Chapter 1 General introduction

Mankind throughout history has been looking for tools that could improve their survival rate. Better materials meant better tools, in particular better weapons, which allowed mankind to spread and conquer. Better materials generally also required improvement(s) in their production technologies and advancements in material processing like steel and aluminum production continue to impact society today. Historians have regarded materials as such an important aspect of civilizations that entire periods of time have defined by the predominant material used (Stone Age, Bronze Age, Iron Age, etc.).

If a poll is taken to decide the most important metallurgical development during the 20th century, it would not be surprising that the discovery of age hardening by Alfred Wilm 110 years ago would be a popular choice. Although this phenomenon has been associated particularly with aluminium alloys, it is now realized that far more types of alloys may be strengthened by this method of heat treatment.

In 1906, the German metallurgist Alfred Wilm [1] accidentally discovered that aluminium containing a small amount of copper showed hardening after quenching, opening the field of age hardenable aluminium alloys. Wilm named the age hardenable aluminum alloy as Duralumin in 1909, which is still recognized today. In similar times the Wright brothers developed their first aircraft from wood and (cotton) fabric to make first successful flights on December 17th, 1903. Although a milestone in engineering, the materials used in the Wright flyer were rather primitive albeit an aluminum block was already used in their engine. In 1919, Professor Junkers in Germany produced the Junkers 13, the first all-aluminium plane [2]. Duralumin was also adopted by Count von Zeppelin for constructing rigid airships at his factory in Germany. Around 100 airships were built during world War I and 750 tons of Duralumin were produced in one year in Germany [3].

Although the notion that aluminium could be age hardened was develop in the early 20th century, a proper explanation for this hardening could not be developed for a long time. Based on experimental work published in 1919 [4] it was proposed that the age hardening after quenching was due to copper atoms precipitating out as particles from supersaturated solid solution. In 1938 Guinier in France [5] and Preston in England [6], independently, interpreted features in diffuse X-ray scattering from aged aluminium alloys as evidence for clustering of copper-rich atoms into very small zones; since then termed as Guinier-Preston zones, or GP zones for short. However, direct observations of GP zones were not possible till transmission electron microscopy (TEM) had become a sufficiently matured technique at the end of the 1950s (leading to first observations by Nicholson and Nutting [7]).

When age hardening could be attributed to precipitates, then it was also relatively logical to understand that slip (of atomic planes) in crystals is hindered by these precipitates, explaining the hardening effect. However, for a proper understanding of precipitation
hardening it is in principle also required to have some basic understanding of dislocation theory. Dislocations as defects in metal crystals were hypnotized for the first time in 1934 [8], but after indirect observations (e.g. by slip traces and etch pits in optical micrographs), they were only for the first time directly observed using TEM by Peter B. Hirsch in work published in 1956 [9]. Only since these seminal TEM works, observing dislocations in 1956 and GP zones in 1958, precipitation hardening can be well understood on the basis of precipitates being obstacles hindering dislocation motion.

In addition to the well-known case of precipitation hardenable aluminium alloys, precipitates also play a crucial role in various types of steels in determining their final structures and properties. In this thesis the focus will be on grain oriented electrical steels and high strength low alloy steels. Developing in-depth understanding of the precipitation behavior in these two steels is of great significance for tailoring the properties of these materials. In this chapter, background information is provided on precipitates and the two types of steels. First, general information on precipitates, such as their classification, formation, nucleation, growth and their role in alloys is described. Next, the two investigated steels are introduced in terms of their application, feature, composition, historical development, manufacturing process and the importance of precipitates in the steels. Finally, an outline of the thesis with a short introduction for each chapter is given.

### 1.1 Precipitates

Metals and its alloys are widely used in our daily life. They exhibit excellent properties, such as high strength, good ductility and conductivity. Advanced electron microscopy techniques enable us to view the inner microstructure at a nanoscale level. In many alloys second phase particles (smaller than 1 μm), which are called precipitates when present with considerable densities, can be observed. A well-known example is precipitation in aluminum alloys as described above and shown in Fig. 1.1. Precipitation in normal language is associated with liquid droplets falling out of the sky, but precipitation in materials science is related to small scale solid particles (with appreciable densities) embedded in larger crystals of the host material.

![Fig 1.1 Precipitates in an Al-Mg-Si alloy [10].](image-url)
Precipitates can be dispersed into the matrix in different ways. Coarse precipitates (100 - 1000 nm) can be formed during solidification [11,12]. Fine precipitates (1-100 nm) can precipitate out from supersaturated solid solution in thermomechanical processes [13,14], which is by far the most commonly used method for producing dispersed precipitates in the matrix. They can also be introduced by diffusion reaction techniques, for instance, by internal oxidation [15,16], by nitriding [17,18], or by mechanical alloying [19].

Based on the interface characteristics between the precipitate and the matrix lattice, precipitates can be classified into coherent, semi-coherent and incoherent precipitates [20]. Fig. 1.2 shows schematic illustrations of the three types of interfaces between the precipitate and the matrix. A coherent interface forms when the precipitate and the matrix match perfectly at the interface plane so that lattice planes continue in a straight manner across the interface (see Fig. 1.2a). For very small, i.e. nanoscale, precipitates the interfacial energy term is still large compared to the energy associated with the volume of the precipitates like for instance strain energy. Therefore, small precipitates are often strained to realize low energy coherent interfaces. In addition, when precipitates and matrix are coherent, then there is no need for straight interfaces and then often spherical precipitates form, because they show the largest volume to interface area ratio, which is energetically the most favorable shape, particularly for very small precipitates. When precipitates grow in size or in case of high misfit strains, it becomes energetically more favorable to replace the coherent interface with a semi-coherent one where the mismatch is periodically taken up by misfit dislocations (see Fig. 1.2b). Such a semi-coherent interface removes most of the strain energy (only local strains remain, but global strains disappear) while it still can be associated with relatively low interfacial energies. In general, there will also be a tendency to produce precipitates where interfaces are straight for certain segments which are called facets. So, the transition from coherent to semi-coherent interfaces is also often associated with the transition from spherical to facetted precipitates. When there is no good lattice matching across the interface or the precipitates are large in size and show large mismatch, incoherent interfaces form (see Fig. 1.2c). So, the coherency is often gradually lost as the precipitate grows in size. A typical example is the phase transformation of GP zone $\rightarrow$ $\beta'' \rightarrow \beta' \rightarrow \beta$ in Al-Mg-Si alloys [21].

![Fig 1.2 Schematic illustrations of interface type between the precipitate and the matrix (adapted from [22]): (a) coherent, (b) semi-coherent, (c) incoherent.](image-url)
Precipitates can nucleate randomly from the supersaturated solid solution and this is called homogeneous nucleation. They can also form on lattice defects, such as vacancies, dislocations and grain boundaries, which is called heterogeneous nucleation. The activation energy for heterogeneous nucleation is lower than that for homogeneous nucleation due to the higher free energy at lattice defect regions and, hence, precipitates preferentially nucleate at these regions [23]. After nucleation, atoms diffuse onto the precipitates and they grow. The growth of precipitates is generally diffusion-controlled. Therefore, precipitates can be randomly distributed in the matrix (see Fig. 1.1), or positioned at grain boundaries (see Fig. 1.3a) or on dislocations (see Fig. 1.3b). Since the diffusion rate increases when going from the perfect lattice to dislocations to grain boundaries also the growth rates of precipitates in general depends in the same manner on the position where the precipitate nucleated. The differences in precipitate spatial distribution can lead to a different pinning effect on grain boundary movement even when the precipitate size and volume fraction are the same.

For precipitates showing a coherent or semi-coherent interface with the matrix, there is an orientation relationship between the crystal lattices of the precipitate and the matrix. This is usually defined by planes and directions in each phase which are parallel, for instance, the crystal orientation relationship (OR) between titanium carbide (TiC) and the ferrite matrix (α) can be written as (100)_{TiC} // (100)_{α} and [011]_{TiC} // [001]_{α} [24]. Note that most often techniques like X-ray diffraction have been used to determine ORs between precipitates and matrix. In such cases the ORs in general do not provide any information on the actual planes and directions that are parallel at the interfaces. Using transmission electron microscopy, that is able to sufficiently resolve precipitates, it becomes possible to determine the shape of the precipitates and to find the actual interface orientations when clear facets are present.

![Fig 1.3 Precipitate distribution in a Nb-Ti micro-alloyed steel [25]. (a) relative big precipitates distributed at a grain boundary in a bright-field TEM image, (b) needle-shaped precipitates distributed on a dislocation in a dark-field TEM image.](image-url)
Precipitates play a very important role in terms of mechanical properties of alloys. The strength and hardness of a large number of metal alloys, for example, aluminum-based alloys, nickel-based super-alloys, titanium alloys and certain types of steels, are enhanced by the formation of finely dispersed precipitates within the matrix in a process known as precipitation or age hardening [23]. After solid solution hardening and cold work this is one of the most widely used mechanisms for the strengthening of metal alloys. The precipitates act as obstacles to dislocation movement and thereby strengthen the alloys.

Moreover, precipitates can affect recrystallization in three distinct manners [26]. Firstly, precipitates modify the deformation structure in terms of heterogeneity sites and stored energy, exerting significant influence on the subsequent recrystallization process. Secondly, precipitates directly interact with recrystallization process by retarding or accelerating recrystallization nucleation, influencing the orientations of the recrystallized grains, and pining the growth of the recrystallized grains. Thirdly, precipitates can also affect the grain growth after the completion of recrystallization, for instance, limiting the grain size and inducing abnormal grain growth. More detailed explanations on how precipitates affect recrystallization can be found in [26].

1.2 Grain oriented (GO) electrical steel

Electrical steel is a soft magnetic material that is used as the core material of electric power appliances. Electrical steel can be divided into grain oriented (GO) electrical steel used mainly in transformers and non-grain oriented (NGO) electrical steel utilized in motors and generators [27].

GO electrical steels, also known as silicon steels or Fe-3% Si alloys, have extraordinary microstructures consisting of centimeter-size grains with the crystal lattice having the so-called Goss orientation: <001> // rolling direction (RD) and the {110} planes // rolling plane [28–30]. The transformer core consists of stacks of thin GO electrical steel plates with their Goss texture oriented in a manner schematically indicated in Fig. 1.4a. Honda and Kaya [31] discovered the existence of magneto crystalline anisotropy in iron and showed that the <001> crystal direction is the most easiest direction of magnetization as illustrated in Fig. 1.4b. Therefore, the microstructure with sharp Goss texture in GO electrical steels results in soft (easy) magnetization and low core losses. Based on the Goss orientation sharpness, the GO electrical steels can be classified into two grades: conventional grain oriented (CGO) electrical steels and high permeability grain oriented (HGO) electrical steels. The average deviation of the <100> axis from the rolling direction is about 7° in CGO and 3° in HGO electrical steels [32].

GO electrical steels have a high silicon (Si) content of 2.9-3.5% (wt%), which increases the electrical resistivity of iron and, therefore, reduces core losses, e.g. by reducing eddy currents. The presence of Si also stabilizes the steel with respect to the deterioration over time of the magnetic properties (magnetic aging) [33]. Yet, the Si content is limited. Arai
and Ohmor mentioned that the steels become more brittle as the Si content increases [34]. Nakashima et al. pointed out that the increase of Si content can result in a reduction in the intensity of the {110} component of the Goss texture [35], i.e. grains become less well oriented. Carbon (C) is added to control dendrite growth during slab reheating and to increase the amount of austenite during hot rolling. The C addition is beneficial for the {110}<001> texture formation [35]. However, C is harmful for electrical steels due to the magnetic aging. Therefore, in a later processing step decarburization must be performed to bring C content to a low level (0.02 - 0.07%). Elements such as manganese (Mn), copper (Cu), sulphur (S), aluminum (Al) and nitrogen (N) are added to form inhibitors that control the grain size. Other trace elements, such as titanium (Ti), chromium (Cr), phosphorus (P), zirconium (Zr), boron (B), nickel (Ni) and tin (Sn), are also added, which have also been reported to be beneficial for the magnetic performance.

The core loss of GO electrical steels has drastically declined to 0.35W/Kg at 1.7 T [36] from 2.8 W/Kg at 1.5 T since the GO electrical steel was invented [37]. The historical development of the core loss reduction has been summarized by Ushigami et al. [36] and is shown in Fig. 1.5. Some key developments are emphasized below. In 1933, Goss invented grain oriented electrical steels which dramatically improved the steel magnetic properties and ARMCO later succeeded in commercial production and gradually improved the properties. In 1956, Nippon Steel developed a new GO electrical steel with high permeability using AlN as the inhibitor which has superior magnetic properties compared to the previous GO electrical steels using MnS as the inhibitor. Since then, the core loss was gradually decreased by reducing the steel thickness and refining magnetic domain using techniques such as mechanical scratching, plasma irradiation, spark ablation, and laser scribing. The manufacturing process of GO electrical steels has been greatly improved over the last few decades with low temperature slab reheating techniques, thin slab technology and thin-casting technology, etc [38].
The manufacturing process of the GO electrical steels is the most difficult one among all possible types of steel and is only mastered by several big steel companies. Any minor change in the process could result in change in the magnetic properties. Therefore, GO electrical steel is honored as an “artistic product of iron”. Fig. 1.6 shows a schematic diagram of the manufacturing process based on the production line of ThyssenKrupp Steel group for HGO electrical steels [39], which utilizes the thin slab technology. Thin-slab technology is an integral chain process starting from the production of liquid steel to the refined hot strip. This technology combines low temperature slab reheating technique with compact process, making the production line more efficient regarding energy usage and running costs, and enables products with higher quality. By nitriding after decarburization, high permeability GO electrical steels can be produced.

Fig. 1.5 Historical development of core loss reduction in GO electrical steels [36].

Fig 1.6 The schematic diagram of the manufacturing process based on the production line of ThyssenKrupp Steel group [39].
During the high temperature coil (HTC) annealing process, a certain very small number (1 out of at least $10^6$) of grains having Goss orientation grow at the expense of other normal primary recrystallized grains. The grain sizes grow from micrometer-size to centimeter-size (see Fig. 1.7 [40]). This phenomenon is called secondary recrystallization.

Several theories have been proposed to explain the secondary recrystallization phenomenon, such as size advantage theory [41], coincident site lattice (CSL) boundaries model [42], high energy (HE) boundaries model [43,44], orientation pinning (OP) model [45] and solid-state wetting model [46,47]. However, none of those models can explain all experimental observations. Yet, it is generally accepted that secondary recrystallization is achieved through the inhibition of normal grain growth by precipitates (also referred to as inhibitors) [48,49] and a sharp primary recrystallization texture [50–55]. During HTC annealing this inhibition is effectively removed, so that secondary recrystallization can occur.

![Figure 1.7](image)

**Fig 1.7** Secondary recrystallization behavior in grain-oriented silicon steel (grain size and structure) [40].

### 1.3 High strength low alloy (HSLA) steels

HSLA steel is a type of alloy steel that provides better mechanical properties or greater resistance to corrosion than carbon steel. It is widely used in automotive industry in response to the increasing demand of lightweight vehicles to reduce energy consumption and CO$_2$ emission in the past few decades [56].

A typical HSLA steel (also referred to as micro-alloyed steel) contains 0.05–0.25% C, up to 2% Mn, small additions of several micro-alloying elements like niobium (Nb), vanadium (V), titanium (Ti), molybdenum (Mo) (all usually max. 0.15%) and some other trace elements like Si, Cu, Ni, Cr, P, Zr and rare earth elements [57]. The role of C is to strengthen the matrix, to retain formability, and to form carbides together with the micro-alloying elements. Mn can delay the austenite decomposition during accelerated cooling.
The micro-alloying elements are used to refine the grain microstructure and facilitate strengthening through precipitation. Si acts as dioxide in molten alloys and as solid solution strengthener. The corrosion resistance of the steel is enhanced by the addition of Cu, Ni, Cr and P whereas Zr and rare earth elements are added for sulfide-inclusion shape control which increases formability [58].

HSLA steels are economically favorable, show good weldability and coatability due to their low carbon and low alloy contents and exhibit excellent formability due to the predominant soft ferrite microstructure (the rest is a small amount of pearlite microstructure) [59,60]. However, the low carbon and low alloy contents also result in insufficient strengthening by solid solution and secondary phase hardening. The main active strengthening mechanisms in HSLA steels are due to grain refinement and precipitation hardening. Current HSLA steels have a yield strength in the range of 350 - 800 MPa, with the potential to exceed 1000 MPa [61].

The use of micro-alloyed elements was first reported in the years 1938–1939 [57] with the addition of Nb as a strengthener of hot rolled C-Mn steels. Much of the early work was concentrated on Nb additions and mainly conducted in the USA and UK. In 1958, the American company National Steel Corporation developed a steel with relatively low cost of Nb addition at 0.005 - 0.03%, obtaining a combined effect on resultant strengthening and good toughness [62]. The Nb was also added to an ordinary C-Mn steel and the yield strength of the steel increased from around 300 MPa to 415 MPa [62]. The term “micro-alloying” was first proposed in 1959 by Beiser [63] who reported the effects of small Nb additions to a carbon steel. Over the past 60 years, the mechanical properties of HSLA steels have been greatly improved by optimizing chemical compositions, such as adding other microalloying elements like V, Ti and Mo, by further understanding strengthening theory, such as Hall-Petch relationship, precipitate hardening and second phase strengthening (where comprehension was also greatly supported by parallel developments in electron microscopy), and by optimizing the hot rolling process [62]. The development of pipeline steels as an example of HSLA steel research is shown in Fig. 1.8, through which the microstructure and properties change over time with advances in alloy design and processing is illustrated.

Thermo-mechanically controlled processing (TMCP), which consists of controlled hot rolling and controlled cooling, is an important and effective rolling technology for microstructural control to obtain excellent mechanical properties, such as high strength, excellent toughness and other performances. Fig. 1.9 shows a schematic diagram of TMCP and microstructures that result from this process [64]. The mechanical properties are greatly affected by different parameters, such as rolling ratio, rolling temperature, cooling rate and the coiling temperature. The main principles behind this process are the ability to refine the austenite grain size, increase the defect density, accelerate the precipitation of micro-alloying elements, and control the type of obtained phases [65].
Cold rolling is a follow-up process after hot rolling. Annealing is therefore necessary after cold deformation to remove the anisotropy of the microstructure and of the mechanical properties. Compared with hot rolled steel strips, cold rolled and annealed HSLA steel strips are thinner and more suitable to be used for various applications in automotive industry to reduce weight, especially as automotive body sheets.
Precipitation of carbides and nitrides can occur in three distinct stages during the microalloyed steel processing. Firstly, precipitates can form in the liquid phase or after solidification. These precipitates, e.g. composed of TiN, are very stable and might retard the austenite coarsening during reheating [11]. Secondly, precipitates such as NbCN and TiC can be induced by strain during controlled rolling, which can retard the austenite recrystallization and lead to grain refinement [66,67]. Thirdly, precipitates such as VC, TiC and NbC can form during or after austenite-ferrite transformation, nucleating in austenite-ferrite interface (known as interface precipitation) or in ferrite (known as random precipitation). They can greatly contribute to strength by precipitation hardening due to their small size and high number density [68–70].

1.4 Thesis outline

The aim of this thesis is to conduct extensive investigations on precipitate evolutions in GO electrical steels and cold-rolled Ti-V HSLA steels mainly using state-of-the-art electron microscopy techniques in order to provide an in-depth understanding of precipitation behavior during annealing and the role the precipitates play in the steels. The experimental techniques and specimen preparation details are described in Chapter 2 and experimental results and their analyses are provided in Chapter 3 for GO electrical steel and Chapters 4-6 for cold-rolled Ti-V HSLA steel.

Chapter 2 gives an overview of the experimental details. The chemical compositions and manufacturing process of the two investigated steels are first described. Then experimental characterization techniques to analyze microstructure, precipitation, recrystallization and mechanical properties are introduced with a brief introduction on basic principle and some detailed experimental parameters.

Chapter 3 focuses on the precipitate evolution in GO electrical steel during HTC annealing (see Fig. 1.6). The composition and size evolution of different types of precipitates were investigated in detail using state-of-the-art transmission electron microscopy (TEM) based techniques. Finally, in-depth understanding is obtained of how precipitates enable secondary recrystallization, e.g. by losing their inhibition effect, but also act as nucleation seeds for other types of inhibiting precipitates.

Chapter 4 deals with the microstructure, mechanical property, especially precipitate evolution during isothermal annealing of cold-rolled Ti-V HSLA steel. The annealed cold-rolled samples were investigated with a unique combination of techniques including visible light microscopy (VLM), advanced TEM, matrix dissolution based analysis, small angle neutron scattering (SANS) and hardness measurements. This chapter also aims at comparing quantification techniques with respect to their ability to determine composition, size and volume fraction of nanoscale precipitates.
Chapter 5 investigates the recrystallization behavior during isothermal annealing of cold-rolled Ti-V HSLA steel. Electron backscatter diffraction (EBSD) measurements were conducted to study the recrystallization kinetics, dislocation density and texture evolution. This chapter is a parallel study with Chapter 4 since Chapter 5 focuses on recrystallization behavior whereas Chapter 4 mainly focuses on precipitation behavior.

Chapter 6 studies the simultaneous precipitation and recrystallization behavior at the early stage of continuous annealing of cold-rolled Ti-V HSLA steel. The effects of different soaking temperatures and times on the microstructure and mechanical properties were revealed after precipitation and recrystallization behavior investigation with techniques employed in Chapters 4 and 5. This acquired knowledge is used to guide the industrial manufacturing process optimizing.

1.5 References


