Formation mechanism of brown etching layers in pearlitic rail steel

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A B S T R A C T

The formation of White Etching Layers (WELs) in rails can lead to the initiation of microcracks, thus reducing the service time of rails. However, the WEL formation mechanism is not yet understood. Brown Etching Layers (BELs) are the intermediate microstructure located between parent pearlite and WEL. In this work, we use BELs as a microstructural tracer to understand the early stages of WEL formation. We study the formation mechanisms of BELs in an industrial R350HT rail steel retrieved from a service application. Atom probe tomography, complementary transmission electron microscopy, and transmission Kikuchi diffraction provide us access to high resolution microstructure characterization. Carbon-depleted cementite lamellae are sheared and cut by dislocations. Several BEL areas with cementite particles exist in the direct vicinity of parent pearlite. Energy dispersive X-ray spectroscopy reveals redistribution of carbon and inhomogeneous distribution of manganese in BEL areas. These results suggest a correlation between cementite decomposition and the formation of BEL. Deformation-induced cementite decomposition causes local alterations in the microstructure regarding defect density and carbon composition, leading to austenite formation in the parent pearlite aided by the temperature ingress during rail/wheel contacts.

1. Introduction

Increasing speed and axle load in train operation urge rails to sustain more severe mechanical loads. The temperature gradient and plastic deformation induced by repetitive rail/wheel contacts cause critical microstructure decay during operation, leading to time- and cost-intensive maintenance. From a microscopic point of view, rail/wheel contacts can be considered as individual thermo-mechanical treatments to the near-surface microstructure of the rails [1]. The severe plastic deformation and rapid heating in the rail/wheel contact regions result in decomposition of the initial pearlite structure (colonies of ferrite with alternating cementite lamellae), crack initiation, and spallation on the rail surface [2,3]. One well-known microstructural alteration is the development of White Etching Layers (WELs). WEL plays a crucial role in initiating microcracks due to its higher hardness than the adjacent parent pearlite. Microcracks can form at stress concentration sites around (i.e. at the pearlite/WEL interface) or inside the hard WEL and propagate into the bulk of the rail material, leading to severe degradation of the service time of the rail [3–5].

The formation mechanism of WELs is primarily discussed along two concepts in literature. The first concept assumes that WEL is generated through martensitic transformation [6,7]. Upon exposure to cyclic loading, pearlite at the rail surface is subjected to rapid frictional heating and reaches austenitization temperatures, triggering the formation of new austenite grains. Subsequent rapid cooling of the rail surface induces the transformation of the newly formed austenite grains into martensite. The second concept correlates the WEL formation with severe plastic deformation [8–10]. Cementite lamellae from the pearlitic microstructure decompose during the cyclic deformation process, releasing C atoms into the surrounding ferritic matrix and stabilizing a nanocrystalline ferrite structure. However, recent studies suggest that WEL formation involves both mechanisms simultaneously. Zhang et al. [11] and Al-Juboori et al. [4] observed that WEL contains multiple microstructure constituents, including martensite, severely deformed pearlite lamellae, austenite, and cementite. Kumar et al. [1] proposed that WEL is generated cumulatively upon a large number of short but intense deformation and heating cycles. Nevertheless, the transition states between pearlite and WEL were never directly observed and investigated. The exact cementite decomposition mechanisms and the redistribution path of C atoms in rail steel microstructures have attracted little attention so far.

Brown Etching Layer (BEL) describes a second zone affected by rail/wheel contacts. While WELs appear white in optical microscopy after nital-etching, BELs, which are more prone to chemical etching, appear darker after the etching treatment. When looking at a rail cross-section, BEL is usually observed directly below the WEL but above the deformed parent pearlitic structure. As a result, BEL is regarded as a
transition zone between the original pearlitic microstructure and WEL [1,12,13]. BEL is interpreted as tempered martensite or tempered WEL [12], whereas it is also explained as a precursor of WEL [13]. In a recent study, Kumar et al. [1] revealed the coexistence of austenite, martensite, C-enriched ferrite, and partially dissolved cementite in BEL, indicating that cementite decomposition and C redistribution occur upon the formation of BEL. Thus, understanding the initial steps of pearlite decomposition and the formation of BEL from the deformed pearlite is essential to unraveling the entire WEL formation mechanism.

This work is a follow-up investigation based on Refs. [1,14] by part of the current authors. In Ref. [1], we characterized the microstructures of deformed pearlite, BEL, and WEL in a fatigued rail steel at the mesoscale and identified two possible paths for the formation of BEL depending on the distance from the rail surface. In the BEL region closer to the rail surface (i.e., close to WEL), BEL is generated through large-scale austenitization followed by martensitic transformation as temperatures frequently reach above the austenitization temperature. On the other hand, in the BEL regions far from the rail surface (i.e., close to deformed pearlite), BEL formation involves deformation-induced cementite decomposition and partial austenitization (followed by martensitic transformation). As temperature spikes only occasionally reach above the austenitization temperature, only a part of the deformed pearlite is transformed first into austenite and then into martensite during subsequent cooling, yielding a mixture of martensite, austenite, C-enriched ferrite, and partially decomposed parent cementite.

However, the exact transition path is still unclear due to the concurrent presence of plastic deformation and temperature ingress. This circumstance makes it challenging to retrace the microstructure evolution precisely. Therefore, in Ref. [14], we investigated the mechanical and thermal effects individually under controlled laboratory conditions. To decouple these two factors, we used a binary Fe-C pearlitic steel, employed a rolling contact fatigue test at a controlled temperature of 60 °C to investigate the impact of mechanical deformation separately, and then conducted heat treatments on the same specimen to investigate the effect of elevated temperatures solely. After the fatigue test, C in cementite was found to be depleted from 25 at% to ~20 at%, and in other positions, cementite was entirely decomposed. After subsequent heating at 250 °C for 30 min, the C-depleted cementite remained surprisingly stable — neither further dissolution nor recovery back to the stoichiometric level of 25 at% occurred. These findings suggest that plastic deformation itself can trigger cementite decomposition and the release of C atoms. The effect of temperature (up to 250 °C) only plays a minor role. Now, with a better understanding of the effects of deformation and temperature on cementite decomposition in a model Fe-C binary system [14], we return to the more complex rail steel scenario, which involves heat and deformation at the same time.

Here, we study the mechanisms of cementite decomposition and the microstructural evolution of deformed pearlite into BEL in the H350RT pearlitic rail steel using scanning electron microscopy (SEM), transmission electron microscopy (TEM), transmission Kikuchi diffraction (TKD), and atom probe tomography (APT). In particular, we focus on the zone directly located between deformed pearlite and BEL, which represents the instance just before complete cementite decomposition. The cementite decomposition mechanisms are compared with the modified solute drag model [14]. The formation mechanisms of BEL are discussed and correlated with deformation-induced cementite decomposition.

2. Materials and methods

2.1. Material

A specimen of R350HT pearlitic steel was extracted from a curved rail track with a curvature radius of 400 m after exposure to service. The composition of the R350HT steel is Fe-0.72C-1.1Mn-0.56Si-0.11Cr (wt%), or Fe-3.23C-1.1Mn-1.09Si-0.11Cr (at%). After casting, the alloy was hot rolled at 1000 °C, annealed at 900 °C for three hours, and cooled in accelerated airflow to room temperature. This treatment yields a microstructure of fine pearlite. The accumulated load passage was estimated to be 200 million tons with an axial load ranging from 120 to 180 kN [1]. Nevertheless, the exact loading history is difficult to quantify due to a large number of unknown parameters, which can vary in each train passage, such as axle load, speed, and friction coefficient [1,6].

2.2. Stress and temperature cycles at rail/wheel contacts

For rail steels, rail/wheel contacts are considered as individual thermo-mechanical treatments of the pearlitic microstructure in the rail subsurface volume [1]. Although the loading conditions of individual rail/wheel contacts are continuously changing during service [15], the peak stresses and temperatures can be approximated with finite element modeling estimations [1]. The highest von-Mises stress is estimated to be ~825 MPa at ~100 μm beneath the rail surface. This is higher than the yield strength of the R350HT pearlitic steel, which is 750 ± 10 MPa [16]. The plastically deformed area extends down to 200 μm below the surface. As for the temperature effect, the entire heating and cooling process occurs within 1 ms [1], i.e., complete cooling down to ambient temperature occurs before the next wheel contact. The highest temperature in the cycle was estimated to be 982–737 °C at a depth of 20–40 μm beneath the rail surface [1]. Therefore, in the transition zone between BEL and deformed pearlite (~40 μm beneath the rail surface), the pearlitic microstructure was subjected to cyclic plastic deformation as well as rapid heating and cooling cycles during the service of the rail.

2.3. Characterization techniques

Electron channeling contrast imaging (ECCI) was carried out using a Zeiss Merlin field emission gun-scanning electron microscope (FEG-SEM) with a voltage of 30 kV and a working distance of 7 mm. A dual-beam FEI Helios NanoLab 600™ focused-ion-beam (FIB) microscope was applied to prepare lamella-shaped TEM and needle-shaped APT samples. A JEOL JEM-2100 transmission electron microscope was employed to characterize the microstructures in conventional TEM mode at 200 kV. Scanning TEM (STEM) together with energy dispersive X-ray spectroscopy (EDX) was performed in a JEOL JEM-2200FS microscope. TKD was conducted in a Zeiss Merlin FEG-SEM equipped with an OPTIMUS™ TKD detector head. The orientation mapping was carried out at 30 kV and at a working distance of 3 mm with a step size of 3–5 nm. APT was conducted using a Cameca LEAP 5000X at in laser mode at a temperature of 60 K. APT data was acquired with a target evaporation rate of 0.8% and pulse repetition rate of 200 kHz. The laser-pulse energy was set to 40 pJ. In addition, 10 pJ laser energy was used to compare the effect of laser pulse energy on C composition quantification. The acquired APT datasets were analyzed with the CAMECA AP Suite 6.1 software. The ranging of mass spectra was conducted according to Tung et al. [14] and widely applied standard protocols [17–21]. To extract more accurate compositions, we conducted separate analyzes on regions of interest (ROIs) using the built-in peak decomposition algorithm in the AP Suite software, where all overlapping peaks (including all ion types) are separated and unmixed in the mass spectrum.

2.4. Reference APT measurement for normalization of carbon composition in cementite

We discuss the quantification of C composition by APT throughout this study. The accuracy of C composition quantification in carbides using APT is discussed in Refs. [19,22]. C tends to field-evaporate as ionic compounds, which can dissociate on the way to the detector and cause detection events close in time and space (referred to as multiple hit events). This leads to detection losses of C, also known as the detector pile-up effect compromising the compositional analysis [23–25]. The related artifacts can be minimized by adjusting experimental parameters.
Fig. 1. APT measurements of undeformed pearlite with different laser energies. 3D distribution of carbon atoms with laser-pulse energy of (a) 40 pJ and (b) 10 pJ, where the analysis of compositions for regions of interest (ROIs) are conducted using the peak decomposition algorithm. (a’) and (b’) 1D composition profiles along arrows in (a) and (b) showing cementite lamellae with carbon compositions of 21.2 and 24.8 at%.

for data acquisition. It is reported that C in cementite comes closer to the stoichiometric composition with decreasing laser-pulse energy [19]. However, lower laser-pulse energies usually cause easier specimen fracture during APT measurements. Therefore, to obtain a better specimen yield, we use a higher laser-pulse energy of 40 pJ for APT measurements and accept the compromised C quantification. Then, the measured C composition with laser-pulse energy of 40 pJ is normalized by a reference APT dataset with laser-pulse energy of 10 pJ. The effect of laser-pulse energy on C quantification is depicted in Fig. 1, which shows two APT measurements with laser-pulse energy of 40 pJ and 10 pJ, respectively. In the APT reconstructions, C atoms are marked with red dots, and areas of C enrichment are enveloped by green 7.0 at% C isocomposition surfaces highlighting cementite lamellae. The specimens were extracted from pearlite at a depth of 5 mm below the rail surface (an undeformed state in the specimen bulk). The peak decomposition analysis from the dataset measured with 40 pJ yields a C composition in the cementite lamellae of only 21.2 ± 0.13 at% (Fig. 1a), which is well below the stoichiometric value of 25 at% C for cementite and affected by APT artifacts. In contrast, with a laser-pulse energy of 10 pJ, the average C composition via peak decomposition analysis yields 24.8 ± 0.34 at% in cementite (Fig. 1b). This is in close agreement with the composition of stoichiometric cementite. The measured C composition in cementite with 40 pJ is underestimated by 17.8%. Hence, knowing that the C composition of 21.2 at% measured at 40 pJ should correspond to a C composition of 25 at%, we normalize the C composition in cementite throughout measurements with 40 pJ. All C composition analyses in cementite measured with 40 pJ are normalized by multiplication with a correction factor of 1.18 to receive the corrected composition. The normalization procedure is applied only to ROIs in crystalline cementite (i.e., the results calculated by the peak decomposition algorithm) and not to 1D composition profiles in cementite. For the analysis of C composition in ferrite matrix, we discuss without the normalized values, as the artifact-related difference between the two measurement conditions is negligible (0.23 ± 0.01 at% with 40 pJ and 0.27 ± 0.01 at% with 10 pJ).

3. Results

3.1. ECCI microstructure characterisation

Fig. 2 shows ECCI micrographs obtained from a cross-section along the rolling direction and reveals the microstructure below the rail surface. Fig. 2a presents an overview image where the WEL and BEL both correspond to the bright contrast regions. This is because the ECCI technique is applied on a polished surface and thereby is not sensitive to the difference in etching resistance between WEL and BEL. Instead, the bright and homogeneous contrast of WEL/BEL in Fig. 2 is due to the high defect density and small grain size in the microstructure, in comparison to the deformed pearlite [26]. The nanoscale grains in the WEL/BEL approach the resolution limit of ECCI and thus yield an averaged-out image contrast. The nanoscale grains in the WEL/BEL make these regions appear in a relatively homogeneous bright contrast, where it is difficult to resolve individual grains. The interface between the WEL/BEL region and deformed pearlite is located at a depth of ~40 μm. However, as shown in Fig. 2b, the microstructure transition is not sharp but appears in a zone consisting of mixed patches. Interestingly, regions of untransformed pearlitic microstructure are surrounded by the BEL. In the deformed pearlite islands (Fig. 2c), ferrite and cementite from the parent pearlitic microstructure can be identified. Deformation-induced bending and fragmentation of cementite are observed.

3.2. TEM and TKD analysis of transition zone between BEL and deformed pearlite

Fig. 3a shows a STEM bright-field (BF) micrograph of a region ~40 μm beneath the rail surface. This region corresponds to the transi-
The microstructure in the BEL is considered mainly martensite for three reasons. First, similar lath martensite-like microstructure was found at the interface of WEL and deformed pearlite in a rail steel [6]. Second, according to our previous study on the same sample [1], austenite grains with the size of 50–100 nm were observed in the BEL, indicating the BEL region witnessed a temperature higher than the austenitization temperature (Ac1) temperature. The temperature higher than Ac1 and subsequent rapid cooling (induced by the rail/wheel contact) could lead to the formation of martensite in the BEL region. Third, an orientation relationship between ferrite and austenite in the BEL is in close agreement with the Kurdjumov-Sachs (K-S) orientation relationship (see Fig. S1), suggesting the presence of martensite in the BEL [27]. Nevertheless, despite the results indicating the presence of martensite in the BEL, additional proof shall be provided in future studies.

In the upper middle of Fig. 3a, an island of untransformed pearlitic microstructure is entirely surrounded by the BEL (as also observed in Fig. 2b). In Fig. 3a, a sharper transition between undeformed pearlite and BEL is observed, with a mixture of microstructural patches of both types co-existing in the close vicinity. This indicates that the formation of BEL may not only be controlled by temperature gradient and stress state, which should be both virtually identical in such spatial vicinity. Furthermore, other factors such as differences in local composition and defect density can play a role (as discussed in Section 4.2). The interface between the BEL and deformed pearlite is not always well-defined, particularly at the bottom of Fig. 3a. The same area as in Fig. 3a is also probed by TKD. The inverse pole figure (IPF) orientation map in Fig. 3b reveals that the parent ferrite of pearlite colonies is separated by low-angle cell boundaries, forming ferritic cells. Data points with confidence index below 0.25 are removed and replaced by black pixels in the orientation map. The areas of omitted data points mostly correspond to the BEL with higher dislocation density and strain in martensite, which renders pattern indexing less reliable. Fig. 3c displays the phase map of the same area, where cementite is excluded as it is not reliably indexed due to overlapping diffraction patterns and the complex crystal structure.

Fig. 4 shows the STEM-EDX analysis of the region marked in Fig. 3a, where a martensite region (included in the BEL) is surrounded by deformed pearlite. The STEM-BF micrograph in Fig. 4a shows a well-defined interface between the martensite and the deformed pearlite. Fig. 4b and c display the EDX maps of carbon (C) and manganese (Mn) distributions. It is known that Mn atoms partition from ferrite into cementite lamellae during pearlite formation. As a result, cementite is both C- and Mn-enriched in the areas of deformed pearlite. In the martensite region, however, C is far more homogeneously distributed; in contrast, Mn is still enriched in locations of prior cementite lamellae (Fig. 4c). Mn redistribution upon cementite dissolution is sluggish during rapid heating and cooling cycles, leading to the inheritance of Mn distribution from the prior pearlite structure into austenite and then martensite [28,29]. Consequently, the Mn distribution can be used to detect prior cementite locations. Yet, the initial pearlitic microstructure has now transformed into martensite. As shown in the magnified STEM-BF (Fig. 4a’) and EDX maps of C (Fig. 4b’) and Mn (Fig. 4c’), the spherical or elongated dark-contrast segments are both C- and Mn-enriched, and their alignment is consistent with the surrounding cementite lamellae orientation of the prior colony. Therefore, these segments are considered as undecomposed cementite in the martensite area. This indicates that the temperature increase during rail operation is sufficient for C redistribution but not for Mn homogenization, which is a much more slowly diffusing substitutional element. Furthermore, it is essential to note that the cementite-free yet Mn-enriched areas in the martensite region are no longer continuous but composed of smaller fragments. This suggests that the transition from pearlite to BEL involves mechanical cementite fragmentation before cementite decomposition.

Fig. 5 shows a correlative TEM and TKD analysis of deformed pearlite at the point of transformation to martensite. Fig. 5a shows an overview TEM-BF micrograph. The magnified TEM-BF micrograph acquired in a two-beam condition (Fig. 5a’) reveals strain contrast in and around ce-
Fig. 3. Correlative STEM and TKD characterization on the transition zone between BEL and deformed pearlite. (a) STEM-BF micrograph, (b) inverse pole figure (IPF) map, and (c) phase map from TKD analysis of the same region as shown in (a). Black pixels in (b) and (c) indicate data points with confidence index < 0.25, mostly corresponding to grain boundaries, cementite, and martensite. The region in the black frame in (a) is further analyzed by STEM-EDX in Fig. 4.

The cementite lamellae Fig. 5b and c show the TKD inverse pole figure (IPF) and phase maps of the same region, respectively. According to Fig. 5b, the entire area stems from the same initial pearlite colony as the ferrite cells show almost identical orientations. Furthermore, we observe three different cementite morphologies, suggesting different decomposition stages. In the bottom region, cementite remains lamellar without severe fragmentation. However, in the left middle region, cementite lamellae are plastically deformed (Fig. 5a’). In the upper left region, cementite lamellae are entirely fragmented and become sphere-like (and elongated) particles, which is similar to the morphology of remaining cementite in the martensite area in Fig. 4.

Fig. 6 shows STEM-BF micrographs of deformed pearlite in the direct vicinity of martensite in the BEL. Fig. 6a shows cementite precipitates with almost spherical morphology in the nearby martensite regions, which is similar to the deformed pearlite region in the upper left of Fig. 5a. The magnified segment in Fig. 6a’ displays cementite particles with rounded edges, which are commonly observed in tempered cementite [30]. In Fig. 6b, twinned martensite is observed directly next to the region containing spherical cementite particles. The interface appears smeared out due to the overlapping of microstructures throughout the thickness of the TEM foil. Fig. 6b’ shows a magnified image area where the shearing of cementite lamellae can be observed. Dislocations are accumulated at the cementite/ferrite interfaces. The martensite is only observed in the region containing both ferrite and spherical cementite instead of pearlite regions with lamellar cementite. These results suggest that fragmentation of cementite occurs prior to the formation of martensite, and cementite fragments with initially sharp edges are spheroidized during the repetitive thermo-mechanical cycles.

3.3. APT analysis of carbon composition

Fig. 7 shows the APT results of lifted-out probe volumes from a depth of ~40 μm below the rail surface. As shown in Fig. 7a, this position corresponds to the transition zone between BEL and deformed pearlite. Fig. 7b shows an exemplary APT reconstruction, where C atoms are shown as red dots and areas of C enrichment are enclosed by green 7.0 at% C isocomposition surfaces highlighting the locations of cementite lamellae. In addition, three regions of interest (ROIs) are marked with dotted frames. In particular, areas of Mn enrichment in ROI2, enclosed by yellow 2.5 at% Mn isocomposition surfaces, are shown in the inset of Fig. 7b. In these ROIs, we analyzed the composition with the peak decomposition algorithm integrated with the IVAS software to obtain the most accurate composition values. The measured C composition in the cementite lamella (ROI1) is 17.9 ± 0.08 at% based on analysis via peak decomposition yielding a reference-corrected C composition of 21.1 at%. This value is calculated based on the reference measurement (see Section 2.4). Compared to the stoichiometric cementite composition, C is depleted in cementite by 3.9 at% in the transition zone. Also, spherical cementite is observed in the reconstructed volume, as indicated by the shape of the isocomposition surfaces. The measured
Fig. 4. STEM-EDX analysis of the martensite region surrounded by deformed pearlite (corresponding to the black frame in Fig. 3a). (a) STEM-BF micrograph. (b) EDX map of carbon showing its enrichment in cementite lamellae in the deformed pearlite areas and a more homogeneous distribution in BEL with less C-enriched zones except for a cloud of C-enriched dust in the middle right. (c) EDX map of manganese showing its enrichment in cementite lamellae in the deformed pearlite areas and also enrichment in smaller fragments of prior cementite locations in the martensite region. Undecomposed cementite particles can be identified in the magnified STEM-BF micrograph (a’) and EDX maps of carbon (b’) and manganese (c’).

Fig. 5. Correlative TEM and TKD analysis of deformed pearlite on the verge of transformation to martensite. (a) TEM-BF micrograph showing the transition of deformed pearlite to martensite. (a’) Magnified segment from (a) showing the strained cementite lamellae in a two-beam diffraction condition. (b) Inverse pole figure (IPF) distinguishing the martensite region from the deformed pearlite. (c) Phase maps of the same area showing three different cementite morphologies: sphere-like, fragmenting, and lamellar cementite.
Fig. 6. STEM-BF micrographs of deformed pearlite in the vicinity of martensite. (a) Cementite fragmentation and spheroidization in pearlite next to the martensite. (b) Shearing of the cementite lamellae and dislocations accumulated at the ferrite/cementite interfaces. (a’) and (b’) showing magnified micrographs.

Fig. 7. APT results of probe volumes extracted from a depth of ~40 μm from the rail surface (i.e. transition zone between BEL and deformed pearlite). (a) Secondary electron (SE) micrograph of the area selected for target preparation by FIB for APT analysis. (b) 3D distribution of C atoms in one exemplary reconstructed tip volume with peak decomposition analysis in the three regions of interest (ROIs), where the reference-corrected values are shown. Areas of Mn enrichment in ROI1 are enveloped by yellow 2.5 at% Mn isocomposition surfaces and displayed in an inset of (b). 1D composition profiles across (c) lamellar cementite and (d) spherical cementite along the cylinders are highlighted in (b).
peak decomposed C composition in the spherical cementite (RO2) is $19.5 \pm 0.10 \text{ at}\%$, which corresponds to a reference-corrected C composition of 23.0 at\%. Hence, the C composition is reduced by 2.0 at\% compared to the initial stoichiometric cementite composition. The spherical cementite shows less C depletion than the deformed lamellar cementite. The C composition in the ferrite matrix is $0.6 \pm 0.02 \text{ at}\%$; an increase of 0.4 at\% as compared to the undeformed state. Fig. 7c and d show 1D composition profiles across the cementite lamella and the spherical cementite highlighted in Fig. 7b, respectively. The Mn profiles in both lamellar and spherical cementite reveal a ‘V-shaped’ composition curve, which is generated upon typical nucleation and growth of cementite from the center to both sides [31] (as can be observed in Fig. 1a’ and b’ as well). The increasing Mn composition from the inner to the outer shell results from the increasing solubility of Mn with decreasing temperature during air-cooling [31]. Such anisotropic Mn enrichment is also observed in the spherical cementite (see the inset in Fig. 7b). Thus, the two similar ‘V-shaped’ Mn profiles indicate that the spherical cementite stems from prior lamellar cementite and is not newly formed during rail wheel contacts. Otherwise, we would observe only C atoms and no substitutional Mn atoms in the cementite precipitate.

4. Discussion

4.1. Decomposition of cementite

We define and understand ‘cementite decomposition’ as the transition process from cementite to ferrite involving plastic deformation, whereas ‘cementite dissolution’ refers to the phase transformation that is purely due to the heating of cementite above its thermodynamically stable regime.

Before discussing possible cementite decomposition mechanisms, we briefly summarize the key results of this work. In the newly formed martensite region (Fig. 4), C is redistributed (Fig. 4b), but isolated Mn-enriched segments still exist at the locations of prior cementite lamellae (Fig. 4c). This indicates that pre-existing cementite lamellae are fragmented before decomposition. Only a small amount of spherical precipitates remains structurally intact as cementite after the rail operation. In deformed pearlite just below the BEL (Fig. 5), which has not yet transformed into martensite, cementite shows a variety of morphologies; some precipitates maintain a relatively complete lamellar structure, some are strained and fragmented, and some are spheroidized which are later maintained in the freshly formed martensite. Dislocation accumulation and pile-up at the cementite/ferrite interfaces are observed (Fig. 6), and the deformed lamellar cementite is C-depleted by $\sim 3.9 \text{ at}\%$ with respect to stoichiometric composition (Fig. 7). These results suggest that martensite is generated after cementite fragmentation and partial decomposition of cementite particles. Hence, deformation-induced cementite decomposition and the release of C play critical roles in the formation of BEL. In the following, we discuss possible cementite decomposition mechanisms in terms of thermodynamic and kinetic driving forces and outline a cementite decomposition process describing the scenario of rail steel exposed to repetitive rail/wheel contacts.

4.1.1. Thermodynamics

One thermodynamic driving force for cementite decomposition arises from the strong interaction energy between C atoms and defects in ferrite [32]. Both the C-dislocation interaction energy and the C-vacancy interaction energy in ferrite ($\sim 0.75 \text{ eV/atom}$ [33,34] and $\sim 0.85 \text{ eV/atom}$ [35], respectively) are higher than the binding energy of C in cementite ($\sim 0.5 \text{ eV/atom}$ [36,37]). Hence, C atoms prefer to be located at defects in ferrite than in cementite. In other words, there is a thermodynamic driving force for C atoms to migrate from cementite to defects in ferrite. Upon repetitive rail/wheel contacts, the number of available defects in ferrite, i.e. dislocations (Fig. 6b) and vacancies, substantially increases, particularly in the highest strained zone below the railway surface. The presence of such new and C-free defects provides a driving force for cementite decomposition.

Another thermodynamic driving force for cementite decomposition occurs upon the fragmentation of cementite and is related to the Gibbs-Thomson effect [38,39]. The shear-induced fragmentation of cementite during severe plastic deformation increases its total interfacial energy. In theory, this raises the instability of cementite and leads to further cementite decomposition. However, the Gibbs-Thomson effect appears to be negligible in the current scenario. The Gibbs-Thomson equation for ferrite and cementite in a binary Fe-C system [40] can be approximated as

$$X_{eq}^c = X_{eq}^f \exp \left( \frac{8\gamma_{eq}^c}{\kappa T} \right)$$

(1)

where $X_{eq}^c$ denotes the solubility of C atoms in ferrite with cementite estimated as spherical particles of radius $r$, $X_{eq}^f$ denotes the solubility limit of C atoms in ferrite with a flat ferrite/cementite interface, $\gamma$ is the surface energy, $\kappa$ the average atomic volume of cementite, $\kappa$ the Boltzmann constant and $T$ the temperature. Using Eq. (1), we calculate the variation of the solubility of C atoms in ferrite with respect to the radius of the cementite particle (as shown in Fig. 8). The temperature is selected as the $A1$ temperature, i.e. 727°C for the binary Fe-C system, which is comparable to temperatures during the rail/wheel contacts. The remaining parameters are chosen as $\gamma = 0.174 \text{ J/m}^2$ [41], $X_{eq}^c = 7.3 \times 10^{-6}$ [41,42], $v_{eq}^c = 1.17 \times 10^{-29} \text{ m}^3$ [41,43], and $k = 1.38 \times 10^{-23} \text{ J/K}^{-1}$. According to Fig. 8, the solubility of C in ferrite hardly changes when the radius of the cementite particle is between 10 and 100 nm. The TEM results (Fig. 4c) show that the fragmented cementite lamellae fall in this regime. Therefore, the Gibbs-Thomson effect only plays a minor role in this case.

4.1.2. Kinetics

Kinetically, cementite decomposition can be accomplished through C transport from cementite to ferrite facilitated by dislocations. In the concept of pipe diffusion [44], dislocations are regarded as paths for accelerated C transport from cementite to ferrite. Due to the lower diffusion barrier than bulk diffusion, C atoms preferentially move through dislocation cores into ferrite and leave C vacancies in cementite. Although this mechanism is considered ineffective in pearlite deformed by rolling contact fatigue at temperatures below 250°C [14], the elevated temperatures involved in the current scenario could render pipe diffusion more feasible. The pipe diffusion rate via dislocation cores is directly linked to the hopping frequency of carbon atoms $v$ [45], which
can be expressed as:

\[ \nu = \nu_0 \exp \left( -\frac{E_{\text{barrier}}}{kT} \right), \]  

(2)

where \( \nu_0 \) denotes the attempt frequency, \( E_{\text{barrier}} \) denotes the minimum energy barrier for C diffusion via a screw dislocation in ferrite, \( k \) is the Boltzmann constant, and \( T \) is temperature. Using \( \nu_0 = 1.2 \times 10^{13} \) \( \text{Hz} \), \( E_{\text{barrier}} = 0.2 \) eV \( \text{[45]} \), and \( k = 8.62 \times 10^{-5} \) eV K\(^{-1} \), we obtain the C hopping frequency \( \nu = 1.27 \times 10^{12} \) s\(^{-1} \) at 737 °C (an estimated temperature during the rail/wheel contacts, as mentioned in Section 2.2). This value is eight times higher than the hopping frequency at 250 °C (\( \nu = 1.42 \times 10^{11} \) s\(^{-1} \)). Hence, C transport from cementite to ferrite might be enhanced by pipe diffusion in the rail steel investigated here.

Another dislocation-driven kinetic process is the solute drag mechanism \( \text{[18,46]} \). Mobile dislocations in ferrite collect C atoms from the cementite/ferrite interface and transport them into the ferrite bulk, where C remains bound in Cottrell atmospheres around dislocation cores. This mechanism requires C atoms to be able to follow the dislocation movement (i.e., the velocity of \( C \geq \) the velocity of dislocation), thereby controlled by temperature and strain rate \( \text{[45]} \). A recent study on cementite decomposition by rolling contact fatigue \( \text{[14]} \) found that lamellar cementite becomes C-depleted throughout its entire thickness. This gives rise to a modified solute drag model, suggesting that C atoms are dragged and carried from cementite into ferrite by dislocations cutting through the entire cementite lamellae. As a result, the initially stoichiometric cementite (25 at\% C) becomes under-stoichiometric with a C composition of only ~20 at\% (i.e. reduced by ~5 at\%) while maintaining the cementite crystal structure. Afterward, cementite decomposition sets in through the dislocation-shuffle mechanism (further explained in Refs. \( \text{[18,47,48]} \)).

Similar microstructural alterations are observed in the current rail scenario, and the APT measurements support the modified solute drag model \( \text{[14]} \). Tangled and jogged dislocations are found at the ferrite/cementite interfaces (Fig. 4), while the C composition in the deformed lamellar cementite reduces by ~3.9 at\% compared to the undeformed cementite (Fig. 7a). In addition, the C composition of the ferrite matrix is ~0.2 at\% in pearlitic regions without cementite decomposition (Fig. 1), and increases to ~0.6 at\% in the deformed pearlite region (Fig. 7), yielding a C composition increment of 0.4. We now validate the measured C-depletion in cementite and C-enrichment in ferrite through an indirect calculation using an estimated volume fraction of cementite before deformation. In the undeformed pearlitic, the thickness of cementite lamellae and the interlamellar spacing are approximately 10 nm and 120 nm, respectively. Thus, the volume fraction of cementite is ~8.4%. Assuming that all C atoms (i.e. ~3.9 at\%) released from cementite (through the solute drag or the pipe diffusion mechanisms) are incorporated in the surrounding ferrite, the C composition increment in ferrite yields ~0.4 at\% after deformation. This value matches the C composition increment measured by APT, further supporting the modified solute drag model \( \text{[14]} \).

Indeed, the unknown loading history poses a challenge to estimating the strain rate. However, if we assume that the strain rate for the rail scenario is comparable to wire drawing, the temperature rises by rail/wheel contacts make the solute drag model highly plausible through enhanced C mobility. According to previous calculations, the hopping frequency of C is 1.27 \times 10^{12} \text{s}^{-1} at 737 °C, yielding a carbon velocity of 1.52 \times 10^{12} \text{Ås}^{-1} (assuming the distance of a jump between two interstitials is 1.2 Å \( \text{[45]} \)). This value is much higher than the dislocation velocity range for wire drawing, 80–1000 Ås\(^{-1} \) \( \text{[45]} \).

Following the argumentation above, the cementite decomposition process in rail steel under service operation can be outlined as follows. As long as the \( \text{Ac}_1 \) temperature is not reached locally in the microstructure, C atoms from cementite are transported to ferrite by dislocations cutting through cementite lamellae (according to the modified solute drag mechanism \( \text{[14]} \)). Also, the transport of C might be further enabled through the pipe diffusion mechanism at elevated temperatures. Slip transmission and slip step formation are induced by dislocations cutting through cementite lamellae, leading to fragmentation of cementite lamellae. At a later stage, C-depleted cementite fragments decompose progressively through the dislocation-shuffle mechanism \( \text{[18,47]} \). When certain conditions are met (as discussed in Section 4.2), the deformation-induced microstructure alterations (e.g. the release of C from cementite into surrounding ferrite and the high defect density) may trigger austenite transformation in the localized regions. Consequently, the remaining undecomposed cementite fragments are incorporated into austenite/martensite during phase transformations upon rail/wheel cycles (as shown in Fig. 4).

However, to uncover the formation mechanisms of BEL, it is essential to understand how cementite decomposition influences the critical conditions for austenite formation. In the following, we discuss the austenite/martensite formation under the condition of the complex interaction of temperature and deformation in the current rail scenario.

4.2. Microstructural factors controlling austenite formation

We observe martensite forming in the deformed pearlite region (see Fig. 6). Martensite formation requires a temperature above \( \text{Ac}_1 \) for austenitization followed by rapid cooling to trigger the diffusion-less transformation from austenite to martensite. Consequently, the local temperatures in the martensitic regions must have been above \( \text{Ac}_1 \) during rail/wheel contacts. Therefore, assessing the \( \text{Ac}_1 \) temperature of the deformed pearlite regions with respect to the temperature ingress induced by rail/wheel contacts is essential for understanding the formation of BEL. This section discusses crucial microstructural factors influencing austenite formation in the deformed pearlite.

We frequently observe islands of BEL (i.e., martensite transformed from temporary austenite grains) directly adjacent to residual deformed pearlite in the transition zone between BEL and deformed pearlite (at the same depth beneath the railway surface, as shown in Figs. 3, 5 and 6), where the local temperature ingress and the \( \text{Ac}_1 \) temperature may be assumed identical. However, there must exist local differences in deformed pearlite regions that facilitate or hinder the nucleation of new austenite grains. In addition, we observe cementite fragments embedded in the martensite (see Figs. 4 and 6). This indicates (i) that austenite can nucleate before the cementite fragments have entirely decomposed and (ii) that austenite formation occurs under non-equilibrium conditions, as otherwise, no cementite would remain in the austenite. Assuming that no additional thermal dissolution of cementite occurs during austenite formation, the austenite nucleation would be associated with the local microstructural characteristics of ferrite, such as the local defect density and C composition in ferrite. Ferrite with higher defect density is preferred for austenite nucleation, as the stored strain and defect energy can be released by the formation of new largely defect-free austenite grains. C enrichment in ferrite from decomposed cementite favors the austenite phase formation as well (later explained in Fig. 9). Apparently, both – defect density and C enrichment in ferrite – are directly related to prior deformation-induced cementite decomposition. Although the local Mn enrichment in prior cementite locations (Fig. 4c) might also favor austenite nucleation \( \text{[28,29]} \), we do not discuss the effect of Mn in this study for two reasons: (i) Mn variations are highly localized (i.e. in prior cementite locations) as the redistribution of Mn in ferrite is limited, and (ii) we do not observe austenite/martensite formation exclusively at prior cementite locations with Mn enrichment. Thus, we primarily focus on the effects of defect density and C composition of the ferrite matrix, which favor or hinder the phase transformation to austenite.

However, austenite formation in the current rail scenario involves a complex interplay of temperature ingress and deformation accumulated from multiple rail/wheel contacts. According to the previous temperature estimation \( \text{[1]} \), a global temperature gradient is introduced upon each rail/wheel contact, i.e. the temperature is highest at the rail surface and decreases with increasing distance from the rail surface. Therefore, if the formation of austenite were only determined by the temperature
can be expressed as [43]:

\[ N \propto C_0 \exp \left( -\frac{\Delta G^* - \Delta G_d}{kT} \right) \]  

where \( C_0 \) is the number of heterogeneous nucleation sites, \( \Delta G^* \) is the Gibbs free energy to form a critical spherical austenite nucleus, \( \Delta G_d \) is the stored strain energy in ferrite, \( k \) is the Boltzmann constant, and \( T \) is the temperature. Here, we estimate \( \Delta G_d \) for dislocations in ferrite, i.e., the released energy if the dislocations are removed from ferrite, and compare it with the austenite nucleation energy barrier. The strain energy of an edge and screw dislocation in ferrite are estimated as \(-4 \text{nJm}^{-1}\) and \(-2.6 \text{nJm}^{-1}\), respectively [54]. Assuming that the rail scenario is comparable to the laboratory-scale rolling contact fatigue experiment that produces WELs [55], the dislocation density \( \rho \) in ferrite could be as high as \(5.69 \times 10^{15} \text{m}^{-2}\). The spacing between dislocations can be approximated as \(\rho^{-0.2} = 1.32 \times 10^{-8} \text{m}[56]\). Considering that one edge dislocation exists in a volume of ferrite with the dimension of \((1.32 \times 10^{-8} \text{m})^3\) and ignoring the interaction among dislocations, \(\Delta G_d\) for this small volume is estimated as \(5.28 \times 10^{-17} \text{J}\), which is in the same order of the austenite nucleation energy barrier of \(1.50 \times 10^{-13} \text{J at 725 °C}\) [57]. Although the strain energy can be reduced by other effects (e.g., C segregation to dislocations and dislocation annihilation at high temperatures), the interaction among dislocations (e.g., the pile-up of dislocations) could raise the strain energy per dislocation [58]; providing a more realistic simulation of the strain energy, however, is beyond the remit of this study. Nevertheless, according to this simplified estimation, the energy barrier of austenite nucleation is further reduced as the dislocation density increases, enabling austenite nucleation at lower temperatures in more severely deformed regions.

### 4.2.2. Effect of carbon composition

The deformation-induced compositional changes in localized regions influence austenite formation as well. Fig. 9 shows the ThermoCalc calculations of austenite formation temperature against the C composition in ferrite. The estimated temperatures (see Section 2.2) for the corresponding distances from the rail surface are marked in Fig. 9. Here, the calculations only consider ferrite transforming to austenite and no cementite involvement. The 'austenite formation temperature' in Fig. 9 represents a temperature at which the Gibbs free energy of ferrite is equal to that of austenite at a given C composition, i.e., above which austenite is energetically more favorable than ferrite with the same C composition. As the C composition in ferrite increases, the required temperature for austenite formation decreases, i.e., ferrite becomes progressively unstable. In the rail microstructure below the surface, deformation-induced cementite decomposition progressively occurs in positions where conditions for austenite formation are not yet met. C atoms are continuously released into the ferrite matrix; firstly through dislocations cutting across cementite lamellae, then cementite lamellae are fragmented and almost completely decomposed. Thus, the C composition in the ferrite matrix gradually increases as the decomposition process proceeds, as evidenced by the three-fold increase measured by APT. Consequently, ferrite regions with higher supersaturation of C are less unstable and more susceptible to austenite transformation at lower temperatures.

Assuming that the thermodynamic properties of the binary Fe-C steel and the current R350H steel are comparable, we now quantitatively discuss the critical condition for austenite formation in C-enriched ferrite based on the APT measurements. According to Fig. 7, the C composition in the ferrite matrix yields 0.6 at% in deformed pearlite regions close to the BEL. Fig. 9 indicates that the release of C from cementite to ferrite is still insufficient for ferrite to transform into austenite in the assumed temperature regime. Considering a perfect ferrite phase, the austenite transformation temperature can be estimated as \(-750 °C\) for a ferrite carbon composition of 0.6 at% according to Fig. 9, which is higher than the estimated temperature of 737 °C at a depth of \(-40 \mu m\) (see Section 2.2). If we solely consider the effect of C composition on the
phase transformation to austenite, ferrite remains untransformed with a C composition of 0.6 at% and a temperature of 737 °C at the early stage of the decomposition process, where C is only released through the solute drag and the pipe diffusion mechanism. At a later stage of the decomposition process, C atoms are further released and enriched in the ferrite matrix through fragmentation and decomposition of cementite. Consequently, the increasing C composition in the ferrite matrix may further reduce the austenite transformation temperature. Therefore, supersaturated ferrite becomes energetically unfavored and may transform into austenite in the following rail/wheel contacts.

In summary, the critical conditions for austenite formation depend on the combined effects of defect density and C composition in ferrite. Higher defect density favors austenite nucleation at lower temperatures; higher C compositions in ferrite lead to lower austenite formation temperatures. Although estimating exact conditions is challenging due to the interplay of these two effects, localized austenite formation is directly linked to deformation-induced cementite decomposition and can be approximated in the context of the progress of the local decomposition process. The critical conditions are not fulfilled at an earlier stage of cementite decomposition (i.e. cementite remains undecomposed but releases its C atoms through the solute drag and the pipe diffusion mechanisms. Only at a later stage, more defects are introduced by extra rail/wheel contacts, and more C atoms are released into the ferrite matrix due to the decomposition of C-depleted cementite through the dislocation-shuffle mechanism; thereby, the critical conditions are fulfilled, and phase transformation to austenite occurs.

5. Conclusion

The formation mechanisms of Brown Etching Layers (BELs) are studied in a pearlitic R350HT rail steel retrieved from a service application. Specifically, the transition region between deformed pearlite and BEL is investigated to identify the microstructural conditions that trigger critical alteration into the martensitic microstructure, which later causes cracking and damage. The key findings from the analyses of the sample at a distance of ~40 µm beneath the rail surface using SEM, TKD, TEM, and APT are:

1. Cementite lamellae in the deformed pearlite areas are cut by dislocations; the carbon composition in lamellar cementite is depleted by ~3.9 at% from the 25 at% stoichiometric level. In contrast, the carbon composition in the surrounding ferrite matrix increases by ~0.4 at%. Sphere-like, fragmenting, and lamellar cementite are found in the transition region.

2. In the direct vicinity of deformed pearlite, BEL forms with a small fraction of residual cementite fragments. Apart from the left-over cementite, the excess carbon from previously decomposed cementite lamellae is redistributed rather evenly across the martensite microstructure. In contrast, manganese remains enriched in prior locations of fragmented cementite.

These findings lead to the following two conclusions:

1. Deformation-induced cementite decomposition can be described by the modified dislocation-driven solute drag model. At an earlier stage, carbon atoms migrate via dislocation gliding through cementite lamellae and pipe diffusion through dislocation cores, transporting carbon atoms into surrounding ferrite and forming carbon-depleted cementite. At a later stage, carbon-depleted cementite decomposes via the dislocation-shuffle mechanism.

2. The formation of BEL involves local austenitization followed by martensitic transformation. Austenite formation is supported by the local progress of deformation-induced cementite decomposition, which reduces the local austenite transformation temperature because of two factors: (a) High defect densities in ferrite with corresponding defect energies encourage the formation of new austenite grains. (b) The enrichment of carbon in the ferrite matrix upon cementite decomposition facilitates austenite formation by reducing the thermodynamic equilibrium temperature between ferrite and austenite.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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References
