Nitriding of White-Solidified Fe–C–Si Alloys: Diffusion Path Concept Applied to Inhomogeneous Microstructures

Stefan Kante, Mykhaylo Motylenko, and Andreas Leineweber

The microstructure formation during nitriding of white-solidified Fe–C–Si alloys, relevant to advanced surface treatments for cast irons, is studied. The as-cast microstructures mainly contain Si-free, C-rich eutectic cementite and Si-enriched, C-lean ferrite/pearlite. The spatial extent of these microstructure regions is significantly larger than the diffusion distance of Si during nitriding. The phases and microstructure forming during nitriding vary with the local Si content in the substrate. Nitriding conditions only allowing to form $\gamma' - Fe_3N$ from pure $\alpha$-Fe generate a compound layer composed of $\gamma' - Fe_3(C, N)$, $\epsilon - Fe_3(C, N)_{1+x}$, and Si-rich nitride, $X$. $\epsilon$ is the main constituent, whereas $\gamma'$ only forms from Si-free eutectic cementite. Different nitriding experiments elucidate the interrelated thermodynamic and kinetic effects of C and Si on the phase evolution and the compound layer growth. A schematic model of the microstructure evolution is developed. Information on the topology of the largely unknown Fe–C–Si–N phase diagram is derived from the experimental observations. For this, the diffusion path concept is adapted to describe the microstructure formation during nitriding of compositionally inhomogeneous alloys, in which substitutional alloying elements are heterogeneously distributed and largely immobile. $\alpha + \varepsilon$ and $\alpha + \varepsilon + X$ phase fields are identified as particular features of the Fe–C–Si–N phase diagram at 540 °C.

1. Introduction

1.1. General Introduction

Gray-solidified cast irons are frequently used to manufacture machine and engine parts due to their low cost, good compressive strength, and high damping capacity.$^{[1,2]}$ Their use is, however, often limited by poor surface hardness and corrosion resistance. Both can be notably improved by a duplex surface treatment developed in recent years.$^{[3-6]}$ First, the surface of the cast iron is remelted, e.g., by an electron beam or plasma arc. This produces a white-solidified, ledeburitic$^{[7,10]}$ surface layer, which is hard and abrasion-resistant. Afterward, the material is nitrided to enhance the corrosion resistance by the formation of a dense surface layer composed of the main Fe (carbo)nitrides, $\gamma' - Fe_4(N, C)$ and $\epsilon - Fe_3(N_C)_{1+x}$ (Table 1), denoted compound layer. Note that nitriding without remelting leads to less favorable microstructures because coarse graphite particles contained in gray-solidified cast irons are detrimental to the compound layer formation.$^{[1,3,4,9-11]}$

Although the general advantages of the previously described duplex treatment have been demonstrated, the nitriding behavior of the white-solidified surface layers turns out to be complex and incompletely understood.$^{[12-19]}$ The research of the current authors$^{[12,18,19]}$ aims at elucidating the complex nitriding behavior of the remelted surface layers by controlled gas nitriding of white-solidified Fe–3.5 wt% C–0/1.5/3 wt% Si alloys, serving as model alloys for commercially available ferritic cast iron grades subjected to remelting and nitriding. Note that, in contrast to ferritic cast irons, pearlitic cast irons often contain non-negligible additions of Mn and Cu, which may additionally affect the nitriding behavior.$^{[17]}$

The microstructure of white-solidified Fe–3.5 wt% C–1.5/3 wt% Si alloys, having C and Si contents typical of cast irons, is mainly composed of coarse eutectic cementite plates, $\theta - Fe_3C_{1-x}$ (Table 1), embedded in ferrite and pearlite.$^{[20,21]}$ The latter result from the decomposition of primary and eutectic $\gamma$-Fe during cooling after solidification. In addition, a minor volume fraction of $Fe_3SiC_4$-type silicocarbide (Table 1) is contained in the alloys.$^{[22-24]}$ The distribution of Si in the white-solidified microstructure is very heterogeneous. The Si/Fe atomic ratio in the eutectic and pearlitic $\theta$ is $u_{Si,\theta} < 3 \times 10^{-4}$ and, here, considered negligible, say $u_{Si,\theta} \approx 0.$$^{[12]}$ The Si/Fe atomic ratio in $Fe_3SiC_4$ is $u_{Si,Fe_3SiC_4} \approx 0.22$; however, it might take also values slightly different from 0.22 due to a possibly mixed Fe/Si site$^{[23,24]}$ and extended lattice defects affecting the composition.$^{[25]}$ The Si content in $\alpha$-Fe relates to the Si content of $\gamma$-Fe, which is affected by Si segregation during solidification. The Si content in the center of $\gamma$-Fe dendrites is typically similar to the Si content of the alloy, while the outer rim of dendrites and last-to-freeze regions are enriched in Si.$^{[25]}$ The Si content in eutectic $\gamma$-Fe is higher.

S. Kante, M. Motylenko, A. Leineweber
Institute of Materials Science
TU Bergakademie Freiberg
Gustav-Zeuner-Str. 5, 09599 Freiberg, Germany
E-mail: andreas.leineweber@tww.tu-freiberg.de

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adem.202100833.

© 2021 The Authors. Advanced Engineering Materials published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adem.202100833
than in primary γ-Fe due to Si rejection from θ and Si segregation to γ-Fe during growth of the γ + θ eutectic. Thus, the Fe/Si atomic ratio in α-Fe typically exhibits various values of the order of $\mu_{Si} > \mu_{Fe} > \mu_{Si,N}$. The heterogeneous Si distribution and the large volume fraction of coarse eutectic θ in white-solidified Fe–C–Si alloys are crucial to the microstructure and phase evolution during nitriding, as indicated in preliminary studies$^{[12,18,19]}$ and will as well be shown in detail in the course of this work. In this regard, the very low to negligible Si solubility in e and γ$^{[12,26–27]}$ in conjunction with the peculiar interaction of Si with N during nitriding is a key factor to the microstructure formation. Si is well known to precipitate in α-Fe as an amorphous Si-rich nitride, here denoted “X”.$^{[12,28–34]}$ X formed in α-Fe was often considered to exhibit the composition $Si_{2-N_xA_1}$.$^{[28,31]}$ It was recently shown$^{[12]}$ that a significant mole fraction of Fe can be contained in X, likely depending on the nitriding conditions (Table 1). The precipitation of X in α-Fe is very sluggish$^{[33,35–37]}$ which relates to the fact that Si is a weak nitride-forming element in α-Fe.$^{[38,39]}$ Upon nitriding of Fe–C–Si alloys, X can also form in a eutectoid fashion by the transformations $Fe_2SiC_4 \rightarrow \alpha + X$ and $\alpha \rightarrow \epsilon + X$, resulting in nanostructures characterized by X rods/lamellae embedded in α-Fe or e.$^{[12]}$

The studies of the current authors have separately analyzed particular features of the microstructure formation during gas nitriding of white-solidified Fe–C–Si alloys in detail, i.e. the aforementioned transformation $\alpha \rightarrow \epsilon + X$ and the transformation of eutectic θ into nitride.$^{[18]}$ Upon nitriding under process conditions only allowing for the formation of γ in a pure Fe reference, here denoted γ’ conditions, γ’ appeared to form only from eutectic θ in white-solidified Fe–C–Si alloys. That formation of γ’ from θ involved the intermediate formation of e, i.e., $\theta \rightarrow \epsilon \rightarrow \gamma'$. This was explained by a higher C solubility in e as compared to γ’ and a structural relation of e and θ.$^{[18,40–43]}$ The transformation e → γ’ requires diffusional redistribution of C, most likely occurring by the outward diffusion and release of C to the gas nitriding atmosphere.$^{[19]}$

Only e formed from Si-rich α-Fe by the reaction $\alpha \rightarrow \epsilon + X$ upon nitriding white-solidified Fe–C–Si alloys under γ’ conditions, and appeared stable against a transformation into γ’.$^{[12]}$ Moreover, the transformation $\alpha \rightarrow \epsilon + X$ occurred at a nitriding temperature of 540 °C, at which the growth of e in contact with α-Fe under conditions of local equilibrium is incompatible with the Fe–C–N phase diagram$^{[44–46]}$ and available thermodynamic databases$^{[47]}$ containing the Fe–Si–N and Fe–C–Si–N systems. A higher Si solubility in e than in γ’ was hypothesized to stabilize e with respect to γ’ in Fe–Si steels.$^{[26,27]}$ Indeed, e formed by the reaction $\alpha \rightarrow \epsilon + X$ was found to exhibit a Si/Fe atomic ratio of about 0.002 $< \mu_{Si,Fe} < 0.02$.$^{[12]}$ It is yet uncertain whether this marginal Si solubility in e is sufficient to stabilize e formed from α-Fe with respect to γ’. Additional effects might contribute to the stabilization of e, e.g., C released by the continuous transformation of θ into nitride; see earlier.

Based on the studies$^{[12,18]}$ reporting partial aspects of the nitriding behavior, the current work comprehensively reviews the overall microstructure evolution during nitriding white-solidified Fe–3.5 wt.%–0/1.5 wt.%Si alloys, subsequently denoted Fe–3.5C–0/1.5/3Si alloys. So far, the overall microstructure evolution was only outlined in a preliminary study$^{[19]}$ based on very incomplete experimental data. Aspects are addressed which are important beyond the particular materials system: the compound layer growth in Si-rich pearlite and the interrelated thermodynamic and kinetic effects of C and Si on the formation, growth, and stability of γ’ and e. Information on the experimentally largely unknown Fe–C–Si–N phase diagram is extracted from the experimental data. For this, the diffusion path concept$^{[48–50]}$—well-established to describe the microstructure formation in the interdiffusion zone of diffusion couples based on phase diagrams—is adapted to describe and interpret the microstructure formation during nitriding of compositionally inhomogeneous alloys.

### 1.2. Microstructure Formation during Gas Nitriding

Gas nitriding in NH$_3$/H$_2$-containing atmospheres allows us to produce Fe nitride compound layers in a thermodynamically controlled fashion. A gradient in the chemical potential of N, $\mu_N$, is generated between the surface and the core of the material, driving the diffusion of N into the material. It is $\mu_N = \mu_N^{surface} - \infty$ in the N-free core of the material. At the surface, $\mu_N = \mu_N^{surface}$ relates to the so-called nitriding potential, $r_N$, given by the partial pressures of NH$_3$ and H$_2$, $p_{NH_3}$ and $p_{H_2}$, according to

| Phase | Space group | Typical lattice parameters | Description | Reference |
|-------|-------------|---------------------------|-------------|-----------|
| α-Fe | $Im\bar{3}m$ | $a = 2.866$ Å | bcc Fe lattice | – |
| γ’-Fe$_3$(N,C) | Pm$\bar{3}$m | $a = 3.790$ Å | fcc Fe lattice; N/C in octahedral sites | [87] |
| ε-Fe$_3$(N,C)$_{1-x}$ | P6$_3$22 | $a = 4.698$ Å, $c = 4.379$ Å$^{[4]}$ | hcp Fe lattice; N/C ordered in octahedral sites; $0.34 < x < 0.47$ | [88–90] |
| θ-Fe$_3$C$_{1-x}$ | Pnma | $a = 5.090$ Å, $b = 6.744$ Å, $c = 4.525$ Å | C trigonal primitively coordinated by Fe; $0 < x < 0.059$ | [91,92] |
| Fe$_2$Si$_3$C$_4$ | $P\bar{1}$ | $a = 6.347$ Å, $b = 6.414$ Å, $c = 9.72$ Å, $\alpha = 84.05^\circ$, $\beta = 99.84^\circ$, $\gamma = 119.98^\circ$ | Si coordinated by partially incomplete Fe icosahedra, C trigonal primitively coordinated | [22–24] |
| X | – | – | Amorphous Si-rich nitride of composition $(Si_{3N4})x(Fe_{\gammaN})y \varepsilon_x = 0.33 < x < 0.43^{[10]}$ | [12,28] |

$^a$The ε lattice parameters refer to a superstructure cell due to N and C ordering with $\Delta_{superstructure} = 3/2\alpha_{hcp}$ and $\Delta_{superstructure} = \alpha_{hcp}$. $^{[12]}$X was reported for X precipitated in α-Fe$^{[28]}$ while $0.33 < x < 0.43$ was reported for X formed by the transformation $\alpha \rightarrow \epsilon + X$.$^{[12]}$ X might exhibit a homogeneity range, with x continuously increasing from 0 to at least 0.43 upon increasing chemical potential of N.$^{[12]}$


\[ \mu_N^{\text{surface}} - \mu_N^{\text{eq}} \propto \ln \left( \frac{p_{N_{2}}^{1/2}}{p_{0}^{1/2}} \right) = \ln(r_{N} p_{0}^{1/2}) \]  

(1)

where \( p_0 \) is the standard pressure, 1 atm. If \( \mu_N^{\text{surface}} (r_N) \) is sufficiently large, a compound layer forms at the material’s surface. The type of Fe nitride forming in contact with the atmosphere, \( \varepsilon \) or \( \gamma' \), at a given temperature can be controlled by the value of \( r_N \). A N-enriched diffusion zone exists underneath the compound layer, in which alloying element nitrides, here X, may precipitate.

The phase and microstructure evolution during nitriding can be related with a respective phase diagram by means of diffusion paths, provided that local equilibria are established at phase boundaries in the nitrided layer. The phase fields, which are crossed by the diffusion path connecting \( \mu_N^{\text{surface}} \) and \( \mu_N^{\text{eq}} \), determine the phases forming during nitriding. \( \mu_N \) must continuously decrease along a diffusion path from \( \mu_N^{\text{surface}} \) to \( \mu_N^{\text{eq}} \), meaning that \( \mu_N \) decreases with increasing distance from the surface, \( z \). Otherwise, \( N \) would need to diffuse into the material against its chemical potential gradient.

When nitriding single-phase Fe–M alloys, where \( M \) is a substitutional alloying element being homogeneously distributed in the microstructure, the diffusion path concept can be used following the description of the formation of \( \delta \)-pearlite upon carburizing Fe–M alloys. The mean \( M/Fe \) atomic ratio, \( u_M \), does not change in a long range upon the introduction of \( N \) into the material because \( M \) diffusion is typically limited to very short distances compared to the diffusion of \( N \). Thus, the diffusion path reduces to a straight line at constant \( u_M \) in the Fe–M–N phase diagram when \( \mu_N \) and \( u_M \) are selected as axes (cf., Hillert).

Likewise, \( u_M \), being averaged over the local microstructure, also remains constant when nitriding Fe–M–C alloys, as in the present case where \( M = Si \). In contrast to \( u_M \), the C/Fe ratio in the alloy may change during nitriding, e.g., due to the decarburizing nature of H-containing nitriding atmospheres. The latter implicates that the chemical potential of \( C \) is \( \mu_C = \mu_C^{\text{surface}} \rightarrow -\infty \) at the material’s surface, driving the outward diffusion of \( C \). In the N-free core of the material \( \mu_M \) may take a constant value \( \mu_M^{\text{core}} \). Given an Fe–M–C–N phase diagram with the axes \( \mu_N, \mu_C, \) and \( u_M \), thus a diffusion path describing the microstructure formation must run in a section of that diagram at constant \( u_M \), and account for the variation of both \( \mu_N \) and \( \mu_C \) between the surface and core. Note that the introduction of \( N \) into the material itself affects \( \mu_C \) i.e., \( \mu_C \) changes with \( \mu_N \) and, thus, with the distance from the surface, \( z \) (cf., earlier).

2. Microstructure Evolution during Nitriding

Mold-Cast Fe–3.5C–0/1.5/3Si

Providing a comprehensive image of the nitriding behavior of white-solidified Fe–3.5C–0/1.5/3Si alloys requires to consider the microstructure formation at different length scales. First, “macroscopic” features of the compound layer growth in Fe–3.5C and Fe–3.5C–1.5/3Si are comparatively described in Section 2.1 with regard to the temporal evolution of the Fe nitride composition of the compound layer and the compound layer thickness. Afterward, “microscopic” features, i.e., the precipitation of X in the diffusion zone and the compound layer formation in Si-rich pearlite of Fe–3.5C–1.5/3Si, are examined in detail in Section 2.2 and 2.3.

2.1. Overview of the Compound Layer in Mold-Cast Fe–3.5C–0/1.5/3Si

Representative microstructures of nitrided Fe–3.5C and Fe–3.5C–3Si are shown in Figure 1a,b. A compound layer has formed in both alloys. Coarse eutectic \( \theta \) plates and coarse ferritic/pearlitic regions are visible in the diffusion zone underneath the compound layer. The position and morphology of the former eutectic \( \theta \) plates is still visible in the compound layer of Fe–3.5C–3Si, which is not the case in Fe–3.5C. In addition, dark rims outline the edges of eutectic \( \theta \) plates underneath the compound layer, indicative of \( Fe_2SiC_4 \) decomposed to \( a + X \) and \( X \) has precipitated in the diffusion zone (see Section 2.2).

XRD reveals that the phase fractions of \( \varepsilon \) and \( \gamma' \) averaged over the volume of the compound layers notably differ in Fe–3.5C and Fe–3.5C–1.5/3Si, and how the average \( \varepsilon \) and \( \gamma' \) phase fractions change with increasing nitriding time (Figure 2a–f). The phase fraction of \( \gamma' \) in the compound layer of nitrided Fe–3.5C is always similar to or slightly larger than the phase fraction of \( \varepsilon \). In the compound layer of nitrided Fe–3.5C–1.5/3Si, by contrast, the phase fraction of \( \varepsilon \) is always larger than the phase fraction of \( \gamma' \). In particular, during short nitriding times of 1–4 h, the phase fraction of \( \gamma' \) contained in the compound of nitrided Fe–3.5C–1.5/3Si is very small. The spatially resolved analysis of the Fe nitride distribution in the compound layers by EBSD (Figure 1c,d) validates and explains these observations.

The Fe nitride formation from Si-free eutectic \( \theta \) is similar in Fe–3.5C and Fe–3.5C–1.5/3Si (Figure 1c, d), pronouncedly following the sequence \( \theta \rightarrow \varepsilon \rightarrow \gamma' \) when nitriding for 16–48 h, as described in Section 1.1. After short nitriding times, particularly after 1 h, the transformation step \( \varepsilon \rightarrow \gamma' \) is very infrequently visible. Occasionally, the direct transformation \( \theta \rightarrow \gamma' \) seems to occur in Fe–3.5C–1.5/3Si without the formation of intermediate \( \varepsilon \) after nitriding for 48 h.

In the microstructure between the eutectic \( \theta \) plates, the Fe nitride formation notably differs in Fe–3.5C and Fe–3.5C–1.5/3Si. Solely \( \gamma' \) has formed in the pearlite of Fe–3.5C, neglecting Fe–3.5C nitrided for 48 h, which is affected by massive pore formation and is not further considered in the course of this work. A \( \gamma' \) interlayer separates \( \varepsilon \)- and \( \alpha \)-Fe in the pearlite of Fe–3.5C. In contrast to Fe–3.5C, only \( \varepsilon \) is visible in microstructure regions associated with transformed ferrite, pearlite, and \( Fe_2SiC_4 \) between former eutectic \( \theta \) plates in Fe–3.5C–1.5/3Si after all nitriding times (Figure 1d and Figure S1, Supporting Information). This implies the existence of \( \alpha/\varepsilon \) phase boundaries during all nitriding times.

The compound layer thickness in both pearlite/ferrite and in eutectic cementite depends on the Si content of the alloy (Figure 2g–i). In ferrite/pearlite, the compound layer thickness generally decreases with increasing Si content of the alloy. This is ascribed to a larger phase fraction of \( X \), forming at higher Si content (see Section 2.2). Therefore, more \( N \) is consumed by the formation of \( X \) and less \( N \) is available for Fe nitride growth. In Fe–3.5C, the compound layer is always thicker in pearlite than
In eutectic θ, in Fe–3.5C–1.5Si, the compound layer thickness is similar in pearlite/ferrite and eutectic θ, at short nitriding times, but larger in pearlite/ferrite after prolonged nitriding. In Fe–3.5C–3Si, the compound layer seems thinner in pearlite/ferrite than in eutectic θ upon short nitriding times, but thicker after prolonged nitriding.

In addition, Fe nitride has grown on top of the original surface of Fe–3.5C–1.5/3Si (Figure 1d). The growth of such surface nitrides is known from nitriding of white-solidified cast irons [12,17] and other alloys [62–64]. It is likely driven by stress relief [65,66] and requires outward diffusion of Fe atoms. As the surface nitrides do not form a dense layer, the nitriding atmosphere should have always been in contact with the original samples’ surface. Therefore, the surface nitrides and their possible effect on diffusion processes and phase transformations in the compound layer underneath are neglected in this work.

2.2. Precipitation of X in the Diffusion Zone of Mold-Cast Fe–3.5C–1.5/3Si

In the diffusion zone, X has formed in α-Fe, at α/θ phase boundaries, and by the decomposition of Fe23Si5C4 into a α + X nanostructure (Figure 3). After nitriding for 1 h, Fe23Si5C4 has already decomposed up to a distance of about 25 μm from the surface (Figure 4a). In ferrite and pearlite, by contrast, X is visible only in the very proximity of the surface and the number density of X seems very small (Figure 3a).

After nitriding for 16 and 48 h, the visible number density of X in the diffusion zone is large. The number density of X typically appears larger in Fe–3.5C–3Si than in Fe–3.5C–1.5Si, which is ascribed to the higher Si content in Fe–3.5C–3Si (Figure S2, Supporting Information). Although X precipitates are rather homogenously distributed in ferrite, they have preferentially formed at α/θ phase boundaries in pearlite (Figure 3b). This might relate to a favorable contribution of interface energy to the nucleation barrier of X, faster Si diffusion at the phase boundary as compared to bulk diffusion in α-Fe, and possibly Si being enriched at the α/θ interface due to Si segregation during pearlite growth [67].

There seems to be no notable difference in the number density of X adjacent to the compound layer after nitriding for 16 and 48 h (Figure 3b,c). In addition, the number density of X precipitates visible after prolonged nitriding decreases with increasing distance from the surface, whereas the size of the precipitates
increases (Figure 3c,d). This is typical of diffusion-controlled internal precipitation. In addition, the onset of the Fe$_2$Si$_5$C$_4$ decomposition occurs at about the same distance from the surface as the presence of visible X precipitates after prolonged nitriding (Figure 3d).

2.3. ε Growth in Si-Rich Pearlite of Mold-Cast Fe–3.5C–1.5/3Si

The volume fraction of ε formed in pearlitic α-Fe is very small after nitriding for 1 h (Figure 4). By contrast, pearlitic θ lamellae are readily transformed into ε, such as eutectic θ. The transformation of pearlitic θ into ε seems to be governed by the same three-phase crystallographic relationship among α-Fe, ε, and θ (Figure S3, Supporting Information), which is known from the formation of ε from eutectic θ and has been suggested to determine also the crystallographic orientation of ε in pearlite. As the transformation of θ → ε runs faster than the growth of ε in α-Fe, a pearlite-like microstructure characterized by alternating α-Fe and ε lamellae results (Figure 4). This pearlite-like microstructure is still very prominent after nitriding.

---

**Figure 2.** a–c) Phase fractions α-Fe, θ, ε, and γ′ estimated by Rietveld analysis of XRD patterns obtained from the surface of mold-cast Fe–3.5C–0/1.5/3Si samples in the as-cast state and after nitriding for 1–48 h at $t_{N} = 1 \text{ atm}^{-1/2}$ and 540 °C, revealing the phase composition in the sample volume averaged over the penetration depth of the X-rays. The volume fraction of Fe$_2$Si$_5$C$_4$ in Fe–3.5C–1.5/3Si is too small to be evaluated by XRD. d–f) γ′/ε weight percentage ratio approximately indicating the Fe nitride composition of the compound layer. g–i) Compound layer thickness measured in nitrided ferrite/pearlite and in nitrided eutectic θ after nitriding for 1–48 h. The pearlite-like α + ε protrusions at the growth front of the compound layer in pearlite (Section 2.3) were not regarded in the measurement.
for 4 h (Figure 5a,b), suggesting that the compound layer growth is preceded by the transformation $\theta \rightarrow \varepsilon$ during short nitriding times. A similar “pearlite-like nitride” morphology has been observed underneath the compound layer in the pearlite of nitrided gray-solidified cast irons.\cite{71}

Once formed from $\theta$, $\varepsilon$ grows into adjacent $\alpha$-Fe by means of the reaction $\alpha \rightarrow \varepsilon + X$ and the $\varepsilon$ lamellae appear to thicken (Figure 4b–d, and Figure S3a, Supporting Information). EDX in Figure 5c indicates that the redistribution of Si during the growth of $\varepsilon$ into $\alpha$-Fe is limited to the very growth front of $\varepsilon + X$ in $\alpha$-Fe. There are notable variations in the Si content only within $\varepsilon + X$, whereas the Si content is constant in $\alpha$-Fe ahead of the transformation front within the limits of measurement noise. $\varepsilon$ formed from Si-free $\theta$ remains Si-free, as previously shown by atom probe tomography.\cite{12}

After prolonged nitriding for 16–48 h, the transformation $\alpha \rightarrow \varepsilon + X$ still seems to occur at the growth front of the compound layer (Figure 6 and Figure S4, Supporting Information). $X$ already existing in the diffusion zone is overgrown by and incorporated into $\varepsilon + X$ forming from $\alpha$-Fe (Figure 7 and Figure S5, Supporting Information).\cite{12} The growth front of the compound layer within pearlite often appears rather even upon prolonged nitriding; i.e., the pearlite-like protrusions frequently observed at the growth front after short nitriding times appear less prominent after prolonged nitriding (Figure 7a). Occasionally, the compound layer growth seems to be preceded rather by the growth of $\varepsilon + X$ in $\alpha$-Fe than by the transformation $\theta \rightarrow \varepsilon$. SEM-BSE contrast images possibly indicate remainders of pearlitic $\theta$ embedded in $\varepsilon + X$ of the compound layer adjacent to the diffusion zone (Figure 7b).

The position of the transformed pearlitic $\theta$ lamellae is still visible in the compound layer after prolonged nitriding, as the former $\theta$ lamellae are X-free and outlined by $X$ formed at the former $\alpha/\theta$ phase boundaries (Figure 7c). EDX in Figure 7d reveals that $\varepsilon$ formed from pearlitic $\theta$ is still Si-free after 48 h. Si, which is contained in $\varepsilon$ of the $\varepsilon + X$ nanostructure formed from pearlitic $\alpha$-Fe\cite{12} adjacent to $\theta$ (Section 1.1), is unlikely redistributed over notable distances during nitriding. Consequently, the Si content of $\varepsilon$ formed from pearlitic $\alpha$-Fe and that formed from pearlitic $\theta$ are retained and remain unequal upon increasing nitriding time.
In contrast to Si-free $\varepsilon$ formed from eutectic $\theta$ (Section 2.1), Si-free $\varepsilon$ formed from pearlitic $\theta$ does not seem to transform into $\gamma$ in contact with the nitriding atmosphere (Figure 7e; compare also EBSD in Figure 1d).

2.4. Summary of the Microstructure Evolution during Nitriding of Mold-Cast Fe–3.5C–1.5/3Si alloys: Kinetic and Thermodynamic Aspects

Generally, the microstructure of the white-solidified Fe–3.5C–1.5/3Si alloys can be divided into different regions characterized by more or less a discrete Si/Fe atomic ratio $u_{Si,\phi}$ ($\phi = \alpha, 0, Fe_{23}Si_{5}C_{4}$; Section 1.1). The mean Si/Fe atomic ratio in these “$u_{Si,\phi}$ regions,” composed of $\alpha$-Fe, 0, or $Fe_{23}Si_{5}C_{4}$ in the as-cast state, is retained during nitriding because the spatial extent of these $u_{Si,\phi}$ regions is larger than the diffusion distance of Si during nitriding. In fact, it appears that Si is not notably exchanged between these regions during nitriding (Figure 5c,e and atom probe tomography in Kante et al.\cite{12}). Therefore, the time-dependent sequence of phase transformations occurring in each of these $u_{Si,\phi}$ regions during nitriding is comparatively sketched in Figure 8 with respect to the distance from the surface, $z$. The latter relates to $\mu_{N}$ and $\mu_{C}$ as shown in Figure 8 and is considered to represent unspecified ($\mu_{N}, \mu_{C}$) value pairs (see Section 1.2 and assumptions in Section 4.1), such that Figure 8 lays the basis for a thermodynamic interpretation of the microstructure evolution by means of diffusion paths in Section 4. The sequence of phase transformations observed after different schematic nitriding times, $t_1$–$t_3$, is discussed in the following.

2.4.1. Short Nitriding Times, $t_1$

In the early stage of nitriding, Figure 8 ($t_1$), the growth of the diffusion zone seems to advance by the transformation $Fe_{23}Si_{5}C_{4} \rightarrow \alpha + X$, occurring at larger $z$ than the visible precipitation of X in $\alpha$-Fe and at $\alpha/\theta$ phase boundaries. This relates to the known sluggish precipitation kinetics of X in $\alpha$-Fe.\cite{33,37} Due to the latter, it appears that a large mole fraction of Si should be still dissolved in $\alpha$-Fe of the diffusion zone after short nitriding.
times, despite a large driving force to precipitate X.\[33\] Thus, α-Fe may be considered as supersaturated with N and Si at a given distance from the surface, \( z \), i.e., at a given local value of \( \mu_N \) (cf., Section 1.2).\[27,37\]

The Si supersaturation of α-Fe obstructs the ε formation in α-Fe, as the low Si solubility in ε\[12\] requires redistributing Si to allow for the growth of ε + X. By contrast, the formation of ε from Si-free θ can readily occur. Consequently, the growth of the compound layer is preceded by the transformation of eutectic and pearlitic θ into ε, occurring at larger depths than the transformation of α → ε + X at short nitriding time. In addition, less N is consumed by the obstructed nitride formation in α-Fe. The resulting excess of N may be supplied to pearlitic and eutectic θ by short-circuit diffusion through α-Fe, further promoting the transformation θ → ε.\[19\]

The pearlite-like α + ε structures at the growth front of the compound layer in pearlitic result (Section 2.3) and the compound layer appears thicker in eutectic 0 than in ferrite/pearlite when nitriding Fe–3.5C–1.5Si for short times (Figure 2g–i).

Furthermore, ε formed from Si-free θ is frequently in contact with the nitriding atmosphere under \( \gamma' \) conditions after short nitriding times. This indicates that local equilibrium with respect to \( \mu_N \) and \( \mu_C \) has unlikely been established yet adjacent to the surface (Section 1.2; \( \mu_C \rightarrow -\infty \) and the applied nitriding potential enforcing the formation of \( \gamma' \) in pure Fe).

2.4.2. Prolonged Nitriding, \( t_2-t_3 \)

Upon prolonged nitriding, Figure 8 (\( t_2 \)), the transformation Fe\(_{23}\)Si\(_5\)C\(_4\) → α + X and the precipitation of X in α-Fe are visible at about the same depth \( z \) (Figure 3d), which contrasts \( t_1 \) and suggests that both transformations occur at similar values of each \( \mu_N \)
and \( \mu_C \). The distribution of \( X \) in the diffusion zone is typical of diffusion-controlled internal precipitation and the visible number density of \( X \) adjacent to the compound layer compares after 16 and 48 h (Section 2.2). This indicates that, in contrast to short nitriding times \( t_1 \), the equilibrium phase fraction of \( X \) has precipitated at a given \( \mu_N \) adjacent to the compound layer (cf., Kante and Leineweber[37]). Nevertheless, the transformation \( \alpha \rightarrow \varepsilon + X \) still occurs in \( \alpha_{\text{Fe}} \) regions after prolonged nitriding. The latter implies that \( \alpha\text{-Fe} \) at the growth front of the compound layer still contains Si despite the large number density of \( X \) formed in the diffusion zone.

It is inferred from this that the phase fraction of \( X \) precipitated in \( \alpha\text{-Fe} \) in front of the compound layer depends on the local value of \( \mu_N \) in \( \alpha\text{-Fe} \), that the phase fraction of \( X \) in \( \alpha\text{-Fe} \) decreases with decreasing \( \mu_N \) (increasing \( z \)), and that the phase fraction of \( X \) in \( \alpha\text{-Fe} \) has taken an equilibrium value at a given \( \mu_N \) in front of the compound layer after prolonged nitriding.[12,37] In contrast to \( t_1 \), thus, \( \alpha\text{-Fe} \) is unlikely supersaturated by Si and N anymore at given \( \mu_N \), but not Si-free. The reaction \( \alpha \rightarrow \varepsilon + X \), therefore, may represent a particular feature of compound layer growth under local equilibrium in \( \alpha\text{-Fe} \).

A decreasing and vanishing Si supersaturation of \( \alpha\text{-Fe} \) allows for faster growth of \( \varepsilon \) in \( \alpha_{\text{Fe}} \) and \( \alpha_{\text{Fe}}\varepsilon_{\text{Fe}}\varepsilon_{3\text{Si}} \) regions. Simultaneously, the diffusional removal of C from the transformation front in \( \theta \) toward the decarburizing nitriding atmosphere may become a limiting factor to the nitride formation from coarse eutectic \( \theta \) due to the increasing thickness of the compound layer. In particular, \( \gamma' \) formed adjacent to the surface in \( \alpha_{\text{Fe}} \) regions may act as a diffusion barrier for C, considering the low C solubility in \( \gamma' \).[19] The C content per volume in pearlite is generally lower than in coarse eutectic \( \theta \) and, thus, the redistribution of C might have little effect on the growth rate of the compound layer in pearlite.

Due to accelerated growth of \( \varepsilon \) in ferrite/pearlite and C-diffusion-limited nitride formation from eutectic \( \theta \), the compound layer becomes thicker in ferrite/pearlite than in eutectic \( \theta \) after prolonged nitriding (Figure 2g–i). In contrast to short nitriding times, thus, the transformations \( \alpha \rightarrow \varepsilon + X \) and \( \theta \rightarrow \varepsilon \) seem to occur mainly at similar \( z \). This means the transformation \( \theta \rightarrow \varepsilon \) simultaneously occurs at different \( z \) in eutectic \( \theta \) and pearlitic \( \theta \) (Figure 8 (t2), Section 2.3), implying local variations of \( \mu_N \) and \( \mu_C \) at a given \( z \) in the transition region between the diffusion zone and compound layer.

After 48 h, \( \gamma' \) occasionally exists in contact with eutectic \( \theta \) (broken arrow in Figure 8 (t2)). The formation of intermediate \( \varepsilon \) from eutectic \( \theta \) (Section 1.1), thus, seems to become less
important after prolonged nitriding. Possibly, a hypothetical state can be reached (Figure 8 (t3)), in which the transformation sequence $\theta \rightarrow \varepsilon \rightarrow \gamma$ in eutectic $\theta$ is fully replaced by the direct transformation $\theta \rightarrow \gamma'$. Within the compound layer, $\varepsilon + X$ formed in $\alpha_{Si,\beta}$ and $\alpha_{Si,Fe_{23}Si_{5}C_{4}}$ regions coexists with $\varepsilon$ formed as well as $\varepsilon$ and/or $\gamma'$ formed from eutectic $\theta$ (Figure 8 (t2–t4)). This implies that Si-free $\gamma'$ and Si-free $\varepsilon$ formed in $\alpha_{Si,\beta}$ regions and $\varepsilon + X$ formed in $\alpha_{Si,\alpha}$ and $\alpha_{Si,Fe_{23}Si_{5}C_{4}}$ ($\varepsilon$ in $\varepsilon + X$ may contain Si$^{[12]}$) regions coexist in contact with the nitriding atmosphere under $\gamma'$ conditions.

3. Stability of $\varepsilon$ in Nitrided White-Solidified Fe–3.5C–1.5/3Si Alloys

Section 2 has shown the prominent formation of $\varepsilon$ in Fe–3.5C–1.5/3Si and the coexistence of different $\alpha_{Si,\beta}$ regions in the microstructure, containing $\gamma'$, $\varepsilon$, or $\varepsilon + X$ in contact with the nitriding atmosphere under $\gamma'$ conditions (Figure 8). It appears uncertain whether the latter phase mixture represents a state of “local equilibrium” with the nitriding atmosphere, and to what extent it is affected by limited rates of Si and C redistribution (cf., Section 2.4). Note that “equilibrium” is written in quotation marks as rather a steady state than true local equilibrium might exist at the surface,$^{[72]}$ which is assumed to be negligible for the considerations in this study. Two-step nitriding of mold-cast Fe–3.5C–1.5/3Si alloys and nitriding of melt-spun Fe–3.5C–0/3Si ribbons were conducted to further determine the effect of Si and C on the formation and stability of $\varepsilon$ and of the aforementioned phase mixture in contact with the nitriding atmosphere. In particular, the effect of C supply from the substrate to the compound layer on the “equilibrium” phase composition of the compound layer in contact with the nitriding atmosphere can be assessed by these experiments.
3.1. Two-Step Nitriding of Mold-Cast Fe–3.5C–1.5/3Si

No Fe nitrides but only X is formed in Fe–3.5C–1.5/3Si upon nitriding at $t_1 = 0.1$ atm$^{-1/2}$ used in the first step of the two-step treatment (Figure 9a). Fe$_2$Si$_3$C$_4$ is decomposed to $\alpha$ + X (see Kante et al.[12] for details). $\theta$ is transformed into $\alpha$-Fe up to a distance of about 10–12 $\mu$m from the surface due to the decarburizing nature of the nitriding atmosphere.

After the second nitriding step at $t_2 = 1$ atm$^{-1/2}$ for 4 h, the distribution of Fe nitrides in the two-step nitrided samples notably differs from the distribution of Fe nitrides in the single-step nitrided samples treated at the same process parameters (Figure 9b–e). Coarse Si- and X-free ferritic regions formed by the dissolution of eutectic $\theta$ during the first nitriding step are almost completely transformed into $\gamma'$, as expected from nitriding pure Fe at the used nitriding conditions. This suggests that $\gamma'$ has a negligible effect on the Fe nitride composition of the compound layer in the two-step nitrided samples. The C-promoted formation of $\varepsilon$ from, in particular, eutectic $\theta$ in the single-step nitrided samples—has a negligible effect on the Fe nitride composition of the compound layer in the two-step nitrided samples. The C-promoted formation of $\varepsilon$ from eutectic $\theta$ is very occasionally visible only at a large distance from the surface (Figure 9b,d).

In formerly pearlitic/ferritic regions, the compound layer is very thin, as compared to regions of former eutectic $\theta$. In contrast to single-step nitrided alloys, $\varepsilon$ and $\gamma'$ exist in former pearlitic/ferrite. $\gamma'$ seems more prominent in formerly pearlitic regions (Figure 9e,f). Here, $\gamma'$ has formed from Si- and X-free pearlitic $\theta$ lamellae, transformed into $\alpha$-Fe during the first nitriding step, but also from $\alpha$-Fe containing X. By contrast, $\varepsilon$ seems to have particularly grown in ferritic regions containing $\alpha$ + X. It may be concluded that Si- and X-free regions associated with dissolved pearlitic $\theta$ are beneficial to the nucleation and growth of $\gamma'$. In regions mainly containing $\alpha + X$, residual Si dissolved in $\alpha$-Fe might promote the nucleation and growth of $\varepsilon$, assuming that the effect of C on the Fe nitride formation is negligible (see earlier).

3.2. Nitriding of Melt-Spun Fe–3.5C and Fe–3.5C–3Si Ribbons

The melt-spun Fe–3.5C and Fe–3.5C–3Si ribbons contain similar microstructure features as their mold-cast equivalents. The size of the microstructure features is notably refined due to rapid solidification (see Kante et al.[21] for details). In Fe–3.5C–3Si, fine-grained and coarse-grained regions can be distinguished, which will be relevant to nitriding. The coarse-grained regions mainly exhibit colonies of elongated eutectic $\theta$ plates with a thickness of typically >100 nm. The plates are mainly embedded in ferrite or pearlite. The fine-grained regions exhibit a more or less completely eutectic microstructure, characterized by colonies of fine 0 plates with a thickness of about 10–100 nm. In addition, a minor phase fraction of Fe silicocarbide should be contained in the Fe–3.5C–3Si ribbon, but was not explicitly studied.

Upon nitriding for 48 h, the entire melt-spun ribbons are transformed into nitride. The Fe–3.5C ribbon is almost completely transformed into equiaxed $\gamma'$ grains (Figure 10a,b). A negligible phase fraction of $\varepsilon$ is detected by XRD (Table 2). In contrast to Fe–3.5C and analogous to the compound layer in mold-cast Fe–3.5C–1.5/3Si, the morphology of microstructure features contained in the as-cast Fe–3.5C–3Si ribbon is still
visible after nitriding (Figure 10c,d). The Fe–3.5C–3Si ribbon mainly contains ε (Table 2). In the formerly fine-grained regions of the ribbon, only ε is visible in EBSD maps. The fine eutectic θ plates in these regions seem not to transform into γ′, analogous to fine pearlitic θ in mold-cast samples (see also Figure S6, Supporting Information). γ′ has only formed from coarse eutectic θ plates in the ribbon. Moreover, γ′ has grown on the ribbon surface (Section 2.1), and occasionally at large pores inside the ribbon. In addition, X embedded in ε is visible in the ribbon. Complementarily, a Fe–3.5C–3Si ribbon was nitrided for 144 h, showing the same distribution of ε and γ′ in the microstructure as observed in the ribbon nitrided for 48 h (Figure S7, Supporting Information).

3.3. “Equilibrium” Nitride Composition of the Compound Layer

The small thickness of the melt-spun Fe–3.5C and Fe–3.5C–3Si ribbons has allowed us to transform the entire ribbons into nitride. Ideally a nitriding-time-independent state is reached, in which μₜ and μᵥ can be considered as equilibrated between the nitriding atmosphere and the bulk of the ribbons. This means μₜ = μₜₑ𝑞 = μₑ𝑞 and μᵥ = μᵥₑ𝑞 = μₑ𝑞 → −∞ (cf., Section 1.2). Thus, the nitride composition and distribution in the ribbons may be regarded as the “equilibrium” nitride composition and distribution in contact with the nitriding atmosphere, with respect to μₜₑ𝑞, μᵥₑ𝑞, and the given Si distribution.

The transformation of the almost entire Fe–3.5C ribbon into γ′ (Table 2) confirms the assumptions μₜ → μₑ𝑞 and μᵥ → −∞. Note the low C solubility in γ′ and the used nitriding conditions enforcing the formation of γ′ upon nitriding pure, C-free Fe. As the Fe–3.5C and Fe–3.5C–3Si ribbons have about the same thickness, μₜ → μₑ𝑞 and μᵥ → −∞ should be valid assumptions also in case of the Fe–3.5C–3Si ribbon. The large phase fraction of ε contained in the Fe–3.5C–3Si ribbon after nitriding at γ′ conditions, hence, is unlikely stabilized by C. The difference in the phase fractions of ε and γ′ in the nitrided Fe–3.5C and Fe–3.5C–3Si ribbons (Table 2) must be due to the presence of Si.

The nitride distribution in the Fe–3.5C–3Si ribbon compares with the nitride distribution in the surface-adjacent compound layer in mold-cast Fe–3.5C–3Si after nitriding for 4–48 h. In both, ε is the only Fe nitride formed in uₜₑ𝑞, uᵥₑ𝑞, and fine-grained uᵥₑq regions (fine eutectic and pearlitic θ), whereas γ′ is only visible in coarse uᵥₑq regions (coarse eutectic θ; Figure 8). Thus, the surface-adjacent compound layer of mold-cast Fe–3.5C–3Si nitrided for 4–48 h exhibits the “equilibrium”
nitride composition and distribution in contact with the nitriding atmosphere, identified by nitriding of the Fe–3.5C–3Si ribbon. Consequently, the stability of ε contained in the surface-adjacent compound layer form can be considered as independent of continuous supply of C from the substrate.

Despite this, C supply from the substrate to the compound layer certainly affects the nitride formation and content in the compound layer at some distance from the surface. This accounts for the transformation θ → ε and, in particular, the continuous growth of ε + X into α-Fe. The latter cannot be explained by the presence of Si in α-Fe only, as continuous growth of ε + X into α-Fe is neither known from nitriding binary Fe–Si alloys\(^{[26,27,37]}\) nor appears very prominent in the present two-step nitrided samples, being decarburized in the proximity of the surface. Note that, on the other hand, C alone cannot stabilize ε in contact with α-Fe at the used process temperature of 540 °C; compare the nitried Fe–3.5C alloy in Figure 1. In this regard, Si dissolved in α-Fe may promote the stabilization of ε in contact with α-Fe by C. This is explained as follows. Si is well known to decrease the C solubility in α-Fe and to increase the chemical potential of C in α-Fe. Adjacent to the compound layer, therefore, α-Fe may become readily saturated with C released by the transformation of θ into ε. The saturation of α-Fe with C in conjunction with an increased chemical potential of C in α-Fe due to Si may stabilize ε in contact with α-Fe. This accounts for both Si-free ε formed from θ and Si-containing ε(þX) formed from α-Fe.

### 3.4. Stabilization of Si-Free ε within the Compound Layer Formed from Pearlite

Si-free ε formed from pearlitic θ and ε of the ε + X nanostructure formed from pearlitic α-Fe do not transform into γ’ in the surface-adjacent compound layer, as observed for ε formed from coarse Si-free eutectic θ (Figure 1d and 7c–e). Likewise, fine eutectic θ plates in the melt-spun Fe–3.5C–3Si ribbon, transformed to ε upon nitriding, do not seem to eventually transform into γ’ (Figure 10 and Figure S6 and S7, Supporting Information). Si contained in ε of the ε + X nanostructure might stabilize ε with respect to γ’, assuming a higher Si solubility in ε than in γ’\(^{[12,26,27]}\). The stability of Si-free ε is puzzling as the C content should be negligible for the stabilization of ε in the decarburized surface-adjacent compound layer and the nitrided sample.

Table 2. Phase fractions of ε and γ’ obtained by Rietveld analysis of XRD patterns obtained of melt-spun Fe–3.5C and Fe–3.5C–3Si ribbons after crushing them to powder. No traces of other phases than ε and γ’ are evident from the diffraction patterns, indicating that the entire ribbons are transformed into nitride.

|         | Fe–3.5C | Fe–3.5C–3Si |
|---------|---------|-------------|
| ε [wt%] | 4       | 83          |
| γ’ [wt%]| 96      | 17          |

![Figure 10. SEM-BSE images and respective EBSD phase maps of melt-spun a,b) Fe–3.5C and c,d) Fe–3.5C–3Si nitrided at 540 °C and \(r_N = 1 \text{ atm}^{-1/2}\) for 48 h being entirely transformed into nitride. Note the massive pore formation, particularly in the nitrided Fe–3.5C ribbon, appearing black in BSE images and as white spots in the EBSD maps. See Figure S6, Supporting Information, for an enlarged image and inverse pole figure map of the nitrided Fe–3.5C–3Si ribbon.](image-url)
ribbons (Section 3.3). Other effects different from Si and C solubilities in ε and γ′ must lead to the stability of Si-free ε formed from pearlitic θ and fine eutectic θ in the ribbons. Exploring these effects is beyond the scope of this work and requires further investigations. Different reasons may be suggested. First, the literature[73–75] has indicated that the stability ranges of Fe nitrides might change at reduced dimensions. ε was observed to form in addition to γ′ upon nitriding nanocrystalline pure α-Fe substrates under γ′ conditions.[76] Size effects on the stability of the Fe nitrides cannot be excluded in case of the nitried pearlite and ribbons, containing nanosized microstructure features. Second, the volume of γ′ is typically larger than the volume of ε.[77] Compressive stresses of at least partially hydrostatic character may be induced by the transformation ε → γ′. An unfavorable contribution of strain energy to the nucleation barrier or the overall stability of γ′ may result.[77] Moreover, considering the large volume density of ε/X phase boundaries at former α/θ phase boundaries in pearlite as well as in the ε + X nanostructure, a higher γ′/X interface energy as compared to the ε/X interface energy could further hamper the nucleation and growth of γ′ in the former Si-containing pearlite. Note that γ′ nucleated in former eutectic θ or on the sample surface (Figure 1d, Section 2.1) does not grow into adjacent transformed pearlite containing ε and X. The nucleation barrier for γ′ might be lower within coarse ε grains formed from eutectic θ, for which, e.g., the formation of possibly unfavorable γ′/X phase boundaries may be negligible.

4. Fe–C–Si–N Phase Diagram In View of the Microstructure Evolution

4.1. Adaption of the Diffusion Path Concept

The u_εSi,θ regions in the white-solidified microstructure (Figure 8, Section 2.4) almost behave like different alloys being nitrided simultaneously. As Si is not notably exchanged between u_εSi,θ regions (Section 2.3), evidently, the microstructure forming during nitriding cannot be described by a single diffusion path in a u_εSi section of the Fe–C–Si–N phase diagram as suggested in Section 1.2 for Fe–C–M–N alloys, in which M is homogeneously distributed. To apply the diffusion path concept to the nitriding of compositionally inhomogeneous alloys such as white-solidified cast irons under conditions of limited mobility of substitutional alloying elements, here Si, additional assumptions are required:

1) the diffusion of N and C is sufficiently fast, such that μ_N and μ_C may always take their equilibrium value at phase boundaries. N and C can be exchanged between u_εSi,θ regions. Therefore, each μ_N and μ_C may take the same value at a given distance from the surface, z. Note that μ_N and μ_C, of course, relate to local contents of N and C, and that phase boundaries under local equilibrium enforce certain values of μ_Si and μ_C. Local variations in μ_N and μ_C due to finite rates of phase transformations and of N, C, and Si diffusion are neglected (cf., Section 2.4.2).

2) Si is not exchanged between u_εSi,θ regions (Figure 5c and Figure 7e). In contrast to μ_N and μ_C (1), therefore, the chemical potential of Si cannot be equilibrated between u_εSi,θ regions. This means the u_εSi,θ regions may be considered to coexist in a paraequilibrium-like state. Phase boundaries between u_εSi,θ regions do not represent local equilibria.

3) Very short-range redistribution of Si during phase transformations inside u_εSi,θ regions is possible, e.g., by the precipitation of X within α-Fe or by the reactions α → ε + X and Fe_23Si_5C_4 → α + X. Thus, phase boundaries inside each u_εSi,θ region represent local equilibria.

Under the assumptions (1–3), the experimentally observed phase boundaries inside u_εSi,θ regions correlate with phase fields in the Fe–C–Si–N phase diagram at a given Si content u_εSi,θ. The microstructure formation in each u_εSi,θ region, therefore, may be simultaneously described by a distinct diffusion path in a respective section of the Fe–C–Si–N phase diagram at u_εSi,θ. The diffusion paths describing the microstructure in different u_εSi sections must coincide when the respective u_εSi sections are overlaid; compare assumption (1)—each μ_N and μ_C having the same value at given z, independent of the value of u_εSi. Characteristic multiphase points must occur in the microstructure whenever one diffusion path crosses a boundary between phase fields in its u_εSi section, whereas another coincident diffusion path simultaneously remains in the same phase field in another u_εSi section. These multiphase points reveal the relative position of phase fields in different u_εSi sections with respect to each other. This relation may be particularly useful in the assessment of unknown higher-order phase diagrams if, for instance, one of the boundary systems is well known; here, the Fe–C–N boundary system at u_εSi,θ = 0.

In the following sections, topological features of the Fe–C–Si–N phase diagram are derived from the experimentally observed phase evolution during nitriding (Figure 8) based on the assumptions (1–3), and difficulties in applying the diffusion path concept to the present materials system are discussed. In doing so, the phase sequence after short nitriding times, Figure 8 (t₁), is neglected as it is notably governed by kinetic effects related to the slow precipitation kinetics of X and diffusional redistribution of Si and C, possibly obstructing the establishment of local equilibria (Section 2.4.1). Likewise, the persistence of Si-free ε formed from pearlitic θ against a transformation into γ′ is assumed to result from size effects or a nucleation barrier to γ′ (Section 3.4), which cannot be accounted for by the diffusion path concept. Pearlitic θ, therefore, is assumed to exhibit the nitriding behavior of eutectic θ in Figure 8.

4.2. Topology of the Fe–C–Si–N Phase Diagram

The transformation of 0 into ε and γ′ and the respective ε/0, ε/γ′, and γ′/0 phase boundaries observed inside the u_εSi,θ regions (Figure 8) are compatible with local equilibria in the well-known Fe–C–N system at 540 °C,[44,45] i.e., the boundary system of the Fe–C–Si–N system at u_εSi = 0. Likewise, the ε + X phase mixture in the surface-adjacent, decarburized part of the compound layer inside u_εSi,α and u_εSi,Fe_23Si_5C_4 regions at z → 0 (μ_C → −∞; see Section 3) in Figure 8 should relate to the Fe–Si–N boundary system, which is experimentally little explored.[77]

The u_ε/k and u_ε/X phase boundaries observed at the growth front of the compound layer in u_εSi,θ and u_εSi,Fe_23Si_5C_4 regions exist in neither the Fe–C–N system[44,47] nor the Fe–Si–N system[31,43] at the used nitriding temperature. The present authors have
previously suggested\cite{12} that these $\alpha/e$ and $\alpha/e/X$ phase boundaries indicate the existence of $\alpha + e$ and $\alpha + e + X$ phase fields in the Fe–C–Si–N phase diagram at nonzero contents of both C and Si, which are not considered in the available thermodynamic databases.\cite{47} The continuous growth of $\epsilon(+X)$ in the $u_{Si,a}$ and $u_{Si,Fe_{23}Si_{5}C_{4}}$ regions and the persistence of that $\epsilon$ against a transformation into $\gamma'$, shown in the current work, corroborate this suggestion and justify accounting for these $\alpha/e$ and $\alpha/e/X$ phase boundaries in a metastable Fe–C–Si–N phase diagram by $\alpha + e$ and $\alpha + e + X$ phase fields.

Based on the experimental data and literature information\cite{44,47} on the respective ternary boundary systems, basic features of the topology of the Fe-rich corner of the Fe–C–Si–N can be deduced.

4.2.1. Fe–C–Si–N Potential Phase Diagram

The Fe-rich corner of a possible Fe–C–Si–N potential phase diagram at 540 °C is schematically constructed in Figure 11 by extrapolating from the Fe–C–N and Fe–Si–N boundary systems into the Fe–C–Si–N space (see the following). The activities of N, C, and Si, $u_{Ni,\alpha}$, $u_{C,\alpha}$, and $u_{Si,\alpha}$, which are related to $\mu_{Ni}$, $\mu_{C}$, and $\mu_{Si}$, are selected as axes to simplify drawings at low contents of N, C, and Si. For convenience, $Fe_{23}Si_{5}C_{4}$ is neglected in the following, such as other phases like SiC and Fe silicides, which were not observed and are unlikely to exist at the investigated alloy compositions.

The Fe–Si–N boundary system exhibits the three-phase fields $\alpha + \gamma' + X$ and $\alpha + e + X$; see corresponding points in the $a_{Si}$–$a_{Si}$ plane at $a_C = 0$ in Figure 11. Both the $\alpha + \gamma' + X$ and $\gamma' + e + X$ fields, and respective $\alpha + \gamma'$, $e + \gamma'$, and $\gamma' + X$ fields, must disappear when extrapolating from the Fe–Si–N boundary system toward $a_C > 0$ to allow establishing the observed $\alpha + e + X$ field (line). The $\alpha + X$ and $e + X$ fields (surfaces) already present in the Fe–Si–N system and bounding the $\alpha + e + X$ field are retained. From all these features, the existence of an $\alpha + e + \gamma' + X$ field (point), being invariant at 540 °C and constant pressure, and a related $\alpha + e + \gamma'$ field follows. Note that phase boundaries indicative of the three-phase fields related to the $\alpha + e + \gamma' + X$ field are principally visible in the surface region of the two-step nitrided samples, where $a_C \rightarrow 0$ (Figure 9).

Figure 11. a) Schematic sketch of the Fe-rich corner of the Fe–C–Si–N potential phase diagram at 540 °C deduced from present experimental data and literature.\cite{44,47} The 3D phase diagram in $a_{Si}$–$a_{Si}$–$a_{Ni}$ space is visualized by projections along the $a_{Si}$ and $a_{Ni}$ axis onto the $a_{Ni}$–$a_{Ni}$ and $a_{Si}$–$a_{Si}$ boundary planes, schematically showing the topology of the Fe–C–N\cite{44,47} and Fe–Si–N\cite{12,37,47} boundary systems (gray). Note that single-phase, two-phase, three-phase, and invariant four-phase fields are volumes, surfaces, lines, and points in $a_{Si}$–$a_{Si}$–$a_{Ni}$ space. The curves are linearized. The line representing the $\epsilon + \gamma'$ field in the Fe–Si–N boundary system is drawn with a negative slope, not evident from the thermodynamic database,\cite{47} as previous studies\cite{12,37} have indicated that Si lowers the chemical potential of N at which $\epsilon$ can form. The Fe–Si–N boundary system,\cite{47} $a_{Si}$–$a_{Si}$ plane, is considered in the region of the phase diagram in which $\alpha$ and $\theta$ are the only stable phases. The positions of invariant points with respect to each other are chosen such that the generalized 180° rule\cite{60,86} is fulfilled; however, the shown solution is not unique. Broken lines illustrate the construction of the hypothesized invariant equilibrium $\alpha + 0 + e + X$. b) Illustrative sketch of a possible $u_{Si}$ section of the Fe–C–Si–N phase diagram accounting for phase boundaries observed in single- and two-step nitrided mold-cast Fe–3.5C–1.5/3Si (see text).
Similar to the this, the extrapolations of the $\alpha + \theta + \gamma'$ and $\theta + \gamma' + \varepsilon$ fields from the Fe–C–N boundary system in the $a_{\text{Si}}$ direction must meet in the $a_{\text{Si}}$–$a_{\text{Si,0}}$ space, giving rise to the experimentally observed $\alpha + \varepsilon$ field. This implies the existence of an $\alpha + \theta + \varepsilon + \gamma'$ field, invariant at 540°C and constant pressure, as well as $\alpha + \varepsilon + \gamma'$ and $\alpha + \theta + \varepsilon$ fields emerging from that point and bounding the $\alpha + \varepsilon$ field. The $\alpha + \theta + \varepsilon + \gamma'$ field likely connects to the previously deduced $\alpha + \varepsilon + \gamma' + \varepsilon$ field, provided that no unknown quaternary Fe–C–Si–N phase exists in the very Fe-rich and Si-poor corner of the Fe–C–Si–N system. Nevertheless, the current experimental evidence of the $\alpha + \theta + \varepsilon + \gamma'$ field is incomplete.

In addition, it might be hypothesized that the $\alpha + \varepsilon + X$ and $\alpha + \theta + \varepsilon$ fields meet in an $\alpha + \theta + \varepsilon + X$ field, indicated by broken lines in Figure 11, if no other phases form during nitriding of Fe–C–Si alloys than those currently observed. This would imply $\alpha + \theta + X$ and $\theta + \varepsilon + X$ fields. Respective phase boundaries exist at the boundaries of $u_{\text{Si,0}}$ and $u_{\text{Si,0}}$, regions in the diffusion zone and in the transition region between the diffusion zone and compound layer (Figure 8); however, they do not represent local equilibrium under the assumptions in Section 4.1. Note that experimentally observed $0/\alpha + X$ and $0/\varepsilon + X$ phase boundaries in the diffusion and transition zone (Figure 8) might relate to a state close to local equilibrium due to the negligible Si solubility in $0/\varepsilon + X$. As a consequence of the latter, a particular situation might arise in which $u_{\text{Si,0}}$ might take a local equilibrium value in $\theta$ in contact with $\alpha + X$ and $\varepsilon + X$ without the need of redistributing Si in $\alpha$ or exchanging Si between $\theta$ and $u_{\text{Si,0}}$ regions; compare assumption (2) in Section 4.1.

4.2.2. Schematic $u_{\text{Si}}$ Section of the Fe–C–Si–N at $u_{\text{Si,0}}$

The Fe–C–Si–N potential phase diagram (Figure 11a) derived in Section 4.2.1 can be used to estimate the phase fields showing up in, e.g., $a_{\text{C}}$ (compare Figure 9 in Kante et al.12) and $a_{\text{Si}}$ or $u_{\text{Si,0}}$ sections of the Fe–C–Si–N phase diagram. For illustration purposes, Figure 11b schematically sketches one of the many possible $u_{\text{Si,0}}$ sections of the Fe–C–Si–N at $u_{\text{Si}} > 0$, representative for the Si content in a $u_{\text{Si,0}}$ region. The shown $u_{\text{Si,0}}$ section accounts for phase fields, which are related to the phase boundaries and phase mixtures observed in the pearlite of single- and two-step nitrided mold-cast samples. Moreover, it is assumed that only the invariant $\alpha + \gamma' + \varepsilon + X$ field, represented by a line in $a_{\text{Si}}$–$a_{\text{Si,0}}$ space, is intersected by the $u_{\text{Si,0}}$ section. The $\alpha + \theta + \gamma' + \varepsilon$ field is assumed to lie outside the section and the hypothetical $\alpha + \theta + \gamma' + \varepsilon + X$ field is neglected.

To illustrate the relative position of the phase fields in $a_{\text{Si}}$–$a_{\text{Si,0}}$ space, the $u_{\text{Si,0}}$ section in Figure 11a is overlaid to the well-known section of the Fe–C–Si–N phase diagram at $u_{\text{Si,0}} = 0$ (Fe–C–N boundary system44–47) in Figure 12. Coincident diffusion paths describing the observed sequence of phases and phase transformations between the substrate and surface in $u_{\text{Si,0}}$ and $u_{\text{Si,0}}$, regions in Figure 8 after $t_2$ and $t_3$ are indicated, together with multiphase points (Section 4.1) determining the position of the phase fields in both $u_{\text{Si,0}}$ sections with respect to each other. Note that the diffusion path in the section at $u_{\text{Si,0}}$ starts from the boundary of the $\alpha$ and $\alpha + \theta$ fields and the coincident diffusion path in the section at $u_{\text{Si,0}}$ starts in the $0$ field—neglecting Fe$_2$Si, C$_4$, and considering $\alpha + \theta$ equilibrium in the substrate.

Regarding the microstructure evolution, the coincident diffusion paths can be read as follows. When the diffusion path in the section at $u_{\text{Si,0}}$ crosses the boundary between the $\alpha$ field and the $\alpha + X$ field, the coincident diffusion path in the section at $u_{\text{Si,0}}$ remains in the $0$ field. This means $X$ starts to precipitate from $\alpha$-Fe, which locally depletes in Si, whereas $\theta$ remains as it is. When the diffusion path in the section at $u_{\text{Si,0}}$ crosses the $\alpha + \varepsilon + X$ field (occurring as a line in the $u_{\text{Si,0}}$ section), all the remaining $\alpha$-Fe decomposes into $\varepsilon + X$ in a eutectoid fashion by means of the reaction $\alpha \rightarrow \varepsilon + X$. Then, this $\varepsilon + X$ coexists

![Figure 12. Overlaid schematic sections of the Fe–C–Si–N phase diagram at $u_{\text{Si,0}}$ (black; redrawn from Figure 11b) and $u_{\text{Si,0}} = 0$ (gray; Fe–C–N boundary system based on ref. [47]; cf., Figure 11a). Coincident diffusion paths (blue) in the overlaid $u_{\text{Si}}$ sections describe the sequence of phases and phase transformation in $u_{\text{Si,0}}$ and $u_{\text{Si,0}}$, regions in Figure 8 after $t_2$ and $t_3$. They start at $a_{\text{C}}$–$a_{\text{Si}}$ and $a_{\text{Si,0}} = 0$ ($z = z_{\text{max}}$ in Figure 8) and end at $a_{\text{C}}$–$0$ and $a_{\text{Si}}$–$a_{\text{Si}}$, regions in Figure 8. Multiphase points (Section 4.1) and respective phase transformations are highlighted, which occur when a diffusion path in one $u_{\text{Si}}$ section crosses the boundary of phase fields while the coincident diffusion path in the other $u_{\text{Si}}$ section remains in the same phase field. Note that $\varepsilon$ in the section at $u_{\text{Si,0}}$ may contain Si, whereas $\varepsilon$ in the section at $u_{\text{Si,0}}$ does not.](image-url)
with $\theta$ of the section at $u_{Si,0}$. From the latter, for instance, it is evident that the $\alpha + e + X$ field in the section at $u_{Si,a}$ must be located at lower $a_{N}$ than the $0 + e + \gamma'$, and $0 + e + \gamma'$ fields in the section at $u_{Si,0}$ to allow for the sequence of phase transformations in Figure 8 ($I_2$–$I_3$).

### 4.2.3. Factors Complicating the Thermodynamic Interpretation of the Experimental Data

In addition to kinetic effects due to slow $X$ precipitation as well as $Si$ and $C$ redistribution (Section 2.4), the interpretation and description of the microstructure formation during nitriding of white-solidified Fe–C–Si alloys with respect to the Fe–C–Si–N phase diagram by means of the here-adapted diffusion path concept is further complicated by two factors, discussed in the following. First, there are different invariant equilibria constituted by phases exhibiting similar and very low Si solubilities. Second, Si is very heterogeneously distributed in $u_{Si,a}$ regions.

**Impact of Low Si Solubility in $e$, $\gamma'$, and $\theta$ on the Extent of Phase Fields:** The possible existence of $\alpha + 0 + e + \gamma'$, $\alpha + \gamma' + e + X$, and $\alpha + 0 + e + X$ fields, being invariant at 540 °C and constant pressure, in the Fe–C–Si–N system was described in Section 4.2.1. Each single-phase field related to these phase fields can connect to the respective four-phase fields in a nitrogen-lean $u_{Si}$ space only at one particular Si content $u_{Si}$. The order in which single-phase fields connect to the invariant four-phase fields (lines of constant $a_{N}$ and $a_{C}$ in a $u_{Si}$–$a_{N}$–$a_{C}$ space only at one particular Si content $u_{Si}$) determines the two- and three-phase fields showing up in $u_{Si}$ sections of the phase diagram. This order could not be experimentally assessed yet in case of the complex and compositionally inhomogeneous microstructures of nitrided white-solidified Fe–3.5C–1.5Si alloys. The presented considerations lay the basis for future investigation and thermodynamic modeling of the metastable Fe–C–Si–N system, relevant to nitriding of Fe–C–Si–based cast irons and steels. Further investigations are required to validate and extend the present considerations and experimental data. In particular, knowledge on the element content in phases at phase boundaries under local equilibrium is required to be able to estimate or calculate the position of phase fields in the phase diagram more precisely.

Moreover, the adapted diffusion path concept presented in this work is not limited to the description of the nitriding of white-solidified Fe–C–Si alloys. It should generally apply to the description of any treatment introducing fast-diffusing interstitial species into alloys, in which the substitutional alloying elements are heterogeneously distributed and largely immobile due to low process temperatures. For instance, such a situation may occur upon nitriding, nitrocarburizing, or carburizing of duplex steels containing ferritic and austenitic regions of different substitutional element contents, or of tool steels containing coarse-alloying-element carbides. Furthermore, nitriding of artificially compositionally graded alloys exhibiting—in contrast to the here-studied alloys—regions of more well-defined levels of alloying element contents may be an efficient approach to evaluate, e.g., experimentally little-known Fe–M–N phase diagrams. A similar approach, i.e., carburizing of Fe–Fe–M diffusion couples exhibiting a continuous gradient in the M content, has already shown its potential.
5. Conclusion

The microstructure formation during nitriding of compositionally inhomogeneous white-solidified Fe–3.5 wt% C–0/1.5/3 wt% Si alloys was investigated, which is relevant to advanced surface treatments of cast iron by surface remelting and nitriding. Phase and microstructure formation during nitriding locally vary, depending on the local Si and C content of microstructure features in the substrate material. In addition, nitriding of melt-spun Fe–3.5 wt% C–0/3 wt% Si ribbons and two-step nitriding of mold-cast Fe–3.5 wt% C–1.5/3 wt% Si alloys have shown how C supply from the substrate to the compound layer affects the Fe nitride formation and the “equilibrium” phase composition of the compound layer in contact with the nitriding atmosphere. The key findings can be summarized as follows:

1) The heterogeneous distribution of Si in the as-cast microstructure is crucial to the microstructure formation because the spatial extent of local variations in the Si content is considerably larger than the diffusion distance of Si during nitriding. A schematic model of the phase formation in microstructure regions of different Si/Fe atomic ratios was derived. It was shown how finite rates of short-range Si and long-range C redistribution affect the local phase composition and thickness of the compound layer after different nitriding times.

2) Limited Si diffusion in conjunction with sluggish precipitation of Si-rich nitride in α-Fe and a very low Si solubility in Fe nitrides obstruct the Fe nitride formation from α-Fe during short nitriding times. Thereby, the transformation of Si-free pearlitic and eutectic 0 into ε is promoted. Local equilibria unlikely establish in α-Fe and adjacent to the surface during short nitriding times. Upon prolonged nitriding, the nitrided layer appears to grow under conditions of local equilibrium inside microstructure regions characterized by different mean Si/Fe atomic ratios, which remains unchanged upon nitriding.

3) The “equilibrium” nitride composition of the compound layer in contact with the nitriding atmosphere is characterized by a heterogeneous mixture of γ’, ε, and ε + X formed from Si-free eutectic 0, Si-free pearlitic 0, and Si-enriched α-Fe, respectively. The persistence of ε formed from Si-free pearlitic 0 against a transformation into γ’ under the used γ’ nitriding conditions cannot be explained by alloying element effects due to C and Si. A large nucleation barrier for γ’ or changed stability ranges of Fe nitrides at reduced dimension may additionally affect the observed stability of ε.

4) The diffusion path concept has been adapted to a thermodynamics-based description of the present microstructure evolution during nitriding compositionally inhomogeneous alloys under limited diffusion of substitutional alloying elements. This has allowed us to extract valuable information on the topology of the Fe-rich corner of the Fe–C–Si–N phase diagram from the current complex microstructures. The transformation α → ε + X and related α + e and α + ε + X phase fields have been identified as particular features of the Fe–C–Si–N system, as hypothesized in a previous study.[12]

The model of the microstructure formation during nitriding of white-solidified Fe–3.5 wt% C–1.5/3 wt% Si alloys developed in this study significantly contributes to the understanding of the nitriding behavior of the white-solidified surface layer produced by remelting of commercially available ferritic cast irons, laying the basis for thermodynamics-based tailoring of the nitriding treatment. In view of the heterogeneous distribution of γ’ and ε in the compound layers obtained under γ’ conditions, nitriding under process conditions already allowing for the formation of ε when nitriding pure α-Fe may be advised to produce macroscopically homogeneous compound layers that are γ’-free and only contain ε (and X) (cf., results in Holst et al.[17]). Also, combined nitriding treatments such as the here-used two-step nitriding might be expedient to tailor the Fe nitride composition and microstructure of the compound layer forming in remelted cast irons. Furthermore, the presented model of the microstructure evolution may require modifications to be applicable also to the nitriding of remelted pearlitic cast irons, containing non-negligible additions of Mn and Cu. The latter effect of Mn and Cu additions on the nitriding behavior of white-solidified cast irons is currently investigated by the authors.

6. Experimental Section

Materials and Processing: Fe–3.5 wt% C–0/1.5/3 wt% Si alloys, denoted Fe–3.5C–0/1.5/3Si, were produced by induction melting and by arc melting of pure Fe granules (99.98%), Si lumps (99.9995%), and graphite rods (99.9999%), supplied by Alpha Aesar, in an Ar atmosphere. The alloys obtained by induction melting were cast into Cu molds measuring 80 × 80 × 5 mm3. The resulting alloy plates were cut into specimens sized 17 × 12 × 2 mm3. The alloy buttons obtained by arc melting were cut, inductively remelted and melt-spun in an Ar atmosphere using a Bühler Melt Spinning SC to produce continuous ribbons measuring 10 mm in width and ≤40 μm in thickness. Further information on the melt-spinning process and the melt-spun ribbons is provided elsewhere.[21] Prior to nitriding, the mold-cast specimens were ground and polished (final step: 1 μm diamond suspension). The melt-spun ribbons were nitrided in an asc state.

Controlled gas nitriding was performed in a laboratory-scale chamber furnace at 540 – 560°C. The mold-cast samples were nitrided at rN = 1 atm/C0 for 1, 4, 16, and 48 h. The melt-spun ribbons were nitrided at rN = 1 atm/C0 for 48 h. Only γ’ but no ε forms in pure Fe at rN = 1 atm/C0 and 540°C (i.e., γ’ conditions (Section 1.1). [46] Fe–3.5C, Fe–3.5C–1.5Si, and Fe–3.5C–3Si samples were nitrided simultaneously. To terminate the nitriding treatment, the samples were pulled into the cold prechamber of the furnace and rinsed with cold process gas. Note that nitriding experiments were also performed in other nitriding furnaces [18,19] and at additional nitriding potentials of rN = 4 atm/C0 and rN = 6 atm/C0. The results of these experiments are compatible with the results presented in this work, focusing only on samples nitrided at rN = 1 atm/C0.

In addition, a two-step nitriding treatment was applied to the mold-cast samples. First, the samples were nitrided at 540°C and rN = 1 atm/C0 for 16 h. No Fe nitrides but only X can form under these conditions.[12] The such nitrided samples were halved. One piece was characterized (see Kante et al.[17]). The other piece was slightly polished using 1 μm diamond suspension to remove contamination and surface oxides possibly formed during cutting. Afterward, it was subjected to a second nitriding treatment under the above γ’ conditions, 540°C and rN = 1 atm/C0 for 4 h.

Characterization: The phase composition of as-cast and nitrided samples was analyzed by X-ray powder diffraction (XRD) in reflection geometry using a Bruker D8 ADVANCE diffractometer operating with Co Kα1 radiation. The measurements were conducted on the surface of as-cast and nitrided specimens in a 2θ range of 30°–125° with a step size of 0.01°. The nitrided melt-spun ribbons were crushed to powder and sieved (grid size: 50 μm) for additional measurements, ensuring that the entire ribbons were transformed into nitride (Section 3.2). Diffraction patterns
were evaluated by means of the Rietveld method using the Bruker-AXS TOPAS 5 software[10] and the crystallographic descriptions of the phases in Table 1.

Metallographic cross-sections were prepared for microstructure investigations by scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). For this, the samples were mechanically cut, electrolytically coated with a protective Ni layer, embedded in Struers Polyfast, ground, and polished (final step: Buehler Master-Met). SEM and EBSD were conducted using a Carl Zeiss LEO 1530 Field Emission SEM equipped with a Nordlys II EBSD detector and Oxford Instruments HKL Channel 5 EBSD system, as well as a JEOL JSM-7800F equipped with an EDAX Hikari Super EBSD system. Images were recorded with Z-sensitive backscattered electron (BSE) contrast, giving dark contrast to interstitial-rich nitrides. EBSD was measured with an acceleration voltage of 20 kV and a step width of 50 nm. EBSD patterns were indexed based on the crystallographic descriptions of the phases in Table 1. EBSD data were plotted using the MATLAB toolbox MTEX.[84,85]

For (scanning) transmission electron microscopy (S)TEM, specimens were prepared from the metallographic cross-sections by focused ion beam (FIB) milling using a FEI Helios Nanolab 600i. Investigations were conducted using a Jeol JEM-2200FS, operating at 200 kV and being equipped with a Gatan Inc. 2 K CCD camera, an in-column field detector, and a 24065JGT field (BF) detector for energy-dispersive X-ray spectroscopy (EDX). Crystalline phases in the TEM specimens were identified by selected area electron diffraction (SAED). STEM images were recorded in bright-field (BF) and dark-field (DF) contrast. Note that the amorphous Si-rich nitride X appears bright in BF images, dark in DF images, and does not contribute to SAED patterns, which only show reflections of the surrounding phases see Kante et al.[11] for details regarding the characterization of X in nitrided Fe–C–Si alloys.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors gratefully acknowledge the German Research Foundation for its financial support of the project LE 1403/1-2. The authors thank Dr.-Ing. A. Dalke and E. Siegismund (Institute of Materials Engineering, TU Bergakademie Freiberg) for providing access to the nitriding facilities and conducting the nitriding experiments. The authors acknowledge Dipl.-Ing. D. Hübben, Dipl.-Ing. (FH) A. Leuteritz, and K. Becker (Institute of Materials Science, TU Bergakademie Freiberg) for providing support in sample preparation. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
- cast irons, diffusion path, Fe–C–Si–N system, microstructure formation, nitriding

[1] H. Berms, W. Theisen, Eisenwerkstoffe - Stahl und Gusseisen, Springer, Berlin, Heidelberg 2008.
[2] Cast Irons (Ed.: J. R. Davis), ASM International, Materials Park, OH 1996.
[3] R. Zenker, A. Buchwalder, K. Rüthrich, W. Griesbach, K. Nagel, Surf. Coat. Technol. 2013, 236, 58.
[4] A. Buchwalder, R. Zenker, K. Rüthrich, K. Nagel, W. Griesbach, S. Hartwig, J. Siedler, HTM, J. Heat Treat. Mater. 2014, 69, 138.
[5] J. Betzold, G. Laudin, S. Strämke, U. Huchel, J. Heat Treat. Mater. 1994, 49, 186.
[6] M. B. Karamış, K. Yıldızlı, Mater. Sci. Eng., A 2010, 527, 5225.
[7] M. Hillert, H. Steinhäuser, Jerrkontorets Ann. 1960, 144, 520.
[8] M. Hillert, V. V. Subba Rao, J. Inst. Met. 1968, 110, 204.
[9] X. Nie, L. Wang, Z. C. Yao, L. Zhang, F. Cheng, Surf. Coat. Technol. 2005, 200, 1745.
[10] E. Roliński, A. Konieczny, G. Sharp, J. Mater. Eng. Perform. 2009, 18, 1052.
[11] J. Baranowska, Surf. Coat. Technol. 1998, 100–101, 271.
[12] S. Kante, P. Künzsteinberger, B. Gault, M. Motyleanko, A. Leineweber, Acta Mater. 2021, 209, 116774.
[13] A. Buchwalder, H. J. Spies, N. Klose, E. Hegelmann, R. Zenker, in Proc. of the 24th IFHTSE Congress, Nice, France 2017.
[14] A. Buchwalder, H. J. Spies, N. Klose, A. Jung, R. Zenker, in Proc. of the 23rd IFHTSE Congress, Savannah, GA 2016, p. 55.
[15] A. Buchwalder, N. Klose, R. Zenker, Metall. Ital. 2020, 112, 28.
[16] A. Holst, A. Buchwalder, P. Hoffmann, R. Zenker, in Proc. of the 26th DTZ, Jihlava, Czech Republic 2017.
[17] A. Holst, A. Buchwalder, R. Zenker, Metall. Ital. 2020, 112, 61.
[18] S. Kante, A. Leineweber, Acta Mater. 2019, 170, 240.
[19] S. Kante, A. Leineweber, in Proc. of the ECHT – European Conf. on Heat Treatment 2018: Nitriding and Nitrocarburising (Eds.: K. Klümp-Westkamp, K. M. Winter), HTM - Carl Hanser Verlag, München 2018, p. 5.
[20] S. Kante, A. Leineweber, Mater. Charact. 2018, 138, 274.
[21] S. Kante, A. Leineweber, A. Holst, A. Buchwalder, Materialwiss. Werkstofftech. 2019, 50, 682.
[22] S. Kante, A. Leineweber, J. Alloys Compd. 2020, 815, 152468.
[23] P. Spinat, C. Brouty, A. Whuler, P. Herpin, Acta Crystallogr., Sect. B 1975, 31, 541.
[24] P. Spinat, J.-P. Sénateur, R. Fruchart, P. Herpin, C. R. Acad. Sc., Ser. C 1972, 274, 1159.
[25] N. Swindells, J. Burke, Metall. Mater. Trans. B 1971, 2, 3257.
[26] S. R. Meka, E. J. Mittemeijer, JOM 2013, 65, 769.
[27] S. R. Meka, A. Schubert, E. Bischoff, E. J. Mittemeijer, Metall. Mater. Trans. A 2020, 51, 3154.
[28] H. P. van Landeghem, M. Gouné, S. Bordère, F. Danoix, A. Redjaimia, Acta Mater. 2015, 93, 218.
[29] H. P. van Landeghem, M. Gouné, A. Redjaimia, Steel Res. Int. 2012, 83, 590.
[30] H. P. van Landeghem, M. Gouné, T. Epicier, A. Redjaimia, Scr. Mater. 2013, 68, 187.
[31] E. J. Mittemeijer, M. H. Biglari, A. J. Böttger, N. M. van der Pers, W. G. Sloof, F. D. Tichelaar, Scr. Mater. 1999, 41, 625.
[32] S. R. Meka, E. Bischoff, B. Rheingans, E. J. Mittemeijer, Philos. Mag. Lett. 2013, 93, 238.
[33] S. R. Meka, K. S. Jung, E. Bischoff, E. J. Mittemeijer, Philos. Mag. 2012, 92, 1435.
[34] G. R. Booker, J. Norbury, Nature 1959, 184, 1311.
