Phase Transformation And Strain Hardening Mechanisms In Advanced Engineering Steels

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PHASE TRANSFORMATION AND STRAIN HARDENING MECHANISMS
IN ADVANCED ENGINEERING STEELS

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PHASE TRANSFORMATION AND STRAIN HARDENING MECHANISMS
IN ADVANCED ENGINEERING STEELS

by

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DISSERTATION

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Abstract

Strain hardening and associated deformation mechanisms play a determining role in the performance of metallic materials. The objective of the doctoral research was to explore and fundamentally understand the strain hardening mechanisms in the next generation of advanced engineering steels. Two main work hardening mechanisms, notably, twinning-induced plasticity (TWIP) and transformation-induced plasticity (TRIP)) were identified that governed strength and ductility. In the nanograined austenitic steel with high strength-high ductility combination, processed by the novel phase reversion concept, twinning-induced plasticity (TWIP) was the governing deformation mechanism and contributed to good ductility. In striking contrast, transformation-induced plasticity (TRIP) was the deformation mechanism in the low strength coarse-grained counterpart, which contributed to high ductility. The difference in the deformation mechanisms in the nanograined and coarse-grained structures was explained in terms of austenite stability – strain energy relationship.

In another instance of Ni-free and Ni-bearing steels, two distinct types of nanostructured bainite were obtained through conventional one-stage and two-stage isothermal treatments, with the aim to study the effect of nickel on strain hardening. The presence of Ni led to reduction in the free energy of bainitic transformation, refinement of bainite structure, and extension of bainite nucleation regime. The uniform nanostructure of Ni-bearing steel promoted the formation of stable film-like retained austenite between the bainitic ferrite laths, leading to higher strain hardening rate and stronger transformation-induced plasticity (TRIP) effect, which was explained in terms of a thermodynamic model.
Table of Contents

Acknowledgements ........................................................................................................ iv

Abstract ............................................................................................................................ v

Table of Contents ........................................................................................................... vi

List of Tables ..................................................................................................................... ix

List of Figures ................................................................................................................... x

Chapter 1: Introduction ..................................................................................................... 1

1.1 Strain hardening in metastable austenitic stainless steel ................................................. 4
  1.1.1 Transformation-induced plasticity (TRIP) ................................................................. 6
    1.1.1.1 The development of transformation-induced plasticity (TRIP) effect ................. 6
    1.1.1.2 The mechanism of transformation-induced martensite and hardening .............. 10
  1.1.2 Twinning-induced plasticity (TWIP) ......................................................................... 18
    1.1.2.1 The development of twinning-induced plasticity (TWIP) effect ...................... 18
    1.1.2.2 The mechanism of twinning-induced plasticity and hardening ....................... 20
  1.1.3 Phase reversion process in TRIP/TWIP steels ......................................................... 27

1.2 Phase transformation hardening phenomenon in bainitic steel ................................. 32
  1.2.1 The development of phase transformation hardening in steel ............................... 33
  1.2.2 The characteristics of low temperature bainitic steel .......................................... 36

1.3 Microalloying elements, heat treatment and precipitation hardening ....................... 44

1.4 Objectives of study ................................................................................................. 48

Chapter 2: Materials and experimental methods ............................................................ 50

2.1 Materials and processing ....................................................................................... 50

2.2 Sample preparation ............................................................................................... 53

2.3 Microstructure observation and characterization ..................................................... 54
  2.3.1 Microstructure observation ................................................................................. 54
  2.3.2 Mechanical tests ................................................................................................. 54
  2.3.3 Phase volume fraction detected by X-ray diffraction (XRD) .............................. 55
  2.3.4 Element distribution measured by electron probe microanalyzer (EPMA) ....... 57
Chapter 3: The significance of phase reversion-induced nanograin/ultrafine-grained (NG/UFG) structure on the strain hardening behavior and deformation mechanism in copper-bearing antimicrobial austenitic stainless steel ........................................ 60
  3.1 Background ........................................................................................................ 61
  3.2 Experimental detail .......................................................................................... 63
  3.3 Experimental results ....................................................................................... 64
    3.3.1 Microstructure ............................................................................................ 64
    3.3.2 Tensile properties and strain hardening behavior ....................................... 66
    3.3.3 Deformation structure ............................................................................... 70
  3.4 Discussion ......................................................................................................... 73
  3.5 Conclusions ..................................................................................................... 78

Chapter 4: Effect of nickel on hardening behavior and mechanical properties of nanostructured bainite-austenite steels .................................................. 80
  4.1 Background ..................................................................................................... 80
  4.2 Experimental detail ........................................................................................ 83
    4.3.1 Materials and heat treatment processes of the samples ......................... 83
    4.3.2 Microstructural analysis .......................................................................... 84
    4.3.3 Mechanical tests ...................................................................................... 85
  4.3 Experimental results ....................................................................................... 86
    4.3.1 Microstructure of the steels after one-stage isothermal treatment ........ 86
    4.3.2 Microstructure of steels after two-stage isothermal treatment ............. 87
    4.3.3 Tensile behavior ...................................................................................... 91
    4.3.4 Strain hardening behavior ....................................................................... 93
    4.3.5 Strain hardening behavior ....................................................................... 96
    4.3.6 Carbon distribution ................................................................................... 97
  4.4 Discussion ......................................................................................................... 100
    4.4.1 The effect of Ni on carbon diffusion and stability of RA .................... 100
    4.4.2 Effect of RA stability on TRIP effect and strain hardening behavior of the steel samples .................................................. 104
  4.5 Conclusions ..................................................................................................... 107

Chapter 5: Effects of cooling after rolling and heat treatment on microstructures and mechanical properties of Mo–Ti microalloyed medium carbon steel ........................................ 109
  5.1 Background ..................................................................................................... 110
Chapter 5: Experimental results

5.2 Experimental detail .................................................................................................112
5.3 Experimental results .................................................................................................114
  5.3.1 Microstructures .................................................................................................114
  5.3.2 Mechanical properties .......................................................................................121
  5.3.3 Fracture surfaces .............................................................................................123
5.4 Discussion ..................................................................................................................124
  5.4.1 Precipitation behavior ......................................................................................124
  5.4.2 Effects of heat treatment on microstructures ......................................................128
  5.4.3 Strengthening and toughening mechanism ........................................................130
5.5 Conclusions ..............................................................................................................133

Chapter 6: Conclusions and future work ....................................................................136

6.1 Conclusions ..............................................................................................................136
  6.1.1 The significance of phase reversion-induced nanograin/ultrafine-grained (NG/UFG) structure on the strain hardening behavior and deformation mechanism in copper-bearing antimicrobial austenitic stainless steel ..........136
  6.1.2 Effect of nickel on hardening behavior and mechanical properties of nanostructured bainite-austenite steels .................................................................137
  6.1.3 Effects of cooling after rolling and heat treatment on microstructures and mechanical properties of Mo–Ti microalloyed medium carbon steel ..........138
6.2 Future work ..............................................................................................................139

References ....................................................................................................................140

Vita 156
List of Tables

Table 1.1 Twenty-four variants of K–S relation

Table 1.2 The typical chemical compositions of low temperature bainitic steel (wt.%) [107, 110].

Table 2.1 The chemical compositions of studied steels in the dissertation (wt.%).

Table 2.2 Lattice constants, atomic spacing and 2θ position for austenite, martensite and ferrite [141].

Table 3.1 Chemical composition (wt.%) of the experimental Cu-bearing austenitic stainless steel.

Table 3.2 Weighted average grain size and tensile properties of NG/UFG and CG copper-bearing antimicrobial austenitic stainless steels.

Table 3.3 Plastic strain in each stage of the samples with different grain sizes based on the C-J analysis.

Table 3.4 Maximum and minimum strain hardening rates of the samples.

Table 4.1 Chemical composition of experimental steels (wt.%)

Table 4.2 Hardness of Ni-bearing and Ni-free steel (HV1).

Table 4.3 The measured average size of bainitic ferrite (thickness), film and block-like RA.

Table 4.4 Mechanical properties of Ni-free and Ni-bearing steels. (A: Total elongation; Z: Reduction of area.)

Table 4.5 The corresponding logarithmic strain values of Ni-free and Ni-bearing steels for each stage of tensile test according to SHR.

Table 5.2 Statistical results of effective grain size.

Table 5.3 Mechanical properties of the test steel under different heat treatment processes.
List of Figures

Figure 1.1: The categories of three generations of AHSS grades according to the total elongation (TE) versus tensile strength (TS) combination (data come from the Ref. [1-4]). ........................................ 5
Figure 1.2: A schematic diagram of transformation-induced plasticity (TRIP) under plastic deformation. ............................................................................................................. 7
Figure 1.3 (a) Gibbs free energy (driving force of thermodynamic transformation) and (b) Critical stress for strain induced martensite transformation versus temperature [30]. .......... 11
Figure 1.4: [001]α’ standard stereographic projection of one of the K–S variants (V1) on which the [001]α’ axes of 23 other variants (V2 to V24) are plotted as solid marks. ......................... 14
Figure 1.5: The classic geometrical model for strain-induced α’-martensite nucleation: situation before (a) and after (b) intersection of localized slip bands proposed by Olson and Cohen [33]. 16
Figure 1.6: The formation of strain induced martensite: (a) Microstructure before and after 5% tensile deformation. (b) Transmission electron microscope (TEM) reveals the α’-martensite nucleated at the intersections of deformation bands [49]. ........................................... 17
Figure 1.7: Typical stress-strain curve for a TWIP steel and optical microstructure of ........... 19
a TWIP steel following deformation, showing a large number of twinning [56]. ..................... 19
Figure 1.8: Typical strain-hardening rate plot with the true strain (logarithmic strain) in a high Mn TWIP steel [61]. .......................................................................................... 21
Figure 1.9: ECCI images of deformed microstructures: highly dense dislocation walls (HDDWs) and dislocation cells (DCs) at (a) 0.05, (b) 0.1, (c) 0.3 and (d) 0.4 true strain [62]. ............... 22
Figure 1.10: Twinning refinement contribution to shear strain. ........................................... 25
Figure 1.11: Galindo-Nava’s model for the formation of ε-martensite and twin [77]........... 28
Figure 1.12: (a) Schematic diagram showing the “phase reversion” process to obtain NG/UFG structure. (b) Schematic diagram of refinement of dislocation cell-type martensite packet by cold deformation [95]. .......................................................... 31
Figure 1.13: Three most common phase transformation process in steels, i.e., (i) austenite to perlite, (ii) austenite to bainite and (iii) austenite to martensite........................................ 33
Figure 1.14: Calculation of parameters related to carbon content, (a) phase transition temperature and (b) bainite transformation incubation period [109]. ............................... 38
Figure 1.15: TEM micrographs of (a) low temperature bainite obtained after 144 h at 200 °C; (b) dislocation debris close to the austenite–bainitic ferrite interface. BF, bainitic ferrite; RA, retained austenite [111]. ........................................................................................................ 42
Figure 1.16 Ti-Mo Precipitates of experiment steel at different cooling rates (a,b) 0.5 °C/s⁻¹, (c) 2 °C/s⁻¹, (d) 20 °C/s⁻¹. [129]. .......................................................................................... 47
Figure 2.1 Heat treatment processes for multi-step nano-bainite transformation (Ni-free and Ni-bearing samples) ............................................................................................. 51
Figure 2.2 Flow chart of the heat treatment process of Ti-Mo sample .................................. 53
Figure 2.3 ASTM E8 standard dimensions and geometry of a flat tensile specimen [140]. .... 55
Figure 2.4 Series of elemental maps showing the distribution of key elements in a Murray Basin ilmenite concentrate. The colored scale bar at the right shows relative concentration [142]. .... 58
Figure 3.1 (a) Light optical and (b) transmission electron micrographs of CG and NG/UFG structure, respectively in Cu-bearing antimicrobial austenitic stainless steels. The NG/UFG steel consisted of nanograins (less than 100 nm) and a few ultrafine grains (~100–500 nm) with a weighted average grain size (\(\bar{d}_v\)) of 350 nm (b), whereas the CG steel was composed of uniform coarse grains with a weighted average grain size of 22 μm (a). ........................................... 65
Figure 3.2 True stress-true strain (logarithmic strain) plots for NG/UFG and CG copper-bearing antimicrobial austenitic stainless steels. ................................................................. 66
Figure 3.3 Strain hardening rate as a function of true strain (logarithmic strain) for NG/UFG and CG copper-bearing antimicrobial austenitic stainless steels................................................. 67
Figure 3.4 The C-J analysis (ln(dσT/dεT) vs. ln(dεT)) for NG/UFG and CG copper-bearing antimicrobial austenitic stainless steels. ................................................................. 69
Figure 3.5 Transmission electron micrographs of antimicrobial copper-bearing austenitic stainless steel with NG/UFG structure illustrating formation of occurrence of (a, b) nanoscale twinning (the inset is the selected area diffraction patterns) and (c, d, e) stacking faults in the tensile deformed structure. ...................................................................................... 71
Figure 3.6 Transmission electron micrographs of CG copper-bearing austenitic stainless steel illustrating (a-d) strain-induced martensitic transformation and (e, f) indexed selected area diffraction patterns. .............................................................................................. 72
Figure 3.7 Elastic strain energy as a function of grain size for martensite nucleation according to single variant equation. ...................................................................................... 78
Figure 4.1 Heat treatment processes for multi-step nano-bainite transformation........................................ 84
Figure 4.2 Optical micrographs of the (a) Ni-free and (b) Ni-bearing steel samples after isothermal treatment. ...................................................................................................................... 87
Figure 4.3 (a) Ni-free and (b) Ni-bearing steel samples after two-stage isothermal treatment. ... 88
Figure 4.4 SEM micrographs of (a) Ni-free and (b) Ni-bearing steel samples after two-stage isothermal treatment .................................................................................................................. 89
Figure 4.5 TEM micrographs of Ni-free (a), (c) and (e) and Ni-bearing steel samples (b), (d) & (f) after two stage isothermal treatment. (c) and (d) are the enlarged TEM images of red rectangular area marked in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.) ................................................................. 90
Figure 4.6 (a) Engineering stress-strain and (b)True stress-logarithmic strain curves for Ni-free (250 °C, 24 h + 200 °C, 48 h) and Ni-bearing (250 °C, 36 h + 200 °C, 72 h) steel samples after two-step isothermal treatment .................................................................................................................. 92
Figure 4.7 Strain hardening rate (SHR) of Ni-free and Ni-bearing steel samples as the function of logarithmic strain. ................................................................................................. 94
Figure 4.8 XRD spectra of (a) Ni-free and (b) Ni-bearing steel before and after tensile tests. .... 95
Figure 4.9 Load displacement plots of film-like RA in Ni-free and Ni-bearing steel samples after two-stage isothermal treatment ........................................................................................................... 96
Figure 4.10 SEM micrographs and carbon distribution maps of (a) Ni-free steel and (b) Ni bearing steel. .......................................................................................................................... 98
Figure 4.11 Point scanning images obtained via electron probe microanalyzer that were used to obtain carbon distribution in (a),(b) Ni-free steel and (c),(d) Ni-bearing steel. ......................... 100
Figure 4.12 Measured values of C-content in (a) Ni-free and (b) Ni-bearing steel samples by EMPA. ................................................................................................................................. 100
Figure 4.13 The free energy variation under quasi-equilibrium state ............................................................................... 101
Figure 5.1 Flow chart of the heat treatment process ......................................................................................... 113
Figure 5.2 Optical microstructures of (a) DQ + T process and (b) (DQ/AC/FC) + RQ + T processes. low chart of the heat treatment process ................................................................................... 115
Figure 5.3 SEM micrographs of (a) DQ + RQ + T, (b) AC + RQ + T and (c) FC + RQ + T processes. ................................................................................................................................. 116
Figure 5.4 TEM micrograph of DQ + T process at different resolutions. ....................................................... 117
Figure 5.5 TEM micrograph of DQ + RQ + T process, (a) (b) were at different resolutions, (c) HRTEM image showing precipitates and (d) IFFT lattice image of one in (c).......................... 118
Figure 5.6 TEM micrographs of AC + RQ + T process at different resolutions................... 119
Figure 5.7 TEM micrographs of FC + RQ + T process at different resolutions...................... 119
Figure 5.8 Inverse pole figures coloring (IPF) grain orientation distribution of (a) DQ + T process, (b) DQ + RQ + T process, (c) AC + RQ + T process and (d) FC + RQ + T process... 120
Figure 5.9 Effective grain size (EGS) of different heat treatment processes........................ 121
Figure 5.10 Longitudinal tensile fracture of (a) DQ + T, (b) DQ + RQ + T, (c) AC + RQ + T and (d) FC + RQ + T processes.......................................................... 123
Figure 5.11 Longitudinal impact fracture of (a) DQ + T, (b) DQ + RQ + T, (c) AC + RQ + T and (d) FC + RQ + T processes. .................................................................................. 124
Figure 5.12 The precipitation behavior under different process conditions...................... 126
Figure 5.13 Large angle grain boundary of (a) DQ + RQ + T, (b) AC + RQ + T and (c) FC + RQ + T processes. (Orientation difference is greater than 15°). ........................................... 129
Figure 5.14 The relationship between the length of a large angle grain boundary and the size of martensite microstructures............................................................ 130
Chapter 1: Introduction

In order to achieve carbon neutrality worldwide, lowering carbon emissions have been the primary motivation in designing automobiles in the two decades. The fundamental strategy to minimize fuel consumption and carbon emissions is to reduce the vehicle's weight, meanwhile, ensure enough frame strength for the safety of passengers in the traffic industry. This has led to the higher crash performance of structures while allowing for a reduction in thickness. The hardening phenomenon plays an essential role in the crash energy absorption and structure deformation. Hardening is a basic metalworking process used to increase the hardness and strength of a metallic material. It also can occur in the application process, i.e., vehicle collision deformation process. The hardness of a metal is directly related to the uniaxial yield stress. A rigid metal shows more excellent resistance to plastic deformation compared to soft metal. There are five well-known hardening processes as below:

Grain refinement. According to the Hall-Petch equation, the yield strength increases with the decrease of grain size. Because smaller grains increase the likelihood of dislocations running into grain boundaries after shorter distances, which are powerful dislocation barriers, in general, a smaller grain size will also make the material harder. When the grain size approaches submicron size, some materials may become softer. This is due to another deformation mechanism that is more prone to occur, i.e., grain boundary sliding. At this time, the dislocation-related hardening mechanism will be invalid.

In strain hardening (work hardening), when the strain of material exceeds its yield point, ductile metal will become harder and harder during plastic deformation. The formation of new dislocations accompanies the plastic strain process. With the increase of dislocation density,
further dislocation movement becomes more difficult because they hinder each other, which results in the increasing hardness of the material.

In solid solution strengthening, the soluble alloy elements are added to the materials to be strengthened to form a "solid solution." A solid solution can be considered a "normal" liquid solution, such as salt in water, but it is solid. According to the size of the dissolved alloy element ions and the size of the base metal ions, they can be dissolved alternatively (the large alloy elements replace the atoms in the crystal) or intermittently (the small alloy elements take up the position between the atoms in the lattice). The size difference of the solid solution hinders dislocation slip from resulting in higher material strength. Different from the precipitation, the alloying element does not precipitate from the solid solution in the solution hardening.

Precipitation hardening (age hardening) is a process in which the second phase dissolved in the base metal as a solid solution and precipitated out from the solution with the metal during quenching so that the particles of the phase are distributed everywhere, thus producing the ability to resist slip dislocation. It can be achieved by first heating the metal to a temperature at which the elements are forming the soluble particles, then quenching it and trapping it in the solid solution. If it is a liquid solution, the elements will form precipitation, just as supersaturated saltwater will precipitate small salt crystals, but at room temperature, the diffusion of atoms in the solid is very slow. Second heat treatment is then required at an appropriate temperature to allow the material to age. The elevated temperature results in the faster diffusion rate of the dissolved elements and to form of the required precipitation particles. Since the material will precipitate during slow cooling, this type of precipitation results in a small number of large particles rather than a large number of small precipitates usually expected, so a high-speed
cooling rate and quenching treatment are required. Precipitation hardening is one of the most common hardening techniques for metal alloys.

Phase transformation hardening, commonly known as martensitic hardening and bainitic hardening, is a hardening mechanism specific to steel. When the crystal structure of steel changes from face-centered cubic (FCC) to body-centered cubic (BCC) by high cooling and high undercooling degrees, the hardness and yield strength performance usually improve. Because steel can dissolve much more carbon in FCC austenitic form than BCC ferrite form. Once the carbon is completely dissolved in austenite, the material is then quenched with a high cooling rate. It is important to quench at a high cooling rate to ensure that the carbon atoms do not have enough time to form carbide precipitates. The steel will try to return to the BCC crystal structure at low temperatures. This transformation process will be completed in a very short time because it does not depend on diffusion and is called displacive phase transformation. Due to the supersaturation of solid solution carbon, the lattice becomes BCT (body-centered tetragonal). This phase is called martensite/bainite. Due to the combined effect of distorted crystal structure and extreme solid solution strengthening, the hardness is extremely high. Both two mechanisms can resist sliding dislocation.

The hardening phenomenon plays a significant role in the property and performance of a metal material, especially in steel. Therefore, it is of great value to understand the mechanism of different hardening effects for material design and application. This research aims to explore the three main hardening mechanisms, including strain hardening, phase transformation, and precipitation in advanced engineering steels. It will provide a theoretical basis for the design of advanced high strength and high ductility steel materials.
1.1. **STRAIN HARDENING IN METASTABLE AUSTENITIC STAINLESS STEEL**

To achieve global carbon neutrality, automakers are searching for a new generation of advanced high-strength steels (AHSS) that help them meet this challenging standard [1]. The AHSS can be divided into three generations according to their strength-ductility combination in Figure 1.1 [1-4]. The first generation of AHSS steel is mainly composed of BCC phase, including martensitic steel, IF (intermediate free) steel [5], DP (dual phase) steel [6] and TRIP (transformation induced plasticity) steel [4]. A small amount of alloying elements such as Si, Mn, Cr, Mo, etc., are usually added to these alloys and less than 5 wt%. The ultimate tensile strength (UTS or TS) ranges from 300 MPa to 2000 MPa, and the product of tensile strength (TS) and total elongation (TE) ranges from 10 to 20 GPa·% (TS × TE). The primary defect of first-generation AHSS is that when the strength is high enough and the matching ductility is very poor. Further, the process formability and collision absorption energy of this kind of steel is not excellent enough. The second-generation AHSS steel mainly consists of FCC phase, including austenitic stainless steel [7] and TWIP (twining induced plasticity) steel [8]. By adding a lot of alloying elements, the second-generation AHSS shows good strength-ductility combination (50 ~ 70 GPa·%) with excellent total elongation (TE, 50 ~ 90 %). However, the high content of precious alloy elements makes the production cost very high and smelting production very difficult with low strength performance. How to reduce the content of alloying elements while maintaining excellent properties is the main difficulty of the third-generation AHSS. Ultimately, the third generation of AHSS has overcome this difficulty and ensure the high ultimate tensile strength (UTS ≥ 1500 MPa) with excellent strength-ductility balance (TS × TE ≥ 30 GPa·%). Their microstructure consists of both BCC and FCC phases, i.e., medium-Mn TRIP steel [9], quench and partitioning (Q&P) steel [10], and carbide-free bainitic (CFB, also called low
temperature bainitic) steel [11]. The products of strength and ductility (TS × TE) of the first, second and third generation AHSS are on the order of 20, 40 and 60 GPa·%, respectively.

![Diagram showing the categories of three generations of AHSS grades according to the total elongation (TE) versus tensile strength (TS) combination (data coms from the Ref. [1-4]).](image)

Figure 1.1: The categories of three generations of AHSS grades according to the total elongation (TE) versus tensile strength (TS) combination (data coms from the Ref. [1-4]).

The transformation-induced plasticity and twinning (TRIP and TWIP) are regarded as the two most common and significant effects for rendering excellent strain hardening to the advanced high-strength steels (AHSS) under severe plastic deformation. For the TRIP effect, the epsilon (ε) martensite and alpha prime (α’) martensite can effectively hinder dislocation movement then contributes to strain hardening rate. The deformation-induced twinning increases
the strength by preventing the dislocation glide and also improves ductility by instantaneous rotating the crystal structure, called as dynamic Hall-Petch effect [12]. Both TRIP and TWIP effects are controlled by many factors, i.e., chemical composition [13, 14], grain size [15], deformation degree [16] and so on.

While maintaining high strength and safety performance, the application of TRIP and TWIP effects in advanced high-strength steels (AHSS) has become one of the primary countermeasures to fuel consumption and air pollution in the steel and automobile industry [2, 17]. Therefore, it is essential to understand the hardening mechanisms of TRIP and TWIP effects and the corresponding processing methods for developing and designing the new generation AHSS steel.

1.1.1. Transformation-induced plasticity (TRIP)

1.1.1.1 The development of transformation-induced plasticity (TRIP) effect

In the 1930s, Scheil et al. [18] observed the formation of martensitic acicular in Fe-Ni alloy, which was formed under shear stress. He put forward two hypotheses to explain this phenomenon: one is the stress hypothesis that martensitic transformation needs minimum shear stress; the other is the hypothesis of spontaneous transformation of unstable martensite. Subsequently, the orientation-dependent martensitic transformation of Fe-Ni alloy under tensile deformation was observed, and it was believed that this transformation contributes to the improvement of ductility [19]. In the following decades, a large number of studies had been carried out on the behavior of austenite martensite transformation in Fe-Ni Alloys.

Until the mid-20th century, Zackey et al. [20] revealed and proposed the classic transformation-induced plasticity (TRIP) effect in metastable austenitic stainless steel. As shown in Figure 1.2, The TRIP effect can be defined as the transformation of (retained) austenite to hard
martensite during the plastic deformation, resulting in improved strength and ductility. This transformation of (retained) austenite to martensite substantially increases the material's strain hardening rate and strength under plastic deformation. Therefore, the deformation transfers to the fabric without transformation around, which effectively alleviates the local concentration of stress and delays the occurrence of necking phenomenon and results in the excellent combination of high strength-high ductility performance.

Figure 1.2: A schematic diagram of transformation-induced plasticity (TRIP) under plastic deformation.

In the 1970s, Fahr et al. [21] further divided TRIP effects into the “strain-induced” and “stress-induced” formation of martensite categories. He first proposed that the stability of austenite was the critical factor in the formation of martensite. The stress-induced formation of martensite due to the low austenite stability provided high tensile strengths and work hardening rate but low yield strength and ductility. Conversely, the high austenite stability prompted the
formation of strain-induced martensite. And a specific amount of strain-induced martensite contributed to an “optimum” work hardening rate and high strength-ductility combination. Later, Matsumura et al. [22] proved that the TRIP effect also existed in low alloy steels. The microstructure mainly consists of 50% alltrioomorphic ferrite, 40% carbide free bainite and a small amount of retained austenite/martensite. Different from metastable AHSS with complete austenite microstructure before deformation, these steels are called low-carbon TRIP steels (or TRIP-assisted low alloy steels). The retained austenite volume fractions varing from 5-15% in typical low-carbon TRIP steels [23]. TRIP steels are generally regarded as first-generation AHSS. Comparing with other first-generation AHSS, the TRIP steels shows a good combination of tensile strength and ductility.

Miller and Tomota et al. [24, 25] found the TRIP effect in Fe-Mn binary alloys system in the 1980s. They observed that the microstructures of Fe-Mn alloys and corresponding transformation (γ→ε and ε→α’) are both strongly dependent on the Mn content. It emphasized that the formation of α’-martensite can significantly improves the work hardening rate in these alloys by creating strong barriers under plastic deformation. The relationship between work hardening rate (strain hardening) and logarithmic strain (true strain) is also charactered in TRIP steel. The ε→α’ transformation is proved to decrease the initial work hardening rate by reducing high local internal stresses and conversely increases the work hardening rate with the accumulated α’-martensite laths become obstacles against the succeeding plastic flow [24, 25].

In the 2000s, the Quenching - Partitioning (Q&P) martensitic steel was novel proposed by Speer et al. [26, 27] based on the chemical composition of C-Si-Mn TRIP steel. The core ideal of Q&P steel is to stabilize the austenite phase by carbon partitioning and maintain more untransformed austenite at room temperature. The deformation-induced transformation of
retained austenite contributes to the high strength-ductility combination and good strain hardening rate. The heat treatment process matched with the typical Q&P martensitic steel is as follows: After austenite homogenization, the steel is quenched to the temperature between the martensite transformation start temperature (MS) and martensite transformation finish temperature (MF), and then increased to the quenching temperature or above the MS temperature for isothermal treatment. In this process, carbon are redistributed from martensite to untransformed austenite to form carbon-rich retained austenite. Finally, after cooling to room temperature, the dual phase microstructure of martensite and retained austenite with excellent strength toughness matching properties is obtained. The microstructure of Q&P martensitic steel is usually composed of micron size martensite laths and retained austenite between laths. The hard phase martensite lath provides the hardness and strength of the steel, while the metastable carbon-rich retained austenite dispersed among the martensite laths. When the steel is subjected to external loading, the retained austenite will transform into strain-induced martensite (TRIP effect), improving the hardness and strength while maintaining the original good ductility.

Recently, Raabe and Schnitzer et al. [28, 29] proposed novel methods to explore the TRIP effect in maraging steels. Raabe [28, 29] found that the TRIP effect and maraging effect simultaneously increase strength and ductility due to the formation of nanosized precipitates during aging providing more nucleation sites for strain-induced martensite. Schnitzer [28, 29] further involved the phase reversed austenite to provide nucleation sites for strain-induced martensite and TRIP effect. The austenite reversion occurs with the partitioning process of carbon(C) and manganese(Mn) between the original austenite/martensite interface resulting in the new austenite formation. Benefiting from both TRIP and maraging effects, the mechanical properties of maraging steels develop a high TS (~1.5 GPa) with a good TE (~20%).
In summary, the TRIP effect plays a vital role in a wide range of steels. The volume fraction and stability of the metastable austenite phase are the critical factors to decide the TRIP effect in steels. It can be controlled by chemical composition design, element enrichment or special treatment.

1.1.1.2 The mechanism of transformation-induced martensite and hardening

The formation of martensite during deformation is the basis of the TRIP effect, and the transformation from austenite to martensite follows the displacement mechanism, that is a diffusionless shear transformation. Figure 1.3 presents the driving force of thermodynamic transformation and corresponding stress conditions for strain induced martensite transformation [30]. The figure 1.3a proved that $\Delta G_{\text{Ms}}^{T'\rightarrow \alpha'}$ is the critical value for the start of martensite transformation at the martensite start temperature (Ms) [30]. At higher temperatures $T_1$, the mechanical driving force $U'$ due to the application of stress can make up for the lack of Gibbs driving force, thus triggering stress assisted martensitic transformation (SAMT) [30]. The mechanical driven force $U'$ can be interpreted as Equation 1.1 [31]

$$U' = \tau \gamma_0 + \sigma \varepsilon_0$$  \hspace{1cm} (1.1)

where $\tau$ is the applied shear stress, $\gamma_0$ is the transformation shear, and $\sigma$ and $\varepsilon_0$ are the nominal stress and dilatation strains, respectively. The mechanical driving force $U'$ has a linear relationship with the applied stress and is also greatly affected by the stress state.

The martensite transformation can be classified into two categories according to driving force shown as Figure 1.3b. (i) The stress-assisted martensitic transformation (SAMT) occurs between the Ms temperature and $M_s^\sigma$ temperature with mechanical driven force $U'$; (ii) the strain-induced martensite transformation (SIMT) is the dominant from $M_s^\sigma$ up to Md temperature.
Figure 1.3 (a) Gibbs free energy (driving force of thermodynamic transformation) and (b) Critical stress for strain induced martensite transformation versus temperature [30].

Many researchers [31-35] have deeply studied the potential nucleation sites and transformation law of deformation induced martensite. The energetically favorable nucleation sites are the intersections of shear bands [35], ε-martensite [33], twinning plates [32] and dislocation pile-ups [34]. In these different transformation methods, the decisive common factor is stacking fault energy (SFE), a function of alloy composition and temperature. SFE of austenite is one of the most critical factors that control the deformation mechanisms during deformation. The dominant deformation mode is shifted from ε-martensite formation to twinning with SFE increases and then to slip. In addition, the different applied stress states can significantly affect the nucleation rate of α’-martensite, even resulting in different microstructures. Murr [36] et al. reported that more intersections of shear bands could be formed in biaxial tension and contributing to the more significant volume fraction of α’-martensite than in uniaxial tension. Patel and Cohen [31] et al. pointed that the compressive applied stress can suppress the transformation from austenite to martensite.
It has been known that there are two transformation mechanisms for face-centered cubic (FCC) austenite transforming into body-centered cubic (BCC) α’-martensite during plastic deformation for an extended period. The first mechanism describes the direct transformation from austenite to martensite ($\gamma \rightarrow \alpha'$ route) [36], while the second route involves a two-steps reaction in which the FCC γ-austenite firstly transformed to an intermediate hexagonal close packed (HCP) ε-martensite, then resulting in BCC α’-martensite ($\gamma \rightarrow \varepsilon \rightarrow \alpha'$ route) [37]. The different deformation temperature sequences enable the transformation to be shifted from one heterogeneous route to one that propagates axially along with the sample [38]. The formation of the α’-martensite directly from the γ-austenite occurs at sufficiently high strains. In contrast, the low temperature accelerates the slide of $\gamma/\varepsilon$ interfaces and resulting in the $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ route [38].

The austenite to martensite transformation follows the displacive mechanism, i.e., diffusionless shear transformation. Further, both $\gamma \rightarrow \alpha'$ and $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ transformations follow the Kurdjumov–Sachs (K–S) orientation relationship with 24 possible variants depending on the stress and strain state. Table 1.1 shows the 24 variants for Kurdjumov–Sachs (K–S) orientation relationship, usually observed in carbon steels [39]. In an idealized case, all variants can appear in an austenite grain with an equal probability during the transformation. However, it has been reported that some variants preferentially appeared during the transformation. In other words, some variants possibly have greater relative probability to be selected. This phenomenon, which is called variant selection, is known to have a significant effect on the texture development in the inherited phase.

Table 1.1 Twenty-four variants of K–S relation.
Table 13

<table>
<thead>
<tr>
<th>No.</th>
<th>Plane parallel</th>
<th>Direction parallel</th>
<th>Rotation from Variant 1</th>
</tr>
</thead>
<tbody>
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<td>(111)γ</td>
<td>/[(01)α′]</td>
<td>0.5774-0.5774</td>
</tr>
<tr>
<td>V2</td>
<td>[1 0 1]</td>
<td>[1 -1 1]</td>
<td>0.0000-0.0000</td>
</tr>
<tr>
<td>V3</td>
<td>(111)γ</td>
<td>/[(01)α′]</td>
<td>0.5774-0.5774</td>
</tr>
<tr>
<td>V4</td>
<td>[1 0 1]</td>
<td>[1 -1 1]</td>
<td>0.0000-0.0000</td>
</tr>
<tr>
<td>V5</td>
<td>[1 -1 0]</td>
<td>[1 -1 1]</td>
<td>0.5774-0.5774</td>
</tr>
<tr>
<td>V6</td>
<td>[1 -1 0]</td>
<td>[1 -1 1]</td>
<td>0.5774-0.5774</td>
</tr>
<tr>
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<td>[1 0 -1]</td>
<td>[1 -1 1]</td>
<td>0.5774-0.5774</td>
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<td>V8</td>
<td>[1 0 -1]</td>
<td>[1 -1 1]</td>
<td>0.5774-0.5774</td>
</tr>
<tr>
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<tr>
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<td>[1 -1 1]</td>
<td>0.5774-0.5774</td>
</tr>
<tr>
<td>V24</td>
<td>[1 0 -1]</td>
<td>[1 -1 1]</td>
<td>0.5774-0.5774</td>
</tr>
</tbody>
</table>

Figure 1.4 shows [001]α′ standard stereographic projection of one of the K–S variants (V1) on which the [001]α′ axes of 23 other variants (V2 to V24) are plotted. The K–S variant of observed martensite lath can be identified by comparing the experimentally measured martensite/martensite orientation relationship with the calculated plot of Figure 1.4. Comparisons were made for 24 different calculated by taking each of the 24 variants as a reference. The slip system of parent phase [40-42], the grain boundary orientation [43], and the existence of stress [44, 45] have been known to affect the variant selection during the transformation and the development of transformation texture. As for the slip activity, the variant selection criterion was imposed in terms of slip distribution and applied to diffusion-controlled transformation [40]. Ray et al. [46] reviewed the various kinds of transformation texture that is normally encountered in austenite-to-ferrite transformation in steel. As for the bainitic transformation in steel, the variant selection had been investigated by an experimental observation [40]. Recently, present authors suggested that the probability for a nucleation site to really act during displacive transformation...
could be derived for each variant as a function of the mechanical interaction energy between externally applied stress and lattice deformation based on the Kurdjumov–Sachs (K–S) relationship [44]. Lee et al. [47] proved that the orientation relationship between the parent austenite and the inherited martensite which had been mechanical induced transformed under both uniaxial tension and compression state was observed by an electron backscattered diffraction (EBSD). The probability of variant selection was assessed with the interaction energy between externally applied stress and lattice deformation for each martensitic variant. The interaction energy was calculated from the Bain deformation and the invariant shear strain based on K–S orientation relationship. It could be confirmed that the calculated interaction energy for the transformed martensitic variant has the relatively very large negative value. The negative value of the interaction energy under the tensile and compressive stress state is related to the favorable interaction with the applied stress and it means that the probability for some specific variants to be selected becomes increased due to the external stress.

Figure 1.4: [001]α’ standard stereographic projection of one of the K–S variants (V1) on which the [001]α’ axes of 23 other variants (V2 to V24) are plotted as solid marks.
Olson and Cohen [48] proposed a classic model for the formation of $\alpha'$-martensite at the intersection of two localized slip bands as in Figure 1.5. According to the Olson-Cohen model, the shear required to transform the FCC crystal lattice structure into the BCC structure can be subdivided into two invariant-plane strains, which can take place either successively or simultaneously. The first shear component of slip band corresponds to one third of the twinning shear in the FCC structure with $\frac{a_{\text{fcc}}}{18} \langle 112 \rangle$ displacement, expressed as $\frac{T}{3}$ in Figure 1.5. The $\frac{T}{3}$ shear can be dissociated from a Shockley partial dislocation $\frac{a_{\text{fcc}}}{6} \langle 112 \rangle$ on every third $\{111\}_{\text{fcc}}$ slip plane. The second shear component corresponds to one half of twinning shear in the FCC lattice structure and expressed as $\frac{T}{2}$ in Figure 1.5. The displacement can be described by $\frac{a_{\text{fcc}}}{12} \langle 112 \rangle$ in FCC lattice and $\frac{a_{\text{bcc}}}{8} \langle 110 \rangle$ in BCC lattice. The $\frac{T}{2}$ shear can be also achieved by the dissociation of Shockley partial dislocation $\frac{a_{\text{fcc}}}{6} \langle 112 \rangle$ on every second $\{111\}$ plane.

Olson and Cohen's model clearly describes the formation of HCP $\varepsilon$-martensite by the relative motion of $\frac{T}{3}$ shear and $\frac{T}{2}$ shear. A shuffle of the atoms over a distance of $\frac{a_{\text{fcc}}}{12} [\overline{1}12]$ every second basal plane of the $\varepsilon$-martensite is required to form the exact $\frac{T}{2}$ shear, which is only available for hard spheres. Further, the shuffle transforms the $(10\overline{1})_{\text{hcp}}$ plane into a distorted $(\overline{1}1\overline{1})_{\text{fcc}}$ plane, because the dislocations are more likely to glide on $(10\overline{1})_{\text{hcp}}$ plane. When the $\frac{T}{3}$ partial dislocations piles up at the intersection with the $\frac{T}{2}$ partial dislocations pass on these
distorted planes, the result will be a BCC structure, i.e., nucleation sites for $\alpha'$-martensite. The intersections of two $\varepsilon$-martensite laths are commonly as the nucleations sites of $\alpha'$-martensite. The $\frac{T}{3}$ and $\frac{T}{2}$ shear intersections are available and applied for other kinds intersections of shear regions in FCC lattice, such as the twin boundary with $\varepsilon$-martensite lath.

![Diagram of strain-induced $\alpha'$-martensite nucleation](image)

Figure 1.5: The classic geometrical model for strain-induced $\alpha'$-martensite nucleation: situation before (a) and after (b) intersection of localized slip bands proposed by Olson and Cohen [33].

Figure 1.6a presents the microstructure evolution under plastic deformation in 1.4301 austenite stainless steel [49]. The lath martensite was obtained by applying 5% tensile deformation to the entire austenite microstructure. Figure 1.6b presents the $\alpha'$-martensite nucleation sites at the intersections of deformation bands by transmission electron microscope (TEM).
Figure 1.6: The formation of strain induced martensite: (a) Microstructure before and after 5% tensile deformation. (b) Transmission electron microscope (TEM) reveals the α'-martensite nucleated at the intersections of deformation bands [49].

Olson an Cohen [50] also proposed a model for the kinetics of strain induced martensite transformation in 1975. The kinetics model describes the relationship between temperature and martensite transformation kinetics based on the observations of shear systems as shown in Equation 1.2 [50]

\[ f^{\alpha'} = 1 - \exp\left[-\beta(1 - \alpha \varepsilon)^n\right] \]  

(1.2)

Where the volume fraction of martensite \( f^{\alpha'} \) is decided by the temperature-dependent parameters, \( \alpha \) and \( \beta \), at strain \( \varepsilon \). The exponent \( n \) is a dimensionless constant as fitting parameter (usually \( \geq 2 \)) affected by the material and process.

The stability of austenite decided by stacking fault energy (SFE) is usually regarded as a critical factor affecting TRIP effect [51]. SFE describes interaction energy between dislocations in a slip band. The low SFE means the mobility of dislocations is greatly suppressed. If the normal stacking sequence of atomic planes is interrupted as defects, the defects will provide the nucleation sites and energy for \( \varepsilon \)-martensite. Thus, in the basic thermodynamic model, SFE is regarded as the sum of the surface energy and volume energy contributions to the formation of \( \varepsilon \)-martensite [52]. Temperature and chemical composition play the most important roles affecting the SFE of austenite.
1.1.2 Twinning-induced plasticity (TWIP)

1.1.2.1 The development of twinning-induced plasticity (TWIP) effect

Mechanical twinning (also called deformation twinning) is an essential mode by which steels can be permanently deformed at ambient temperature, without recourse to diffusion [53]. Mechanical twinning results in a much larger shear strain compared with displacive transformations. Twinning-induced plasticity (TWIP) effect refers to that the austenitic alloys maintain austenitic phase during mechanical deformation and adjust the strain through both the glide of a single dislocation and mechanical twins on the \( \{111\} \gamma \langle 1 \overline{1} 2 \rangle \gamma \) system. The alloys usually contain large amount of manganese, some aluminum and silicon (e.g. Fe-25Mn-3Si-3Al wt%) in some versions present essentially as impurities. Higher concentrations of carbon can be added to enhance strength. At high manganese concentration, austenite tends to transform into HCP \( \varepsilon \)-martensite during deformation. \( \varepsilon \)-martensite can be dissociated from a perfect \( a/2 \langle 011 \rangle \gamma \) dislocation into Shockley partials dislocation on a close-packed \( \{1 \overline{1} 1\} \gamma \) plane. A faulted region occurs between the dissociated partials and presents as a three-layer thick plate of \( \varepsilon \)-martensite [53]. Therefore, a reduction in the fault energy is conducive to the formation of \( \varepsilon \)-martensite. The addition of aluminum offset this due to the raising stacking fault energy of austenite. Silicon has the effect of reducing stacking fault energy, but both silicon and aluminum will reduce the density of steel.

Although the TWIP effect was discovered very early in steels, it has not been put into large-scale application. Until the early 1990s, Kim et al. [54] reported a TWIP steel with excellent mechanical performance, whose tensile strength was 2.5 times higher than other automotive ferritic sheet steels due to the well-developed mechanical twins during plastic deformation. The pioneering contributions of Grässel et al. [55] and Frommeyer et al. [56] to the
understanding of high manganese (Mn) TWIP steels promoted a global attention on TWIP steels. Grässel and Frommeyer observed that large-scale deformation twinning occurred when the Mn content of TWIP steel was greater than 25 wt%, the Al content was more than 3 wt%, and the Si content was in the range of 2–3 wt%. Under this chemical composition, the steel has a rather low yield strength (YS) at 200–300 MPa but the ultimate tensile strength (UTS) can be much higher, in excess of 1100 MPa as shown in Figure 1.7. This is because the large strain hardening coefficient results in a great total elongation (TE) up to 80%. The twins add to plasticity, but they also have a powerful effect in increasing the work-hardening rate by subdividing the untwinned austenite into finer regions. TWIP steels can obtain a very excellent strength-ductility balance through the appropriate treatment process. Corresponding strength-ductility value exceeds 50 GPA-% (TS × TE). Since then, High Mn TWIP Steel has entered the public's vision as a second-generation advanced high-strength steels (AHSS).

Figure 1.7: Typical stress-strain curve for a TWIP steel and optical microstructure of a TWIP steel following deformation, showing a large number of twinning [56].
1.1.2.2 The mechanism of twinning-induced plasticity and hardening

Many factors affect the TWIP effect and microstructural evolution during plastic deformation, such as chemical composition, SFE, deformation condition, grain size, grain orientation, etc.

The chemical composition of TWIP steel usually contains a large amount of manganese, some aluminum and silicon (e.g. Fe-25Mn-3Si-3Al wt%) in some versions present essentially as impurities. According to both the Mn concentration and the ratios of the Al and Si concentrations, ε martensitic transformation and mechanical twinning compete to form during plastic deformation owing to the change in SFE with chemical composition [57].

It is well known that mechanical twins are formed in austenite when the SFE is in ranges of 20 to 40 MJ/m$^{-2}$ [58, 59]. Allain et al. [58] showed that strain-induced ε-martensite occurs if SFE was lower than 18 MJ/m$^{-2}$, whereas mechanical twinning is formed if the SFE value is between 12 and 35 MJ/m$^{-2}$. It is not difficult to see an overlapping region of SFE between mechanical twinning and strain-induced ε-martensite transformation. Within a specific SFE range, both mechanical twins and ε-martensite can be observed simultaneously [59]. However, it is difficult to accurately determine the SFE range required to obtain mechanical twinning and ε-martensite structures at the same time. In the range of SFE that can produce mechanical twins, the increase of SFE delays the kinetics of mechanical twins because the perfect dislocation is difficult to dissociate. In high Mn steel, when the SFE value exceeds MJ/m$^{-2}$, microbands rather than mechanical twins will be formed during austenite deformation [60].

The deformation condition plays an essential role on strain hardening and mechanical twinning. Strain hardening rate is investigated as a function of the true strain by the tensile test. Barbier et al. [61] reported that the plastic deformation of a high Mn TWIP steel can be divided
into five stages (A-E) as shown in Figure 1.8. The primary mechanical twinning (occurs in Stage B) and secondary mechanical twinning (occurs in Stage D) can effectively increase the strain hardening rate and strength during deformation. Recently, the mechanical twins evolution during deformation was further precisely analyzed by electron channeling contrast imaging (ECCI) as shown in Figure 1.9 [62]. The result shows that highly dense dislocation walls (HDDWs) contribute to the strain hardening rate at the early deformation stage. The planar slip promotes the formation of intersections between HDDWs consisting of two different slip systems. In contrast, the wavy slip encourages the formation of equiaxed dislocation cells (DCs) in materials with medium-to-high SFE values [62].

Figure 1.8: Typical strain-hardening rate plot with the true strain (logarithmic strain) in a high Mn TWIP steel [61].
The deformation condition plays an essential role on strain hardening and mechanical twinning. Strain hardening rate is investigated as a function of the true strain by the tensile test. Barbier et al. [61] reported that the plastic deformation of a high Mn TWIP steel can be divided into five stages (A-E) as shown in Figure 1.8. The primary mechanical twinning (occurs in Stage B) and secondary mechanical twinning (occurs in Stage D) can effectively increase the strain hardening rate and strength during deformation. Recently, the mechanical twins evolution during deformation was further precisely analyzed by electron channeling contrast imaging (ECCI) as shown in Figure 1.9 [62]. The result shows that highly dense dislocation walls (HDDWs) contribute to the strain hardening rate at the early deformation stage. The planar slip promotes the formation of intersections between HDDWs consisting of two different slip systems. In contrast, the wavy slip encourages the formation of equiaxed dislocation cells (DCs) in materials with medium-to-high SFE values [62].
The grain size and grain orientation are also important factors referring to microstructure evolution during the deformation in TWIP steels [63-66]. Ueji et al. [63] investigated the relationship between mechanical twinning behavior and various grain sizes in Fe-31Mn-3Al-3Si TWIP steel by tensile tests. The results show that ~50% of the grains with 49.6 μm were observed mechanical twins at 0.2 true strain, but only 18% of grains with 1.8 μm included mechanical twins at the same strain. Recent research [64] found that there were well-developed planar dislocation structures observed in 72.6 μm grains and non-planar dislocation structures in 2.1 μm grains at the early stage of deformation. It was reported that mechanical twinning occurred more easily in steels with planar dislocation structures than non-planar dislocation structures. And the different dislocations between fine-grained (FG) and coarse-grained (CG) structures are likely associated with the origin of the grain-size-dependent mechanical twinning. The differences of mechanical twinning behaviors in FC and CG structures will be discussed in this dissertation. Yang et al. [65] reported the mechanical twinning behavior depends on the grain orientation in Fe–33Mn–3Al–3Si TWIP steel. The result shows mechanical twins commonly occur in 〈111〉 grains parallel to the tensile axis; in contrast, they rarely occur in 〈001〉 grains. However, the compression tests showed an opposite rule that mechanical twinning is more likely to occur in 〈001〉 grains rather than in 〈111〉 grains parallel to the compressive axis in Fe–33Mn–3Al–3Si TWIP steel [66].

Since deformation twinning is the core of mechanical properties of TWIP Steel, the mechanism of deformation twinning will be described in detail as below.

Deformation twinning results from a homogeneous shearing of the matrix caused by the highly coordinated glide of partial dislocations with the same Burgers vector, with exactly one dislocation gliding on each successive {111} plane [53]. In polycrystalline materials twin
formation by \{111\}(112) slip results in a volume orientation change of a certain fraction of the twinned grains, affecting the crystallographic texture. \{111\}(112) slip should be separated from partial dislocations or the dislocation sources [53]. The spontaneous formation of twins is improbable because it requires very high stress. Fontaine [67] proposed the model in 1968 considered the first model for deformation twinning. In Fontaine’s model [67], broad stacking faults are formed first, then overlapped stacking faults generate twin embryos, followed by the occurrence and growth of twins on the twin plane. The stacking faults can either result from suitable dislocation reactions or interfaces such as grain boundaries. However, the conditions for nucleation of twins from stacking faults emitted from grain boundaries are not well established.

The classical models of deformation twinning are deeply described in the literature as follows:

1. Reed-Hill’s venables pole mechanism [68].
2. Cohen’s cross slip mechanism [69].
3. Fujita’s cross slip mechanism [70].
4. Miura’s primary Frank slip mechanism [71].
5. Byun’s partial dislocation breakaway mechanism [72].
6. Bouaziz’s gliding dislocation-shear strain mechanism [73].

The common point of these models is that deformation twinning needs high enough dislocation density and high local stress environments to trigger the nucleation and growth of twins. Both dislocation glide and deformation twinning are straining processes caused by applied stresses and are highly limited on the \{111\} slip planes of austenitic steels. The latest research results of Byun showed that partial dislocation pile-ups at twin band-grain boundary intersections, indicating that deformation twins were formed by the glide of Shockley partial dislocations of
the same sign on successive \{111\} slip plane [72]. Further, these deformation twins mainly originate from defects, such as grain boundary, twin matrix interface or other defects, and can extend from grain boundary to grain boundary [72]. Many research results support pile-up/glide mechanisms for twinning, rather than pole, homogeneous nucleation, or other mechanisms [72]. Therefore, this dissertation only introduces and discusses pile-up/glide mechanisms for the twinning mechanism.

The latest dislocation gliding mechanism for the twinning formation proposed by Bouaziz will be discuss in details [73]. Considering the contribution of twinning to the total plastic shear strain as Figure 1.10, the mixing law expressed as follows is used [74]:

$$d\gamma = 1 - F d\gamma_g + \gamma_t dF$$

(1.3)

Where, $\gamma_g$ is the shear strain caused by dislocation gliding, $\gamma_t$ is the twining shear strain equal to 12 and $F$ is the volume fraction of twins.

Figure 1.10: Twinning refinement contribution to shear strain.
At the same time, Bouaziz assumes that its mechanical behavior obeys the classical relationship between flow stress and total dislocation density as below:

\[ \sigma = \sigma_0 + \alpha \cdot M \cdot \mu \cdot b \cdot \rho \]  

(1.4)

Where, \( \alpha \) is a constant of order 0.4; \( M \) is the average Taylor factor; \( \mu \) and \( b \) are the shear modulus and Burgers vector, respectively.

The evolution of dislocation density with gliding dislocation shear strain is the result of accumulation and annihilation competition caused by dynamic recovery as below [75]:

\[ d \rho d \gamma_g = lb \cdot \Lambda - f \cdot \rho \]  

(1.5)

Where, \( \Lambda \) refers to the dislocation average free path, and \( f \) is a constant value. It is assumed that a twin can be regarded as an impenetrable obstacle for dislocations, therefore the dislocation average free path can be expressed as follow:

\[ 1 \Lambda = 1d + 1t + k \cdot \rho \]  

(1.6)

where \( d \), \( t \) and \( k \) are grain size, average twins spacing and constant value, respectively. Applying Fullman [76] quantitative metallographic relation as below:

\[ t = 2e \cdot 1 - FF \]  

(1.7)

with \( F \) and \( e \) are twin volume fraction and average twin thickness, respectively. Combining all the above formulas, dislocation density can be expressed as follows:

\[ d \rho d \gamma_g = lbld + 12e \cdot F1 - F + k \cdot \rho - f \cdot \rho \]  

(1.8)

The classical Olson and Cohen’s twinning kinetic formula [50] is introduced:

\[ dF = 1 - F \cdot md \varepsilon \]  

(1.9)

Here, \( m \) is a function of stacking fault energy and increases with the decrease of SFE. By integration, the twin volume fraction of Bouaziz’s gliding dislocation-shear strain model can be calculated as below [73]:
\[ F = 1 - \exp(-m \cdot \varepsilon) \]  

(1.10)

1.1.3 Phase reversion process in TRIP/TWIP steels

As mentioned above, the occurrence of both TRIP and TWIP effects depend on the stacking fault energy (SFE), the initial microstructure and deformation conditions [58]. The strain-induced \(\varepsilon\)-martensite occurs if SFE was lower than 18 MJ/m\(^2\), whereas mechanical twinning is formed if the SFE value is between 12 and 35 MJ/m\(^2\) [58]. It is not difficult to see an overlapping region of SFE between mechanical twinning and strain-induced \(\varepsilon\)-martensite transformation. Within a specific SFE range, both mechanical twins and \(\varepsilon\)-martensite can be observed simultaneously. Recently, Galindo-Nava et al. [77] proposed a unified model to explain the evolution from \(\varepsilon\)–martensite to twinning and then to \(\alpha'\)–martensite in austenitic steel. The model illustrates that both the micro \(\varepsilon\)-martensite and twin band structures consist of hierarchically arranged periodic sequences of nanosized embryos and the bands grow by overlapping additional embryos, as shown in Figure 1.11 [77]. Figure 1.11a describes a stacking fault forms on \(\{111\}\)\(_{\text{fcc}}\) a slip plane from the dissociation of a perfect dislocation under an applied stress. Figures 1.11b and 1.11c presents a number of stacking faults (1 for \(\varepsilon\)-martensite and 3 for twin ) overlap in adjacent \(\{111\}\)\(_{\text{fcc}}\) planes to form \(\varepsilon\)-martensite and twin embryos, respectively. After the increase of \(\varepsilon\)/twinning volume fraction by the overlapping of new embryos(Figures 1.11c and 1.11d), the micro–bands will occurs as shown in Figure 1.11f.
Figure 1.11: Galindo-Nava’s model for the formation of ε-martensite and twin [77]. Based on the research model of Galindo-Nava, TRIP effect and TWIP effect can be expressed simultaneously in TRIP/TWIP steel through specific treatment process, e.g., phase reversion process.

“Phase reversion” proposed by Misra [78, 79] is an innovative concept involving repetitive thermo-mechanical sequence that develops nanograin (NG)/ultrafine grained (UFG) structure with bimodal grain size distribution and characterized by a high strength/high ductility combination.
Grain refinement is an important access to improve both strength and toughness of engineering materials at the same time. The methods to obtain UFG materials in bulk can be classified into two primary groups. The first group comprises severe plastic deformation (SPD) techniques and the second group relates to advanced thermo-mechanical processing (TMP).

The typical severe plastic deformation (SPD) techniques to obtain nanograined/ultrafine grained (NG/UFG) structure include equal channel angular pressing (ECAP)[80, 81], upsetting extrusion[82], multiple compression[83], accumulative roll bonding (ARB)[84, 85] and high-pressure torsion[86]. Previous research suggests that the accumulated logarithmic plastic strain required to obtain submicron-sized grains by SPD is ~ 4 in ECAP and ~ 5-6 in the ARB process[87].

The advanced thermo-mechanical processing (TMP) adopts alternative strategies to obtain ultrafine ferrite grains, such as strain-induced ferrite transformation[88], dynamic recrystallization of austenite during hot deformation with subsequent austenite to ferrite transformation, hot rolling in the inter-critical two-phase region, dynamic recrystallization of ferrite during warm rolling[87], and multi-pass rolling or forging[89]. The TMP methods require a low accumulated logarithmic strain of ~ 2-4 to produce ultrafine grained steels, as compared to SPD methods[87, 90].

However, there is a serious drawback of these methods is that they require multiple stages of deformation to obtain large plastic strain and the ductility is generally low compared with the coarse grained (CG) counterpart. One of the primary reasons for low ductility in NG/UFG metals is instability[91]. In materials with grain size exceeding ~1 mm, the unit dislocations control plasticity, while in small grain size, grain boundary shear is considered to be an operating deformation mechanism[91], which encourages the activation of shear bands or
localized deformation during the early stages of straining [92, 93]. It is also suggested that ultrafine grains are unable to accommodate a high density of dislocations, which results in a reduction in the strain hardening ability of UFG metals. These 'non-equilibrium' boundaries produce long-range stress fields, and strain localization (shear band/slip lines) is not only limited to a single grain but extends to grain boundaries with high atomic mobility [94]. Uniform strain during plastic deformation in UFG materials can be obtained by controlling instability and delaying the necking process [91, 94]. Thus, to obtain uniform strain during deformation in UFG materials, the strain hardening ability is required as a stabilizing effect to control the instability and to delay/diffuse necking [91]. One approach to control instability is to obtain a UFG structure with bimodal grain size distribution. First, the preferential accommodation of strain in large grains would lead to an excellent strength-ductility combination. Second, the bimodal grain size distribution will enable significant strain hardening, restricting localized deformation.

The phase reversion approach results in a nanograin/ultrafine grained (NG/UFG) structure in austenitic stainless steels with high strength–high ductility combination. Figure 1.12 shows the phase reversion process's schematic illustration and dislocation cell-type martensite in the cold rolling reduction deformation [95]. In this approach, severe deformation (60-80%) of austenite at room temperature leads to the strain-induced diffusionless transformation of austenite (FCC $\gamma$) to martensite (BCC $\alpha'$). Upon annealing, this heavily deformed strain-induced martensite transforms backs to austenite. By repeating this sequence, a very fine-grained structure is achieved. An optimized deformation-phase reversion annealing sequence has been observed to lead to the formation of NF/UFG microstructure, which not only results in significantly higher strength but also renders the material significantly ductile. The reverted austenite may partially or fully transform back to the martensite phase during subsequent
deformation, further enhancing the strength. This method is especially suitable for a wide range of metastable austenite alloys, because the transformation from austenite to ferrite is not involved in alloys with austenite microstructure. Secondly, austenite recrystallization occurs at temperatures above 900 °C. The critical factor to obtain NG/UFG structure by 'phase reversion' method is to get high-density dislocation cell type martensite.

![Diagram](image)

**Figure 1.2:** (a) Schematic diagram showing the “phase reversion” process to obtain NG/UFG structure. (b) Schematic diagram of refinement of dislocation cell-type martensite packet by cold deformation [95].

In this dissertation, the TRIP/TWIP effects and strain hardening behaviors of NG/UFG and CG microstructures will be systematically explored and studied by the phase inversion process.
1.2 **Phase transformation hardening phenomenon in bainitic steel**

There are three most common phase transformation process in steels as shown in Figure 1.13, i.e., (i) austenite to perlite, (ii) austenite to bainite and (iii) austenite to martensite. Phase transformation hardening, commonly known as martensitic hardening and bainitic hardening, is a hardening mechanism specific to steel. When the crystal structure of steel changes from face-centered cubic (FCC) to body-centered cubic (BCC) by high cooling and high undercooling degrees, the hardness and yield strength performance usually improve. Because steel can dissolve much more carbon in FCC austenitic form than BCC ferrite form. Once the carbon is completely dissolved in austenite, the material is then quenched with a high cooling rate. It is important to quench at a high cooling rate to ensure that the carbon atoms do not have enough time to form carbide precipitates. The steel will try to return to the BCC crystal structure at low temperatures. This transformation process will be completed in a very short time because it does not depend on diffusion and is called displacive phase transformation. Due to the supersaturation of solid solution carbon, the lattice becomes BCT (body-centered tetragonal). This phase is called martensite/bainite. Due to the combined effect of distorted crystal structure and extreme solid solution strengthening, the hardness is extremely high. Both two mechanisms can resist sliding dislocation.
1.2.1 The development of phase transformation hardening in steel

Iron-based materials have a long historical record. The earliest man-made steel can be traced back to about 2500 BC. The historical ironmaking centers in pre-Roman times include Anatolia, Mesopotamia, East Africa, India and China [96]. Before 1863, any inspection by naked eye or low power optical microscope (LOM) was carried out on an unprepared surface (intact or broken), resulting in corrosion, overheating, wear, etc. This method conceals more than it reveals [97]. In 1863, Henry Clifton Sorby examined a kind of carburized Swedish iron with a reflected light microscope, which made a great step forward in the direct observation of microstructure. It was not until 1880 that the framework of modern metallography was roughly established and used to study metal materials [97]. Sorby [98] first reported the discovery of “pearlite” by optical microscope in 1886. Roberts Austin [99] drew the first Fe-C phase diagram, from which the concept of “phase transformation” in steel has been intuitively expressed and widely accepted in
The X-ray diffraction (XRD), discovered by Max von Laue in 1912, brought great impetus to metal research. The basic structure of metals and alloys was finally revealed as the vast majority of crystals, which accumulated in the form of atoms rather than molecules, and have defects. Adolf Martens (1850-1914) forward the concept of "martensite" as early as the 1890s. However, it was not directly observed and confirmed by Westgren et al. through XRD until 1922 [100]. Bain et al. made great contributions in drawing TTT diagrams of a large number of steels and revealed a new microconstituent “bainite” in the 1930s [97]. By the end of 1930s, isothermal transformation, XRD and LOM were established as the preferred methods to study and explain “phase transformations”.

Quenching from high temperatures was a known as the most basic phase transformation process for hardening. The Greeks and Romans knew that iron could be hardened by heating and quenching, but little progress was made until the 17th and 18th centuries when chemists studied the problem with their analytical methods. The “quenching hardening” models from the 17th and 18th centuries were purely academic and in fact, useless for practice. These models can not describe the relation between the quenching product and the quenching temperatures [101]. It was not until the early 20th century that martensite was confirmed by XRD technology that material scientists confirmed that the essence of “quenching hardening” was “martensitic transformation hardening”. Nowadays, as the most basic hardening process in the iron and steel manufacturing industry, “quenching martensite hardening” is widely used all over the world.

The austenite transformation products formed below the reconstruction transformation temperature are identified as Widmanstätten ferrite, bainite and martensite. The bainite phase is observed below the temperature required for the formation of Widmanstätten ferrite. Bhadeshia [102] believes that the properties of bainite nuclei are similar to those of Widmanstätten ferrite.
Unlike Widmanstätten ferrite, carbon diffuses into retained austenite not during the growth of bainite plate, but after the growth of bainite plate in bainitic transformation. Therefore, the thermodynamic conditions are the decisive factor for the evolution of nuclei growing into Widmanstätten ferrite or bainite. On the premise that the free energy required for Widmanstätten ferrite transformation is about 50 J/mol, while the free energy needed for bainite transformation is about 400 J/mol [103]. The much higher stored energy in bainite was rationalized based on the absence of favorable strain interactions within bainite sheaves [103]. Hillert [104] proposed the edgewise growth mechanism of bainite is the same as for Widmanstätten ferrite with carbon diffusion controlling growth velocity. And the carbides precipitation occurs in the vicinity of advancing bainite plate-tips which results in a shorter diffusion distance for carbon away from the advancing tip. Aaronson et al. [105] believe that the short-range diffusion of carbon is the main predominant aspect of bainite transformation mechanism. However, Speer et al [27] proposed that bainite may grow through a growth mechanism similar to martensite, which is displacive and non-diffusion, followed by or accompanied by the distribution of carbon into austenite. Bainite has some characteristics of diffusional or displacive mechanism, so its formation mechanism has aroused controversy. The long-term confusion and controversy of bainite should not hide that it has become many ways of technology related microstructure, which is very important for the superior strength, toughness and weldability of many advanced steels. Compared with ferrite pearlite microstructure, the finer scale of bainite provides many advantages, and ferrite pearlite microstructure is the basis of more traditional steel. “Bainite transformation hardening” has excellent research and development prospects and potential application fields, and is gradually entering the market.
In the past two decades, ultrafine (<500 nm) and nanocrystalline (<100 nm) polycrystalline metals with excellent mechanical properties have been found [106]. Bhadeshia and Caballero [11, 102, 107-109] have developed a high carbon, high silicon carbide-free bainite steel with very thin austenite films forming an intimate composite, i.e., low-temperature bainitic steel. After austenitizing, the low-temperature bainite transformation zone above the martensitic transformation (MS) temperature will be isothermal treated for a long time to obtain the composite two-phase structure of very fine bainite ferrite lath and carbon rich retained austenite, namely “low-temperature bainite”.

The microstructure of low temperature bainitic steel is usually composed of submicron/nano bainitic ferrite laths and retained austenite between laths. The microstructure exhibits a good combination of strength and ductility, which comes from the following two aspects. On the one hand, it can play a good role in fine grain strengthening and improve the strength and hardness due to the fine size of the bainitic ferrite lath. On the other hand, metastable retained austenite distributed between bainite laths will cause strain-induced martensitic transformation (TRIP effect) when subjected to external stress. The strain-induced martensite can further improve the strength and hardness of the material while maintaining good plasticity, as mentioned above in the strain hardening section [53]. Therefore, the relatively simple heat treatment process and excellent strength toughness matching of low-temperature bainitic steel make the development space of this steel better.

1.2.2 The characteristics of low temperature bainitic steel.

Professor Bhadeshia and Caballero [11, 102, 107-109] proposed that when designing the chemical composition of low temperature bainitic steel, in order to obtain the structure dominated by bainite, it is necessary to reduce the starting temperature of bainite and martensite
transformation and delay the pearlite transformation to inhibit the emergence of martensite and pearlite. The chemical composition of typical low temperature bainitic steel [107, 110] is shown in Table 1.2.

Table 1.2 The typical chemical compositions of low temperature bainitic steel (wt.%)[107, 110].

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Co</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.79</td>
<td>1.59</td>
<td>1.94</td>
<td>1.33</td>
<td>0.30</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0.98</td>
<td>1.46</td>
<td>1.89</td>
<td>1.26</td>
<td>0.26</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0.83</td>
<td>1.57</td>
<td>1.98</td>
<td>1.62</td>
<td>0.24</td>
<td>-</td>
<td>1.54</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>0.78</td>
<td>1.49</td>
<td>1.95</td>
<td>0.97</td>
<td>0.24</td>
<td>-</td>
<td>1.60</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Bhadeshia and Caballero put forward alloy design principle of low temperature bainitic steel. Assuming that there is no alloying element in the steel for diffusion, the free energy variable of austenite transformation to bainite ferrite is \( \Delta G_{\gamma \rightarrow \alpha} \). Considering that the bainite transformation is incomplete, it is necessary to introduce the elastic strain energy due to volume change in the transformation process, which can be expressed as \( G_{SB} \approx 400 \text{ J/mol} \) [108]. In the nucleation process of bainite ferrite, including the redistribution of carbon content, the change of free energy can be expressed as \( \Delta G_m \). The nucleation driving force of bainitic ferrite must be higher than a certain value to make it nucleate normally, and the numerical function can be expressed as \( G_N \). The starting condition of bainite transformation must meet the following Equation 1.11

\[
\Delta G_{\gamma \rightarrow \alpha} < -G_{SB}, \Delta G_m < G_N
\] (1.11)

Bhadeshia et al. calculated the simulation calculation results of Fe-2Si-3Mn-C steel by Equation 1.11 as shown in Figure 1.14 [109]. The results showed that bainite ferrite transformation can occur at very low temperature. As shown in Figure 1.14(b), Bhadeshia et al.
obtained the carbon content as a function of the time required to start the transformation below bainite start (BS) temperature. The results showed that there was an exponential relationship between the beginning time of bainite transformation and carbon content. When the carbon content reached about 1.1 wt.%, the time required for bainite transformation was nearly 10 years, which indicated that there were many kinetic constraints for low-temperature bainite transformation at extremely low temperatures. Therefore, when designing chemical composition and heat treatment process, it is necessary to specially consider the dynamic conditions of bainite transformation, add alloy elements to improve the driving force of phase transformation, such as Co and Al.

When designing the chemical composition of low temperature bainitic steel, in order to obtain the structure dominated by bainite, it is necessary to reduce the starting temperature of bainite and martensite transformation, i.e., BS and MS, and delay the pearlite transformation to inhibit the emergence of martensite and pearlite.

![Figure 1.14: Calculation of parameters related to carbon content, (a) phase transition temperature and (b) bainite transformation incubation period [109].](image-url)
The chemical composition of typical low temperature bainitic steel designed by Caballero et al. [107, 110] is shown in Table 1.2. The effects of elements in low temperature bainitic steel are shown as below:

Carbon (C): The increase of carbon can significantly reduce the starting temperature of bainite (BS)/martensite transformation (MS) and expand the temperature difference between them. At the same time, the carbon element in steel is also the main element of solid solution strengthening, which has a great influence on the strength and properties of microstructure.

Silicon (Si): In low temperature bainite steel, silicon can obviously inhibit the precipitation of carbide in isothermal process, which is the key to obtain the low temperature carbide free bainite. At the same time, an appropriate amount of Si can also improve the hardenability and tempering stability of steel.

Nickel (Ni): Non carbide forming element(Ni) can be well dissolved in austenite. Ni forms an infinite solid solution with $\gamma$-Fe and forms a limited solid solution with $\alpha$-Fe, which reduces A3 and increases A4 in steel and makes the body centered cubic $\alpha$-phase vanishing, then face centered cubic $\gamma$-phase would be retained at room temperature. Ni plays an important role in stabilizing $\gamma$-phase in steel, promoting the acquisition of metastable retained austenite at room temperature. In addition, Ni has good acid and alkali corrosion resistance, rust prevention and heat resistance at high temperature, which can improve the corrosion resistance of steel to a certain extent.

Cobalt (Co) and Aluminum (Al): According to the alloy design theory, the transformation of low temperature bainite has great kinetic limitations, and its transformation cycle is very long. Therefore, Garcia Mateo et al. [108] proposed the alloy design principle of increasing the driving force of bainite transformation by adding Co and Al. The addition of Co and Al will increase the
bainite nucleation density and reduce the size of bainite ferrite lath, so as to achieve the purpose of fine grain strengthening and greatly accelerate the bainite phase transformation.

In addition to the above alloy elements, Mn, Cr, Mo and other alloy elements will be added to low temperature bainitic steel. Among them, Mn element is similar to Ni element, which plays the role of stabilizing austenite phase, makes it easier to obtain metastable retained austenite, and is also the main element to improve the hardenability of steel. Cr element can reduce the starting temperature of bainite and martensite transformation and improve the stability of undercooled austenite. It is also the main element to enhance the hardenability of steel. Mo element can delay pearlite transformation and eliminate certain tempering brittleness.

Low temperature bainitic steels often add high content of silicon (Si), which can significantly inhibit the precipitation of carbides in the isothermal process. Therefore, the obtained low temperature bainite structure usually has little or no carbides, and the structure is composed of acicular or lamellar bainite ferrite laths and carbon-rich retained austenite.

On the whole, the structural morphology of low temperature bainite is similar to that of carbide free bainite. The difference between them is that the formation temperature of carbide free bainite is close to the beginning temperature of bainite transformation (BS), and the formation temperature of low temperature bainite is close to the beginning temperature of martensite transformation (MS). The bainite lath without carbide bainite is thicker and the lath spacing is wide (micron size), while the bainite lath of low-temperature bainite is narrow (nano size). In addition, compared with other traditional bainites, low temperature bainite has a large distinction between upper bainite, lower bainite or granular bainite, which is usually not easy to be confused.
The chemical composition of typical low temperature bainitic steel designed by Caballero et al. [107, 110] is shown in Table 1.2 above. The matching heat treatment process is: first heat to 1000 °C for complete austenitizing and holding for 15min, and then isothermal quenching for 1 ~ 60 days in the range of 125 ~ 325 °C. As shown in Figure 1.15, it is the low temperature bainite transmission electron microscope (TEM) microstructure after the above heat treatment process and holding at 200 °C for 144h [111]. It can be seen from Figure 1.5 that the structure of low temperature bainitic steel is composed of only bainitic ferrite and retained austenite, in which the thickness of bainitic ferrite laths is about 30 nm size, while retained austenite exists between bainitic ferrite laths, and the thickness of thin film retained austenite is also nano size. The research shows that the content of retained austenite in low-temperature bainite steel is generally ≥ 20 vol.%.
Figure 1.15: TEM micrographs of (a) low temperature bainite obtained after 144 h at 200 °C; (b) dislocation debris close to the austenite–bainitic ferrite interface. BF, bainitic ferrite; RA, retained austenite [111].

Low-temperature bainite steel has an excellent matching of strength and toughness, with a tensile strength of 1.77 - 2.2 GPa, yield strength of 1.5 GPa, elongation of 5 - 30%, and fracture toughness of 40 MPa·m1/2[112]. In the low temperature bainite structure, the bainite ferrite is nanoscale and in supersaturated state, which plays a strong role in fine grain strengthening and solid solution strengthening of bainite structure; secondly, there is a high dislocation density in bainite ferrite, which has a specific role in dislocation strengthening. The low-temperature bainite structure has good plasticity and toughness, partially due to the bainite ferrite lath substructure's high dislocation. The other reason is that the thin film retained austenite is
reasonably distributed between the bainitic ferrite laths to enhance the crack absorption effect. Further, the high stability film retained austenite will transform into strain-induced martensite to improve the hardness and plasticity under considerable deformation, presented as transformation induced plasticity (TRIP) effect.

Austenite is a face-centered cubic (FCC) structure. Compared with BCC and HCP, austenite has the most slip systems (12) and lowest the Peierls-Nabarro stress (dislocation slip force) for sliding at the same temperature. Therefore, the austenite phase can cooperate with other phases in plastic deformation. There are many thin-film retained austenite distributed between bainitic ferrite or martensite laths in nanostructured dual-phase steel. Strain-induced martensite transformation can occur under high plastic deformation, which can effectively alleviate the local stress concentration, delay the crack formation, prevent crack propagation, and effectively improve the structure's overall deformation ability to delay the occurrence of necking.

Caballero et al. [113] adjusted the chemical composition of steel (reduced the C-content and increased the Ni-content simulatenously) and obtained mixed structure of martensite and RA with nano-size (100-200 nm width) laths of bainitic ferrite. Singh [114] pointed out that the strength of austenite and the chemical free-energy change responsible for the transformation are the primary factors influencing the plate-thickness. Cornide et al. [115] studied the influence of austenite strength on the thickness of bainite laths and demonstrated an increase in the austenite strength decreases the lath thickness. These studies indicate that high stability austenite is more favorable for producing thinner bainitic ferrite laths. Meanwhile, the TRIP effect is also strongly affected by the retained austenite. Chiang et al. [116] have reported that work hardening behavior is directly related to the transformation rate of retained austenite, which is correlated with the C content and grain size of the RA in the respective TRIP microstructure. Zhang et al. [117] have
shown that block-like RA quickly transforms into martensite, resulting in high deformability. The highly stable film-like RA is beneficial to arrest crack propagation. However, systematic studies on the relationship among bainite transformation kinetics, microstructural features, mechanical properties, and TRIP effect of bainitic steels are currently limited.

Hence, in this paper, two types of steels are chosen to investigate the effect of Ni on the free energy of bainitic transformation to explore the relationship among bainite transformation kinetics, microstructural features, mechanical properties, and TRIP effect of bainitic steels.

1.3 MICROALLOYING ELEMENTS, HEAT TREATMENT AND PRECIPITATION HARDENING

In all steels, there is usually more than one phase. In fact, several phases can usually be identified in the microstructure. The matrix is usually ferrite (BCC Structure) or austenite (FCC structure), which is strengthened by grain refinement and solid solution addition, and further strengthened by controlling the precipitation (dispersion) of other phases in the microstructure. The most common other phases are carbides formed as a result of the low solubility of carbon in α-iron (Figure 1.16). In ordinary carbon steel, this carbide is usually Fe₃C (cementite), which can occur in a variety of forms, from rough and obvious layers in pearlite to fine platelet or spherical precipitation in tempered martensite. In alloy steels, the same range of structures is encountered, except that in many cases, the iron-rich carbide is replaced by alloy carbides such as Mo₂C that are thermodynamically more stable. Other precipitation (dispersed phases) encountered include nitrides, intermetallic compounds, and graphite in cast iron.

Precipitation strengthening (hardening) has been widely used in various metal systems for a long time. In essence, precipitation strengthening is achieved by generating particle dispersion that prevents dislocation movement. The particle dispersion is achieved by the second
phase precipitation process. Most precipitates lead to hardening and strengthening, but they usually have an adverse effect on ductility and toughness. The degree of strengthening obtained depends largely on the metal system involved, the volume fraction and size of particles, and the nature of the interaction between particles and dislocations. Precipitation strengthening is used extensively in ferrous system, such as quenching and aging of low carbon steel, microalloyed steel and tempered martensitic steel. This strengthening mechanism may be more important in non-ferrous metal systems. The most well-known are Al – Cu and Al – Si based alloys, and the more recently is Al – Li based alloys, whose structural refinement is limited by absence of allotropic changes. The detailed interaction between precipitated particles and dislocations is important to the degree of strengthening observed. Various mechanisms have been proposed, including particle bypassing by Orowan looping, or bypassing slip, or particle shearing.

Considering the relationship between applied stress and dislocation bowing, the Orowan equation is widely used in hard precipitate particle [118]:

\[
\Delta \tau_y = G b / L \tag{1.12}
\]

where \( \Delta \tau_y \) is the increase of the yield stress caused by the precipitate particles; \( G \) is the shear modulus of the matrix; \( b \) is the Burgers vector of the dislocation, and \( L \) presents the spacing of precipitate particle. The \( L \) value in Orowan equation is usually considered as the distance between particles arranged on a square grid on the slip plane.

Ashby [119] further considers the influence of particle spacing and statistical distribution, and obtains the Ashby-Orowan relationship as shown below:

\[
\Delta \tau_y = 0.84(1.2Gb / 2\pi L)\ln(x / 2b) \tag{1.13}
\]

Involving the Taylor factor of polycrystalline materials, the microstructure parameters are expressed by volume fraction and actual diameter, and the shear stress is converted into tensile
stress. The increase in yield strength by precipitation strengthening can be described by Orowan-Ashby equation as follow:

\[
\Delta \sigma_y = \left(0.538 \frac{Gbf^{1/2}}{X} \right) \ln \left( \frac{X}{2b} \right)
\]  

(1.14)

where \(\Delta \sigma_y\) is the yield strength increase associated with precipitates; \(G\) is the shear modulus (MPa); \(b\) is the Burgers vector of the dislocation (mm); \(f\) presents the volume fraction of precipitate particles, and \(X\) is the diameter of the precipitate.

Low carbon microalloyed steel plates are widely used in buildings, bridges, ships, vessels, industrial equipment, and offshore platforms because of the high strength-high toughness combination [120, 121]. Of particular significance in microalloyed steels is the role of microalloying elements, such as niobium (Nb), vanadium (V) and titanium (Ti), which helps in optimizing the microstructure and mechanical properties. Microalloying elements are generally present in steels as solute atoms or precipitates to inhibit austenite recrystallization and grain growth of ferrite \(\alpha\)-phase. Nb is generally considered very effective as compared to other microalloying elements [122, 123]. In recent years, researchers have advocated that the incorporation of second-phase particles can effectively improve the strength and the toughness of low-carbon martensitic steels through interactions between dislocations and grain boundaries [124]. Nanoscale precipitates (carbides, nitrides and carbonitrides) significantly enhance the strength of microalloyed steels through precipitation strengthening involving Orowan mechanism [125-128]. Deng [129] and Kim [130] studied the effects of rolling, cooling, and heat treatment on precipitates and mechanical properties of medium-carbon Mo–Ti martensitic steel. It pointed out the precipitation of Ti and Mo carbides can occur during austenite-to-ferrite, austenite-to-bainite and even during austenite-to-martensite transformations by different cooling rate in Ti–Mo bearing high-strength medium-carbon steel. However, how to control the
precipitate's shape and size by chemical composition and processes is a critical problem for precipitate hardening.

Funakawa et al. [120, 121] developed a 780 MPa high-strength ferritic steel using Ti and Mo microalloying in low-carbon steel and obtained a precipitation hardening increment of ~300 MPa. Zhang et al. [131] reported that a finer microstructure was achieved in the latter and many nanometer-size (Nb, Mo)C carbides (< 10 nm) precipitated, which significantly improved the strength of Nb-Mo microalloyed low carbon steel. Mo addition led to significant refinement of precipitated carbides and provided resistance to coarsening during the heat treatment [132]. The results indicated that the interaction of Nb, Ti, and Mo microalloying elements led to a high
density of fine and stable precipitates, playing a decisive role in further increasing the strength. Furthermore, Patra et al. [133] studied the effect of coiling temperature from 520 °C to 580 °C on microstructure and mechanical properties of 700 MPa Nb-Ti bearing low carbon microalloyed steel. However, a systematic study and a physical model to predict the precipitation behavior and quantify the strengthening mechanism as a function of coiling temperature for Ti-Nb-Mo bearing microalloyed steel has not been attempted to the best of our understanding.

Cooling after rolling and heat treatment are important methods to control precipitation. For example, the cooling rate after rolling and coiling temperature (auto tempering) had a great impact on precipitation behavior and the mechanical properties of Nb, V, Ti alloyed steel[134-136], and the quenching-partitioning-tempering (Q-P-T) process for Nb, V, Ti microalloyed ultra-high strength steel was also studied[137]. However, the research on cooling rate and RQ + T complex process is relatively rare.

Thus, in this study, the effect of controlled cooling and treatment processes on microstructure, mechanical properties, and precipitation behavior in Ti-Nb-Mo low-carbon microalloyed steels and quantitative analysis of strengthening mechanism has been carried out. A model was utilized to predict the precipitation behavior in terms of size, number density, and volume fraction that provides guidelines for processing of microalloyed steels.

1.4 Objectives of Study

The objectives of the research were the following:

1) Fundamentally explore the strain hardening behavior of tensile strained NG/UFG copper containing austenitic stainless steel by combining tensile data and post-mortem electron microscopy and compare with the coarse-grained (CG) counterpart.
2) Elucidate the effect of Ni on the free energy of bainitic transformation by designing Ni-free and Ni-bearing steels. In this regard, steels with two distinct nano-bainite structures were obtained through conventional one-stage and two-stage isothermal treatments. Also, study the effect on work hardening behavior and accompanying strain on martensitic transformation of two nano-bainite structures.

3) Identify the effects of controlled cooling and heat treatment on martensite morphology and precipitation in Mo-Ti microalloyed medium carbon steel and elucidate the relationship between microstructural evolution and mechanical properties. In this regard, a facile and cost-effective process for martensitic steels with high strength and toughness combination was proposed, and strengthening and toughening mechanisms elucidated. Furthermore, develop a model to predict the precipitation behavior in terms of size, number density, and volume fraction that provides guidelines for processing of microalloyed steels.
2.1 MATERIALS AND PROCESSING

The chemical compositions of studied steels are presented as Table 2.1.

Table 2.1 The chemical compositions of studied steels in the dissertation (wt.%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.02</td>
<td>0.55</td>
<td>0.85</td>
<td>17.4</td>
<td>-</td>
<td>3.15</td>
<td>7.43</td>
<td>-</td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>Ni-free</td>
<td>0.59</td>
<td>1.54</td>
<td>2.03</td>
<td>1.03</td>
<td>0.280</td>
<td>-</td>
<td>-</td>
<td>0.11</td>
<td>0.02</td>
<td>0.04</td>
<td>Bal.</td>
</tr>
<tr>
<td>Ni-bearing</td>
<td>0.60</td>
<td>1.55</td>
<td>2.07</td>
<td>1.01</td>
<td>0.278</td>
<td>-</td>
<td>1.47</td>
<td>0.11</td>
<td>0.02</td>
<td>0.04</td>
<td>Bal.</td>
</tr>
<tr>
<td>Ti-Mo</td>
<td>0.31</td>
<td>0.22</td>
<td>1.43</td>
<td>-</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

The studied austenitic stainless steel containing 3.15 wt.% Cu was used for strain hardening research by a phase reversion process (hereinafter referred to as Cu steel). The received steel sample was a hot-rolled sheet of ~3 mm thickness. The as-received steel was cold-rolled in a laboratory rolling mill to 1 mm thickness (66.7% reduction) and subsequently annealed in a Gleeble 3800 thermo-mechanical simulator. The annealing temperature and holding time to obtain NG/UFG structures were 800°C and 10 s, and the values were 950°C and 100 s for CG structures.

Two types of bainite-austenite dual-phase steels of nomination listed in composition Table 1 were prepared in the laboratory using standard melting process. Briefly, the steel specimens in the form of a forged billet with a cross-section of $50 \times 50$ mm$^2$ were obtained. The as-received steels were austenitized at 950 °C for 30 min and then transferred to a sealed box furnace at 250 °C for isothermal treatment for different duration (varying from 1 h to 48 h). In a multi-stage bainitic transformation, the first stage was a conventional bainite transformation to obtain partially transformed bainitic microstructure. The next stage involved the transfer of samples to a sealed box furnace at 200 °C to facilitate the transformation of untransformed
austenite to nanostructured bainite. The isothermal holding time of the second stage was twice the first stage (The heat treatment process is shown as Figure 2.1). We studied one-step transformation to ensure that the degree of bainite transformation in the two samples was similar prior to adopting the second isothermal step.

Medium carbon Ti-Mo composite microalloyed test steel was smelted for precipitation hardening research in a 50 kg vacuum induction furnace. The chemical composition of the test steel is presented in Table 2.1 (Ti-Mo sample). The carbon equivalent (CEV) index and the weld crack sensitivity index (Pcm) of the test steel were 0.597 wt% and 0.403 wt%, respectively. An appropriate amount of B was added to the test steel in order to improve its hardenability as well
as to obtain a uniform martensite structure. Moreover, the contents of N and S were controlled to avoid Ti precipitation during solidification [138]. The ingot was forged into 170 mm × 170 mm × 220 mm rectangular specimens and heated to 1230 °C for 3 h in order to ensure the complete solution of alloy elements as well as to avoid the excessive austenite grain growth. The controlled rolling was then carried out on an 800 mm two-high rolling mill, and austenite grains became fully deformed by rolling at low temperatures and high reduction rates. The specimens were cooled to room temperature by different cooling processes after rolling and then heat treated to prepare 250 mm × 250 mm × 14 mm steel plates (Fig. 1; Process A: direct quenching + tempering (DQ + T), Process B: direct quenching + reheating and quenching + tempering (DQ + RQ + T), Process C: forced air cooling + reheating and quenching + tempering (AC + RQ + T), Process D: furnace cooling + reheating and quenching + tempering (FC + RQ + T). The starting temperature of the cooling processes was 950 °C. The cooling rates of DQ, AC, and FC were 40 °C/s, 1 °C/s, and 0.1 °C/s, respectively. Process A was tempered after cooling, whereas processes B, C, and D were cooled first, then reheated to an austenitization temperature of 880 °C for 15 min, and finally, quenched and tempered. Tempering parameters were kept at 180 °C for 2 h during all processes.
Figure 2.2 Flow chart of the heat treatment process of Ti-Mo sample.

2.2 SAMPLE PREPARATION

The heat-treatment pieces for characterization were cut from bulk samples after each processing procedure by Buehler ISOMET 2000 Precision Cutting with feeding speeds of 5-10 mm/s. The pieces of samples were then hot mounted for optical microscope (OM) and scanning electron microscope (SEM) observation. Another group of samples prepared for X-ray diffraction (XRD) and transmission electron microscope (TEM) analyses were not mounted. Mechanical grinding and polishing process with extremely care to make sure produce good image. The grinding operation was carried out successively on 400, 800, 1200 and 2400 grade silicon carbide papers. After grinding, the samples were then mechanical polishing by Buehler ECOMET 2500 with 3 μm diamond suspension for 20 min at 500 RPM and etched with nital solution (4 vol%). All samples were washed and dried with isopropanol after each step and finally cleaned with ultrasonic stirring. Thin foils for transmission electron microscope (TEM)
were polished down to 50 µm thickness followed by electropolishing at 50 V and at room temperature. The electrolyte consisted of 80% methanol, 15% glycerol and 5% perchloric acid.

2.3 MICROSTRUCTURE OBSERVATION AND CHARACTERIZATION

2.3.1 Microstructure observation

Microstructural studies were carried out using optical microscopy (OM, Olympus BM51), scanning electron microscopy (SEM, Sirion 200), and transmission electron microscopy (TEM, Hitachi H7600, 120 kV).

The measurement of grain size involved two different methods. In the first approach, the grain size of at least 50 grains in the micrographs were estimated by Image J software and subsequently, mean linear intercept grain size ($\bar{d}$) was determined. The second method considered the grain size distribution to measure the weighted average grain size ($\bar{d}_w$) [139]. An optimum bin size of 200 nm was selected for a statistically relevant distribution of 100 detected grains in the micrographs. Denoting the number of grains in the $i$-th bin as $n_i$ and dividing it by the total number of grains, $N$, the weight of the $i$-th bin is [139]

$$w_i = \frac{n_i}{N} \quad (2.1)$$

Moreover, the square root of the areal mean of $n_i$ grains in the $i$-th bin provides the average grain size ($\bar{d}_i$) in the $i$-th bin. The weighted average grain size was calculated by the following equation [139]

$$\bar{d}_w = \sum_{i=1}^{N} w_i \bar{d}_i \quad (2.2)$$

2.3.2 Mechanical tests

The tensile tests were carried out by ASTM E8 standard [140] using an MTS testing machine. Once the sample is fixed, the load is set to zero to neglect force set manually because
the load set by fixing the sample hand tight is not the original load. An extensometer set helps in finding the instantaneous change in the cross-section during the test on the specimen while the strain is extracted. Vickers hardness test was conducted using Vickers hardness tester (THV-1MD) with 1.0 kg indentation load. An average of at least ten tests were carried out. The nanoindentation tests were conducted in the load-controlled mode to obtain load-displacement plot and understand the deformation mechanism in steels. The experimental set-up (Keysight Nanoindenter G200) consisted of a Berkovich three-sided pyramidal diamond indenter with an angle of 65.3° and an indenter tip of 20 nm diameter. Each load-displacement plot was recorded at a constant loading rate (2 μNs⁻¹) and the load varied from 0 to 0.5 mN. An array of indents (10 × 10) were made with a gap of 10 μm between each indent.

Figure 2.3 ASTM E8 standard dimensions and geometry of a flat tensile specimen [140].

2.3.3 Phase volume fraction detected by X-ray diffraction (XRD)

Quantitative phase analysis was carried out by an x-ray diffractometer (XRD, Xpert Pro MPD) operated at 40 kV and 45 mA using Mo-Kα radiation to determine the volume fraction of
austenite before and after the tensile test. Quantitative phase analysis is based on the premise that crystalline materials have unique diffraction patterns and that the intensity of the peaks in each particular pattern varies directly with its concentration. The XRD patterns were compared to standard diffraction patterns by software to identify phases. Each phase has characteristic X-ray peaks and corresponding to d spacing. Accurate d-spacings were calculated using Bragg’s law, \( \lambda = 2dsin\theta \) (\( \lambda \) is the wavelength of target radiation, Mo-K\( \alpha \) radiation, and \( \theta \) is half of the angle where the peak presents). The volume fraction calculation of this dissertation followed the ASTM standard E975-03 [140]. The integrated intensities of the austenite (\( \gamma \)) and ferrite (\( \alpha \)) diffraction peaks are determined by equations as follow [140]:

\[
I_{\alpha}^{hkl} = \frac{KR_{\alpha}^{hkl}V_{\alpha}}{2\mu} \\
I_{\gamma}^{hkl} = \frac{KR_{\gamma}^{hkl}V_{\alpha}}{2\mu}
\]

(2.3)

where \( K \) is the instrument geometric constant and \( R \) is the theoretical integrated intensity affected by interplanar spacing (hkl), Bragg angle \( \theta \), crystal structure and composition of the phase. \( V \) is the volume fraction of each phase and \( \mu \) is the linear absorption coefficient of steels.

The volume fraction of retained austenite (RA) was calculated using integrated intensities of (110), (211), (200), and (202) peaks of BCC structure and (111), (220), (200), and (311) peaks of FCC structure as equation below:

\[
V_i = \frac{1}{1 + G \left( \frac{I_{\alpha}}{I_{\gamma}} \right)}
\]

(2.4)

where \( V_i \) is the volume fraction of RA. \( I_{\alpha} \) and \( I_{\gamma} \) are the integrated intensities of ferrite and austenite. The experimental error was about 0.015 in the calculation of volume fraction. \( G \) is the ratio of intensity related factors corresponding to ferrite and austenite diffraction rays. The experimental error was about 0.015 in the calculation of volume fraction. There are many factors that prevent the direct comparison of concentration through peak intensity.
According to the principle of X-ray diffraction, the volume fraction of the measured phase is positively correlated with the cumulative intensity of X-ray. The lattice constants, atomic spacing and 2θ position for austenite, martensite and ferrite were shown in Table 2.2 [141]. The 2θ scan angle was in the range of 20°-120°, with scanning step size of 0.03342°. After the tensile test, the fracture surface was characterized by SEM and XRD.

Table 2.2 Lattice constants, atomic spacing and 2θ position for austenite, martensite and ferrite [141].

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>d (Å)</th>
<th>2θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1,1)</td>
<td>2.100</td>
<td>43.081</td>
</tr>
<tr>
<td>(2,0,0)</td>
<td>1.818</td>
<td>50.170</td>
</tr>
<tr>
<td>(2,2,0)</td>
<td>1.286</td>
<td>73.679</td>
</tr>
<tr>
<td>(3,1,1)</td>
<td>1.096</td>
<td>89.346</td>
</tr>
<tr>
<td>(2,2,2)</td>
<td>1.050</td>
<td>94.500</td>
</tr>
<tr>
<td>(1,0,1)</td>
<td>2.081</td>
<td>43.367</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>2.006</td>
<td>45.077</td>
</tr>
<tr>
<td>(0,0,2)</td>
<td>1.532</td>
<td>60.293</td>
</tr>
<tr>
<td>(2,0,0)</td>
<td>1.419</td>
<td>65.650</td>
</tr>
<tr>
<td>(1,1,2)</td>
<td>1.217</td>
<td>78.363</td>
</tr>
<tr>
<td>(2,1,1)</td>
<td>1.173</td>
<td>81.902</td>
</tr>
<tr>
<td>(2,0,2)</td>
<td>1.041</td>
<td>95.286</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>2.028</td>
<td>44.645</td>
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<tr>
<td>(2,0,0)</td>
<td>1.434</td>
<td>64.979</td>
</tr>
<tr>
<td>(2,1,1)</td>
<td>1.171</td>
<td>82.275</td>
</tr>
<tr>
<td>(2,2,0)</td>
<td>1.014</td>
<td>98.865</td>
</tr>
</tbody>
</table>

2.3.4 Element distribution measured by electron probe microanalyzer (EPMA)

The distribution of carbon was measured by electron probe microanalyzer (EPMA, JXA–8530F). EPMA is an instrument with the function of SEM and the additional parts of reflected light microscope, energy dispersive spectrometer (EDS), and wavelength Dispersive.
spectrometer (WDS) for microanalysis. EPMA involves bombarding a specimen with a focused electron beam and analyzing the emitted X-rays. It generally combines two related analytical techniques – wavelength-dispersive spectroscopy and energy-dispersive spectroscopy – in a single instrument known as a microprobe. Both techniques work by collecting characteristic X-rays and continuum released when the surface of a specimen is bombarded with electrons. As their names suggest, wavelength-dispersive spectroscopy separates emitted X-rays according to their wavelengths while energy-dispersive spectroscopy separates them according to their energies. The typical result of elemental distribution by EPMA shown as in Figure 2.4 [142].

Figure 2.4 Series of elemental maps showing the distribution of key elements in a Murray Basin ilmenite concentrate. The colored scale bar at the right shows relative concentration [142].

After the standard polishing process and etching (with 4 vol% nital solution), the target area of the sample was marked by a focused ion beam (FIB) under OM. The corresponding X-ray peak intensity of C and Ni in the marked area was recorded using 15 kV voltage, 20 nA current, and 0.08 μm scanning step size. The scanning result consisted of 300 × 225 test points.
(24 × 18 µm²), showing the distribution of carbon. The C-content was determined by point scanning mode, and the field of view (FoV) was randomly selected on a 10 × 10 mm sample surface to confirm the C-content in different microstructural constituents. Statistically, twenty different effective FoV were selected to determine the overall level of the C-content.
Chapter 3: The significance of phase reversion-induced nanograin/ultrafine-grained (NG/UFG) structure on the strain hardening behavior and deformation mechanism in copper-bearing antimicrobial austenitic stainless steel

Abstract

The unique concept of phase reversion involving severe deformation of parent austenite into martensite, followed by annealing for a short duration, whereby the strain-induced martensite reverts to austenite, was adopted to obtain nano-grained/ultrafine-grained (NG/UFG) structure in a Cu-bearing biomedical austenitic stainless steel resulting in high strength-high ductility combination. Work hardening and accompanying deformation mechanism are two important aspects that govern the mechanical behavior of biomedical devices. Thus, post-mortem electron microscopy of the strained region was carried out to explore the differences in the deformation mechanisms induced by grain refinement, while the strain hardening behavior was analyzed by Crussard-Jaoul (C-J) analysis of the tensile stress-strain data. The strain hardening behavior consisted of four stages and was strongly affected by grain structure. Twinning-induced plasticity (TWIP) was the governing deformation mechanism in the NG/UFG structure and contributed to good ductility. In striking contrast, transformation-induced plasticity (TRIP) contributed to high ductility in the coarse-grained (CG) counterpart and was the governing strain hardening mechanism. When the grain size is less than ~1 μm, the increase in the strain energy and the austenite stability significantly reduces the possibility of strain-induced martensite transformation such that there is a distinct transition in deformation mechanism from nanoscale twinning in the NG/UFG structure to strain-induced martensite in CG structure. The differences in the deformation mechanisms are explained in terms of austenite stability – strain energy relationship.
3.1 BACKGROUND

Austenitic stainless steels are commonly used materials, besides titanium alloys for biomedical applications, such as in joint replacement, bone fixation, and coronary stents [143-145]. Biomedical devices manufactured from stainless steels are expected to have a life span of 20–25 years, but unfortunately, they tend to fail prematurely because of the inadequate build-up of bone mass around the implants. Furthermore, the debris generated with time due to wear may be absorbed in the surrounding areas of biomedical implants and may induce inflammation, tissue death, and even failure of the biomedical device. Stainless steel is also used as a biomedical device in Parkinson's disease and neurological problems [146].

In order to increase the long-term stability of metallic implants, significant efforts have been made to decrease the grain size and induce nanostructured features to favorably tune protein-material and cell-material interactions [146-148]. Moreover, grain refinement and alloying with copper address the challenge of microbial infections induced by microorganisms, thereby thwarting the risk of infection through the inhibition of bacterial colonization and biofilm formation on biomedical implants [149-152]. Copper has been considered as an antimicrobial element for a long time [153]. The release of Cu$^{2+}$ ions damages the bacteria and is envisaged to destroy the permeability of the bacterial membranes, which helps in reducing sugars and proteins from the cells. Furthermore, they promote the formation of bacteria-killing reactive oxygen species (ROS). Thus, the antibacterial role of Cu encourages its potential use in inhibiting bacterial infection and materials containing copper are now being increasingly considered as antimicrobial biomaterials [151].

The ingenious concept of phase reversion has gained significance attention in recent years since it provides a route to enhance mechanical properties through extensive grain
refinement [154-156]. In austenitic stainless steels, the strain induced martensitic transformation is categorized into two types: the body centered cubic (BCC) or body centered tetragonal (BCT) α’-martensite and the hexagonal close packed (HCP) ε-martensite [157, 158]. It is generally noted that ε-martensite forms as a transition phase and assists in the formation of bcc α’-martensite by providing favorable conditions [158]. According to Lagneborg [157], α’-martensite forms at the intersection of ε-martensite sheet, as it is observed in contact with the ε-martensite. In AISI 304 steel, ε-martensite is observed for even small strains at room temperature and then it transforms completely to α’-martensite with continued deformation. According to one study, ε-martensite forms in steels with relatively low stacking fault energy (SFE), much lower than when only α’-martensite forms in austenitic stainless steels (SFE < 20 mJ/m²) [159]. In essence, the SFE controls the possibility of strain induced martensite transformation and the rate of work hardening of austenite. The reversion concept involves severe cold deformation of parent austenite to strain-induced martensite followed by short duration annealing and has been adopted to obtain nano-grained/ultrafine-grained (NG/UFG) structure in austenitic stainless steels including a Cu-bearing biomedical steel, resulting in high strength-high ductility combination [156, 160-165]. The concept was effectively used to critically analyze the interplay between the load-controlled deformation response and strain-rate sensitivity of NG/UFG austenitic stainless steel via nanoscale deformation experiments and compare with its coarse-grained (CG) counterpart. The study demonstrated that the strain-rate sensitivity of NG/UFG was ~1.5 times that of the CG structure [163]. While a study on biological functions indicated the occurrence of favorable modulation of osteoblast cellular activity on Cu-containing austenitic stainless steel in relation to the Cu-free counterpart.
Strain-induced hardening (also known as work hardening) is an important property for biomedical devices from the perspective of restricting deformation and providing wear resistance. Thus, in sequel to our recent studies on Cu-containing austenitic stainless steels [163, 165], the objective of the present study is to fundamentally explore the strain hardening behavior of tensile strained NG/UFG Cu-containing austenitic stainless steel by combining the tensile data and post-mortem electron microscopy and to compare the behavior with the coarse-grained (CG) counterpart.

3.2 EXPERIMENTAL DETAIL

The investigated austenitic stainless steel was received as a hot-rolled sheet of ~3 mm thickness. It was made using standard melting process in a laboratory, and its chemical composition is presented in Table 3.1, showing alloying with 3.15 wt.% Cu. The typical features of this steel composition are its low C content (0.023% C) and high stability as estimated using the stability index, Md30 = −11.2 °C (for grain size ASTM #7). Md30 is the temperature at which an amount of 50% austenite will be transformed to martensite through cold-deformation of 0.3 true strain (corresponding ca. 0.35 engineering strain) and is estimated using the following equation [166]:

$$M_{d30}^\circ (\text{C}) = 552 - 462(C + N) - 9.2Si - 8.1Mn - 13.7Cr - 29(Ni + Cu) - 18.5Mo - 68Nb - 1.42(GS - 8)$$

Table 3.1 Chemical composition (wt.% of the experimental Cu-bearing austenitic stainless steel.

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.02</td>
<td>0.55</td>
<td>0.85</td>
<td>17.40</td>
<td>3.15</td>
<td>7.43</td>
<td>0.011</td>
<td>0.025</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

As regards the SFE, none of the empirical equations in literature can precisely estimate the SFE. However, the Brofman and Ansell equation for SFE calculation is somewhat better than
the other ones. The SFE value of the investigated austenitic stainless steel computed using the Brofman and Ansell equation [167] as well as a more recent equation proposed by de Bellefon et al. [168], is estimated to be about 17 mJ/m² at room temperature. Since both the equations do not show any influence of copper, the actual SFE can be relatively higher, as Cu is one of the elements that increases the SFE of the austenitic stainless steel and increases the stability of the steel and decreases the $M_{d30}$ temperature.

The as-received steel sheet was further cold-rolled in a laboratory rolling mill to 1 mm thickness (66.7% reduction) and subsequently annealed in a Gleeble 3800 thermo-mechanical simulator. The optimized reversion annealing temperature and holding time to obtain NG/UFG structures were 800 °C and 10 s, respectively, and the corresponding values were 950 °C and 100 s for CG structures.

According to Schaeffler diagram, the steel is in the austenitic-ferritic-martensitic region corresponding to the % Ni equivalent ($Ni_{eq} = 9.7$) and % Cr equivalent ($Cr_{eq} = 18.6$) given by the following equations [169]:

$$Ni_{eq} \text{ (in wt.\%)} = Ni + Co + 30C + 25N + 0.5Mn + 0.3Cu \tag{3.2}$$

$$Cr_{eq} \text{ (in wt.\%)} = Cr + 2Si + 1.5Mo + 5V + 5.5Al + 1.75Nb + 1.5Ti + 0.75W \tag{3.3}$$

In annealed condition, the 2.95 mm thick sheet used in this study had about 1.5% ferrite. The $\alpha'$-martensite fraction after reversion annealing at 950 °C for 100 s was 2.3% and the corresponding strain induced $\alpha'$-martensite fraction after tensile deformation was about 65.5% estimated near the fractured ends.

### 3.3 Experimental results

#### 3.3.1 Microstructure
The optical and TEM micrographs of NG/UFG and CG steels are displayed in Figure 3.1. The weighted average grain size of NG/UFG and CG steels after cold rolling and annealing are presented in Table 3.2. The NG/UFG steel consisted of nanograins (less than 100 nm) and a few ultrafine grains (~100–500 nm) with a weighted average grain size of 350 nm, whereas the CG steel was composed of uniform coarse grains with a weighted average grain size of 22 μm. The samples did not show formation of any ε-Cu particles under these conditions of reversion. However, another study by Somani et al. showed formation of ε-Cu precipitates following reversion annealing treatments at 650–700 °C for long holding times of 1–1.5 h [165].

![Figure 3.1](image_url)

Figure 3.1 (a) Light optical and (b) transmission electron micrographs of CG and NG/UFG structure, respectively in Cu-bearing antimicrobial austenitic stainless steels. The NG/UFG steel consisted of nanograins (less than 100 nm) and a few ultrafine grains (~100–500 nm) with a weighted average grain size ($\bar{d}_w$) of 350 nm (b), whereas the CG steel was composed of uniform coarse grains with a weighted average grain size of 22 μm (a).

<table>
<thead>
<tr>
<th></th>
<th>Weighted average grain size</th>
<th>Average yield strength, MPa</th>
<th>Average elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG/UFG</td>
<td>350 nm</td>
<td>769</td>
<td>38</td>
</tr>
<tr>
<td>CG</td>
<td>22 μm</td>
<td>297</td>
<td>68</td>
</tr>
</tbody>
</table>
3.3.2 Tensile properties and strain hardening behavior

The tensile properties of NG/UFG and CG steels are presented in Table 3.2. The yield strength and elongation of the NG/UFG steel were 769 MPa and 38% respectively, whereas corresponding values for the CG steel were 297 MPa and 68%, respectively. The yield strength of NG/UFG steel was ~ 2.5 times higher than that of the CG steel, and the elongation was also reasonably good. The true stress-true strain (σ_T-ε_T) curves of NG/UFG and CG Cu-bearing steels obtained from the tensile data are presented in Figure 3.2.

![Graph showing true stress-true strain curves for NG/UFG and CG steels](image)

Figure 3.2 True stress-true strain (logarithmic strain) plots for NG/UFG and CG copper-bearing antimicrobial austenitic stainless steels.

The strain-hardening rates (SHR = dσ_T/dε_T) of the two steels with remarkably different grain sizes obtained from the true stress-true strain plots in Figure 3.2 are presented as a function of true strain in Figure 3.3. In the early stage, the SHR of NG/UFG steel decreased sharply and
attained a small plateau of ~1858 MPa in the range $\varepsilon = 0.02–0.05$. This was followed by a very slow decrease of SHR in the strain range of $\varepsilon = 0.05–0.22$, and finally a sharp drop until the onset of necking. The SHR of CG steel also decreased rapidly in the initial stage, but in contrast to NG/UFG steel at $\varepsilon_T < 0.02$, the SHR of CG steel decreased at a relatively higher rate and attained a plateau of ~ 1089 MPa in the strain range $\varepsilon = 0.26–0.40$, and finally, decreased sharply with the onset of necking to fracture.

Figure 3.3 Strain hardening rate as a function of true strain (logarithmic strain) for NG/UFG and CG copper-bearing antimicrobial austenitic stainless steels.

The strain-hardening behavior of the two steels was further analyzed by the Crussard-Jaoul (C-J) method ($\ln(\frac{d\sigma_T}{d\varepsilon_T})$ vs. $\ln(\varepsilon_T)$) and is presented in Figure 3.4. The differential C-J plot assumes the Ludwik power relation and can describe changes in the slope of a line segment,
facilitating further insight into the differences in deformation mechanisms [170, 171]. Though limited in applicability, the C-J analysis of the tensile deformation was employed to show the changes in the strain hardening behavior of the two materials with widely different grain structures. The idea was to identify and reveal different stages characterized by the decrease or increase in \( \ln(d\sigma_T/d\varepsilon_T) \) with \( \ln(\varepsilon_T) \), including plateaus and valleys. These stages are marked by the occurrences of mechanisms that are characteristic of NG/UFG and CG structures. In earlier studies on the C-J analysis [172-175], the natural logarithmic values of SHR (i.e., \( \ln(d\sigma_T/d\varepsilon_T) \)) was divided into various stages characterized by the decrease or increase in \( \ln(d\sigma_T/d\varepsilon_T) \) with true strain, including plateaus, valleys and peak positions. It is evident from the C-J plot in Figure 3.4 that the strain hardening behavior can be divided into three stages (A, B, D) for the NG/UFG steel and four stages (A, B, C, D) for the CG counterpart. The characteristic data points corresponding to these stages are summarized in Table 3.3. For the NG/UFG structure, the logarithmic value of SHR (\( \ln(d\sigma_T/d\varepsilon_T) \)) decreased rapidly in stage A \((\varepsilon < 0.030)\) followed by a period of slow decrease in stage B \((0.030 < \varepsilon < 0.172)\) and then a rapid decrease corresponding to the necking region in stage D \((0.172 < \varepsilon < 0.268)\). The \( \ln(d\sigma_T/d\varepsilon_T) \) of the CG structure decreased relatively slowly compared to the NG/UFG structure in stage A \((\varepsilon < 0.022)\), but maintained a near similar rate of decrement before reaching the valley level of stage B \((\varepsilon = 0.195)\). This was followed by a small but gradual increase of \( \ln(d\sigma_T/d\varepsilon_T) \) to attain the minor peak of stage C \((\varepsilon = 0.339)\). This behavior was not observed in the NG/UFG structure. Lastly, the onset of necking in CG steel until fracture was characterized by stage D \((0.339 < \varepsilon < 0.461)\). The main differences in the strain hardening behavior of NG/UFG and CG steels are summarized below:
(a) In stage A, the SHR decreased rapidly in the case of NG/UFG steel compared to the CG steel. Also, the NG/UFG steel had a wider SHR ($\ln(d\sigma_T/d\varepsilon_T)$) range and considerable strain in stage A; the corresponding decrease in SHR was gradual and characterized by a slower decrease with strain.

(b) Both structures experienced a small decrease in SHR in stage B at nearly similar $\ln(d\sigma_T/d\varepsilon_T)$.

(c) Stage C was absent in NG/UFG steel, whereas there was presence of a small stage C in CG steel.

(d) Stage D in the CG structure occurred at a higher strain, obviously as a result of greater elongation.

Figure 3.4 The C-J analysis ($\ln(d\sigma_T/d\varepsilon_T)$ vs. $\ln(d\varepsilon_T)$) for NG/UFG and CG copper-bearing antimicrobial austenitic stainless steels.
Table 3.3 Plastic strain in each stage of the samples with different grain sizes based on the C-J analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stage A</th>
<th>Stage B</th>
<th>Stage C</th>
<th>Stage D</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG/UFG</td>
<td>$\varepsilon &lt; 0.030$</td>
<td>$0.030 &lt; \varepsilon &lt; 0.172$</td>
<td>-</td>
<td>$0.172 &lt; \varepsilon &lt; 0.268$</td>
</tr>
<tr>
<td>CG</td>
<td>$\varepsilon &lt; 0.022$</td>
<td>$0.022 &lt; \varepsilon &lt; 0.195$</td>
<td>$0.195 &lt; \varepsilon &lt; 0.339$</td>
<td>$0.339 &lt; \varepsilon &lt; 0.461$</td>
</tr>
</tbody>
</table>

The plastic strain range for NG/UFG and CG steels based on C-J analysis is presented in Table 3.3 and the maximum and minimum SHR for the different stages are presented in Table 3.4.

Table 3.4 Maximum and minimum strain hardening rates of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SHR in stage B, MPa</th>
<th>SHR in stage C, MPa</th>
<th>SHR in stage D, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>NG/UFG</td>
<td>1858</td>
<td>1464</td>
<td>-</td>
</tr>
<tr>
<td>CG</td>
<td>2510</td>
<td>1089</td>
<td>1134</td>
</tr>
</tbody>
</table>

3.3.3 Deformation structure

Illustrations of post mortem electron microscopy of the tensile deformed region in the vicinity of the fracture surface are presented in Figure 3.5, Figure 3.6 for the NG/UFG and CG steels, respectively. For the NG/UFG structure, a number of representative electron micrographs are presented, which clearly depict formation of stacking faults (SF) and nanoscale twins during tensile deformation (Figure 3.5). A number of intersecting nanoscale twins were detected along with the stacking faults in various regions. The formation of stacking faults is contemplated as a precursor to the occurrence of twinning. In striking contrast, strain-induced martensite was observed in the case of CG steel (Figure 3.6). Prior to tensile deformation, the fraction of martensite in the steel was very small (~2.3%). However, a significant strain induced martensite (65.5%) formed in the microstructure following tensile testing, measured near the fracture end. Thus, we can unambiguously conclude that there was a distinct change in the deformation mechanism, when the grain structure was refined from CG to NG/UFG structure.
Figure 3.5 Transmission electron micrographs of antimicrobial copper-bearing austenitic stainless steel with NG/UFG structure illustrating formation of occurrence of (a, b) nanoscale twinning (the inset is the selected area diffraction patterns) and (c, d, e) stacking faults in the tensile deformed structure.
Figure 3.6 Transmission electron micrographs of CG copper-bearing austenitic stainless steel illustrating (a-d) strain-induced martensitic transformation and (e, f) indexed selected area diffraction patterns.

Figures 3.5 and 3.6 confirm that the deformation mechanism was altered from stacking faults and nanoscale twinning in the NG/UFG structure (Figure 3.5) to strain-induced martensitic
transformation in the CG structure (Figure 3.6). In the NG/UFG structure, twinning contributed to good ductility, while in the CG counterpart, the high ductility was associated with the formation of strain-induced martensite.

3.4 DISCUSSION

The deformation-induced martensite is achieved by the cooperative shear movement of atoms, where the applied stress aids the transformation and the role of plastic strain on the martensitic transformation is significantly more complicated [176]. It is clear from Figures 3.5 and 3.6 that the deformation mechanism changed from nanoscale twinning in the NG/UFG structure to strain-induced martensitic transformation in the CG structure, and this transition was closely associated with the increase of strain energy and stability of austenite with the decrease of the grain size, as discussed below.

Stage A in C-J analysis plots (Figures 3.3 and 3.4) can be characterized as the elastic deformation stage with dislocation nucleation [13, 177]. It is pertinent to indicate that slip or dislocation glide is precursor to any deformation mechanism (twinning or strain induced martensite) and is a major mechanism accommodating the strain. In stage A, the logarithmic value of SHR ($\ln(d\sigma_T/d\varepsilon_T)$) of NG/UFG steel was significantly greater than CG steel.

Stage B was characterized by a continuous decrease in SHR from 1858 to 1464 MPa (Table 3.4), and is attributed to the nucleation of stacking faults and twins in the NG/UFG steel. In the NG/UFG structure, emission of multiple partial dislocations from grain boundaries promotes twin nucleation. During this process, when a perfect dislocation in the matrix is stopped by an obstacle, such as a twin boundary, it dissociates into Frank sessile and Shockley partial dislocations ($\frac{1}{2}[\overline{1}01] \rightarrow \frac{1}{3}[\overline{1}\overline{1}1] + \frac{1}{6}[\overline{2}1])$ [178]. Stage B in the CG structure compromised of two sub-regions (I and II) of different slopes. The decrease of SHR in region I is slower, while
in region II, the decrease occurs relatively rapidly[13, 172, 177-181]. The SHR dropped from a maximum of 2510 MPa to about 1089 MPa in stage B for the CG steel, see Table 4. The accumulation of strain energy leads to an increase in the transformation of austenite to martensite with consequent increase in dislocation density, which provides more nucleation sites for the new strain induced martensite and increases the strain hardening effect. Moreover, a high density of dislocations hinders the movement of partial Shockley dislocations.

In stage C, both the strain-induced transformation as well as generation of high dislocation density slightly increased the SHR of the CG structure from 1089 to 1134 MPa (Table 3.4). In contrast, stage C did not exist in the NG/UFG structure, because it just corresponded to nucleation rather than the growth of twins with increasing strain. Generally, twins tend to nucleate in the high-stress concentration regions, and the stress required for twins to nucleate is far greater than the growth of twins. During the plastic deformation stage for the NG/UFG structure (0.030 < ε < 0.172), the formation of different twin configurations resulted in a significant increase in the twin density, thus hindering the glide of dislocations and providing the strain hardening effect [180]. Finally, necking (stage D) occurred beyond the endurance limit of the steel, resulting in a rapid decrease of SHR leading to fracture.

Considering that both mechanical twinning and strain-induced martensite formation contributed to the strain hardening effect, it can be inferred that the strain hardening characteristics associated with twinning and strain-induced martensite formation were similar. However, subtle differences were noticed between these two strain hardening mechanisms, due to the significant weighted average grain size difference between NG/UFG (350 nm) and CG structures (22 μm).
Although it is considered that grain size greatly controls the thermal stability of austenite, the impact of grain size on the mechanical stability of austenite continues to be unclear [182, 183] and is revisited here. It is generally believed that the transformation of γ-austenite to α'-martensite leads to anisotropic strains in the neighboring untransformed austenite. Matsuoka et al. [182] suggested that when the grain size was large, 24 variants were equally obtained to minimize the total strain energy. However, when the grain size was equal to or smaller than the martensite lath width, for instance, in the case of NG/UFG structure, a majority of the variants of martensite are restricted to operate within an austenite grain because of the spatial restriction effect. Thus, during tensile straining, only a particular variant is selected for strain-induced martensitic transformation in the NG/UFG structure, where <101>α' direction is parallel to the tensile direction [182]. In view of this reason, austenite is envisaged to transform to strain-induced martensite via a single variant. But the strain energy generated by martensitic transformation cannot be minimized by the limited variant transformation, leading to suppression of martensitic transformation in the NG/UFG structure.

In a recent study, different initial microstructures with various bimodal grain size distributions (BGSD) were obtained in a high Mn austenitic steel (TRIP/TWIP) through rolling at different temperatures [184, 185]. The corresponding room temperature mechanical properties and the related strain hardening behavior were assessed via tensile testing. The results indicated that in the microstructure with high grain size bimodality, the length and amplitude of rapid strain hardening region were greater, a behavior attributed to the higher capability to α'-martensite formation. Furthermore, different transformation paths were identified as the BGSD changed [186]. The austenite directly transformed to α'-martensite (γ→α’) in the case of the microstructure with lower BGSD. In contrast, nucleation occurred at the intersections of ε-
martensite platelets in the case of the microstructure with higher BGSD. The co-existence of these transformation paths provided an extended transformation induced plasticity effect leading to higher elongation. In summary, the higher possibility of strain-induced transformation and twinning in coarser grains as compared to finer grains was observed to dictate the material work hardening potential during tensile deformation. The material characterized by more homogeneous grain size and low level of BGSD showed austenite to martensite transformation as the primary mechanism during tensile deformation at room temperature. In contrast, materials with bimodal grain size largely depicted the occurrence of mechanical twinning, which induced rapid hardening region and prompted work hardening behavior. The aforementioned effects were correlated to the length of work hardening region (dictated by twinning), and the magnitude of hardening rate (controlled by transformation of austenite to α′ martensite).

In this study, the texture effect has not been determined, but a separate recent study carried out to understand the microstructure and properties of this Cu-bearing austenitic stainless steel revealed that the fully reverted CG structure had fully random orientation suggesting a very weak texture, though the grain size varied slightly due to a mixture of reversion-refined fine grains formed from deformation induced martensite and recrystallized grains formed from deformed austenite [165]. With lower reversion temperatures corresponding to NG structure, similar features were present with weak to very weak textures, but some large grains with numerous low angle grain boundaries were also present. However, no attempt has been made to exclude the effect of these features on the mechanical properties.

The mechanism of austenite stabilization induced by grain refinement can be discussed in terms of physical energy [186]. If austenite is transformed to martensite through a single variant mode, the increase of the elastic strain energy can be described by equation (3.4) [186].
\[ \Delta E_v = \left( \frac{1}{2} \right) E_1 \varepsilon_1^2 + \left( \frac{1}{2} \right) E_\text{II} \varepsilon_\text{II}^2 + \left( \frac{1}{2} \right) E_\text{III} \varepsilon_\text{III}^2 \] (3.4)

where \( E \) and \( \varepsilon \) are Young's modulus and elastic strain in each lattice, respectively. The transformation of fcc \( \gamma \)-austenite into bcc \( \alpha' \)-martensite experiences lattice displacement consisting of two types of atomic movement: (I) \(~36\%\) shear deformation along the [\( \bar{1}10 \)] direction and (II) anisotropic deformation with a volume expansion of \(~4.5\%\). This volume expansion includes \(~13.9\%\) \( (\varepsilon_\text{I}) \) expansion along the [001] direction, \(~7.0\%\) \( (\varepsilon_\text{II}) \) contraction along the [\( \bar{1}10 \)] direction and \(~1.4\%\) \( (\varepsilon_\text{III}) \) contraction along with the [\( \bar{1}1\bar{0} \)] direction, and the corresponding Young's moduli are 132.1 GPa \( (E_\text{I}) \), 220.8 GPa \( (E_\text{II}) \), and 220.8 GPa \( (E_\text{III}) \), respectively [186]. The increase of elastic strain energy calculated using equation (3.3) is \(~1839\) MJ/m\(^3\). Given that the maximum displacement occurs along the [001]\(_{\text{BCC}}\) direction, it can be assumed that the nucleation of thin-plate martensite would minimize the elastic strain energy. Moreover, lattice strain is controlled by austenitic grain size. Thus, equation (3.4) can be modified to equation (3.5):

\[ \Delta E_v = \left( \frac{1}{2} \right) E_1 \varepsilon_1^2 \left( \frac{x}{d} \right)^2 + \left( \frac{1}{2} \right) E_\text{II} \varepsilon_\text{II}^2 \left( \frac{x}{d} \right) + \left( \frac{1}{2} \right) E_\text{III} \varepsilon_\text{III}^2 \left( \frac{x}{d} \right) \] (3.5)

where \( x \) is the thickness of thin-plate martensite, and \( d \) is austenitic grain size. Substituting the value of Young's modulus and strain in equation (3.5), the increase of elastic strain can be obtained as equation (3.6) [186]:

\[ \Delta E_v = 1276.1 \left( \frac{x}{d} \right)^2 + 562.6 \left( \frac{x}{d} \right) \] (3.6)

The elastic strain energy \( (\Delta E_v) \) as a function of grain size \( (d) \) for martensite nucleation is plotted in Figure 3.7 for the martensite lath thickness of 0.2 \( \mu \)m. It is noted that when the grain size is
smaller than \( \sim 1 \mu m \), the elastic strain energy increases rapidly. For the NG/UFG structure, the weighted average grain size of 350 nm results in a significantly high elastic strain energy of \( \sim 850 \) MJ/m\(^3\). In contrast, the CG structure had a relatively low elastic strain energy of \( \sim 5 \) MJ/m\(^3\) because of larger weighted average grain size (22 \( \mu m \)). Thus, the possibility of multi-variant transformation to occur is restricted and the transformation of strain-induced martensite was significantly suppressed in the NG/UFG structure.

Figure 3.7 Elastic strain energy as a function of grain size for martensite nucleation according to single variant equation.

3.5 CONCLUSIONS

The significance of grain refinement on the strain hardening behavior and TWIP/TRIP deformation mechanisms in Cu-bearing NG/UFG and CG antimicrobial stainless steels was
elucidated on the basis of Crussard-Jaoul analysis of tensile deformation data of the steels and post-mortem electron microscopy of the strained region near the fractured ends. The plastic deformation process can be divided into four stages based on the change in SHR. Grain refinement strongly affected the strain hardening ability. The good ductility and high SHR of the NG/UFG structure is attributed to the occurrence of mechanical twinning, whereas the strain-induced martensite transformation was the underlying reason for the excellent strain hardening ability and ductility of the CG structure. Both mechanisms were effective in inhibiting the movement of dislocations. In nano-grained austenitic stainless steel with grain size less than \(~1\) μm, the high strain energy and austenitic stability significantly reduced the possibility of multivariant transformation and led to the suppression of strain-induced martensitic transformation. Extensive grain refinement due to reversion annealing was responsible for the transition of the deformation mechanism from a strain-induced martensitic transformation in the CG structure to mechanical twinning in the NG/UFG structure, besides manifestation of a large number of stacking faults, a precursor to the occurrence of twinning.
Chapter 4: Effect of nickel on hardening behavior and mechanical properties of nanostructured bainite-austenite steels

Abstract

Ni-free and Ni-bearing steels were designed to elucidate the effect of Ni on the free energy of bainitic transformation. Steels with two distinct nano-bainite structures were obtained through conventional one-stage and two-stage isothermal treatments. The effect of work hardening and accompanying strain on martensitic transformation of the two nano-bainite structures was also studied. Microstructure of both the steels consisted of bainitic ferrite and film-like and block-like retained austenite (RA). The total carbon concentration, degree of Fe–C cluster formation, and stability of RA were significantly affected by the free energy of bainitic transformation. The presence of Ni leads to reduction in the free energy of bainitic transformation, refinement of bainite structure, and extension of bainite nucleation regime. The carbon-content in block-like and film-like RA microstructure of Ni-bearing steel was 5.5% and 19.1%, respectively, which was greater than Ni-free steel. The load-displacement behavior indicated superior strain hardenability and higher strain hardening rate (SHR) in Ni-bearing steel. The uniform nanostructure of Ni-bearing steel promoted the formation of stable film-like RA between bainitic ferrite, leading to higher strain hardening rate and stronger transformation-induced plasticity (TRIP) effect at large strain. The Ni-bearing steel was characterized by superior plasticity (13.7%–10.3%) and product of tensile strength and % elongation (25.9 GPa·% to 20.9 GPa·%) in comparison to the Ni-free steel.

4.1 BACKGROUND

The low-temperature bainite (super-bainite) proposed by Bhadeshia et al. [11, 187] is a new generation nanostructured bainitic steel with an excellent combination of tensile strength
(-2.3 GPa), toughness (~30 MPa m\(^{1/2}\)), and ductility (~30%). These properties were obtained because of bainitic lath of nano-thickness dispersed in the retained austenite (RA) matrix. This was obtained by isothermal transformation for a long period of time at 200–300 °C (slightly above the martensite formation temperature, MS). The small size of bainitic ferrite lath in the low-temperature bainitic steel can play an important role in improving the strength and hardness of steel because of refinement. Nevertheless, the metastable RA distributed between the bainite laths may transform to martensite (strain-induced martensitic transformation) on being subjected to external stress, which renders good plasticity and toughness and further enhances the strength and hardness of steel. This is known as transformation-induced plasticity (TRIP) effect [116, 188]. Therefore, to maximize the TRIP effect, the shape, size, and volume fraction of RA should be effectively controlled while producing nanoscale bainite lath. However, there is a continued challenge to obtain excellent properties in bainitic steel.

Hu et al. [189] reported that the addition of niobium (Nb) improved the strength of steel through grain refinement by hindering bainitic transformation, while molybdenum (Mo) was effective in improving the strength of low carbon (C) bainitic steel by promoting the bainitic transformation. The results of the study conducted by García-Mateo et al. [108] showed that the addition of cobalt (Co) and aluminum (Al) increased the driving force of bainite transformation, thereby, accelerating the transformation process and increasing plasticity and toughness without loss of strength of low-temperature bainite. Caballero et al. [113] optimized the chemical composition of steel (reduced the C-content and simultaneously increased the Ni-content) and obtained mixed structure of martensite and RA with nano-size (100–200 nm width) laths of bainitic ferrite. Singh [114] pointed out that the strength of austenite and chemical free-energy change responsible for the transformation were governing factors influencing plate-thickness.
Cornide et al. [115] studied the influence of strength of austenite phase on the thickness of bainite lath and demonstrated that an increase in austenite strength decreased lath thickness. These studies indicated that highly stable austenite was more favorable in obtaining thinner bainitic ferrite laths. Meanwhile, the TRIP effect was also strongly affected by RA. In this regard, Chiang et al. [116] reported that work hardening behavior was directly related to the transformation rate of RA, which in turn depends on the C-content and grain size of RA in the respective TRIP microstructure. Moreover, the transformation of block-like RA to martensite easily occurred, resulting in high deformability [188]. The highly stable film-like RA was beneficial in arresting crack propagation. However, systematic studies on the relationship between bainite transformation kinetics, microstructural features, mechanical properties, and TRIP effect in bainitic steel are currently limited.

Yang et al. [190] added Ni to decrease martensite/bainite start temperature and successfully attained low-temperature bainite in low carbon steel. Far et al. [191] reported that Ni addition increased the content of retained austenite and mechanical properties. Moreover, the addition of Ni can effectively strengthen hydrogen embrittlement in bainite steel [192]. However, a systematic understanding on the effect and mechanism of Ni addition on low-temperature nanostructured bainite transformation and mechanical properties is rare. In the present study, the effect of Ni on the free energy of bainitic transformation on the two types of steels is elucidated. The microstructure and hardness of both the samples after conventional one-stage and two-stage isothermal treatment (for different holding period) were studied using different microscopic techniques. Tensile properties and strain hardening rate of both the steels after two-stage isothermal treatment were also studied. The C-content of block-like and film-like RA was measured to understand its effect on bainitic transformation. The load-displacement plots of
film-like RA in Ni-free and Ni-bearing structures were obtained by nanoindentation process to understand the strain hardenability of steels (after two-stage isothermal treatment). Lastly, the volume fraction of austenite before and after the tensile test was calculated from the XRD data, and the effect of external strain on austenite-bainite transformation investigated.

4.2 EXPERIMENTAL DETAIL

4.3.1 Materials and heat treatment processes of the samples

Two types of bainite-austenite dual-phase steels of nomination listed in composition Table 4.1 were prepared in the laboratory using standard melting process. Briefly, the steel specimens in the form of a forged billet with a cross-section of $50 \times 50$ mm$^2$ were obtained. The as-received steels were austenitized at 950 °C for 30 min and then transferred to a sealed box furnace at 250 °C for isothermal treatment for different duration (varying from 1 h to 48 h). In a multi-stage bainitic transformation, the first stage was a conventional bainite transformation to obtain partially transformed bainitic microstructure. The next stage involved the transfer of samples to a sealed box furnace at 200 °C to facilitate the transformation of untransformed austenite to nanostructured bainite. The isothermal holding time of the second stage was twice the first stage (The heat treatment process is shown as Figure 4.1). We studied one-step transformation to ensure that the degree of bainite transformation in the two samples was similar prior to adopting the second isothermal step. Ni addition significantly extended the bainite nucleation and contributed to refinement of bainite structure in the second isothermal. The second stage isothermal time was set according to bainite transformation degree in one-step isothermal, with the objective to make this premise clear. This is the significance of one-step isothermal process in the study described here.
Table 4.1 Chemical composition of experimental steels (wt.%)  

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>V</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-free</td>
<td>0.59</td>
<td>1.54</td>
<td>2.03</td>
<td>1.03</td>
<td>0.280</td>
<td>-</td>
<td>0.11</td>
<td>0.02</td>
<td>0.04</td>
<td>Bal.</td>
</tr>
<tr>
<td>Ni-bearing</td>
<td>0.60</td>
<td>1.55</td>
<td>2.07</td>
<td>1.01</td>
<td>0.278</td>
<td>1.47</td>
<td>0.11</td>
<td>0.02</td>
<td>0.04</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Figure 4.1 Heat treatment processes for multi-step nano-bainite transformation

4.3.2 Microstructural analysis

After the heat treatment, the samples were polished with 1500 mesh SiC sandpaper, followed by mechanical polishing with diamond paste W2.5 (4000 mesh, Ra < 0.025 μm) for 20 min at 800 RPM and etched with nital solution (4 vol%). Microstructural studies were carried out using optical microscopy (OM, Olympus BM51), scanning electron microscopy (SEM, Sirion 200), and transmission electron microscopy (TEM, Hitachi H7600, 120 kV). Thin foils for TEM studies were ground to ~50 μm thickness, followed by twin-jet electropolishing (50 V) at room temperature (RT). The electrolyte consisted of 80% methanol, 15% glycerol, and 5% perchloric acid.

X-ray diffraction studies were carried out using an x-ray diffractometer (XRD, Xpert Pro MPD) operated at 40 kV and 45 mA using MoKα radiation to determine the volume fraction of austenite before and after the tensile test (by Rietveld analysis). The 2θ scan angle was in the range of 20°–120°, with scanning step size of 0.03342°. The volume fraction of RA was
calculated using integrated intensities of (110), (211), (200), and (202) peaks of bcc structure and (111), (220), (200), and (311) peaks of fcc structure. The experimental error was about 0.015 in the calculation of volume fraction. After the tensile test, the fracture surface was characterized by SEM and XRD.

Furthermore, the distribution of C and Ni was measured by electron probe microanalyzer (EPMA, JXA–8530F). After the standard polishing process and etching (with 4 vol% nital solution), the target area of the sample was marked by a focused ion beam (FIB) under OM. The corresponding X-ray peak intensity of C and Ni in the marked area was recorded using 15 kV voltage, 20 nA current, and 0.08 μm scanning step size. The scanning result consisted of 300 × 225 test points (24 × 18 μm2), showing the trend of change in C/Ni ratio. The C-content was determined by point scanning mode, and the field of view (FoV) was randomly selected on a 10 × 10 mm sample surface to confirm the C-content in different microstructural constituents. The results of twenty different FoV were selected to determine the overall C-content.

The prior grain size of the austenite was measured using the oxidation method [193]. In the first approach, the average austenite grain size was obtained by measuring at least 300 grains in the micrograph by Image J software, and subsequently, the mean linear intercept grain size ( ) and error were determined.

4.3.3 Mechanical tests

The tensile tests were carried out using round bar samples with 8 mm diameter and 50 mm gage length according to GB/T 228.1–2010 Chinese standard, and the impact test was carried out using ZBC 2452–3 pendulum impact tester at room temperature. Standard Charpy v-notch impact sample of dimensions 10 mm × 10 mm × 55 mm was used. Vickers hardness test was conducted using Vickers hardness tester (THV-1MD) with 1.0 kg indentation load. An
average of at least ten tests were carried out. The nanoindentation tests were conducted in the load-controlled mode to obtain load-displacement plot and understand the deformation mechanism in steels. The experimental set-up (Keysight Nanoindenter G200) consisted of a Berkovich three-sided pyramidal diamond indenter with an angle of 65.3° and an indenter tip of 20 nm diameter. Each load-displacement plot was recorded at a constant loading rate (2 μNs⁻¹) and the load varied from 0 to 0.5 mN. An array of indents (10 × 10) were made with a gap of 10 μm between each indent.

4.3 EXPERIMENTAL RESULTS

4.3.1 Microstructure of the steels after one-stage isothermal treatment

The microstructure of Ni-bearing and Ni-free steels after conventional one-stage isothermal treatment for bainitic transformation was characterized by OM and is shown in Figure 4.2. The hardness values corresponding to each holding time are listed in Table 4.2. After the isothermal treatment at 250 °C for 6 h, the microstructure of Ni-free sample showed a combination of acicular bainite, RA, and martensite (Figure 4.2a, the black part is acicular bainite, and the white part is the mixed structure of RA and martensite) with a hardness of 679 ± 12 HV1. On the other hand, the microstructure of Ni-bearing steel (under identical experimental conditions) consisted of only martensite (white) with 744 ± 5 HV1 hardness. On increasing the holding time to 12 h, the acicular bainite content was also found to increase in Ni-free sample with a significant decrease in RA/martensite content and hardness was reduced to 611 ± 17 HV1. However, under identical experimental conditions, the Ni-bearing sample showed the presence of a small amount of acicular bainite with slight reduction in hardness to 718 ± 14 HV1. This indicated that the incubation period for Ni-bearing sample was ~12 h. When the duration of isothermal transformation was increased to 24 h, the RA content in Ni-free sample was also
decreased and transformed to bainite along with the decrease in hardness to $568 \pm 5$ HV1. In contrast, the microstructure of Ni-bearing sample showed a combination of martensite and bainite, and the hardness of the sample remained relatively high at $636 \pm 19$ HV1. When the bainite transformation duration was extended to 48 h, the morphology and hardness of Ni-free sample were almost similar to the previous case (24 h), while the microstructure of Ni-bearing sample indicated a complete transformation of austenite to acicular bainite and the corresponding hardness value was similar to Ni-free sample ($554$ HV1 to $563$ HV1). The results indicated that bainitic transformation in Ni-free sample was completed after isothermal treatment at $250 \degree C$ for 24 h, while in Ni-bearing sample, the bainitic transformation was completed at $250 \degree C$ after 36 h.

![Optical micrographs of the (a) Ni-free and (b) Ni-bearing steel samples after isothermal treatment.](image)

**Figure 4.2** Optical micrographs of the (a) Ni-free and (b) Ni-bearing steel samples after isothermal treatment.

<table>
<thead>
<tr>
<th>Samples</th>
<th>250°C-6h</th>
<th>250°C-12h</th>
<th>250°C-24h</th>
<th>250°C-36h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-free</td>
<td>$679 \pm 12$</td>
<td>$611 \pm 17$</td>
<td>$568 \pm 5$</td>
<td>$563 \pm 4$</td>
</tr>
<tr>
<td>Ni-bearing</td>
<td>$744 \pm 5$</td>
<td>$718 \pm 14$</td>
<td>$636 \pm 19$</td>
<td>$554 \pm 9$</td>
</tr>
</tbody>
</table>

### 4.3.2 Microstructure of steels after two-stage isothermal treatment

In order to obtain a microstructure with finer nano-bainite, Ni-free ($250 \degree C$-24 h) and Ni-bearing ($250 \degree C$-36 h) steel samples (after one-step isothermal bainitic transformation) were
subjected to two-stage isothermal treatment at 200 °C for 48 and 72 h, respectively. The OM microstructures after two-stage isothermal treatment were shown in Figure 4.3. The microstructure of both the steel samples consisted of acicular bainite (black) and RA (white) with similar hardness of 558 ± 3 HV1 and 547 ± 4 HV1, respectively. The prior austenite grain size of Ni-free and Ni-bearing steel was 14.09 ± 5.90 μm and 13.04 ± 5.72 μm, respectively.

![Figure 4.3](image.jpg)

Figure 4.3 (a) Ni-free and (b) Ni-bearing steel samples after two-stage isothermal treatment.

SEM micrographs of Ni-free and Ni-bearing samples after two-stage isothermal treatment are shown in Figure 4.4. The microstructure mainly consisted of large bainitic packets (BP) with a small amount of RA blocks in both the steel samples. The content of RA in the Ni-bearing steel was significantly greater as compared to the Ni-free sample. The SEM images showed two different sizes of bainitic ferrite in both Ni-free and Ni-bearing samples. B1 corresponds to bainitic ferrite produced in the first stage of isothermal treatment, while B2 corresponds to bainitic ferrite produced in the second stage of isothermal treatment. While both B1 and B2 had nanoscale dimensions, the size of B2 (bainitic ferrite) was smaller than B1. It may be noted that the orientation of bainitic ferrite in Ni-bearing steel was more uniform as compared to Ni-free steel. On the other hand, two different morphologies of RA, i.e., micrometer-size block-like RA
(existed between BPs) and the nanometer size thin film-like RA (present between two bainitic ferrites in BP), were observed.

![Figure 4.4 SEM micrographs of (a)Ni-free and (b)Ni-bearing steel samples after two-stage isothermal treatment.](image)

TEM micrographs of Ni-free and Ni-bearing samples after two-stage isothermal treatment are shown in Figure 4.5. The TEM results are in agreement with SEM results and confirmed the presence of bainitic ferrite of different sizes, B1 and B2, in Ni-free samples (Figure 4.5a). The measured average size of bainitic ferrite and RA (film and block) are shown in Table 4.3. The thickness of conventional isothermal bainitic ferrite (B1) was significantly greater (>500 nm) than the two-stage bainitic ferrite (B2), which was ~100–200 nm thick. Furthermore, the growth direction of B2 was almost perpendicular to B1, and both grew between RA, forming a network structure. Moreover, the irregular blocks of RA of different size were observed. The enlarged image of the corresponding rectangular area of Figure 4.5a, marked in red, is shown in Figure 4.5c. Numerous Fe–C clusters [111, 194] formed by the decomposition of unstable RA were observed in bainitic ferrite (Figure 4.5e). However, in some instances, stable thin film-like RA was present between the bainitic ferrite.
Figure 4.5 TEM micrographs of Ni-free (a), (c) and (e) and Ni-bearing steel samples (b), (d) & (f) after two stage isothermal treatment. (c) and (d) are the enlarged TEM images of red rectangular area marked in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
Table 4.3 The measured average size of bainitic ferrite (thickness), film and block-like RA.

<table>
<thead>
<tr>
<th>Samples</th>
<th>α (B1), nm</th>
<th>α (B2), nm</th>
<th>γ (film), nm</th>
<th>γ (block), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-free</td>
<td>681 ± 193</td>
<td>267 ± 70</td>
<td>186 ± 41</td>
<td>1242 ± 297</td>
</tr>
<tr>
<td>Ni-bearing</td>
<td>565 ± 119</td>
<td>114 ± 35</td>
<td>93 ± 22</td>
<td>1408 ± 357</td>
</tr>
</tbody>
</table>

On the other hand, in Ni-bearing samples, the orientation direction of bainitic ferrite laths, B1 and B2, was more uniform, and the size of block-like RA was larger (Figure 4.5b). However, it was noted that thin-film type RA formed between bainitic ferrite laths did not decompose to Fe–C clusters and remained stable (Figure 4.5f), resulting in the formation of A-B-A-B repetitive nanostructure with similar orientation and size (40–90 nm) between bainitic ferrite and thin film-like RA (Figure 4.5d). The comparison of dimensions of different phases (Table 4.3) confirmed that Ni-free steel had a larger average size of B1, B2, and film-like RA, while the Ni-bearing steel showed a larger average size of block type RA.

4.3.3 Tensile behavior

Mechanical properties of steels were evaluated by tensile tests and are presented in Table 4.4. The yield strength and tensile strength of Ni-free steel were ~1083 MPa and 2036 MPa, respectively, while for Ni-bearing steel, the values were 1059 MPa and 1889 MPa, respectively. The tensile strength of Ni-free steel was slightly greater than Ni-bearing steel (2036 MPa vs. 1889 MPa), but the elongation of Ni-bearing steel was greater than Ni-free steel (13.7%–10.3%). Consequently, the product of tensile strength and elongation (Rm × A) of Ni-bearing steel was ~24% greater compared to Ni-free steel (25.9 GPa·% to 20.9 GPa·%). Engineering stress-strain and true stress-logarithmic strain (σT-εT) curve plotted from the tensile data are shown in Figure 4.6. Both the steel samples showed a similar behavior in the elastic region (εT < 0.01). However, after a short period of yielding, Ni-free steel attained peak (tensile strength) relatively earlier and
fractured, while Ni-bearing steel was characterized by a steady and slow increase until peak tensile strength is reached with a wide range of strain ($0.04 < \varepsilon_T < 0.11$), followed by fracture.

Table 4.4 Mechanical properties of Ni-free and Ni-bearing steels. (A: Total elongation; Z:Reduction of area.)

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_{p0.2}$, MPa</th>
<th>$R_m$, MPa</th>
<th>A, %</th>
<th>Z, %</th>
<th>$K_V$, J</th>
<th>$R_m \times A$, GPa-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-free</td>
<td>1172</td>
<td>2183</td>
<td>9.5</td>
<td>27.0</td>
<td>13(13/14/12)</td>
<td>20.7</td>
</tr>
<tr>
<td>Ni-bearing</td>
<td>1107</td>
<td>2068</td>
<td>13.2</td>
<td>33.0</td>
<td>21(21/21/22)</td>
<td>27.3</td>
</tr>
</tbody>
</table>

Figure 4.6 (a) Engineering stress-strain and (b) True stress-logarithmic strain curves for Ni-free (250 °C, 24 h + 200 °C, 48 h) and Ni-bearing (250 °C, 36 h + 200 °C, 72 h) steel samples after two-step isothermal treatment.

Typical characteristic features like dimples (microvoids) and cleavage planes were observed in Ni-free steel, while large dimples with a higher density and almost no evidence of cleavage was observed in Ni-bearing steel. This implied greater plasticity of Ni-bearing steel (13.7%–10.3%), which was also evident from superior Charpy v-impact results (Table 4.4) of Ni-bearing steel and quasi-cleavage in Ni-free steel. The formation of dimples represents microvoid coalescence, implying ductile fracture in both the steels. The product, $R_m \times A$, of Ni-bearing steel was ~24% greater compared to Ni-free steel (25.9 GPa-% to 20.9 GPa-%).
4.3.4 Strain hardening behavior

The strain hardening rate (dσT/dεT; SHR) was calculated from true stress-logarithmic strain curve (Figure 4.6) and is presented as a function of logarithmic strain in Figure 4.7. The corresponding logarithmic strain values of Ni-free and Ni-bearing steels in each stage of the tensile test according to the strain hardening rate (SHR) are listed in Table 4.5. In the case of Ni-free steel, the SHR initially showed a steep decrease in the elastic region (ε < 0.009) followed by large fluctuation with a minimum plateau (~40458 MPa) at 0.009–0.028 strain. Both first fluctuation and plateau indicated the end of the elastic region and beginning of plastic stage in Ni-free steel. The plastic stage could be classified into two stages separated by the second fluctuation. In stage A (0.009 < ε < 0.028), the sample experienced yielding, and the original microstructure gradually deformed, accompanied by a sharp decline in SHR. The declining rate of SHR in stage B was lower than stage A, and the trend of the overall curve was slightly moderate than stage A. This indicated the presence of TRIP effect in the structure, and the transformation of a part of soft RA into hard martensite enhanced the strength of steel. When the logarithmic strain reached a value of 0.072, the value of SHR decreased to zero, and the strength of Ni-free steel reached the maximum point (tensile strength was 2036 MPa). Consequently, Ni-free steel sample entered the failure zone (0.072 < ε < 0.095), followed by rapid fracture.
Figure 4.7 Strain hardening rate (SHR) of Ni-free and Ni-bearing steel samples as the function of logarithmic strain.

Table 4.5 The corresponding logarithmic strain values of Ni-free and Ni-bearing steels for each stage of tensile test according to SHR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic stage</th>
<th>Plastic Stage</th>
<th>Failure stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stage A</td>
<td>Stage B</td>
</tr>
<tr>
<td>Ni-free</td>
<td>$\varepsilon &lt; 0.009$</td>
<td>$0.009 &lt; \varepsilon &lt; 0.028$</td>
<td>$0.028 &lt; \varepsilon &lt; 0.072$</td>
</tr>
<tr>
<td>Ni-bearing</td>
<td>$\varepsilon &lt; 0.013$</td>
<td>$0.013 &lt; \varepsilon &lt; 0.033$</td>
<td>$0.033 &lt; \varepsilon &lt; 0.123$</td>
</tr>
</tbody>
</table>

The SHR values of Ni-bearing steel showed a trend similar to Ni-free steel (declining rate) in the elastic stage ($\varepsilon < 0.013$) and zone A of the plastic stage ($0.013 < \varepsilon < 0.033$). However, after the yielding process (stage A), the SHR of the Ni-bearing steel was similar to that of the Ni-free steel at $\varepsilon = 0.04$ (SHR≈10456 MPa) and then became significantly lower than Ni-free steel, leading to the higher SHR value and plastic strain range of the Ni-bearing steel in stage B ($0.033 < \varepsilon < 0.123$) until the failure point. This showed that the intensity and duration of TRIP effect in Ni-bearing steel was significantly greater than in Ni-free steel. It may be noted that during the entire tensile test, the data fluctuation in Ni-free steel was greater than the Ni-bearing steel at each transition stage ($\varepsilon = 0.028, 0.072, 0.095$), which is attributed to the unique interlocked
acicular bainite structure (Figure 4.5a) of Ni-free steel. Whereas, the presence of Ni in the Ni-bearing steel led to the production of a large amount of nanoscale RA film, which hindered the growth of bainitic ferrite, resulting in a finer and uniform nanoscale bainite structure (114 ± 35 nm) with regular orientation.

The volume fraction of austenite (in both the steels) before and after the tensile test was calculated from XRD pattern (shown in Figure 4.8). The results showed that both the samples were composed of γ-fcc phase and α-bcc phase before and after the tensile tests. The γ-fcc phase corresponded to austenite, while the α-bcc phase corresponded to martensitic ferrite or bainitic ferrite. After the tensile test, both the samples showed a decrease in the intensity of (111)γ, (200)γ, and (220)γ peaks with a simultaneous increase in the intensity of (200)α and (211)α peaks. This indicated a phase transition from γ-fcc phase to α-bcc phase during the tensile test of both the samples, thereby ascertaining the TRIP effect. The austenite volume fraction in Ni-free steel decreased from 17.2% to 10.5% (i.e., by 6.7%), whereas in Ni-bearing steel, it was reduced from 24.6% to 13.2% (i.e., by 11.4%). The Ni-bearing steel observed a higher percentage of change in austenite volume fraction as compared to Ni-free steel, indicating a stronger TRIP effect. These results were consistent with the SHR results.

![Figure 4.8 XRD spectra of (a) Ni-free and (b) Ni-bearing steel before and after tensile tests.](image-url)
4.3.5 Strain hardening behavior

Load-controlled nanoindentation experiments were carried out to obtain load-displacement curve and study the deformation mechanism. It was difficult to use strain rate-controlled mode because the minimum available strain rate setting of the instrument was too high to observe dislocation nucleation or phase transformation. The representative load-displacement curves of film-like RA in Ni-free and Ni-bearing steels at a constant loading rate of 2 μNs$^{-1}$ are shown in Figure 4.9. The indentation hardness is usually related to the strength of the materials. Thus, the loading rate can be considered to be equivalent to strain rate.

A few abrupt discontinuities (pop-ins) were observed in the load-displacement curve of both Ni-free and Ni-bearing steels. The first pop-in stress fluctuation (9–11 nm displacement) is related to the thermally activated process of dislocation nucleation [195-197] in both the structures, corresponding to the first fluctuation in the SHR of the tensile test (Figure 4.7). The
second pop-in is related to the following two factors: (i) strain-induced transformation of austenite to martensite/bainite ($\gamma \rightarrow \alpha'$) phase and (ii) geometric softening caused by martensite variant formation to consume the increased strain energy [177, 198]. Between the first two pop-ins (11–25 nm displacement), both the samples showed identical behavior, consistent with the change in SHR in the yielding stage (stage A) of tensile test. However, after the third pop-in (~33 nm displacement), the increase in the rate of the load-displacement curve of Ni-bearing steel became significantly greater than Ni-free sample. This indicated that Ni-bearing steel had a stronger strain hardening ability and a higher SHR value. The initial regions in the structure of both Ni-free and Ni-bearing samples followed Hertzian elastic contact equation (4.1) [199],

$$P \propto h^{1.5}$$  \hspace{1cm} (4.1)

where $P$ is load and $h$ is depth of contact. It should be emphasized that the soft FCC phase (RA) can completely transform into hard BCC phase under steady and large strain rate (2 μNs$^{-1}$ loading rate) conditions of the nanoindentation experiment, compared to the tensile test. This may result in larger TRIP effect and lower penetration depth in Ni-bearing steel (~42 nm) in comparison to Ni-free steel (~45 nm).

4.3.6 Carbon distribution

The C distribution in Ni-free and Ni-bearing samples was studied by EPMA and is shown in Figure 4.10, the left hand side images are SEM micrographs, and the right hand side images show distribution of C for the corresponding area. The results suggested that both Ni-free and Ni-bearing samples consisted of BP and micro block-like RA and had similar C distribution in the corresponding regions. The BP region was composed of bainitic ferrite with low C-content and thin film-like RA (A/C) region had high C-content, along with a light green region (A'/C') referring to the uniform distribution of C. Whereas, in the block-like RA regions (B/D), the C-
content was significantly lower than the surrounding structure corresponding to the dark-blue regions (B’/D’).

Figure 4.10 SEM micrographs and carbon distribution maps of (a) Ni-free steel and (b) Ni-bearing steel.

EPMA is an important analytical technique to study the distribution of elements. However, its resolution is not adequate to separate BF around the film-RA. Therefore, we adopted statistical analysis to analyze the samples. In the EPMA experiment, the scanning was carried at a scanning step size of 0.08 μm and consisted of 300 × 225 test points (24 × 18 μm²). Although the measured data is not highly accurate, but they clearly show the trend in the distribution in carbon content in different phases.
The quantitative analysis and the difference between the two structures was further studied by point analysis using EPMA (electron probe microanalyzer) (Figure 4.11). The C-content in the blocky and film-like RA were measured by considering 20 effective fields in each case. The average value of the measured data was used to represent the carbon content. The corresponding statistical analysis is shown in Figure 4.12. In the case of Ni-free steel, the C-content in film-like RA was ~70% greater than the blocky RA, whereas it was ~92% in Ni-bearing steel. Moreover, the C-content in blocky and film-like RA in Ni-bearing steel was greater by ~5.5% and ~19.1%, respectively, in comparison to Ni-free steel. In both the steels, the calculated C-content of the block-like RA had a similar error margin (Ni-free and Ni-bearing steels, ±0.044 wt % and ±0.047 wt%, respectively). In contrast, for the film-like RA, the error in Ni-free steel (±0.172 wt %) was almost twice that of Ni-bearing steel (±0.092 wt %). A large size difference in film-like RA was observed between Ni-free (186 ± 41 nm) and Ni-bearing steels (93 ± 22 nm).
Figure 4.11 Point scanning images obtained via electron probe microanalyzer that were used to obtain carbon distribution in (a),(b) Ni-free steel and (c),(d) Ni-bearing steel.

Figure 4.12 Measured values of C-content in (a) Ni-free and (b) Ni-bearing steel samples by EMPA.

### 4.4 DISCUSSION

#### 4.4.1 The effect of Ni on carbon diffusion and stability of RA

Thermodynamic analysis was performed using MUCG database software ver. 83 [200] to analyze the effect of chemical composition (especially Ni content) on phase transformation kinetics of both the steels. The corresponding free energy (driving force) from austenite transition to bainite under quasi-equilibrium state is shown in Figure 4.13. During the process of
bainite transformation (at a constant temperature), the corresponding free energy determines the driving force of transformation [201]. The presence of Ni shifted the bainite transformation curve of Ni-bearing steel to the right, relative to Ni free steel, indicating that Ni reduced starting temperature (from 348 °C to 303 °C) and increased the incubation time and completion time of the bainite transformation. In Figure 4.13, at 250 °C the absolute value of the free energy of Ni-free steel was 1762 J/mol, whereas it decreased to 1585 J/mol in the Ni-bearing steel. This indicated a decrease in the free energy of the bainitic transformation by 177 J/mol at 1.47 wt % of Ni. In the case of Ni-free steel, it was found that more than 50% of bainitic transformation was completed after 6 h of conventional isothermal treatment (as seen from the OM images, Figure 4.2), whereas Ni-bearing steel stayed in the incubation period at that time and the bainitic transformation started after 12 h. Moreover, because of higher driving force of the phase transformation, the pre-nucleated bainitic ferrite in Ni-free steel had a higher growth rate, which prevented the growth of post-nucleated bainitic ferrite, resulting in higher B1 lath size (681 ± 193 nm) compared to Ni-bearing steel (565 ± 119 nm).

![Figure 4.13](image-url)

Figure 4.13 The free energy variation under quasi-equilibrium state.
Silicon (Si) is known to suppress cementite formation and affect C diffusion. In the present study, Si inhibited the precipitation of C from bainitic ferrite and shifted the bcc bainitic ferrite lath (supersaturated in C) transition to fcc RA, while it also increased the C-content and decreased the martensite start temperature (Ms) of RA (Figure 4.12). However, during this process, a large number of carbon-rich defects were formed, thereby reducing the stability of RA [111, 194]. In Ni-free steel, during the two-stage nano-bainite transformation (200 °C, 48 h), nano-bainitic ferrite (B2) grew in the interior of RA and formed an interlocked acicular structure (Figure 4.5a) because of relatively high driving force (1762 J/mol) and low stability of RA [202]. Lan et al. [203] reported that the secondary bainitic ferrite (B2) is more likely to nucleate on pre-existing ferritic lath rather than at the grain boundary because of the mechanism of sympathetic nucleation. The authors also observed an interlocked distribution of bainitic ferrite packets on coarse austenite grains. Timokhina et al. [204] pointed out that at lower bainite transformation temperature (e.g., 200 °C), the C-content in RA is unevenly distributed. During diffusion of C from bainitic ferrite to austenite, continuous segregation of C occurred near high-density dislocations, resulting in the formation of Fe–C clusters in bainitic ferrite. The stress distribution in interlocked acicular bainitic ferrite was uneven and generated a large number of dislocations and defects to form irregular Fe–C clusters (Figure 4.5e). Fe–C clusters that existed between bainitic ferrite laths consumed a large amount of C from the nearby region, thus, reducing the C diffusion rate and making the formation of a stable film-like RA between the bainitic ferrite laths difficult (Figure 4.5c). In contrast, the presence of Ni in Ni-bearing steel formed thin film-like RA with relatively high stability due to low driving force (1585 J/mol). It largely reduced the growth rate of nano bainitic ferrite and contributed to the formation of a “side-by-side” uniform bainitic ferrite structure with higher density and smaller thickness (114 ± 35 nm, 72 h) compared
to the Ni-free steel (267 ± 70 nm, 48 h) even under a prolonged period of isothermal treatment. Moreover, the low driving force in Ni-bearing steel led to longer diffusion time for C to diffuse into RA. Furthermore, the high-density interface of film-like RA created more vacancies for C segregation and reduced the possibility of Fe–C cluster formation. Thus, in the case of Ni-bearing steel, C did not form Fe–C cluster, but was distributed uniformly in the form of film-like RA between bainitic ferrite that produced a uniformly oriented microstructure (Figures 4.5d and f).

The stability of RA is affected by a variety of factors, including heat treatment [205, 206] and C-concentration. However, C-content in RA is the most critical factor governing the stability of austenite [207]. Phase interface and grain boundaries act as sinks for defects. The relative surface area of film-like RA was significantly higher than block-like RA, which facilitated C segregation and attained high stability. In the case of Ni-free and Ni-bearing steels, the C content of film-like RA was significantly higher than block-like RA (Figure 4.12) because of relatively higher surface area of the former (Table 4.3). On comparing the difference in the prior austenite grain size (14.09 μm–13.04 μm) of two steel samples, it was noted that the smaller prior austenite grain size in Ni-bearing steel provided a larger number of grain boundary segregation sites for C atoms. Moreover, Fe–C cluster may consume a lot of C from the nearby zone, which might play a critical role in affecting the C-content of film-like RA in Ni-free structure. Thus, the C-content in film-like RA in Ni-bearing steel was ~19% greater than in Ni-free steel (1.289 wt % to 1.082 wt %). This is attributed to Fe–C clusters and size of film. The reduction in the C-content in film-like RA may directly affect the austenite stability, TRIP effect, and the mechanical properties of the structure discussed in the following section.
4.4.2 Effect of RA stability on TRIP effect and strain hardening behavior of the steel samples

The nanoindenter-induced stress can reach up to the theoretical strength of the materials [177]. When the radius of the indenter tip (20 nm) is small enough to produce a highly stressed region with a size smaller than the average spacing between the dislocations (~500–800 nm), then the probability of the presence of a pre-existing dislocation in that small region is very low [194]. Therefore, the small volume beneath this region can be initially regarded as defect-free [194]. Many studies [188, 208, 209] have shown that when RA exists between the bainite substructure as a film, it significantly contributes to TRIP effect, while the block-like RA is shown to deform easily under small stress and has little contribution to the strength of the material. Thus, it can be ascertained that only film-like RA contributes to the TRIP effect, as discussed below.

During the loading segment (Figure 4.9), the rising trend in Ni-free and Ni-bearing structures indicated their theoretical strength before deformation at low displacement (less than ~20 nm). The theoretical Hertzian elastic behavior is shown by broken line in Figure 4.9 and was consistent with the experimental curve at low displacement. It implied that the region before the first discontinuity was initially elastic and later plastic in nature [194]. The Hertzian solution indicated superior mechanical performance of Ni-free steel compared to Ni-bearing steel without plastic deformation. This can be attributed to the interlocked microstructure of Ni-free steel, which prevents dislocation slip and improves yield strength [210].

After entering the incipient plasticity stage (~11 nm displacement), a first pop-in (Arrow 1 in Figure 4.9) was observed in both the samples due to the thermally activated process of dislocation nucleation. Dislocation nucleation in a defect-free crystal is often assumed to occur
when the shear stress beneath the indenter reaches some critical value. This shear stress can be prompted by high temperature and low strain rate to generate the first displacement pop-in, which is attributed to a stress-based and thermally-activated yielding mechanism [195-197]. The second pop-in (Arrow 2) occurred at 20–25 nm displacement in both structures. According to the previous TEM studies [177], the second dislocation in both samples was related to the formation of strain-induced martensite during the indentation. This arises from the geometrical softening that occurs in the lattice because of the formation of a favorable martensite variant based on the mechanical interaction energy between the externally applied stress and the lattice deformation. After the third pop-in (Arrow 3) at ~34 nm displacement in the Ni-bearing steel, the rising rate of the load-displacement curve was higher than Ni-free steel. In contrast, no third pop-in phenomenon was observed in the Ni-free structure. This difference in the behavior of two steel samples can be ascribed to (1) high-density interface of the film-like RA in the Ni-bearing structure, which provided more vacancies for C segregation and reduced the possibility of Fe–C cluster formation, resulting in higher C-content and stability of film-like RA in Ni-bearing steel than the Ni-free sample (Figure 4.12). Chiang reported that C content played a key role in the stability of RA and the TRIP strengthening effect [116]. This implied that the highly stable film-like RA might transform into strain-induced martensite under high stress and provide more TRIP strengthening effect during the deformation of the Ni-bearing structure, and (2) the Fe–C clusters in the Ni-free structure reduced the C content, diffusion rate, and stability of the RA [204]. The less stable film-like RA contributed less to the TRIP strengthening effect when transformed to martensite (strain-induced). Thus, it can be concluded that Ni increases the stability of film-like RA, resulting in a stronger TRIP effect, observed as more pop-ins and lower penetration depth phenomenon in the Ni-bearing steel.
The TRIP effect significantly affects the strain hardening behavior of the material during deformation. The strain hardening behavior is presented as SHR in Figure 4.7. The two samples exhibited similar SHR values in the initial elastic deformation stage, which is attributed to the dislocation nucleation through stacking fault [13, 177]. The plastic deformation region is characterized by a continuous and slow decrease in the SHR, corresponding to the strain-induced transformation of austenite (FCC) to α′-martensite (BCC), i.e., the TRIP effect. Bracke et al. [33] have shown that the formation mechanism of HCP ε-martensite arises due to the formation of stacking faults by the movement of partial dislocations, and thus, depends highly on the degree of deformation. The plastic deformation region can be further divided into two sub-stages, A and B, based on their different slopes (Table 4.5). Both the steel samples maintained the same decreasing rate in stage A due to the nucleation of the hcp ε-martensite from the stacking faults, formed by the partial dislocation \( \frac{a}{6} \langle 112 \rangle \) at low strain [13, 61, 177]. Meanwhile, the Ni-free sample provided higher SHR in stage A since the uniform interlocked bainitic ferrite hindered the dislocation slip and resisted the deformation as reflected in the improved yield strength [210]. However, the interlocked structure of the Ni-free steel lost its strengthening effect under high strain (stage B). The quasi-cleavage plane proved the poor deformation of interlocked structure of Ni-free steel to provide strength at high strain. In contrast, ultra-high RA stability of Ni-bearing steel continued to transform to α′-martensite and provided a TRIP effect at high strain. The Ni-bearing steel showed a greater change in austenite volume compared to Ni-free steel, indicating a stronger TRIP effect (Figure 4.8). Thus, SHR of the Ni-bearing structure decreased slowly and surpassed the performance of Ni-free steel in stage B. The higher density of dimples might also provide greater deformation in the Ni-bearing sample. Finally, occurrence of necking
(failure stage) phenomenon beyond the endurance limit of steel resulted in a rapid drop of SHR in both the steel samples.

It may be pertinent to mention that the change of retained austenite before and after tensile tested can not sufficiently characterize its stability. Thus, we carried out load-controlled nanoindentation experiments described above to suggest stronger TRIP effect and work hardening in Ni-bearing steel under applied load. Furthermore, the carbon diffusion detected by EMPA also demonstrated that the retained austenite stability in Ni-bearing was higher than Ni-free steel. The above three experiments together suggested that retained austenite in Ni bearing had higher stability.

The presence of Ni was found to (i) reduce the free energy of bainitic transformation during low-temperature isothermal treatment, (ii) extend the bainite nucleation period, and (iii) refine the bainite structure. Unexpectedly, we also noted that the presence of Ni altered the orientation of bainite nanostructure from “interlocked” to “uniform” and corresponding hardening behavior indicated significant differences. These results are of significance in the design of nanostructured bainite.

In summary, the “interlocked” structure of Ni-free steel can effectively prevent dislocation slip and improve the strength of the material, but it also reduces the stability of film-like RA, resulting in weak TRIP effect and elongation. While, the “side-by-side” uniform structure of Ni-bearing steel contributed to high volume and stability of film-like RA between the nano bainitic ferrite, leading to a stronger TRIP effect and elongation.

4.5 Conclusions

The influence of Ni on microstructure, strain hardening behavior, and TRIP effect of medium C nano bainitic-austenitic dual-phase steel produced by two-stage isothermal
transformation at low-temperature was studied. The microstructure of Ni-free and Ni-bearing steels consisted of nano-bainitic ferrite, film-like, and block-like RA. The presence of Ni was found to (i) reduce the free energy of the bainitic transformation during the low-temperature isothermal treatment, (ii) extend the bainite nucleation period, and (iii) refine the bainite structure. The average size of nano-bainitic ferrite (B2) and film-like RA was smaller in Ni-bearing steel (114 ± 35 nm and 93 ± 22 nm, respectively) compared to the Ni free steel (267 ± 70 nm and 186 ± 41 nm, respectively). The relatively high free energy of austenite to bainite transformation in Ni-free steel resulted in “interlocked” distribution of coarse bainitic ferrite and further promoted the formation of the Fe–C clusters to consume C-content and stability of film-like RA. The presence of Ni was shown to effectively reduce free energy to obtain uniformly-oriented finer nano bainitic ferrite and highly stable film-like RA, exhibiting a “side-by-side” structure in Ni-bearing steel. The interlocked nanostructure of Ni-free steel can effectively prevent dislocation slip and provide higher SHR at low strain, but the “side-by-side” uniform nanostructure of Ni-bearing steel resulted in higher SHR and stronger TRIP effect at high strain. This resulted in Ni-bearing steel with superior plasticity (13.7%–10.3%) and product of tensile strength and elongation (25.9 GPa·% to 20.9 GPa·%) compared to the Ni-free steel.
Chapter 5: Effects of cooling after rolling and heat treatment on microstructures and mechanical properties of Mo–Ti microalloyed medium carbon steel

Abstract

The effects of four different processes, direct quenching + tempering (DQ + T), direct quenching + reheating and quenching + tempering (DQ + RQ + T), forced air cooling + reheating and quenching + tempering (AC + RQ + T), and furnace cooling + reheating and quenching + tempering (FC + RQ + T), on microstructures and precipitates of Mo–Ti microalloyed medium carbon steel were investigated by OM, SEM, TEM, EBSD and mechanical tests. The width of martensite laths (0.22 ± 0.01 μm) produced in DQ + RQ + T was similar to that generated in DQ + T and was narrower than those formed during AC + RQ + T and FC + RQ + T. The effective grain size of the DQ + RQ + T sample was found to be the smallest (0.98 ± 0.38 μm), thus it yielded the finest (Ti, Mo) C precipitates, manifested high strength and excellent plastic toughness, and generated uniform transverse and longitudinal properties. The strength of the DQ + RQ + T sample (longitudinal Rm = 1773 MPa) was slightly lower than that of the DQ + T samples and its elongation (A = 11.0%) and impact energy at −40 °C (AkV = 50 J/cm²) were greater than those of the other three samples. Before the RQ process, the DQ cooling process was employed in order to generate large angle grain boundaries to provide more nucleation sites for austenitization. Moreover, the DQ process inhibited the precipitation of Ti during cooling and then formed fine (Ti, Mo) C precipitates during reheating of RQ to prevent austenite grain growth. Therefore, the DQ + RQ + T process generated fully refined austenite grains, made the martensite structure and (Ti, Mo) C precipitates more uniform, and enhanced the effects of fine grain strengthening and precipitation strengthening. In addition, the plasticity and the toughness
of the fine and uniform equiaxed grains were also significantly improved, and the formation of acicular cementites was impeded.

5.1 BACKGROUND

Martensite microstructures, due to their high strengths and hardness, are widely used in wear-resistant steels, armor steels, abrasive steels, and other special purpose steels. However, complex service environments demand advanced martensitic steels with comprehensive properties. It is already proved that the proper control of carbon addition is an effective way to strengthen martensite microstructures. The strength of martensite steel with 0.3% carbon content can reach more than 1200 MPa with considerable adverse effects on toughness, plasticity, and weldability. Therefore, on the premise of controlling carbon content and ensuring weldability, iron, and steel industries are continuously searching for a new route to improve the strength, the toughness, and the plasticity of martensitic steels through process control.

In recent years, researchers have advocated that the incorporation of second-phase particles can effectively improve the strength and the toughness of low-carbon martensitic steels through interactions between dislocations and grain boundaries [211]. Moreover, the existence of second-phase particles at high temperatures prevents grain growth in coarse grained heat-affected zone (CGHAZ) and improves the weldability of steels [212]. Other recent studies on second-phase particles, such as Ti–V [213], Ti-Mo [214-216], Ti–V–Mo [217], Ti–V–Nb [218], and Ti–Nb–Mo [127], mainly concentrate on the type, quantity, size, the shape of precipitates. However, very few studies have investigated the roles of precipitates in strengthening and toughening mechanisms of medium-carbon martensitic steels. Deng [219] and Kim [130], studied the effects of rolling, cooling, and heat treatment on precipitates and mechanical properties of medium-carbon Mo–Ti martensitic steel. However, the change in precipitates
during austenitizing is still questionable. At the same time, there were some disadvantages such as high cost of alloys and complex production process. Thus, at present, the toughness, plasticity, and weldability of medium-carbon martensitic steels are not sufficient to meet the requirements of iron and steel industries. Hiroshi and Funakawa [121, 220, 221] have studied the microstructure and properties of 0.12–0.21C-1.5Si-2.3Mn martensite steel and 0.04C-0.09Ti-1.5 Mn-0.2 Mo ferrite steel. In reference 12, by controlling the martensite/ferrite ratio, toughness was improved, only 0.02Ti was added in the steel to play the role of fixing N. In references 13 and 14, the strength and toughness were improved through the nano-precipitation of Ti. In this paper, the above research was integrated and referenced. 0.09Ti was added to medium carbon steel, and the nanometer precipitation of Ti was expected to improve the strength and toughness of martensite steel.

Cooling after rolling and heat treatment are important methods to control precipitation. For example, the cooling rate after rolling and coiling temperature (auto tempering) had a great impact on precipitation behavior and the mechanical properties of Nb, V, Ti alloyed steel [134-136], and the quenching-partitioning-tempering (Q-P-T) process for Nb, V, Ti microalloyed ultra-high strength steel was also studied [137]. However, the research on cooling rate and RQ + T complex process is relatively rare. Therefore, the effects of controlled cooling and heat treatment on martensite morphology and precipitates of Mo–Ti microalloyed medium carbon steel were investigated and the relationship between microstructural evolution and mechanical properties are discussed. A facile synthesis process was proposed to prepare martensitic steels with high strength and toughness at low costs, and its strengthening and toughening mechanisms are discussed.
5.2 EXPERIMENTAL DETAIL

Medium carbon Mo–Ti composite microalloyed test steel was smelted in a 50 kg vacuum induction furnace. The chemical composition of the test steel is presented in Table 5.1. The carbon equivalent (CEV) index and the weld crack sensitivity index (Pcm) of the test steel were 0.597 wt% and 0.403 wt%, respectively. An appropriate amount of B was added to the test steel in order to improve its hardenability as well as to obtain a uniform martensite structure. Moreover, the contents of N and S were controlled to avoid Ti precipitation during solidification [222].

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Mo</td>
<td>0.31</td>
<td>0.22</td>
<td>1.43</td>
<td>-</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

The ingot was forged into 170 mm × 170 mm × 220 mm rectangular specimens and heated to 1230 °C for 3 h in order to ensure the complete solution of alloy elements as well as to avoid the excessive austenite grain growth. The controlled rolling was then carried out on an 800 mm two-high rolling mill, and austenite grains became fully deformed by rolling at low temperatures and high reduction rates. The specimens were cooled to room temperature by different cooling processes after rolling and then heat treated to prepare 250 mm × 250 mm × 14 mm steel plates (Figure 5.1; Process A: direct quenching + tempering (DQ + T), Process B: direct quenching + reheating and quenching + tempering (DQ + RQ + T), Process C: forced air cooling + reheating and quenching + tempering (AC + RQ + T), Process D: furnace cooling + reheating and quenching + tempering (FC + RQ + T). The starting temperature of the cooling processes was 950 °C. The cooling rates of DQ, AC, and FC were 40 °C/s, 1 °C/s, and 0.1 °C/s, respectively. Process A was tempered after cooling, whereas processes B, C, and D were cooled
first, then reheated to an austenitization temperature of 880 °C for 15 min, and finally, quenched and tempered. Tempering parameters were kept at 180 °C for 2 h during all processes.

The mechanical properties and the fracture surfaces of all four heat-treated specimens were tested and analyzed. Tensile tests of round bar specimens (diameter of 8 mm) were carried out on a hydraulic tensile testing machine in both transverse and longitudinal directions. Impact toughness measurement tests were performed on 10 mm × 10 mm × 55 mm samples in both transverse and longitudinal directions. All impact work specimens were tested on a ZBC2452–3 pendulum impact tester (U.S.A.) at −40 °C. Moreover, tensile and impact fractures were observed by scanning electron microscopy (SEM). The microstructures of the specimens before and after heat treatment were also characterized. All metallographic specimens were polished and etched with 4% nitric acid. The microstructures of the specimens were observed by a LEI2CAQ5501IW optical microscope (OM), a cold field emission SEM, and an electron backscatter diffractometer (EBSD). All EBSD samples were electropolished at room temperature at 50 V for 15 s, and the electrolyte consisted of 80% methanol, 15% glycerol, and 5% perchloric acid. The EBSD system was operated at 20 kV with a resolution of 0.2 μm (close to the size of
martensite laths). Grain boundaries with misorientations greater than 15° were considered as effective grain boundaries. Fine microstructures and precipitates were observed by a JEM–2100F transmission electron microscope (TEM) and an INCA energy dispersive spectrometer (EDS). Thin film specimens were prepared by the electrolytic double-jet thinning technique. The electrolyte was prepared with 6% perchloric acid at 25 V and at −20 °C.

5.3 EXPERIMENTAL RESULTS

5.3.1 Microstructures

The OM micrographs of the specimens are displayed in Figure 5.2, and it is observable that tempered martensite was the main element of all microstructures. It is evident at lower magnifications that the microstructures of the DQ + T and the (DQ/AC/FC) + RQ + T specimens were flattened and equiaxed, respectively. Figure 5.2a presents the OM micrograph of the DQ + T specimen, which was rolled at a high reduction rate in the non-recrystallized austenite region, thus austenite grains were flattened and parallel to the rolling direction. After rolling, austenites were quenched directly and the martensitic transformation occurred. Martensite laths in flattened strips were inclined to the rolling direction at a certain angle. The flattened grain width measured by the truncation method was found to be ~9.2 ± 0.5 μm. Figure 5.2b illustrates the OM micrographs of the (DQ/AC/FC) + RQ + T specimens, which were cooled to room temperature by different methods (DQ/AC/FC) after rolling. Flattened grains were transformed into equiaxed austenite grains after reheating and subsequently, to tempered martensites by quenching and tempering.
Figure 5.2 Optical microstructures of (a) DQ + T process and (b) (DQ/AC/FC) + RQ + T processes. Low chart of the heat treatment process.

The microstructures of (DQ/AC/FC) + RQ + T samples were further observed at higher magnifications by scanning electron microscopy (SEM). Grains obtained by DQ + RQ + T, AC + RQ + T, and FC + RQ + T processes exhibited equiaxed characteristics (Figure 5.3). The average diameters of equiaxed grains in the DQ + RQ + T, the AC + RQ + T, and the FC + RQ + T samples were $\sim 3.3 \pm 0.21 \, \mu m$, $\sim 5.7 \pm 0.19 \, \mu m$, and $9.6 \pm 0.24 \, \mu m$, respectively. During tempering at low temperatures, martensite laths merged partially and lath boundaries became blurred gradually, consequently, supersaturated carbon precipitated from martensites and formed flaky and granular carbides at grain boundaries and lath boundaries.
Figure 5.3 SEM micrographs of (a) DQ + RQ + T, (b) AC + RQ + T and (c) FC + RQ + T processes.

The TEM micrograph of the DQ + T specimen is presented in Figure 5.4. Figure 5.4a reveals that most tempered martensites were lath-shaped of width ~0.18 ± 0.02 μm and ran through flattened grains with clear directionality. A large number of fine cementite particles were present at the interface and also in the matrix of martensite laths. The local enlargement is exhibited in Figure 5.4b. High-density dislocations and a few large precipitates were noticed on martensite laths. It is confirmed from EDS results that spherical particles with diameters larger than 40 nm were TiC and square particles with diameters about 50 nm were TiN.
The TEM micrograph of the DQ + RQ + T specimen is presented in Figure 5.5. Martensite packets and blocks existed in equiaxed grains, and martensite laths of width ~0.22 ± 0.01 μm intersected each other (Figure 5.5a). The local enlargement is presented in Figures 5.5b and 5.5c, and the high-resolution image is displayed in Figure 5.5d. A large number of precipitates with diameters less than 15 nm were distributed on the matrix. The energy spectrum reveals that the obtained smaller precipitates were composed of Ti, Mo, and C and the atomic ratio of Ti/Mo was about 0.85. The dislocation density of the DQ + RQ + T specimen was lower than that of the DQ + T specimen.
Figure 5.5 TEM micrograph of DQ + RQ + T process, (a) (b) were at different resolutions, (c) HRTEM image showing precipitates and (d) IFFT lattice image of one in (c).

The TEM micrographs of the AC + RQ + T and the FC + RQ + T specimens are exhibited in Figure 5.6, Figure 5.7, respectively. The sub-structures of equiaxed grains in Figure 5.6, Figure 5.7a are similar to those in Figure 5.5a; however, the sizes of grains and sub-structure (martensite packets and blocks) increased significantly, especially martensite laths became wider and longer. Figure 5.7a expresses that more large TiC precipitates were present on the matrix of the FC + RQ + T specimen. A large number of (Ti, Mo)C precipitates with diameters about 20
nm were observed on the matrix, and the atomic ratio of Ti/Mo was about 1.27 (Figure 5.6b). However, only a small amount of fine acicular cementites (no fine precipitates of (Ti, Mo)C) was observed on the martensite matrix (Figure 5.7b). The dislocation densities of DQ + RQ + T, AC + RQ + T, FC + RQ + T were almost the same and were lower than that of DQ + T.

Figure 5.6 TEM micrographs of AC + RQ + T process at different resolutions.

Figure 5.7 TEM micrographs of FC + RQ + T process at different resolutions.
Figure 5.8 and Figure 5.9, respectively, present the inverse pole figures (IPFs) and the effective grain size (EGS) statistics of the samples. Effective grains with grain orientation greater than $15^\circ$ are marked with different colors. Effective grains mainly consisted of grains and sub-grains (martensite blocks and packets), and these results are consistent with OM, SEM, and TEM observations. A few abnormal large grains of diameters about 20 μm were observed in the DQ + T specimen, and sub-grains were dominated by long-striped martensite packets. In the DQ/AC/FC + RQ + T specimens, the grains were more uniform and sub-grains were mainly composed of short martensite blocks and packets. The statistical results of effective grain size are depicted in Table 5.2.

Figure 5.8 Inverse pole figures coloring (IPF) grain orientation distribution of (a) DQ + T process, (b) DQ + RQ + T process, (c) AC + RQ + T process and (d) FC + RQ + T process.
Table 5.2 Statistical results of effective grain size.

<table>
<thead>
<tr>
<th>Processes</th>
<th>Min</th>
<th>Max</th>
<th>Average</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>DQ+T</td>
<td>0.41</td>
<td>21.28</td>
<td>1.13</td>
<td>±0.76</td>
</tr>
<tr>
<td>DQ+RQ+T</td>
<td>0.42</td>
<td>6.54</td>
<td>0.98</td>
<td>±0.38</td>
</tr>
<tr>
<td>AC+RQ+T</td>
<td>0.42</td>
<td>7.18</td>
<td>1.20</td>
<td>±0.46</td>
</tr>
<tr>
<td>FC+RQ+T</td>
<td>0.42</td>
<td>7.39</td>
<td>1.63</td>
<td>±0.58</td>
</tr>
</tbody>
</table>

5.3.2 Mechanical properties

Table 5.3 presents the mechanical properties of the DQ + T, the DQ + RQ + T, the AC + RQ + T, and the FC + RQ + T samples. It is noticeable that the mechanical properties of the DQ + T specimen were directional. The transverse (perpendicular to the rolling direction) properties
(R_p0.2, R_m, A, A_kV) of the DQ + T sample were lower than its longitudinal (parallel to the rolling direction) properties, whereas other three specimens manifested uniform transverse and longitudinal properties. The strength (R_p0.2 = 1591 MPa, R_m = 1780 MPa) of the DQ + T specimen was the highest among all four samples, whereas its plasticity (A = 7.2%) and low-temperature impact toughness (A_kV = 26 J) were the lowest. The strength of the DQ + RQ + T specimen was slightly lower than that of the DQ + T specimen; however, it yielded the highest plasticity (A = 11%) and low-temperature impact toughness (A_kV = 50 J). The mechanical properties (R_p0.2, R_m, A, A_kV) of DQ + RQ + T, AC + RQ + T, and FC + RQ + T decreased gradually due to the different cooling processes before reheating. Therefore, the DQ + RQ + T sample yielded the best comprehensive properties (high strength, good plasticity, and toughness) and manifested uniform lateral and longitudinal properties.

<table>
<thead>
<tr>
<th>Processes</th>
<th>Specimen Orientation</th>
<th>Tensile test</th>
<th>Impact test A_kV(−40 °C), J/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R_p0.2, R_m, A, A_kV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DQ+T</td>
<td>Transverse</td>
<td>1483</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>Longitudinal</td>
<td>1591</td>
<td>7.2</td>
</tr>
<tr>
<td>DQ+RQ+T</td>
<td>Transverse</td>
<td>1583</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>Longitudinal</td>
<td>1586</td>
<td>11.0</td>
</tr>
<tr>
<td>AC+RQ+T</td>
<td>Transverse</td>
<td>1442</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>Longitudinal</td>
<td>1450</td>
<td>9.3</td>
</tr>
<tr>
<td>FC+RQ+T</td>
<td>Transverse</td>
<td>1387</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>Longitudinal</td>
<td>1396</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Table 5.3 Mechanical properties of the test steel under different heat treatment processes
5.3.3 Fracture surfaces

The SEM morphology of the longitudinal tensile fracture surface is exhibited in Figure 5.10. DQ + T process, as shown in Figure 5.10a, the cracks generated during the cleavage brittle fracture propagated along the flattened grain boundaries and caused delamination. The longitudinal tensile fracture morphologies of the DQ + RQ + T, the AC + RQ + T, and the FC + RQ + T specimens are displayed in Figures 5.10b, 5.10c, and 5.10d, respectively, and it is evident that all samples presented quasi-cleavage characteristics. The quasi-cleavage section had tearing edges, and some smaller subunits (similar to dimples) also existed in this section. However, in comparison to Figure 5.10a, there were no steps in the cleavage unit (fluvial) in Figures 5.10c and 5.10d, due to the decrease in dislocation density and the increase in lath width.

![Figure 5.10 Longitudinal tensile fracture of (a) DQ + T, (b) DQ + RQ + T, (c) AC + RQ + T and (d) FC + RQ + T processes.](image_url)
The impact fracture morphologies of different samples are presented in Figure 5.11. The fracture morphology of the DQ + T specimen had fluvial cleavages with uneven cross-sections. The DQ + RQ + T process generated shallow dimples. The AC + RQ + T process formed shallower dimples with larger diameters. The FC + RQ + T process formed cleavages with a small number of dimples.

![Figure 5.11 Longitudinal impact fracture of (a) DQ + T, (b) DQ + RQ + T, (c) AC + RQ + T and (d) FC + RQ + T processes.](image)

5.4 DISCUSSION

5.4.1 Precipitation behavior

It is evident from Figures 5.4, 5.5, 5.6, 5.7 that precipitates of the four samples mainly consisted of square TiN particles with edges about 50 nm, spherical TiC particles with diameters greater than 40 nm, spherical (Ti, Mo)C particles with diameters less than 20 nm, and needle-like
fine cementites. The precipitates of Mo–Ti microalloyed steels generally manifest different characteristics during solidification, rolling, post-rolling cooling, and heat treatment. Hu et al. [223] calculated the solid solution content of N in Mo–Ti–C–N microalloyed steel and found that most N precipitated at temperatures >1300 °C and the size of precipitated TiN particles was generally larger than 50 nm. However, the solid solubility of N was less than 0.00002% at temperatures below 1300 °C, thus no N was observed in the precipitated phase. In the actual rolling process, a thermodynamic equilibrium state of Ti precipitates exists in the γ-Fe region under deformation [224]. Due to the high temperature of the deformed γ-Fe region (in comparison to the undeformed α-Fe region), less precipitates (of larger sizes) are generally formed. Chen [225] investigated the effects of Mo on the precipitation behavior of Ti. The activity value of Mo was almost zero above 950 °C. Mo precipitated with Ti only at lower temperatures and caused a reduction in precipitate size. Therefore, the effects of different heat treatment processes on precipitation behavior can be studied by the morphology, quantity, size, elemental composition, and kinetics of precipitates.

In the current experiment, the main difference among the four processes was the mode of cooling and heat treatment after rolling. During the cooling process, the precipitation kinetics of microalloyed carbides was described by the Avrami kinetic equation based on the classical nucleation and growth theory. The relationship between precipitate amount and time (in terms of driving force and diffusion) generated a C-shaped curve (PTT curve) [226]. During heating, when microalloying elements were in the state of oversaturation, low temperatures were not conducive to diffusion and a large precipitation driving force was generated. At high temperatures, although the diffusion speed of elements was accelerated, the precipitation driving force was low; therefore, the PTT curve in the heating process followed a “C” shape [227]. After
precipitation, the process of particle coarsening occurred, namely Ostwald ripening. Ostwald ripening is a competitive growth process in which a system lowers its total energy by reducing its precipitate-matrix interfacial area. During coarsening, large particles grow at the expense of small particles, which shrink and finally dissolve [228, 229]. The precipitation behavior under different heat treatment processes is displayed in Figure 5.12.

![Figure 5.12](image)

Figure 5.12 The precipitation behavior under different process conditions.

In the DQ + T process, the specimen was cooled to room temperature at a rate of 40 °C/s after rolling. Due to the fast cooling speed of DQ, supersaturated Ti, Mo, and other alloying elements could not precipitate in time. In the subsequent low-temperature tempering process, the free energy of microalloyed carbides was found to be lower than that of cementites, it implies that microalloyed carbides were thermodynamically more stable than cementites. Therefore, only fine cementites precipitated from the supersaturated matrix (Figure 5.4a), whereas square TiN particles with edges larger than 50 nm and spherical TiC particles with diameters greater than 40
nm precipitated during the solidification and rolling processes, respectively (Figure 5.4b). These large precipitates also existed in other three specimens.

In the DQ + RQ + T process, the deformation energy and the high dislocation density obtained during rolling were retained in the matrix after direct quenching (DQ) and all alloy elements were in the supersaturated state. Therefore, in the subsequent reheating process (RQ), a large number of fine cementites ((Ti, Mo)C) continued to precipitate. With the increase in reheating temperature, cementites dissolved completely and only fine (Ti, Mo)C precipitates were obtained (Figure 5.5b).

In the AC + RQ + T process, some microalloyed carbides precipitated during the cooling process due to the slow cooling rate of AC and subsequently, supersaturated microalloyed elements completely precipitated during reheating. The Ostwald ripening of precipitated (Ti, Mo)C occurred at high temperatures, and Ti atoms accumulated continuously to larger (Ti, Mo)C. Therefore, in comparison to the DQ + RQ + T sample, the size of (Ti, Mo)C in AC + RQ + T was larger and the atomic ratio of Ti/Mo was higher (Figure 5.6b).

In the FC + RQ + T process, the specimen was cooled (at the slowest cooling speed) after rolling. After the slow cooling of FC, alloy elements reached the equilibrium precipitation state. In the subsequent reheating process, fine (Ti, Mo)C precipitated gradually dissolved; thus only large particles were observed (Figure 5.7a). Due to the dissolution of (Ti, Mo)C, the supersaturation of C and alloy elements after RQ was comparable to that of the DQ state, and led to the precipitation of cementites during low-temperature tempering. Cementites nucleated in martensite laths and grew into fine needles along the (110) habit plane of martensites [230] (Figure 5.7b).
5.4.2 Effects of heat treatment on microstructures

The results of OM, SEM, TEM, and EBSD revealed that the morphology, grain size, and sub-structure of microstructures were noticeably different for different heat treatment processes. Both DQ and RQ yielded lath martensite microstructures. DQ maintained the flattened grain shape and the high dislocation density during rolling; hence, deformation energy increased the driving force of martensite transformation and formed fine martensite laths. Most plate-shaped martensites penetrated through grains, thus subgrains were dominated by lath bundles. However, RQ formed equiaxed austenites and hindered the growth of dislocations (deformation energy disappeared completely), thus resulting in a relatively low driving force of martensite transformation and wide martensite laths. Martensite nucleated on equiaxed grain boundaries mostly during quenching process, that was beneficial for martensites growing multi-directionally and intercrossing to generate subgrains. Therefore, effective grains mainly consisted of grains and subgrains (martensite blocks and packets) will be more uniform, as shown in Figures 5.8b, c and d.

During (DQ/AC/FC) + RQ + T processes, different cooling methods (DQ/AC/FC) affected the degree of austenite grain refinement after reheating and then influenced the martensite structure formed after quenching. The grain size of austenites is generally determined by nucleation and growth. The nucleation of reheated austenites occurs mainly on large-angle grain boundaries and dislocations. Hence, a longer large-angle grain boundary and dislocation cause more nucleation per unit area and generates finer austenite grains. Figure 5.13 presents the EBSD results of the specimens cooled by DQ, AC, and FC. The black line signifies large-angle grain boundaries (orientation difference is greater than 15°). The relationship between the total length of large-angle grain boundaries and the effective grain size of the final martensite
microstructure is displayed in Figure 5.14. It is discernible that a longer large-angle grain boundary can generate finer martensite microstructures. It has been known that dislocations can act as the sites for nucleation of new phase [231, 232]. For DQ/AC/FC + RQ + T process, dislocation density decreased in turn, because of the different levels of recovery at different situation, resulting to the different degrees of grain refinement correspondingly, i.e. the higher dislocation density, the finer the grain. That was matched with the result of effective grains size shown in Table 5.2 and Figure 5.14.

Figure 5.13 Large angle grain boundary of (a) DQ + RQ + T, (b) AC + RQ + T and (c) FC + RQ + T processes. (Orientation difference is greater than 15°).
Figure 5.14 The relationship between the length of a large angle grain boundary and the size of martensite microstructures.

Large-angle grain boundaries and dislocations can promote the nucleation of austenites, and the precipitates profoundly affect the growth of austenite grains. In the DQ + RQ + T process, the fine precipitates, which continuously precipitated during heating, effectively prevented the growth of austenite grains. In the FC + RQ + T process, the fine precipitates dissolved and matured continuously during the heating process and promoted the growth of austenite grains. Therefore, the effective grain size and the martensite lath width during DQ + RQ + T, AC + RQ + T, and FC + RQ + T processes increased significantly.

5.4.3 Strengthening and toughening mechanism

The strength of lath martensitic steels can be determined by different strengthening mechanisms as equation (5.1).

$$\sigma = \sigma_0 + \sigma_s + \sigma_p + \sigma_p + \sigma_g$$  (5.1)
Where $\sigma_0$ is the constant lattice frictional stress of pure iron, $\sigma_s$, $\sigma_p$, $\sigma_\rho$, and $\sigma_g$ represent the increase in strength by solution strengthening [233], precipitation strengthening, dislocation strengthening [234], and fine grain strengthening [235], respectively.


$$\sigma_p = 0.538Gbd^{-1}f^{1/2}\ln(d/2b) \quad (5.3)$$

$$\sigma_\rho = \alpha MGb \rho^{1/2} \quad (5.4)$$

$$\sigma_g = k_y d^{-1/2} \quad (5.5)$$

In Equation (5.3), $G$ and $b$ are shear moduli and the Bernoulli vector, respectively, $f$ and $d$ are the volume fraction and the diameter of the precipitated phase, respectively. In Equation (5.4), $\alpha$ and $M$ are constants and $P$ is dislocation density. In Equation (5.5), $k_y$ is the Hall-Petch slope and $d$ is the effective grain size.

It is discernible that $\sigma_p$, $\sigma_\rho$, and $\sigma_g$ are the main reasons for strength difference in the four specimens. $\sigma_p$ was dependent on the volume fraction and the size of (Ti, Mo)C precipitates, it happened because when the average diameter of particles was greater than 40 nm, the precipitation strengthening effect was not effective [236]. For process of DQ + T, Ti did not precipitate nearly after rolling, so $\sigma_p$ was not the primary method of strengthening. For process of DQ/AC/FC + RQ + T, Ti could precipitate in different stages after rolling. However, the volume fraction of (Ti, Mo)C precipitates were almost the same for these three processes, because the solid solubility would be almost at the same state after reheating at 880 °C for 15 min. The difference was the size of precipitates due to different cooling processes as analyzed in section 5.4.1, and DQ + RQ + T process had the highest precipitation strengthening. $\sigma_p$ was determined by the number of dislocations and small-angle grain boundaries in martensite laths. In lath martensite steels, small-angle grain boundaries are mainly formed from lath boundaries;
hence, a finer lath generated more small-angle grain boundaries. The value of $\sigma_g$ was determined by the effective grain size. However, due to the thermodynamic non-equilibrium state of tempered martensites at low temperatures, it was very difficult to accurately calculate the aforesaid parameters and only qualitative comparative analysis can be done, combining the morphology of longitudinal tensile fracture as given in Figure 5.10.

In the DQ + T process, the uneven longitudinal and transverse strengths were mainly generated from flattened martensite structures and inclined martensite laths. The cracks generated during the cleavage brittle fracture propagated along the flattened grain boundaries and caused delamination, thus the plasticity of the sample started to deteriorate. However, high-density dislocations and fine martensite laths contributed mainly to increase strength. In addition, cementites precipitated at low-temperature tempering also manifested a certain strengthening effect [232].

In the processes of the DQ + RQ + T, the AC + RQ + T, and the FC + RQ + T, finer effective grains caused more dimples. With the increase in effective grain size, the cleavage characteristics of fracture surfaces became more prominent (Figure 5.10c and 5.10d). Moreover, the refinement of effective grain size caused improvements in both strength and plasticity. In addition, it is noticeable from Section 5.4.1 and Equation (5.3) that the precipitated phase was consistent with the changes in strength. Smaller grains generated more precipitates and made the precipitation strengthening effect stronger.

Toughness is generally measured by brittle transition temperature, and the linear relationship between brittle transition temperature and effective grain size can be expressed by Equation (5.6).

$$V_{Trs} = B - A d^{-1/2}$$  \hspace{1cm} (5.6)
Where VT\textsubscript{rs} signifies brittle transition temperature, \(A\) and \(B\) are constants, \(d\) is the effective grain size. Except for the DQ + T process, the effective grain size (Table 5.2) values were consistent with low-temperature impact energies (Table 5.3), thus larger effective grains caused a severe deterioration in toughness. Large-angle turning generally occurs when cracks propagate through the effective grain interface (large-angle interface), consequently, it hinders crack propagation and improves the toughness of steels [237]. Therefore, it can be inferred that when the effective grain size of equiaxed grains was small enough, dimples were formed and the toughness of the steel was improved. Precipitates were not beneficial for improving fracture toughness directly, however, which had function of refining effective grains by effectively preventing the growth of austenite grains during reheating process, and promoted fracture toughness indirectly.

In addition, toughness is also related to crack nucleation. It is clear from Figure 5.11a and d that small cracks at the edge of the cleavage section were the main reason for low toughness of the DQ + T and the FC + RQ + T samples. High-density dislocations were observed in the matrix of the DQ + T specimen. Cracks nucleate under shear stresses when dislocations merge or fold into obstacles. The austenite grain coarsening in the FC + RQ + T specimen caused more chances of crisscross impacts of primary martensite laths, thus resulting in a greater probability of crack occurrence. Furthermore, more acicular cementites (their morphologies were unfavorable to toughness) were also formed by these two processes.

5.5 CONCLUSIONS

In the present study, the effects of controlled cooling and heat treatment on martensite morphology and precipitates of Mo–Ti microalloyed medium carbon steel were investigated and
the relationship between microstructural evolution and mechanical properties was discussed. The key observations are presented below.

The DQ + RQ + T sample yielded high strength and excellent plastic toughness and manifested uniform transverse and longitudinal properties. The strength of the DQ + RQ + T sample (longitudinal Rm = 1780 MPa) was slightly lower than that of the DQ + T samples; however, its elongation (A = 11.0%) and impact energy at −40 °C (Akv = 50 J/cm²) were larger than those of other three samples.

Deformation energy generally increases the driving force of martensite transformation, thus the DQ + T sample generated the finest martensite lath with the highest dislocation density and strength. For (DQ/AC/FC) + RQ + T processes, the number of large-angle grain boundary increased with the increasing cooling rate (DQ > AC > FC). Large-angle grain boundaries generated more nucleation sites during reheating and refined the microstructure of austenite grains and martensites. The effective grain size of the DQ + RQ + T sample was found to be the smallest (0.9 μm), thus resulting in an improvement in fine grain strengthening.

Ti precipitated in the form of (Ti, Mo)C during cooling and reheating after rolling, and the “C”-shaped precipitation kinetics curve was obtained. The increase in cooling rate (DQ > AC > FC) inhibited the formation of (Ti, Mo)C precipitates during reheating and heating, thus made the size of precipitates smaller (diameter of <15 nm) and enhanced the effects of precipitation strengthening and grain refinement. The highest supersaturation of carbon during DQ + T and FC + RQ + T processes led to the formation of acicular cementites at low temperatures and manifested a certain strengthening effect, which was not conducive to toughness.
(4) Flattened microstructures had directional anisotropy and yielded lower plasticity and toughness. In equiaxed microstructures, with the decrease in effective grain size, some dimples appeared on fracture surfaces, thus resulting in an improvement in both plasticity and toughness.
Chapter 6: Conclusions and future work

6.1 Conclusions

The strain hardening behavior of tensile strained NG/UFG copper containing austenitic stainless steel was explored by combining tensile data and post-mortem electron microscopy and compare with the coarse-grained (CG) counterpart.

The effect of Ni on the free energy of bainitic transformation was elucidated by designing Ni-free and Ni-bearing steels. In this regard, steels with two distinct nano-bainite structures were obtained through conventional one-stage and two-stage isothermal treatments. Also, study the effect on work hardening behavior and accompanying strain on martensitic transformation of two nano-bainite structures.

The effects of controlled cooling and heat treatment on martensite morphology and precipitation was identified in Mo-Ti microalloyed medium carbon steel, and the relationship between microstructural evolution and mechanical properties was elucidate. In this regard, a facile and cost-effective process for martensitic steels with high strength and toughness combination was proposed, and strengthening and toughening mechanisms elucidated. Furthermore, develop a model to predict the precipitation behavior in terms of size, number density, and volume fraction that provides guidelines for processing of microalloyed steels.

6.1.1 The significance of phase reversion-induced nanograined/ultrafine-grained (NG/UFG) structure on the strain hardening behavior and deformation mechanism in copper-bearing antimicrobial austenitic stainless steel

The significance of grain refinement on the strain hardening behavior and TWIP/TRIP deformation mechanisms in Cu-bearing NG/UFG and CG antimicrobial stainless steels was elucidated on the basis of Crussard-Jaoul analysis of tensile deformation data of the steels and
post-mortem electron microscopy of the strained region near the fractured ends. The plastic deformation process can be divided into four stages based on the change in SHR. Grain refinement strongly affected the strain hardening ability. The good ductility and high SHR of the NG/UFG structure is attributed to the occurrence of mechanical twinning, whereas the strain-induced martensite transformation was the underlying reason for the excellent strain hardening ability and ductility of the CG structure. Both mechanisms were effective in inhibiting the movement of dislocations. In nano-grained austenitic stainless steel with grain size less than ~1 μm, the high strain energy and austenitic stability significantly reduced the possibility of multivariant transformation and led to the suppression of strain-induced martensitic transformation. Extensive grain refinement due to reversion annealing was responsible for the transition of the deformation mechanism from a strain-induced martensitic transformation in the CG structure to mechanical twinning in the NG/UFG structure, besides manifestation of a large number of stacking faults, a precursor to the occurrence of twinning.

6.1.2 Effect of nickel on hardening behavior and mechanical properties of nanostructured bainite-austenite steels

The influence of Ni on microstructure, strain hardening behavior, and TRIP effect of medium C nano bainitic-austenitic dual-phase steel produced by two-stage isothermal transformation at low-temperature was studied. The microstructure of Ni-free and Ni-bearing steels consisted of nano-bainitic ferrite, film-like, and block-like RA. The presence of Ni was found to (i) reduce the free energy of the bainitic transformation during the low-temperature isothermal treatment, (ii) extend the bainite nucleation period, and (iii) refine the bainite structure. The average size of nano-bainitic ferrite (B2) and film-like RA was smaller in Ni-bearing steel (114 ± 35 nm and 93 ± 22 nm, respectively) compared to the Ni free steel (267 ± 70
nm and 186 ± 41 nm, respectively). The relatively high free energy of austenite to bainite transformation in Ni-free steel resulted in “interlocked” distribution of coarse bainitic ferrite and further promoted the formation of the Fe–C clusters to consume C-content and stability of film-like RA. The presence of Ni was shown to effectively reduce free energy to obtain uniformly-oriented finer nano bainitic ferrite and highly stable film-like RA, exhibiting a “side-by-side” structure in Ni-bearing steel. The interlocked nanostructure of Ni-free steel can effectively prevent dislocation slip and provide higher SHR at low strain, but the “side-by-side” uniform nanostructure of Ni-bearing steel resulted in higher SHR and stronger TRIP effect at high strain. This resulted in Ni-bearing steel with superior plasticity (13.7%–10.3%) and product of tensile strength and elongation (25.9 GPa·% to 20.9 GPa·%) compared to the Ni-free steel.

6.1.3 Effects of cooling after rolling and heat treatment on microstructures and mechanical properties of Mo–Ti microalloyed medium carbon steel

The DQ + RQ + T sample yielded high strength and excellent plastic toughness and manifested uniform transverse and longitudinal properties. The strength of the DQ + RQ + T sample (longitudinal Rm = 1780 MPa) was slightly lower than that of the DQ + T samples; however, its elongation (A = 11.0%) and impact energy at −40 °C (Akv = 50 J/cm2) were larger than those of other three samples.

Deformation energy generally increases the driving force of martensite transformation, thus the DQ + T sample generated the finest martensite lath with the highest dislocation density and strength. For (DQ/AC/FC) + RQ + T processes, the number of large-angle grain boundary increased with the increasing cooling rate (DQ > AC > FC). Large-angle grain boundaries generated more nucleation sites during reheating and refined the microstructure of austenite
grains and martensites. The effective grain size of the DQ + RQ + T sample was found to be the smallest (0.9 μm), thus resulting in an improvement in fine grain strengthening.

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6.2 FUTURE WORK

In this dissertation, the TRIP/TWIP mechanisms and strain hardening behaviors of were systematically explored and studied by the phase reversion process. The bainitic phase transformation was explored by kinetics, microstructural features and mechanical properties. Furthermore, the controlled cooling and treatment processes were compared on microstructure, mechanical properties, and precipitation behavior in Ti-Nb-Mo low-carbon microalloyed steels and quantitative analysis of strengthening mechanism has been carried out.

Future research will focus on applying phase reversion technology to bainite transformation to obtain ultra-fine prior austenite grains. The driving force of bainite transformation will be limited by ultra-fine prior austenite grains, then the orientation of bainitic ferrite and the stability of retained austenite can be controlled by the limited driving force.
References

141


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Vita

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