κ-carbide in a high-Mn light-weight steel: precipitation, off-stoichiometry and deformation

Von der Fakultät für Georessourcen und Materialtechnik
der Rheinisch-Westfälischen Technischen Hochschule Aachen

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genehmigte Dissertation

vorgelegt von M.Sc.

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Symbols and abbreviations

Symbols

$\alpha$  Ferrite
$\delta$  Lattice misfit
$\varepsilon$  True strain
$\varepsilon_p$  Partitioning coefficient
$\gamma$  Austenite
$\gamma_{APB}$  Anti-phase boundary energy
$\gamma'$  Gamma-prime phase in superalloys
$\kappa$  Kappa-carbide
$\mu$  Chemical potential
$\theta$  Diffraction angle
$\sigma$  Stress
$r$  Particle radius
$a$  Lattice parameter
$b$  Burgers vector
$c$  Composition
$d_{\{hkl\}}$  Interplanar distance of the \{hkl\} lattice planes
$D$  Diffusion coefficient
$E$  Formation energy
f  Mole fraction
G  Shear modulus
kB  Boltzmann constant
M  Taylor factor
t  Time
T  Temperature
Vf  Volume fraction
X  Diffusion length
Z  Atomic number

**Abbreviations**

1D  One-dimensional
2D  Two-dimensional
3D  Three-dimensional
APB  Anti-phase boundary
APT  Atom probe tomography
BSE  Backscattered electron
DF  Dark field
DP  Discontinuous precipitation
EBSDD  Electron backscatter diffraction
ECCI  Electron channeling contrast imaging
EDX  Electron dispersive x-ray spectroscopy
EPMA  Electron probe microanalysis
ER  Evaporation rate
fcc  Face-centered cubic
FEG  Field emission gun
FM  Ferromagnetic
FIB  Focused ion beam
FOV  Field-of-view
GB  Grain boundary
GI  Grain interior
HAADF  High angle annular dark field
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>HAGB</td>
<td>High angle grain boundary</td>
</tr>
<tr>
<td>HR</td>
<td>High-resolution</td>
</tr>
<tr>
<td>LEAP</td>
<td>Local electrode atom probe</td>
</tr>
<tr>
<td>LRO</td>
<td>Long-range ordering</td>
</tr>
<tr>
<td>MBIP</td>
<td>Microband-induced plasticity</td>
</tr>
<tr>
<td>OM</td>
<td>Optical microscopy</td>
</tr>
<tr>
<td>OPS</td>
<td>Oxide polishing suspension</td>
</tr>
<tr>
<td>PF</td>
<td>Pulse fraction</td>
</tr>
<tr>
<td>RDF</td>
<td>Radial distribution function</td>
</tr>
<tr>
<td>ROI</td>
<td>Region of interest</td>
</tr>
<tr>
<td>SAD</td>
<td>Selected area diffraction</td>
</tr>
<tr>
<td>SDM</td>
<td>Spatial distribution map</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SFE</td>
<td>Stacking fault energy</td>
</tr>
<tr>
<td>SIP</td>
<td>Shear-band induced plasticity</td>
</tr>
<tr>
<td>SQS</td>
<td>Quasi random structure</td>
</tr>
<tr>
<td>SRO</td>
<td>Short-range ordering</td>
</tr>
<tr>
<td>SS</td>
<td>Solid-solution</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>SXRD</td>
<td>Synchrotron X-ray diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-of-flight</td>
</tr>
<tr>
<td>TRIP</td>
<td>Transformation induced plasticity</td>
</tr>
<tr>
<td>TWIP</td>
<td>Twinning induced plasticity</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZA</td>
<td>Zone axis</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

There is a strong demand for the development of advanced high-strength steels for automotive applications, in order to reduce energy consumption and greenhouse gas emission. Austenitic ($\gamma$) high-Mn (15-30 wt.%) Fe-Mn-Al-C steels show particularly outstanding mechanical properties (Frommeyer et al., 2006; Chang et al., 2010; Springer et al., 2012; Gutierrez-Urrutia et al., 2013; Park et al., 2013; Raabe et al., 2014; Rana et al., 2014) and are therefore highly promising candidates for such applications. Due to their good oxidation and corrosion resistance (Banerji et al., 1978), these steels were originally developed in an attempt to substitute Cr-containing stainless steels, but recently they have regained substantial interest due to their excellent strength-ductility balance and significantly reduced mass density because of alloying with Al.

Austenitic Fe-Mn-Al-C steels, containing high Al (5-12 wt.%) and high C (0.5-1.3 wt.%), are age-hardenable. Through an ageing treatment at a temperature of 470-710 °C (Sato et al., 1989; Tjong et al., 1990; Sato et al., 1990; Choo et al., 1997), nanometer-scale ordered $\kappa$-carbide precipitates can be introduced into the disordered face-centered cubic (fcc) austenite matrix, which can remarkably strengthen the material while preserving great ductility. Due to the great importance of $\kappa$-carbide precipitates, numerous studies have been conducted to understand their precipitation and deformation behavior, which, however, are not fully clear.
Chapter 1. Introduction

Pronounced planar slip is generally observed in deformed ϰ-carbide-containing γ-alloys (Gutierrez-Urrutia et al., 2013; Park et al., 2013; Raabe et al., 2014; Welsch, 2016). Though a few transmission electron microscopy (TEM) micrographs of sheared particles have been reported (Choi et al., 2010; Welsch, 2016), controversial opinions still exist over the predominant interaction mechanism between ϰ-carbide precipitates and dislocations. Gutierrez-Urrutia et al. concluded that the primary mechanisms are Orowan bypassing of particle stacks and subsequent expansion of dislocation loops assisted by cross-slip (Gutierrez-Urrutia et al., 2014). Since the ϰ-carbide precipitates are finely dispersed in the γ-matrix, it is challenging to make a clear observation of them in the presence of dislocations. The current existing two-dimensional (2D) TEM micrographs are not convincing enough.

Moreover, no matter which mechanism dominates, a better microstructural characterization is yet necessary to quantitatively analyze the strengthening behavior. As for the “Orowan looping” case, the particle size and inter-spacing are critical which however are not unambiguous in 2D projected micrographs. In the case of “particle shearing”, besides particle size, its feasibility is associated with the antiphase boundary (APB) energy on the slip plane (Ardell et al., 1988), which depends on the stoichiometry and site-occupancy of the ordered particle.

Commonly, the composition of ϰ-carbides is given as (Fe,Mn)$_3$AlC$_x$, where the exact chemical composition of this phase is still unknown (Sato et al., 1988; Tjong, 1990; Sato et al., 1990; Choo et al., 1997). It is tacitly assumed to be a derivative from the Fe$_3$AlC$_x$-type ternary ϰ-carbide (Oshima et al., 1972). Due to the difficulty in determining C concentrations in small precipitates and also obtaining single-phase ϰ-carbide, the exact composition of the Fe$_3$AlC$_x$-type ϰ-carbide was uncertain for a long time (Palm et al., 1995; Sanders et al., 1997). In 1995, Palm et al. revealed a composition range for this phase between Fe$_{3.2}$Al$_{0.8}$C$_{0.71}$ and Fe$_{2.8}$Al$_{1.2}$C$_{0.42}$, i.e. Fe$_{3+y}$Al$_{1-y}$C$_x$ (-0.2 <y<0.2, 0.42<x<0.71), based on electron probe microanalysis (EPMA) (Palm et al., 1995). The C content does not reach the stoichiometric 20 at.% and the Fe to Al ratio can vary between 2.3 and 4.0 instead of being equal to 3. Despite the fact that the deviation of the Fe to Al ratio is not appropriately considered in the common Fe$_3$AlC$_x$ formula, it is still generally adopted. As for the (Fe,Mn)$_3$AlC$_x$ ϰ-carbide precipitates in Fe-Mn-Al-C alloys, since they are finely dispersed and only a
few nanometers in size, their direct chemical characterization is challenging. Atom probe tomography (APT) is the ideal tool to resolve this composition uncertainty since it offers near-atomic spatial resolution and equal detection sensitivity to all elements (Miller et al., 1996; Gault et al., 2012b; Larson et al., 2013; Miller et al., 2014). However, in contrast to intensive studies on κ-carbide-containing alloys, little APT data have been published on κ-carbide precipitates in quaternary austenitic Fe-Mn-Al-C alloys.

The crystal structure of κ-carbides is reported to be L’1₂ perovskite-type (Tjong, 1986; Tjong, 1990; Han et al., 1986; Choo et al., 1985). In such a variant of the conventional fcc crystal structure, the unit cell contains 5 atoms at 3 kinds of sites. In addition to the 4 atoms at one corner and three face-centered sites, as per fcc conventional unit cell, there is also one atom at the body-centered site. Conventionally, as shown in Figure 1.1, the elemental site-occupancy of the κ-carbide phase is such that Al occupies the corner site of the unit cell, Fe and Mn the face-centered positions, and C occupies the body-centered octahedral interstitial site, which is based on observations of electron diffraction patterns and calculations of structure factors (Tjong, 1986; Han et al., 1986; Tjong, 1990). In terms of atomic percentage, the stoichiometric (Fe,Mn)₃AlC κ-carbide has 60% (Fe+Mn), 20% Al and remaining 20% C. However, the κ-carbides are commonly expected to be off-stoichiometric and thus the elemental site-occupancy remains unresolved.

![Figure 1.1](image.png)

**Figure 1.1.** Schematic sketch of the unit cell of the ideal stoichiometric (Fe,Mn)₃AlC L’1₂ κ-carbide with Fe, Mn, Al and C atoms shown by red, orange, green and purple balls, respectively.
In addition, nanometer-sized κ-carbide precipitates are often regarded as coherent particles with respect to the γ-matrix according to x-ray diffraction (XRD) analyses (Huang et al., 1994) or simply tacitly assumed. The interfacial structure between κ-carbide precipitate and γ-matrix is little known, which, however, could significantly affect the morphology and arrangement of κ-carbide precipitates due to elastic constraining if any and the dislocation motion if misfit dislocation occurs.

Besides the beneficial intragranular precipitation of κ-carbide, detrimental intergranular precipitation of coarse κ₀-carbide via discontinuous precipitation (DP) has also been noticed in Fe-Mn-Al-C alloys (Chao et al., 1993; Hwang et al., 1993; Huang et al., 1994; Choo et al., 1997; Kimura et al., 2004). The resultant lamellae colonies, composed of κ₀-carbide and other solute-depleted phase(s), gradually wipe out the GI structure by GB migration. Though the DP product phases were identified in these works, the initiation and evolution of such a phase transition has not been investigated. From the mechanical performance perspective, it is of great importance to understand this process. Also, from a thermodynamic point of view, the phase equilibria and elemental partitioning in such a microstructure need a better understanding.

To address the questions discussed above, a quaternary model Fe-29.8Mn-7.7Al-1.3C (wt.%) steel was chosen in this work. An ageing treatment at 600 °C was utilized for the κ-carbide precipitation. The well-precipitated 24 hours-aged sample was subjected to tensile deformation in order to study the deformation mechanisms. Given that the nanometer-sized κ-carbide precipitates are dense and chemical analysis is compulsory for the phase composition and elemental partitioning study, three-dimensional (3D) APT is the optimal tool for the κ-carbide characterization, thus employed as the primary technique. Besides, synchrotron x-ray diffraction (SXRD), high-resolution scanning electron microscopy (SEM) and (scanning) transmission electron microscopy ((S)TEM) are also utilized to obtain a general overview of the microstructure or complementary information to APT results. Theoretical calculations in the framework of density functional theory (DFT) is additionally employed to understand the atomistic structure of the off-stoichiometric κ-carbide.

This thesis is organized in the following way.

Chapter 1: Introduction.
Chapter 2: Materials and methods. The details of material synthesis and thermomechanical processing is introduced in this chapter. The devices and methods utilized in this work for microstructure characterization and the theoretical approach are described in detail.

Chapter 3: Dislocation-particle interaction during plastic deformation. In this chapter, the 3D morphology and arrangement of κ-carbides in γ-matrix are firstly studied by APT and the κ/γ alloy deformed to different strains are studied via correlative TEM and APT technique, revealing the dislocation-particle interaction mechanism.

Chapter 4: Elemental partitioning and κ/γ interface structure. In this chapter, the κ/γ elemental partitioning and chemical compositions of κ/γ phases are studied by APT, the compositional accuracy of which is discussed. The κ/γ interfacial structure, in terms of chemical gradient, interfacial width and coherency, are investigated using SXRD, STEM and APT.

Chapter 5: Off-stoichiometry and site-occupancy of κ-carbide. In this chapter, attempts are made to resolve the site-occupancy of off-stoichiometric κ-carbide from both the experimental and theoretical perspective. DFT calculations successfully predict the off-stoichiometry and explains such a phenomenon.

Chapter 6: Phase equilibria in the κ/γ microstructure. In this chapter, the prolonged-aged κ/γ microstructure is characterized via SXRD, SEM and APT, revealing the co-existence of coherency equilibrium of GI κ/γ phases and thermodynamic equilibrium of GB κ₀/γ₀/α-ferrite phases. The thermal stability of GI κ-carbide and initiation & evolution mechanisms of GB κ₀/γ₀/α-ferrite phases are discussed.

Chapter 7: Summary and outlook.
Chapter 2

Materials and methods

2.1 Material processing

A high-Mn Fe-30Mn-8Al-1.3C (wt.%) steel was synthesized as a rectangular bar (12 kg, thickness of 40 mm) via melting and casting in an induction furnace under argon atmosphere. Due to evaporation of the melt and its interaction with the crucible during the production process, extra amounts of the alloying elements were added in order to achieve a target composition. According to empirical experience, a Fe-30.8Mn-8.2Al-1.34C alloy was produced aiming at the final Fe-30.0Mn-8.0Al-1.3C composition (all in wt.%). The composition of the as-cast alloy, as determined by wet chemical analysis, is listed in Table 0.1.

Table 0.1. Chemical composition of the studied alloy obtained by wet chemical analysis.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>61.2</td>
<td>29.8</td>
<td>7.74</td>
<td>1.28</td>
</tr>
<tr>
<td>at. %</td>
<td>53.9</td>
<td>26.7</td>
<td>14.12</td>
<td>5.25</td>
</tr>
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</table>

In order to remove microstructural heterogeneities inherited from the solidification process, the cast ingot was reheated to 1200 °C for 30 min and subsequently hot-rolled at 1100 °C to a thickness reduction of 75%, followed by water-quenching. The bar sample of 11×11×60 mm³, cut from the hot-rolled sheet, was then subjected to a solid-
solution (SS) treatment at 1200 °C for 2 h in a furnace under argon atmosphere and quenched to room temperature in an oil bath. At 1200 °C, the alloy is fully austenitic (Chin et al., 2010).

To induce the precipitation of κ-carbides and study their evolution and phase stabilities upon ageing, the SS-treated sample was isothermally annealed at 600 °C for various times from 24 hours up to three months and oil quenched. The aged samples are referred to ‘x-aged’, where ‘x’ indicates the ageing time.

The 24h-aged alloy with well-precipitated nanometer-scale κ-carbides was chosen as a representative case for the study on the dislocation-particle interaction during plastic deformation. Cylindrical tensile test samples with a gauge dimension of Φ 6 mm × 40 mm were prepared and interruptedly tested to true strains of ε=0.02, 0.05 and 0.15 in a Zwick ZH 100 tensile machine with an initial strain rate of 5×10⁻⁴ s⁻¹.

2.2 Microstructure characterization

Microstructure characterization of various samples was conducted using multi-scale techniques, including synchrotron X-ray diffraction (SXRD), optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atom probe tomography (APT).

2.2.1 Synchrotron X-ray diffraction

Due to the high coherency between the κ-carbide precipitates and γ-austenite matrix (Sato et al., 1988; Sato et al., 1989; Sato et al., 1990; Tsay et al., 2011), i.e. little lattice misfit, as well as potential grain boundary (GB) phases formed in small amounts (Chao et al., 1993; Hwang et al., 1993), it is difficult to identify phases and trace their evolution upon ageing by laboratory X-ray diffraction. High-resolution SXRD with a superior signal-to-background ratio was hence employed. Thin cylindrical film samples of 3 mm in diameter were machined from alloys under different ageing states and mechanically grinded by SiC abrasive papers of grits from 120 up to 2000 (European P-grade) till reaching a sample thickness of ~1 mm. The SXRD measurements were carried out by Wenwen Song from the Lehrstuhl und Institut für Eisenhüttenkunde (IEHK), Rheinisch-Westfälische Technische Hochschule Aachen (RWTH Aachen) at
Chapter 2. Materials and methods

the high-resolution powder diffraction beamline P02.1 PETRA III Bessy with a wavelength of 0.20727 Å. The detected 2D diffraction patterns were first calibrated and integrated into one-dimensional (1D) data (intensity versus 2θ) by the software Fit2D (Hammersley et al., 1994) and further analyzed by the Rietveld method using the software MAUD (Lutterotti et al., 1999).

2.2.2 Scanning electron microscopy

Samples for microscopy studies were all prepared following the standard metallographic procedure:

- firstly, grinded by SiC abrasive papers of grit from 120 up to 4000 (European P-grade) under flowing water;
- then mechanically polished using 3 μm-grained diamond suspension with lubricant;
- finally, polished by colloidal silica oxide polishing suspension (OPS) with a few drops of soap to remove mechanically induced surface deformation and ensure a clean surface.

For the sake of simplicity during sample preparation and handling, disc samples machined from gauges of tensile test samples were embedded into thermosetting bakelite with carbon filler of standard cylindrical geometry (Φ 25 mm) by a hot-mounting process under 180 °C and 25 kN (Struers PolyFast). To better reveal the multi-phase microstructure, some samples were etched with a 1% Nital solution (a mixture of nitric acid and ethanol) for 30-90 seconds. Prior to electron microscopy analysis, OM was often used to get a rough overview of the microstructure.

Further microstructural characterization was performed in two field emission gun (FEG) HR-SEMs, i.e. JEOL JSM 6500F (JEOL GmbH) and ZEISS Crossbeam XB 1540 (Carl Zeiss SMT AG), both operated at 15 kV and equipped with EDAX electron backscatter diffraction (EBSD) system. The ZEISS microscope was mainly employed for secondary electron (SE) and backscattered electron (BSE) imaging, whereas most EBSD measurements were carried out in the JEOL tool. The EBSD data was acquired and analyzed using the TSL OIM software (version 6.5-7.0).
2.2.3 Transmission electron microscopy

TEM was employed for nanometer-sized precipitate analysis. The TEM work, including phase analysis by selected area diffraction (SAD) and precipitate observation using dark-field (DF) imaging, was mainly completed by Emanuel Welsch from the Department of Microstructure Physics and Alloy Design, Max-Planck-Institut für Eisenforschung GmbH (MPIE) and reported in his PhD dissertation (Welsch, 2016). Marta Lipinska-Chwalek from the Peter Grünberg Institut (PGI), Forschungszentrum Jülich also kindly helped for Scanning-TEM (STEM) measurements on the coherency of κ-carbide precipitate with respect to the γ-matrix in a FEI Titan G2 80-200 ChemiSTEM operated at 200 kV.

High angle annular dark field (HAADF) STEM samples were prepared by focused ion beam (FIB) using two FIB/SEM dual beam devices - FEI Helios Nano-Lab 600 and FEI Helios Nano-Lab 600i. Since the κ-carbides have a {001} cube-cube orientation relationship with the γ-matrix (Choo et al., 1997), <001> is the optimal direction for an edge-on view of the κ/γ interface, which was therefore adopted as the primary analysis axis. Moreover, for a fcc-metal, dislocation slip is typically activated along <110> directions on {111} planes, whose edge-on observation direction would be <011>. Hence, thin lamellas for misfit dislocation study were prepared along {001} and {011} planes, i.e. lifted out along {001} and {011} plane traces in a {100}-oriented grain (plane normal), respectively. The aim of orientation-specific preparation is to simplify TEM operation, i.e. minimizing the tilting required to achieve target zone axes and the increase in sample thickness caused by tilting. The crystallographic directions of bulk samples for lift-out were determined by prior EBSD measurements. The FIB-prepared lamellae were first cleaned by oxygen plasma for 30 seconds before performing STEM studies.

2.2.4 Atom probe tomography

TEM/STEM is good at crystallography, phase identification, defect and strain analysis down to atomic scale whereas it is difficult to map the distribution of light elements like carbon with electron dispersive x-ray spectroscopy (EDX). TEM images are also 2D projections of a 3D microstructure, which could also cause an ambiguous
interpretation of precipitate morphologies and alignments. Alternatively, APT, a combination of ion projection microscopy and a time-of-flight (TOF) spectroscopy, has a near-atomic resolution with equal sensitivity to all elements (Gault et al., 2012b). It was thereby employed for a three-dimensional (3D) chemical mapping of the nanometer-sized \( \kappa \)-carbides embedded in the \( \gamma \)-matrix.

Needle-shaped APT specimens were all prepared by FIB using the two FIB/SEM dual beam devices as mentioned above. The usual lift-out procedure (Thompson et al., 2007) was employed for most specimens. To minimize the Ga implantation into specimens, during specimen sharpening the ion beam energy was reduced from 30 kV/\~0.26 nA to 16 kV/\~0.14 nA after the 1\textsuperscript{st} annular ion milling step and 2 kV/ \~24 pA was adopted for the final cleaning.

For GB studies, it is challenging to prepare a specimen with a GB in the analysis volume since GBs are probably inclined with respect to sample surface and not visible by FIB/SEM during annual ion milling. To increase the success rate of capturing a GB, the GB was aligned parallel to the analysis direction by a tilted lift-out and then simply kept as the center of the annular milling patterns. A pre-cutting deep into the bulk sample across GB was first made to obtain the GB inclination angle, i.e. the angle between the GB and the bulk sample’s surface. During the lift-out, the stage was then tilted by an angle complementary to the GB inclination angle, which directly made the GB perpendicular to the specimen post (parallel to the analysis direction).

During the analysis of the reaction front of GB discontinuous precipitation (DP), considering the field-of-view (FOV) of an APT specimen is much larger longitudinally than laterally, the reaction front was oriented perpendicular to the analysis direction by the method described in (Felfer et al., 2012), to enlarge the analysis volume in front of and behind the reaction front. Commercial Mo-grids (1GM 100, Pyser-SGI) were used as specimen posts in this case to realize the 90\degree rotation, simply by switching the Mo-grid holder adaptor with two perpendicular stage-mounting pins. The preparation of Mo-grids and its corresponding special home-made holder and holder adapters for FIB and APT instruments are explained in detail in (Herbig et al., 2015a).

Two local electrode atom probe (LEAP) devices were used in this work for APT measurements. The LEAP 3000X-HR (CAMECA instruments) with a reflectron has a detection efficiency of \~37\% while the LEAP 5000X-S (CAMECA instruments), a
Chapter 2. Materials and methods

straight path system, has a high detection efficiency of ~80%. Atom probe instrument equipped with a reflectron is usually expected to have improved mass resolutions (the peak width in a mass spectrum normalized by the mass of the peak) (Cerezo et al., 1998). Most measurements were performed in the LEAP 3000X-HR tool. The LEAP 5000X-S was used for a comparable study on the mass spectra and crystallography. Needle-shaped specimens were measured in voltage-pulsing mode at ~70 K with a pulse repetition of 200 kHz, a pulse fraction (PF) of 15% and a target evaporation rate (ER) of 5 ions per 1000 pulses. Choosing such a set of parameters is based on a detailed study of the influence of measurement parameters on phase compositions, which will be explained in detail in section 4.3.1.2. The collected APT data were reconstructed and analyzed using the IVAS software (version 3.6.6 - 3.6.14) by CAMECA instruments.

Figure 2.1. APT mass spectrum of κ-carbide containing austenitic alloy obtained by LEAP 3000X-HR: (a) 5-15 Da, (b) 18-26 Da, (c) 26-30 Da, (d) 33-57 Da. Ranges of mass-to-charge-state ratios without peaks are omitted. Peaks with ion overlap are marked with constituent ions.

Figure 2.1 shows a representative mass spectrum of the studied austenitic alloy with κ-carbide precipitation. Peaks at 6, 6.5, 12, 13 Da are identified as carbon
monomers. Apart from them, several peaks can be assigned to carbon molecular ions, similar to previous studies on other high-C containing alloys and carbides (Miyamoto et al., 2012; Marceau et al., 2013; Takahashi et al., 2011; Li et al., 2011; Kitaguchi et al., 2014; Thuvander et al., 2011). Peaks at 18, 18.5, 36 and 37 Da belong to carbon trimer ions. The carbon dimers $^{12}\text{C}_2^{1+}$ and $^{13}\text{C}^{12}\text{C}^{1+}$ are detected at 24 and 25 Da, respectively. The presence of 24.5 Da peak, which can be assigned to $^{13}\text{C}^{12}\text{C}_3^{2+}$, indicates the detection of carbon tetramers (Takahashi et al., 2011; Li et al., 2011; Sha et al., 1992). Hence, the peak at 24 Da does not only result from the carbon dimer $^{12}\text{C}_2^{1+}$ but also partly from $^{12}\text{C}_4^{2+}$. This overlapped peak can be decomposed by considering the peak at 24.5 Da $^{13}\text{C}^{12}\text{C}_3^{2+}$. According to the natural abundance of carbon isotopes $^{12}\text{C}$ and $^{13}\text{C}$, the contribution of $^{12}\text{C}_4^{2+}$ to peak 24 Da can be estimated by its relative abundance ratio to $^{13}\text{C}^{12}\text{C}_3^{2+}$ (Takahashi et al., 2011; Li et al., 2011; Sha et al., 1992). The decomposition via the IVAS software indicates that $^{12}\text{C}_4^{2+}$ gives a contribution of about 37% to the peak at 24 Da. The $^{12}\text{C}_2^{2+}$ peak could in principle overlap with the $^{12}\text{C}_4^{1+}$ peak at 12 Da. However, the absence of a peak belonging to $^{12}\text{C}^{12}\text{C}^{2+}$ suggests that there is a negligible fraction of $^{12}\text{C}_2^{2+}$ at the peak at 12 Da. Regarding substitutional elements, Fe$^{2+}$ is detected at 27, 28, 28.5 and 29 Da and its primary isotope can also be detected at 56 Da ($^{56}\text{Fe}^+$) and 18.7 Da ($^{56}\text{Fe}^{3+}$). Mn$^{2+}$ is detected at 27.5 Da. Peaks at 9 and 13.5 Da can be ascribed to Al$^{3+}$ and Al$^{2+}$, respectively. Here, it is also noted that according to the natural abundance of the isotopes of Fe, the peak at 27 Da cannot be completely assigned to $^{54}\text{Fe}^{2+}$. Al$^{1+}$ ions must give a contribution to it as well (Seol et al., 2012; Seol et al., 2013). The peak decomposition algorithm in IVAS indicates that 45% of this peak can be assigned to Al$^{1+}$. The measured total impurity concentration Si (14 Da) and Cr (26 Da) is less than 0.1 at.%. The material is a rather clean quaternary Fe-Mn-Al-C model alloy.

### 2.2.5 Correlative transmission electron microscopy and atom probe tomography

The particle-matrix interface and deformed microstructure of the 24h-aged alloy were further studied by the correlative TEM/STEM and APT approach (Herbig et al., 2015a). Although APT is capable of mapping a 3D microstructure with sub-nm resolution, due to different evaporation fields of $\kappa$-carbides and $\gamma$-austenite, local
magnification could occur and complicate the 3D reconstruction of the $\kappa/\gamma$ interface (Gault et al., 2012b). Also, it is often difficult to resolve crystal defects, such as dislocations and slip bands, only by APT due to the lack of the crystallographic information. Combining TEM/STEM and APT enables a correlative and complementary understanding on the interface structure and particle-dislocation interaction.

Electro-polished Mo-grids were used as specimen posts for the correlative study, which could be easily transferred between FIB, TEM and APT with a grid holder (Herbig et al., 2015a). Similar to STEM lamella analysis, to optimize the measurement conditions, needle-shaped specimens are preferred to be orientation-specific. Due to the $\{001\}$ cube-cube $\kappa/\gamma$ orientation relationship, the specimens for $\kappa/\gamma$ interface study were prepared orthogonally along $<001>$-directions and put into a double-tilting TEM holder in such a way that the $(\alpha, \beta)$ tilting axes and electron beam were all parallel to the $<001>$ direction. Thereby the electron beam would directly observe edge-on the $\{001\}$ $\kappa/\gamma$ interface. Also, there would be $\kappa/\gamma$ interfaces perpendicular to the APT analysis direction, minimizing the local magnification effect during field evaporation and utilizing the higher resolution along the in-depth direction (Gault et al., 2012b). Owing to the dense distribution of the $\kappa$-carbides, there are often enough precipitates for interface analysis within the FOV of STEM and APT, i.e. $\sim 80$ nm from apex, beyond which the specimen thickness would be too large for STEM analysis.

In contrast, the correlative study on slip bands is challenging in terms of specimen preparation. Due to the limited FOV of APT and common premature failure of deformed APT specimen, the slip bands have to be within the top $\sim 100$ nm from the needle’s apex in order to be detected in APT before a specimen facture. This is challenging since there is no image contrast of slip bands at all during annular FIB milling. For heavily deformed samples, e.g. $\varepsilon=0.15$, it is possible to realize that, owing to the high density of slip bands with an average spacing of $\sim 250$ nm, as well as the activation of multiple groups of slip bands (Welsch, 2016). However, the slip bands in slightly deformed samples ($\varepsilon<0.05$) are much sparser, in the order of 1-2 $\mu$m (Welsch, 2016). Instead of blind lift-out targeting slip bands only by chance, site-specific specimen preparation is preferred in this case. Also, to minimize electron beam
exposure during the zone axes search process affecting the specimen survival rate in subsequent APT measurements, an orientation-specific specimen is desirable.

The optimal direction for observing particle shearing along typical \{111\} fcc slip planes is \(<011>\). The strategies employed for such a specimen preparation are as follows.

- Prior EBSD and electron channeling contrast imaging (ECCI) (Zaefferer et al., 2014) were utilized to search for one set of \{011\} dense sharp slip lines in a \{011\}-oriented grain (done by Emanuel Welsch). Slip lines parallel to the longest \{011\} plane trace were preferred since they are less inclined from the sample surface, i.e. with a higher probability of being captured in the analysis volume.
- The relative distance and angle between the slip lines and microstructural features such as GB and inclusions, which could be visible by FIB/SEM, were measured.
- The target set of slip lines was located by FIB/SEM according to its relative position with respect to the microstructural features.
- The lift-out was carried out in such a way that the long-axis of the wedge was perpendicular to the slip lines.
- Specimens prepared in this way would directly fit the \(<011>\) TEM zone axis (ZA) and should include several inclined slip bands in the top volume. The subsequent TEM characterization could manifest the distance between slip bands and needle apex and a further controlled FIB re-sharpening could bring the target slip band to the FOV of APT measurement.

In order to minimize beam contamination and surface oxidation, all the specimens were freshly prepared just before loading into TEM double-tilting holders. Christian Liebscher from Department of Structure and Nano-/ Micromechanics of Materials, MPIE and Marta Lipinska-Chwalek performed STEM measurements on \(\kappa/\gamma\) interface in a probe-corrected FEI Titan 80-300 S/TEM microscopy operated at an accelerating voltage of 300 kV. The TEM observation on deformed specimens was done by Emanuel Welsch in a Philips CM20 device. After the TEM work, the specimens were directly transferred into the FIB for re-sharpening when necessary and a re-cleaning at 2 kV for a few seconds to remove the contamination and oxidized layer before APT measurements.
2.3 Density functional theory study

To understand the site-occupancy of ordered κ-carbide and the influence of elastic strain on its stoichiometry, ab-initio work was employed in this work. Poulumi Dey and Tilmann Hickel from Department of computational materials design, MPIE performed the calculations using density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP) (Kresse et al., 1993). Projector augmented wave (PAW) potentials were used to describe the electron-ion interaction (Blöchl, 1994). The generalized-gradient approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE) (Perdew et al., 1996) was employed. The single-electron wave functions were expanded using plane waves up to an energy cut-off of 500 eV. The Methfessel-Paxton method (Methfessel et al., 1989) was used for the Fermi surface smearing with a 6x6x6 Monkhorst-Pack grid for 2x2x2 atomic supercells of both stoichiometric and off-stoichiometric κ-carbides. The energies converged to a precision of 1 meV/atom. Structural relaxations were performed until the forces on each atom were below 0.01 eV/Å. Cell shape and atomic positions were fully relaxed in all calculations, unless specified otherwise.

The 2x2x2 supercell of stoichiometric (Fe,Mn)3AlC κ-carbide is composed of 8 unit cells in the L’12 structure with 5 sites/unit cell and occupied by 40 atoms ((Fe16Mn8)Al8C8). Here, Fe/Mn are situated at face-centered sites of each unit cell, Al at corner sites and C atoms occupy the body-centered octahedral sites (Figure 2.2(a)). An Fe to Mn ratio of 2:1 was employed based on the APT results. DFT studies reveal that configurational entropy is more favorable than chemical ordering in the face-centered Fe/Mn sub-lattice of κ-carbide above ~75 K (Dey et al., 2016). The Fe/Mn chemical disorder was taken into account by a special quasi-random structure (SQS) generation scheme (Zunger et al., 1990) for the 2x2x2 supercell. It is important to note that all calculations were performed for ferromagnetic (FM) κ-carbide since the (Mn) anti-site formation energies computed for FM and paramagnetic states differed only by a small amount (~0.05 eV). Therefore, the consideration of paramagnetism, which is computationally much more demanding, does not qualitatively alter the results on structural properties and estimated point defect concentrations in κ-carbide (Dey et al., 2016).
Figure 2.2. Schematic visualization of the supercell of (a) stoichiometric L’1₂ κ-carbide, (Fe₁₆Mn₈)Al₈C₈, and (b) off-stoichiometric κ-carbide with a Mn anti-site at the Al sub-lattice and C vacancies, (Fe₁₆Mn₈)(Mn₁Al₇)(C₅Vac₃), with chemical disorder in the Fe/Mn sub-lattice with an Fe:Mn ratio of 2:1. Fe, Mn, Al and C atoms are shown by red, orange, green and purple balls, respectively. The theoretical calculations were done by Poulumi Dey and Tilmann Hickel.
Chapter 3

Dislocation-particle interaction during plastic deformation

3.1 Introduction

A common characteristic of alloys showing excellent strength and ductility is a pronounced strain hardening capability, which continuously increases the strength and delays local necking during deformation. Transformation induced plasticity (TRIP) and twinning induced plasticity (TWIP) steels are typical examples for alloys showing high strain hardening capabilities (Herrera et al., 2011; Gutierrez-Urrutia et al., 2011), where martensitic transformation and formation of deformation twins are the respective dominant deformation and strain hardening mechanisms. The active deformation mechanisms are closely related to the stacking fault energy (SFE). Generally, as the SFE increases, the dominant deformation mechanism changes from TRIP to TWIP and from TWIP to dislocation gliding (Allain et al., 2004; Pierce et al., 2014).

Gutierrez-Urrutia et al. attributed the excellent strain hardening capacity of solid solution austenitic Fe-Mn-Al-C alloys containing <5 wt.% Al to multiple stages of deformation during which sequential dislocation cell structures and, at higher loads, twin substructures are gradually formed (Gutierrez-Urrutia et al., 2012). For alloys with >5 wt.% Al, intragranular precipitation of nanometer-sized κ-carbides leads to a
substantial increase in yield strength without a significant loss in ductility. Planar dislocation substructures were observed in deformed κ-carbide containing austenitic Fe-M-Al-C alloys. The occurrence of planar dislocation substructures in these alloys, which have high SFE values ranging from 80 to 110 mJ/m² (Park et al., 2013), was ascribed to shearing of ordered κ-carbides by dislocations and a mechanism referred to as “glide plane softening” (Gerold et al., 1989). According to this mechanism, the local order is destroyed by a leading dislocation shearing the ordered particle and thus facilitating the glide of consecutive trailing dislocations. For high strain levels, the mechanisms of shear-band-induced plasticity (SIP) (Frommeyer et al., 2006) and microband-induced plasticity (MBIP) (Yoo et al., 2009; Park et al., 2013) have been suggested, referring to homogeneous shear deformation and bands of very high dislocation density, respectively.

However, the interaction between dislocations and κ-carbide precipitates in age-hardened austenitic Fe-Mn-Al-C steels is still not well understood. Debates still exist over the dominant co-deformation mechanism during plastic deformation, i.e. the competition between dislocation looping and precipitate shearing. Choi et al. claimed that κ-carbide precipitates are sheared by slip bands since misalignment of particle stacks was observed along a specific direction by TEM DF imaging (Choi et al., 2010). However, Gutierrez-Urrutia et al. suggested that Orowan bypassing of stacks of κ-carbides is predominant, followed by expansion of dislocation loops by cross-slip while shearing of κ-carbides occurs only rarely (Gutierrez-Urrutia et al., 2014). Convincing observations are still missing to illustrate the dislocation interaction with κ-carbide precipitates. The answer to this question is the prerequisite to understand the nature of the strengthening by κ-carbide precipitates and thereby accurately predict the yield strengths of the precipitation-hardened κ/γ alloys.

This chapter aims at providing a comprehensive understanding of the interaction of dislocations with κ-carbide precipitates, as well as the associated strengthening and deformation mechanisms. First of all, the 3D morphology and arrangement of κ-carbide precipitates in the non-deformed γ-matrix are unveiled by APT analysis. Then correlative TEM-APT analyses are employed to systematically characterize the deformed κ/γ microstructure under various strain states. Crystallographic and chemical mapping are correlated to each other, demonstrating the dislocation interaction with κ-
carbide precipitates. Finally, the strengthening effect of $\kappa$-carbide precipitates, how they are affected by plastic deformation and its reverse effects on deformation are discussed. The 24h-aged sample is chosen for this work as a state, for which precipitation is pronounced and is similar to the previously reported, typical $\kappa/\gamma$ microstructure (Choo et al., 1997; Choi et al., 2010; Sato et al., 1988-1990; Tjong et al., 1990).

3.2 Results

3.2.1 Morphology and arrangement of $\kappa$-carbides

Precipitation of coherent $\kappa$-carbides in the $\gamma$-matrix introduces an elastic stress field due to the lattice mismatch between precipitates and matrix (Choo et al., 1997). The shape and arrangement of $\kappa$-precipitates are determined by the minimization of the sum of the elastic energy and the interfacial energy, arising from the $\kappa/\gamma$ phase boundaries (Doi et al., 1996).

Figure 3.1(a) shows the ordered L’12-type $\kappa$-carbide precipitates within the austenitic matrix observed by APT. The $\kappa$-carbides in the reconstructed 3D atom maps are visualized by 9 at.% C iso-concentration surfaces. APT reveals that cuboidal and plate-like $\kappa$-carbide particles are arranged in 3D in the form of stacks along three orthogonal directions which are identified by TEM observations as the elastically soft <001> crystallographic directions (Gutierrez-Urrutia et al., 2012; Gutierrez-Urrutia et al., 2014; Choo et al., 1997). The cuboidal particles have a size of 15-20 nm. The largest cross-sections of plate-like particles perpendicular to the particle stack directions are often square-shaped with an edge length of 15-20 nm, while the thickness of the plates is on the order of 5-10 nm. The spacing between two parallel stacks is on the order of 10-40 nm and will be referred to as broad $\gamma$-channels. The spacing between individual precipitates within a stack is about 2-5 nm and will be referred to as narrow $\gamma$-channels.

Figure 3.1(b) shows a schematic sketch of $\kappa$-carbide precipitates’ 3D morphology and arrangement based on APT observations. Two possible corresponding 2D transect-projections along <001> zone axes, which are often employed for imaging $\kappa$-carbides with TEM, are shown in Figure 3.1(c). Particles that might be assumed to have a cuboidal morphology based on their square-like appearance in the TEM DF images
(Gutierrez-Urrutia et al., 2012; Gutierrez-Urrutia et al., 2014; Choo et al., 1997) have very often a much smaller size in the third dimension according to APT. Thus, they show plate-like morphology (see the particles outlined in red). At the intersection between two stacks of precipitates a preference for a cuboidal morphology is often observed, e.g. the particles outlined in green. Long rectangular particles observed in TEM micrographs (particles highlighted in yellow outlines) are found to be rectangular parallelepipeds.

Figure 3.1. Morphology and arrangement of κ-carbide precipitates in 3D space (APT) and 2D observation (e.g. TEM): (a) three representative reconstructed 3D APT maps of C (purple), Al (green) and Mn (yellow) atoms. The κ-carbide precipitates are visualized with a 9 at.% C iso-concentration surface. (b) A schematic illustration of the 3D morphology and arrangement of κ-carbide precipitates based on APT observations. (c) 2D projections of the κ/γ microstructure along <001> directions highlighted in (b), simulating the TEM observation.
3.2.2 Dislocation/κ-carbide interaction

![Figure 3.2](image)

**Figure 3.2.** TEM dark-field (DF) images of deformed microstructures at different true strains of (a) $\varepsilon=0.05$ and (b) $\varepsilon=0.15$ utilizing the superlattice diffraction spot of κ-carbides. Two different zone axes (ZA) (a) [011] and (b) [001] were employed to show the shearing of κ-carbides and sheared κ-carbides, respectively. The TEM measurements were carried out by Emanuel Welsch.

The deformed microstructure of the 24h-aged samples are shown in Figure 3.2, which displays TEM micrographs obtained from APT specimens. The TEM observations were obtained by Emanuel Welsch. At a low strain level of 0.05, clear shearing of κ-carbide stacks is observed along the [011] ZA as indicated by arrows in Figure 3.2(a). The κ-carbide precipitates have a (001) cube-cube orientation relationship with the γ-matrix. Along the [011] ZA, i.e. looking edge-on the (11̅1) plane, the nanometer-sized κ-carbides with a 2-5 nm inter-spacing in the narrow γ-channels
overlap with each other in the 2D TEM projection. Instead of individual precipitates, a stack of precipitates is observed. The misalignments of several stacks along a single slip line is captured (Figure 3.2(a)), clearly revealing the shearing of \( \kappa \)-carbides by slip. As the true strain increases to 0.15, more slip systems are activated and intensive slip bands appear (highlighted by arrows in Figure 3.2(b)), which, along the [001] ZA, are manifested by dense precipitate fragments concentrating on certain directions. In comparison to the relatively complete precipitates at the apex of the needle-shaped specimen, the \( \kappa \)-carbide precipitates within these slip bands are fragmented into small debris. At the intersection of slip bands, the superlattice phase contrast is almost completely lost, indicating either the loss of ordering or even dissolution of precipitates.

It is worth noting that from low-strain to high-strain states, slip bands are observed throughout the specimens, not only in these two representative ones shown in the Figure 3.2, but also in another approx. 10 specimens. Particle shearing is a general phenomenon, observed in the deformed \( \kappa/\gamma \) microstructure, and therefore believed to be the prevalent deformation mechanism. The previous debates in the literature on either shearing or Orowan looping is probably due to the lack of clear observation of such deformed microstructures. The high density of particles and specific crystallographic orientation add difficulties onto that. Here, these difficulties are circumvented by optimized specimen preparation, adopting thin needle-shaped specimens specifically oriented with the help of a prior EBSD measurement.

The deformed microstructure with 3D chemical mapping, accomplished by correlative TEM -APT on a 0.05-strained specimen, is presented in Figure 3.3. In the TEM micrograph (Figure 3.3(a)), two originally cuboidal or plate-like \( \kappa \)-carbide precipitates are clearly split into two parts - one major part and another smaller one at the corner, as highlighted by blue arrows. The slight mismatch between these two parts, particularly for the right plate-like \( \kappa \)-carbide, indicates that these two precipitates are sheared by dislocation slip. The slip directions of the two precipitates are parallel to each other. Since the needle-shaped specimen is prepared orthogonally along the \(<001>\) direction, the slip direction can be characterized as \( \sim 45^\circ \) from [001] and [010], i.e. close to [011]. Besides, as highlighted by yellow arrows, there are also some small fragments of the ordered precipitates, which probably have been heavily fragmented by deformation.
Chapter 3. Dislocation-particle interaction during plastic deformation

Figure 3.3. Correlative TEM and APT analysis of a deformed microstructure at a true strain of \( \varepsilon = 0.15 \): (a) TEM dark-field (DF) micrograph along [001] zone axis with the blue arrows highlighting the shearing of \( \kappa \)-carbides and yellow ones indicating the fragments of \( \kappa \)-carbides; (b) an overlay of reconstructed APT analysis volume with purple \( \kappa \)-carbides visualized by carbon iso-concentration surface at a threshold value of 9.0 at.% on top of the TEM DF micrograph of the same specimen taken before APT measurement; (c-e) 3D elemental atom maps of the reconstructed APT volume with different elemental iso-concentration surfaces of (c) \( \geq 9.0 \) at.%, (d) \( \geq 7.5 \) at.% and (e) \( \geq 14.5 \) at.%, showing the dissolution of \( \kappa \)-carbides. The TEM measurements were carried out by Emanuel Welsch.

The same specimen was subsequently analyzed by APT. Figure 3.3(b) shows an overlay of the reconstructed APT analysis volume on top of the DF-TEM micrograph. The latter utilizes the superlattice diffraction contrast to reveal the ordered \( \kappa \)-carbide precipitates whereas the former employs carbon iso-concentration surfaces at a threshold value of 9.0 at.% to show the carbon-enriched \( \kappa \)-carbides. The size, shape and position of \( \kappa \)-carbide precipitates in the reconstructed APT volume fit well with the DF-TEM image, illustrating that the employed APT reconstruction algorithm, tip profile
reconstruction, could perform properly for this \( \kappa/\gamma \) alloy. Despite the well reconstructed APT volume, particle splitting by dislocation slip is not clearly observed, conversely to what was highlighted by blue arrows in the DF-TEM image (Figure 3.3(a)). This is probably due to shearing of the precipitate by a single dislocation glide rather than dense slip bands of high dislocation density, as captured in the TEM micrograph. The signal is likely smoothed out by voxelization and delocalization of APT data. Instead of two split parts of one precipitate, only one complete \( \kappa \)-carbide is visualized by carbon iso-concentration surface in the APT volume. In addition to large \( \kappa \)-carbides both observed in TEM and APT, there are also small, irregularly shaped fragments with no obvious visual match between TEM and APT measurements: the region of which is marked by a yellow dash circle in Figure 3.3(b). Some fragments observed in the DF-TEM image are not found in APT analysis via 9.0 at.% C iso-concentration surface, and vice versa. This is probably due to the limited FOV of APT so that the outer shell of the specimen observed in TEM are not registered at the APT detector (Herbig et al., 2015a). Or the \( \kappa \)-carbides at this region fragmented by deformation preserve local ordering and solute enrichment to some extent, but not necessarily both at the same time.

To better reveal the 3D solute distribution after deformation, further APT elemental maps and iso-concentration surfaces of different elements at varying threshold values are created (Figure 3.3(c-e)). As highlighted by a black dashed circle in Figure 3.3(c), the elements are not homogeneously distributed at this region. A lower threshold value for the C iso-concentration surface of 7.5 at.% unveils that there are not only small C-enriched fragments but also C segregation along certain directions, as indicated by black arrows in Figure 3.3(d). Such a linear solute enrichment is also correspondingly found for Al at the same positions (Figure 3.3(e)), but not for Mn (not shown here). Completely differing from the common particle morphology (Figure 3.1), these line features imply that the \( \kappa \)-carbides in this region have been fragmented and dissolved during deformation. The dislocation slip might destroy the \( \kappa \)-carbides and drag the solutes along with its movement. Considering the affinity between segregated solutes and crystalline defects (Kirchheim et al., 2007), it is highly possible that the solute segregation zones are dislocation lines. The reason why such an enrichment only takes place for Al and C, not Mn, is that the \( \kappa \)-carbides are enriched with Al and C, not Mn (details for \( \kappa/\gamma \) elemental partitioning are referred to Chapter 4.2.1).
Owing to the <001>-oriented specimen, as well as the (001) cube-cube orientation relationship between κ-carbide precipitates and γ-matrix, the <001> directions can be easily figured out for the reconstructed 3D APT analysis volume (Figure 3.4). Therefore, a crystallographic analysis can be performed on the linear solute segregation zones, highlighted by black arrows in Figure 3.3(d).

**Figure 3.4.** Crystallographic analysis of three solute-segregated line features in a deformed κ/γ alloy at a true strain of 0.15 as highlighted by black arrows in Figure 3.3(d) based on the orientation of the needle-shaped specimen.
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All three line segregation zones (Figure 3.4(a), (b) and (c)) are well associated to \{111\} planes, which are the typical slip plane for fcc metals. Along with the aforementioned \langle110\rangle slip direction (Figure 3.3(a)), the activated slip system can be identified as \{111\}<110>, that is the typical slip system for fcc metals. Among these three linear segregation zones, one line is found to be perpendicular to the \langle110\rangle slip direction (Figure 3.4(a)) and the other two are inclined to that (Figure 3.4(b)(c)), which implies that probably the former is an edge dislocation while the latter have a mixed character.

3.3 Discussion

3.3.1 Particle shearing and ordering strengthening

The microstructure of the 24h-aged alloy deformed to different strain states have been studied by correlative TEM and APT. It is revealed that \{111\}<110> dislocation slip and shearing of κ-carbide precipitates occurs during plastic deformation rather than Orowan looping.

The ordered κ-carbide with a L’1₂-type perovskite structure deform differently from the disordered fcc γ-matrix. For dislocation slip on a crystallographic plane, a shear stress, the so-called Peierls stress, has to be exerted on the slip plane, which depends exponentially on the ratio of lattice spacing \(d\) to the Burgers vector \(b\) and thereby ought to be smallest for a slip along the close-packed direction on the close-packed plane (Gottstein, 2004). In disordered fcc γ, this corresponds to the \(a/2<1\bar{1}0>{111}\) slip system (\(a\) is the lattice parameter). However, in chemically ordered L’1₂ κ-carbides the preferred slip system could be \(a<100>{001}\) or \(a<1\bar{1}0>{111}\), since the shortest lattice vectors \(a<100>\) do not lie in the close-packed \{111\} planes. Experimentally, the observed activated slip system is the latter one. Given that the Burgers vector of a perfect dislocation in the γ-matrix (\(a/2<1\bar{1}0>\)) is only half of the closing vector to restore the ordered κ-carbide to its perfect lattice, it cannot enter the κ-carbide unless a planar defect is formed (Ardell, 1985; Reed, 2008). A pair of superpartial \(a/2<1\bar{1}0>{111}\) dislocations must travel together through the κ-carbides, forming the so-called superdislocation. The resultant planar fault in-between two
superpartials is known as an anti-phase boundary (APB) and the APB energy $\gamma_{APB}$ represents the associated energy barrier for the occurrence of particle cutting.

Depending on $\gamma_{APB}$, volume fraction $V_f$ and the mean particle radius $r$ (assumed spherical for simplicity) of the $\kappa$-carbides, the pair of superpartial dislocations could reside in the same $\kappa$-carbides or there could be faulted particles between the leading and trailing superpartials, i.e. ‘strongly coupled’ or ‘weakly coupled’ superpartials, respectively (Reed, 2008). Their anticipated order strengthening contribution are different considering the elastic stress between the superpartials. In the SS-treated alloy, free of precipitates, the spacing between the superpartials intersecting the short-range ordering (SRO) was found to be ~20 nm (Welsch et al., 2016). Since the APB energy is usually relatively high and should be much higher in the 24h-aged alloy with $\kappa$-carbide precipitates of long-range ordering (LRO) than that in SS-treated alloy, the superpartials would experience more resistance in the $\kappa$-carbide containing alloy. The superpartial spacing should be less than ~20 nm and comparable to the particle size. Hence, the superdislocation in this case is more inclined to strong-coupling, whose ordering strengthening contribution is

$$
\Delta\sigma_{ordering} = \sqrt{\frac{3}{2}} M \left(\frac{G b}{r}\right) V_f^\frac{1}{2} \frac{w}{\pi^2} \left(\frac{2\pi \gamma_{APB} r}{w G b^2} - 1\right)^\frac{1}{2},
$$

(3.1)

where $M$ is the Taylor factor of 3.06 to convert the resolved shear strength for dislocation motion into an equivalent uniaxial yield strength of a polycrystal (Stoller et al., 2000), $G$ represents the shear modulus, $b$ denotes the Burgers vector and $w$ is a dimensionless constant of the order of unity. No $\gamma_{APB}$ data is reported specifically for $\kappa$-carbides, but similarities with superalloys with a L1$_2$ ordered structure and the activated $\{111\}<1\bar{1}0>$ slip system (Reed, 2008)) allow us to use values reported for those alloys ($\gamma_{APB} \sim 0.1$ J/m$^2$) as a rough estimate. Taking $G=70$ GPa, $b=0.26$ nm (Welsch et al., 2016), $r=10$ nm (half of the particle size ~ 20nm) and $V_f \sim 0.21$ (experimental results refer to section 4.2), $\Delta\sigma_{ordering}$ is estimated to be 321 MPa. This is much lower and more reasonable than what is estimated for Orowan stress

$$
\Delta\sigma_{Orowan} \sim M \frac{G b \sqrt{V_f}}{r} = 2.55 \text{ GPa} \quad \text{(Gottstein, 2004)},
$$

supporting that particle cutting is the preferred mechanism rather than Orowan bypassing.

Experimentally, the ageing-introduced $\kappa$-carbides was found to significantly increase the yielding strength of the alloy by ~480 MPa (Welsch, 2016). Given that the
two samples, SS-treated and 24h-aged, have similar grain sizes and the solute concentration is lower in the aged alloy as a result of precipitation, the order strengthening contribution, estimated as 321 MPa for κ-carbide shearing, is relatively low in comparison to the strength increase of ~480 MPa. One reason could be that there are additional contributions arising from the elastic strain field due to coherency, shear modulus mismatch between κ-carbide precipitates and γ-matrix, and creation of additional matrix-precipitate interface during particle shearing (Ardell, 1985). On the other hand, a few assumptions are made for the estimation of order strengthening. Firstly, for the sake of simplicity, the κ-carbides are assumed to be homogeneously distributed. In fact, as shown in Figure 3.1, they form particle stacks with different widths for broad and narrow γ-channels. Locally, along the particle stacks, the volume fraction is much higher than the averaged ~0.21. Secondly, there is actually no reported data of $\gamma_{APB}$ for κ-carbides. ~0.1 J/m$^2$ is only based on the γ’ precipitates in superalloys with a similar crystal structure and a similar slip system, which may lead to an inaccurately estimated strength increase.

3.3.2 Particle dissolution and solute segregation

Despite having a high SFE, the 24h-aged alloy exhibits pronounced planar slip during deformation (Welsch, 2016). It has been ascribed to the so-called glide plane softening phenomenon, which states that the cutting of ordered precipitates on a single slip plane by superdislocations results in a continuous decrease of obstacle strength on this individual plane and only minor strength needs to be overcome by the following dislocation pairs until all particles of the activated slip plane are completely cut (Gerold et al., 1989). Thereby, dislocation motion and particle shearing is restricted to the slip plane, giving rise to the planar slip with isolated active slip planes. As strain increases, multiple slip bands are activated and the spacing between slip bands is continuously reduced (Welsch, 2016). The refinement of planar slip bands progressively destroys the κ-carbides (Figure 3.2-3.3). Inside the slip bands, particularly at their intersections, κ-carbides are found fragmented or even dissolved.

Similar dissolution of shearable particles under plastic deformation has been reported in severe plastic deformed metals, e.g. dissolution of metastable fine precipitates in equal-channel angular pressed Al alloys (Murayama et al., 2001;
Chapter 3. Dislocation-particle interaction during plastic deformation

Gutierrez-Urrutia *et al.*, 2005), and in fatigued metals, e.g. precipitate dissolution within the persistent slip bands or shear bands (Vogel *et al.*, 1982; Vinogradov *et al.*, 2002). In those cases, the intensive strain, either applied by severe deformation or accumulated by cycling, cut the particles into smaller nanoscale fragments, leading to the instability of the phase because of high surface energy and their eventual dissolution. Such a particle fragmentation is also observed in the present κ/γ alloy by massive slip bands in high-strain states (Figure 3.2-3.3), which promotes the dissolution of κ-carbides.

It is known, on the other hand, that the dislocation interaction with solute atoms of precipitates might also cause the dissolution or decomposition of particles. One well-studied case is the cementite decomposition in heavily drawn pearlitic steels (Li *et al.*, 2011). During the motion of dislocations, looping around the interfaces in that case, carbon atoms are dragged out of the cementite and segregate to dislocation structures. As for shearable particles, the penetration of dislocations through particles might lead to the transfer of interstitial atoms from the particles to the matrix due to drifting of atoms under the stress field of dislocations (Sagaradze *et al.*, 1997). In the present case, the observed solute-segregated line features are likely dislocations, the crystallographic orientations of which follows the typical fcc slip system (Figure 3.4). A compositional analysis of such a segregation is illustrated in Figure 3.5 using proxigram (proximity histogram, Hellman *et al.*, 2000) and 1D concentration profile. Figure 3.5(b) shows the proxigram generated around the line segregations highlighted in purple in Figure 3.5 (a) by a 7.5 at.% C iso-concentration surface. The 1D concentration profiles of cylindrical regions of interest (ROIs) placed perpendicular to dislocation lines, as shown in Figure 3.5(a), are plotted in Figure 3.5(c-d). Both methods clearly reveal the enrichment of C and Al to the dislocation lines, the enrichment factor of which are about 2.8 and 1.2 in comparison to the neighborhood compositions, respectively. This result suggests that upon particle cutting, indeed the solutes of the κ-carbide precipitates are dragged along with the moving dislocations, which facilitates precipitate fragmentation and dissolution. Regarding the composition, no obvious difference is observed between the two solute-segregated dislocation lines in Figure 3.5(c) and Figure 3.5(d), which are probably of edge and mixed characters according to the analysis in Figure 3.4(a) and Figure 3.4(b), respectively.
Figure 3.5. Concentration analysis on solute segregation to dislocations: (b) Proxigram of the magenta-highlighted interface generated by a carbon iso-concentration surface of 7.5 at.% in (a). (c)(d) Two individual 1D concentration profiles of cylindrical regions of interest (ROIs) perpendicular to two dislocation lines as highlighted in (a).
Chapter 4

Elemental partitioning and $\kappa/\gamma$ interface structure

4.1 Introduction

The precipitation of nanometer-sized $\kappa$-carbides in austenitic Fe-Mn-Al-C alloys significantly strengthens these grades while maintaining substantial formability. This is realized by a dramatic increase in yield strength and an excellent strain hardening ability comparable to that of $\kappa$-carbide-free alloys (Welsch, 2016). Since particle-shearing is found to be the dominating deformation mechanism, the significant strengthening effect results from ordering strengthening, as well as contributions of coherency, shear modulus mismatch and creation of additional matrix-precipitate interface (section 3.3.1). In order to better understand the strengthening and strain hardening behavior of the studied alloy, it is essential to analyze the internal $\kappa/\gamma$ microstructure, especially the elemental partitioning and the interfaces between the precipitates and the matrix.

The partitioning of solutes is decisive for the lattice misfit between the $\kappa$-carbides and the $\gamma$-matrix. In a coherent system, elastic strain energy arises from this mismatch and the precipitates experience an elastic strain field. The critical influence of the elastic strain field on resultant morphology and arrangement of coherent precipitates has been noticed in many alloy systems (Doi, 1996; Lee, 1996). As the lattice misfit increases,
the shape of the particles may evolve from sphere to cube and plate, or even needle. The corresponding elastic anisotropy can lead to a directional alignment of particles instead of a random distribution. In this chapter, APT is employed for the chemical mapping of the $\kappa/\gamma$ microstructure at the atomic scale, illustrating the elemental partitioning between phases and measuring the chemical composition of $\kappa$-carbides. The initial state before ageing (SS-treated) and the 24h-aged alloy with well-developed $\kappa$-carbides are investigated. To ensure the compositional accuracy of APT measurements, the influence of measurement parameters on apparent compositions are systematically studied and the measurement conditions are optimized.

Commonly, $\kappa$-carbides are regarded as coherent precipitates according to their nanometer-scale sizes observed by DF-TEM imaging and small lattice parameter difference with that of the $\gamma$-matrix based on XRD measurements (Sato et al., 1988; Choo et al., 1997; Bartlett et al., 2014). To my knowledge, there is no direct atomic-scale observation of the $\kappa/\gamma$ interface with respect to compositional and structural transitions. Due to the small lattice misfit between the $\kappa$-carbides and $\gamma$-matrix, the $\kappa$-peaks often appear close to the $\gamma$-peaks as small shoulders. Thus, an accurate determination of the lattice misfit between $\kappa$ and $\gamma$ is challenging. Moreover, to understand the non-uniform anisotropic $\kappa/\gamma$ microstructure (section 3.2.1), the interfaces between cuboidal/plate-like $\kappa$-carbides and broad/narrow $\gamma$-channels have to be individually studied. Possibly existing local incoherency cannot be detected via XRD. The existence of misfit dislocation at some point, however, could interact with mobile dislocations and affect their movement. Hence, another primary aim of this chapter is to gain a thorough view of the $\kappa/\gamma$ interfaces at the atomic scale. SXRD is used for an accurate evaluation of lattice misfit; APT and HAADF-STEM are exploited to study the interface structure.

### 4.2 Results

#### 4.2.1 $\kappa/\gamma$ elemental partitioning and phase compositions

The reconstructed 3D elemental maps for the SS-treated specimens are shown in Figure 4.1(a). All elements, i.e. Fe, Mn, Al and C, are homogeneously distributed
throughout the specimen without any sign of clustering or phase separation. For a better assessment of the homogeneity of the elemental distributions, nearest neighbor (NN) distributions (Gault et al., 2012b) are evaluated (Figure 4.1(b)), where the experimentally measured distributions are compared against artificially randomized, i.e. correlation-free datasets. For the first as well as higher order NN distribution analyses, the experimental frequency histograms show a very good match with ideal random distributions for all detected elements. No elemental partitioning is detected for the SS-treated state. However, in the same SS-treated alloy, Welsch observed weak superlattice diffraction spots in TEM and finely dispersed ordered regions in a size of <2 nm (Welsch, 2016). Apparently, local ordering occurred during quenching without chemical partitioning. To differentiate these ordered regions from κ-carbides with a certain chemical composition, they were referred to as ‘long-range-ordered clusters’.

The elemental compositions of the supersaturated SS-treated specimens $c_n$ as determined by APT are listed in Table 4.1.

**Figure 4.1.** APT analysis on the SS-treated specimen: (a) reconstructed 3D elemental maps (b) nearest neighbor (NN) distribution analysis.
Chapter 4. Elemental partitioning and κ/γ interface structure

Table 4.1. Chemical compositions (at.%) of supersaturated single austenitic SS-treated specimens $c_n$, and κ-carbides $c_\kappa$ and γ-matrix $c_\gamma$ in the 24h-aged specimens determined by APT. Error bars indicate compositional fluctuations between different APT measurements, where the statistical errors are negligible.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_n$</td>
<td>52.6±0.3</td>
<td>24.5±0.5</td>
<td>17.0±0.2</td>
<td>5.9±0.3</td>
</tr>
<tr>
<td>$c_\kappa$</td>
<td>43.4±0.3</td>
<td>23.7±0.3</td>
<td>19.8±0.2</td>
<td>13.2±0.4</td>
</tr>
<tr>
<td>$c_\gamma$</td>
<td>53.8±0.2</td>
<td>25.8±0.3</td>
<td>16.1±0.1</td>
<td>4.3±0.2</td>
</tr>
</tbody>
</table>

After isothermal ageing at 600°C for 24 hours, κ-carbide precipitates are clearly observed both in TEM as ordered particles (Welsch, 2016) and in APT as a C-enriched phase (Figure 4.2(a), delineated by a C iso-concentration surface at a threshold value of 9.0 at.%). Figure 4.2(b) shows a 1D concentration profile along a particle stack through a cylindrical ROI, which is highlighted in green in Figure 4.2(a). Al and C atoms clearly partition to the κ-carbides, whereas Mn exhibits only slight partitioning to γ. In order to closely compare the elemental partitioning of smaller plate-like and larger cuboidal κ-carbides with respect to their neighborhoods, proxigrams are employed to calculate the concentrations at fixed distances from their respective iso-concentration surfaces (9 at.% C). Figure 4.2(c) depicts proxigrams from one large cuboidal κ-carbide $\kappa_1^L$ and three small plate-like κ-carbides $\kappa_1^S$, $\kappa_2^S$ and $\kappa_3^S$, which are highlighted in blue in Figure 4.2(a). The proxigrams of the plate-like particles show slightly higher statistical errors due to smaller probed volumes as compared to the large cuboidal κ-carbide, but no compositional difference related to precipitate size and shape is observed. All compositional profiles are rather smooth and symmetric. No elemental segregation or pile-up at κ/γ interfaces is noticed.

When evaluating phase compositions, contributions from overlapping mass-to-charge peaks must be considered. Those are however not taken into account in the above-shown concentration profiles and proxigrams. For a more accurate composition analysis, decomposition of overlapping mass-to-charge peaks has to be performed. Hence, phase compositions were determined by clipping out the phases in the 3D atom maps by iso-concentration surfaces and subsequently analyzing their individual mass spectra by decomposition of overlapping mass peaks ($C_2^+/C_2^{2+}$ and $Al^+/Fe^{2+}$).
Threshold values for iso-concentration surfaces that isolate the κ-carbides and γ-matrix were chosen as ≥10 at.% C and ≤7 at.% C, respectively. These values correspond to the respective plateau of the C concentrations in κ and γ in the 1D concentration profiles and exclude the interfacial region from the analyses (Figure 4.2(b)). Since no compositional differences were found between κ-carbides of different size and shape, an average composition value from all κ-carbides in the analyzed volume was determined.

**Figure 4.2.** (a) Reconstructed APT maps of C (purple), Al (green) and Mn (yellow) atoms. κ-carbide precipitates are visualized by a 9 at.% C iso-concentration surface; (b) 1D concentration profile of elements along the green cylinder (Φ=10 nm) in (a) with a bin size of 0.3 nm. (c) Proxigrams with respect to interfaces between γ-matrix and κ-carbides highlighted in blue in (a), calculated with a bin size of 0.3 nm.

The compositions determined, as listed in Table 4.1, reveal the same partitioning trend to that obtained from the proxigram analysis: κ-carbides are enriched with Al and C but depleted in Mn. The elemental partitioning between κ and γ can be quantified in terms of the corresponding partitioning coefficients \( \varepsilon_{\text{p}} = c_{\kappa} / c_{\gamma} \), where \( c_{\kappa} \) and \( c_{\gamma} \) are the
concentrations of element i (at.%) in the κ and γ phase, respectively. The values of the elemental partitioning coefficients ε are 0.92, 1.23 and 3.07 for Mn, Al and C, respectively. In terms of atomic percentage, the stoichiometric (Fe,Mn)$_3$AlC κ-carbide has 60% (Fe+Mn), 20% Al and 20% C. However, the compositions of the κ-carbides measured with APT reveal an off-stoichiometry in carbide composition, which will be further studied in detail in chapter 5.

As the phase compositions of the κ/γ two-phase microstructure are determined, their phase mole fractions can be obtained according to the lever rule (Povstugar et al., 2014). It is worth pointing out here that the 24h-aged alloy has a κ/γ two-phase microstructure free of GB precipitates, which will be studied later in chapter 6. Thus, the mass balance of the κ/γ two-phase microstructure reads:

$$c_n^i = c_\gamma^i (1 - f_\kappa) + c_\kappa^i \cdot f_\kappa,$$

where $f_\kappa$ is the mole fraction of κ-carbides, $c_n^i$ represents the nominal composition of the alloy. A reformulation of equation (4.1) gives:

$$f_\kappa = (c_n^i - c_\gamma^i)/(c_\kappa^i - c_\gamma^i).$$

Hence, the mole fraction of the κ-carbides $f_\kappa$ can be extracted by plotting $(c_n^i - c_\gamma^i)$ against $(c_\kappa^i - c_\gamma^i)$. Since the atomic density difference between κ-carbide and γ-matrix is negligible, the volume fractions of phases are approximately equal to their mole fractions. Figure 4.3 shows such a lever rule plot applied on the 24h-aged alloy with the phase compositions listed in Table 4.1 (solid spherical markers). Its linear regression analysis (dashed black line) gives a volume fraction of κ-carbide $V_{f_\kappa}$ of 16.3%. However, it is noted that the linearity of the fit is not satisfactory. Similar to other high-Mn steels, the conventionally thermo-mechanically treated alloy exhibits chemical inhomogeneities, particularly for Mn as a result of substitutional alloying element segregation during dendritic solidification (section 4.3.1). The Mn concentration could vary ~4 wt.% (~4 at.%) between different regions (Figure 4.7). The regions for SS-treated and 24h-aged samples lifted-out for FIB milling might have had different Mn concentrations, leading to deviations from linearity (mass balance). It is therefore difficult to extract the exact general volume fraction of κ-carbides based on local APT compositions. But since Mn barely partitions during the κ-carbide precipitation (Figure 4.2(b)), the deviation induced by its heterogeneity can be simply taken into account by studying its variation range. At least a range can be estimated for $V_{f_\kappa}$. 

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Due to the Mn inhomogeneity, instead of an exact value, a range is determined with varied nominal Mn composition $c_{n}^{Mn}$. In addition to the lower locally measured $c_{n}^{Mn}$ by APT (Table 4.1), the higher $c_{n}^{Mn}$ expected by wet chemical analysis (Table 2.1) is used as the upper bound. Fe serves as the balance element. The former lower bound is plotted with solid spherical markers and linearly fitted with a black dash line while hollow square markers and a grey dash line are correspondingly used for the upper bound.

The nominal Mn composition locally measured for the SS-treated specimen (24.5 at.%, Table 4.1) is noticed to be lower than the bulk one determined by wet chemical analysis (26.7 at.%, Table 2.1). If the latter is further used as the upper bound (hollow square markers & grey dash line) while the former is regarded as the lower bound (solid spherical markers & dark black dash line) (Figure 4.3), the volume fraction of κ-carbides can be determined to be within a range of 16.3-25.0%.

### 4.2.2 κ/γ interface structure

#### 4.2.2.1 Chemical gradient and interfacial width

Figure 4.2(b) and (c) reveal that the κ/γ interface has a thickness of ~2 nm, which might be larger than the actual value due to systematic measurement errors and APT-
related artifacts. Firstly, there is the local magnification effect as a result of different evaporation fields of two adjoining phases, especially for interfaces parallel to the analysis direction (Miller et al., 2014; Gault et al., 2012b). If trajectories of neighboring surface atoms cross each other during field evaporation the x-y positions of such ions reconstructed using simple point projection algorithms are biased with an error and the apparent interface width in APT datasets is increased. Secondly, compositional signals can be smeared out due to data sampling. Since the detected $\kappa/\gamma$ interfaces are not perfectly flat and exhibit some roughness and curvature, concentration gradients in 1D profiles become broadened even if the ROI is placed perpendicular to the interfaces. The finite sampling bin width (0.3 nm) leads to averaging of compositions of both abutting phases, increasing the apparent interface width. As for the proxigrams, the calculated distance of an atom to the nearest iso-concentration surface is to a certain extent smeared out depending on voxel size and delocalization (smoothing) values.

To better assess the $\kappa/\gamma$ interfacial width, specific $<001>$-oriented APT specimens were further studied, where the crystallographic $<001>$ direction is aligned parallel to the analysis direction. Due to the special $<001>$ alignment of the $\kappa$-carbide arrays and their (001) cube-cube relationship with the $\gamma$-matrix, there are sets of $\kappa/\gamma$ interfaces perpendicular to the depth direction. Thus, interface broadening caused by the above-mentioned local magnification effect is minimized and maximal spatial resolution is achieved for compositional profiles across these interfaces. Additionally, such a special crystallographic alignment facilitates the observation of $\{002\}$ fcc pole in the detector hit map, which helps optimize the reconstructions with clearly resolved $\{002\}$ lattice planes as depicted later in section 5.2.1.1.

One big cuboidal $\kappa$-carbide close to the $\{002\}$ pole is selected for this interfacial analysis. The overall $\kappa/\gamma$ interface, as well as the single top and bottom ones, delineated by C iso-concentration surface, are individually examined (Figure 4.4(a)). The former (‘overall’) yields better data statistics due to its larger probed volume while the latter (‘top’, ‘bottom’) offers better spatial resolution by avoiding lateral analysis. Their proxigrams are summarized into Figure 4.4(b). C, as the most significant partitioning element (Figure 4.2(b,c)), is chosen to depict the chemical transition across the interfaces. Indeed the proxigrams of the ‘top’ and ‘bottom’ interfaces show stronger statistical scatters. Since the compositional profiles of $\kappa/\gamma$ interfaces are symmetric
without exhibiting any elemental segregation (Figure 4.2(b,c)), their carbon proxigrams can be described by a sigmoid function (Luna et al., 2008):

\[ c = \frac{c_0}{1 + e^{-d/L}}, \]

where \( c_0 \) denotes the intermediate composition at the inflection point, \( L \) is a fitting parameter defining the range around the inflection point, \( d \) represents the distance away from the interface. The fitted profiles of these three interfaces exhibit slight differences between each other in terms of gradients and plateau compositions. In general, the interfaces perpendicular to the analysis direction (‘top’, ‘bottom’) have slightly lower \( \gamma \) plateau concentrations and bit steeper gradients as compared to the ‘overall’ encompassing interface.

**Figure 4.4.** Chemical analysis across the \( \kappa/\gamma \) interfaces using C concentration: (a) Illustration of three chosen interfaces - ‘overall’ (the overall interface of one big cuboidal \( \kappa \)-carbide particle whose constituent interfaces are either parallel or perpendicular to the APT analysis direction), ‘top’ and ‘bottom’ (its top and bottom interfaces perpendicular to the analysis direction, respectively); (b) The carbon proxigrams of these three interfaces and their fitted sigmoidal profiles; (c) Normalized sigmoidal fitting showing their interfacial widths (10% to 90% of plateau values).
According to the common definition of interfacial width as the distance of the 10%-90% plateau variation (Luna et al., 2008; Hwang et al., 2009), the widths of the ‘overall’, ‘top’ and ‘bottom’ interfaces are determined to be 1.8, 1.9 and 2.1 nm, respectively (Figure 4.4 (c)). No remarkable difference is found between the encompassing and perpendicular interfaces. Interfacial broadening caused by local magnification is therefore negligible. Although the analysis here has been optimized in many aspects including reconstruction, interface orientation and data sampling, the determined width (~2 nm) is similar to the value obtained above from the composition profiles of interfaces inclined to the analysis direction, suggesting that the κ/γ interface is most likely not atomically sharp.

### 4.2.2.2 Interface coherency

The continuity of lattice planes across a phase boundary is determined by the similarity of crystal structures and lattice parameters of the adjacent phases. Since the κ-carbide precipitates possess a fcc-based L’12 structure, the coherency of the κ/γ interface depends on the lattice misfit between the κ-carbides and γ-matrix. Figure 4.5 shows a SXRD spectrum of the 24h-aged sample, the measurement of which was carried out by Wenwen Song. Two sets of peaks are labelled, which belong to the κ-carbides and γ-austenite, respectively. As a fcc-structure, γ-austenite exhibits reflections only if the individual Miller indices h, k, l of the reflecting {hkl} planes are all odd or all even. However, for the ordered L’12 κ-carbide, superlattice reflections prevail, since scattering factors of different atoms can differ. Peaks which are supposed to be missing in a basic fcc-reflection exhibit weak intensities in the superlattice structure and are referred to as superlattice peaks (Engler et al., 2010). It is difficult to identify the low-index, non-superlattice peaks of the κ-carbides at small Bragg angles since they coincide with the γ-peaks of the same plane indices (e.g. (111)) or appear as side-shoulders (e.g. (200), (220)). Clear κ/γ peak separation is visible for non-superlattice reflections as the plane indices increase to (311). The peak coincidence suggests that the κ-carbides have a lattice parameter \(a_\kappa\) very close to that of the γ-matrix \(a_\gamma\). The lattice parameters obtained from the SXRD data are 3.722 Å and 3.679 Å for the κ-carbides and γ-matrix, respectively. The corresponding lattice misfit, \(\delta=(a_\kappa - a_\gamma)/a_\gamma\), is determined as 1.16%.
The volume fraction of the κ-carbides gained by Rietveld profile fitting is 20.1%, which is in good agreement with the lever rule plot (Figure 4.3).

**Figure 4.5.** Synchrotron X-ray diffraction (SXRD) spectrum of the 24h-aged sample. Peaks for κ-carbide precipitates and γ-matrix are identified and labelled. The measurement was performed by Wenwen Song.

Due to the lattice parameter difference between precipitates and matrix, precipitation always introduces an elastic distortion into the crystal. As the lattice misfit or precipitate size increases, the elastic energy of the interface boundary increases until it is energetically more favored to have an interface edge dislocation to compensate the lattice mismatch. The coherent interface becomes partially coherent or semi-coherent when a misfit dislocation appears. The critical precipitate radius $r_c$ for such a transition is assumed to be the lattice distance compensating the matrix burgers vector $b$ by the lattice misfit $\delta$ (Royset et al., 2005):

$$r_c = \frac{b}{2\delta}.$$  

(4.4)

The calculated critical precipitate size for the κ/γ interface $r_c^{\kappa/\gamma}$ is 22.4 nm. This value is larger than the observed κ-carbide size, i.e. 15-20 nm (section 3.2.1), suggesting that the interface between the κ-carbide and γ-matrix is coherent.

The κ/γ interface can be directly observed by HAADF-STEM imaging (Figure 4.6). This measurement was performed by Marta Lipinska-Chwalek.
Figure 4.6. HAADF-STEM images of the 24h-aged sample along zone axes of (a) [001] and (b) [011]; (c) Atomic arrangements of the measured κ-carbides with respect to those of the ideal L’1₂ (Fe,Mn)₃AlC structure along the [001] and [011] zones. HAADF-STEM: High angle annular dark field – scanning transmission electron microscopy. The measurements were performed by Marta Lipinska-Chwalek.
Two different zone axes, [001] and [011], are utilized to check the edge-on lattice continuity of the {100} and {111} planes, respectively. The long range ordered κ-carbides can be clearly recognized by the periodicity of atomic columns with alternative contrasts, whereas the disordered γ-matrix exhibits a more homogeneous contrast. Cubic-shaped and plate-like κ-carbides, as well as broad and narrow γ-channels, can be well identified. From both zone axes and for different interfaces between cubic-shaped (or plate-like) κ-carbides and broad (or narrow) γ-channels, all atomic planes continue across the κ/γ phase boundaries and no interface edge dislocation is detected (Figure 4.6(a,b)). This is a general observation, not limited to the present local images but seen at different sites across several micrometers. It is hence safe to conclude that the κ-carbides are completely coherent to the γ-matrix.

Owing to sensitivity of HAADF-STEM with respect to the atomic number Z, the images could help shed light on the ordering and site-occupancy of the κ-carbides, which are off-stoichiometric according to APT analysis (section 4.2.1). For the ideal L’12 (Fe,Mn)3AlC structure, there should be three kinds of atomic columns along the [001]κ direction, i.e. pure Al, pure Fe/Mn and Fe/Mn with additional C (Figure 4.6(c)). Since C is far lighter than Fe/Mn, while Fe and Mn have very similar atomic numbers, it is practically difficult to distinguish the latter two. In the HAADF-STEM image (Figure 4.6(a,c)), mainly two sets of atomic columns with different contrasts are observed in the κ regions. Provided that Al is lighter than Fe and Mn, the brighter spots should contain Fe/Mn atoms whereas the darker ones should correspond to the Al columns. Unlike the grid contrast variation along the [001]κ zone axis, the image contrast varies linearly from the [011]κ direction (Figure 4.6(b)). From the ideal L’12 (Fe,Mn)3AlC structure perspective, there should be two alternative vertical atomic lines, where one is composed of Fe/Mn/Al atomic columns and the other consists of alternative pure Fe/Mn and pure C columns (Figure 4.6(c)). The two experimentally observed sets of vertical lines in part fulfill this expectation (Figure 4.6(b,c)). The darker spot line represents the Fe/Mn/Al column line containing Al while the brighter one should indicate the alternative pure Fe/Mn and pure C column line. However, only one set of spots is noticed along the brighter line. Their contrast are comparable to each other and the inter-spacing fits with the Fe/Mn column distance. Hence, all observed spots on the bright line should be Fe/Mn columns and the pure C columns are missing.
Theoretically, [011] is a proper direction for single C column measurement, avoiding any overlap with other elements and hence providing insights into the evaluation of commonly expected C vacancies. However, in practice it is difficult to obtain the C column signal due to (i) the inherent difficulty in detecting light elements and (ii) the small distance between C columns away from the brightest Fe/Mn spots. Overall, according to the measured atomic contrasts of the κ-carbides, their site-occupancy seems generally follow the ideal L’12 (Fe,Mn)3AlC structure. However, the existence of C vacancies or other point defects cannot be assessed with the current data.

In addition, it is noticed that the κ/γ interfaces are not atomically sharp but rough. The diffuse interfaces observed in APT by iso-concentration surface (Figure 4.2(a), Figure 4.4(a)) are not artefacts but real. The width of ordering transition can be about 1-5 lattice units, i.e. up to ~1.9 nm, which is consistent with the compositional transition width measured by APT as ~2.0 nm (Figure 4.4(c)).

4.3 Discussion

4.3.1 Compositional accuracy of APT measurements

4.3.1.1 Microstructural chemical homogeneity

Despite its sub-nm spatial resolution, a limitation of APT is its limited FOV and analysis volume (tens to hundreds of nanometers), which raises questions about the statistical relevance of this technique. In the circumstance of a chemically heterogeneous microstructure, it is of great importance to evaluate the inhomogeneity in order to avoid biased judgements. High-Mn steels are well-known alloys susceptible to dendritic micro-segregation during solidification (Majka et al., 2002; Daamen et al., 2015). To evaluate the chemical homogeneity of the studied high-Mn alloy, electron probe microanalysis (EPMA) mapping was carried out at the μm-scale on an SS-treated alloy sample. It was performed by Philippe T. Pinard from the Gemeinschaftslabor für Elektronenmikroskopie (GFE), RWTH Aachen on a JEOL JXA-8530F FEG-SEM (JEOL GmbH) using an accelerating voltage of 15 kV and a beam current of 100 nA.

As shown in Figure 4.7, micro-segregation zones are identified, typically appearing in a banded structure. It is most pronounced for Mn whereas Al and C are
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relatively more homogeneous. The Mn concentration could vary $\sim$4 wt.% from the core of segregated bands to the regions between bands. The variation ranges for Al and C are only about $\pm$0.4 wt.% and $\pm$0.3 wt.%, respectively. The wavelength of the Mn banding, i.e. the average distance between the segregation cores and valleys perpendicular to the bands, is $\sim$70 $\mu$m. The SS treatment at a temperature of 1200 °C for 2 hours after a hot-rolling process (section 2.1) could not fully remove Mn segregation inherited from casting.

![Figure 4.7. EPMA compositional maps of constituent elements in the SS-treated alloy with a step size of 3 $\mu$m. All compositions are shown in wt.%. EPMA: electron probe microanalysis. The measurement was carried out by Philippe T. Pinard.](image)

Such Mn micro-segregation zones found in the SS-treated sample are expected to be preserved in other samples aged at 600 °C, including the 24h-aged sample. An estimation of the diffusion length $X_i$ with a diffusion coefficient $D_i$ within a time frame reads (Gottstein, 2004):
Table 4.2 lists the diffusion coefficients (Mehrer, 1990) and correspondingly calculated diffusion lengths for solute elements. Note that due to the lack of diffusion data for concentrated alloys, they are estimated based on the D_i in dilute \( \gamma \)-Fe at a temperature of 950°C (lower temperatures, e.g. 600 °C, are inaccessible for \( \gamma \)-Fe because of the insufficient \( \gamma \)-stability of a dilute alloy). Taking t=24 hours as an example (Table 4.2), the estimated diffusion length for Mn is only about one tenth of the Mn band wavelength. Even much shorter diffusion lengths are expected, as the actual temperature is only 600 °C. In contrast, the solutes Al and C with little inhomogeneities show much higher diffusivity. It is therefore plausible that in the aged alloys Al and C are rather homogeneous while Mn exhibits similar segregation behavior as shown in Figure 4.7.

Fortunately, as manifested in Figure 4.2, Mn barely partitions during the precipitation of \( \kappa \)-carbides. The exact Mn compositions measured for the \( \kappa \)-carbide and \( \gamma \)-matrix phases might be slightly affected by the local Mn compositions, which however should have little influence on the elemental partitioning behavior of the \( \kappa \)-carbide precipitation, as well as the Al- and C- contents of phases.

**Table 4.2.** Estimation of solute diffusion lengths \( X_i \) at a temperature of 950°C in \( \gamma \)-Fe.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Al</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_i ) (m²/s)</td>
<td>1.07×10⁻¹⁶</td>
<td>3.23×10⁻¹⁴</td>
<td>1.34×10⁻¹¹</td>
</tr>
<tr>
<td>( X_i ) (μm/s)</td>
<td>0.02</td>
<td>0.44</td>
<td>8.96</td>
</tr>
<tr>
<td>( X_i ) (μm, t=24 hours)</td>
<td>7.43</td>
<td>129.5</td>
<td>2600</td>
</tr>
</tbody>
</table>

### 4.3.1.2 Influence of measurement parameters

Chemical compositions as determined by APT can be significantly affected by measurement conditions (Larson *et al.*, 2013; Miyamoto *et al.*, 2012; Takahashi *et al.*, 2011; Gault *et al.*, 2012b). The effects of measurement parameters, including pulse fraction (PF), base temperature and evaporation rate (ER), on the apparent compositions of highly alloyed Fe-Mn-Al-C steels are studied using the single-phase austenitic SS-treated alloy, whose wet chemical analysis (Table 2.1) and EPMA measurement (section 4.3.1.1) results can be employed as references. Considering the high multiple-
hit-event proportion of the studied alloy and its important role in compositional accuracy, special attention is paid against it as measurement parameters vary.

Firstly, the effect of PF on apparent compositions is examined in a range of 10%-20% on one needle specimen with a detection rate of 0.5% at 70 K. The PF and base temperature combination is critical for a decent pulse-controlled evaporation. An improper selection of parameters may result in preferential evaporation or retention of specific ions leading to incorrect compositions or degraded depth resolution as a result of ion loss or retardant detection, respectively (Gault et al., 2012b; Larson et al., 2013; Miller et al., 2014). A high temperature of 70 K is chosen here since usually with a fixed PF preferential field evaporation or retention is more prone to take place at high temperatures and thereby can be better recognized if there is any. A constant PF is ensured for each measurement without reaching the maximum pulse voltage of the device.

As shown in Figure 4.8, the apparent compositions of Al and C are hardly affected by the variation of PF while that of Mn is reduced as PF decreases. In general, high PF is recommended to avoid potential preferential field evaporation of elements with low evaporation fields and preferential field retention of elements having high evaporation fields (Larson et al., 2013). According to the image hump model predictions for evaporation fields of pure elements (Tsong, 1978; Gault et al., 2012b), Al has the lowest evaporation field among the component elements and therefore the highest risk of encountering DC evaporation (field evaporation by a standing electrostatic field without voltage pulses). C, having a much higher evaporation field than other elements (Tsong, 1978; Gault et al., 2012b), might be the one most probably being prevented from evaporation, giving rise to an enhanced formation of molecular and multiple events (Thuvander et al., 2011). If the applied PF is insufficient for a proper evaporation of all elements with equal probability at this temperature, it might be indicated either by a lower Al composition (Al loss due to preferential evaporation) or via an abnormal inhomogeneous distribution of C atoms (C retardation as a result of preferential retention), both of which should be alleviated as PF increases. In fact, the measured apparent Al composition is higher than the bulk composition and does not show any obvious difference as the PF changes (Figure 4.8(a)). Preferential evaporation of Al is hence less likely to occur as PF varies from 20% to 10% at 70K. The steep increase of
multiple-hit-event proportion as PF decreases to 10% (Figure 4.8), however, implies that retention of C might take place, leading to the accumulation of C atoms on the surface which helps form multiple events. In contrast, the multiple events are at a much lower steady level in the range of 15-20% PF. The C atoms are also found to be homogeneously distributed throughout the analysis volume at a PF of 15% (Figure 4.1). Retention of C is effectively restricted when PF lies in the range of 15-20%.

**Figure 4.8.** Influence of pulse fraction (PF) on apparent compositions at 70 K; the dash lines indicate the nominal compositions obtained by wet chemical analysis.

In comparison to the invariable apparent compositions of Al and C as PF increases from 10% to 20%, there is an obvious increment of Mn concentration about ~2 at.%. It is probably associated with the Mn inhomogeneity problem (section 4.3.1.1). Thanks to the serial PF measurements on one needle specimen, the effect of chemical gradient on apparent Mn concentration can be evaluated by a slicing study of the analysis volume. 10 nm-thick slices are cut at different depths and their individual compositions as a function of depth are plotted in Figure 4.9. The values obtained from the same needle part (measured with a same PF) are connected by solid lines to reveal the Mn compositional gradient in this part, leaving the influence of PF out. Such a plot reveals that there is an ascending trend of Mn composition as the depth increases before a
decline occurs in part III. This, to some extent, explains the increase in Mn concentration with increasing PF (Figure 4.8) since increasing PF equals increasing depth here.

Figure 4.9. Illustration of possible causes for the effect of pulse fraction (PF) on Mn concentration variation in Figure 4.8: (1) existence of compositional gradient along depth direction as depicted by solid trend lines; (2) effect of PF on measured Mn% - red arrows indicating jumps from expected values to measured ones due to the change of PF. The dash lines are the average bulk compositions of needle parts, as given in Figure 4.8.

Apart from the chemical gradient, it seems that there are abrupt Mn concentration jumps as the PF changes. Since the specimen is well aligned after the first measurement, the initiation of a following measurement with a varying PF barely consumes material. It is safe to assume that the top of the following part is directly attached to the bottom of the previous part. Then the top slice of the following part is about 10 nm (slice thickness) away from the bottom slice of the previous part, as sketched in Figure 4.9. Assumining the Mn chemical gradient changes continuously, the composition of the following top slice expected by an unchanged PF can be estimated by extending the
concentration gradient trend of previous part to this depth, as indicated by red open circles in Figure 4.9. The gaps between these values and those actually measured result from the change of PF (highlighted by red arrows). This implies that there might be Mn loss between pulses at low PFs, i.e. preferential evaporation of Mn.

According to the image hump model predictions for evaporation fields of pure metals (Tsong, 1978; Gault et al., 2012b), Al, rather than Mn, is the component most susceptible to preferential evaporation. However, the PF analysis clarifies that it is Mn that seems to encounter such a problem. One explanation could be that the evaporation behavior of alloys is complex and differs from pure metals, as reported also for dilute steels by Yamaguchi et al. (Yamaguchi et al., 2009). The Fe-Mn-Al-C alloy studied here is heavily alloyed with a sum of solute concentration up to 46 at.%. Quaternary alloying makes its field evaporation complicated due to the complex atomic bonding environment. Quenched directly from 1100°C, the studied SS-treated alloy is supersaturated and exhibits local C and/or Al ordering in a size of ~2 nm (Welsch, 2016). The local ordering in a few unit cells might have caused volumetric strain due to unit cell expansion. An ab-initio study on the binding energy between Al and C in pure γ-Fe reveals that Al and C atoms are attracted to each other under constrain (details in section 5.3.2). Hence, the local atomic ordering makes the binding of Al atoms to their neighbors stronger than that of Mn atoms and their surroundings, resulting in the higher field evaporability of Mn over Al species.

Nevertheless, if the inherent Mn inhomogeneity is subtracted, there would be a ~1 at.% underestimation of Mn concentration as the PF decreases from 20% to 10% at 70 K due to its preferential evaporation while Al and C concentrations are not affected (Figure 4.9). A high PF of 20% would be preferred for a more accurate compositional measurement of Mn while considering specimen yielding and keeping a constant PF throughout a dataset, a moderate PF of 15% would be an appropriate choice. Despite an optimized PF, it is noticed that generally there is an overestimation of Al and C concentrations in comparison to the reference concentrations, which needs to be explained by other effects.

ERs of 0.2%, 0.5% and 0.8% are tested on one needle specimen to reveal the effect of ER on apparent concentrations. As shown in Figure 4.10, the apparent Al and C compositions are higher than the nominal compositions. Such an overestimation is
relieved, especially for C, at a low ER of 0.2%, where a simultaneous reduction of multiple events is found. The apparent composition of Mn is not much affected by the change of ER. It seems that a lower ER less than 0.5% can offer a better accordance to the nominal compositions due to the reduction of multiple events, implying that the overestimation of Al and C may be related to multiple events. Since the apparent compositions do not strongly depend on ER and, to ensure a rapid but robust measurement, a moderate ER of 0.5% is chosen.

![Figure 4.10. Influence of evaporation rate (ER) on apparent compositions at a pulse fraction (PF) of 15% and a base temperature of 70 K; the dash lines indicate the nominal compositions obtained by wet chemical analysis.](image)

The specimen base temperature is commonly found to have a significant influence on apparent concentrations of C-containing alloys (Takahashi et al., 2011; Marceau et al., 2013; Miyamoto et al., 2012). The temperature dependence of apparent concentrations of the SS-treated alloy is studied on one needle specimen from 70 K to 30 K with a fixed PF of 15% and an ER of 0.5% (Figure 4.11). There is a general overestimation of Al and C but an underestimation of Mn as compared to the nominal compositions. As the base temperature decreases from 70 K to 30 K, the C concentration remains nearly constant while the apparent Al and Mn compositions increase.
accompanied by an increase in multiple events. According to the basic theories of field evaporation, the image hump and charge exchange models, at a given constant ER, as temperature decreases the evaporation fields of atomic species increase and the difference of evaporation fields between different atomic species decreases (Miller et al., 1996). Hence, at a fixed PF, the risk of preferential field evaporation and/or retention should be alleviated at lower base temperatures if there is any. This could help to explain the relief of Mn deviation from the nominal composition with a temperature reduction if such a deviation is indeed resultant from measurement artifacts instead of inherent elemental inhomogeneity. However, Al and C species are not involved into preferential evaporation or retention even at 70K (Figure 4.8), let alone lower temperatures. Their overestimations have to be explained by other reasons.

Figure 4.11. Influence of base temperature on apparent compositions at a pulse fraction (PF) of 15% and an evaporation rate (ER) of 0.5%; the dash lines indicate the nominal compositions obtained by wet chemical analysis.

In previous reports, the significant influence of the base temperature on apparent compositions of C-containing alloys was found to be closely related to multiple events (Miyamoto et al., 2012; Marceau et al., 2013; Takahashi et al., 2011). When multiple ions evaporated by a single pulse are of the same isotope and hit the detector very close
to each other, the so-called pile-up effect can take place, i.e. only one ion is registered at the detector, leading to a preferential loss of specific species. For steels, Fe, being the primary alloying element, is usually believed to produce the highest number of multiple events and thus encounter the most severe detection losses (Miyamoto et al., 2012; Marceau et al., 2013; Takahashi et al., 2011). As shown in Figure 4.8, 4.10, 4.11, no matter how measurement parameters are tuned in this work, there is always an overestimation of Al and C with a corresponding underestimation of Fe (Mn is not considered here due to the lack of true reference). Intuitively, it might be a result from a detection loss of Fe. After all, the multiple-event proportion keeps at a high level of over 30% under all conditions. An analysis on the constituents of multiple events and their dependence on base temperature reveals that Fe$_{2+}$ indeed takes the majority part of multiples (41-47%) (Figure 4.12). The other two main constituents of multiple events are Mn$_{2+}$ (25-27%) and Al$_{2+}$ (17-21%).

![Figure 4.12. Influence of base temperature on the constituents of multiple events at a pulse fraction (PF) of 15% and an evaporation rate (ER) of 0.5%. The atomic species of fractions less than 0.1% are not shown.](image-url)
The possibility of Fe detection loss can be quickly checked by comparing the apparent ratio of Fe isotopes against natural abundance (Takahashi et al., 2011). If Fe loss occurs as a result of the pile-up effect, the main Fe isotope $^{56}\text{Fe}$ would suffer much more than other minor isotopes at a possibility of the square of its abundance (assuming two-ion multiple impact) and thereby its apparent fraction would be lower while fractions of minor isotopes are higher than natural abundance. The measured apparent isotope ratios of Fe as a function of base temperature are plotted in two forms in Figure 4.13. The peak at 27 Da is either decomposed into $^{54}\text{Fe}^{2+}$ and $^{27}\text{Al}^{+}$ by IVAS or undecomposed with a complete assignment to $^{54}\text{Fe}^{2+}$. Since there is a peak overlap at 27 Da between $^{54}\text{Fe}^{2+}$ and $^{27}\text{Al}^{+}$ (Figure 2.1), the $^{54}\text{Fe}^{2+}$ contribution to the 27 Da peak is calculated in IVAS by its relative abundance ratio to other Fe isotope (Al is a monoisotopic element) (Larson et al., 2013). Such a direct decomposition, however, eliminates the signal of Fe detection loss since it tacitly assumes that the Fe isotope ratios follow the nature abundance, which is not true when pile-up effect occurs. On the other hand, if the peak at 27 Da is not decomposed and fully assigned to $^{54}\text{Fe}^{2+}$, the counts of $^{54}\text{Fe}^{2+}$ would be overestimated, amplifying the severity of detection loss.

![Figure 4.13. Apparent isotope ratio of Fe$^{2+}$ species at 27, 28 and 28.5 Da. The dash lines indicate the natural abundance of Fe isotopes.](image-url)
As shown in Figure 4.13, the isotope ratios of $^{54}\text{Fe}^{2+}$ without peak decomposition obviously indicates the occurrence of a pile-up effect, which is almost not realized after decomposition. Nevertheless, the higher isotope ratios of the $^{57}\text{Fe}^{2+}$ isotope than the natural abundance are not affected by the peak decomposition at 27 Da and clearly suggest the occurrence of a pile-up effect. This then in turn implies that the automated peak decomposition of the peak at 27 Da in IVAS is improperly executed without taking the Fe loss into account. Or in other words, the contribution of $^{54}\text{Fe}^{2+}$ to this peak is underestimated since its primary reference isotope $^{56}\text{Fe}^{2+}$ is much lost during detection. This explains the universal Al overestimation (Figure 4.8, 4.10, 4.11), because the Al$^{1+}$ contribution to the peak at 27 Da is overestimated (that of $^{54}\text{Fe}^{2+}$ is underestimated).

The global overestimation of Al composition is therefore a result of the chain reaction of Fe detection loss and peak decomposition via IVAS without taking that into consideration. To perform a proper decomposition of the peak at 27 Da ($^{54}\text{Fe}^{2+}$ vs. Al$^{1+}$), a prior correction on Fe detection loss has to be carried out. Miyamoto et al. proposed a correction method for the detection loss of Fe in dilute Fe-C binary alloys based on the isotope abundance of Fe (Miyamoto et al., 2012). Here, given that the count of $^{54}\text{Fe}^{2+}$ is unknown (the peak at 27 Da needs to be decomposed), the Miyamoto’s method is modified here in such a way that the evaluation of Fe detection loss leaves the $^{54}\text{Fe}^{2+}$ out. The correction on Fe loss is only employed for Fe$^{2+}$ species, since the multiple hits of Fe$^{1+}$ and Fe$^{3+}$ are negligible (Figure 4.12). Since ~75% of the multiple events in the temperature range of 70-30 K are found as evaporation of two ions in one pulse (not shown here), it is reasonable to consider only these hits for the sake of simplicity. Then the probability of encountering a count loss for Fe$^{2+}$ species ($i=54, 56, 57, 58$) is proportional to the square of its natural abundance $X_{Fe_i}$ ($X_{Fe54} = 0.05845, X_{Fe56} = 0.91754, X_{Fe57} = 0.02119, X_{Fe58} = 0.00282$ (Böhlke et al., 2005)). With a parameter $\alpha_{Fe^{2+}}$ representing the count loss probability, the detected counts of Fe$^{2+}_i$ species $n_{Fe^{2+}_i}$ can be expressed as:

$$n_{Fe^{2+}_i} = N_{Fe^{2+}}X_{Fe_i} - \alpha_{Fe^{2+}}N_{Fe^{2+}}(X_{Fe_i})^2,$$  \hspace{1cm} (4.6)

where $N_{Fe^{2+}}$ is the total number of Fe$^{2+}$ ions hitting the detector. A multiplication on equation (4.6) with $X_{Fe_i}$ and the sum of all Fe$^{2+}$ isotopes except $^{54}\text{Fe}^{2+}$ gives rise to:
Chapter 4. Elemental partitioning and $\kappa/\gamma$ interface structure

\[
\sum_{i=56,57,58} n_{Fe_i^{2+}} = N_{Fe^{2+}} (0.94155 - 0.8423 \alpha_{Fe^{2+}}) = A, \quad (4.7)
\]

\[
\sum_{i=56,57,58} \left( n_{Fe_i^{2+}} X_{Fe_i} \right) = N_{Fe^{2+}} (0.8423 - 0.7725 \alpha_{Fe^{2+}}) = B. \quad (4.8)
\]

Having $n_{Fe_i^{2+}}$ from mass spectra analysis, values of A and B can be calculated. The detection loss parameter of $Fe^{2+} \alpha_{Fe^{2+}}$ and the total $Fe^{2+}$ count $N_{Fe^{2+}}$ then can be obtained as:

\[
\alpha_{Fe^{2+}} = \frac{0.8423 \left( \frac{A}{B} \right) - 0.94155}{0.7725 \left( \frac{A}{B} \right) - 0.8423}, \quad (4.9)
\]

\[
N_{Fe^{2+}} = \frac{A}{0.94155 - 0.7725 \alpha_{Fe^{2+}}}. \quad (4.10)
\]

With equation (4.6), the contribution of $Fe_{54}^{2+}$ to the peak at 27 Da $n_{Fe_{54}^{2+}}$ can be calculated and thereby that of $Al^{1+}$ $n_{Al^{1+}}$ is obtained -- the peak at 27 Da is well decomposed:

\[
\begin{align*}
\alpha_{Fe^{2+}} = n_{27Da} - n_{Fe_{54}^{2+}} = & n_{27Da} - (N_{Fe^{2+}} X_{Fe_{54}} - \alpha_{Fe^{2+}} N_{Fe^{2+}} (X_{Fe_{54}})^2)
\end{align*} \quad (4.11)
\]

The corrected counts of $Fe^{2+}$ species are:

\[
n_{Fe_i^{2+}}^c = N_{Fe^{2+}} X_{Fe_i} \quad (4.12)
\]

With the detection loss of Fe corrected and the peak at 27 Da better decomposed, the corresponding corrected compositions are plotted in Figure 4.14. Excellent agreements to the nominal compositions are achieved for Al at the high temperature regime (60-70 K). After such a correction, the peak at 27 Da is found to be composed of only 35% $Al^{1+}$ ions at 70 K instead of 49% $Al^{1+}$ obtained by direct peak decomposition via IVAS. This discrepancy is exacerbated at lower temperatures, e.g. correspondingly 14% vs. 36% at 30 K, which helps to explain the severer deviation of Al composition at low temperatures. The value of $\alpha_{Fe^{2+}}$, as a parameter indicating the severity of Fe loss, does not show significant difference upon temperature change. There is only a slight increase from 0.25 to 0.31 when temperature decreases from 70 K to 30 K. The corresponding total detection loss of Fe, $100 \times 0.846 \alpha_{Fe^{2+}}$ (Miyamoto et al., 2012), shows a slight increase from 21.2% to 26.2%. A drastic increase in Fe loss from 15% to 40% when base temperature decrease from 80 K to 20 K as observed in a Fe-1.03C (wt.%) alloy (Miyamoto et al., 2012) is not found here. This is consistent with
the relatively constant deviation of apparent isotope ratios as base temperature changes (Figure 4.13) and can be explained by the relatively constant proportion of Fe$^{2+}$ species among multiple events (Figure 4.12).

The correction on Fe loss strongly alleviates the global overestimation of both the Al and C compositions (Figure 4.14). At 60-70 K, great consistencies to nominal compositions are achieved for Al. However, there is a slight underestimation of C within this temperature regime.

![Figure 4.14](image)

**Figure 4.14.** Temperature dependence of compositions with the detection losses of Fe and C corrected.

A check on carbon loss is performed by comparing the count ratio between $^{12}$C and $^{13}$C isotopes to their natural abundance ($X_{^{12}C} = 0.9889$, $X_{^{13}C} = 0.0111$), for example $^{12}$C$^{2+}$ versus $^{13}$C$^{2+}$, $^{12}$C$_2$$^{2+}$ versus ($^{12}$C$^0$)$^{13}$C$^{2+}$, etc (Thuvander et al., 2011; Sha et al., 1992). It is found that detection loss of C mainly happens among the carbon monomer species, i.e. C$^{1+}$, C$^{2+}$. Such a loss can be simply corrected by the amount of $^{13}$C ions as follows since the probability of count loss for $^{13}$C$^i$ species ($i=1, 2$) is negligible (Thuvander et al., 2011):
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\[ n_{i+}^{\varepsilon} = n_{i+}^{\varepsilon} \times \frac{98.89}{1.11}. \]  

(4.13)

The results of such a further correction are immerged into Figure 4.14, where the corrected C contents are found to have an excellent agreement with the nominal.

Moreover, it is noticed that although after corrections on Fe and C losses the apparent compositions of Al and C agree well with the nominal compositions, the Al composition at low temperatures are still overestimated and the deviation of Mn composition from the nominal composition deteriorates. As discussed above, the compositional accuracy of Mn is difficult to determine due to its inhomogeneity. A local variation of ~4 wt.% (~4 at.%), as observed here (Figure 4.14), is possible according to the EPMA mapping (Figure 4.7). The residual overestimation of Al composition after correction is probably due to a Mn loss at low temperatures since Mn$^{2+}$ is the successive species after Fe with the highest proportion of multiples. However, as a monoisotopic element, its possibility cannot be evaluated by isotope ratios as conducted above for Fe and C species.

Nevertheless, a good agreement with the nominal compositions can be achieved at high temperatures of 60-70 K after data correction. This is consistent with some previous work on binary Fe-C and ternary Fe-Mn-C alloys (Miyamoto et al, 2012; Marceau et al, 2013), where the best agreement between APT results and nominal bulk composition is obtained at 80 K and 60 K, respectively. Therefore, in this work, a base temperature of 70 K is chosen.

To summarize, the optimal measurement parameters for the studied SS-treated alloy are a PF of 15%, a ER of 0.5% and a base temperature of 70 K. Due to the pile-up effects, the measured apparent compositions of Al and C would be overestimated. Fortunately, Mn, whose compositional accuracy is unsure due to the lack of a true reference, is an element barely subjected to elemental partitioning during the κ-carbide precipitation and having little effect on the precipitation process. Note that the acquisition parameters are optimized on homogenized single phase (γ) specimens, but the field evaporation behavior of ordered κ-carbides is expected to be different from that of the disordered γ-phase. The κ-carbides enriched with C is expected to be more susceptible to multiple evaporation, which is confirmed by the measurement of μm-scale GB κ-carbide (section 6.2). Therefore, even under optimized measurement...
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conditions stronger detection loss of data and overestimation of Al and C apparent compositions can be anticipated in κ-carbides than those in the γ-phase. Since the overall Al and C concentrations are overestimated, the actual Al and C depletion in κ-carbides may be underestimated.
Chapter 5

Off-stoichiometry and site-occupancy of κ-carbides

5.1 Introduction

The primary contribution of κ-carbide to strengthening originates from the ordering strengthening by particle shearing (chapter 3). The effect of ordering strengthening is closely associated with the APB energy on the slip planes, which highly depends on the stoichiometry and site-occupancy of the ordered κ-carbides. An accurate determination of the stoichiometry and site-occupancy of κ-carbides is therefore critical for understanding the ordering strengthening in age-hardened austenitic Fe-Mn-Al-C alloys. Also, the exact sub-lattice occupancy in such a two-phase material containing ordered precipitates affects the elastic misfit across the hetero-interfaces. This will also contribute to the total system energy and to the strain hardening behavior.

If the κ-carbide had ideal stoichiometry, i.e. (Fe,Mn)₃AlC, its composition should be 60% (Fe+Mn), 20% Al and 20% C (at.%). However, the measured composition of the κ-carbides in the 24h-aged alloy deviates from these values (Table 4.1). At first glance, there is an excess of Fe and Mn and a lack of C whereas the value for Al is close to the ideal value. The measured C content lower than 20 at.% indicates that the body-centered octahedral sites are not completely occupied by C atoms but are either left
vacant or occupied by metal atoms, e.g., the excess Fe or Mn atoms. Regarding the experimentally measured lattice parameter of the \( \kappa \)-carbides \( a_c=3.722 \ \text{Å} \) (section 4.2.2.2), its fcc octahedral gap cannot tolerate an extra Fe or Mn atom with a radius of \( \sim 1.2 \ \text{Å} \) (Takeuchi et al., 2005). Hence, C vacancies must be the cause for the off-stoichiometric C concentration. Moreover, the ratio of the Fe/Mn content (sharing the same face-centered sub-lattice) to the Al content (corner sub-lattice) is experimentally observed to be 3.4:1, instead of the stoichiometric 3:1, thereby indicating an excess of Fe and Mn and/or a depletion of Al. The underlying reason could be: (i) the presence of Al vacancies instead of a full occupation of this sub-lattice, or (ii) excess Fe or Mn atoms occupying the Al sub-lattice, i.e., the formation of anti-site defects. The experimentally measured \( \kappa \)-carbide is, therefore, off-stoichiometric, not only due to vacancies but also substitutional defects. Hence, the \( \kappa \)-carbide formed in the present \( \kappa/\gamma \) microstructure must be studied in more detail with respect to its site-occupancy.

Efforts are made first by means of APT study with optimized data reconstruction trying to resolve the atomic distribution in \( \kappa \)-carbides. Also, a theoretical approach using DFT is employed to elucidate the site-occupancy and explain the off-stoichiometry from the energetic perspective.

### 5.2 Results

#### 5.2.1 APT-based analysis of site-occupancy

The elemental site-occupancy of an ordered phase directly determines its element-specific atomic distributions in space. In principle, APT, capable of 3D atomic mapping with a near-atomic resolution and an equal sensitivity to all elements, could provide insights into the site-occupancy of ordered phases.

One approach recently reported is the utilization of the so-called spatial distribution maps (SDM) (Geiser et al., 2007; Gault et al., 2012a). They are based on an algorithm examining the local neighborhood of atoms by creating histograms of vectors between all atoms and their respective surrounding neighbors in three dimensions (Gault et al., 2012b). The SDM usually employed for site-occupancy analysis is the 1D- or \( z \)-SDM, which is a 1D distribution of the offset between atoms and their respective reference atoms along a specific direction (often near the \( z \) direction where the resolution is best).
Chapter 5. Off-stoichiometry and site-occupancy of κ-carbides

A 1D-SDM can be computed perpendicular to a set of crystallographic planes, which then reveals the atomic distribution of a pair of species along the specific plane normal. A set of peaks will show up, corresponding to the relative positions of atomic planes with respect to the reference atoms. Ion-specific 1D-SDMs, thereby, can unveil the relative distributions of ion species on particular crystallographic planes, which give hints on the probabilities of ion species occupying certain positions. Here, in this work, firstly the SDM analysis is applied onto the experimental data and subsequent SDM simulations are executed as an attempt to better understand the experimental results.

5.2.1.1 Experimental spatial distribution maps

Crystallographic information is compulsory for such an analysis. Also, the APT reconstruction should be optimized to resolve the lattice planes in the analysis volume (Moody et al., 2009).

For the studied 24h-aged alloy, a {002} fcc crystallographic pole is observed in the vicinity of the detector center (Figure 5.1(a)). The SDMs can then be created along the [002] plane normal (Figure 5.1(b)). The reconstruction parameters of the voltage reconstruction algorithm are tuned in such a way that the peaks in the SDMs exhibit distinct Gaussian shapes and the peak-to-peak distance, i.e. the {002} inter-planar distance \( d^{(002)} \), fits well with the experimental lattice parameter of the \( \gamma \)-matrix \( \sim 0.37 \) nm (section 4.2.2.2) (Gault et al., 2012b). Instead of single \( \gamma \)-phase, the computed data might encompass a few κ-carbide precipitates embedded in the \( \gamma \)-matrix. Due to the slight lattice misfit between \( \gamma \) and κ, the peaks are slightly broadened, or even split into twin peaks. The pole position is set as the reconstruction center. Figure 5.1(c) shows an exemplar thin slice of the resultant reconstructed volume with well resolved {002} lattice planes, allowing for the further atomic distribution analysis of ion species. The \( \kappa/\gamma \) interface is visualized by a C iso-concentration surface at a threshold value of 9.0 at.%. The atomic planes are seen to be continuous across the \( \kappa/\gamma \) interface, confirming coherent κ-carbide precipitates.
Chapter 5. Off-stoichiometry and site-occupancy of κ-carbides

Figure 5.1. A demonstration of the optimized reconstruction with resolved lattice planes using spatial distribution maps (SDMs): (a) The detector event histogram with the presence of a {002} fcc crystallographic pole; (b) z-SDM of all elements computed within a cylindrical region around the pole with a radius of 2 nm, the peak-to-peak distance of which is tuned to fit with the experimental lattice parameter of the fcc γ-matrix ~0.38 nm; (c) A thin slice of the resultant reconstructed volume near the pole, clearly showing the {002} lattice planes. The κ-carbide is visualized by a C iso-concentration surface of 9.0 at.%. z-SDMs: spatial distribution maps along the z-direction, i.e. perpendicular to {002} planes here.

To study the elemental site-occupancy of the ordered κ-carbide precipitates, a square zone with an edge length of 6 nm around the pole position are cropped throughout the reconstructed volume. As an analogy to the way described for the composition determination in section 4.2.1, C iso-concentration surfaces of ≥10 at.% and ≤7 at.% are again exploited here to isolate the data for the κ-carbides and γ-matrix, respectively. The γ-matrix is also of interest since its SDM analysis will answer the haunting suspicion about whether there is any ordering in the γ-matrix, affecting the dislocation motion.
The SDMs created for substitutional element pairs in both sub-datasets are present in Figure 5.2(a,b). C-atom-related pairs are not plotted because the C distribution on atomic planes are almost overwhelmed by noises as a result of the complex evaporation behavior of carbon in such a high C-containing alloy (Marceau et al., 2013). For a completely disordered γ-phase, all the substitutional atoms should occupy all the fcc sub-lattices with a same probability and are equally away from each other, resulting in the theoretical {002}-SDMs shown in Figure 5.2(c). The experimentally observed γ(002)-SDMs (Figure 5.2(a)) exhibit similar peak shapes to the theoretical results, suggesting that the substitutional atoms are randomly distributed. The γ-matrix is a disordered phase.

**Figure 5.2.** z-SDMs of substitutional element pairs along the {002} pole of (a) γ-matrix and (b) κ-carbide precipitates in comparison to corresponding theoretical expectations for (a) disordered γ-phase and (b) ideal stoichiometric (Fe₂Mn)AlC κ-carbide with their unit cells schematically shown in the inset images. z-SDMs: spatial distribution maps along the z-direction, i.e. perpendicular to {002} planes here.
In contrast to the clearly resolved SDMs of the γ-matrix, those of κ-carbide are noisy (Figure 5.2(b)). On the one hand, this is due to the limited atomic data. The κ-carbide precipitates with a volume fraction of ~20% (section 4.2) have a much smaller sub-volume in the pole vicinity as compared to that of the γ-matrix. On the other hand, with higher solute contents, particularly carbon, the κ-carbides show a more complicated evaporation behavior. Nevertheless, in the plotted κ_{(002)}-SDMs (Figure 5.2(b)), there seem to be small humps, as highlighted by black arrows, at the half {002} interplanar distance in the SDM of Al-Al pair, which is surprising. Given the classical κ-carbide of L’12 crystal structure, the Al atoms should solely occupy the corner sites whereas Fe and Mn atoms sit only at the face-centered positions. Following this, unlike Fe or Mn atoms occurring on all planes, Al atoms should only reside alternative planes and the peak-to-peak distance of the Al-Al distribution along [002] should be equal to the {002} interplanar distance $d_{(002)}^{\kappa}$ instead of half of it (Figure 5.2(d)). The presence of the in-between humps indicates that there might be Al atoms sitting at the face-centered positions. The noisy κ_{(002)}-SDMs, however, are not convincing enough to make a solid conclusion. It is not completely sure whether the humps or the fluctuations are simply a result of noise or what the contribution of the noise is. One approach to find it out is via data simulation as present in the next section.

### 5.2.1.2 Data simulation for spatial distribution map analysis

SDM simulation is one possibility to evaluate the effect of noise on the plotted SDMs. In addition, usually the probability that one species occupies a specific sub-lattice site is inaccessible simply by plotting the SDM. Data simulation can be an attempt for such a quantitative analysis. The core idea of the SDM simulation is to understand the experimental SDMs by comparing them with SDMs of a series of simulated data taking into account of varying parameters, such as noise levels and site-occupancy scenarios.

The bottleneck for a quantitative SDM analysis is to determine the peak damping function, which describes how the peak intensities attenuate from the central to side peaks due to radial data analysis. Since SDM is principally a modified 3D radial distribution function (RDF) (Gault et al., 2012b), the inter-atomic distances between one reference atom and its surrounding neighbors are recorded in a histogram radially.
from the center reference atom to a series concentric shells in 3D volume. As the offset distance increases, i.e. further away from the central lattice plane, the total atom count decreases as a result of the reduced probed volume. Therefore, the intensities of peaks in a z-SDM along a crystallographic direction would naturally damp from the center to both sides. Such a peak damping is inherited from the RDF algorithm. The isolation of this damping, as a result of the algorithm itself, from the material signal is the prerequisite for a quantitative SDM analysis. This is not simple. Moreover, embedding a specific phase in an analysis volume adds complexity to the determination of the algorithmic damping. Commonly, the data of this phase is filtered out from the matrix by an elemental iso-concentration surface, the 3D contour of which, probably varies from site to site. This effect could be too intricate to be expressed by analytical functions. In short, it is almost impossible to directly quantify the algorithmic damping of SDMs for precipitates or secondary phases.

In this work, a short-cut is proposed to circumvent the above-mentioned problems during SDM simulation. Instead of trying to determine the algorithmic damping of the experimental data and apply it to simulated data, the SDM is performed on simulated data delineated by the same filtering contour (iso-concentration surface) used for experimental SDMs. Therefore, when comparing simulated and experimental SDMs, there should be no difference coming from algorithmic damping and any difference should be explained by other factors.

In this spirit, the SDM simulation was carried out as follows.

1. An artificial atomic dataset of κ-carbide (L’12 structure) was generated in the form of a ‘.POS’ file, the format of which was explained in (Gault et al., 2012b). A custom Matlab script was developed for it. The site-occupancy of the L’12 unit cell, including atom species and their probabilities of occupying different sub-lattices, can be tuned. For the sub-lattice having more than one kind of atom or with vacancies, atoms, as well as vacancies, are all randomly distributed.

2. The simulated dataset and the experimental data (limited to the vicinity of the pole as described above) were merged together into one ‘.POS’ file. To distinguish the two datasets, they were differentiated by a mass spectrum shift: the ions in the experimental data of a mass-to-charge-state ratio above 100 were erased (no valuable information in this regime) and 100 Da were added to the
mass-to-charge-state ratio values of ions in the simulated data. The noise and detection efficiency of 37% (to compare with the experimental data obtained from LEAP 3000X-HR) (Larson et al., 2013) for the simulated data were introduced at this step.

3. The 10 at.% C iso-concentration surfaces based on the experimental data were used to filter out and subsequently export the core part of the κ-carbides, including the experimental and simulated data.

4. z-SDMs of substitutional element pairs are plotted for both datasets. The influence of noise level and site-occupancy on SDMs are studied by varying corresponding parameters in the simulated data.

Figure 5.3 summarizes the [002] SDMs of simulated data with varying noise levels and site-occupancy scenarios (Figure 5.3 (b-h)) in comparison to those of the experimental data (Figure 5.3(a)). Firstly, the influence of noise level on the SDMs is studied using the ideal (Fe2Mn1)Al1C1 structure (Figure 5.3(b-d)). Then at a fixed noise level, the effect of MnAl (Figure 5.3(e-f)) and AlMn (Figure 5.3(g-h)) anti-sites are evaluated.

Since the APT spatial resolution can be estimated by a Gaussian function fitting to atomic distribution (Gault et al., 2012b), the noise is introduced by adding a displacement Δ to each atomic coordinate in all x, y, z dimensions, which is a product of a random scalar drawn from the Gaussian distribution and the resolution δ. The depth resolution (z-δ) is considered one fourth of the lateral resolution (x/y-δ) because it is found that the spatial resolution is much better in z-dimension than in x-y plane (Gault et al., 2012b). Three different noise levels (z-δ= 0.05, 0.1 or 0.15 nm) are studied (Figure 5.3(b-d)).

**Figure 5.3.** (Figures see below on the next page) Spatial distribution maps (SDMs) along the [002] of (a) experimentally measured and (b-h) simulated κ-carbides: (b-d) simulated ideal (Fe2Mn1)Al1C1 κ-carbides with varying noise levels: (b) z-δ= 0.05 nm; (c) z-δ= 0.1 nm; (d) z-δ= 0.15 nm; (e-h) simulated off-stoichiometric κ-carbides (z-δ= 0.05 nm): (e) (Fe2Mn1)(Mn0.1Al0.9)C1, (f) (Fe2Mn1)(Mn0.5Al0.5)C1, (g) Fe2(Mn0.9Al0.1)(Mn0.2Al0.8)C0.6, (h) Fe2(Mn0.5Al0.5)(Mn0.6Al0.4)C0.6. To distinguish the simulated data, ‘S.’ prefixes are added to their legends.
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In the ideal \((\text{Fe}_2\text{Mn}_1)\text{Al}_1\text{C}_1\ \text{L’1}_2\) structure (Figure 1.1), there are two sub-lattices for substitutional atoms, i.e., the corner Al and face-centered Fe/Mn sites in the unit cell. With a low noise level (\(z-\delta=0.05\) nm, Figure 5.3(b)), such a site-occupancy can be well resolved by the \(\kappa_{[002]}\)-SDMs. The peak-to-peak distance of the Al-Al distribution is equal to the lattice parameter of the κ-carbide, indicating that Al atoms only reside on alternative \(\{002\}\) planes and therefore the corner sub-lattice. In contrast, the peak-to-peak distances of the Fe-Fe and Mn-Mn distributions correspond to the \(\{002\}\) interplanar distance, suggesting that Fe and Mn atoms appear on all \(\{002\}\) planes, i.e., the face-centered sub-lattice. This can also be noticed from the Fe-Al and Mn-Al distributions whose first prominent peaks show up at a \(z\)-offset of \(\pm 0.2\) nm instead of 0 nm. This finding implies that most atom pairs do not share the same \(\{002\}\) lattice plane but they are \(\pm 0.2\) nm away from each other in \(z\). However, for the distribution of Fe/Mn-Al in the ideal structure, there should also be a small probability of sharing the same plane (a small hump at the \(z\)-offset equal to 0 nm), which is now not obviously seen due to the fluctuation caused by noise. It is worth noting that although the general peak shape and relative distance fit with the expectation, a low noise level of \(z-\delta=0.05\) nm has added zig-zag fluctuations to the peaks.

As the noise level increases to \(z-\delta=0.1\) nm (Figure 5.3(c)), more fluctuations are introduced to the atomic distribution peaks, which have significantly broadened. Peak broadening and fluctuations overwhelm most material signals. Only the Al-related distributions, Al-Al, Mn-Al and Fe-Al, still maintain peaks beyond background, among which only the Al-Al pair has decent peak shape. This is due to the fact that in the ideal \((\text{Fe}_2\text{Mn}_1)\text{Al}_1\text{C}_1\ \text{L’1}_2\) structure, Al atoms are more sparsely distributed along the \([002]\) direction than Fe and Mn atoms and hence less sensitive to the depth resolution. When the noise level reaches \(z-\delta=0.15\) nm (Figure 5.3(d)), no effective peak can be identified in any distribution of atom pairs. The noise completely obscures the atomic distribution.

From Figure 5.3(b-d), it is found that the noise level has a critical effect on the accessibility of atomic distribution information. Even for the same ordered structure, the limited resolution can remarkably alter the SDMs, including peak intensity, broadening and local fluctuation. This points out the necessity of a proper evaluation of spatial resolution for the quantitative site-occupancy analysis.
To clearly reveal the influence of substitutional anti-site on z-SDMs, a low noise level of $z-\delta = 0.05$ nm is used to examine different scenarios with varying anti-sites. The Mn$_{\text{Al}}$ anti-site, i.e. occupation of Al sites by Mn atoms, is first studied (Figure 5.3(e-f)). This is because the experimentally measured $\kappa$-carbide composition is Fe$_2$Mn$_{1.1}$Al$_{0.9}$C$_{0.6}$. As compared to the ideal Fe$_2$Mn$_1$Al$_1$C$_1$, the first guess would be whether there are extra Mn atoms substituting corner-site Al atoms. With the increase of the Mn$_{\text{Al}}$ anti-site fraction from 0, 10% to 50%, i.e. from (Fe$_2$Mn$_1$)Al$_1$C$_1$ (Figure 5.3(b)), (Fe$_2$Mn$_1$)(Mn$_{0.1}$Al$_{0.9}$)C$_1$ (Figure 5.3(e)) to (Fe$_2$Mn$_1$)(Mn$_{0.5}$Al$_{0.5}$)C$_1$ (Figure 5.3(f)), the observed most remarkable trend is the appearance and enhancement of peaks at $z$-offsets of 0 or $a_k$ in the Mn-Al distribution. As more Mn atoms occupy the Al corner sites, more Mn atoms share the corner-site-containing {002} planes with Al atoms. Other than this, there are only slight peak intensity changes for Fe-Mn and Mn-Mn distributions.

Recalling the possible presence of Al$_{\text{Fe/Mn}}$ anti-site defects (Figure 5.2), its effects on SDMs are also investigated. Here two assumptions are made: (i) Al atoms substitute Mn atoms forming Al$_{\text{Mn}}$ anti-site; (ii) the total composition sticks to the experimentally measured composition Fe$_2$Mn$_{1.1}$Al$_{0.9}$C$_{0.6}$, i.e. the increase of Al$_{\text{Mn}}$ anti-site fraction is accompanied by a simultaneous increase of Mn$_{\text{Al}}$ anti-site fraction. As the Al$_{\text{Mn}}$ anti-site fraction increases from 10% to 50%, i.e. from Fe$_2$(Mn$_{0.9}$Al$_{0.1}$)(Mn$_{0.2}$Al$_{0.8}$)C$_{0.6}$ (Figure 5.3(g)) to Fe$_2$(Mn$_{0.5}$Al$_{0.5}$)(Mn$_{0.6}$Al$_{0.4}$)C$_{0.6}$ (Figure 5.3(h)), the peak-to-peak distance of the Al-Al distribution becomes half of the lattice parameter. The relative peak intensities of Al-related pairs are also obviously affected in terms of relative peak intensities.

Although the effect of various potential site-occupancy scenarios on the SDMs are well revealed and quantitative analysis could be viable by tuning defect concentrations (Figure 5.3(e-h)), the simulated SDMs do not really reproduce the original experimental data in terms of peak shapes and relative peak intensities (Figure 5.3(a)). The primary discrepancy is the peak damping. The non-central peaks in the experimental SDMs rapidly dampen and their intensities are only slightly above the noise level (Figure 5.3(a)), while at a spatial resolution of 0.05 nm the peaks in the simulated data have a much weaker damping (Figure 5.3(b,e-h)). Since the simulated data follow the same contour as the experimental data, the damping difference is not resultant from the edge
effect of radial distribution examination or the surface roughness of the κ-phase. Instead, it is probably due to the spatial noise, which is found to have much stronger influence on the profiles of SDMs (Figure 5.3(b-d)) than site-occupancy variants (Figure 5.3(e-h)). Because of trajectory aberrations and local magnification, the determination of spatial resolution in APT is challenging (Gault et al., 2012b). Instead of the chosen test value of $z-\delta= 0.05$ nm, the actual spatial resolution of atoms is unknown and might not be constant throughout the dataset.

5.2.2 DFT-based investigations of off-stoichiometry and site-occupancy

Since the experimental analysis of site-occupancy is challenging, a viable theoretical approach to elucidate the site-occupancy in κ-carbides is DFT. Therefore, in the following, the energetics and probabilities of different site-occupancy scenarios are evaluated within DFT, trying to explain the off-stoichiometry of κ-carbides. This part of work was done by Poulumi Dey and Tilmann Hickel.

5.2.2.1 Metal and C sub-lattices interchange

The possibility of C vacancies is first evaluated by computing the energy of Mn-free Fe$_{24}$Al$_8$C$_8$ κ-carbide with an interchange of a metal atom (Fe/Al) and an interstitial atom (C). It is found to be approximately 11 eV higher than the κ-carbide without such an interchange. Also the scenarios that Al (or Fe) from the matrix occupies the interstitial C site yielding a κ-carbide with Fe$_{24}$Al$_8$(Al$_1$C$_7$) or that C from the matrix occupies a Fe (or Al) metal site yielding Fe$_{24}$(Al$_1$C$_1$)C$_8$ are all found energetically unfavorable, which in turn indicates that metal atoms stick to substitutional sites, i.e. face-centered and corner sites, and C vacancies exist.

5.2.2.2 Al vacancies and Fe$^{\gamma}_{Al}$/Mn$^{\gamma}_{Al}$ anti-sites

Since the experiments anticipate rather large defect concentrations in the order of 10% (discussed explicitly in section 5.3.1), the Fermi distribution

$$c = 1/[1 + \exp(E_f/k_B T)]$$

(5.1)
rather than the Boltzmann distribution (Centoni et al., 2005) is used to account for the defect configurational entropy at finite temperatures. Here, $E_f$ is the 0 K formation energy as obtained from DFT, $T$ is the temperature and $k_B$ the Boltzmann constant. The Fermi distribution prevents that two or more defects are placed at the same lattice site.

In order to consider off-stoichiometric configurations for Al, the impact of Al vacancies in the $\kappa$-carbide is investigated by calculating the formation energy of a vacancy at the Al site using the expression

$$E_f(Vac_{Al}) = E[(Fe_{16}Mn_8)(Al_7Vac_1)C_8] + (\mu_{Al} + \mu_{Al}^0) - E[(Fe_{16}Mn_8)Al_8C_8].$$

Assuming thermodynamic equilibrium between the carbide and the surrounding matrix, the chemical potential $\mu_{Al}$ is determined by the composition of the matrix material (Table 4.1), whereas $\mu_{Al}^0$ is the T=0 K reference energy (Dey et al., 2016). $E[(Fe_{16}Mn_8)(Al_7Vac_1)C_8]$ and $E[(Fe_{16}Mn_8)Al_8C_8]$ are bulk energies of $\kappa$-carbide with and without a vacancy, respectively. The calculations show that the vacancy formation energy can be as large as 2.62 eV, if an unstrained $\kappa$-carbide is assumed, yielding a diminishingly low Al vacancy concentration ($\sim 10^{-16}$) at the aging temperature of 600°C. The Al vacancy formation energy decreases to $\sim 2.47$ eV under consideration of hydrostatic strain induced by the coherency between the matrix and precipitate, which does not significantly alter the Al vacancy concentration. Interestingly, the strain dependence is much more severe in the case of C vacancies as shown in (Dey et al., 2016). In fact, the experimentally observed C off-stoichiometry is a direct consequence of the reduction of inherent elastic strain in the coherent $\kappa/\gamma$ system. The crucial role of elastic strain in pushing away C from $\kappa$-carbide is further demonstrated by the lower C concentration in coherently strained grain interior (GI) $\kappa$-carbides than the incoherent GB $\kappa$-carbides (see section 6.2). However, for the formation of Al vacancies, the elastic strain field is found to have a negligible effect which is consistent with the chemical composition measured by APT (Dey et al., 2016). While there exists a noticeable difference in the C concentrations in GI and GB $\kappa$-carbides, the difference in Al concentration is smaller. It can be thus concluded that the formation of Al vacancies in $\kappa$-carbides at 600°C is not energetically favorable and fails to explain the off-stoichiometric Al concentrations in $\kappa$-carbides, which also indicates that the substitutional sites are completely occupied by metal atoms.
The next possible scenario considered to explain the Al depletion in the κ-carbides is the presence of Fe or Mn anti-site atoms at the Al sub-lattice. Considering the trend observed by APT that during precipitation Al partitions into κ-carbides while Fe and Mn out of them (Figure 4.2(c), Table 4.1), this is a consequence of an incomplete de-mixing of the metal atoms on the fcc sub-lattices during precipitate formation. The point defect would still obey stoichiometry, if at the same time an Al anti-site on the Fe/Mn sub-lattice is formed. However, the results reveal that the formation of such stoichiometry conserving defect pairs is energetically not favored, because the Al anti-site has a high formation energy of more than 1 eV. The incomplete de-mixing must therefore be explained assuming a thermal equilibrium with the surrounding matrix material, as captured by the following expressions for the formation energies of such MnAl or FeAl anti-sites:

\[
E_f(Mn^{\gamma}_{Al}) = E[(Fe_{16}Mn_8)(Mn_1Al_7)C_8] - (E[(Fe_{16}Mn_8)Al_8C_8] + (\mu_{Mn} + \mu_{Mn}^0) - (\mu_{Al} + \mu_{Al}^0)),
\]

\[
E_f(Fe^{\gamma}_{Al}) = E[(Fe_{16}Mn_8)(Fe_1Al_7)C_8] - (E[(Fe_{16}Mn_8)Al_8C_8] + (\mu_{Fe} + \mu_{Fe}^0) - (\mu_{Al} + \mu_{Al}^0)).
\]

Here, E[(Fe_{16}Mn_8)(Mn_1Al_7)C_8] and E[(Fe_{16}Mn_8)(Fe_1Al_7)C_8] are the bulk energies of a κ-carbide with a Mn or Fe anti-site atom at the Al sub-lattice. As before, \(\mu_X\) (X=Mn, Al or Fe) is the chemical potential of element X in the surrounding γ matrix and \(\mu_X^0\) are the T=0 K reference potentials. The anti-site formation energies are computed as a function of lattice constant in order to elucidate the impact of strain induced by the surrounding γ matrix on anti-site formation (yellow shaded region in Figure 5.4). Comparing the results for the pure anti-sites (squared symbols in Figure 5.4), it is found that the Fe anti-site formation energies are substantially higher than for Mn and will be therefore excluded in the subsequent analysis.

The formation energies can then be used to calculate the equilibrium concentrations of Mn and Fe anti-sites using equation (5.1). However, the resulting concentration of Mn anti-sites at the equilibrium lattice constant (approx. 3.78 Å) in the absence of C vacancies is low (~10^{-5}) and undergoes only a negligible increase (to 10^{-4}) under volumetric compression (to 3.6 Å, the lattice constant of the γ matrix). These values are still much lower than the Al depletion measured by APT (~10^{-1}), which is discussed in
detail later in Section 5.3.1. Hence, a strain effect alone is unable to explain the Al depletion within the κ-carbides.

Figure 5.4. Formation energies and concentrations of Fe\textasciigreek{\textalpha{}}\textsubscript{Al} and Mn\textasciigreek{\textalpha{}}\textsubscript{Al} anti-sites as a function of lattice constant for different C environments. The squared symbols in the upper panel mark the pure anti-site, whereas the circles mark complexes of anti-sites with a certain number of adjacent C vacancies, Vac\textsubscript{C}. In the lower panel a sensitivity analysis for the dependence of Mn anti-site concentration for different equilibrium temperatures and total C concentrations in the carbide is performed. The possible change of the κ lattice constant constant (with composition Fe\textsubscript{2.0}Mn\textsubscript{1.125}Al\textsubscript{0.875}C\textsubscript{0.625}) due to coherency strain to the γ matrix is highlighted by the yellow shaded region, where a\textsubscript{γ+κ} indicates the situation for an equal volume fraction of both phases. This DFT work was done by Poulumi Dey and Tilmann Hickel.
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5.2.2.3 Combined C depletion and elastic strain effect on Mn\textsuperscript{γ}Al

antisites

The experimental determination of κ-carbide composition suggests that not only Al but also C is depleted. The experimental composition (Table 4.1) has a C concentration of 13.2 at.%, i.e. lower than the stoichiometric 20 at.% C. Therefore, next the combined effect of C vacancies and elastic strain on the Mn anti-site formation in a supercell (Fe\textsubscript{16}Mn\textsubscript{8})(Mn\textsubscript{1}Al\textsubscript{7})(C\textsubscript{8}zVac\textsubscript{z}) is studied, where the 40 sites contain z vacant body-centered interstitial sites (C vacancies) and an excess Mn atom on a Al-site as compared to the ideal (Fe\textsubscript{16}Mn\textsubscript{8})Al\textsubscript{8}C\textsubscript{8} with all sites (40) being completely occupied. Choosing only z=3, which would be closest to the experimental composition, would correspond to a highly ordered vacancy distribution. Since the C vacancy interaction energies are too small (approx. 0.1 eV) to stabilize ordering effects at the annealing temperature of 600°C, a random distribution of C vacancies is assumed. The probability \(P(z)\) of \(z\) vacancies on the C sub-lattice adjacent to the considered anti-site, i.e., in the second nearest neighbor position, can be calculated using the following expression,

\[
P(z) = \frac{N!}{(z!)(N - z)!} (p)^z (1 - p)^{(N-z)}
\]  

(5.5)

where \(N\) is the total number of adjacent sites on the C sub-lattice (i.e., \(N=8\)) and \(p\) is the probability that a particular site is vacant (i.e., \(p=0.392\), see Table 5.1). Using this combinatorial approach, not only three (\(P=28\%\)), but also one (\(P=10\%\)), two (\(P=22\%\)) and four (\(P=23\%\)) second neighbor vacancies have a high probability to occur in a sample with the given composition.

In Figure 5.4, the presence of C vacancies next to the Mn\textsuperscript{γ}Al anti-site is clearly noticed to reduce the anti-site formation energy. While the stabilization of the anti-site increases with increasing number of adjacent C vacancies, the strongest effect is observed for the first vacancy (i.e. (Fe\textsubscript{16}Mn\textsubscript{8})(Mn\textsubscript{1}Al\textsubscript{7})(C\textsubscript{7}Vac\textsubscript{1}), see also section 5.3.2). The effect of vacancies alone is, however, not sufficient to explain the experimental anti-site concentrations. Even configurations with no adjacent C atoms (i.e. \(z=N=8\)) have at the equilibrium lattice constant \(a_c^{\text{DFT}}\) still an anti-site formation energy of \(~0.4\) eV, which is too large to yield substantial anti-site concentrations. A remarkable result is the strong dependence of the anti-site formation energy on volumetric strain, as soon as C vacancies are present on adjacent sites (Figure 5.4). Under large volumetric
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compression, e.g., if the volume fraction of κ-carbides is too small and thus the lattice constant of the coherent composite is close to that of the γ-phase, the κ-carbide even becomes unstable, as indicated by the negative formation energy of the anti-site.

Using the above approach, the anti-site concentration for a given temperature can be computed by superimposing all possible configurations of adjacent C atoms. The results are shown in the lower panel in Figure 5.4 and show an increase by several orders of magnitude (from $10^{-4}$ to $10^{-1}$) as the κ-carbide undergoes volumetric compression due to the lattice misfit with the surrounding γ-matrix. Depending on the degree of compression of κ-carbide to the lattice constant of the surrounding γ-matrix (3.6 Å), the corresponding anti-site concentration is in the order of $10^{-1}$ (see section 5.3.2 for details).

5.3 Discussion

5.3.1 Off-stoichiometry and site-occupancy of κ-carbides

The DFT calculations have revealed that (a) metal atoms are unlikely to occupy interstitial C sites and vice versa (section 5.2.2.1); (b) there is a full occupation of substitutional sites since the formation of Al vacancies is not favored (section 5.2.2.2). Considering (a) and the APT-measured reduced C content (13.2 at.% as shown in Table 4.1) as compared to the ideal stoichiometry (20 at.%), the existence of C vacancies is confirmed. Since the existence of vacancies scales the elemental composition differently, the description in terms of atomic percentage (Table 4.1) is translated into a chemical formula $\text{Fe}_a\text{Mn}_b\text{Al}_c\text{C}_x$. Here $a+b+c=4$ is the number of substitutional metal sites in a unit cell of L’12 structure and $x\leq 1$ is the portion of body-centered interstitial sites occupied by C. The fitting of the measured composition into such a form gives ($\text{Fe}_{2.00}\text{Mn}_{1.09}\text{Al}_{0.91})(\text{C}_{0.61}\text{Vac}_{0.39})$, fulfilling the substitutional/body-centered interstitial site ratio of 4:1. As compared to the nominal (Fe,Mn)$_3$AlC perovskite, there is not only C vacancies but also an Al depletion in conjunction with an excess of (Fe+Mn). As shown in Table 5.1, instead of occupying 25% of the substitutional sites (corner sites), Al atoms only occupy 22.8% of them. In other words, 8.8% of the corner sites are not occupied by Al. This is not apparent, if the overall Al concentration of almost 20 at.% is considered.
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Table 5.1. Comparison of elemental site-occupancy of κ-precipitates between stoichiometric composition, APT analysis and DFT calculations.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Stoichiometry</th>
<th>APT analysis</th>
<th>DFT calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Fe, Mn)\textsubscript{3}AlC</td>
<td>Fe\textsubscript{2.00}Mn\textsubscript{1.09}Al\textsubscript{0.91}C\textsubscript{0.61}</td>
<td>Fe\textsubscript{2.00}Mn\textsubscript{1.125}Al\textsubscript{0.875}C\textsubscript{0.625}</td>
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<td>Occupation of substitutional sites (%)</td>
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<td>62.5</td>
</tr>
<tr>
<td>Concentration of C depletion (%)</td>
<td>0</td>
<td>39.2</td>
<td>37.5</td>
</tr>
</tbody>
</table>

The calculations show that Mn atoms rather than Fe atoms can fill the corner sites unoccupied by Al, if there is a C vacancy in the nearest-neighbor configuration and if the carbide is under volumetric compressive strain (Figure 5.4). If this is applied to the chemical formula, one obtains (Fe\textsubscript{2.00}Mn\textsubscript{1.09}Al\textsubscript{0.91}C\textsubscript{0.61})(Mn\textsubscript{0.09}Al\textsubscript{0.91})(C\textsubscript{0.61}Vac\textsubscript{0.39}). In terms of a 40 atom DFT supercell this composition is best represented by (Fe\textsubscript{16}Mn\textsubscript{8})(Mn\textsubscript{1}Al\textsubscript{7})(C\textsubscript{5}Vac\textsubscript{3}) (Figure 2.2(b)). The corresponding Mn\textsubscript{γ}/Al anti-site concentration at the experimental temperature of 600°C found by DFT calculations (Figure 5.4) is ~0.1 in the strained regime, which fits well with the experimental value of 8.8% (Table 5.1). The experimentally observed Al depletion can therefore be explained by the combination of Mn\textsubscript{γ}/Al anti-sites and C vacancies under compressive strain caused by the coherency of the κ-carbides. It is driven by the minimization of the lattice misfit and hence the elastic strain between the coherent κ-carbide precipitates and the γ-matrix.
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5.3.2 Underlying issues related to DFT

The amount of Al depletion derived from the ab initio approach is affected by uncertainties, for which a sensitivity analysis is performed. First, the calculations are based on the assumption of a thermal equilibrium that is determined by the experimentally employed annealing temperature of 600°C. The impact of this assumption is estimated by considering in addition two other temperatures that are 300 K below and above the annealing temperature, respectively (Figure 5.4, lower panel, color gradient). For these (rather extreme) choices, the anti-site concentration changes depending on the strain state by up to one order of magnitude. However, the qualitative picture remains unchanged.

Second, the derived Al depletion is based on the assumption that in the experimental samples the C vacancies are mesoscopically homogeneously, but locally randomly distributed. To estimate the impact of C fluctuations, the overall C concentration is therefore changed from the experimental value (13.2 at.%) to 11 at.% and 16 at.%, respectively (Figure 5.4, lower panel, red shading). As can be seen this has only little impact (approx. factor 2) on the resulting anti-site concentration.

Consequently, as outlined in the result part, the predicted anti-site concentration mainly depends on the volumetric strain, which is a direct consequence of the coherency to the γ-matrix. Depending on the volume fraction of both phases (Dey et al., 2016), the equilibrium value of lattice parameter of the carbide-matrix composite can vary between the lattice parameter of κ-carbide and that of the γ-matrix (Figure 5.4, yellow shaded region). For the latter synchrotron radiation yielded 3.679 Å (section 4.2.2.2), slightly deviating from 3.6 Å as predicted by our DFT calculations. This discrepancy can be due to the approximation of the exchange-correlation functional in DFT. Further, the finite supercell size yields a small deviation between the experimental and theoretical composition (53.8Fe-25.8Mn-16.1Al-4.3C vs 54.5Fe-27.3Mn-15.2Al-3C, at.%, respectively), in particular a lower Al concentration that can result in different lattice constants. Another reason may be the assumption of an anti-ferromagnetic rather than a paramagnetic spin configuration. For consistency reason, in Figure 5.4 the DFT lattice constant of 3.6 Å is used for the lower boundary. Due to the above considerations, the lattice constant $a_{κ+γ}$ highlighted in Figure 5.4 for the composite (determined by taking
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the elastic strain energy into account) can only serve as an estimate, indicating that anti-site concentrations of several percent are predicted by the ab-initio approach.

In order to understand the surprisingly strong dependence of the anti-site formation energy on the C vacancy content in the regime of large volumetric strain, the effect of strain on the binding energy between Al and C in pure γ-Fe is investigated. The results show that this binding energy changes from repulsion to attraction when going from the strain free to the maximum strained configuration. The negligible effect of large volumetric strain on the anti-site formation in the absence of C vacancies (Figure 5.4) can, therefore, be explained such that the energy gain from the formation of Mn anti-site under strain is compensated by the stronger loss of Al-C binding energy. Once the first C vacancy is present, i.e. there are less C atoms than Al atoms in the system, the formation energy of Mn\textsubscript{Al} anti-site is significantly reduced (Figure 5.4).
Chapter 6

Phase equilibria in the κ/γ microstructure

6.1 Introduction

To meet miscellaneous application requirements, different Fe-Mn-Al-C steel grades have to be developed. A prerequisite for alloy design is the fundamental knowledge on phase equilibria and evolution during the production and thermomechanical treatment process. Though a lot of efforts have been spent in studying the microstructure and mechanical properties of various Fe-Mn-Al-C alloys, a general thermodynamic and kinetic database has not been fully developed for this quaternary system, except for a few thermodynamic modelling attempts offering partial maps (Chin et al., 2010; Lee et al., 2013; Kim et al., 2015). The construction of these thermodynamic descriptions for this multicomponent system was mainly realized by combining and modifying existing binary and ternary databases of constituents. Further experimental work is necessary to assess their validation. Moreover, in real applications, steel grades are commonly not in phase equilibria. The effect of factors other than thermodynamic properties, such as kinetics and elastic strain, on the microstructural evolution has to be evaluated. Hence, for the database development, more experimental contribution is required.
To this end, the alloy studied in this work is aged at 600°C for a prolonged time of 4 weeks or 12 weeks, referred to as the 4w-aged or 12w-aged samples, respectively. The aim is to reveal its phase equilibrium at this temperature and trace the microstructural evolution towards that. In order to better understand the evolution process, various techniques of different resolutions, ranging from μm- down to atomistic-scale, are utilized to characterize the microstructure, including SXRD, SEM-imaging/EBSD and APT.

6.2 Results

6.2.1 Prolonged-aged microstructure

Figure 6.1 shows the SEM microstructure of the 4w-aged and 12w-aged samples. At a low magnification (Figure 6.1(a)(c)), it is clearly shown that some GBs are decorated with coarse phases in a cellular morphology while most twin boundaries (TBs) are free of those. As the ageing time increases from 4 weeks (Figure 6.1(a)) to 12 weeks (Figure 6.1(c)), there is no obvious microstructural difference in terms of size and volume fraction of the GB phases. A zoom-in into a decorated GB region (Figure 6.1(b)) reveals that the cellular zones at GBs mainly consist of alternating lamellar phases which initiate at GBs and grow into GI.

The sample etching unveils the co-existence of GI and GB precipitates (Figure 6.1(d)). The precipitates in GI are the κ-carbides studied previously, which preserve the nanometer-scale size and seemingly not coarsen much after a prolonged ageing. Their grid appearance is probably due to particle stacks (Figure 3.1) inclined to the sample surface or agglomeration of particles within a stack as a result of slight coarsening. At the TB highlighted by blue arrows, no other phase is found apart from the κ-carbide precipitates.
Figure 6.1. SEM Microstructure of the (a)(b) 4w-aged and (c)(d) 12w-aged samples: (a)(c) overview of decorated grain boundaries (GBs); (c) alternative lamellar phases near GBs manifested by BSE contrast; (d) nanometer-sized grain interior (GI) and μm-scale GB protruding precipitates after etching. A GB with coarse precipitates along it and a twin boundary (TB) free of those are highlighted by red and blue arrows, respectively. The reaction fronts are marked by yellow dashed lines with the yellow arrows indicating their aggressing directions.

In contrast, additional coarse precipitates show up along the GB highlighted by red arrows. The nanometer-sized κ-carbides in the GB vicinity are not much affected; no precipitate free zone is observed next to this GB. Besides, there are two other GBs captured in this figure, which have cellular μm-scale colonies attached to them. The coarse colonies result from a phase decomposition behind the moving GBs (dashed yellow lines), which advance into the GI matrix at the expense of the GI microstructure, as highlighted by yellow arrows. This is a typical phase transition termed as ‘discontinuous precipitation’ (DP) (Hillert, 1972; Williams et al., 1976; Hirth et al., 1998; Manna et al., 2001). As an isothermal solid state phase transformation, DP is characterized by an abrupt discontinuous change in orientation and composition across
a migrating boundary. The swept regions of the matrix by advancing boundaries often transform into alternating lamellar phases which are more stable than the mother phase(s). The initial matrix could be a single phase supersaturated solid solution or have pre-existing fine-dispersed or lamellar precipitates embedded in the matrix. Hence, in the current alloy aged at 600 °C, the alternating lamellar phases behind migrating GBs are the more thermodynamically stable phases at this temperature than the previous coherent (κ+γ) phases in GI.

To identify the constituent phases of the GB DP colonies, a SXRD measurement was conducted on the 4w-aged sample. Wenwen Song performed this experimental work. The spectrum is plotted in Figure 6.2, together with that of the 24h-aged sample (Figure 4.5) as a comparison. In addition to the previously existing GI κ-carbides and γ-matrix, three new phases come up as ageing time increase from 24 hours to 4 weeks, i.e. GB κ₀-carbides, solute-depleted GB γ₀-phase and α-ferrite (Figure 6.2(a)). The GB κ₀/γ₀-phases are basically also κ-carbide and γ-austenite in terms of crystal structure but their morphology (Figure 6.1) and chemical compositions (see below in section 6.2.2 & section 6.2.3) are different from those of the GI κ-carbide and γ-austenite. For discrimination, subscript is used for the GB κ₀/γ₀-phases. Due to the same crystal structure and slight compositional difference (see below in Table 6.2 & Table 6.3), the lattice parameter differences between the two κ/κ₀-carbide phases are small. Twin κ/κ₀-peaks are therefore observed in the SXRD spectrum, especially at low 2θ angles (e.g. Figure 6.2(b)(c)). The compositional difference between γ/γ₀-phases (see below in Table 6.2 & Table 6.3), i.e. lattice parameter difference, is even smaller so that broad overlapped γ/γ₀-peaks are observed (e.g. Figure 6.2(c)). Since the GB κ₀-carbide precipitate is more solute-enriched of C as compared to the GI κ-carbide (see below in Table 6.2 & Table 6.3), the carbide with a bigger lattice parameter, i.e. SXRD peaks at smaller Bragg angles, should correspond to the GB κ₀-carbide. Likewise, the more solute-depleted GB γ₀-phase should have a smaller lattice parameter than the GI γ-phase. Besides the twin κ/κ₀- and overlapped γ/γ₀-peaks, small α-peaks are also found in the spectrum (Figure 6.2(a)(c)). Therefore, instead of alternating two product phases, the GB DP colonies contain three phases - κ₀, γ₀ and α.
Chapter 6. Phase equilibria in the κ/γ microstructure

Figure 6.2. Synchrotron x-ray diffraction (SXRD) spectrum of the 8Al-4w-aged sample in comparison to that of the 8Al-24h-aged sample: (a) overall spectra; (b) 2θ= (3.1-3.3) rad; (c) 2θ= (5.3-5.9) rad. The measurement was performed by Wenwen Song.

The lattice parameters and volume fractions of the phases obtained by the Rietveld method are listed in Table 6.1. The lattice parameters of the GI κ/γ-phases barely change as the ageing time increases from 24 hours to 4 weeks. In the 4w-aged GI κ/γ microstructure, the volume fraction of the κ-carbides is approx. 18.3% (\( \frac{12.0}{12.0+53.7} \times 100\% \)), which is close to the 20.1% in the 24h-aged sample. The 4w-aged GB DP (κ₀+γ₀+α) colonies have taken approx. one third of the whole microstructure. Within the colonies, the volume fraction of the γ₀-phase is about twice of that of the κ₀-carbide while there is only a small fraction of α-ferrite. Therefore, the observed alternating lamella phases (Figure 6.1(b)(d)) are primarily composed of κ₀-carbide and γ₀-phase. In contrast to the small lattice misfit of 1.4% for the GI coherent κ/γ-phases, the GB κ₀/γ₀-
phases have a much larger lattice misfit as 3.5%. Concerning their lamellar morphology, it is plausible that the GB $\kappa_0/\gamma_0$-phases are semi-coherent or even incoherent.

Table 6.1. Lattice parameters (a) and volume fractions ($V_f$) of the phases in the 4w-aged sample obtained by Synchrotron x-ray diffraction (SXRD) in comparison to those in the 24h-aged sample. N/A represents ‘not available’.

<table>
<thead>
<tr>
<th>Samples</th>
<th>a or $V_f$</th>
<th>$\kappa$</th>
<th>$\gamma$</th>
<th>$\kappa_0$</th>
<th>$\gamma_0$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4w-aged</td>
<td>a (Å)</td>
<td>3.733</td>
<td>3.681</td>
<td>3.792</td>
<td>3.663</td>
<td>2.899</td>
</tr>
<tr>
<td></td>
<td>$V_f$(%)</td>
<td>12.0</td>
<td>53.7</td>
<td>12.6</td>
<td>21.1</td>
<td>0.6</td>
</tr>
<tr>
<td>24h-aged</td>
<td>a (Å)</td>
<td>3.722</td>
<td>3.679</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>$V_f$(%)</td>
<td>20.1</td>
<td>79.9</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

6.2.2 Coarsening of grain interior precipitates

The low-magnification SEM observation (Figure 6.1(d)) and SXRD results (Table 6.1) suggest that there is no obvious difference between the GI $\kappa/\gamma$ microstructures of the 24h-aged and 4w-aged samples in terms of nanometer-scale particle size, phase lattice parameters and volume fractions. The coarsening behavior of the coherent GI $\kappa$-carbide precipitates is further studied in details by subsequent SEM measurement at a higher magnification and APT analysis at a near-atomic resolution on the 12w-aged sample, the longest aged sample in this study.

Figure 6.3(a) shows a SE micrograph of the etched 12w-aged sample. The $\kappa$-carbide precipitates, in a protruding and bright appearance, are clearly unveiled by the Nital etching. They are uniformly dispersed throughout the $\gamma$-matrix as “grids”. A closer examination of the “grids” reveals that they consist of individual particles with a small inter-spacing (Figure 6.3(b)), similar to the particle stacks previously observed in the 24h-aged sample (Figure 3.1). The particles in stacks are not agglomerated after the prolonged ageing. Figure 6.3(b) also distinctly shows a typical TB free from DP. It is noted that there are some regions of specific patterns, as highlighted by blue arrows (Figure 6.3(a)(c)). A zoom-in observation (Figure 6.3(c)) reveals that they are areas which are not etched sufficiently. The sensitivity of SE imaging to surface tomography gives rise to such shadow patterns. The regular alignment of these patterns to a certain direction is probably due to residual surface mechanical deformation induced by sample preparation.
Figure 6.3. SEM micrographs of the grain interior (GI) κ/γ microstructure of the etched 12w-aged sample: (a) uniform, protruding, bright, nanometer-sized κ-carbide precipitates embedded in the γ-matrix; (b) particle stacks composed of individual precipitates and a typical twinning boundary (TB) free from discontinuous precipitation (DP); (c) a zoom-in into a region containing surface patterns as highlighted by blue arrows, which result from inhomogeneous etching.
The GI κ/γ microstructure observed by APT is depicted in Figure 6.4. In the reconstructed 3D atom maps, the κ-carbides are visualized by 9 at.% C iso-concentration surfaces (Figure 6.4(a)). Cuboidal and plate-like particles in a size range of approx. 10-30 nm align into particle stacks along certain orthogonal directions, which is similar to the morphology and arrangement of the κ-carbides in the 24h-aged specimens (Figure 3.1). The κ/γ partitioning is revealed in Figure 6.4(b) by a 1D concentration profile along a particle stack through a cyan-highlighted cylindrical ROI in Figure 6.4(a). In analogy to the profile observed for the 24h-aged specimen (Figure 4.2(b)), Al and C atoms partition to the κ-carbides while the Mn partitioning is not obvious. The degree of Al and C partitioning between the κ-carbide precipitates and γ-matrix also looks similar to that in the 24h-aged specimen. No partitioning difference is noticed between these three particles and their γ-neighborhoods in this profile, which are of different sizes and shapes. The chemical compositions of the κ-carbides and γ-matrix are determined by individual mass spectrum analysis, same as the method adopted for the 24-aged specimen (section 4.2.1). The obtained compositions of the κ/γ-phases in the 12w-aged specimen (Table 6.2) are almost same as those in the 24h-aged specimen (Table 4.1), so do the corresponding elemental partitioning coefficients. A fitting of the measured κ-carbide phase compositions into the chemical formula \( \text{Fe}_a\text{Mn}_b\text{Al}_c\text{C}_x (a+b+c=4, x\leq1) \) (section 5.3.1) returns \( (\text{Fe}_{1.99}\text{Mn}_{1.10}\text{Al}_{0.91})(\text{C}_{0.60}\text{Vac}_{0.40}) \), which barely changes with respect to the off-stoichiometric formula of the κ-carbide precipitates in the 24h-aged specimens, i.e. \( (\text{Fe}_{2.00}\text{Mn}_{1.09}\text{Al}_{0.91})(\text{C}_{0.61}\text{Vac}_{0.39}) \) (section 5.3.1). Therefore, overall, as the ageing time increases from 24 hours to 4 weeks, the GI κ/γ microstructure barely changes in terms of precipitate size, volume fraction and chemical compositions. There is almost no coarsening of the GI nanometer-sized κ-carbide precipitates upon the prolonged ageing.
Figure 6.4. APT analysis of the grain interior (GI) κ/γ-phases in the 12w-aged sample: (a) reconstructed APT maps of C (purple), Al (green) and Mn (yellow) atoms. κ-carbide precipitates are visualized by a 9 at.% C iso-concentration surface; (b) 1D concentration profile of elements along the cyan cylinder (Φ=10 nm) in (b) with a bin size of 0.3 nm.

Table 6.2. Chemical compositions (at.%) of the grain interior (GI) κ-carbides $c_\kappa$ and γ-matrix $c_\gamma$ in the 12w-aged specimens determined by APT. Error bars indicate compositional fluctuations between different APT measurements, while the statistical errors are negligible.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_\kappa$</td>
<td>43.2±0.1</td>
<td>23.9±0.2</td>
<td>19.8±0.2</td>
<td>13.0±0.2</td>
</tr>
<tr>
<td>$c_\gamma$</td>
<td>54.3±0.1</td>
<td>25.8±0.1</td>
<td>16.1±0.1</td>
<td>3.8±0.1</td>
</tr>
</tbody>
</table>
6.2.3 Grain boundary discontinuous precipitation

The SXRD results indicate that in GB DP colonies, there is an α-ferrite phase in addition to the primary κ₀-carbide precipitates and solute-depleted γ₀-phase. To elucidate the phase morphology and distribution within the DP colonies, correlated fine EBSD scan and BSE imaging are utilized to study the GB regions in the 4w-aged sample.

A BSE image and corresponding EBSD phase map of the same region are shown in Figure 6.5(a-b). The DP colonies are mainly composed of alternating κ₀-carbide and γ₀-phase, the dark and bright phases of the lamellae in Figure 6.5(a), respectively. Although a fine step size of 50 nm is used for EBSD mapping, the lamellar constituents of the DP colonies are not resolved (Figure 6.5(b)). The alternating phases are entirely recognized as one austenitic phase. This is, on the one hand, due to the thin width of the κ-carbide lamellae in the order of 50-200 nm (the dark phase in Figure 6.5(c)) and probably their inclined alignment with respect to the sample surface, which leads to an overlay of the κ-carbide lamellae and γ-surrounding in the interaction volume. On the other hand, the similarity between the basic fcc and superlattice L’₁₂ crystal structures also adds difficulty onto the phase separation by diffraction patterns. In contrast, owing to its completely different bcc crystal structure and relatively thicker/more spherical morphology, the fine α-ferrite phase is well recognized by EBSD (Figure 6.5(b)). The volume fraction of the α-ferrite as determined by EBSD is only 0.4%, which is consistent with the SXRD result (Table 6.1). To better reveal the morphology and distribution of the α-ferrite with respect to the κ₀/γ₀-lamellae, they are highlighted in yellow in Figure 6.5(c), a zoom-in micrograph of the blue-outlined region in Figure 6.5(a), by comparing the corresponding BSE image and EBSD phase map at the same region in Figure 6.5(a,b). It is found that the α-ferrite phase sparsely scatter in the DP colonies and are often in close contact with κ₀-carbides, either occurring between two κ₀-carbides as small islands or showing up as a thin interlayer between the κ₀/γ₀-lamellae. Similar α-ferrite morphology and volume fraction is also found in the 12w-aged sample by EBSD and BSE imaging.
Figure 6.5. SEM microstructure of the grain boundary (GB) discontinuous precipitation (DP) colonies in the 4w-aged sample: (a) a BSE image showing the lamella morphology; (b) EBSD phase map of the region (a); (d) a zoom-in BSE image of the blue-outlined region in (a) with the α-ferrite phases outlined in yellow according to (b).
Chapter 6. Phase equilibria in the κ/γ microstructure

The chemical analysis of the GB DP phases, including phase compositions, interfaces and elemental partitioning between phases, is realized using APT. Needle-shaped specimens are prepared from DP colonies’ centers, away from both original GBs and reaction fronts. Figure 6.6 shows the APT analysis of the primary κ₀/γ₀-lamella without α-phases in the vicinity. In the reconstructed atom maps (Figure 6.6(a)), the κ₀-carbide is visualized by a 10.0 at.% C iso-concentration surface. Unlike the small cuboidal or plate-like GI κ-carbides embedded in the γ-matrix (Figure 6.4), a GB κ₀-carbide interlayer with a thickness of approx. 100 nm is observed between two γ₀ layers (Figure 6.6(a)). The κ₀/γ₀-interfaces are not completely planar but a bit curved, not parallel but inclined to each other, which is consistent with some κ₀/γ₀-lamellae observed in SEM micrographs (Figure 6.5(a)(c)).

A 1D concentration profile is generated across the κ₀/γ₀-interface (Figure 6.6(b)), revealing that all the solute atoms, including Mn, Al and C, partition to the κ₀-carbide. Despite the similar Al and C partitioning to carbides, an obvious distinction between the GI κ/γ- and GB κ₀/γ₀- partitioning is the clear Mn enrichment in κ₀-carbide with respect to the slight Mn depletion in κ-carbide (Table 6.2). Similar partitioning behavior is observed in several other κ₀/γ₀-specimens of the 4w-aged sample, as well as 12w-aged specimens. No apparent difference is noticed between the concentration profiles across the 4w-aged and 12w-aged GB κ₀/γ₀-lamellae.

The chemical compositions of the κ₀/γ₀-lamellae are determined by cropping out cuboidal ROIs and analyzing mass spectra for individual phases. Table 6.3 summarizes the obtained results. It is found that the Al and C compositions of the κ₀/γ₀-lamellae are almost same for the 4w-aged and 12w-aged specimens while the Mn compositions are slightly higher in the 12w-aged κ₀/γ₀-lamellae. The κ₀/γ₀ partitioning coefficients of the Mn, Al and C solutes in the 4w-aged and 12w-aged DP lamellae are determined as (1.09, 1.32, 7.04) and (1.10, 1.33, 7.21), respectively. The similar partitioning coefficients between the 4w-aged and 12w-aged κ₀/γ₀-lamellae suggest that the studied DP κ₀/γ₀-lamellae in the 4w-aged sample, and of course also the 12w-aged sample, have reached a chemical equilibrium state. The determined κ₀/γ₀ phase compositions are the thermodynamic equilibrium compositions at this ageing temperature of 600 °C. It is plausible that the generally higher Mn compositions of the 12w-aged κ₀/γ₀-lamellae as
Chapter 6. Phase equilibria in the $\kappa/\gamma$ microstructure

compared to those of the 4w-aged $\kappa_0/\gamma_0$-lamellae is due to a local Mn inhomogeneity (section 4.3.1.1).

Figure 6.6. APT analysis of grain boundary (GB) discontinuous precipitation (DP) $\kappa_0/\gamma_0$-lamella in the 4w-aged sample: (a) reconstructed maps of C (purple), Al (green) and Mn (yellow) atoms. The $\kappa_0$-carbide precipitate is visualized by a 10.0 at.% C iso-concentration surface; (b) 1D concentration profile of elements along the cyan cylinder ($\Phi=10$ nm) in (a) with a bin size of 0.3 nm.

Given that the $\kappa$-carbides have a chemical formula of $\text{Fe}_a\text{Mn}_b\text{Al}_c\text{C}_x$ where $a+b+c=4$ and $x\leq1$ (section 5.3.1), the fitting of the measured chemical compositions into such a form results in $(\text{Fe}_{1.7}\text{Mn}_{1.3}\text{Al}_{0.96})(\text{C}_{0.81}\text{Vac}_{0.2})$ for the GB $\kappa_0$-carbides ($\text{(Fe}_{1.70}\text{Mn}_{1.25}\text{Al}_{0.96})(\text{C}_{0.81}\text{Vac}_{0.19})$ and ($\text{Fe}_{1.69}\text{Mn}_{1.35}\text{Al}_{0.95})(\text{C}_{0.84}\text{Vac}_{0.16})$ for the 4w-aged and 12w-aged GB $\kappa_0$-carbides, respectively). In comparison to the GI $\kappa$-carbides ($\text{Fe}_{1.99}\text{Mn}_{1.10}\text{Al}_{0.91})(\text{C}_{0.60}\text{Vac}_{0.40})$ (section 6.2.2), the concentrations of the off-
stoichiometric defects, including Mn\textsubscript{Al} antisites and C vacancies, are distinctly reduced in GB \kappa_0-carbides.

**Table 6.3.** Chemical compositions (at.%) of the grain boundary (GB) \kappa_0/\gamma_0-lamellae \ci_0, \ci_0 in the 4w- and 12w-aged specimens determined by APT. Error bars indicate compositional fluctuations between different APT measurements, while the statistical errors are negligible.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>c</th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4w-aged</td>
<td>\ci_0</td>
<td>37.1±0.1</td>
<td>26.0±0.2</td>
<td>20.0±0.2</td>
<td>16.9±0.2</td>
</tr>
<tr>
<td></td>
<td>\ci_0</td>
<td>58.7±0.1</td>
<td>23.8±0.2</td>
<td>15.1±0.2</td>
<td>2.4±0.1</td>
</tr>
<tr>
<td>12w-aged</td>
<td>\ci_0</td>
<td>35.0±0.5</td>
<td>28.0±0.3</td>
<td>19.7±0.4</td>
<td>17.3±0.1</td>
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<tr>
<td></td>
<td>\ci_0</td>
<td>57.3±0.1</td>
<td>25.3±0.1</td>
<td>14.8±0.1</td>
<td>2.5±0.2</td>
</tr>
</tbody>
</table>

Besides the primary alternating \kappa_0/\gamma_0-lamellae, there are also some regions having the additional \alpha-phase. One needle-shaped APT specimen is prepared in such a way that all three phases (\kappa_0+\gamma_0+\alpha) are present in the same analysis volume (Figure 6.7). The inhomogeneous distribution of atoms (Figure 6.7(a)), especially the Mn and C atoms (Figure 6.7(c)(e)), demonstrates the presence of different phases. According to the Mn atom map (Figure 6.7(c)), it seems that there are two regions – one region I depleted of Mn and the rest other region II enriched with Mn. However, the C atom map reveals that the region II in Figure 6.7(c) seemingly having a homogeneous Mn distribution can be divided into several regions – two regions (III) with a similarly high C concentration are separated by one region (III) depleted of C. Hence, there are three phases of different Mn and C concentrations while their Fe or Mn compositional distinction is not straightforward. Given that Al is a ferrite former and Mn and C help stabilize austenite, the region I, repulsing both Mn and C, should be the \alpha-ferrite phase. Moreover, concerning that all solutes, Mn, Al and C, tend to partition to the \kappa_0-carbide in \kappa_0/\gamma_0-lamella (Figure 6.6), the region II having a higher C concentration should correspond to the \kappa_0-carbide while region III should represent the solute depleted \gamma_0-phase. The \alpha-phase in this specimen has a typical morphology as observed in SEM micrograph (Figure 6.5(c)), i.e. thin lamella attached to \kappa_0-carbide lamella.
Figure 6.7. 3D atom maps of an APT specimen containing $\kappa_0$, $\gamma_0$ and $\alpha$. three phases from the 4w-aged sample: (a) all atoms; (b) Fe (red); (c) Mn (yellow); (d) Al (green); (e) C (purple). The dashed lines outline the phase boundaries according to atom distributions.

The phase identification is further substantiated by generating iso-concentration surfaces and investigating elemental partitioning between phases (Figure 6.8). The iso-concentration surfaces of 9.0 at.% C (Figure 6.8(a)), 20.0 at.% Mn (Figure 6.8(b)) and 15.0 at.% Al (Figure 6.8(c)) clearly illustrate the $\kappa_0$-carbide, $\alpha$-ferrite and $\gamma_0$ phases, respectively. Correspondingly, 1D concentration profiles across the phase interfaces are used to qualitatively study the elemental partitioning between $\kappa_0$, $\alpha$ and $\gamma_0$ phases.
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- κ₀ vs. γ₀ (Figure 6.8(a)). Though having an α-ferrite phase in the vicinity, the κ₀/γ₀ partitioning is similar to that between the κ₀/γ₀-lamellae (Figure 6.6), i.e. Mn, Al and C atoms partition to the κ₀-carbide.

- κ₀ vs. α (Figure 6.8(b)). When a κ₀-carbide is in contact with an α-ferrite phase, it is not surprising that Mn and C are repulsed from the α-ferrite into the κ₀-carbide since they are generally recognized as austenite stabilizers (not favored by ferrite) (Klueh et al., 1988; Speer et al., 2003; Bleck, 2007) and found to be enriched in κ₀-carbides even with an austenitic surrounding (Figure 6.6, Figure 6.8(a)). In contrast, both having affinity with Al, the κ₀-carbide and the α-ferrite compete for Al. The concentration profile suggests that Al is slightly enriched in the α-ferrite. Similar elemental partitioning trends between the κ/α phases were also reported for the κ-carbide precipitation in a ferritic Fe-Mn-Al-C steel (Seol et al., 2013).

- α vs. γ₀ (Figure 6.8(c)). It is observed that Mn and C show clear partitioning to the γ₀-phase while Al partitions to the α-ferrite. This is consistent with the classical understanding of the stabilization effect of elements on ferrite and austenite phases, i.e. Mn and C facilitate austenite formation while Al is a ferrite stabilizer (Klueh et al., 1988; Speer et al., 2003; Bleck, 2007).

For a quantitative comparison of elemental partitioning between the κ₀/γ₀-lamellae and the (κ₀+γ₀+α) phases, the chemical compositions of the κ₀, γ₀ and α phases in the specimen in Figure 6.8 are determined by the same way as utilized for κ₀/γ₀-lamellae, i.e. cropping phases out via cuboidal ROIs and analyzing their mass spectra individually. The two κ₀-carbides are discriminated by κ₀₁ and κ₀₂ (Figure 6.8). Table 6.4 summarizes the results. The κ₀/γ₀ solute partitioning coefficients with an α-ferrite phase in the vicinity is obtained between the γ₀ and κ₀ phases, resulting in (1.05, 1.40, 5.31) for (Mn, Al, C) solutes. In comparison to the pure κ₀/γ₀-lamellae given in Table 6.3 (1.09, 1.32, 7.04), a distinct characteristic is the weaker C partitioning. This is due to the higher C content of the γ₀-phase in contact with the α-ferrite. The Al and C contents of the κ₀/γ₀-phases, having an α-ferrite phase in the vicinity, are similar to those of pure κ₀/γ₀-lamellae (Mn contents are not compared concerning its local heterogeneity). Overall, as an α-ferrite phase shows up, the elemental partitioning trend of adjacent κ₀/γ₀ phases is
not affected but the phase compositions and partitioning coefficients could slightly differ from those of pure $\kappa_0/\gamma_0$-lamellae as a result of solute exchange with the $\alpha$-ferrite.

**Figure 6.8.** Illustrations of $\kappa_0$, $\gamma_0$ and $\alpha$ phases in the APT specimen in Figure 6.7 by iso-concentration surfaces of (a) 9.0 at.% C; (b) 20.0 at.% Mn; (c) 15.0 at.% Al and corresponding analysis of the elemental partitioning between $\kappa_0$, $\gamma_0$ and $\alpha$ phases by 1D concentration profiles across (a) $\kappa_0/\gamma_0$ interface; (b) $\kappa_0/\alpha$ interface; (c) $\gamma_0/\alpha$ interface.
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Table 6.4. Chemical compositions (at.%) of the grain boundary (GB) κ0/γ0/α-phases in the 4w-aged specimen in Figure 6.8 determined by APT. Error bars indicate the statistical errors.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>κ01</td>
<td>34.19±0.05</td>
<td>27.74±0.05</td>
<td>19.76±0.05</td>
<td>18.28±0.03</td>
</tr>
<tr>
<td>κ02</td>
<td>38.01±0.28</td>
<td>25.04±0.23</td>
<td>20.64±0.21</td>
<td>16.31±0.15</td>
</tr>
<tr>
<td>γ0</td>
<td>58.37±0.13</td>
<td>23.78±0.10</td>
<td>14.71±0.09</td>
<td>3.07±0.03</td>
</tr>
<tr>
<td>α</td>
<td>68.85±0.08</td>
<td>11.49±0.05</td>
<td>19.61±0.07</td>
<td>0.005±0.004</td>
</tr>
</tbody>
</table>

6.3 Discussion

6.3.1 Influence of strain state on the off-stoichiometry of κ-carbides

According to APT measurements, both the coherent GI κ-carbides ((Fe1.99Mn1.10Al0.91)(C0.60Vac0.40), section 6.2.2) and semi-coherent/incoherent GB κ0-carbides ((Fe-1.7Mn-1.3Al0.96)(C-0.8Vac-0.2), section 6.2.3) are found to deviate from the ideal L’12 (Fe,Mn)3AlC stoichiometry. DFT calculations reveal that elastic strain stabilizes a composition that is C-deficient and favors MnγAl anti-sites (section 5.2.2). The different compositions of the coherent GI κ-carbides and semi-coherent/incoherent GB κ0-carbides, as determined by APT, substantiate this explanation. The coherency strain, facilitating the formation of off-stoichiometric defects in the GI, does not exist anymore at the semi-coherent/incoherent GB κ0/γ0 lamellae, which leads to a reduction of C vacancies and MnγAl anti-sites in GB κ0-carbides.

Moreover, it is noticed that despite the similar Al & C partitioning behavior between the GI κ/γ and GB κ0/γ0 phases, the Mn partitioning exhibits a reverse trend, i.e. repelled from GI κ-carbides (Figure 6.4(b), Table 6.2) while enriched in GB κ0-carbides (Figure 6.6(b), Table 6.3). As the ageing time increases, the GB (κ0+γ0+α) phases gradually progress into the GI regions at the expense of the GI (κ+γ) phases (Figure 6.1, 6.5) while the GB phases behind the migrating GB have reached a chemical equilibrium (section 6.2.3). Therefore, the observed GB (κ0+γ0+α) phases in the 4w- and 12w-aged samples are the thermodynamically more stable phases than the GI (κ+γ) phases and are the equilibrium phases of the studied alloy at this ageing temperature of
600°C. The partitioning of Mn to the GB κ₀-carbide is driven by thermodynamics to reach its equilibrium composition. In contrast, the reason for the depletion of Mn in GI κ-carbides is not so clear. Probably it is also related to the effect of elastic strain on the elemental partitioning of the GI κ₀ phases. The role of Al and C in the expansion of the κ-carbide’s unit cell and its resultant off-stoichiometry has been demonstrated by DFT calculations. However, little attention was paid to Mn atoms since they have a close atomic volume to the matrix Fe atoms and would not cause obvious lattice expansion. Further work is required to find out other factors, probably atomic interaction and magnetic properties, responsible for such a phenomenon.

6.3.2 Thermal stability of coherent GI κ-carbide precipitates

It is found that the coherent nanometer-sized GI κ-carbide precipitates are extremely stable at 600°C even subjected to prolonged ageing. No obvious difference, in terms of precipitate size, volume fraction, lattice parameter and phase composition, is noticed as the ageing time increases from 24 hours to 12 weeks.

In previous studies about the coarsening of the coherent GI κ-carbide precipitates (Choo et al., 1997; Choi et al., 2010; Lin et al., 2014), more attention was drawn to shortly aged stages, i.e. from the initiation of phase decomposition in a supersaturated matrix, through the formation of fine dispersed precipitates, to the development of modulated microstructure. Post-modulation stages after extended ageing are barely reported. To the best knowledge of the author, it is for the first time that the prolonged-aged GI κ-carbides are thoroughly characterized down to the atomistic scale and their thermal stability is noticed.

The precipitation of coherent κ-carbides introduces an elastic strain field around them due to the lattice misfit between the precipitates and the matrix. The effects of the elasticity, including elastic energy and anisotropy, on the coarsening behavior of coherent precipitates have been observed in Ni-alloys (Miyazaki et al., 1994; Lund et al., 2002; Maebashi et al., 2004) and studied via numerical approaches (Vaithyanathan et al., 2002; Li et al., 2004; Thornton et al., 2004). In addition to a morphological transition, a time-dependent law is commonly found for the evolution of particle size (distribution) in the presence of elastic stress while the coarsening rate constant depends on the elastic interaction energy. In the current alloy, concerning the dense ‘grid-like’
microstructural appearance composed of individual precipitate stacks (Figure 6.3), intensive elastic stress should be distributed throughout the \( \gamma \)-channels in-between the \( \kappa \)-carbide precipitates, as well as the elastic interaction between them. Further elemental partitioning or mass transition for the coarsening is strongly prohibited by such elastic stress. As a result, the precipitate coarsening is remarkably decelerated and negligible. The nanometer-sized coherent \( \kappa \)-carbide precipitates are stabilized by elasticity effects.

### 6.3.3 Grain boundary discontinuous precipitation

#### 6.3.3.1 Initiation of GB discontinuous precipitation

The DP transformation is generally recognized to initiate with heterogeneous nucleation of precipitates on GBs followed by GB migration (Manna et al., 2001). Despite the fact that DP has been observed in various alloys based on Pb, Cu, Ni, Al, Mg, Fe, etc., the question why it occurs in some alloy systems but not in others is not fully understood. A suspicion is whether solutes segregate at GBs, which could effectively reduce the GB energy and offer a driving force for the GB migration (Meyrick, 1976). Since GB segregation of trace elements, including C and substitutional Si, Cu, has been reported in a similar austenitic Fe-Mn-C alloy (Herbig et al., 2015b), it is worth investigating the possibility of GB segregation and its relationship with GB DP in the current Fe-Mn-Al-C alloy.

In the 4w- and 12w-aged samples, the DP colonies are often found at general GBs rather than TBs (Figure 6.1(a)(c)), whereas the segregation of solutes at general GBs was clearly detected in the Fe-Mn-C alloy (Herbig et al., 2015b). Therefore, needle-shaped APT specimens are prepared from a random high angle grain boundary (HAGB) in the SS-treated sample. The reconstructed atom maps of primary elements (Figure 6.9(a-d)) do not show obvious chemical inhomogeneity while the B map (Figure 6.9(e)) distinctly reveals the presence of a GB within the analysis volume. B, as a foreign element not detected in any other APT measurements (e.g. Figure 2.1), seemingly solely appears at GBs but significantly help highlight GBs. A 1D concentration profile of a cylindrical ROI across the GB in Figure 6.9(e) shows that there is no obvious segregation of Mn, Al and C to the GB (Figure 6.9(f)). Instead, the C and Al concentrations are slightly lower at the GB Figure 6.9(g), the reason for which is not
clear. Nevertheless, no GB segregation of solutes Mn, Al and C is observed in the current alloy. Hence, it is other mechanisms instead of GB solute segregation that contribute to the initiation of DP.

**Figure 6.9.** (a-e) 3D atom maps of a SS-treated specimen containing a random large angle grain boundary; (f-g) 1D concentration profiles of the cylindrical cyan region of interest (ROI) in (e) across the grain boundary (GB).

Though there is no pre-existing solute enrichment at HAGBs, their high diffusivity and mobility make them optimal initial sites for DP. Figure 6.10(a) shows the reconstructed atom maps of an APT specimen from a GB with coarse κ₀-carbide precipitates along it (see the inset micrograph).
Figure 6.10. (a) Reconstructed C map of a 12w-aged specimen prepared from a grain boundary (GB) with coarse \( \kappa_0 \) precipitates along it (highlighted by white arrows in the inset SEM micrograph). The GB is visualized by a 0.4 at.% P iso-concentration surface. (b-c) 1D concentration profiles of the cylindrical cyan region of interest (ROI) in (a) across the GB.

Besides B, P is detected in this specimen and its segregation is more significant than that of B. Therefore, a P iso-concentration surface is employed for the visualization of the GB (Figure 6.10(a)). It is apparent that the C concentration is higher to one side of the GB than the other, suggesting the nucleation of \( \kappa_0 \)-carbide at the GB and its growth into the GI from one side. A 1D concentration profile of the cyan cylindrical ROI in Figure 6.10(a) is generated (Figure 6.10(b)). The similar partitioning behavior to the GB \( \kappa_0/\gamma_0 \) lamellae (Figure 6.6) supports that \( \kappa_0 \)-carbide is formed on one side while on the other side austenite is preserved. Despite the overall analogous partitioning of solutes to the \( \kappa_0 \)-carbide (Figure 6.10(b)), a close-up on the solute concentration profiles in the lower pane (Figure 6.10(c,d)) reveals that instead of smooth profiles, solutes are enriched in front of the GB as spikes and then depleted behind (the GB
position is illustrated by the P and B humps). Such a local solute distribution is conspicuous for Mn while relatively subtle for C and Al, suggesting that it is a diffusion-related phenomenon due to the diffusivity difference between Mn and Al/C (section 4.3.1.1). Moreover, on the $\kappa_0$-carbide side, concerning the higher solute concentrations adjacent to the GB, it is plausible that HAGBs are serving as high diffusion paths for the initiation of DP, while it would take longer for the solute transportation via bulk diffusion, leading to the local solute enrichment in front of the GB. Away from the interface, the chemical compositions of the embryo $\kappa_0$-carbide is determined as $(\text{Fe}_{1.70}\text{Mn}_{1.34}\text{Al}_{0.96})(\text{C}_{0.86}\text{Vac}_{0.14})$ and found to be almost the same as that of well-grown lamellar $\kappa_0$-carbides in the center of cellular colonies (section 6.2.3). The invariant precipitate composition substantiates the occurrence of heterogeneous nucleation at GBs.

In addition, the GB interface is observed to be curved rather than planar (Figure 6.10 (a)). This could be associated to GB puckering induced by precipitation, which has been observed in many other alloy systems as the initiation mechanism of GB migration (Hirth et al., 1998; Manna et al., 2001; Nedjad et al., 2008). The pucker mechanism, proposed by Tu and Turnbull (Tu et al., 1967), emphasizes that boundary deflection is necessary upon precipitate nucleation in order to minimize the interfacial energy and accommodate the orientation relationship between the nucleus and the matrix. Curved boundary segments between nuclei would then activate the advancement of boundaries into the matrix, triggering DP.

### 6.3.3.2 Growth of GB discontinuous precipitation colonies

Since the GB DP reaction generally degrades the performance of alloys, it is of great interest to elucidate the growth of DP in the current alloy. Figure 6.11 shows a typical advancing reaction front of DP colonies in the 12w-aged sample. The alternate $(\kappa_0+\gamma_0+(\alpha))$ lamellae behind the reaction front and nanometer-sized GI $\kappa$-carbides ahead of that are well manifested by sample etching. The GI $\kappa$-carbides appear to maintain their original morphology even when they are in contact with the advancing boundary. No conspicuous particle dissolution or precipitate free zone is observed in front of the boundary.
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**Figure 6.11.** The propagation of grain boundary (GB) discontinuous precipitation (DP) colony at the expense of grain interior (GI) (κ+γ) in the etched 12w-aged sample.

In order to clarify the interaction between the progressing DP colonies and the sacrificing GI structure, needle-shaped specimens are prepared from an advancing boundary. A successful measurement with the presence of a boundary in the analysis volume is shown in Figure 6.12. The GI κ-carbides are visualized by a 9.0 at.% C iso-concentration surface as usual. Though not fully coincided, iso-concentration surfaces of 2.3 at% C and 20.0 at.% Mn help manifest the advancing boundary. It is found that the phase behind the boundary is enriched in Al but depleted in Mn, suggesting that rather than the primary κ0 or γ0 phases, the rare α-ferrite phase is captured behind the boundary in this specimen (Figure 6.8). As shown in Figure 6.5(c), this could take place but not on a large scale. The reconstructed 3D maps (Figure 6.12) reveal the GI κ-carbides in front of the boundary well preserve their original cuboidal or plate-like morphology and chemical compositions even the advancing boundary is a few of nanometers away. The dissolution of GI κ-carbides appears to occur only when they are in contact with the boundary and only locally at the contact area - the rest of the κ-carbides is not much affected.
Figure 6.12. APT analysis of discontinuous precipitation (DP) reaction front in the 12w-aged specimen. The grain interior (GI) κ-carbides embedded in γ-matrix are visualized by a 9.0 at.% C iso-concentration surface. The reaction front is manifested by a 20.0 at.% Mn and 2.3 at.% C iso-concentration surface.

The elemental partitioning between phases at the reaction front is revealed by generating 1D concentration profiles across the boundary. Two cylindrical ROIs perpendicular to the boundary, one across γ/α (Figure 6.13(a)) and the other across κ/α (Figure 6.13(c)), are utilized for this purpose. For the sake of simplicity, the analysis volume is cropped here so as to clearly manifest the interfacial regions. The corresponding concentration profiles are plotted in Figure 6.13(b) and Figure 6.13(d), respectively. The γ/α or κ/α partitioning generally follow the same trend as observed between GB (γ₀+κ₀+α) phases (Figure 6.8(b,c)) unless that there are compositional differences between γ₀/γ and κ₀/κ. In addition to the plateau composition differences, it is worth noting that there are solute enrichments locally at the interfacial regions. In Figure 6.13(b), the repulsion of Mn out of the α-ferrite into γ-phase is apparently slower than the partitioning of Al and C. The interfacial region of Mn partitioning is much
wider than that of Al and C, as marked by dashed lines. Also, unlike Al and C that quickly reach plateau compositions, a broad Mn hump is observed in front of the boundary. This explains the offset between the C and Mn iso-concentration surfaces showing the reaction boundary (Figure 6.12, Figure 6.13(a)). In Figure 6.13(d), as GI κ-carbides are consumed by the advancing boundary, similar local enrichments in front of the boundary are observed for substitutional Mn and Al, as highlighted by black arrows. Therefore, it is clear that the atomic redistribution during the growth of DP colonies only takes place within a few nanometers away from the reaction front and there is no long-range diffusion of any solute elements. The local enrichments ahead of the boundary can be associated to the limited volumetric diffusivities, especially for Mn.

**Figure 6.13.** Elemental partitioning between the α-ferrite behind the migrating reaction front and the grain interior (GI) (κ+γ) structure ahead. The γ/α partitioning is illustrated by a 1D concentration profile (b) of the cyan region of interest (ROI) in (a), whereas the cyan ROI in (c) is utilized to generate a 1D concentration profile across κ/α (d).
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Given that morphologically there is no distinct difference whether either α-ferrite or κ₀/γ₀ phase is advancing into the GI (κ+γ) structure (Figure 6.5(c)) and chemically the compositional differences between κ₀/γ₀ and (κ+γ) phases are actually less in comparison to those between α and (κ+γ), it is reasonable to speculate that also local equilibrium is established in a short range as κ₀/γ₀ interacts with (κ+γ) phases. The atomic redistribution only occurs within a few nanometers away from migrating boundary, which might serve as a short-circuit path for elemental diffusion.
Chapter 7

Summary and outlook

7.1 Summary

The precipitation and deformation of κ-carbides in an austenitic Fe-29.8Mn-7.7Al-1.3C light-weight steel have been investigated. The main conclusions are listed as follows:

- In the solid-solution (SS) treated alloy, though small long-range-ordered clusters (<2 nm) are observed in transmission electron microscopy (TEM), no elemental partitioning is detected by atom probe tomography (APT).
- An isothermal ageing of the SS-treated alloy at 600°C introduces precipitation of nanometer-scale ordered L'12-type κ-carbides in the γ-matrix. After 24 hours, well-precipitated κ-carbides exhibit cuboidal and plate-like shapes, which are arranged in the form of stacks along <001> crystallographic directions. The κ/γ interface is fully coherent but not atomically sharp. The width of ordering and chemical transition is about 2 nm.
- Particle shearing is the dominant co-deformation mechanism in the 24h-aged alloy. The significant strengthening by κ-carbide precipitation primarily arises from shearing of the ordered L’12-type κ-carbides. The shearing follows the typical fcc slip system {111}<110> and is accompanied by particle dissolution and solute segregation.
• The chemical composition of the κ-carbides determined by APT is found to be off-stoichiometric. Compared to the expected stoichiometric bulk L’12 perovskite composition, sub-lattice depletion was detected not only for the interstitial C sites but also for the substitutional Al sites.

• DFT calculations elucidate that the off-stoichiometry can be explained by the formation of C vacancies and Mn\(^{\gamma}\)/Al anti-sites as a result of that the alloy tends to minimize the elastic strain energy caused by precipitation. Due to the atomic interaction, Mn\(^{\gamma}\)/Al anti-sites are energetically favored only if neighboring C vacancies are present. This off-stoichiometry is expected to modify the strengthening effect by the precipitate due to reduction in anti-phase boundary (APB) energy.

• The nanometer-scale κ-carbides exhibit remarkable thermal stability at 600°C. As ageing time increases from 24 hours to 4- or even 12-weeks, no distinct differences are recognized in terms of particle size, volume fraction and chemical composition. It is plausible that the elastic strain accounts for such an abnormal coarsening behavior.

• Discontinuous precipitation (DP), however, occurs as ageing is prolonged to a few months. It initiates by heterogeneous nucleation of κ\(_0\)-carbides at grain boundaries (GBs) and advances into the grain interior (GI) at the expense of GI (κ+γ) phases by GB puckering. Besides α-ferrite of a small portion (<1%), the generated cellular colonies are mainly composed of alternating lamellar GB κ\(_0\)-carbide and solute-depleted γ\(_0\)-phase, which are of the same structure but different chemical compositions from the GI (κ+γ) phases. The propagation of DP colonies is sluggish since the atomic redistribution is limited to a few nanometers away from reaction front, i.e. via a local equilibrium mode.

• Despite the similar elemental partitioning of Al and C to κ/κ\(_0\)-carbides from their respective γ/γ\(_0\)-neighbors, Mn is depleted in GI κ-carbide while enriched in GB κ\(_0\)-carbide. The partitioning coefficients of all elements are larger in GB DP than in GI precipitation. This is associated with the elastic constrain in the GI while thermodynamic equilibrium is established in GB (κ\(_0\)+γ\(_0\)+α) DP colonies.
7.2 Outlook

The elastic strain, introduced by κ-carbide precipitation and determined by κ/γ elemental partitioning, is found to be critical for the particle morphology and off-stoichiometry of the κ-carbide precipitates. Among the solutes, the partitioning of Al and C are stronger and more decisive for the coherency constrain. From the alloy design perspective, κ/γ alloys can be further optimized by tuning the relative Al and C alloying contents. In the further modeling of the plasticity mechanisms such as SIP or MBIP, the off-stoichiometry of ordered shearable κ-carbide needs to be taken into account. Since the coherent κ-carbide is extreme stable at the ageing temperature and the propagation of deleterious GB DP reaction is sluggish (controlled by local equilibrium ahead the reaction front), additional minor alloying can be tested to impede the GB migration and, thus, the mechanical performance of κ/γ alloys at moderate temperatures (~200-600 °C) is worth studying.


Choo, W.K. and Han, K.H. (1985). Phase constitution and lattice parameter relationships in rapidly solidified (Fe0.65Mn0.35)0.83Al0.17.xC and Fe3Al.xC pseudo-binary alloys. Metallurgical Transactions A, 16(1); 5-10.


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**Figure 5.4.** Formation energies and concentrations of \( \text{Fe}^{\gamma}_{\text{Al}} \) and \( \text{Mn}^{\gamma}_{\text{Al}} \) anti-sites as a function of lattice constant for different C environments. The squared symbols in the upper panel mark the pure anti-site, whereas the circles mark complexes of anti-sites with a certain number of adjacent C vacancies, \( \text{Vac}_C \). In the lower panel a sensitivity analysis for the dependence of Mn anti-site concentration for different equilibrium temperatures and total C concentrations in the carbide is performed. The possible change of the \( \kappa \) lattice constant constant (with composition \( \text{Fe}_{2.0}\text{Mn}_{1.125}\text{Al}_{0.875}\text{C}_{0.625} \)) due to coherency strain to the \( \gamma \) matrix is highlighted by the yellow shaded region, where \( a_{\kappa+\gamma} \) indicates the situation for an equal volume fraction of both phases. This DFT work was done by Poulumi Dey and Tilmann Hickel.

**Figure 6.1.** SEM Microstructure of the (a)(b) 4w-aged and (c)(d) 12w-aged samples: (a)(c) overview of decorated grain boundaries (GBs); (c) alternative lamellar phases near GBs manifested by BSE contrast; (d) nanometer-sized grain interior (GI) and \( \mu \text{-} \text{m} \) scale GB protruding precipitates after etching. A GB with coarse precipitates along it and a twin boundary (TB) free of those are highlighted by red and blue arrows, respectively. The reaction fronts are marked by yellow dashed lines with the yellow arrows indicating their aggressing directions.

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Abstract

Nanometer-sized κ-carbides are efficient strengtheners making light-weight austenitic (γ) Fe-Mn-Al-C steels ultra-strong yet highly ductile. However, they lack fundamental understanding. Not only their interaction with dislocation during deformation, but also their atomistic structure, off-stoichiometry and effect of elemental partitioning on those, are not fully clear. These, however, are essential to instruct alloy design and optimization. This work aims at clarifying these pending questions by an atomistic-scale investigation of aged or deformed κ/γ microstructure.

A quaternary model Fe-29.8Mn-7.7Al-1.3C (wt.%) steel aged at 600 °C for 0-2016 hours was chosen for this study. The 24h-aged sample with well-precipitated grain interior (GI) κ-carbides was thoroughly investigated in terms of particle morphology and arrangement, elemental partitioning and off-stoichiometry, κ/γ interface and particle-dislocation interaction upon deformation; whereas more attention was paid to the phase evolution in the 4- or 12-weeks-aged samples. The microstructural characterization was carried out by exploiting various cutting-edge techniques, including synchrotron x-ray diffraction (SXRD), high-resolution scanning electron microscopy (HR-SEM), (scanning) transmission electron microscopy ((S)TEM), atom probe tomography (APT) and correlative TEM and APT. Density functional theory (DFT) was employed to elucidate the atomistic site-occupancy of κ-carbide and understand its off-stoichiometry.

The results reveal that particle shearing is the predominant co-deformation mechanism in the studied κ/γ alloy and ordering strengthening is the primary
contribution to the precipitation strengthening. Though rough and not atomically sharp, the $\kappa/\gamma$ interface is fully coherent, causing an elastic strain around $\kappa$-carbide precipitates and an elastic interaction between them. As a result, in comparison to the ideal bulk L’12 perovskite, the measured $\kappa$-carbide is off-stoichiometric with a depletion in C and Al compositions due to the formation of C vacancies and Mn$^\gamma_{\text{Al}}$ anti-sites. The elastic stress not only results in their nanometer-scale size, stack alignment, thermal stability upon prolonged ageing, but also leads to a limited elemental partitioning. In comparison to the thermodynamic stable grain boundary (GB) $\kappa_0$-carbide, the elemental partitioning of solutes for the grain interior (GI) precipitation are all restricted, giving rise to the different chemical compositions and morphologies between GI $\kappa$-carbide and GB $\kappa_0$-carbide.
Zusammenfassung


Die Mikrostrukturcharakterisierung wurde durchgeführt unter Verwendung aufwendiger Methoden wie Synchrotron Röntgenbeugung (SXRD), hochauflösende
Rasterelektronenmikroskopie (HR-SEM), (Raster-) Transmissionselektronenmikroskopie ((S)TEM), Atomsondentomographie (APT) und korrelative TEM und APT Charakterisierung. Density functional theory (DFT) wurde eingesetzt, um die Gitterplatzbesetzung von κ-Karboid und die beobachtete Abweichung von der Stöchiometrie zu erklären.