel along the [011] zone axis, while Figure 3b shows the ω phase in a Ti-10V-3Fe-3Al (wt.%) metastable β -Ti alloy along the [100] $_{\omega}$ zone axis [13], respectively². It is seen that the projected atomic structure in both images is similar but fundamentally different; with the main difference being 4 distinct atomic positions within a unit cell of the high carbon steel and only 2 distinct atomic positions within the unit cell of the β -Ti alloy. The shortest distance between atoms within the unit cell is 80 pm in the [011] projection; a value that is at the resolution limit of aberration-corrected STEMs. It follows that conventional HRTEM is inadequate to identify and/or confirm the ω phase as the technique lacks the resolution to resolve the atomic positions.

An important point to emphasise is that the HAADF images in Figure 3 are directly interpretable due to the lack of contrast reversal [16]. This is opposed to previous reports [2, 8, 10] where conventional HRTEM was used to identify and confirm the existence of the ω phase in high carbon steel. It is emphasised that interpreting HRTEM images is not straight-forward as the contrast transfer function of such images exhibits contrast reversal, i.e. - the atomic columns can also be dark; a significant fact that is very often overlooked by researchers in recent times.

² The reader may also refer to Figure 1b in Ref. [14] of a HAADF-STEM image of large ω phase in a Ti-20V wt.% alloy.

The above also explains situations where double diffracted spots appear in diffraction patterns, but no twins are observed in the image. This happens when the twins are in face-on condition (Figure S2a) with respect to the electron beam such that double diffraction becomes evident as shown in Figure S2b. Darkfield imaging in Figures S2c to S2f formed by selecting each of the marked spots in the diffraction pattern in Figure S2b provides further evidence that the twins are in a face-on condition. However, such images have been misinterpreted as proof of the existence of the ω phase.

Finally, using the SimulaTEM software suite [17], we calculated electron diffraction patterns (Figures S3a and S3b) of: (i) a perfect (112) $\langle 111 \rangle$ twin and (ii) an overlapped twin-matrix region using the atomic models in Figures 2c and 2d, respectively. As seen in the diffraction patterns, the extra spots are: (i) stronger when there is an overlap between a twin and the matrix (Figure S3b) and, (ii) very weak when there is no overlap (Figure S3a). However, Ref. [7] takes this observation as proof confirming the existence of the ω phase. In that study, the authors state that in a [112] orientation, their simulated twin boundaries do not overlap; hence the diffraction spots are absent. But this argument is erroneous, as an electron beam diffracted at twin boundaries can always diffract: (i) from the matrix towards the twin and then diffract a second time within the twin or, (ii) from a neighbouring twin towards the twin and then diffract a second time within the latter twin; hence the term, double diffraction, meaning that the intensity at the double diffracted spots would asymptote to zero as the thickness of the specimen approaches zero. Simulations can overlook real life factors such as thickness and scattering power, which is why electron diffraction alone is insufficient to confirm the existence of the ω phase.

The above experimental and simulation results unequivocally confirm that the double diffracted spots in high carbon steels originate from overlapped twin-matrix or multiple twin regions. Furthermore, in situations when a bcc unit cell transforms to the ω phase, aberration-corrected HAADF-STEM imaging is useful to definitively identify the latter phase. Conventional HRTEM simply lacks the resolution to identify and/or confirm the ω phase.

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Author contributions

G.C. and A.A.G. conceived the experiments and co-wrote the paper. G.C. undertook STEM analysis and simulations. W.S. undertook sample processing. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Figures

Figure 1: (a) Bright field image of a region containing multiple twins seen in edge-on condition along the $[110]$ zone axis. (b) Selected area diffraction pattern from the region marked by the white circle in (a) along the $[110]$ zone axis where the twins can be easily identified. (c) and (d) Dark field images formed using the $[0\bar{1}1]$ twin

spot and the leftmost double diffracted spot (red circle), respectively. (e) Colour mix image of (c) in green and (d) in red. (f) Relative intensity profile along the white arrow in (e).

Figure 2: (a) HAADF-STEM image of twins. Inset is the FFT of (a) revealing the double-diffracted spots shown using white arrows. (b) HAADF-STEM image of the atomic structure of the matrix, the twin and the overlapping

region. Atomistic models of (c) a $(112) \langle 111 \rangle$ twin plane with no overlap and (d) an overlapping region comprising a $(112) \langle 111 \rangle$ twin (red) and the matrix (blue) shown in edge-on condition. (e) HAADF-STEM image where the superimposed structure of the overlapping twin and matrix show a good match. (f) The overlapped region in (d) rotated 90° into the screen or paper around the local horizontal (or x) axis to cross-sectional edge-on condition.

Figure 3: HAADF-STEM images of (a) $(112) \langle 111 \rangle$ twins in bcc steel and (b) the ω phase in a β -Ti alloy [13].

Atomistic models of (c) a $(112) \langle 111 \rangle$ twin plane with no overlap and (d) a unit cell of the ω phase. In Figure 3a, the atomic columns to the right of the ball-and-stick schematic exhibits a motif of three atoms and not four due to a partial overlap between matrix and twin.

Supplementary material

Twins or the omega phase: Which is it in high carbon steels?

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Figure S1: (a) False-coloured DF TEM image formed with the yellow $[0\bar{1}1]$ spot in Fig. 1b corresponding to the matrix. (b) False-coloured DF TEM image formed with the green $[0\bar{1}1]$ spot in Fig. 1b corresponding to the twins. (c) False-coloured DF TEM image formed with the double diffracted spot marked by the right red circle in Fig. 1b. (d) Colour mix of all (a,b and c).

(a)

(b)

(c)

(d)

(e)

(f)

Figure S2: (a) Bright field image of a twinned grain with the twin boundary in face-on condition. (b) Selected area electron diffraction from the region marked by the white circle in (a). (c-f) Dark field images from the corresponding diffracted spots in (b).

(a)

(b)

Figure S3: Simulated diffraction patterns of (i) a perfect (112) $\langle 111 \rangle$ twin and (ii) an overlapped twin-matrix region using the atomic models in Figures 2c and 2d, respectively.