Precipitate evolution in grain oriented electrical steel and high strength low alloy steel

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Chapter 3* Precipitate evolution in grain oriented electrical steel during high temperature coil annealing

Abstract: To correlate the abnormal growth of grains having sharp Goss texture with the precipitate evolution, decarburized and nitrided GO electrical steel was annealed to different temperatures simulating high temperature coil annealing. The precipitate evolution in this steel was studied in detail using various state-of-the-art TEM-based techniques. Results show that three types of precipitates are present in the steel. Majority type I precipitates are mainly large irregular (Mn,Cu)S-(Al,Si)N core-shell precipitates. Type II precipitates are mainly medium-size six-sided prismatic (Al,Si)N-(Mn,Si)N or (Al,Si)N-CuS precipitates, which are present in distinct areas with high and low number density. The precipitate size evolution in both areas was quantitatively assessed. Precipitates in both the two areas coarsen up to 900°C and dissolve rapidly above 1100 °C. Type III precipitates are small spherical face-centered (FCC) \( \text{Cu}_2\text{S} \) \( (0<x<0.6) \) precipitates. They first dissolve between 830 °C and 900 °C and then precipitate out again as FCC \( \text{Cu}_2\text{S} \) precipitates during (slow) cooling from annealing above 900 °C. Secondary recrystallization responsible for the extraordinary grain growth occurs between 1100 °C and 1175 °C. The present work demonstrates that the dissolution of type II precipitates is responsible for activating the abnormal grain growth process whereas type III precipitates only indirectly affect this process by acting as nuclei on which type II precipitates can grow.

3.1 Introduction

GO electrical steels are classified into two grades: conventional grain oriented (CGO) electrical steels and high permeability grain oriented (HGO) electrical steels, in which MnS [1] and AlN [2] are the main inhibitors, respectively. AlN precipitates usually contain Si and Mn, and they are thus written as (Al,Si)N or (Al,Si,Mn)N [3]. The average deviation of the \(<100>\) axis from the rolling direction is about 3° in HGO electrical steels and about 7° in CGO electrical steels [4]. The sharper \{110\}<001> orientation in HGO electrical steels results in lower core loss and higher permeability, and therefore HGO electrical steels were extensively studied.

Extensive investigations have been carried out on AlN precipitates, such as the morphology and structure [5,6], composition [7,8], thermodynamics [9–12] and the evolution of AlN in different manufacturing processes (hot rolling, hot-band annealing, decarburization and HTC annealing) [2,13,14]. However, there is still a lack of detailed study of AlN and its

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evolution (such as composition, size and distribution) during the HTC annealing because conventional TEM investigations employed in previous studies do not suffice to reveal the required detailed information.

In Cu-containing HGO electrical steels, the inhibitor types remain controversial during HTC annealing: Cu$_2$S precipitates were observed apart from AlN precipitates [15], whereas no Cu$_2$S was reported in [7]. In addition, the Cu-based precipitates were reported to finely disperse in Cu-added GO electrical steels, even after secondary recrystallization [16]. According to Zener [17], the pining force of these precipitates should be much higher than that of AlN-based precipitates due to their smaller size and higher density. Yet, this has not been discussed before. So, the evolution of Cu-based precipitates during HTC annealing and the role they play in secondary recrystallization are to date still not clarified.

Precipitate characterization in GO electrical steels is difficult. The composition of individual precipitates is generally complex (often co-precipitates [8]), and conventional TEM is not sufficient to provide detailed chemical information. Moreover, nanoscale precipitates (especially AlN precipitates between 10 nm and 100 nm) have low number density and are not uniformly distributed [2]. To obtain statically accurate precipitate size distributions, the imaging requires both high resolution as well as large investigated areas, which means that neither conventional TEM nor scanning electron microscopy (SEM) is suitable. These issues hinder the further understanding of the precipitate evolution during (HTC) annealing.

The aim of the present work is to provide an in-depth understanding of precipitate (composition and size) evolution during simulated HTC annealing and to finally illuminate the role precipitates with different compositions and sizes play in the secondary recrystallization process. In order to address the precipitate characterization problems as mentioned above, high resolution scanning TEM (STEM) elemental mapping based on energy dispersive X-ray spectrometry (EDS) was employed to investigate precipitate composition and 30 kV high-angle annual dark field (HAADF) - scanning transmission electron microscopy (STEM) image stitching over larger areas was used to obtain precipitate size distribution in the range of 10-100 nm.

### 3.2 Experimental

A schematic diagram of the simulated HTC annealing is shown in Fig. 3.1. The D-line samples were annealed from room temperature at a heating rate of 2 °C/min in a pure hydrogen (H$_2$) atmosphere to different interrupted temperatures (900 °C, 950 °C, 1100 °C, 1175 °C), and finally to 1250 °C and held for 24 h to simulate the HTC annealing process. The annealed samples were slowly cooled down within the furnace after reaching the desired temperatures, which took several hours. The annealed samples are named after the temperature in the following text, for instance, the sample annealed to 900 °C is written as the 900°C sample.
Microstructures were investigated on the ND-RD plane of the samples. Specimens for electron microscopy investigations were prepared by electrochemical polishing, carbon replica extraction and FIB. Precipitates were investigated with TEM imaging, TEM-EDS, SAD, HRTEM, STEM EDS elemental mapping. 30 kV HAADF-STEM image stitching was employed over large areas to measure precipitate diameter between 10 nm and 100 nm. Experiment details can be found in Chapter 2.

![Graph showing temperature vs. time for HTC annealing procedure](image)

**Fig. 3.1** Schematic diagram of the simulated HTC annealing procedure used to produce the samples investigated in the present work.

### 3.3 Results

#### 3.3.1 Overview and type I precipitates

Examples of bright field TEM images of the D-line sample, from thin foils and carbon replicas, are shown in Fig. 3.2. Three types of precipitates with different morphologies and sizes are discerned. Type I precipitates are large irregular precipitates of several hundred nanometers; type II precipitates are medium-size precipitates of several tens of nanometers; type III precipitates are small precipitates of several nanometers. Precipitate number densities of type I and type II are low and they are not uniformly distributed, whereas type III precipitates are uniformly distributed with a high number density.

![Image showing HAADF-STEM and EDS mapping](image)

**Fig. 3.3** shows a HAADF-STEM image and EDS elemental mapping of a typical type I precipitate in the D-line sample. Contrasts are clearly seen inside of the precipitate from the HAADF-STEM image. The contrast originates from two effects: local variations in thickness and composition (Z contrast). The sudden contrast change inside of the precipitate suggests composition changes. EDS elemental mapping shows that the precipitate contains Al, Si, N, Mn, Cu and S. Al, Si and N show the same spatial distribution. This also holds for Mn, Cu and S, demonstrating that the precipitate is composed of two distinct phases, namely (Al, Si)N and (Mn, Cu)S. In projection, the area of the (Al, Si)N is bigger than that of (Mn, Cu)S, with (Al, Si)N more towards the outside, suggesting that (Al, Si)N precipitates upon (Mn, Cu)S.
Type I precipitates in the D-line sample were mainly identified as (Mn,Cu)S-(Al,Si)N core-shell precipitates, ranging from 150 nm to 700 nm. Small amounts of other precipitates, such as TiN (also the core of co-precipitates) and FeSi (separate precipitates), were also detected. Another example of a core-shell co-precipitate is shown in Fig. S3.1 (see...
supplementary material (SM) Section S3.1). Type I precipitates are not of primary interest, because, due to their large sizes, they are not relevant to secondary recrystallization [16].

3.3.2 Type II precipitates

3.3.2.1 Composition characterization

The composition of type II precipitates in all the samples was first investigated in thin foils with EDS. Almost all of them were identified as AlN-based precipitates in the D-line, 900 °C, 950 °C, 1100 °C and 1175 °C samples (see Fig. S3.2a in SM) with minor compositional differences. Occasionally cuboidal TiN and spherical Cu$_{2-x}$S precipitates can be also observed. In the 1250 °C 24 h sample, still a very small amount of precipitates with sizes between 50 nm and 200 nm were observed and identified as Cu particles (see Fig. S3.2b in SM). As will be discussed below the type II AlN-based precipitates were characterized in much more detail in carbon replicas.

Fig. 3.4a shows three type II precipitates with six-sided prismatic shape as observed with HAADF-STEM. Contrast can be observed in the image for each precipitate, indicating that their composition is complex corresponding to core-shell co-precipitates. EDS spectra of typical type II precipitates show that they contain Al, Si, N, Mn, Cu and S (see Fig. 3.4b). This is consistent with the EDS spectra of precipitates in thin foils, indicating that there is no difference for precipitates in between carbon replicas and thin foils. Figs. 3.4c and d show HRTEM images of a precipitate. The corresponding fast Fourier transform (FFT) shown in Fig. 3.4e indicates that viewing is along the [0001] zone axis. The (01\bar{1}0) plane distance is determined to be 0.270 nm (Fig. 3.4d). This precipitate is identified as hexagonal AlN with an a lattice parameter of 0.311 nm, which agrees well with what is reported previously [6].

STEM EDS elemental mapping was performed to further investigate precipitate composition. Fig. 3.5a shows that the precipitate has an (Mn, Si)N core upon which (Al, Si)N is precipitated. The contrast in the bottom part of the image suggests that the brightest area might be Cu$_{2-x}$S (the EDS signal is quite weak due to the very small local region of the complex precipitate). Cu$_{2-x}$S is brighter compared to (Mn, Si)N which in return is brighter than AlN due to their respective Z values, with Cu > Mn, Si > Al and S > N. Fig. 3.5b clearly shows that this precipitate has a Cu$_{2-x}$S core and an (Al, Si)N shell. These results indicate that (Al, Si)N precipitates have a low homogeneous nucleation rate and require a seed. They form on the already existing precipitates, either upon (Mn, Si)N or Cu$_{2-x}$S precipitates.
Fig. 3.4 (a) HAADF-STEM images showing the shape and contrast of the type II precipitates, (b) EDS spectrum of a typical precipitate, showing that the precipitate is rich in Al and N, but also contains some minor part of Si, Mn, Cu and S, (c) HRTEM image of the precipitate, (d) zoom in area of (c), (e) FFT of the HRTEM of (d), showing that imaging is along [0001] of hexagonal AlN.

Fig. 3.5 HAADF-STEM image and EDS elemental mapping showing (a) (Al, Si)N precipitated upon an (Mn, Si)N seed, (b) (Al, Si)N precipitated upon a Cu$_2$S core.
3.3 Results

3.3.2.2 Size characterization and size evolution

The number density of type II precipitates is very low in TEM images (see Fig. 3.2). Even recording hundred TEM images may not be enough for a proper quantitative analysis. In addition, these hundred images may still not truly reflect the real spatial distribution of type II precipitates. To accurately characterize size distribution and number density of type II precipitates, both large areas with enough precipitates and sufficient spatial resolution images are required. 30 kV HAADF-STEM image stitching was employed to address this issue.

Fig. 3.6a shows a stitched 30 kV HAADF-STEM image with an area of 49.8 × 31.3 µm² and pixel resolution of 9 × 9 nm² of the D-line sample. All the three types of precipitates can be seen (although type III precipitates are not very obvious). Type I precipitates distribute along the rolling direction (indicated by the blue arrow). Regarding type II precipitates, two types of areas with low and high (some are indicated by red ellipses) number density are discerned. A stitched bright-field SEM image of etched bulk D-line sample is shown in Fig. S3.3, where the high and low precipitate number density areas can be clearly discerned. The stitched SEM image shows that the high number density areas are not confined to individual grains. Instead, they align in lines across grains. The precipitate distributions on the carbon replica and on etched bulk sample are almost the same. This guarantees that the following precipitate investigations on carbon replicas over large areas are reliable and can reflect the precipitate distribution in the steel. Fig. 3.6b shows another stitched 30 kV HAADF-STEM image with an area of 13.2 × 9.7 µm² and pixel resolution of 1.5 × 1.5 nm², clearly illustrating precipitates in both the low (lower part) and high (upper part) number density areas. Figs. 3.6c and d show individual 30 kV HAADF-STEM image of precipitates in high and low number density area in the D-line sample, respectively. Type II precipitates in the high number density areas are on average bigger than those in the low number density areas. For the 900 °C, 950 °C and 1100 °C samples, both low and high number density areas for type II precipitates were found (see Figs. 3.6e-f for the 900 °C sample, Figs. S3.4a-b for the 950 °C sample in SM and Figs. S3.4c-d for the 1100 °C sample in SM). Note that in the 1175 °C sample, precipitates in high number density areas are no longer observed and only the low number density area was found (Fig. 3.6g). When the sample was annealed at 1250 °C for 24 h, type II AlN-based precipitates are absent, i.e. totally disappeared (see Fig. S3.4e in SM).
Fig. 3.6 Stitched HAADF-STEM images of D-line sample showing both high and low number density areas for type II precipitates (a) low magnification, (b) high magnification, HAADF-STEM images showing type II precipitates in (c) high number density areas of the D-line sample, (d) low number areas of the D-line sample, (e) low number density areas of the 900 °C sample, (f) high number density areas of the 900 °C sample, (g) low number density areas of the 1175 °C sample.
3.3 Results

Figs. 3.7a and b show size distributions of type II precipitates in low and high number density areas, respectively. An area of 600-1000 µm² was investigated for precipitates in low number density areas and 500-1200 precipitates in high number density areas were measured for each sample. Precipitates grow up to 950 °C in low number density areas and dissolve afterwards. Precipitate size and number density evolution in high number density areas follow the same trend as those in low number density areas. In the D-line sample, precipitate size in the high number density areas is larger than that in the low number density areas. Yet, precipitates in the low number density areas coarsen and dissolve faster than those in the high number density areas (the peak size is 68.5 nm in the low number density areas whereas it is only 43.3 nm in the high number density areas).

Fig. 3.7c shows the total number density of precipitates in both high and low number density areas. This density in both types of areas decreases with the increase of annealing temperature. The precipitate number density in the high number density areas is around 11 times higher than that in the low number density areas. The slow drop of the type II precipitate number density before 950 °C is due to the precipitate coarsening. The type II precipitates present in the 1175 °C sample can be attributed to dissolving type I precipitates and for a part (the initially biggest) type II precipitates.

![Figure 3.7](image-url)

**Fig. 3.7** Size distribution of type II precipitates in (a) low number density areas, (b) high number density areas, (c) total precipitate number density in low and high number density areas, (d) high number density area fraction.
The area fraction of the high number density area for type II precipitates was assessed for the D-line, 900 °C, 950 °C, 1100 °C samples (see Fig. 3.7d). An area of 3000 to 5000 µm² was investigated in each sample. Around 16% of the total area is the high number density area. For samples annealed to 1100 °C, this area fraction decreases because precipitates have been partly dissolved and became small, resulting in an underestimation of the area fraction.

3.3.3 Type III precipitates

Figs. 3.8a-c show TEM images of type III precipitates in the thin foil of the D-line, 1100 °C and 1250 °C 24 h samples, respectively. There is no observable size difference for the type III precipitates. The presence of type III precipitates in Fig. 3.8c is contrary to the expectation that there should be no precipitates after the final annealing because they affect domain walls (and their dynamics), leading to higher power loss of transformers in which this steel is used as core. Keith et al. [16] also observed these fine precipitates in a final annealed Cu-added CGO electrical steel. However, the magnetic performance seems not deteriorate even with the presence of those fine precipitates [16]. Turner et al. [18] explained that the residual presence of Cu precipitates (5-10 nm) does not affect domain wall motion because the diameter of Cu precipitates is relatively small compared to the domain wall thickness.

Fig. 3.8 Type III precipitates in the thin foil of the samples (a) D-line, (b) 1100 °C, (c) 1250 °C 24 h.

Fig. 3.9 shows EDS spectra of the type III precipitates in the D-line and 1175 °C samples investigated with carbon replicas. Type III precipitates in the D-line sample are identified as Cu₂₋ₓS (x is between 0 and 0.6, see Fig. 3.9a) and they keep similar composition in the samples annealed up to 1175 °C. In contrast, in the 1250 °C 24 h sample, the precipitates are identified as Cu (see Fig. 3.9b).

Fig. 3.10a shows an SAED pattern taken along the [001] ferrite zone axis from the D-line sample. Big bright spots originate from the ferrite matrix and small weak spots (as indicated by blue arrays) come from Cu₂₋ₓS precipitates. The distance of the small weak spots is half of that of the bright spots, which is consistent with the previous report that the lattice
parameter of BCC ferrite is around twice that of FCC Cu$_{2-x}$S precipitates. The very weak diffraction intensities from Cu$_{2-x}$S precipitates indicate that their size is very small. Some weak ring-like intensity can be observed in the diffraction pattern, most probably due to surface contamination of the sample, which shows an amorphous phase. Fig. 3.10b shows an SAED pattern taken along the [001] ferrite zone axis from the 1100 °C sample, which is the same as that from the D-line sample. Fig. 10c schematically illustrates the diffraction patterns from the matrix and the precipitates, from which we can derive that the orientation relationship (OR) of the ferrite matrix and Cu$_{2-x}$S precipitates is cube-on-cube ([001]$_{\text{Cu}_2-x\text{S}}$ // [001]$_{\alpha}$, (010)$_{\text{Cu}_2-x\text{S}}$ // (010)$_{\alpha}$). The SAED patterns of the samples annealed to 900 °C and 950 °C also show the same OR as that of the D-line sample (see Figs. S3.5a and b in SM). The precipitates in the 1250 °C 24 h sample, according to the small size, should be the coherent BCC Cu precipitates [19], which is formed during cooling. It does not make sense to obtain the SAED pattern from the 1250 °C 24 h sample because the diffraction patterns of the Cu precipitates coincide with those of the iron matrix.

A HAADF-STEM image and EDS elemental mapping of a precipitate in the 900 °C sample is shown in Fig. 3.11, which shows that an outer region of Cu$_{2-x}$S is present surrounding...
(Al, Si)N which in return seems to have been precipitated upon a (Mn, Si)N core. More results can be found in Fig. S3.6. The peculiar structure supports the conclusion that cubic Cu$_2$-xS precipitates dissolve into the matrix below 900 °C and do not exist at high temperatures. The presence of the Cu$_2$-xS precipitates in the samples is because they are formed during the cooling to room temperature.

Fig. 3.11 HAADF-STEM image and EDS elemental mapping showing (Al, Si)N precipitate upon MnSiN and Cu$_2$-xS precipitate out upon (Al, Si)N during cooling in the 900 °C sample.

TEM images of Cu$_2$-xS precipitates on carbon replicas and their corresponding precipitate size distribution are shown in Fig. 3.12. 200~300 precipitates were analyzed in each sample. There is no observable size difference for Cu$_2$-xS precipitates.
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Fig. 3.12 Type III precipitates in the samples (a) D-line, (b) 900 °C, (c) 950 °C, (d) 1100 °C, (e) 1175 °C, (f) size distribution evolution of Cu_{2-x}S precipitates. 200–300 precipitates were analyzed in each sample.

### 3.3.4 MatCalc phase simulation

Fig. 3.13 shows the equilibrium phases and their mole fractions in the investigated HGO electrical steel with the composition of the D-line sample (see table 1) based on MatCalc simulations. Note that denitrification and desulphurization that occur in reality are not considered here. The simulation results are consistent with a previous report [20]. AlN still exists at high temperatures (> 1400 °C). MnS, instead of Cu_{2-x}S, is present in equilibrium and completely dissolves at around 1250 °C. MnSiN_{2} exists at low temperature (< 800 °C).

Fig. 3.13 The equilibrium phases and their mole fractions with the composition of the D-line sample based on MatCalc simulations.
3.3.5 Grain size evolution

Fig. 3.14 shows optical micrographs of the ND-RD plane of all the samples. There is almost no difference for the grain size between the D-line sample and the samples annealed to 900 °C, 950 °C and 1100 °C due to the strong pinning force by the precipitates. There is also no observable difference for the grain size near the surface and center of the foil. The grains in the sample annealed to 1175 °C clearly demonstrate abnormal growth, indicating that secondary recrystallization occurs between 1100 °C and 1175 °C. When the sample was annealed at 1250 °C for 24 h, the grains finally grow to sizes of centimeters (which can be readily observed by visual inspection).

Fig. 3.14 Micrographs of the ND-RD plane showing that secondary recrystallization occurs between 1100 °C and 1175 °C.

3.4. Discussion

3.4.1 Origin of high and low number density areas of type II (AlN-based) precipitates

The inhomogeneity of the precipitate distribution in GOES has been investigated before, but most of the work then focused on the inhomogeneity in the thickness direction by investigating layers at certain depths, such as at the surface, a quarter depth and in the middle [1,13,21]. However, only very few investigations have reported an inhomogeneous precipitate distribution for a layer at a certain depth.

An inhomogeneous distribution of AlN precipitates in a Fe-3%Si alloy has been reported, which was attributed to the orientation of grains with respect to the foil surface [22,23]. Zaveryukha et al. [22] found that the number density of AlN precipitates is about $11.8 \times 10^{13}$ cm$^{-3}$ in {111}<uvw> type grains, whereas $8.9 \times 10^{13}$ cm$^{-3}$ on average in {110}<uvw> type grains with a minimum value between $3 \times 10^{12}$ cm$^{-3}$ and $6 \times 10^{12}$ cm$^{-3}$. Different
annealing experiments after hot rolling, 1st cold rolling, decarburization annealing and 2nd cold rolling were conducted in their later research [23] to investigate the reason that cause the inhomogeneous precipitate distribution. Zaveryukha et al. [23] claimed that the number density difference of AlN precipitates in different types of grains are due to the different dislocation densities that remained after recrystallization. The high and low dislocation densities in grains are caused by different recrystallization mechanisms, i.e., the \{111\}_{uvw}-oriented grains form by the sub-grain coalescence and low-angle boundary movement, whereas the \{110\}_{uvw}-oriented grains in the narrow deformed bands form by high-angle boundary movement, and this results in higher dislocation density in the former type grains.

In the present work, low and high number density areas of type II (mainly AlN-based) precipitates are discerned in the D-line sample and samples annealed below 1100 °C (see Fig. 3.6 and Fig. S3.4). The number density of AlN-based precipitates in the high number density areas is over 10 times higher than that in the low number density areas, whereas the precipitate number density in \{111\}_{uvw}-oriented grains is only 1.3 times higher than that in \{110\}_{uvw}-oriented grains [22]. Also note that the high number density areas only occupy parts of the grain and extend across grain boundaries (see Fig. S3.3). Therefore, the explanation proposed by Zaveryukha et al. [23] cannot hold here. The high and low number density areas of AlN-based precipitates cannot be formed on dislocations during decarburization and nitriding process, otherwise, the precipitate number density difference should be relatively small.

Sakai et al. [2] investigated the types and distributions of AlN precipitates before and after hot-band annealing. A large amount of fine plate-like AlN precipitates with diameters between 20 nm and 50 nm, referred to as type B AlN precipitates, were observed to be formed after hot-band annealing. The type B AlN precipitates are believed to precipitate out during austenite - ferrite transformation that occurs continuously on cooling after hot-band annealing. This is because the N solubility in austenite is calculated to be 10 times higher than that in ferrite at 1000 °C [2] and AlN precipitates out in these (former) austenite regions due to the sharp decrease of N solubility during austenite - ferrite transformation. The type B AlN precipitates are observed to be distributed only within the transformed regions. This mechanism very well explains the precipitate distribution in high number density areas in the present work, indicating that the high number density areas originate from the former austenite regions.

The area fraction of the high number density areas is estimated to be around 16%. However, this area fraction is most likely to be underestimated since small areas with high number density are easily overlooked and then not counted. EBSD study on the hot-band annealed sample shows that the area fraction of austenite is around 20-30%, which will be reported in detail in another paper since this is beyond the scope of the present work. These two fractions are reasonably close, further supporting that the high number density areas most
likely originate from the austenite regions. Additional experiments can be conducted to investigate precipitates in hot rolled, hot-band annealed and cold rolled samples. However, this is beyond the scope of the present work.

For the low number density areas, precipitates form both during hot-band annealing, decarburization and nitriding, mainly on sub-grain boundaries, as can be inferred from Figs. 3.6a and b.

### 3.4.2 Evolution of AlN-based precipitates

Wilson and Gladman [24] pointed out that AlN has difficulty to nucleate unless precipitation is enhanced by thermal or mechanical treatments. Therefore, AlN precipitates nucleate on dislocations or on (sub-)grain boundaries and their composition is not pure AlN, but contains a small amount of Si and Mn. Bernier et al. [7] reported a detailed composition of \((\text{AlN})_{x} (\text{SiMn}_{0.25} \text{O}_{x})_{1-x}\) \((0<x<1)\) with a Si:Mn ratio of \(4:1\) for the AlN-based precipitates in a Cu-added HGO electrical steel. The mechanism of forming such a precipitate is that \((\text{Mn}, \text{Si})\text{N}\) precipitates first form due to their easier nucleation and faster kinetics \((\text{Si}, \text{Mn} >> \text{Al})\%), then Al is incorporated into the \((\text{Mn}, \text{Si})\text{N}\) due to the high affinity of Al for N and the high thermal stability of AlN [7]. Pure AlN was also detected. However, based on our investigation, we have reasons to argue that even the so-called “pure AlN” is not really pure, but very likely contains a small \(\text{Cu}_{2-x}\)S core.

AlN-based precipitates in high number density areas form during austenite to ferrite transformation. Their compositions are mainly \((\text{Al}, \text{Si})\text{N}-(\text{Mn}, \text{Si})\text{N}\). Seldom \((\text{Al}, \text{Si})\text{N}-\text{Cu}_{2-x}\)S can be detected because \(\text{Cu}_{2-x}\)S precipitates then have been dissolved into the austenite and do not exist during the transformation (as will be discussed in Section 3.4.3). On the contrary, \(\text{Cu}_{2-x}\)S precipitates exist during decarburization and nitriding, thus acting as nucleation seeds for AlN precipitates, mainly in low number density areas. \((\text{Al}, \text{Si})\text{N}-(\text{Mn}, \text{Si})\text{N}\) can be also detected in low number density areas. During annealing, Al and N diffusion towards the precipitates is responsible for their growth. The composition of AlN-based precipitates remains almost the same in this way. This is consistent with previous reports [7,8].

The solubility product of AlN in ferrite and austenite are expressed as Eqs. (3.1) and (3.2), respectively [11]:

\[
\log([\% \text{Al}] [\% \text{N}]) = 1.69 - 8296/T \tag{3.1}
\]

\[
\log([\% \text{Al}] [\% \text{N}]) = 1.95 - 7400/T \tag{3.2}
\]

The calculated dissolution temperature is 1469.5 °C in ferrite and 1201.0 °C in austenite based on the Al and N content in the investigated steel. This agrees with MatCalc simulation that AlN still exists above 1400 °C (see Fig. 3.13). However, AlN-based precipitates started to dissolve after annealing to 950 °C in the present work. This
discrepancy can be well understood because denitrification (by the hydrogen environment) is not considered both in the MatCalc simulation and in the solubility product calculation.

### 3.4.3 Dissolution of Cu$_{2-x}$S

MatCalc phase simulations (Fig. 3.13) shows that MnS instead of Cu$_{2-x}$S is present in equilibrium in the steel. However, Cu$_{2-x}$S precipitates were identified in this study. They have also been reported in earlier works [25–29]. Liu et al. [29] performed thermodynamic calculations and found that Cu$_2$S has much lower activation energy of nucleation compared to MnS in ferrite due to its coherent relationship with the matrix (in agreement with our observation in Fig. 3.10a) and therefore exists in steels. A thermodynamic calculation based on the CALPHAD method predicted that Cu$_{2-x}$S is a metastable phase which can precipitate when thermodynamic equilibrium is not reached [20].

Previous TEM investigations show that hexagonal Cu$_{2-x}$S precipitates out at high cooling rates, i.e., after water quenching [26,28]. Ishiguro et al. [28] indicated that Cu$_{2-x}$S precipitates form between 620 °C and 750 °C, and Lee et al. [20] used thermodynamic calculations to obtain 740 °C as the precipitation temperature. Yet, the hexagonal Cu$_{2-x}$S precipitates transform into cubic Cu$_{2-x}$S precipitates during isothermal holding at 700 °C [26]. In the present work, cubic Cu$_{2-x}$S precipitates instead of hexagonal ones form during furnace cooling after heating in the range from 950 °C and 1100 °C, because the slow cooling within the furnace can be regarded as annealing at lower temperature (like 700 °C) where the transformation to the cubic phase occurs.

The Cu$_{2-x}$S size distributions are almost the same for the D-line, 900 °C, 950 °C and 1100 °C samples. This is because Cu$_{2-x}$S precipitates in the D-line sample have already been well developed after decarburization and nitriding whereas Cu$_{2-x}$S in the 900 °C, 950 °C and 1100 °C samples have been grown to similar sizes during the slow furnace cooling.

The dissolution of Cu$_{2-x}$S precipitation in electrical steels is not well understood, also because the results in the literature are not consistent. Sakai et al. [30] proposed a value of 1200 °C for the dissolution temperature of Cu$_{2-x}$S in a Fe-3%Si steel with 0.05%Cu and 0.02%S. On the other hand, Kataoka et al. [26] investigated the Cu$_{2-x}$S precipitation behavior in a cast ferrite steel with the composition of Fe-3.2%Si-0.4%C-0.02%S (wt%) after annealing the as-cast samples to different temperatures. X-ray diffraction (XRD) and TEM results show that cubic Cu$_{2-x}$S precipitates existed in the cast steel and dissolved when annealing to 900 °C, whereas hexagonal Cu$_{2-x}$S precipitates appeared after water quenching from the annealing temperature of 1100 °C and 1340 °C.

In the present work, we showed an AlN precipitate with a Cu$_{2-x}$S core (see Fig. 3.5b), indicating that Cu$_{2-x}$S is present during decarburization at 830 °C. However, the Cu$_{2-x}$S shell outside of the AlN-based precipitate shown in Fig. 3.11 indicates that Cu$_{2-x}$S has
already dissolved into the matrix at 900 °C and precipitated out during cooling. Therefore, we believe that we now have convincing results to state that cubic Cu\textsubscript{2-x}S precipitates dissolve between 830 °C and 900 °C. This is also supported by [11] that hexagonal Cu\textsubscript{2-x}S precipitates were identified by SAED in a Fe-3% Si steel after quenching from 900 °C.

Table 3.1 shows the calculated dissolution temperature of Cu\textsubscript{2-x}S based on the composition in the investigated steel and Cu\textsubscript{2-x}S solubility products from previous reports. None of the solubility products can give a reasonable prediction of the dissolution temperature of Cu\textsubscript{2-x}S in our steel: either too high or too low, and one solubility product predicts even a non-physical negative dissolution temperature. The most probable reason is that Cu\textsubscript{2-x}S has several phases [29] and the essential thermodynamic data (for instance, solubility and interfacial energy) of all these phases is incomplete. It is not clear for which phase the solubility products shown in Table 3.1 are valid. Moreover, all these solubility products do not consider the effect of the other elements, especially Mn, on the behavior of Cu and S in the steel. In addition, the pure H\textsubscript{2} atmosphere causes desulphurization and leads to a continuous reduction of the sulphur concentration during the annealing process which has major impact on the Cu\textsubscript{2-x}S phase stability and its apparent dissolution temperature.

**Table 3.1** The calculated dissolution temperature of Cu\textsubscript{2-x}S based on the composition in the investigated steel and Cu\textsubscript{2-x}S solubility products.

<table>
<thead>
<tr>
<th>Solubility</th>
<th>Reference</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\log([%Cu]^2 %S])=60.58-103550/T</td>
<td>[30]</td>
<td>1324.2</td>
</tr>
<tr>
<td>\log([%Cu]^2 %S])=6.62-9693.75/T</td>
<td>[31]</td>
<td>617.8</td>
</tr>
<tr>
<td>\log([%Cu]^2 %S])=6.2582-9693.75/T</td>
<td>[26]</td>
<td>648.5</td>
</tr>
<tr>
<td>\log([%Cu]^2 %S])=8.1209-12158/T-(1.0844-1511.5/T)[%Cu]-0.081925[%Si]</td>
<td>[32]</td>
<td>&lt; 0</td>
</tr>
</tbody>
</table>

### 3.4.4 Role of Cu in precipitation

Cu is often added into GO electrical steels, which has been proven to be beneficial for obtaining sharp Goss texture and improved magnetic properties [33]. Yet, the role of Cu in precipitation has not been fully understood. The role of copper in GO electrical steels are summarized below based on previous studies and including some of our own research results.
3.4. Discussion

(1) Cu reacts together with Mn and forms (Cu,Mn)S. In CGO electrical steels where MnS is the main inhibitor, Cu is incorporated into MnS and forms (Cu,Mn)\textsubscript{1.8}S [34–36], which is more effective in pinning the normal grain growth than MnS in Cu-free CGO electrical steels because the precipitate volume fraction increases whereas the size decreases with Cu addition [34]. However, in HGO electrical steels where AlN is the main inhibitor, (Cu,Mn)S often precipitates out with a size of several hundred nanometers (see Fig. 3.3). This size is too big to effectively prevent grain boundary movement.

(2) Cu directly combines with S and forms Cu\textsubscript{2-x}S precipitates to inhibit normal grain growth [15]. In the present work we show that Cu\textsubscript{2-x}S is finely dispersed within the matrix below 830 °C, which can exert a strong pinning force. However, we also demonstrate that the Cu\textsubscript{2-x}S precipitates dissolve above 900 °C and thus do not pin the grain boundaries.

(3) Cu atoms can segregate at grain boundaries and exert a solute-drag effect [37]. However, the distribution of type III precipitates indicates that Cu atoms are uniformly distributed in the matrix, do not show enrichment at grain boundaries, making a solute drag effect less likely.

(4) The addition of Cu increases the volume fraction and stability of austenite during hot rolling in the two phase (austenite and ferrite) region [37]. As discussed in Section 3.4.1, the higher the austenite volume fraction, the larger the area with a high precipitate number density, and the stronger the precipitate inhibition strength. Therefore, Cu can indirectly increase the inhibition strength by promoting the precipitation of AlN precipitates during hot-band annealing.

(5) In addition, we clearly demonstrated that precipitation of Cu\textsubscript{2-x}S precipitates could positively affect the distribution of AlN precipitates in this work, because Cu-based precipitates act as the cores of AlN precipitates in low number density areas.

To summarize, Cu can affect the inhibition strength directly (points 1-3), or indirectly affect the nucleation and distribution of AlN-based precipitates (points 4-5).

3.4.5 Effects of precipitates on secondary recrystallization

From our combined observations on grain growth (secondary recrystallization) and evolution of the three types of precipitates, we can derive the following conclusions:

Type I precipitates in the GOES analyzed in the present work are so large that they are not effective in pinning grain boundary movement and therefore they are not relevant to secondary recrystallization.

Type II AlN-based precipitates grow below 950 °C and start to dissolve afterwards, where most effective dissolution occurs in the temperature range from 1100 to 1175 °C. Considering the precipitate size and number density evolution in Fig. 3.7a-c, we show that it is the dissolution of the type II precipitates that lowers the pinning effect on grain
boundary movement and leads to the secondary recrystallization. This agrees with the work done by Yim et al. [8], who annealed a decarburized HGO steel to different temperatures (600 °C, 800 °C, 900 °C and 1000 °C) at a heating rate of 20 °C/h in a 50% H₂ + 50% N₂ atmosphere, and found that AlN precipitates dissolve (between 900 °C and 1000 °C) before secondary recrystallization occurs. However, Huang et al. [25] showed that AlN precipitates continue to coarsen before secondary recrystallization occurs (at ~1040 °C) in an annealing atmosphere of 75% H₂ + 25% N₂. Jenkins and Lindenmo [16] investigated a Cu-added CGO electrical steel and pointed out that the onset of secondary recrystallization starts when the CuMnS precipitates coarsen (above ~100 nm). Note the inhibition strength is depended by the precipitate size and number density instead of its type.

A likely reason for the discrepancy between our work and [25] is that we annealed the samples in a pure H₂ atmosphere which leads to faster decomposition of AlN-based precipitates (on top of the effective desulphurization) whereas a mixed H₂ and N₂ atmosphere was used in the previous study to maintain the N content in the steel so that AlN could continuously to grow. This is due to an important difference in the manufacturing processes used: the present sample was nitrided before HTC annealing whereas nitriding was not performed before HTC annealing in [25]. Nevertheless, for our steel and annealing conditions it is clear that the dissolution of type II precipitates, and not their growth beyond 100 nm, explains why grain boundary pinning becomes ineffective and why secondary recrystallization occurs. In fact, it is the decrease of inhibition strength of precipitates, which can be caused by both precipitate coarsening and dissolution, that triggers the onset of secondary recrystallization.

The precipitates in high number density areas should play a major role in the development of Goss grains compared to those in low number density areas. As pointed in [2], three regions can be distinguished after hot-band annealing: large ferrite regions without austenite-ferrite transformation, cell structured regions with carbides where the austenite-ferrite transformation has occurred upon cooling after hot-band annealing, and the extended narrow ferrite regions between such cell structured regions. Taguchi et al. [38] pointed out that the sharp Goss grains exist in the extended narrow ferrite region. As discussed in Section 3.4.1, the high number density areas originate from the cell structured region. The precipitates in high number density areas surround the Goss grains. Therefore, the dissolution of precipitates in the high number density areas is most likely responsible for the onset of Goss grain abnormal growth.

Type III Cu₂₃S precipitates exist in the sample below 850 °C and pin grain boundary movement together with type II AlN-based precipitates in the early stage of annealing. They dissolve above 900 °C and do not exist at the higher temperatures between 1100 °C and 1175 °C, where the actual abnormal grain growth occurs. They have therefore no direct effect on the secondary recrystallization. However, as shown in Figs. 3.4 and 3.5, type II precipitates are not pure AlN precipitates but they generally contain Mn and particularly Cu.
and S, often with a clear copper sulphide core. So, it is therefore likely that Cu₂₋ₓS precipitates play an important role in the nucleation of type II AlN-based precipitates and thus still have an important indirect effect on secondary recrystallization. Moreover, a second (but small) indirect effect of the dissolved Cu₂₋ₓS precipitates is that the higher Cu (and S) concentration in the matrix may alter the solubility product of AlN slightly and thus its solvus (or dissolution) temperature.

### 3.4.6 Secondary recrystallization mechanism

On the assumption of spherical particles as extracted by the replicas, the precipitate volume fraction \( f \) is given by [39]:

\[
f = \frac{\pi}{6} \left( \frac{N_s^2}{\alpha} (x_A^2 + \sigma_A^2) \right)
\]

where \( N_s \) is the measured number of precipitates per unit area on the extraction replica, \( \alpha \) is the extraction efficiency (here the surface depth replicated is taken as \( 2X_A \), and the extraction efficiency thus incorporates this variable), \( X_A \) is the precipitate mean diameter, \( \sigma_A \) is the standard deviation from this mean diameter. Note that although AlN precipitates show six-sided prismatic shapes, still its equivalent diameter is obtained as shown in Figs. 3.7a and b.

According to Zener, the pinning force \( Z_p \) of the small precipitates on grain boundaries can be quantified as [17]:

\[
Z_p = \frac{3\gamma_{GB} f}{2r}
\]

where \( \gamma_{GB} \), \( f \) and \( r \) are grain boundary energy, precipitate volume fraction and precipitate mean radius, respectively. The value of \( \gamma_{GB} \) is taken as 0.75 J/m² [40].

Combining Eqs. (3.3) and (3.4), the Zener pinning force can be calculated. Although the accuracy of Eq. (3.3) has been doubted since the effective thickness where the precipitates were extracted is impossible to measure. Still, it makes sense because the inhibition force evolution trend can be obtained even though the calculated inhibition forces may be different from the real ones. First the pinning force \( Z_p \) for both the AlN precipitates in high and low number density areas is calculated separately. Then the total pinning force \( Z_p \) of AlN precipitates is obtained by first multiplying the \( Z_p \) values holding for the two areas by their corresponding area fractions and then summing them (see Fig. 3.7d).

A schematic diagram showing the relationship of the evolution of total inhibition force \( Z_p \) of AlN and the grain size during the simulated HTC annealing is shown in Fig. 3.15. Before annealing to a temperature slightly above 1100 °C, the grain sizes remain unchanged. The inhibition strength is slowly decreasing due to the dissolution of AlN-based precipitates (both number density and average size decrease). The inhibition force decreases to the critical value between 1100 °C and 1175 °C, which triggers the onset of secondary
recrystallization. The inhibition force keeps decreasing towards zero and grains rapidly grow to centimeter-size during secondary recrystallization. During annealing at 1250 °C for 24 h, grain sizes remain almost the same and the inclusions are purified.

![Diagram showing the relationship of the evolution of total inhibition force Zp of AlN and the grain size during the simulated HTC annealing.](image)

The inhibition force $Z_p$ of Cu$_{2-x}$S precipitates is also roughly calculated for the D-line sample based on the number density and size distribution shown in Fig. 3.12. The inhibition force $Z_p$ of Cu$_{2-x}$S precipitates is calculated to be around 0.52 MPa, two orders of magnitude higher than that of AlN precipitates. However, the $Z_p$ value of Cu$_{2-x}$S is not shown in Fig. 3.15 since it is only valid for the D-line sample and not for the annealed samples, because Cu$_{2-x}$S dissolves between 830 °C and 900 °C.

### 3.5 Conclusions

Decarburized and nitrided HGO electrical steel was annealed to different temperatures in a pure H$_2$ atmosphere to simulate the HTC annealing that is used in practice to invoke secondary recrystallization leading to large (centimeter-size) grains with sharp Goss texture. The precipitate evolution in this steel was studied in detail using TEM related techniques. The main conclusions are:

1. Three types of precipitates with different compositions, size ranges and morphologies are present.
2. Type I precipitates are mainly large irregular (Mn,Cu)S-(Al,Si)N core-shell precipitates with sizes ranging from 150 nm to 700 nm.
3.6 References

(3) Type II precipitates are mainly six-sided prismatic precipitates with sizes between 10 nm and 150 nm. Their compositions correspond to (Mn, Si)N-(Al, Si)N- or Cu₅S-(Al, Si)N core-shell structures. Two types of areas with high and low number density of type II precipitates were observed and quantitatively assessed. Precipitates in both the two areas coarsen before 900 °C and start to dissolve after 950 °C, where strongest dissolution occurs just above 1100 °C. It is rationalized that the high number density areas originate from the austenite to ferrite transformation during hot-band annealing.

(4) Type III precipitates are spherical precipitates smaller than 10 nm. FCC Cu₂₅-S precipitates are present in the D-line sample and then dissolve between 830 °C and 900 °C. After annealing at temperatures above 900 °C, they precipitate out again as FCC Cu₂₅-S precipitates during cooling. BCC Cu precipitates form during cooling when annealing at 1250 °C for 24 h, because of the desulphurization that occurred during annealing in the H₂ atmosphere.

(5) Secondary recrystallization occurs between 1100 °C and 1175 °C. The present work demonstrates that the dissolution of type II precipitates is responsible for activating this process. Note however, that type II precipitates, like stated under conclusion (3), have a complex structure often requiring a Cu-S type core and it is therefore the total interplay of (copper) sulphide and (aluminum) nitride precipitation and their dissolution that paves the way for secondary recrystallization and thus the extraordinary sharp Goss texture with centimeter-size grains.

3.6 References


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3.6 References


3.7 Supplementary material

S3.1 Type I core-shell co-precipitates

Fig. S3.1 STEM elemental mapping of a type I precipitate showing (Al, Si, Mn)N form on the Cu$_2$S shell and TiN core.

S3.2 Type II precipitates

Fig. S3.2 (a) Example of typical EDS spectra of type II precipitates in the D-line, 900 °C, 950 °C, 1100 °C and 1175 °C samples, (b) big precipitates between 50 nm and 200 nm in the 1250 °C 24 h sample, (c) EDS spectra of the big precipitates in (b), showing they are Cu particles. Small precipitates of several nanometers are also observed.
S3.3 Stitched SEM image of bulk D-line sample

![Stitched SEM image of bulk D-line sample](image)

**Fig. S3.3** Stitched bright-field SEM image of the bulk D-line sample, clearly showing the low and high (indicated by red circles) precipitate number density areas. The bulk sample were etched in 3% Nital solution for 20 s after final polishing.

S3.4 HAADF-STEM images

![HAADF-STEM images](image)

**Fig. S3.4** HAADF-STEM images showing type II precipitates in (a) low number density area of the 950 °C sample, (b) high number density area of the 950 °C sample, (c) low number density area of the 1100 °C sample, (d) high number density areas of the 1100 °C sample, (e) the 1250 °C 24 h sample.
S3.5 SAED patterns

Fig. S3.5 SAED pattern recorded along the [001] zone axis of ferrite from the sample (a) 900 °C and (b) 950°, and (c) the schematic illustration of (a) and (b).

S3.6 STEM EDS elemental mapping in the 900 °C sample

Fig. S3.6 STEM EDS elemental mapping of precipitates in high number density areas in the 900 °C sample, showing that the main composition of the precipitates is (Al,Si)N. Cu$_{2-x}$S is observed to be on (Al,Si)N precipitates, indicating the Cu$_{2-x}$S has already dissolved at 900 °C and precipitate upon (Al,Si)N during furnace cooling.