A Molecular Dynamics Simulation of Alloy Carbide Cluster Formation

by

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M. S.

Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Deakin University
August, 2015
I am the author of the thesis entitled

A Molecular Dynamics Simulation of Alloy Carbide Cluster Formation

submitted for the degree of Doctor of Philosophy

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List of publications


Abstract

The interest in High-Strength Low-Alloy (HSLA) steel has been motivated by its better mechanical properties than general carbon steel due to the fine carbide precipitates. Recent experimental work has identified the existence of carbide clusters that consist of several to several tens of atoms and play an important role during the precipitation process. As the precursor of precipitates, the clusters are generally formed at the initial annealing stage, which govern the precipitate formation and determine the microstructure. As in-situ experiments at atomic scale are often very difficult, the mechanisms through which carbide clusters form and grow during the phase transformation and their structure and thermodynamic properties are not as well understood as the mature precipitates.

Consequently the formation and evolution of titanium carbide clusters in ferrite during the early isothermal annealing process were investigated in detail via molecular dynamics (MD) simulation in the current work, aiming to approach the formation and growth mechanisms of carbide precipitate clusters, fill the lack of understanding of the atomic configuration, properties of clusters and the driving force for precipitation. Therefore in this work the titanium carbide clusters formed in a ferrite matrix, dislocation cluster formation and cluster growth were sequentially investigated with the development of corresponding simulation models and methods.

The titanium carbide clusters that could form in the ferrite matrix were revealed by examining the dependence of their energy property on the structure. Their constitution was characterised by three serials of carbide components proposed. The atomic configuration and energy of these clusters and the dependence on size and composition were determined, which provided a systematic description on the morphology and property of the titanium carbide clusters. This is the first time there has been such a theoretical study these carbide clusters formed in ferrite matrix by the MD simulation technology. The comparison of properties of the titanium carbide clusters formed in ferrite to the corresponding independent carbide clusters, which have been the objects of interest in this research area, indicated a large difference in atomic structure between these clusters and a significant influence of the atomic interactions between the ferrite matrix and clusters.
The formation mechanism of titanium carbide clusters in ferrite was disclosed based on a dislocation-motivated formation model developed in this work. This model has the ability to describe a ternary Fe-Ti-C system and supply a proper expression of titanium carbide cluster formation. The analysis of the atomic interactions of titanium and carbon atoms during the initial formation process explained the aggregation of the carbon and titanium atoms. A mechanism of a combination of single atom adsorption and cluster uniting was discovered for carbide cluster formation in ferrite. As a considerable progress the MD results demonstrated the influences of the parameters that dominate the evolution and structural properties of clusters during the formation process.

To further investigate the evolution process of clusters to mature precipitates, the simulation of the growth of titanium carbide clusters in ferrite matrix was extended. The typical kinetic of carbide cluster growth was studied in detail through analysing the atomic interactions of a carbide cluster with scattered carbon atoms, which provided useful information for building up the dependence of the structural and property of mature precipitates on their precursors, carbide clusters. It was found that a two-step growth mechanism was responsible for single atom absorption kinetics. The two steps are the diffusion in ferrite matrix and absorption in the interaction region of TiC cluster. The growth kinetic improved the understanding of precipitate evolution at the atomic level.

Based on the molecular dynamics simulations, this work presented the properties of the titanium carbide clusters, cluster formation mechanism, and cluster growth mechanism in iron matrix. These together provided a better fundamental understanding of the cluster formation and firm information for the investigation of the precipitate growth, structural and mechanical properties, and their functions in high-strength low-alloy steel in the future.
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<tbody>
<tr>
<td>$\varepsilon$</td>
<td>Thermal expansion</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Ferrite</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Austenite</td>
</tr>
<tr>
<td>$a$</td>
<td>Lattice parameter</td>
</tr>
<tr>
<td>$b$</td>
<td>Burgers vector</td>
</tr>
<tr>
<td>$B$</td>
<td>Bulk modulus</td>
</tr>
<tr>
<td>$c/a$ ratio</td>
<td>Lattice parameter in $hcp$ structure</td>
</tr>
<tr>
<td>$d_{ij}$</td>
<td>Interatomic distance</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$D_o$</td>
<td>Pre-exponential factor of Arrhenius law</td>
</tr>
<tr>
<td>$d_c$</td>
<td>Minimum distance of cluster definition</td>
</tr>
<tr>
<td>$E$</td>
<td>Total energy of a system</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Cohesive energy parameter of 2NN.MEAM</td>
</tr>
<tr>
<td>$E_{coh}$</td>
<td>Cohesive energy per atom</td>
</tr>
<tr>
<td>$E_{\text{cluster}}, E_{\text{Ti}}, E_{\text{C}}$</td>
<td>Total energies of TiC clusters, titanium atom and carbon atom</td>
</tr>
<tr>
<td>$E_d$</td>
<td>Dissociation energy of cluster</td>
</tr>
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List of symbols or abbreviations

\begin{itemize}
    \item \(E_f\) Formation energy of cluster
    \item \(E_i\) Formation energy of self-interstitial
    \item \(E_{int}\) Interfacial energy of 2NN.MEAM
    \item \(E_m\) Activation energy of Arrhenius law
    \item \(E_v\) Formation energy of vacancy
    \item \(fs\) Femtosecond
    \item \(F^{ABF}\) Force to overcome the free energy barrier by ABF
    \item \(\langle F_i \rangle / \xi\) Current average force of ABF
    \item \(g(r)\) Pair distribution function
    \item \(\Delta G\) Change in PMF
    \item \(k_B\) Boltzmann constant
    \item \(N\) Number of atoms
    \item \(P\) System pressure
    \item \(r\) Distance from original site of PDF
    \item \(r_e\) Nearest neighbour distance of 2NN.MEAM
    \item \(r_i(t)\) Distance travelled by molecule \(i\) over some time interval of length \(t\) of MSD
    \item \(r_{ij}\) Distance between atoms \(i\) and \(j\)
    \item \(t\) Computational time
    \item \(\Delta t\) Time step
    \item \(T\) Temperature
\end{itemize}
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<table>
<thead>
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<tbody>
<tr>
<td>$T_m$</td>
<td>Melting point</td>
</tr>
<tr>
<td>$v_j$</td>
<td>Atom velocity</td>
</tr>
<tr>
<td>$V$</td>
<td>System volume</td>
</tr>
<tr>
<td>$W_{se}$</td>
<td>Work of separation</td>
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Abbreviations

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<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>2NN.MEAM</td>
<td>Second nearest-neighbour modified embedded atom method</td>
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<tr>
<td>ABF</td>
<td>Adaptive biasing force method</td>
</tr>
<tr>
<td>APT</td>
<td>Atom-probe tomography</td>
</tr>
<tr>
<td>Bcc</td>
<td>Body-centred cubic</td>
</tr>
<tr>
<td>CD</td>
<td>Cluster dynamics method</td>
</tr>
<tr>
<td>CNT</td>
<td>Classical nucleation theory</td>
</tr>
<tr>
<td>COM</td>
<td>Centre of mass</td>
</tr>
<tr>
<td>DFT</td>
<td>Density-functional theory</td>
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<tr>
<td>EAM</td>
<td>Embedded-atom method</td>
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<td>Face-centred cubic</td>
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<tr>
<td>FS</td>
<td>Finnis-Sinclair potential</td>
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<tr>
<td>Hcp</td>
<td>Hexagonal close-packed</td>
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<tr>
<td>HSLA</td>
<td>High strength low carbon alloy</td>
</tr>
<tr>
<td>Ind-</td>
<td>Independent cluster</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>JMAK</td>
<td>Johnson–Mehl–Avrami–Kolmogorov model</td>
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<tr>
<td>KMC</td>
<td>Kinetic Monte Carlo</td>
</tr>
<tr>
<td>KNT</td>
<td>Kinetic nucleation theory</td>
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<tr>
<td>KWN</td>
<td>Kampmann–Wagner-Numerical model</td>
</tr>
<tr>
<td>LAMMPS</td>
<td>Large-scale Atomic/Molecular Massively Parallel Simulator</td>
</tr>
<tr>
<td>L-J</td>
<td>Lennard-Jones (L-J) potential</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
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<td>MD</td>
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<td>MEAM</td>
<td>Modified Embedded Atom Method</td>
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<td>MS</td>
<td>Materials Studio</td>
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<td>MSD</td>
<td>Mean-squared displacement</td>
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<td>RMS</td>
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<tr>
<td>TTT</td>
<td>Time Temperature Transformation</td>
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<td>VC</td>
<td>Vanadium carbides</td>
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<td>VMD</td>
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<td>XMD</td>
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Chapter 1 Introduction

1.1 Motivation

High-Strength Low-Alloy steels are attracting much attention due to their good mechanical properties. Alloy carbide precipitation, which occurs at the interphase boundary during phase formation, plays an important role in strengthening the HSLA steel. It has been found that, in many cases, some atoms first aggregate during precipitation, and the formed atom group is termed a cluster [1]. The cluster involves typically a couple to several tens of atoms, and to some extent, may act as the precursor of mature precipitate.

A great deal of experimental work has been carried out in exploring the precipitation mechanism, but as the cluster observations are quite new there are still only a few systematic studies and even these are quite limited. Several kinetic models have been proposed for the classical interphase precipitation, such as the ledge mechanism model [2], the solute-drag nucleation model [3], and the eutectoid decomposition model [4], but the limitations of the detection and individual assumptions of these models make the mechanism of interphase precipitation still not completely resolved, this is further exacerbated for the cluster formation. Computational modelling method has been adopted to study the precipitation and precipitate microstructure [5]. However, the modelling which was performed at the mesoscopic scale [6, 7] encountered a large number of unidentified input parameters [8], which leads to a diversity of modelling methods and likewise a diversity of precipitation results [9-13]. Although the nucleation and properties of carbide precipitates has been investigated by atomic simulation [14-16], the majority of atomic simulations have only been performed to study the dislocation-precipitate interaction in binary alloy/alloy and alloy/carbon systems, and they neglected the precipitate formation and evolution process, which is essential to the understanding of the clusters. Therefore, the most important reason that these models cannot provide an accurate precipitation mechanism is the lack of
understanding of the first stage of precipitate formation, as the clusters determine the microstructure and govern the precipitate formation in the HSLA steels.

A clear understanding of the cluster is vital to support the exploration of precipitation mechanism. Unfortunately, experiments of clusters can be very difficult at the atomic level due to the small size-scale of clusters. The difficulty in conducting critical experiments motivates the use of atomistic simulations to reveal the formation mechanism of clusters and to eventually help interpret the limited experimental results available. Molecular dynamics simulation has been efficiently used in analysing the cluster evolution of binary alloy-alloy systems after solidification [17-19]. However, these existing atomic models show an incapability in describing the precipitation phenomena in an alloy-C-Fe ternary system because of the different formation procedures and complicated interactions in a multicomponent system. To date, besides those experiments that confirmed the existence of clusters and the explanation of relationship between cluster and precipitates based on experimental results, there is little study on cluster in alloy-C-Fe system at atomic level.

The investigation of the carbide clusters at the atomic level offers the potential to be able to examine the atomic interactions and clustering dynamics during the precipitation process that cannot be observed directly in experiments. It provides a better fundamental understanding of the cluster formation and firm information for the investigation of the precipitate growth, structural and mechanical properties in high-strength low-alloy steel. Due to the limited work in the area of alloy carbide cluster in iron matrix, there are a multitude of research questions that need to be addressed.

Although the structure of TiC cluster has been studied through MD [19] and quantum mechanics [20], the objects were independent clusters, i.e., there was no bulk matrix in the system. The iron matrix presents a significant influence on the structure and energy property of the formed cluster due to the interactions of matrix atoms and cluster atoms, which can lead to a different cluster morphology to the independent clusters. During the precipitation process, the structure and property of titanium carbide cluster are highly sensitive to their configurations, but it is difficult to discover the atomistic property of carbide clusters experimentally. Additionally, cluster structures with different size and composition are important to determine the configurations of the precipitate during subsequent formation and growth process. However, the interactions
between iron matrix and TiC clusters and the influence of iron matrix on the configurations and properties of titanium carbide clusters is unclear. Therefore, it is necessary to obtain the minimum energy equilibrium structure and understand the characteristics of the clusters in the ferrite matrix.

Identifying the formation process and examining the various properties of titanium carbide clusters is a critical issue in understanding of precipitation mechanism. To provide a clear picture of cluster formation, the atomic interactions between matrix and cluster constituted titanium and carbon atoms are the key information to be collected. Also, the analysis of the formation behaviour as a function of the various system variables is complicated but necessary. However, there is a distinct lack of understanding of the aforementioned issues during the cluster formation process in a ternary Fe-Ti-C system. Thus, the question that arises from this is how the formation of titanium carbide cluster occurs in ferrite at atomic level.

The formation model is the first key point for accuracy and comparability of the simulation results. Furthermore, the development and implementation of the calculation methodology incorporating a suitable analysis technique for characterising those thermodynamics properties is required. Building an efficient model for the Fe-Ti-C ternary system is a challenge in the study of precipitate cluster formation and growth mechanism in the iron matrix during the isothermal annealing process.

As a subsequent step after the nucleation stage, the fine growth of the cluster determines the final property of the mature precipitate. The growth behaviour of titanium carbide cluster within the ferrite is the most important step to obtain the fine precipitate to strengthen the HSLA steel. However, it cannot be studied by the current computational modelling methods due to the complicated environment, such as the unclear distinction between nucleation and growth and the complex influence of the system variables. If the growth of a carbide cluster can be achieved then potentially a correlation between the cluster and mature precipitate could be obtained. A dynamics process that can investigate the growth behaviour of atoms interacting with atoms could contribute eventually to the understanding of the formation and evolution of precipitates during the precipitation process.

The research objectives will be met through designing and performing systematic studies to answer the aforementioned research questions and any subsequent questions
that arise. The outcomes will provide a fundamental understanding of the characteristics of titanium carbide formed in the matrix and the formation and growth mechanisms of clusters in a ferrite matrix. Once the atomic scale formation mechanisms of titanium carbide cluster in iron matrix are better understood, this insight can be incorporated into multi-scale models to further explore the cluster characteristics in steel materials and have a potential application in material development in the future.

1.2 Thesis outline

The objective of this thesis is to investigate the formation mechanism of titanium carbide cluster in a ferrite matrix and the cluster properties via molecular dynamics simulation. The contents of the work are outlined as the follows:

Chapter 2 reviews the previous work concerning the precipitation kinetics and the previous studies on the clusters. The precipitate types, main parameters for precipitation, and the wide investigations of interface precipitation models are introduced and compared. The advantages and drawbacks of various kinetic models of precipitation at the macroscopic and mesoscopic levels are discussed, respectively. In this chapter, the experiments on clusters and their role in precipitation are summarized. The evolution models of clusters and theoretical investigation on cluster structures are also presented, and the gaps in knowledge that prompted this work are given in the conclusions.

Chapter 3 will introduce the simulation methodology used for titanium carbide in ferrite. It provides detailed information of the MD simulation for the Fe-Ti-C system, including the generation of the simulation cell and the determination of the general simulation conditions during cluster formation and growth. This chapter will also discuss the fundamentals of the modified embedded atom method with detailed comparison with other types of potentials and will verify the force field. Finally, the methods for analysing and evaluating the atomic interactions during cluster formation and the structure and energy properties of clusters in a ferrite matrix are outlined and explained in this chapter.

In Chapter 4 the simulations of the structure and energy properties of titanium carbide clusters and the interactions of cluster and iron matrix are presented. TiC clusters with
different sizes and compositions are developed and examined, and the properties of
the clusters, including structure and structural features, interatomic interaction and
binding potential are analysed to identify the stable titanium carbide clusters in the
iron matrix. The atomic configurations and property of the cluster units which
constitute the titanium carbide cluster are studied to investigate the cluster stability and
activity.

Chapter 5 presents the molecular dynamics simulation of cluster formation in the iron
matrix during the isothermal annealing process. A dislocation-motivated simulation
model for the formation of titanium carbide cluster is developed. The simulation
reveals the atomic interactions between titanium and carbon atoms in ferrite at the
initial formation stage and evaluates the energetic driving force for atom aggregation.
Particular attention is paid to the formation mechanism of the titanium carbide cluster,
cluster evolution and properties, and the characteristics of cluster components. The
system variables, such as carbon concentration and temperature, have great influences
on the cluster properties, which are examined in detail.

Chapter 6 examines the growth mechanism of titanium carbide clusters in the iron
matrix, which is realized through a specific growth molecular dynamics model. A main
growth dynamic is proposed in this chapter, which explains the continuous evolution
of cluster and mature precipitation. The characteristics of the steps of the growth
dynamic are clarified. The growth model suggests a common mechanism of the
titanium carbide cluster formation and growth processes in ferrite.

The main findings and the significant contributions of this thesis are summarized in
Chapter 7. The recommendations for future research, which build upon the results in
this work, are described in Chapter 8. Overall, it will be shown that, with some
limitations, the formation and growth mechanism of titanium carbide clusters in ferrite
can be investigated and proposed via molecular dynamics simulation.
Chapter 2  Literature Review

Precipitation is an important phenomenon observed in alloys and steel. As a thermo-mechanical treatment technique, it has been used for the control of strength, texture and grain size to strengthen metallic materials. This chapter reviews recent development on precipitation with a focus on simulation of the process which will lead to the formulation of the major research questions of the current work. Recent investigations on precipitate types and interphase precipitation are firstly introduced in Section 2.1. Various kinetic models that have been proposed to understand the precipitation mechanism are examined in Section 2.2, including the modelling methods at macroscopic and mesoscopic levels. The advantages and drawbacks of these models are outlined, with an emphasis on the gaps in knowledge that prompted this work. As the precursor of precipitates, carbide clusters have now been observed and their role in steel strengthening has been identified experimentally (Section 2.3). A few evolution models of clusters and theoretical investigation on cluster structures show a lack of understanding of the formation mechanism of carbide clusters and cluster characteristics in ferrite.

2.1 Precipitates in steel

High-strength low-alloy steels, as a type of alloy steels, can provide better mechanical properties than carbon steels do. HSLA steels have a carbon content of up to 0.25% and small-quantities of alloying elements. The alloying elements, such as vanadium, titanium, and niobium, are added for strengthening purposes by refining the grain microstructure or facilitating the formation of precipitates [21].

Precipitation strengthening occurs from the formation of finely dispersed carbides/carbonitrides during heat treatment, which is one of the most important approaches for enhancing the strength of the HSLA steels. Investigation of precipitation in HSLA steels can be tracked back to 1960’s. To date, research is still ongoing for better control over the precipitation process to get more reliable performance of the steels.
In low carbon steels, the precipitation are generally classified into three ways: (1) precipitation in austenite; (2) precipitation during γ/α transformation, and (3) precipitation after transformation in the ferrite [22].

### 2.1.1 Precipitation in austenite

During thermo-mechanical processing, the carbide/carbonitride precipitation (Fig. 2-1) in austenite relates to the decrease in alloy solubility with a decreasing temperature. Precipitation in austenite, which plays a major role in controlling the steel structure and the strength of low alloy steels [23] has been widely studied.

The preferential nucleation sites for precipitation in austenite are at the regions of dislocations, grain boundaries and deformation bands. For instance, deformation can not only greatly promote the nucleation of precipitates but also reduce the time necessary for the completion of precipitation [24].

![Fig. 2-1. Carbonitride precipitates in austenite [25].](image)

The formation of carbide/carbonitride precipitates carries out with continuous consumption of alloy and carbon/nitrogen elements in austenite. If there were a large number of precipitates formed in austenite, the amount of alloy elements available for subsequent precipitation would be greatly reduced [23]. Therefore, the precipitation in austenite is very important, because it determines the quantity and quality of the precipitates before the
phase transformation [26], which has a significant influence on the amount of alloy elements for interphase precipitation and precipitation in ferrite.

### 2.1.2 Precipitation during phase transformation

#### 2.1.2.1 Interphase precipitation

During the phase transformation from austenite to ferrite, the solubility of the alloy elements at interphase boundary decreases dramatically, which drives the precipitation of carbides/carbonitrides on the migrating $\gamma/\alpha$ interface (Fig. 2-2) [27, 28]. This kind of precipitations is termed as interphase precipitation. The interphase precipitation reaction can occur during both isothermal and continuous cooling transformations after austenitization, and results in a characteristic sheet-like microstructure of alloy carbide precipitates, which have been widely found in many HSLA steels [29].

![Fig. 2-2. Interphase precipitates [27].](image)
The interphase precipitates have several characteristics which distinguish them from other kinds of precipitates. The precipitates show a regular row arrangement. The formation of precipitates and the migration of interphase boundaries are successive so that the precipitate rows are nearly parallel to the interphase boundary [30] and follow any sharp changes in direction of the ferrite growth front, as shown in Fig. 2-3 [2]. Furthermore, the interphase precipitates with ferrite follow a Baker-Nutting orientation relationship (\{100\} carbide//\{100\} ferrite and <110> carbide//<100>ferrite) [28].

Various shapes of interphase precipitates have been observed, and can be classified into three major types [31]: planar interphase precipitate (Fig. 2-4 (a)), curved interphase precipitate (Fig. 2-4 (b)), and fibrous interphase precipitate.
Fig. 2-4. (a) Planar interphase precipitate [32] and (b) curved interphase precipitate [33].

To improve the understanding of the formation of interphase precipitates with different types, many formation mechanisms and models have been developed, which will be discussed in the following section.
2.1.2.2 Mechanism of interphase precipitation

2.1.2.2.1 Ledge mechanism

The ledge mechanism [2] was developed to explain the nucleation and growth of interphase precipitates at the interphase boundaries migrating with regular and irregular ledge heights, as illustrated in Fig. 2-5. This mechanism assumes that precipitation occurs on planar, low energy, semi-coherent and immobile interfaces during the growth of ferrite. The lateral passage of the mobile ledge leads to the motion of the planar $\gamma/\alpha$ boundary which is normal to the direction of ledge migration. The nucleation of the precipitates on the straight semi-coherent interface should be in sheets, which have a spacing equal to the ledge height. However, there are repeated nucleation of precipitates along the planar $\gamma/\alpha$ boundary, the uniform size of precipitates, and the inter-sheets spacing which cannot explained properly with the ledge mechanism. And so is the formation of curved interphase precipitates. Overall, the ledge mechanism only explained the formation of planar type precipitates, which led to the developments of the quasi-ledge mechanism.

Fig. 2-5. Illustration of precipitate nucleation and growth on the interface with: (a) regular ledge heights, and (b) irregular ledge heights [33].
2.1.2.2 Quasi-ledge mechanism

The quasi-ledge mechanism [33] (Fig. 2-6 (b)) was proposed for the curved interphase precipitates at the disordered interphase boundaries with high energy. The ledges laterally traverse the interphase boundary, and the migration occurs similar to that illustrated for the low energy immobile boundaries (Fig. 2-6 (a)). The quasi-ledge mechanism involves the following steps. First, the interphase precipitates nucleate at the interphase boundary; then, the precipitates pin the mobile interface and bow the ledges between the widely spaced precipitates; and lastly, the subsequent precipitation forces the ledges to move sideways.

![Diagram](image)

Fig. 2-6. Schematic diagram of (a) ledge mechanism and (b) quasi-ledge mechanism [33].
2.1.2.2.3 Bowing mechanism

The bowing mechanism was developed by Ricks and Howell [34] to interpret the interphase precipitation at the interphase boundaries with high energy mobility. In the mechanism, four stages were assumed to explain the boundary growth process, as illustrated in Fig. 2-7. Firstly, the interface bows between two pinned precipitate particles (Fig. 2-7 (a)). When the bowed segments turn semi-circular in cross section (Fig. 2-7 (b)), the precipitates unpin, so the interface can move forward (Fig. 2-7 (c)) until the precipitate nulceation and bowing process restart (Fig. 2-7 (d)). The bowing mechanism adopts an energy balance criterion and gives a calculated value for the critical precipitate spacing. If the precipitate spacing along the interphase boundary is less than the critical precipitate spacing required for bowing, it is not energetically possible for the boundary to bow but migrate by the quasi-ledge mechanism.

Fig. 2-7. Illustration of bowing mechanism [34].
2.1.2.2.4 Solute-drag model

The solute-drag model [3] was introduced to explain the interphase precipitates and fibrous precipitates for vanadium carbides (VC), as shown in Fig. 2-8. It is assumed that the carbon aggregates ahead of the moving interphase boundary and the possible collection of vanadium on the interface restrict the carbon movement and drag the migration of interphase boundary, so the VC precipitates can nucleate and grow. The growth of VC precipitates continuously consumes the carbon and vanadium on the interfaces, so the carbon and vanadium concentrations on the interface are reduced, which drives the interphase boundary migrating front to a new position where new precipitates nucleate (Fig. 2-8 (a)). The model can also explain the formation of fibrous precipitates at the conditions of that the growth direction of vanadium carbides is parallel to the movement direction of the interface and the interphase migration is very low, as shown in Fig. 2-8 (b).

![Diagram of solute-drag model](image)

Fig. 2-8. Illustration of solute-drag model for (a) planar interphase precipitation, and (b) fibrous precipitation [3].
2.1.2.2.5 Eutectoid decomposition mechanism

Fig. 2-9. Illustration of eutectoid models [35]: (a) a structure of planar carbides developed with small $\theta_1$ and $\theta_2$, (b) a curved carbides sheet with increase in $\theta_1$ and $\theta_2$, (c) a fibrous structure with further increment of $\theta_1$ and $\theta_2$, and (d) a pearlite structure with $\theta_1$ and $\theta_2$ of high values.
Another approach treating the interphase precipitation is an eutectoid decomposition model [4]. It was presented for Fe-0.11C-1.95 Mo alloy [35], as seen in Fig. 2-9. The formation of all interphase precipitates, including planar precipitate, curved precipitate, and fibrous precipitate, can be explained by two related factors, $\theta_1$ and $\theta_2$, of the eutectoid decomposition model. $\theta_1$ is the angle between the slowest moving $\gamma/\alpha$ boundary orientation and grain boundary plane, and $\theta_2$ is the angle between the slowest moving $\gamma/\alpha$ boundary and the slowest moving $\alpha$/carbide boundary. A planar structure of carbide precipitates develops at small $\theta_1$ and $\theta_2$ (Fig. 2-9 (a)). When $\theta_1$ and $\theta_2$ increase, a curved carbide sheet can be seen (Fig. 2-9 (b)). In Fig. 2-9 (c), a fibrous structure is observed with the further increase of $\theta_1$ and $\theta_2$, and a pearlite structure forms at high values of $\theta_1$ and $\theta_2$ (Fig. 2-9 (d)). This model thermodynamically predicts the various shapes of the precipitates with different factors of $\theta_1$ and $\theta_2$. However, the eutectoid decomposition model leads to a problem in predicting the sheet spacing of interphase precipitates.

From the above discussion on mechanism models of interphase precipitation, it can be seen that extensive research has been carried out to interpret the formation mechanism of interphase precipitate. All these precipitation mechanisms are based on their individual assumptions for specific systems.

### 2.1.3 Precipitation in ferrite

Precipitates after the phase transformation (Fig. 2-10) are produced due to the low solubility of carbon and alloying elements in supersaturated ferrite. During the heat treatment within the ferrite range precipitates mainly nucleate on the dislocation defects in the matrix [36].

There is a dispute in the observation of precipitates in ferrite. Some believed that homogeneous precipitation of NbC was suppressed below about 700°C [37] and no precipitation was observed during coiling [38], while others claimed that when some Nb was left in solution after hot working, precipitation can take place during the coiling [39]. Charleus *et al.* [40] claimed that the nucleation and growth of needle shaped Nb/Ti carbides could take place in ferrite and made an important contribution to the strengthening. However, Kestenbach *et al.* [38] suggested the precipitates observed by Charleux *et al.*
were carbonitride precipitates formed in austenite rather than in ferrite. Afterwards, Charleux et al. confirmed their results by providing the diffraction pattern of the precipitates and interpreted the differences of experimental conditions between their experiment and others’ work. In 2009, the precipitation of Nb carbides in ferrite during coiling was clearly observed by using TEM, and its effect on strengthening the steel was well demonstrated [41].

![Fig. 2-10. Precipitates in ferrite [40].](image)

It can be summarized that the precipitate can form in ferrite when there are abundant soluble alloying elements and available carbon after phase transformation, and the precipitate in ferrite can lead to a significant increase in strength of the low carbon steels.
2.2 Current state of precipitation modelling

The mechanical properties of steels depend on the steel microstructure which closely relates to the distribution, size and morphology of the precipitates [22, 42-44]. If the precipitation can be analysed directly in the detail of microstructure evolution, it would be possible to approach the mechanisms of precipitation [5].

A wealth of research has been carried out to model the microstructure evolution of phase transformation. The available models for steel microstructure are usually in the macro-level and based on the parameters such as stress and temperature. Since the 40’s, a Johnson–Mehl–Avrami–Kolmogorov (JMAK) model has been widely used in different systems to study the kinetics of isothermal phase transformation through nucleation and growth [45] and predict the recrystallization kinetics and microstructure with calibrated parameters [46]. However, this model is at the macroscopic level where the average microstructure property is considered for an entire system.

Computer simulation can provide explanation, description and prediction, and it is suitable for revealing the details behind experiments. An increasing attention has been paid to the computer modelling to understand the phase transformation and kinetics of precipitation in metallic alloy at mesoscopic level [47].

The mesoscopic modelling can not only predict the actual microstructures but also combine with morphology and spatial distribution of microstructure constituent [44, 48]. Phase field modelling and cluster dynamics (CD) methods, etc. are widely used in such scale modelling. The mesoscopic modelling methods have been widely used in figuring out the evolution of precipitates in various alloy systems like V-Fe, Cu-Co, Ni-Al, [49], Al-Sc [7], Fe-Ni [50], and C-Mn steel [51].

Cluster dynamics method has been proven to be able to simulate processes over a wide range of spatial scales. Mesoscopic modelling with CD method could perform the quantitative multi-scale modelling [52]. As a fast and simple method, CD method was used for the kinetics modelling of Al₃Sc and Al₃Zr precipitation [53] in aluminium supersaturated solid solution and for dynamics simulation of the relationship of discrete dislocation and interphase precipitation [54]. CD method can give similar results to Monte Carlo simulations for Cu precipitation [55], which supported the important effects of
coherent cluster mobility on Cu precipitation. However, the absence of real space considerably limits the ability of the CD method to treat concentrated alloys [56].

In some other modelling methods, the growth of precipitates is usually calculated by diffusion equations under the Zener’s assumption [22, 57], while precipitates behave differently depending on various parameters, such as temperature and heating rate. It is irrefutable that modelling using classical theory is qualified in describing order and disorder transformations, and is reasonable in modelling a heterogeneous phase transformation [58]. However, it is found that the description in the classical theory is different from the actual nucleation process. The nucleation, growth and coarsening of precipitates occur simultaneously but the classical method describes nucleation and growth as a continuous process, so the overlap of these processes is unavoidable. In 1992, a concept of ‘nucleation window’ [59] was introduced to discuss the overlap between nucleation and coarsening. To deal with this phenomenon, many valid measures were utilized to approve the methods, such as modifying the parameters or directly neglecting the nucleation stage [7, 60].

Although the mesoscopic modelling methods are useful in managing some complex problems like the multi-component or multi-phase precipitation [61], there are some shortages that restrict their applications. One of the main drawbacks is that the mesoscopic modelling is not as predictive as atomic models, especially for ternary alloys due to the less precise description of precipitation process [48]. Another major problem is about the input parameters. The simulation results of precipitate microstructure in some modelling were proved to be contrary to experiments because of the parameters setting [62], especially in modelling discontinuous precipitation in a multi-phase [11]. It is a challenging task to measure the most of the input parameters involved in the mesoscopic modelling due to the large number of parameters [8] and their sensitive dependences on the diffusivity on interphase. These unidentified parameters led to a diversity of modelling methods and therefore results [9-13]. A precise description of the initial composition of precipitates would be important for setting the parameters to improve the accuracy of modelling.

To date, a precipitation mechanism at the mesoscopic scale that could explain the carbide precipitates formation and growth in HSLA steels is still unavailable.
2.3 Cluster during precipitation process

2.3.1 Cluster/clustering

A non-equilibrium phase was observed during the phase transformation in Al-Mg-Si alloy [1] and Ni-Al-V alloy [63]. This phase has a close chemical composition and a similar crystal structure to the stable precipitated phase, which somewhat governs the subsequent precipitation behaviour, the steel microstructure, and further the mechanical properties. Atom groups constituted this phases were observed by the atom probe field ion microscope [1]. The small atom aggregates were identified and named as “clusters” [64].

The difference of the clusters to the classical nucleus caught some interests. Both have at least two atoms and aggregate with the loss of potential energy. As it is clearly known, the definition of classical nucleation is based on the first irreversible formation of a nucleus of the new phase [65]. The nucleus was generally assumed to have a uniform shape of planar or spherical. “Clusters” with various structures and compositions were observed in precipitation process of steel and alloy.

The clusters serve as the precursors for further precipitation at longer annealing time [64, 66]. Dutta and Allen [64] suggested the precipitation process of Al-Mg-Si alloy consisting of the formations of solute clusters as the first step and the subsequent shaped precipitate as the second step. Edwards et al. [1] confirmed the occurrence of Mg-Si clusters in ageing process. It has been demonstrated that the compositions of the clusters, GP zone and mature precipitates are similar. The process of precipitation can be assumed to include the stages of the formations of clusters, minor precipitates of unidentified structure, and shaped precipitates. The clusters could be reverted in artificial ageing [67]. The clusters observed in Al-1.1Cu-(0.2-0.7)Mg alloys involve a few atoms to tens of atoms [68].

Carbide clusters were detected during the precipitation process in HSLA steels. In 2011, titanium rich clusters were observed with Atom-probe tomography (APT) in severely deformed and annealed steels [69]. Timokhina et al [66] focused on the microstructures of high strength steels with a composition of 0.05C-1.6Mn-0.3Si-0.05Nb-0.2Mo and reported that most of the fine clusters containing Nb and C appeared with an average thickness of 2.5 ± 0.5 nm. The carbide precipitates and carbide clusters of C-Ti-Mo are illustrated in Fig. 2-11.
Fig. 2-11. Three dimensional atom maps for (a, b) Ti-Mo-C interphase precipitates and clusters and (c) a disc-shaped particle [70].

Although carbide clusters have been observed experimentally, the details of their structure, composition, and properties are rarely reported. Because of the close relationship of carbide clusters and precipitates, it is meaningful to investigate the formation mechanism of carbide clusters in HSLA steel. As one of the strength-enhancing carbides, titanium carbide precipitate has attracted much attention due to its ability to maintain nano-scale size and enhance hardness [71, 72] in HSLA steels.

2.3.2 Numerical models of clusters

Due to the small size-scale of carbide clusters, it is very challenging to investigate their atomistic property experimentally. Several distinct approaches have been proposed to
model the nucleation and growth of precipitates. The parameters describing the carbide clusters and precipitates include carbide size, morphology, chemical composition, spatial distribution, and number density, etc [73]. The properties of transition-metal carbide clusters are highly sensitive to their size [74] and shape [75, 76].

A numerical model of precipitation was proposed by Kampmann and Wagner [77], in which the nucleation rate was calculated from the homogeneous or heterogeneous nucleation theory and the concept of critical nucleation radius. Dem Ouden [78] extended the Kampmann-Wagner (KW) numerical model with Robson’s formalism [79] for nucleation and growth of precipitates. Another model which can address the problem of precipitation in multicomponent alloys is the mean-field approach [80, 81]. There is also a modelling approach which is based on the integration of Time Temperature Transformation (TTT) diagrams [82]. Several models, such as the thermodynamic extremum principle [83, 84] and the phase field model [85], have also been used to describe the growth or dissolution of a single precipitate within the matrix.

Another main approach is based on a classical nucleation theory (CNT) [86, 87], which can be used to describe the size distribution, nucleation rate and growth rate. The classical nucleation theory plays a prominent role in the investigation of cluster formation. In CNT, there is an important parameter, a pre-exponential factor, which is derived in terms of the monomer attachment and detachment rates. However, this factor greatly depends on the concentration of potential nucleation sites, which is difficult to be precisely determined. Although CNT method is easily comprehensible, in many cases it cannot accurately predict the nucleation of clusters [88].

The aforementioned models can predict the growth and dissolution of the carbide clusters and precipitates to a certain extent. The majority of these studies just focused on the time evolution of the clusters growth, which cannot describe the formation mechanism of clusters and cluster property in iron matrix. Fortunately, atomic simulation showed its possibility of studying the formation mechanism of carbide clusters.

2.3.3 Atomic simulation of clusters

The computer simulation at atomic level becomes increasingly powerful in fundamental study of material processes, physical properties, and material design. Monte Carlo method (MC) and Molecular Dynamics (MD) simulation are widely used in the material behaviour
simulation at the atomic scale, providing a precise description of alloy carbide microstructure and phase transformation.

The system structures of both MC and MD are typically in the same manner. Both require the molecular depiction, application of force fields and boundary conditions. Their key difference is in the sampling method of the configuration space in system. MC is based on exploring the energy surface by randomly probing the configuration space, which specifies the initial atom coordinates, selects the atom randomly, moves it by random displacement, and then calculates the change of potential energy corresponding to the displacement. MD solves the motion equations of Newton applied for new configurations over a time step. In both methods, it is the force field that decides the system progress by controlling the energy and forces, separately. Due to the current development of computer, it is feasible to use MD or MC to model the phase transformation process clearly and reasonably [5, 20, 56].

The MC simulation provides a substantial description of the kinetic path to understand precipitation kinetics in a great detail. MC simulation can perform the physical rules accurately without restriction to binary alloys [56]. MC simulation suggested that the solute clusters were formed first by the atom migration. This observation was proved at the early stage of precipitation in Al–Zn–Mg–Cu alloy [20]. The MC simulation also was coupled into a multi-scale model to study precipitate morphology in Al–Cu [89] and Fe-Al alloys [90], and the energy contributions to alloy clusters were calculated with the first-principles calculations.

However, the limitation is that in MC performance the atomic positions are determined by the random movements, so an amount of samples are required to obtain a reasonable precision of the results, which is an inefficient process. In addition, only small size system can be considered, making the coarsening out of reach in simulating precipitation process and unable to explain the relationship between clusters and precipitates.

To date, several MD simulations have been performed for the study of precipitate and cluster properties in different systems. For instance, the MD was used to study the interactions between the misfit dislocation and \( \gamma' \) precipitation and got reasonable results [14, 15]. The simulation of a Fe-Cu system with Finnis-Sinclair (FS) potential [91] showed that the interaction between dislocation and precipitation depended on the precipitate size and system temperature. Also, Singh et al. [92] proved the significance of dislocation cross-slip in precipitation hardening by MD simulation. The MD simulation of precipitation in
Ni-Ti thin films predicted a lower energy precipitate which was the same as experimental results, but the MD was not well predicted in the martensite nucleation [93]. Zirkelbach et al. [94] found that the positions of interstitial carbon atoms had an important influence on the formation of C-Si precipitates, and a high system temperature was required for the precipitate formation even at a high C concentration. Overall, the MD simulation can give some valuable information of the interactions between dislocation and precipitation at atomic level. However, the atom clustering mechanism has not been considered in these MD models.

With respect to the atomic modelling of clusters, the MD method showed its ability to reveal atomic structures and structural transformation of binary alloy-alloy clusters such as Fe-Al, Ti-Al and Cu-Ni, etc. Li et al.’s [17] revealed the cluster evolution of Fe-Al in fast solidification with a constant pressure. Shimono and Onodera [18] investigated an amorphous alloy with various Al concentrations in Ti-Al binary system by MD. It was pointed out that there were two regions of structural inhomogeneity in the amorphous state and the structures varied with Al concentration. A cluster type index method was used to define the clusters in MD modelling of Al-Mg clusters during quick solidification [19], by which an icosahedral cluster of Al-Mg amorphous structure was identified during cooling. The MD study of Zhang [95] proved the structural transformation of an Au$_{54}$Cu$_1$ cluster by pair distribution functions. Besides, the influences of size and composition of Cu-Ni clusters were modelled by Li et al.’s [96], in which a good agreement of the MD results with experimental phase diagram was obtained.

Molecular dynamics simulation has been proven to be a powerful and reasonable technique to discover the precipitation process and cluster property. However, these existed atomic models show an incapability of describing the precipitation phenomena in a Fe-Ti-C ternary system due to the complicated interactions in the multi-component system. To date, besides those experiments that confirmed the existence of clusters and the explanation of relationship between clusters and precipitates based on experimental results, there is little study on titanium carbide cluster in Fe-Ti-C system at atomic level.

Therefore, in this work molecular dynamics simulation is used to examine the atomic interactions during initial precipitation process that cannot be observed directly in experiments and provide a better fundamental understanding of the carbide cluster
formation and firm information for the investigation of the precipitate growth, structural
and mechanical properties in high-strength low-alloy steel.

2.4 Summary

Precipitates and clusters form during phase transformation, which can significantly
enhance the strength of the HSLA steel. The precipitation in steels has three main types:
precipitation in austenite, interphase precipitation and precipitation in ferrite. Many kinetic
models explained the process of interphase precipitation in metallic alloys but provided an
inadequate understanding of the mechanism of interphase precipitation.

The clusters are the precursors for precipitates, which determine the subsequent
precipitation process and the structure and property of the mature precipitates, but the
formation mechanism and property of the clusters are unclear. It is meaningful to reveal
the structure and formation mechanism of titanium carbide clusters, and the relationship
between the formation and growth of the clusters, in order to investigate the mechanism of
cluster formation in HSLA steels and thereafter to understand the precipitation mechanism.

Despite an increasing attention has been put on the significance of carbide clusters during
precipitation process, the formation, and structural and mechanical properties of the
clusters are not fully understood. MD simulation has been widely used in the study of
evolution and structure property of alloy clusters and shown to be an efficient and powerful
tool in the simulation of clusters, which can provide information of atomic interaction and
fundamental statistic to understand the clusters behaviour. However, there is no MD
simulation of the titanium carbide cluster formation process in a ternary Fe-Ti-C system.
Chapter 3 Simulation Methodology

Molecular dynamics (MD) simulation technology will be used to investigate the atomistic structure and properties, formation mechanism, and growth behaviour of titanium carbide clusters in ferrite matrix. The details of the MD simulation, including the cluster-matrix systems, implementation strategy, force field, and characterization methods of titanium carbide clusters, are outlined in this chapter. Two basic strategies of MD simulation, i.e., the force field that can be used to sufficiently and accurately describe the interatomic interaction energy for the atomistic system of interest and the atomistic models, and the unified computational methods that can approach the properties of interest without significantly depending on the model, are discussed in detail.

3.1 Molecular dynamics system

The most important step of the art of MD simulation is to build a molecular model that represents the real material properties and interactions at molecular level but does not considerably increase the computational effort. The construction of a model generally includes system configuration, minimization and equilibrium.

The generation of the initial configuration for the model is the first and the most significant step, including the determination of cell size and the type and location of each of atoms constituting the model. In the present work, the domain of the model was determined based on the crystal structure and lattice parameters of the respective phases: it was large enough to produce reliable results that can represent the materials properties and be as small as possible in order to, productively, implement the computations with physical infrastructures available.

As the present work will focus on the precipitation of TiC from ferrite, a matrix of ferrite was firstly created. The ferrite model is a cell box of body-centred cubic (bcc) Fe, \(a = 2.87\) Å with periodical boundary conditions, as shown in Fig. 3-1 (a). In a bcc Fe unit cell, one atom is located in the centre of the cubic unit, and other atoms locate at each corner of the unit. Each atom in the bcc iron matrix has a coordination number of eight.
As mentioned above, the titanium carbide (TiC) cluster will be the subject of this work. Titanium displays a typical hexagonal close-packed (hcp) crystal structure with a lattice parameter of 2.95 Å. Each atom in hcp titanium has twelve nearest neighbours, six in the same close packed layer, three in the layer above and three in the layer below [97]. The lattice parameter for diamond carbon is 3.56 Å. Diamond cubic is in the Fd3m space group, following the face-centred cubic Bravais lattice. The diamond crystal structure is a repeating pattern of eight atoms [98]. In the ferrite matrix, titanium as a solute atom takes the place of an iron atom, and carbon as an interstitial atom is located at the hollow sites of iron atoms. In the creation of the initial structure of the model, the change in local matrix structure (coordinates of iron atoms) due to the addition of titanium and carbon atoms were not considered at this step, as shown by an example in Fig. 3-1 (b). The non-equilibrium initial structure will be minimized to create the modelling system, which will be discussed in the end of this section.

![Fig. 3-1. (a) Bcc Fe cell and (b) the locations of Ti and C atoms in matrix (Fe in white, Ti in Black, and C in red).](image)

Precipitation of TiC greatly depends on the variation of solubility conditions of Ti and C atoms in steel. In ferrite, the maximum solubility of titanium is 8.4 wt.% at 1562 K, 0.53 wt.% at 873 K and 0.15 wt.% at 673 K; the maximum solubility of carbon is 0.02% at 996 K and 0.008% at 0 K [99]. Note that a relatively high content of titanium would lead to the
formation of intermetallic compounds, such as Fe$_2$Ti and Fe$_3$Ti in Fe-C alloys [100]. Ti at a low content rarely dissolves in cementite but can form carbides [101]. Thus, the content of Ti should be controlled in a reasonable high level in the ferrite matrix to facilitate the formation of carbide cluster and avoid the formation of Fe$_x$Ti$_y$.

The results of MD simulations somewhat depend on the atomistic/molecular models used, such as the model size. Generally, models should be large enough to produce the properties of interest, without significantly depending on the model, through effective computational methods. However, simulations of a large model usually require a long computational times. The most CPU intensive task is the evaluation of the potential (force field) as a function of the internal coordinates of the particles in the model. In the present work, a force field that also contains the interactions of atoms with their second layer neighbours will be used. The computational cost will be significantly increased, because, in a classical MD simulation, the most expensive one is the calculation of the non-bounded parts.

To determine a suitable simulation cell, MD simulations were carried out for the models with different sizes (a 10×10×10 bcc iron box, a 15×15×15 bcc iron box, and a 20×20×20 bcc iron box) to compare the dependence of simulation results on model size. It was found that the activation energy of carbon in the simulation cell of 20×20×20 bcc iron matrix was only 0.08 % higher than that from 15×15×15 bcc iron cell and 0.12 % higher than that from 10×10×10 bcc iron cell. The simulation results and detailed comparison will be given in Section 3.3.2.2. It was also observed that the titanium and carbon atoms were successfully aggregated in all the models, which meant the formation of small titanium carbide clusters was independent on the cell size. Considering the calculation accuracy and computational efficiency, an iron matrix with 10×10×10 bcc Fe (28.7 Å × 28.7 Å × 28.7 Å in volume) is expected to be large enough to study the characteristics and formation of the small clusters of interest in the present work. Besides, large rectangle cells will be used to investigate the growth and aggregation of titanium carbide clusters in ferrite matrix.

It is well known that the preferential nucleation sites for precipitation are at the regions of dislocations, grain boundaries, deformation bands and second-phase particles [102] and the dislocations are the most favourable sites [103-105]. The dislocations can prominently accelerate the precipitation kinetics [106, 107], because they change the spatial distribution of diffusion paths, leading to precipitate nucleation and coarsening. This is also the reason that dislocations always act as solute collectors for the formations of NbC [101] and TiC.
In that context, as one of objectives of the present work, the investigation of the formation and growth of titanium carbide clusters will focus on dislocations. Ferrite matrices containing designed dislocation defects were then created for the simulations.

The initial simulation systems are non-equilibrium, so an energy minimization is required for each system to relax strained local conformations. In the present work, a fine mathematical algorithm [109] was applied in the energy minimization. After the simulation systems reach equilibrium, dynamics simulations were performed to approach the behaviours and properties concerned. The details of the performance of MD simulations will be introduced in next section.

### 3.2 Performance of MD simulation

#### 3.2.1 MD codes

There are some molecular dynamics codes, such as TINKER [110], Material Studio, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [111], Nanoscale Molecular Dynamics program (NAMD) [112], and XMD (Molecular Dynamics for Metals and Ceramics) [113].

The selection of modelling technique should be closely aligned with the material system, the force field for the materials and the material properties of interest in the research. LAMMPS has been widely applied in the simulation of metal process and was adopted in this work. LAMMPS [111] was released by Sandia National Laboratories as a classical MD code. A wide range of potentials, such as Lennard-Jones (L-J) potential [114], Finnis-Sinclair (FS) potential [115], Embedded Atom Method (EAM) [116] force field, Modified Embedded Atom Method (MEAM) [117], and second nearest-neighbour modified embedded atom method (2NN.MEAM) [118] force field can be applied. More important is that LAMMPS is majorly designed for solid systems, which can appropriately and efficiently to disclose the phenomenon of metal field at atomic level.

Post-processing of the atomic information requires various techniques and computational tools to effectively analyse and visualise simulation results. Several software can be used to visualize cluster activity. Visual Molecular Dynamics (VMD) [119] is a graphical front end for LAMMPS code, which provides a wide range of rendering and colouring the atoms and the animation and displaying the simulation trajectory. Origin (OriginLab,
Northampton, MA), a statistical calculation program, will be used for data analysis and standard graphing.

### 3.2.2 Simulation conditions

Boundary conditions for the simulation cells need to be set in all MD simulations. Periodic boundary conditions were used in all directions (x, y, and z) of the models. With periodic boundary conditions, when an atom passes through one side of the cell, it can enter in the cell from the opposite side with the same velocity, which enables the simulation cell to maintain a constant atom number during the cluster formation and growth processes. Also, each individual atom in the simulation also interacts with the closest image of the remaining atoms in the system, so the boundary effect on the simulation domain can be avoided.

In a simulation, a statistical ensemble is required to be defined to represent the states of the modelling system. One ensemble is Isobaric-Isothermal (NPT) ensemble with constant particle number, pressure and temperature [120]. Gibbs free energy is the characteristic state function of the NPT, while its thermodynamic potential relates to Helmholtz free energy. In order to get good simulation results with no external pressure effect, the NPT ensemble could be considered during the simulation of phase transformation. In the present work, the NPT ensemble was used in the minimization of the models and equilibrium dynamics. The temperature and pressure was controlled by modified Nose and Hoover’s equations [121, 122]. Another important ensemble is canonical ensemble (NVT) [121], in which the atom number, the system volume and the system temperature are constant. The NVT ensemble is treated as a measure of Gibbs free energy because it relates to the Markov property of statistical independence. The NVT ensemble is extensively applied for the thermodynamic calculation under a fixed temperature. It does well in maintaining a stable atomic relationship and preventing the structure deformation by stress at fixed box volume and temperature. In the present study, this ensemble was applied in the dynamic simulation of the carbide cluster formation and growth during the isothermal annealing process.

Implementation of MD simulations is through the calculation of forces and solution of the motion equations. It contains two steps, namely predictor and corrector, to solve the motion equations and other extra steps such as the control, analysis and output of temperature and pressure. With the development of MD simulation technology, a series of mathematical algorithms have been proposed for the integration of motion equations. The popularly adopted algorithms are Verlet [123], Velocity Verlet [124], Leap-frog [125] and Beeman’s
algorithms [126]. The decision in choosing algorithm should be based on the following criteria. Firstly, the algorithm should have the ability to record energy and momentum of atoms. Secondly, the algorithm must be efficient for computer running. Lastly, it should be capable of performing the calculation at a long time step for system integration.

Verlet algorithm has been the most popular time integration algorithm since 1967 [123]. This algorithm is welcomed among MD simulators due to its simplicity of implementation and its accurate and stable properties. However, it has the drawback that velocity is not directly generated. Furthermore, the computational error from the calculation positions is of order $\Delta t^2$ ($\Delta t$, time step) rather than $\Delta t^4$. Thus, variations of the Verlet algorithm have been developed to solve this problem. Velocity Verlet is a better algorithm than the basic one, in which the positions at the time $t+\Delta t$ is predicted by the positions and accelerations at the time $t$ and the positions at the time $t-\Delta t$. For Velocity Verlet, it asks for $9N$ ($N$, number) memory locations for the storage of $3N$ positions, velocities and accelerations. The standard for an excellent algorithm is that it can reach the global or local minimum and be able to easily approach the minimum energy from another situation. Therefore, the Velocity Verlet algorithm will be adopted in this study for its efficient and effective performance.

The time step, which defines the integration time, is to ensure the stability of numerical time integration. The time step in mathematical algorithms is significant, and the determination of the time step should keep the error of the integration method within a certain level of accuracy to maintain the stable atom motions and structures and also improve the computation efficiency. Thus, a suitable time step is one of the key points to achieve a good MD performance. In most cases, integration time is usually fixed to about 1 femtosecond (fs) to keep an efficient and accurate MD simulation for metals.

3.3 Force fields for Fe-Ti-C system

The principles that control the atomic interactions in molecular systems are defined in terms of interatomic potentials for either classical or semi-classical atomic simulations. A suitable potential is fundamental for the atomic simulation, so the accuracy, transferability and computational speed should be considered in choosing potential.

Lennard-Jones potential [114] is effective for gases. For metal phase transformation simulations, L-J potential is not suitable. The controlling potentials that could be applicable to solve this problem are Finnis-Sinclair potential [115], ReaxFF potential [127], and
Embedded Atom Method [116]. EAM was improved to replace the volume-dependent energy of pair potential by accounting for the electron density-dependence. Due to its advantage in the definable electron density, the EAM is frequently adopted in MD simulations of crystal structure, dynamics and phase transformation and diffusions [128]. The initial EAM potential was extended by adding the angular forces and the Modified Embedded Atom Method (MEAM) [117] can well describe the alloys of bcc, hcp, fcc, and diamond cubic structures, in which the system total energy is presented by

\[ E = \sum_i \left[ F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi_j(R_{ij}) \right] \]  

where \( F_i \) is the embedding function, \( \bar{\rho}_i \) is the background electron density at site \( i \), and \( \phi_j(R_{ij}) \) is the pair interaction between atoms \( i \) and \( j \) at a distance \( R_{ij} \).

The energy per atom of MEAM is calculated from the equation of Rose et al. [129], relating to the nearest-neighbour distance \( R \):

\[ F\left[ \rho^0(R) \right] + \frac{1}{2} \sum \phi(R) = E^u(R) = -E_c \left( 1 + \alpha^* \right) e^{-\alpha^*} \]  

and

\[ \alpha^* = \alpha \left( \frac{R}{r_c} - 1 \right) \]  

and

\[ \alpha = \left( \frac{9B\Omega}{E_c} \right)^{1/2} \]  

where \( E^u(R) \) represents the functions for structure expansion or contraction, \( B \) represents the bulk modulus, and \( \Omega \) is the equilibrium atomic volume. The expression for the pair potential between two atoms with distance \( R \), \( \phi(R) \), is deduced as follows, in which \( Z_i \) represents the number of the first nearest-neighbour atoms.
The modified embedded-atom method potential can describe the interatomic relationship of many metals with various crystal structures using the same formalism, but the MEAM was formulated to consider only nearest neighbour interactions by using a screening function. Although the second nearest neighbours have a larger distance than the first nearest-neighbour in bcc structure, their interaction with the concerned atom cannot be neglected to approach a more accurate physical properties of the considered system.

### 3.3.1 2NN.MEAM Force field

A second nearest-neighbour modified embedded atom method (2NN.MEAM) [118] was developed to modify the MEAM, which involves the second nearest-neighbour interactions. 2NN.MEAM has been adopted to measure the parameters for both bcc and hcp transition metals, such as Fe, Ti, V, Mo [130], for binary alloy systems, like Fe-C [131], Fe-Ti, Fe-Mo, Fe-W, Ti-C [132], Mo-C and W-C, and for ternary systems such as Fe-Ti-C and Fe-Nb-C [133].

In 2NN.MEAM, the energy per atom in a specific structure is calculated by:

\[
E^\alpha(R) = F(\rho^\alpha(R)) + \frac{Z_1}{2} \phi(R) + \frac{Z_2 S}{2} \phi(aR)
\]

where the third term in the right hand side is the contribution of the second nearest neighbour. \(Z_2\) is the numbers of second nearest-neighbour atom and \(a\) is the ratio between the second and first nearest-neighbour distance. \(S\) is a many body screening function between atoms \(i\) and \(j\), which is defined as the product of the screening factors, \(S_{kj}\), due to all other neighbour atoms \(k\),

\[
S = \prod_{k \neq i, j} S_{kj}
\]
where $S_{ikj}$ is identified using an ellipse construction, which passes through atoms, $i$, $k$ and $j$ with the $x$ axis of the ellipse determined by atoms $i$ and $j$. The screening factor, $S_{ikj}$ is defined as a function of $C$ as follows:

$$S_{ikj} = f_i\left[\frac{(C - C_{\text{min}})}{(C_{\text{max}} - C_{\text{min}})}\right]$$

where $C_{\text{min}}$ and $C_{\text{max}}$ are the limiting values of $C$ determining the extent of screening.

Generally, 2NN.MEAM formalism has fourteen main parameters for pure elements: cohesive energy ($E_c$), nearest neighbour distance ($r_e$), bulk modulus ($B$), and $d$ for the universal equation of state, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, $t^{(1)}$, $t^{(2)}$, and $t^{(3)}$ for the electron density, $A$ for the embedding function, and $C_{\text{min}}$ and $C_{\text{max}}$ for the many-body screening.

The body-centred cubic ($bcc$), diamond and hexagonal close-packed ($hcp$) structure were selected as the reference structure of iron, carbon and titanium, and the values of the above parameters were obtained from experimental information on $bcc$ Fe, diamond C and $hcp$ Ti. The potential parameters of Fe, Ti, and C are listed in Table 3-1.

Fig. 3-2. A schematic illustration for the interaction screening in ternary Fe-Ti-C systems. The symbols, $i$, $j$ and $k$, represent Fe, Ti and C, respectively.
Table 3-1. 2NN.MEAM potential parameters for Fe [130], Ti [134] and C [131].

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ti</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c$ (eV)</td>
<td>4.29</td>
<td>4.87</td>
<td>7.37</td>
</tr>
<tr>
<td>$r_e$ (Å)</td>
<td>2.48</td>
<td>2.92</td>
<td>1.54</td>
</tr>
<tr>
<td>$B$ ($10^{12}$dyn/cm²)</td>
<td>1.73</td>
<td>1.1</td>
<td>4.45</td>
</tr>
<tr>
<td>$A$</td>
<td>0.56</td>
<td>0.66</td>
<td>1.18</td>
</tr>
<tr>
<td>$\beta^{(0)}$</td>
<td>4.15</td>
<td>2.7</td>
<td>4.25</td>
</tr>
<tr>
<td>$\beta^{(1)}$</td>
<td>1</td>
<td>1</td>
<td>2.8</td>
</tr>
<tr>
<td>$\beta^{(2)}$</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>$\beta^{(3)}$</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>$\tau^{(1)}$</td>
<td>2.6</td>
<td>6.8</td>
<td>3.2</td>
</tr>
<tr>
<td>$\tau^{(2)}$</td>
<td>1.8</td>
<td>-2</td>
<td>1.44</td>
</tr>
<tr>
<td>$\tau^{(3)}$</td>
<td>-7.2</td>
<td>-12</td>
<td>-4.48</td>
</tr>
<tr>
<td>$C_{max}$</td>
<td>2.8</td>
<td>1</td>
<td>2.8</td>
</tr>
<tr>
<td>$C_{min}$</td>
<td>0.36</td>
<td>1.44</td>
<td>1.41</td>
</tr>
<tr>
<td>$S$</td>
<td>0.91</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>$d$</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>/</td>
<td>/</td>
<td>0.3</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>/</td>
<td>/</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Note: $E_c$: sublimation energy, $r_e$: equilibrium nearest-neighbour distance, and $B$: bulk modulus.
Table 3-2. 2NN.MEAM potential parameters for the Fe–C [131], Fe-Ti [135] and Ti-C [132] binary systems.

<table>
<thead>
<tr>
<th></th>
<th>Fe-C</th>
<th>Fe-Ti</th>
<th>Ti-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c$ (eV)</td>
<td>$0.75E_c^{Fe} + 0.25E_c^{C} + 0.95$</td>
<td>$0.5E_c^{Fe} + 0.5E_c^{Ti} - 0.22$</td>
<td>$0.5E_c^{Ti} + 0.5E_c^{C} - 0.78$</td>
</tr>
<tr>
<td>$r_e$ (Å)</td>
<td>2.364</td>
<td>2.58</td>
<td>2.21</td>
</tr>
<tr>
<td>$B$</td>
<td>$(10^{12}\text{dyn/cm}^2)$</td>
<td>$(10^{12}\text{dyn/cm}^2)$</td>
<td>$(10^{12}\text{dyn/cm}^2)$</td>
</tr>
<tr>
<td>$d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{min}(\text{Fe-C-Fe})$</td>
<td>0.36 $C_{max}(\text{Fe-C-Fe})$ 2.80</td>
<td>$C_{min}(\text{Fe-Ti-Fe})$ 1.21</td>
<td>$C_{min}(\text{Ti-C-Ti})$ 0.64</td>
</tr>
<tr>
<td>$C_{min}(\text{C-Fe-C})$</td>
<td>0.16 $C_{max}(\text{C-Fe-C})$ 1.44</td>
<td>$C_{min}(\text{Fe-Ti-Ti})$ 0.78</td>
<td>$C_{min}(\text{Ti-C-Ti})$ 0.64</td>
</tr>
<tr>
<td>$C_{min}(\text{Fe-Fe-C})$</td>
<td>0.16 $C_{max}(\text{Fe-Fe-C})$ 2.80</td>
<td>$C_{min}(\text{Ti-C-Ti})$ 0.64</td>
<td>$C_{min}(\text{Ti-C-Ti})$ 0.64</td>
</tr>
<tr>
<td>$C_{min}(\text{Fe-C-C})$</td>
<td>0.16 $C_{max}(\text{Fe-C-C})$ 2.80</td>
<td>$C_{min}(\text{Ti-C-Ti})$ 0.64</td>
<td>$C_{min}(\text{Ti-C-Ti})$ 0.64</td>
</tr>
<tr>
<td>$C_{min}(\text{Fe-C-C})$</td>
<td>0.16 $C_{max}(\text{Fe-C-C})$ 2.80</td>
<td>$C_{min}(\text{Ti-C-Ti})$ 0.64</td>
<td>$C_{min}(\text{Ti-C-Ti})$ 0.64</td>
</tr>
<tr>
<td>$C_{min}(\text{Fe-Ti-Fe})$</td>
<td>$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$ $C_{max}(\text{Fe-Ti-Fe})$ 2.80</td>
<td>$C_{min}(\text{Fe-Ti-C})$ $[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$ $C_{max}(\text{Fe-Ti-C})$ 2.80</td>
<td></td>
</tr>
<tr>
<td>$C_{min}(\text{Ti-Fe-Ti})$</td>
<td>$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$ $C_{max}(\text{Fe-Ti-Ti})$ 2.80</td>
<td>$C_{min}(\text{Fe-Ti-C})$ $[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$ $C_{max}(\text{Fe-Ti-C})$ 2.80</td>
<td></td>
</tr>
<tr>
<td>$C_{min}(\text{Fe-Fe-Ti})$</td>
<td>$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$ $C_{max}(\text{Fe-Ti-C})$ 2.80</td>
<td>$C_{min}(\text{Fe-Ti-C})$ $[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$ $C_{max}(\text{Fe-Ti-C})$ 2.80</td>
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</tr>
<tr>
<td>$C_{min}(\text{Fe-C-C})$</td>
<td>$[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$ $C_{max}(\text{Fe-Ti-C})$ 2.80</td>
<td>$C_{min}(\text{Fe-Ti-C})$ $[0.5(C_{min}^{Fe})^{1/2} + 0.5(C_{min}^{Ti})^{1/2}]^2$ $C_{max}(\text{Fe-Ti-C})$ 2.80</td>
<td></td>
</tr>
<tr>
<td>$\rho_o$</td>
<td>$\rho_o^{Fe}/\rho_o^{C}=6$</td>
<td>$\rho_o^{Fe}/\rho_o^{Ti}=1$</td>
<td>$\rho_o^{C}/\rho_o^{Ti}=6$</td>
</tr>
</tbody>
</table>

Note: The reference structures for Fe-C, Ti-C, and Fe-Ti are the L1$_2$ Fe$_3$C, NaCl-type (B1) TiC, and CsCl-type (B2) FeTi, respectively.
Chapter 3: Simulation Methodology

Table 3-3. Parameter sets of $C_{\text{max}}$ and $C_{\text{min}}$ for Fe-Ti-C ternary systems [133].

<table>
<thead>
<tr>
<th>Type</th>
<th>$C(i-k-j)$</th>
<th>$C(i-j-k)$</th>
<th>$C(j-i-k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$0.5(C_{\text{Fe--Fe}})<em>{1/2}+0.5(C</em>{\text{Ti--Ti}})_{1/2}$</td>
<td>$0.5(C_{\text{Fe--Fe}})<em>{1/2}+0.5(C</em>{\text{Ti--Ti}})_{1/2}$</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>$0.5(C_{\text{Fe--Fe}})<em>{1/2}+0.5(C</em>{\text{Ti--Ti}})_{1/2}$</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
</tr>
<tr>
<td>C</td>
<td>$0.5(C_{\text{Fe--Fe}})<em>{1/2}+0.5(C</em>{\text{Ti--Ti}})_{1/2}$</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
</tr>
<tr>
<td>D</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
<td>$0.5(C_{\text{Fe--Fe}})<em>{1/2}+0.5(C</em>{\text{Ti--Ti}})_{1/2}$</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
</tr>
<tr>
<td>F</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
</tr>
<tr>
<td>G</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
<td>$0.5(C_{\text{Fe--Fe}})<em>{1/2}+0.5(C</em>{\text{Ti--Ti}})_{1/2}$</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
</tr>
<tr>
<td>I</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
<td>Ti-C binary ($C_{\text{Ti--Ti}}$)</td>
<td>Fe-C binary ($C_{\text{Fe--Fe}}$)</td>
</tr>
</tbody>
</table>

*Note: The symbols, $i$, $j$ and $k$ represent Fe, Ti and C, respectively.*

Table 3-2 lists the parameters of 2NN.MEAM potential for Fe-C [131], Fe-Ti [135] and Ti-C [132] binary systems. A B2 FeTi compound was used to serve as a reference structure for Fe-Ti system. A NaCl-type TiC ordered structure was chosen as reference structure for Ti-C system. Although many (semi-)empirical interatomic potentials have been developed for the Fe-C binary system [136-138], these investigations either ignored the carbon-carbon interaction in iron matrix or cannot describe the physical properties of pure-carbon well. The 2NN.MEAM can give an accurate description of the physical properties over the entire composition range.
It is difficult to develop a (semi-) empirical interatomic potential that can deal with a ternary system of Fe, Ti, and C in order to investigate the effects of carbide precipitates on steel properties at atomistic level. In a ternary Fe-Ti-C system, a new screening factor of 2NN.MEAM is introduced for the screening of interactions between two neighbour atoms of different types by a third element atom, which is illustrated in Fig. 3-2. The parameter sets for the Fe-Ti-C system are listed in Table 3-3.

### 3.3.2 Force field verification

#### 3.3.2.1 Structural, physical and thermal properties

The 2NN.MEAM potential was adopted to calculate several structural, physical and thermal properties of iron, titanium and carbon in order to evaluate its reliability in the application of titanium carbide study in iron matrix. The lattice parameters, cohesive energy, vacancy formation energy, formation energy of self-interstitial, melting point, and thermal expansion were calculated and compared with data from references (Table 3-4).

<table>
<thead>
<tr>
<th></th>
<th>Bcc Fe</th>
<th>Hcp Ti</th>
<th>Diamond C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>Ref.</td>
<td>MD</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>2.864</td>
<td>2.866</td>
<td>2.945</td>
</tr>
<tr>
<td>(E_{coh}) (eV)</td>
<td>-4.29</td>
<td>/</td>
<td>-4.87</td>
</tr>
<tr>
<td>(E_v) (eV)</td>
<td>1.759</td>
<td>1.79 [97]</td>
<td>1.783</td>
</tr>
<tr>
<td>(E_i) (eV)</td>
<td>4.343</td>
<td>/</td>
<td>3.738</td>
</tr>
<tr>
<td>(T_m) (K)</td>
<td>2200</td>
<td>1811 [141]</td>
<td>1706</td>
</tr>
<tr>
<td>(\varepsilon) (10^{-6}/K)</td>
<td>12.4</td>
<td>12.1 [142]</td>
<td>10.2</td>
</tr>
</tbody>
</table>

**Note:** \(a\): the lattice parameter, \(E_{coh}\): cohesive energy per atom, \(E_v\): vacancy formation energy, \(E_i\): formation energy of self-interstitials, \(T_m\): melting point, and \(\varepsilon\): thermal expansion.
For unary systems, the lattice parameters calculated for bcc Fe, hcp Ti and diamond C are in good agreement with the experimental data [97, 139]. The calculated cohesive energy per atom, $E_{coh}$ (eV), vacancy formation energy, $E_v$ (eV), and self-interstitial formation energy, $E_i$ (eV), agree well with the experimental results, although the $E_v$ of C is smaller than the result in Ref. [97]. The 2NN.MEAM gives a higher melting point of Fe than the experimental data, which is caused by the influence of the large radial cut-off distances used. For Ti, as the potential cannot predict the phase transformation from hcp to bcc at 1155 K, the calculated melting point in this study comes from the metastable melting of hcp Ti, which is different to the experimentally measured melting point. The thermal expansion of Fe with 2NN.MEAM is in good agreement with the experiment, while the thermal expansions of Ti and C are slightly larger than the experimental data. For the unitary systems of iron, titanium and carbon, it can be seen that 2NN.MEAM can well produce the bulk properties.

2NN.MEAM can reasonably predict the experimental results and well reproduce the physical, structural and thermal properties of the Fe-Ti, Fe-C, and Ti-C systems. In binary Fe-Ti system, 2NN.MEAM can give a lattice parameter of 2.98 Å for FeTi, which agrees well with the experimental data [144], and the elastic constant of FeTi from this potential is the same as experimental results [145]. In Fe-C system, the dilute heat of solution of carbon (1.22 eV) is comparable to the experimental value [146]. The migration energy barrier of carbon in iron (0.9 eV) agrees well with the experimental results [147, 148]. The vacancy-carbon binding energy is in the range of the values obtained from experiments [147, 149, 150], but the self-interstitial-carbon energy (0.68 eV) is a little larger than the calculation from the experiment [136]. In Ti-C system, the melting point of titanium carbide calculated with the potential is 3000–3500 K [132]. The NaCl-type of TiC is the most stable structure with 2NN.MEAM force field. The calculated enthalpy of titanium formation is the same as the experimental results.

It can be concluded that the 2NN.MEAM can well produce the structural, physical and thermal properties of Fe, Ti and C systems. As it is noticed that the 2NN.MEAM gives a high melting point of Fe and a different melting point for Ti with the experimental work, a stable matrix should be maintained by setting a reasonable temperature range to avoid the phase transformation in cluster simulations.
3.3.2.2 Transport property

The diffusion of solute and interstitial elements generally governs the precipitate formation and growth. A force field that can precisely describe the diffusion properties of the elements constituted the metal system is essential to accurately model the formation and growth of clusters.

To verify the force field, the diffusions of carbon and titanium in iron, carbon in cementite, and carbon in titanium carbide were simulated with the force field. For the carbon and titanium diffusions in iron, the diffusion of one atom in an iron matrix (10×10×10 \textit{bcc} Fe) over a temperature range from 950 K to 1050 K was simulated. For the calculation of carbon diffusion in cementite, 768 iron atoms and 256 carbon atoms were used and the simulations were at temperatures ranging from 1200 K to 2500 K. For the carbon diffusion in titanium carbides, 2248 titanium atoms and 2249 carbon atoms were included in the simulation box, and the temperature ranged from 1000 K to 2000 K.

The models were initially minimized to allow the atoms occupy their equilibrium positions in local potential minima. After that, the NPT ensemble with periodic boundary conditions was used for each diffusion simulation at different temperatures. Velocity Verlet algorithm is used as time integration. The MD simulations run with a time step of 1 fs. Thermodynamic averages were computed over 10 ps. All the simulations were performed for up to 5 ns.

The diffusivities of carbon and titanium were calculated from MD simulations based on the Einstein’s equation [151] (see section 3.4.1 for details). If assuming that the results follow the Arrhenius law [151], the estimated pre-exponential factor, $D_0$, (m$^2$/s) and the activation energy, $E_m$, (eV) are calculated by,

$$D = D_0 \exp(-\beta E_m)$$  \hspace{1cm} 3-9

where $D$ is the diffusion coefficient, $\beta=(k_B T)^{-1}$, $T$ is the absolute temperature, and $k_B$ is the Boltzmann constant.

3.3.2.2.1 Mechanisms of carbon and titanium diffusions in iron

The atom trajectories from the simulations of Ti and C diffusion in Fe matrix are summarized in Fig. 3-3 and 3-4.
Fig. 3-3 illustrates that carbon diffuses mainly via an interstitial jumping diffusion mechanism, jumping from a four-hold hollow site to another hollow site of Fe through a path between two iron atoms. The atomic mechanism of carbon movement in iron crystal has also been found experimentally and by atomic simulation [152-155].

Fig. 3-3. The interstitial diffusion of carbon in iron matrix. To clearly illustrate the path of carbon, only one Fe layer is shown. The diffusion follows that (A) C vibrates in the hollow site, and then (B) jumps to a new site through a path between iron atoms.

Fig. 3-4. The exchange diffusion of titanium in Fe matrix. Only one Fe layer is shown. The diffusion follows that (A) Ti vibrates at the site, and then (B) moves to a new site that was occupied by a Fe atom.
The titanium atom trajectories (Fig. 3-4) show that the Ti takes a site of Fe. An exchange diffusion mechanism was found for Ti. The diffused Ti atom moves from its location to one of its neighboured Fe sites, while the Fe atom is drifted away. This observation corresponds to the vacancy exchange mechanism found experimentally [156, 157].

3.3.2.2.2 Diffusivities of carbon and titanium in Fe

*Diffusion of C in Fe*

From the calculated diffusivities, the activation energy is estimated to be 0.81 eV for C diffusion in iron, and the value of $E_m$ agrees well with the experimental result (0.81 eV [158]). The pre-exponential factor $D_0$ is estimated to be $1.6\times10^{-7}$ m$^2$/s. $D_0$ from the present MD results is smaller than the experimental results ($1.67\times10^{-7}$ m$^2$/s [158] and $2\times10^{-6}$ m$^2$/s [159]). Fig. 3-5 displays the difference of the MD results with the experimental data [158, 159]. Considering the impurity in the experimental environment and different temperature range, this difference is acceptable.

![Graph showing comparison of carbon diffusion in iron matrix with experimental results](image_url)

Fig. 3-5. Comparison of carbon diffusion in iron matrix with the experimental results (Ref a, [158]; derivation from Ref b, [159]).
The activation energy of carbon in a $15\times15\times15\ bcc$ iron matrix and a $20\times20\times20\ bcc$ iron matrix were also calculated. There is a slight change of the activation energy of carbon in the matrix with different sizes. In the $15\times15\times15\ bcc$ iron matrix, the activation energy calculated is only 0.04\% larger than that in the $10\times10\times10\ bcc$ iron box, while the activation energy calculated from the $20\times20\times20\ bcc$ iron matrix is 0.08\% larger than that from the $15\times15\times15\ bcc$ iron matrix. The influence of the matrix size on the activation energy is little.

It can be concluded that the 2NN.MEAM of Fe-C is able to well produce transport property. As a result, this potential can be adopted with confidence to describe the interactions between carbon and iron.

*Diffusion of Ti in Fe*

![Graph](image)

Fig. 3-6. Comparison of titanium diffusion in iron matrix with the experimental results (Ref a, [156]; Ref b, [157]).

For titanium diffusion in iron, the pre-exponential factor $D_0$ is estimated to be $7.37 \times 10^{-2}$ m$^2$/s and the activation energy is estimated to be 2.24 eV. The active energy, $E_m$, obtained in this work is close to the experimental value (2.52 eV) [156]. The comparison of the MD
results with experimental data is shown in Fig. 3-6. It was found that the pre-exponential factor is larger than the experimental data. The calculation of the diffusivity of Ti was based on 5.0 ns MD dynamic. This simulation is not sufficiently long to produce a significant Ti migration for calculating diffusivity.

3.3.2.2.3 Carbon diffusion in cementite

The simulation results were compared with experimental data (Fig. 3-7). From simulation results, the calculated activation energy for carbon diffusion in cementite is 1.56 eV and the calculated pre-exponential factor $D_0$ is $1.15 \times 10^{-6}$ m$^2$/s. It is found out that the estimated $D_0$ is close to the experimental values ($1.30 \times 10^{-6}$ m$^2$/s) from the summary of Hillert [160] and Ozturk et al [161] and another experimental data from Levchenko et al ($0.14 \times 10^{-6}$ m$^2$/s) [162]. The agreement between the $E_m$ from this work (1.60 eV) and the experimental data (1.81 eV) [162] is also reasonable. The potential produced a good representation for the carbon diffusion in cementite. This result provided a solid support for the subsequent studies.

![Fig. 3-7. Comparison of carbon diffusion in cementite with the experimental results (Ref a, [162]; Ref b, summary of [160, 161]).](image-url)
3.3.2.4 Carbon diffusion in titanium carbides

From the simulation results, the activation energy for C diffusion in titanium carbides is 0.98 eV and the pre-exponential factor $D_0$ is $1.56 \times 10^{-9} \text{ m}^2/\text{s}$. Fig. 3-8 shows the comparison of the MD results with the values obtained experimentally. In view of the scarcity of the experimental and simulation data, it is not easy to determine the activation energy and pre-exponential factor accurately. Nevertheless, it can be still concluded that $D_0$ estimated in this study is close to the value derived from the experimental data at 673~873 K [163] and has a good agreement with the experimental data at 873~1073 K [164]. The activity energy $E_m$ of this study is also in the range of the experimental results (0.41~3.81 eV). Overall, this potential can well predict the carbon diffusion in titanium carbides.

The above MD simulations showed that the 2NN.MEAM force field can produce a reasonable results for C and Ti diffusion in iron, C diffusion in cementite, and C diffusion...
in titanium carbides. It is difficult to estimate the deviation of MD results to the experimental data due to the large difference in diffusivity between the experimental data obtained by various methods for different impurities in materials; however the predicted dependence of diffusion on temperature is in good agreement with the experimental results.

Consequently, the 2NN.MEAM potential was proved to be qualified to describe the Fe-Ti-C system and it will be used in the simulations of the formation and growth of titanium carbide clusters. However, long computational time, large storage memory and disc space will be required for the simulations of the Fe-Ti-C system, because the interactions of each atom with its second nearest neighbours are also involved in this potential. This drawback of 2NN.MEAM should be considered in building MD models.

### 3.4 Characterization of clusters

The properties and the formation and growth processes of carbide clusters are obtained by analysing the dump files containing the evolution of the system conditions with time, such as locations, temperatures, pressures, and potential energy during the MD simulations.

#### 3.4.1 Atomic diffusivity

The performance of titanium and carbon atoms during cluster formation in iron matrix can be directly identified through their transport properties, which not only contributes to the cluster formation but also determines the growth of formed clusters. To measure the diffusion behaviour of the atoms in matrix, the mean-squared displacement (MSD) and diffusion coefficients were calculated.

The mean-squared displacement is defined by the displacement of an atom from its original position, which is used to measure the average distance of one reference group. The MSD is defined by [151],

\[
MSD(t) = \left\langle \Delta r_i(t)^2 \right\rangle = \left\langle (r_i(t) - r_i(0))^2 \right\rangle
\]

where \(r_i(t) - r_i(0)\) is the (vector) distance migrated by atom \(i\) over time \(t\), and the squared magnitude of this vector is averaged.

The diffusion coefficient, \(D\), is calculated from MSD by Einstein’s equation,
where \( MSD(t) \) is the MSD for time \( t \).

### 3.4.2 Structure identification

As it is known that carbide clusters are not well-shaped, especially these formed at the initial formation stage, identifying and comparing the structure of clusters are of great importance. In iron matrix, cluster structure refers to the patterns and correlations that atoms exhibit in their placement in space, which is important because it has direct effects on the behaviour of the bulk material.

To examine the structural features of clusters, pair distribution function, \( g(r) \), was used to quantify the average structure, which describes the probability of finding an atom \( b \) with distance \( (r) \) from an atom \( a \) [169].

\[
g(r) = \frac{1}{N_a N_b} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \langle \delta(|\mathbf{r}_i - \mathbf{r}_j| - r) \rangle
\]

where \( N_a \) and \( N_b \) are the atom numbers of atom \( a \) and atom \( b \).

### 3.4.3 Energy property

The variation of various energies in system contains a very abundant information in explaining cluster stability, binding ability and energy driving force.

#### 3.4.3.1 Formation energy

The formation energy of TiC clusters in iron matrix was calculated to compare the stability of formed clusters. For cluster of Ti\( _x \)C\( _y \) the formation energy \( (E_f) \) was determined by,

\[
E_f = E_{\text{cluster}} - xE_{Ti} - yE_{C},
\]

where \( E_{\text{cluster}}, xE_{Ti} \) and \( yE_{C} \) are the total energies for Ti\( _x \)C\( _y \) cluster, titanium atoms and carbon atoms, respectively. Forming bond is always exothermic, which causes a negative value. Thus, the cluster with larger formation energy should be more stable.

#### 3.4.3.2 Dissociation energy

The dissociation energy was also used to evaluate the stability. It is defined by
for dissociation process of Cluster → A + B [170]. The right-hand terms, $E_A$, $E_B$, and $E_{\text{cluster}}$, are the energies of the products A and B and the total energy of the cluster, respectively. It is known that breaking bond is always endothermic; clusters with a negative dissociation energy should be taken as unstable.

3.4.3.3 Free energy

The variation of free energy was determined using Adaptive Biasing Force method (ABF), which adopts an average force to overcome the free energy barriers in the simulations. The development of ABF is mainly based on three aspects, including the unconstrained thermodynamic integration, adaptive bias based on a local estimate, and a unique representation for the free energy derivative. The average biasing force approach [171, 172] is through the accumulated $F_\zeta$ in small bins of finite size to estimate the derivative $dA(\zeta)/d\zeta$. The force that applied along the reaction coordinate to overcome free energy barriers is calculated by,

$$ F_{\text{ABF}} = \nabla_\zeta \tilde{A} = -\left\langle F_\zeta \right\rangle \nabla_\zeta \zeta $$

where $\tilde{A}$ represents the current estimate of the free energy, and $\left\langle F_\zeta \right\rangle$ is the current average force of instantaneous component, $F_\zeta$.

The aim of the ABF method is therefore twofold: to serve as an adaptive significant sampling approach, and to figure out free energy differences quickly. In this method, it is the self-diffusion property that controls the evolution of the system along $\zeta$. The evaluation of the force is under the classical thermodynamics integration formulation. During the molecular simulation, the derivation of free energy is locally collected, which leads to the update of biasing force. This ABF method can give an accurate computation of free energy, because of its ability in sampling the values of the reaction coordinate with an equal probability.

3.5 Summary

Based on the brief introduction of molecular dynamics simulation technology, the key issues in MD simulation, including models, force field, periodic boundary conditions,
ensembles and calculation algorithms, were determined for studying the properties and the formation of small titanium carbide clusters in ferrite.

As one of the most important problems that are normally encountered in molecular dynamics simulation, the selection of force field was discussed by comparing the potentials available for the Fe-Ti-C system. The force field of named 2NN.MEAM was chosen due to its capability in describing ternary systems and the consideration of the second nearest-neighbour interactions. The force field was evaluated through comparing the resulting structural, physical and thermal properties of iron, titanium and carbon and the predicted diffusion coefficients of carbon in iron, titanium in iron, carbon in cementite, and carbon in titanium carbides with the experiments. The potential of 2NN.MEAM shows reliable in describing the interatomic interactions for Fe-Ti-C system.

Because 2NN.MEAM force field includes the interactions of the atoms with their second nearest neighbour atoms, which will significantly increase the computational time, as another basic problem in MD simulation, the size of the atomistic models becomes more important to approach the properties that do not significantly depend on the model. To determine the model size, the carbon diffusion in different iron matrices was calculated. The simulation of titanium carbide clusters in the matrix was also performed and the results showed that a $10\times10\times10$ bcc Fe matrix is efficient for achieve model-independent properties of small clusters.

The main methods and techniques used to characterise the structural properties and formation features of clusters in ferrite were introduced, including the mean-squared displacement method for the calculation of diffusion coefficient, pair distribution function for cluster structure identification. The methods for calculating formation energy and dissociation energy were proposed to evaluate the stability of clusters. The Adaptive Biasing Force method was introduced to calculate the driving force of cluster formation.
Chapter 4 Atomic Structure of TiC Clusters in Ferrite

In this chapter the TiC clusters that can form in ferrite are determined. The properties of the titanium carbide clusters, including structure and structural features, atomic interaction, formation potential and dissociation property, are analysed to identify the stable titanium carbide clusters in ferrite. The comparison of TiC clusters in ferrite with corresponding independent TiC clusters are carried out to reveal the interaction between the cluster and the matrix.

4.1 Introduction

Computer simulation presents a strong capability to analyse the properties of clusters at the atomic level. The studies on the titanium carbide clusters were mainly focused on the crystal growth, equilibrium structure, and the dependence of structural and electronic properties on cluster size [173-175], for some specific compositions, such as TiC$_n$ ($n = 2 - 5$) [176], TiC$_4$ and TiC$_4$ [177], TiC$_n$ ($n \leq 8$) [170], Ti$_4$C$_4$ and Ti$_{14}$C$_{13}$ [178], Ti$_6$C$_{12}$ [179], and Ti$_6$C$_6$ and Ti$_{12}$C$_{12}$ [180]. For TiC$_n$ ($n \leq 8$) clusters [170], it was found that the stable structure was closely related to the atom number and isomers. The structures of Ti$_6$C$_6$ and Ti$_{12}$C$_{12}$ clusters that exhibit the bulk-like rock salt structure appear to be the most energetically stable [180]. The above studies are for independent clusters, i.e., the interaction between carbide cluster and the host material, such as iron matrix, is not considered in the modelling.

The host material presents a significant influence on the structural and energy properties of clusters due to the interactions of the matrix atoms with the cluster atoms. To date, the structure and energy properties of titanium carbide clusters and the interactions between cluster and iron matrix are still unclear.
4.2 Determination of clusters in ferrite

It has been experimentally found that the size of carbide clusters formed in ferrite, defined as the total number of Ti and C atoms, can up to several tens [68, 181]. It is impossible to consider all the titanium carbide clusters, as a large cluster includes numerous isomers. Here the term of “isomer” is used to state those clusters with the same atom number of each element but having different arrangements of their atoms in space. As seen in Fig. 4-1, most studies on the structure of titanium carbide clusters only considered the clusters with less than thirty atoms. This work also focuses on the titanium carbide clusters formed in ferrite at the initial stage of precipitation, and clusters of no more than twenty atoms are considered here.

Fig. 4-1. The size and composition of clusters (Ref. 1 [178], Ref. 2 [180], Ref. 3 [182], Ref. 4 [179], Ref. 5 [183], Ref. 6 [177], Ref. 7 [176], and Ref. 8 [170]).

The titanium carbide clusters chosen for the present work are Ti$_{x}$C$_{y}$ ($x+y \leq 4$) clusters, Ti$_{x}$C$_{y}$ ($x = 4$ and $y = 6 - 12$) clusters, and Ti$_{y}$C$_{x}$ ($x+y = 20$) clusters. This design allows us to examine and compare the structure and stability of titanium carbide clusters with
the same composition but different sizes and with the same size but different compositions. The TiC clusters and according independent (ind)-TiC clusters are investigated and compared. Here, the ind-TiC clusters are the titanium carbide clusters not in the iron matrix.

For ind-Ti$_x$C$_y$ ($x+y \leq 4$) clusters, the one-dimensional, two-dimensional, and three-dimensional isomers are considered. For the clusters having the same size but different compositions, Ti$_x$C$_y$ ($x+y = 20$, $y \geq x$), the ind-TiC clusters are generated by replacing the Ti sites of the NaCl-type Ti$_{10}$C$_{10}$ cluster with C atoms [184]. For the clusters that have different sizes and different compositions, Ti$_x$C$_y$ ($x = 4$ and $y = 6 - 12$), the ind-TiC clusters are generated by adding carbon atoms in pairs to the NaCl-type Ti$_4$C$_4$ cluster.

The structural optimization was performed for all generated clusters to determine the stable ind-TiC clusters. The generated clusters were minimized in vacuum by the steepest descent algorithm [109] for 500 ps in the NPT ensemble. The potential energy was used to evaluate the stability of the structure. Only the isomer out of all isomers for each ind-cluster which has the minimum potential energy after MD equilibration was considered as the stable one [185]. Each of the stable ind-TiC clusters was then located in a ferrite matrix and then minimized to investigate the interaction between matrix and cluster atoms. The formation energy calculation was based on the equation 3-13.

### 4.3 Ti$_x$C$_y$ ($x+y \leq 4$) clusters

#### 4.3.1 Structure

The clusters, Ti$_x$C$_y$ ($x+y \leq 4$), investigated include TiC, Ti$_2$C, Ti$_3$C, TiC$_3$, Ti$_4$C and Ti$_2$C$_2$ with different structures, as shown in Fig. 4-2. For TiC, there is only a 1D-linear structure. In addition to a linear structure, a 2D-ring structure exists in TiC$_2$, Ti$_2$C, TiC$_3$, Ti$_3$C and Ti$_2$C$_2$, and the last three also have a structure in 3D. Some of the clusters have more than one structure, for instance, Ti$_x$C$_y$ ($x+y = 4$) clusters have a 2D four-atom ring structure and a 2D structure where a single atom is located outside a three-atom ring. Only the one which has the minimum potential energy after MD equilibration is considered as the stable structure [185] and presented in Fig. 4-2.
Chapter 4: Atomic Structure of TiC Clusters in Ferrite

Fig. 4-2. Structures of Ti$_x$C$_y$ ($x+y \leq 4$) clusters in iron matrix and corresponding structures of independent clusters.
The optimized structures for Ti$_x$C$_y$ ($x+y \leq 4$) clusters can be classified into three main types: (i) 1D-linear; (ii) 2D-ring, where titanium and carbon atoms are bonded in a circle; (iii) 3D-tetrahedral.

### 4.3.2 Formation energy

Table 4-1 presents the interatomic distance and formation energy of Ti$_x$C$_y$ clusters. The results were compared with those from the density functional theory (DFT) calculation for some structures [170]. For linear *ind*-TiC$_2$, the DFT gives $d_{12} = 1.86$ Å and $d_{23} = 1.281$ Å, which are approximately the same as the MD values of 1.83 Å and 1.29 Å in this study. The interatomic distances of linear *ind*-TiC$_3$ from the two methods are also in good agreement. For the ring structure of *ind*-TiC$_2$, the DFT values of $d_{12}$, $d_{23}$ and $d_{13}$ are 1.973 Å, 1.291 Å and 1.973 Å, respectively; the distances from MD are 1.95 Å, 1.31 Å and 1.95 Å. The differences may be attributed to the calculation methods and the precision of the force field used in this work.

Ti$_x$C$_y$ clusters in an iron matrix are different to the *ind*-Ti$_x$C$_y$ clusters, which can be concluded by comparing the structural parameters between them. The calculation of the root mean square (RMS) of the interatomic distances for all clusters in iron matrix gives 2.36 Å for $d_{\text{Ti-Ti}}$ and 2.23 Å for $d_{\text{C-C}}$, which are larger than those of the *ind*-clusters ($d_{\text{Ti-Ti}, \text{RMS}} = 2.08$ Å and $d_{\text{C-C}, \text{RMS}} = 1.86$ Å). The changes in RMS of Ti-C distances between the clusters in iron matrix and the *ind*-cluster are different for the different types of structures. For linear and ring structures, the RMS values of $d_{\text{Ti-C}}$ in the iron matrix (line: 1.65 Å, ring: 1.66 Å) are smaller than those not in the matrix (line: 1.74 Å, ring: 1.86 Å), indicating a smaller size of clusters in the iron matrix. On the contrary, the quadratic mean of the Ti-C atomic distances of the tetrahedral clusters (RMS 2.09 Å) is larger than that without the matrix (RMS 1.79 Å).
Table 4-1. Interatomic distance, $d_{ij}$ (Å) and formation energy, $E_f$ (eV) of the Ti$_x$C$_y$ ($x+y \leq 4$) clusters.

<table>
<thead>
<tr>
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<th>$d_{14}$</th>
<th>$d_{23}$</th>
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<td>(1.94)</td>
<td>-</td>
<td>(1.70)</td>
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Notes: $d_{ij}$ is the distance between atoms $i$ and $j$ (refer to Fig. 4-2); the values in the brackets are for the $nnd$ Ti$_x$C$_y$ clusters.
Fig. 4-3. Potential energy of Ti$_x$C$_y$ clusters with (a) line, (b) ring and (c) tetrahedron structures.
Due to the different structures, the clusters in the iron matrix show a different property compared to the *ind*-clusters. The potential energy of each cluster was calculated in order to compare the clusters in the iron matrix with the *ind*-clusters and to analyse the contribution of the interaction of cluster with matrix to the total energy of the cluster. Fig. 4-3 clearly shows the change in the potential energy between the clusters in the iron matrix and the *ind*-clusters. When considering the numbers of interactions of both Ti-Fe and C-Fe, it is not hard to understand that the energy change has a close relationship with the cluster size and structure. The energy change of linear TiC is not obvious due to the small size and simple structure, compared to other structures. Normally, a cluster in an iron matrix has a lower total energy than an *ind*-cluster that has the same atomic number and equilibrium structure, due to the contribution of interatomic interaction energy of the cluster with its surrounding Fe atoms. Furthermore, the formation energies of *ind*-cluster and cluster in matrix are different. For instance, the clusters in an iron matrix have lower formation energies than *ind*-Ti$_x$C$_y$ clusters, except TiC and Ti$_2$C$_2$.

The stability of titanium carbide clusters depends on both the composition and structure. For the clusters of Ti$_x$C$_y$ ($x+y = 3$), the atomic distances of ring TiC$_2$ ($d_{12} = 1.4$ Å, $d_{13} = 1.32$ Å, $d_{23} = 1.89$ Å) are smaller than ring Ti$_2$C ($d_{12} = 1.6$ Å, $d_{13} = 1.47$ Å, $d_{23} = 2.48$ Å). TiC$_2$ also has a higher formation energy (0.85 eV for a linear structure and 0.90 eV for ring structure) than Ti$_2$C (0.71 eV for linear and 0.74 eV for ring). It is found that the ring Ti$_x$C$_y$ ($x+y = 3$) clusters are more stable than the linear structures. This finding was also confirmed with the DFT study [170] which showed the ring TiC$_2$ was the most stable isomer.

For the clusters of Ti$_x$C$_y$ ($x+y = 4$), both the theoretical study of Largo [170] and photoelectron spectra results of Wang’s [176] ignored the three-dimensional structure and the ring structure of TiC$_3$ was identified to have a stronger stability than the linear structure. Besides the ring and linear structures, the present MD study considered the
three-dimensional tetrahedral structure for the $\text{Ti}_x\text{C}_y (x+y=4)$ clusters. The largest formation energy of the tetrahedral structures among the three structures shows that the 3D tetrahedral structure of $\text{TiC}_3$, $\text{Ti}_2\text{C}_2$ and $\text{Ti}_3\text{C}$ is the most stable one.

### 4.3.3 Dissociation property

The dissociation properties, in particular the dissociation path and energy, of the $\text{Ti}_x\text{C}_y$ clusters in iron matrix were characterized. To define the dissociation energy for the dissociation path of $\text{Ti}_x\text{C}_y$ Cluster $\rightarrow$ A + B, the energies of the products A and B and the total energy of the cluster were calculated, respectively, as the equation 3-14 shows. The dissociation of clusters were carried out in an iron matrix, and all the $\text{Ti}_x\text{C}_y$ clusters and the products are minimized by the steepest descent algorithm [109] for 500 ps in the NPT ensemble.

It can be seen in Table 4-2, for the $\text{Ti}_x\text{C}_y (x+y=3)$ clusters in an iron matrix, linear structures ($E_d$: 0.21 eV for $\text{TiC}_2$ and 0.07 eV for $\text{Ti}_2\text{C}$) more easily decompose than the ring structures (0.26 eV for $\text{TiC}_2$ and 0.10 eV for $\text{Ti}_2\text{C}$), indicating the ring structures are more stable, which agrees with the results of the formation energy. For the ring structures, $\text{Ti}_2\text{C}$ is easier than $\text{TiC}_2$ to decompose to one $\text{TiC}$ and a single Ti/C atom. This can be interpreted by the tighter interatomic structure of the $\text{TiC}_2$ cluster in the matrix than $\text{Ti}_2\text{C}$.

In the case of $\text{Ti}_x\text{C}_y (x+y=4)$ clusters, the dissociation characteristics apparently depend on the dissociation channel. The tetrahedral-$\text{TiC}_3$ decomposes via releasing one C atom, $\text{TiC}_3 \rightarrow \text{TiC}_2 + \text{C}$. The dissociation of $\text{Ti}_2\text{C}_2$ is through releasing a single Ti or C atom or decomposing to two $\text{TiC}$ clusters. The transfer of $\text{Ti}_3\text{C} \rightarrow \text{Ti}_2\text{C} + \text{Ti}$ in iron matrix is easier compared with $\text{Ti}_2\text{C}_2 \rightarrow \text{TiC}_2 + \text{Ti}$.
Table 4-2. Dissociation path and dissociation energy, $E_d$, (eV) for the Ti$_x$C$_y$ clusters in an iron matrix.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Type</th>
<th>Path</th>
<th>$E_d$</th>
</tr>
</thead>
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</tr>
<tr>
<td></td>
<td>Ring</td>
<td>TiC+C</td>
<td>0.26</td>
</tr>
<tr>
<td>Ti$_2$C</td>
<td>Line</td>
<td>TiC+Ti</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Ring</td>
<td>TiC+Ti</td>
<td>0.10</td>
</tr>
<tr>
<td>TiC$_3$</td>
<td>Line</td>
<td>TiC$_2$+C</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Ring</td>
<td>TiC$_2$+C</td>
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<td>Tetrahedron</td>
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</tr>
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</tr>
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</tr>
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</table>

4.4 Structures of Ti$_4$C$_y$ ($y = 6 - 12$) and Ti$_x$C$_y$ ($x+y = 20$) cluster

4.4.1 Cluster configuration

The structures of ind-TiC clusters and TiC clusters in an iron matrix are presented and compared in Fig. 4-4. For ind-Ti$_4$C$_y$ clusters, there are two main series of structures: one has an approximate NaCl-type structure (structure a) and the other is a multi-layer
structure (structure b). In this study the carbon atoms that were added in pairs to create the structures of Ti$_4$C$_y$ were identified as C$_{add}$. In ind-Ti$_4$C$_6$ that has an approximate NaCl-type structure (a), the bond lengths of C$_{add}$-Ti and C$_{add}$-C are 2.05 Å and 1.41 Å, respectively. The multi-layer ind-Ti$_4$C$_6$ (b) is composed of C$_{add}$-C$_{add}$ pairs (1.34 Å) and Ti$_4$-C$_4$ pairs (1.97 Å). Ind-Ti$_4$C$_8$ (a) can be assumed as the result of two C atoms taking the places of two Ti sites in NaCl-type Ti$_6$C$_6$, where the bond length of C$_{add}$-C is 1.52 Å. Ind-Ti$_4$C$_8$ (b) shows a layer-by-layer structure (C layer - Ti layer - C layer) and the value of $d_{Ti-C}$ is 2.01 Å. The structure of ind-Ti$_4$C$_{10}$ (a) looks like two extra C atoms locating in the opposite corners of Ti$_4$C$_8$ (a); the bond length of C$_{add}$-C is shortened to 1.34 Å. Ind-Ti$_4$C$_{10}$ (b) consists of a top pentagon C layer, a middle Ti layer and a bottom pentagon C layer. Likewise, one stable structure of Ti$_4$C$_{12}$, (Ti$_4$C$_{12}$ (a)), is a deformed NaCl-type structure with a value of $d_{Ti-C}$ ranging from 1.95 Å to 2.18 Å, while the other (Ti$_4$C$_{12}$ (b)) is packed by two hexagon C layers with 1.43 Å of $d_{C-C}$ and one square Ti layer in the middle.

Comparing clusters with a similar size but different compositions, ind-Ti$_x$C$_y$ (each $x+y$ is approximately the same, while C/Ti ratio varies), it can be found that with the increase in C/Ti ratio (from Ti$_9$C$_{11}$, Ti$_8$C$_{12}$, Ti$_7$C$_{14}$, Ti$_6$C$_{15}$ to Ti$_5$C$_{15}$), the NaCl-type structure in the ind-clusters disappears gradually. Both structures of each ind-Ti$_x$C$_y$ cluster are without a clearly defined structure.

It is found that most of the values of $d_{Ti-C}$ for ind-TiC clusters are approximately the same as the value for TiC bulk, 2.161 Å [180], but a slight contraction is observed in the TiC clusters. The contraction in structure (Ti-C bonds reduced to 1.94 Å~2.07 Å) was also confirmed by DFT calculation [180] which can be attributed to the low coordination of these surface atoms together with the relatively small cluster size. On the contrary, a higher $d_{Ti-C}$ value (2.18 Å) is found in the ind-Ti$_4$C$_{12}$ cluster compared to the TiC bulk. This larger bond distance is normally observed in the innermost part of the structure.
Chapter 4: Atomic Structure of TiC Clusters in Ferrite

| Ti₄Cₓ | Geometry     | | Ti₆Cₓ | Geometry     |
|-------|-------------| |-------|-------------|
|       | Ind-cluster | In matrix |       | Ind-cluster | In matrix |
|       | (a)         |           |       | (a)         |           |
| Ti₄C₆ | (b)         |           | Ti₉C₁₁| (b)         |
| Ti₄C₈ | (a)         |           | Ti₈C₁₂| (a)         |
| Ti₄C₁₀| (b)         |           | Ti₇C₁₄| (b)         |
| Ti₄C₁₂| (a)         |           | Ti₆C₁₅| (a)         |
| Ti₅C₁₅| (b)         |           | Ti₃C₁₅| (b)         |

Fig. 4-4. Geometries of Ti₄Cₓ (x=6, 8, 10, and 12) and Ti₆Cₓ (x+y=20 or 21) clusters
(Ti in black, C in red, Fe in white and only Fe atoms close to the clusters are presented).
Fig. 4-5. RMS of $d_{\text{Ti-C}}$, $d_{\text{Ti-Ti}}$ and $d_{\text{C-C}}$ of (a) $\text{Ti}_4\text{C}_y$ clusters and (b) $\text{Ti}_x\text{C}_y$ clusters in an iron matrix.
There is a significant difference in the structure between the TiC clusters in an iron matrix and the ind-clusters. It is found that the structures of ind-Ti,xC,y (x+y ≤ 4) clusters can be maintained in the matrix. Different to the interaction of ind-Ti,xC,y (x+y ≤ 4) clusters with the matrix the structures of ind-Ti4C,y (y = 6 - 12) and ind-Ti,xC,y (x+y = 20) clusters are totally changed in the iron matrix (Fig. 4-4), as the interactions of the matrix atoms and the cluster atoms become stronger with the increase in cluster size. The influence of the matrix can be analysed by comparing the root mean square of atom distances for clusters in an iron matrix and all ind-TiC clusters. For ind-TiC clusters, the calculation gives 2.89 Å for dTi-Ti, 1.55 Å for dC-C and 2.24 Å for dTi-C, which are larger than those of the TiC clusters in the matrix (dTi-Ti, RMS = 2.74 Å, dC-C, RMS = 1.45 Å and dTi-C, RMS = 2.02 Å), indicating a smaller size of clusters in the iron matrix.

The TiC cluster structure in the iron matrix has a close relationship with cluster size and composition. For Ti4C,y clusters (Fig. 4-5 (a)), the RMS of dTi-C slightly increases from 1.99 Å of Ti4C6 to 2.03 Å of Ti4C12, and the dTi-Ti increases from 2.62 Å of Ti4C6 to 2.82 Å of Ti4C12, while dC-C is in the range of 1.38 Å to 1.52 Å. For the Ti,xC,y (x+y = 20) clusters in ferrite, the change of dTi-C with the C/Ti ratio is not obvious (Fig. 4-5 (b)), whereas both dTi-Ti and dC-C decrease with the increase in the C/Ti ratio, indicating a more compact cluster in iron matrix.

4.4.2 Stability

The formation energy of ind-TiC cluster, scaled by per atom, is calculated to evaluate the stability of clusters [173]. Cluster formation is always exothermic, which causes a negative value. The cluster with a larger formation energy per atom is more stable.

The formation energy has a close relationship with cluster size, composition and structure. Table 4-3 shows that the formation energy per atom increases from 0.87 eV of ind-Ti4C6 isomer (a) to 1.17 eV of ind-Ti4C10 isomer (a) and then decreases to 0.7
eV of \textit{ind}-Ti$_4$C$_{12}$ (a), indicating the most stable \textit{ind}-cluster is Ti$_4$C$_{10}$ with an approximate NaCl-type structure. The size dependence of \textit{ind}-TiC cluster stability (Table 4-3) was also confirmed by the density functional theory study of TiC$_n$ ($n \leq 8$) clusters [170].

In regards to the influence of structure on the stability, \textit{ind}-Ti$_4$C$_y$ with approximate NaCl-type structure (a) has a larger formation energy per atom than the layer by layer structure (b), because, normally, the extra carbons in NaCl-type clusters would cause the inner core structure to be almost intact [186]. However, an exception is for \textit{ind}-Ti$_4$C$_8$. The layer by layer structure (\textit{ind}-Ti$_4$C$_8$ (b)) has a larger formation energy per atom than the approximate NaCl-type structure (\textit{ind}-Ti$_4$C$_8$ (a)), implying that doping atom does not always enhance cluster stability [186].

The dependence of the stability of \textit{ind}-Ti$_x$C$_y$ ($x+y=20$) clusters on their composition can be found by comparing the formation energy (Table 4-4). The \textit{ind}-Ti$_x$C$_y$ (b) has a higher formation energy per atom than the \textit{ind}-Ti$_x$C$_y$ (a), which means the former is more stable for Ti$_x$C$_y$ clusters. The comparison of energy of \textit{ind}-Ti$_x$C$_y$ clusters shows that Ti$_6$C$_{15}$ (b) has the highest formation energy per atom and it is 1.26 eV, indicating Ti$_6$C$_{15}$ is the most stable cluster in the interested independent clusters. It can be concluded that the \textit{ind}-TiC cluster with about a C/Ti ratio of 2.5 is the most stable.

Table 4-5 and Table 4-6 show the formation energy per atom for TiC clusters in an iron matrix. For each cluster the formation energies of the two types of structures are somewhat different. Also, the variation of formation energy indicates a significant size and composition dependence of cluster stability in an iron matrix, as the \textit{ind}-TiC clusters do. For Ti$_x$C$_y$ clusters the relative stable structures are Ti$_4$C$_6$ (b), Ti$_4$C$_8$ (a), Ti$_4$C$_{10}$ (b) and Ti$_4$C$_{12}$ (b). For Ti$_x$C$_y$ ($x+y=20$) the structures with higher formation energy are Ti$_9$C$_{11}$ (a) Ti$_8$C$_{12}$ (a), Ti$_7$C$_{14}$ (a), Ti$_6$C$_{15}$ (b) and Ti$_5$C$_{15}$ (b). Among these concerned clusters the most stable small cluster is Ti$_4$C$_8$, which has a C/Ti ratio of 2, while for large clusters ($x+y = 20$) Ti$_8$C$_{12}$ has the highest formation energy.
Table 4-3. Formation energy per atom of $ind$-Ti$_4$C$_y$ clusters.

<table>
<thead>
<tr>
<th>$ind$-Ti$_4$C$_y$</th>
<th>Geometry</th>
<th>$-E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_4$C$_6$</td>
<td>(a)</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.85</td>
</tr>
<tr>
<td>Ti$_4$C$_8$</td>
<td>(a)</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.00</td>
</tr>
<tr>
<td>Ti$<em>4$C$</em>{10}$</td>
<td>(a)</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.09</td>
</tr>
<tr>
<td>Ti$<em>4$C$</em>{12}$</td>
<td>(a)</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 4-4. Formation energy per atom of $ind$-Ti$_x$C$_y$ clusters.

<table>
<thead>
<tr>
<th>$ind$-Ti$_x$C$_y$</th>
<th>Geometry</th>
<th>$-E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>9$C$</em>{11}$</td>
<td>(a)</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.71</td>
</tr>
<tr>
<td>Ti$<em>8$C$</em>{12}$</td>
<td>(a)</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.08</td>
</tr>
<tr>
<td>Ti$<em>7$C$</em>{14}$</td>
<td>(a)</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.08</td>
</tr>
<tr>
<td>Ti$<em>6$C$</em>{15}$</td>
<td>(a)</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.26</td>
</tr>
<tr>
<td>Ti$<em>5$C$</em>{15}$</td>
<td>(a)</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>1.12</td>
</tr>
</tbody>
</table>
Table 4-5. Formation energy per atom of Ti$_4$C$_y$ clusters in a matrix.

<table>
<thead>
<tr>
<th>Ti$_4$C$_y$ in matrix</th>
<th>Geometry</th>
<th>-$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_4$C$_6$</td>
<td>(a)</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.25</td>
</tr>
<tr>
<td>Ti$_4$C$_8$</td>
<td>(a)</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.27</td>
</tr>
<tr>
<td>Ti$<em>4$C$</em>{10}$</td>
<td>(a)</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.20</td>
</tr>
<tr>
<td>Ti$<em>4$C$</em>{12}$</td>
<td>(a)</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 4-6. Formation energy per atom of Ti$_x$C$_y$ clusters in a matrix.

<table>
<thead>
<tr>
<th>Ti$_x$C$_y$ in matrix</th>
<th>Geometry</th>
<th>-$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>9$C$</em>{11}$</td>
<td>(a)</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.33</td>
</tr>
<tr>
<td>Ti$<em>8$C$</em>{12}$</td>
<td>(a)</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.39</td>
</tr>
<tr>
<td>Ti$<em>7$C$</em>{14}$</td>
<td>(a)</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.26</td>
</tr>
<tr>
<td>Ti$<em>6$C$</em>{15}$</td>
<td>(a)</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.19</td>
</tr>
<tr>
<td>Ti$<em>5$C$</em>{15}$</td>
<td>(a)</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.16</td>
</tr>
</tbody>
</table>
The stability of clusters depends on the matrix, for instance, the most stable Ti$_4$C$_y$ cluster in the iron matrix is Ti$_4$C$_8$, and whereas the simulation for *ind*-clusters gives that the most stable cluster is *ind*-Ti$_4$C$_{10}$. In the iron matrix, titanium atoms tend to take place of Fe sites and carbon atoms locate the in iron matrix as interstitial atoms. This restriction together with the interatomic interaction forces lead to the difference in structure, and then the stability.

In this study even though it was found that the most stable clusters in iron matrix are Ti$_4$C$_8$ and Ti$_8$C$_{12}$ for Ti$_4$C$_y$ and Ti$_x$C$_y$ ($x+y=20$) clusters, respectively, the cluster can be present in any of its structure formula during precipitation. The formation of clusters greatly depends on the local environment in the system, such as the concentration of carbon and titanium atoms, other alloy elements, temperature and structural defect.

### 4.5 Summary

In this chapter, the characteristics of titanium carbide clusters in a ferrite matrix were investigated for the first time through examining the properties of the clusters, including structure, atomic interaction and stability. The main conclusions are as follows.

1. Results of Ti$_x$C$_y$ ($x+y \leq 4$) clusters show that the TiC clusters in iron matrix are different to the *ind*-TiC clusters. The root mean square of $d_{Ti-Ti}$ and $d_{C-C}$ for clusters in an iron matrix are larger than those of the *ind*-clusters, and the RMS change of $d_{Ti-C}$ between the clusters in an iron matrix and the *ind*-clusters depends on the structure types. The Ti$_x$C$_y$ ($x+y \leq 4$) clusters in the iron matrix have lower formation energies than *ind*-clusters, except TiC and Ti$_2$C$_2$.

2. The analysis of formation energy and dissociation energy of clusters in ferrite show that the stability of Ti$_x$C$_y$ ($x+y \leq 4$) clusters depends on their structures. The ring
**Chapter 4: Atomic Structure of TiC Clusters in Ferrite**

Ti\(_x\)C\(_y\) \((x+y = 3)\) clusters are more stable than the linear structures. For the clusters of Ti\(_x\)C\(_y\) \((x+y = 4)\), it is observed that the 3D tetrahedral structure is the most stable.

3. The main difference between the *ind*-cluster and cluster in the iron matrix is due to the atomic interaction of matrix atoms with cluster atoms. The structures of *ind*-Ti\(_4\)C\(_y\) \((y = 6 - 12)\) and *ind*-Ti\(_x\)C\(_y\) \((x+y = 20)\) clusters are greatly different to these in the iron matrix. The interactions of the matrix atoms and the cluster atoms become stronger with an increase in cluster size.

4. It is observed that the TiC cluster structure in iron matrix has a close relationship with cluster size and composition. Although the change of \(d_{C-C}\) for Ti\(_x\)C\(_y\) clusters is not obvious, the RMS of \(d_{Ti-C}\) and \(d_{Ti-Ti}\) increases with the cluster size. For Ti\(_x\)C\(_y\) \((x+y = 20)\) clusters, the decrease in \(d_{Ti-Ti}\) and \(d_{C-C}\) with the increase in the C/Ti ratio indicates the cluster with a larger C/Ti ratio is more compact in the iron matrix.

5. The calculation of formation energy indicates size and composition dependence of the cluster stability in the iron matrix. The formation energy analysis elucidates that the most stable Ti\(_x\)C\(_y\) \((x+y \leq 20)\) cluster in ferrite has a C/Ti ratio of 1.5 to 2.
Chapter 5 Cluster Formation in Ferrite

This chapter presents the MD results of atom clustering behaviour in ferrite and discloses the formation process of titanium carbide clusters during the isothermal annealing process. Firstly, a dislocation-motivated formation model is introduced. After that, the sources for titanium carbide cluster formation in ferrite is discussed by (i) analysing the atomic interactions during formation process; and (ii) evaluating the driving force for atomic aggregation. The cluster evolution with time is analysed, including cluster structural and energy property and characteristics of cluster components. Lastly, the influences of temperature, carbon concentration, and defect on the cluster formation are examined in detail.

5.1 Formation model and MD procedure

It has been identified experimentally that the preferential nucleation sites for precipitation are at the regions of dislocations, grain boundaries, deformation bands and second-phase particles [102], among them dislocation is primarily responsible for the nucleation of precipitates [104, 105]. A dislocation-motivated formation model was then generated in this study to investigate the cluster formation. The model was built in a cubic box of \textit{bcc} Fe with periodic boundary conditions. An edge dislocation was allocated in the centre of box, and the Burgers vector for this dislocation was along the \textit{x}-axis (\(b=1/2[100]\) Fe). The simulation box consists twenty solute titanium atoms which take the place of Fe atoms and twenty interstitial carbon atoms which are located at the hollow sites of Fe atoms. The system was then initially minimized by the steepest descent algorithm [109] for 500 ps at 300 K in NPT ensemble to ensure the system to approach the equilibrium. An initial atomic configuration with an edge dislocation was obtained to calculate the atomic interactions between titanium, carbon and iron atoms and investigate the formation of titanium carbide clusters during the isothermal annealing process.
The dynamics simulations to investigate the cluster formation were performed in the NVT ensemble. Thermal equilibrium was controlled by rescaling temperature by Nose-Hoover method [121, 187] and statistical averages were maintained every 10 ps. The motion equations were integrated using Velocity Verlet algorithm [124] with a 1 fs time step.

The formation of TiC clusters depends on temperature, carbon concentration and matrix defect. The influence of each parameter was studied individually by holding all others constant during the simulation.

Fig. 5-1. Illustration of cluster definition in matrix.
In this study, TiC cluster in a ferrite matrix is defined as a network of atoms with an atom-atom distance of equal and less than $d_c$ based on the Stillinger’s definition [188], as Fig. 5-1 shows. The choose of $d_c$ is usually based on the locations of the peaks of the pair distribution function [189]. Fig. 5-2 plots the pair distribution functions of site to site for the formed TiC clusters and matrix at 1100 K (Fig. 5-2 (a)) and Ti to C for the clusters at different temperatures (Fig. 5-2 (b)). It can be seen that the locations of the peaks of Ti to C, C to C, and Ti to Ti at 1100 K and the peaks of Ti-C at different temperatures are less than 4.06 Å which is the location of the second peak of site to site for matrix. In this study, the distance of 4.06 Å is used for $d_c$. Although precipitates generally contain a certain amount of iron, depending on the precipitate size, it is hypothesised that the TiC clusters concerned in this work contain only titanium and carbon elements considering the small size of them.
5.2 Interatomic interactions and energy during cluster formation

5.2.1 Titanium and carbon interactions

Based on the atomic trajectories, the atomic interactions between Ti and C atoms are illustrated in Fig. 5-3. During the formation process, single Ti and C atom (a) are first combined to form a pair of Ti-C (b). Subsequently, the Ti-C pair interacts with another atom to form a triplet cluster, Ti₂C or TiC₂ (c). The clusters expand either by combining a single atom or a neighbour cluster (d, e, f, and g). The simulations clearly demonstrate the atom groups consisting C atoms and Ti atoms in iron matrix after 2 ns dynamics.

The simulations show that the aggregation of titanium carbide clusters is through two processes, i.e., (1) an adsorption process whereby cluster/atom adsorbs the nearby titanium or carbon atom one by one, and (2) a uniting process of two clusters with the similar size. The titanium carbide cluster formation can be regarded as a local re-distribution of the solute Ti atoms and interstitial C atoms in matrix. It was found that in the region of dislocation defect interstitial C atoms tend to surround the Ti atoms, so the cluster nucleation occurs. The re-distributions of atoms are directly controlled by the diffusion of Ti and C atoms. Picu and Zhang [190] found that the solute aggregation near the nuclei core can be accelerated by dislocation defect, which provided an high energetic driving force for enhancing the diffusion.

The dissociation of clusters was also detected during the simulations. This observation points out that the titanium carbide cluster is possible to split into sub-clusters at the initial formation stage. The simulation of TiC cluster displays a typical formation behaviour that the aggregation and dissociation occur simultaneously [191].
Fig. 5-3. Atomic interactions of Ti and C atoms during the cluster formation in ferrite at different times (Fe in white, Ti in black, and C in red; after the equilibrium (0 ns) there are a few atom groups existed based on the cluster definition). Single Ti and C atom (a) are combined to form a pair of Ti-C (b), and then forms a triplet cluster (c). The clusters grow by combining a single atom or a neighbour cluster (from d to h).
5.2.2 Energy barrier for Ti and C diffusions in ferrite

To analyse the driving forces that are responsible for the binding of C and Ti atoms, the interactions of C to Fe, Ti to Fe and C to Ti in iron matrix were analysed during the cluster formation process. The potential of mean forces (PMF) of C in Fe and Ti in Fe were calculated with the ABF method, and one period of the force change is displayed in Fig. 5-4. The peaks of the energy profile denote the energy barrier for atomic interactions of carbon and titanium in iron matrix, and the distance between the valleys corresponds to the change in the site of the atoms.

The calculation of PMF for C in Fe without dislocation defect gives a local minimum at 1.45 Å, with an energy barrier of height 0.71 eV (Fig. 5-4 (a)). Although the MD calculation is slightly smaller than the experimental results (0.81 eV [158] and 0.86 eV [152]), here, the main attention is put to the change in energy barrier with the defect in matrix. When the dislocation defect is applied in system, the inspection of the PMF shows the energy barrier for C decreases to 0.41 eV (Fig. 5-4 (a)), which is hardly observed experimentally and has rarely be reported.

The energy barrier for Ti in iron matrix without dislocation defect calculated is 1.87 eV which is larger than the value for Ti in Fe with the fixed dislocation (1.13 eV), as shown in Fig. 5-4 (b). It can be seen that both positions of C and Ti in matrix without dislocation defect are at 1.45 Å, while the positions in matrix with defect shift to 1.5 Å, suggesting that the Fe layers are stretched due to the dislocation defect.

In the present work, the dislocation defect, as the atom collector, significantly reduces the energy barrier for atom diffusion and therefore facilitates the cluster formation. Furthermore, the lower energy barrier for carbon atoms than for Ti atoms implies a higher C diffusivity.

The PMF of interaction of C to Ti in Fe is also calculated and compared (Fig. 5-4 (c)). The ΔG are 0.54 eV and 0.20 eV for the conditions without and with dislocation defect, respectively. The dislocation defect decreases the interactive energy for C to Ti, leading to an increased probability of the atom aggregation. So that the nucleation sites supplied by dislocation defect not only enhance the migration of solute and interstitial atoms in ferrite matrix, but also reduces the energy barrier for the combination of Ti and C atoms.
Fig. 5-4. PMF of (a) C in pure Fe, (b) Ti in pure Fe and (c) C in Fe containing Ti.
5.3 Evolution of clusters

5.3.1 Size and composition

The distributions of Ti and C atoms at the initial state and after 2 ns dynamics MD are displayed in Fig. 5-5. The atoms disperse in the iron matrix after equilibrium, as Fig. 5-5 (a) indicates. After 2 ns MD, the Ti and C atoms aggregate in the centre of iron matrix, where the dislocation defect is located and provides the nuclei sites. It can be seen that almost all the carbon atoms involve in the cluster, while there are some “free” Ti atoms at this stage.

![Atomic distributions of Ti and C atoms at 0 ns and 2 ns](image)

Fig. 5-5. Atomic distributions of Ti and C atoms (a) at 0 ns and (b) at 2 ns, (Fe in white, Ti in black and C in red).

Fig. 5-6 shows the time evolution of TiC cluster size during the formation process at 1100 K. The size of clusters quickly increase with the time. It can be pointed out that the cluster formation follows three main stages. One is the fast atom aggregation, which occurs in the first 0.5 ns, as shown in Fig. 5-6. After the rapid growth of clusters, the slight increase in the cluster size indicates that the cluster growth reaches a peak-aging region [192] with nearly fifteen atoms. After that, a growth stage of titanium carbide clusters was observed after 1.4 ns. The drops of cluster size at $t=0.6$ ns and $t=1.1$ ns can be explained by the cluster dissociation.
The carbide constituents will, at a certain extent, determine the structure and energy properties of titanium carbide clusters and further mature precipitates. However, there are no experimental data of the composition of TiC clusters formed in ferrite. In the present work, the composition features of titanium carbide clusters were analysed with the variation of the C/Ti ratio of clusters (Fig. 5-7).

It can be seen that that the composition of clusters is in a wide range of C/Ti ratio, especially for the small clusters (less than ten atoms) the C/Ti ratio is from 0.5 to 2. It indicates the randomness of the cluster constituent at the very beginning stage of nucleation, agreeing with the experiments [70] which show the composition of (Ti, Mo)C nano-clusters varied over a wide range.
With the increase in the size, the C/Ti ratio of clusters tends to be a constant, which is larger than 1 that is the C/Ti ratio of standard NaCl-type TiC. The Mukherjee et al. also found that the formed (Ti, Mo)C nano-clusters in thermomechanically treated titanium-molybdenum steels were mostly rich in C [70]. Carbon atoms can efficiently gather and form clusters in iron matrix, which shows a stronger participation than Ti at the very initial stage [193]. In addition, the clusters would keep growing with the time, and the C/Ti ratio of large titanium carbide clusters will approximate the composition of mature TiC precipitates.

The mean square displacements of Ti and C atoms are shown in Fig. 5-8. The diffusion coefficients calculated based on Einstein’s equation are $3.22 \times 10^{-11}$ m$^2$/s and $0.52 \times 10^{-11}$ m$^2$/s for C and Ti, respectively. Although C atoms constituting the titanium carbide cluster show a larger diffusivity than Ti does, the diffusion-controlled precipitate nucleation [194] relies on the co-work of interstitial and solute atoms.
5.3.2 Potential and formation energy

Fig. 5-9 displays the relationship of the potential energy and formation energy of clusters with their composition and size. The potential energy of TiC clusters increases with cluster size, while the change with the composition is slight.

The formation energy increases with the clusters size. Note that the formation energy of clusters with the same size also changes with the cluster composition, which indicates that the cluster stability closely depends on its composition. This result has been confirmed by the study of structure and energy property of Ti$_x$C$_y$ clusters in iron matrix (Chapter 4).
Fig. 5-9. Potential energy and formation energy of TiC cluster during formation process.
5.4 Influence of temperature

5.4.1 Cluster size and number

The influence of temperature on the TiC cluster size and number was analysed by comparing the MD results at different temperatures (Fig. 5-10). It can be found that the clusters grow quickly at high temperature, which is in good agreement with the experimental study of (Ti, Mo)C precipitate [195] and the observation in the As-cast precipitation-hardening stainless steel [196]. This observation is easily understood, as the cluster formation is a result of the atom diffusion which depends on the temperature. There is no an obvious change in the cluster size when the temperature is in the range of 600 K~800 K, because the migrations of solute titanium atoms are weak at these temperatures (Fig. 5-11), which restricted the cluster formation. When the temperature increases, there is a marked rise of the cluster size. The enhancement of atoms aggregation is attributed to the active migrations of Ti and C atoms.

Fig. 5-10. Effect of temperature on TiC cluster size and number.
It was also observed that the cluster number reduced with the increase in temperature. The increase in cluster number from 600 K to 700 K indicates a quick nucleation. From 700 K to 1100 K, the gradual decrease in the cluster number reveals the notable cluster aggregation.

Although there is no direct experimental investigation of the TiC clusters, the researcher conducted many purposeful lab works on precipitation behaviours of Ti-containing precipitates. It was suggested by Kaspar et al. [197] that when all kinds of micro alloy carbonitrides precipitated in ferrite, the nucleation rate reached at maximum at about 873 K, and the fastest precipitation occurred at about 973 K. Huang and co-workers [198] pointed out that the precipitation of titanium carbide reached the peak in the temperature range of 833 K and 933 K, while it was 823 K for high content Ti steel in Kashima and Muka [199]'s report. In Wang et al.’s [200] study of the isothermal temperature influence on TiC precipitate, plentiful titanium carbide particles were observed and randomly distributed at low annealing temperatures of 923 K in the ferrite. Although this work cannot predict the peak clustering temperature in quantitative terms, MD results show that the titanium carbide cluster has a great increase in size at 900 K, confirming the experimental findings.

Although there is no direct experimental investigation of the TiC clusters, many lab works on precipitation behaviours of Ti-containing precipitates have been conducted. It was suggested by Kaspar et al. [197] that when all kinds of micro alloy carbonitrides precipitated in ferrite, the nucleation rate reached at maximum at about 873 K and the fastest precipitation occurred at about 973 K. Huang and co-workers [198] pointed out that the precipitation of titanium carbide reached the peak in the temperature range of 833 K and 933 K, while Kashima and Muka [199] reported it was 823 K for high Ti-content steels. In Wang et al.’s [200] study of the isothermal temperature influence on TiC precipitate, plentiful titanium carbide particles were observed and randomly distributed at annealing temperature of 923 K in the ferrite. Although the present work cannot quantitatively predict the peak clustering temperature, MD results show that the titanium carbide cluster has a great increase in size at 900 K.
Fig. 5-11. MSD of (a) C and (b) Ti in matrix at different temperatures.
Table 5-1. Diffusion coefficients, $D$, ($10^{-11}$ m$^2$/s) of Ti and C at different temperature, T, (K) during formation process.

<table>
<thead>
<tr>
<th>T</th>
<th>$D$ of C</th>
<th>$D$ of Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>700</td>
<td>0.44</td>
<td>-</td>
</tr>
<tr>
<td>800</td>
<td>0.95</td>
<td>-</td>
</tr>
<tr>
<td>900</td>
<td>1.24</td>
<td>0.38</td>
</tr>
<tr>
<td>1000</td>
<td>2.11</td>
<td>0.46</td>
</tr>
<tr>
<td>1100</td>
<td>3.22</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Although the diffusion coefficient of carbon is higher than that of titanium in ferrite matrix, the investigation of Wang [194] showed that the main determined factor for the growth rate of precipitate was the diffusion rate of solute atoms. At the low isothermal temperature, the weak diffusivity of titanium cannot support the growth of carbide cluster, so there are a large amount of carbide cluster with small size. When the temperature is relatively high, the stronger diffusivity of titanium makes the growth of carbide clusters possible.

### 5.4.2 Cluster structure

The variation of cluster structure with temperature was investigated in terms of the pair distribution function. The calculation was performed for Ti to C, Ti to Ti and C to C for titanium carbide clusters with a correlation distance of 10 Å and a resolution of 0.1 Å as shown in Fig. 5-12.

The pair distribution functions reveal the various structures of clusters during the initial formation process via the wide distributions of peaks of Ti to Ti, C to C and Ti to C for titanium carbide clusters. It confirms that the titanium carbide cluster has a not well-defined structure in iron matrix during the initial formation process [70].
Chapter 5: Cluster Formation in Ferrite

Fig. 5-12. PDF of Ti to C, Ti to Ti and C to C of TiC cluster at different temperatures.
Chapter 5: Cluster Formation in Ferrite

The PDF functions exhibit a significant structure change of the TiC cluster at different temperatures. The first peak of $r_{Ti-C}$ locates at 2.7 Å at 800 K, and at 2.2 Å at 900 K, 1000 K and 1100 K, which indicates the compact clusters formed at high temperature. This change is also shown by the distributions of Ti to Ti and C to C. The location of the first peak of Ti to Ti is 4.2 Å at 800 K and 900 K, and it decreases to 3.2 Å at 1000 K and 2.2 Å at 1100 K. The distribution of C to C shows that the first peak locates at a large distance at low temperature, 800 K, and the distance decreases to 3.2 Å at 1100 K.

5.5 Influence of carbon concentration

5.5.1 Cluster size and composition

![Fig. 5-13. Atomic distribution of TiC cluster in matrix with (a) C/Ti=1, (b) C/Ti=1.5, (c) C/Ti=2, and (d) C/Ti=2.5.](image)
The distributions of Ti and C atoms in iron matrix with different carbon concentrations (C/Ti ratio) after 2 ns dynamics MD are shown in Fig. 5-13. In all cases, it clearly shows that the Ti and C atoms aggregated in the centre of the iron matrix, where the dislocation defect was located. Some Ti atoms that did not aggregate with C, when C/Ti is less than 2.5. Almost all the titanium and carbon atoms formed the cluster as C/Ti ratio equals to 2.5.

The influence of C/Ti ratio in iron matrix on TiC cluster formation was investigated with respect to cluster size and composition (Fig. 5-14). The increase in cluster size with C/Ti ratio shows the cluster formation is faster at a larger C/Ti ratio. This finding is consistent with previous simulation [201], which showed the precipitation of M$_{23}$C$_6$ increased with C content in a high nitrogen austenitic stainless steel. However, large C/Ti ratios can depress the diffusion of C and Ti atoms in iron matrix (Fig. 5-15), especially for carbon atoms, as the carbon diffusion in titanium carbide clusters requires a larger activation energy than that in iron matrix (Chapter 3).

![Fig. 5-14. Dependence of TiC cluster size and composition on carbon concentration.](image)
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The cluster composition is also dependent on the C/Ti ratio of the matrix, which agrees with the experimental [202] and theoretical study [203] of transition metal carbide. The C/Ti ratio of formed cluster shows a marked rise with the increase in C concentration in the matrix. However, when the C/Ti ratio in matrix is 2 or 2.5, the C/Ti ratio of the cluster is nearly to 3, which is larger than that of the stable TiC clusters at the initial formation stage (Chapter 4). Thus, the C/Ti ratio in the matrix should be maintained in a reasonable range, no more than 1.5.

5.5.2 Cluster structure

Fig. 5-16 plots the PDF functions of Ti to C, Ti to Ti and C to C for the clusters formed with different carbon concentrations. For all C/Ti ratios, the first peak of $r_{Ti-C}$ locates at 2.2 Å, and the first peak of $r_{C-C}$ is at 3.2 Å. The C/Ti ratio has lightly influence on the atomic distances of Ti to C and C to C of the TiC cluster.
Fig. 5-16. Variation of PDF of Ti to C, Ti to Ti and C to C of TiC clusters with the C/Ti ratio in matrix (10 Å correlation distance and 0.1 Å resolution).
For the Ti-Ti distribution, the first two peaks for C/Ti=1 are at 2.2 Å and 3.2 Å, respectively. For C/Ti=1.5, the first two peaks locate at 2.7 Å and 4.2 Å, respectively. When the ratio of C/Ti increases to 2, the first peak of $r_{Ti-Ti}$ is at 2.7 Å, which is the same as the location of the first peak at C/Ti=1.5. The first two peaks for C/Ti=2.5 are at 2.7 Å and 4.7 Å, respectively. These show that the structures of the titanium carbide clusters formed at different C/Ti ratios are different.

### 5.6 Influence of defect

A MD system with two edge dislocation defects along the $x$-axis in the centre of box (b=1/2[100] Fe) was generated. The results of produced clusters were compared with that from the system with one edge dislocation defect to study the influence of defect number on cluster formation.

Fig. 5-17 displays the atomic distributions of Ti and C atoms in matrix with one defect and two defects after 2 ns dynamics. It can be seen that almost all the Ti and C atoms are centralized in one atom group in the iron matrix with one defect, while more atoms aggregates can be found in the iron matrix with two dislocation defects. This confirms the fact that the dislocation defect greatly determines the nucleation sites for the formation of titanium carbide clusters and further the precipitates [101].

![Fig. 5-17. Atomic distribution of TiC cluster in matrix with (a) single defect and (b) two defects at 2 ns and C/Ti of 1.](image)
The time evolution of titanium carbide cluster in matrix with two dislocation defects during the formation process is shown in Fig. 5-18. In the ferrite matrix with two defects, the cluster size quickly increased in the first 0.4 ns. However, there is no obvious change in cluster size after 0.4 ns, and the slight decrease of cluster size after 0.9 ns can be explained by the cluster decomposition.

Fig. 5-18. Time evolution of TiC cluster in ferrite with two defects.

The comparison with the results from the matrix with one defect is displayed in Fig. 5-19. The maximum cluster formed in the matrix with two defects has thirteen atoms, which is smaller than the size of the clusters formed in the matrix with single defect.

Fig. 5-20 shows the mean square displacements of C and Ti in the iron matrix with two dislocation defects. Comparison with the MSD of atoms in matrix with one defect (Fig. 5-8) indicates that both the migrations of the C and Ti were enhanced by the defects, as they created more vacancies. Although the carbon diffusion is still faster than titanium atoms, the difference in the diffusion coefficient between carbon and titanium decreases from 83.98 % (one defect) to 58.87 % (two defects).
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Fig. 5-19. Influence of defect on TiC cluster size and number (at 2 ns).

Fig. 5-20. MSD of C and Ti in ferrite with two defects.
Overall, the defect, as one of the most important conditions for precipitation, can promote the cluster and precipitate nucleation at isothermal process by providing additional nucleation sites and enhancing atoms diffusion [194].

5.7 Summary

In this chapter, the characteristics of atom clustering, interatomic interactions, formation mechanism, and the influences of temperature, carbon concentration and dislocation defect on cluster formation and cluster property were investigated.

1. The simulations showed that the formation of titanium carbide clusters was through both an adsorption process that cluster/atom adsorbed nearby titanium or carbon atom one by one and a uniting process of two clusters with the similar size. The dissociation of clusters was observed during the simulations, which indicated that the aggregation and dissociation occurred simultaneously.

2. From the dislocation-motivated formation model, the calculation of free energy profile produced that the energy barrier for C diffusion in iron matrix was 0.41 eV and the energy value for Ti in Fe was 1.13 eV. It revealed that the dislocation defect significantly reduced the energy barrier for atom diffusion and therefore facilitated the cluster formation.

3. The simulations of cluster evolution revealed that the composition of clusters was from 0.5 to 2 in C/Ti ratio, especially for the clusters with less than ten atoms. The constituent of small clusters formed at the very beginning formation stage is random, whereas the C/Ti ratio of large titanium carbide clusters would have an approximate same composition as mature TiC precipitates.

4. Cluster formation can be influenced by temperature only it is higher than 800 K. There was no an obvious change in the cluster size when the temperature is in the range of 600 K~800 K.

5. The pair distribution functions revealed that the titanium carbide cluster had a not well-defined structure in iron matrix during the initial formation process, and the structure of clusters formed at high temperature was compact.
6. The atoms aggregated fast at high C concentrations, but the C/Ti ratio in matrix should be no more than 1.5.

7. The dislocation defect in matrix greatly influenced the cluster formation and evolution. Two defects led to more clusters but with smaller cluster size, compared with the result from one defect. The dislocation defect determined the nucleation sites for the formation of titanium carbide clusters and further the precipitates.
Chapter 6 Growth of Titanium Carbide Clusters

This chapter aims to reveal the features of the growth of titanium carbide clusters in an iron matrix through molecular dynamics simulations. Growth of clusters will be studied by analysing the atomic interactions of a titanium carbide cluster with interstitial carbon atoms in the matrix and the energy variation of the system. The process will be further discussed with the details of the influence of carbon concentration, the interaction of carbon atoms with the cluster at the boundary of the cluster, the structural evolution of clusters, and the dissociation of small titanium carbide clusters. The simulations suggest common mechanisms for the formation and growth processes of titanium carbide clusters in ferrite, which can explain the continuous evolution of carbide clusters during precipitation.

6.1 Growth models

An atomistic model was designed to investigate the growth of a large TiC (TiC(L)) cluster (Fig. 6-1 (a)) due to the interaction with interstitial atoms (ad-atoms) (Fig. 6-1 (b)). The simulation box of bcc Fe has a size of $a=14.35$ Å, $b=14.35$ Å, and $c=57.4$ Å with periodic boundary conditions. The TiC(L) cluster located in the iron matrix consists of 120 atoms with periodic boundary conditions in the $x$ and $y$ directions. Therefore the cluster can be considered as a very large cluster. A C/Ti ratio of less than 1 was used to create some vacancies in the TiC(L) cluster to enhance its absorption ability. As the structure of titanium carbide clusters during precipitation is atypical [70], the TiC(L) cluster is not-well shaped in ferrite in this work, as Fig. 6-1 (a) shows. The structure was minimised by the steepest descent algorithm [109] for 500 ps. The distributions of Ti and C atoms in TiC(L) along the z-axis before and after the equilibration are shown in Fig. 6-2.
Fig. 6-1. Configurations of (a) a large cluster in ferrite, TiC(L) and (b) TiC(L) and interstitial carbon atoms in ferrite, (Fe in white, Ti in black and C in red).

The interstitial carbon atoms are initially located at the coordinates generated one by one by using a specified generation number seed of LAMMPS [111]. The interstitial atoms were located beyond the boundary of Fe/TiC(L). The boundary is defined by the positions (centres of mass) of the Ti and C atoms located at the outermost layer of the cluster. The centre of mass (COM) of TiC(L) is at \( z = 43.2 \) Å, and the average distance of the Ti and C atoms at the outermost layer to the COM of TiC(L) is 4.3 Å (Fig. 6-2). To ensure the system at local minima, the matrix was initially minimized by the steepest descent algorithm [109] for 500 ps in the NPT ensemble.
The simulation of cluster growth in the iron matrix was performed for 2 ns in the NVT ensemble. The temperature was controlled at 1100 K, which is below the transition temperature (1184 K) of fcc Fe to bcc Fe.

6.2 Interaction of TiC cluster with interstitial atoms

The atomic interactions of TiC(L) with the interstitial atoms after 0 ns, 0.4 ns, 0.8 ns, 1.2 ns, 1.6 ns and 2 ns are displayed in Fig. 6-3. The potentials of the iron matrix, interstitial C and TiC cluster during the growth process are shown in Fig. 6-4.

It can be found that the carbon atoms diffused in the iron matrix before 1.2 ns, and then quickly migrated to TiC(L) after they moved to a certain distance to the cluster. At 2.0 ns, the C atoms finally merged into the cluster. The carbon atoms crossed the z-boundary of the model during the simulation (one at about 1.2 ns and the other at about 1.6 ns). This confirmed the experimental finding that the growth of some clusters were carried out by the diffusion of atoms in ferrite [204].
Fig. 6-3. Atomic interactions between a large cluster, TiC(L), and interstitial C atoms. The interstitial C atoms diffused in the iron matrix (0 - 0.8 ns), crossed the z-boundary of the model and migrated to TiC(L) (1.2 and 1.6 ns), and entered into TiC(L) (2 ns).
A close inspection of the behaviour of the interstitial carbon atoms at the boundary of Fe and TiC(L) shows that the carbon atoms pass over the Fe/TiC(L) boundary and occupy the vacancy sites of TiC(L), which is different to the atom-vacancy exchange process for the formation of surface alloys [205]. Also, it was observed that no C atom separated from the large cluster, TiC(L), during the growth process. This finding supports the assumption of no atoms migrating from solid clusters, which has been applied in many studies [191].

Fig. 6-4. Potentials of iron matrix, TiC(L) and interstitial C during cluster growth.
Chapter 6: Growth of Titanium Carbide Clusters

The potentials of the interstitial C atoms, TiC cluster, and iron matrix during the cluster growth process are displayed in Fig. 6-4. Two reductions in the potential of the TiC cluster were observed. The drops at 1.67 and 1.72 ns correspond to the absorption of the two C atoms at the surface of the TiC cluster. By analysing the change of TiC cluster potential, it is found that the contribution of each interstitial C atom is 4.78 eV.

A close inspection of the fluctuation of carbon potential shows that the average fluctuation amplitude is 2.41 eV before 1.67 ns and reduces to 1.79 eV after one C atom was absorbed by TiC at that time and to 1.71 eV after the other carbon atom was absorbed at 1.72 ns. The change in potential of the iron matrix also has a relationship to C atoms. After 1.67 ns, the fluctuation of potential of iron matrix was at a smaller value.

Fig. 6-5. Trajectories of interstitial carbon atoms (C₁ and C₂). Δd is the distance from C atoms to the COM of TiC(L).
As shown in Fig. 6-5, the trajectories of interstitial C atoms can be divided into four stages: stages of before about 1.39 ns, about 1.39 ns - 1.65 ns, 1.65 ns - 1.67 ns, and after 1.67 ns.

Before 1.39 ns, the diffusion of the atom, C₁, was mainly in the region of 15 Å - 30 Å to the COM of TiC(L), while the other atom, C₂, diffused in the region of 20 Å - 30 Å before 1.25 ns and then moved to about 14 Å at 1.39 ns. Both interstitial C atoms transferred in the far iron matrix to TiC(L) at the first stage. The carbon atoms fluctuated in the area of 10 Å-14 Å at the stage of 1.39 ns -1.65 ns. There is a slight increase in the distance at about 1.62 ns. The rapid decrease in the distance from 10 Å to 4.2 Å of C₁ and to 5.5 Å of C₂ in the short time of from 1.65 ns to 1.67 ns indicates that the interaction of TiC(L) with C occurred very fast at this stage. At 1.68 ns, carbon C₁ arrived the TiC(L) boundary. It was observed that C₂ first migrated to the position of 5.5 Å to the mass centre of TiC(L) at 1.68 ns and then moved to a more stable site (Δd= 4.40 Å) 0.06 ns later. After 1.68 ns, the C atoms were absorbed at the boundary of TiC(L) and no further migration in the cluster was detected.

### 6.3 Growth of clusters through atom absorption

Based on the analysis of the behaviour of the interstitial carbon atoms during the absorption process (Fig. 6-3), it can be found that the migration of C atoms in the matrix was carried out by jumping between the hollows sites of Fe. In other words, it is a carbon diffusion process. After C atoms diffused to the region close to TiC(L)/Fe boundary, they were quickly absorbed by the cluster, as the vacancies of the cluster supply sites for the nearby C atoms.

Therefore, the cluster growth is a two-stage process of a diffusion stage in iron matrix and an absorption stage in the interaction region of cluster. This two-step process for cluster growth is named as DA in this work.

To further explain the DA process and explore the driving force responsible for each stage, the potential of mean force (PMF) of an interstitial carbon atom in the iron matrix and in the interaction region as a function of the distance of the atom to the cluster, \( r \), was calculated with the ABF method (Fig. 6-6). In Fig. 6-6, the valleys of the energy profile denote the local minima of the system. The differences between a
valley and its neighbour peaks (right and left peaks), $\Delta G$, represent the energies that are needed to be overcome for carbon migration along the corresponding directions (backwards and towards the cluster). The distance between the valleys, $d$, corresponds to the change in the site of the carbon.

Fig. 6-6. PMF of an interstitial C ($r$ is the distance of the interstitial carbon to the COM of TiC(L), and $r=4.3$ Å denotes the boundary of TiC(L)/Fe).

In the iron matrix ($r >$about 13 Å), the PMF shows the approximate same energy barriers ($\Delta G=0.54$ eV) for carbon diffusion in this region. Fig. 6-6 shows that the valley-valley distance, $d$, is 1.4 Å, which is the distance between two nearest hollow sites formed by Fe atoms in $bcc$ Fe (the $a$ for $bcc$ Fe is 2.87Å). In the iron matrix, carbon atoms diffuse through jumping between hollow sites. Also, there is no change in $d$ in this region. Thus, there is no interaction of the interstitial C atoms with TiC(L) in the region of $r >$13 Å.

When carbon atoms diffused into the region of about 10 Å - 13 Å, the energy barrier gradually decreased from 0.52 eV at 13 Å to 0.43 eV at 11.6 Å and 0.25 eV at 10 Å. This indicates that for carbon atoms the energy needed to escape from the minima of
the free energy landscape decreased as they diffuse to the cluster. The lower $\Delta G$ for the transport of the carbon towards the cluster, compared to that for the transport away the cluster, indicates faster diffusion of carbons to the cluster in this region, as shown in Fig 6-4. The valley-valley distance increased from 1.4 Å to 1.6 Å, showing the Fe layers in this region was partly distorted.

In the region of $5.5 \text{ Å} < r < 10 \text{ Å}$, the rapid decrease in PMF (Fig. 6-6) well explains the fast transport of C to the TiC(L) boundary in 1.65 ns - 1.67 ns (Fig 6-4). The $\Delta G$ for the transport from the site at 8.3 Å to next closer site to the cluster (0.48 eV) is larger than that from sites at 10 Å and 11.6 Å. This shows the C atom requires a larger energy to jump out of the local energy minimum. Also the distance between the local minima increased to 1.7 Å, which suggests that the Fe layers close to the TiC(L)/Fe boundary were stretched. This region is the main interaction region of the TiC(L) and interstitial C atoms.

Close to the boundary of TiC(L)/Fe, the PMF shows a minimum at $r = 5.5 \text{ Å}$, where the interstitial C atoms should be trapped. The deep local minimum indicates a strong interaction of the interstitial atoms with the TiC cluster. The low PMF also indicates the difficulty for C in transporting to the deep of the cluster and in separating from the cluster.

The behaviours and free energy of the interstitial carbon atoms show that there is a critical distance to the cluster, in which the carbon atoms exhibit an obvious interaction with the cluster. Fig. 6-5 shows that this distance is about 11 Å for the cluster. The corresponding area is therefore defined as the interaction region of interstitial C atoms with the cluster. When a carbon diffuses into this region, it will quickly transport to the cluster, as shown in Fig 6-5.

**6.4 Behaviours of carbon in matrix and TiC**

**6.4.1 Diffusion of interstitial C atoms in matrix**

To analyse the influence of the concentration of interstitial carbons on their diffusion in the matrix, the mean square displacements (MSDs) of interstitial C atoms at different carbon concentrations in the matrix during the growth process of TiC cluster were calculated (Fig. 6-7).
When the content of interstitial C atoms is 0.2 %, the MSD of the interstitial C atoms increased before 1.7 ns. After 1.7 ns it becomes constant. This is because the carbon atoms entered into the cluster at this time. When the C content is 0.5% and 1% in the matrix, the MSDs show a continuous increase with time. It is noticed that the MSD shows a constant value or a decrease at some stages, such as at the stages of 0.8 - 0.9 ns and 1.7-1.8 ns for 0.5% C, and at 1.4 - 1.5 ns for 1% C. This might be explained by that some interstitial C atoms arrived at the TiC(L) boundary at that time and their diffusion discontinued.

It was observed that the diffusion of interstitial carbons in matrix increases with C concentration. For the carbons in the systems with a cluster, the MSD results give the diffusion coefficients of $0.46 \times 10^{-7}$ m$^2$/s for 0.2% C, $2.05 \times 10^{-7}$ m$^2$/s for 0.5% C and $6.12 \times 10^{-7}$ m$^2$/s for 1% C. These values are higher than the results of carbon diffusion in a pure iron matrix ($0.16 \times 10^{-7}$ m$^2$/s, Chapter 3). This is because the TiC cluster led to local deformation of iron layers close to the cluster, resulting in a decrease in the energy barrier for carbon diffusion.
High C concentration in the iron matrix can strengthen the absorption of C atoms and accelerate the growth of TiC cluster. It was observed that 100% C atoms were absorbed by the TiC cluster for the system having a low interstitial C concentration (0.2%). At C concentrations of 0.5% and 1%, only 65% and 50% of the interstitial C atoms were involved in the cluster at 2 ns, respectively.

### 6.4.2 Self-diffusion of C in TiC$_x$

After C atoms merge into the TiC$_x$ ($x<1$) cluster, they will diffuse in the TiC$_x$. Here, several systems were generated for studying the self-diffusion of C in TiC$_x$ ($x=0.5 - 0.9$) through the calculation of MSD and diffusion coefficients at different temperatures (1200 K, 1500 K and 1800 K) in NPT.

Fig. 6-8 displays the mean square displacements of interstitial C atoms in TiC$_x$ ($x=0.5 - 0.9$) at 1500 K. All the MSDs of carbon in TiC$_x$ with different carbon contents continuously increase with the time. However, it is noticed that the diffusion of C atoms were suppressed in TiC$_x$ (about $x>0.7$), as there were less vacancy sties of TiC$_x$ with a higher carbon content.

![Graph](image.png)

Fig. 6-8. MSD of carbon in TiC$_x$ ($x=0.5 - 0.9$) at 1500 K.
The self-diffusion coefficients of carbon atoms in TiC$_x$ were calculated (Fig.6-9). The carbon content-dependence coefficient is observed, especially at high temperatures. The less carbon atoms means more vacancies in TiC$_x$, which facilitates the carbon self-diffusion. The content dependence of carbon diffusivity in titanium carbides was also confirmed by the experiments of Van Loo and Bastin’s [165]. However, a contrary result that the diffusion coefficient increases with the increase of carbon atoms was reported by Kohistedt, Williams and Woodhouse [206]. They used a single crystal of TiC$_{1-x}$ and high-purity graphite powder.

Fig.6-9. Diffusion coefficients of carbon atoms in TiC$_x$ ($x=0.5 - 0.9$).

The self-diffusion significantly depends on the temperature. A larger diffusion coefficient can be reached at a higher temperature. However, the carbon diffusion coefficient does not change much with the temperature when $x$ is more than 0.7.
Due to the strong dependence of carbon diffusion on the carbon content of TiC, there is not an Arrhenius equation that can be used to describe all the diffusivities for C in TiC\(_x\) (x=0.5 - 0.9).

### 6.4.3 Structural evolution of TiC clusters

It has been found that the growth of TiC cluster can be realized by absorbing the interstitial C atoms. In the TiC\(_x\) (x<1) clusters, the absorbed C atoms occupy the vacancy sites, so the structure of TiC\(_x\) (x<1) cluster will change with carbon absorption. To study the structure variation of TiC\(_x\) cluster during growing, a series of MD systems consisting of the same number of Ti atoms (864 atoms) but different number for C atoms (432 - 778 atoms) were generated and the TiC\(_x\) (x=0.5 - 0.9) clusters formed were analysed.

Each of the initial structures was generated by locating C atoms in the Ti lattice at specified coordinates one by one [111]. The structures were then minimised by the steepest descent algorithm [109] for 500 ps at 300 K. The dynamics simulations were performed in the NPT ensemble. As the melting point of titanium carbide calculated with the potential adopted is 3000-3500 K for Ti-C system [132], a high temperature (3000 K) was firstly applied in the simulations, at which the fast self-diffusion of the atoms facilitated the global energy minimum of TiC\(_x\) clusters. The TiC\(_x\) structures were then approached by rapidly cooling (cooling rate 5.0×10\(^{11}\) K/s) the high temperature system. During the cooling process, the temperature was rescaled by using a Berendsen thermostat [207] every 1000 steps.

The structure change in TiC\(_x\) was presented by the PDF, \(g(r)\). The calculations of Ti-Ti, C-C, and Ti-C functions were performed with a correlation distance of 10 Å and a resolution of 0.1 Å, as shown in Fig. 6-10. The variations of the Ti-C, Ti-Ti and C-C distribution functions are the direct response to the structure change in TiC\(_x\).
Fig. 6-10. Pair distribution functions of Ti to C, Ti to Ti and C to C for TiC$_x$ with different carbon contents.
For all clusters, the first peak of Ti-C does not change with the carbon content, and it locates at 2.2 Å. The main change in the structure with carbon content is in the distributions of the second and third peaks. When \( x = 0.5 - 0.7 \) the locations of the two peaks are at 4.1 Å and 4.7 Å, respectively. For \( x > 0.7 \), the third peak disappears, and the position of the second peak shifts to a larger distance (4.5 Å) than that for \( x \leq 0.7 \). The Ti-C correlation functions of TiC\(_{0.8-0.9}\) indicates that TiC\(_{0.8-0.9}\) has an approximate NaCl-type TiC structure.

Another notable change is the Ti-Ti distribution. It is clear that the distance of the second peak becomes smaller at higher carbon contents, from the 4.3 Å of TiC\(_{0.5-0.7}\) to 4.1 Å at TiC\(_{0.8}\) and 4.0 Å at TiC\(_{0.9}\). When the carbon content is low, TiC\(_{0.5-0.7}\), the carbon atoms absorbed take the places of the hollow sites of the TiC\(_x\) cluster, which does not change the original structure. When \( x > 0.7 \), the TiC\(_x\) cannot supply sufficient hollow sites for C atoms, so its structure is deformed by the absorbed carbons and the distribution function changes, accordingly.

The obvious change in the first two peaks of the C-C distribution also confirms the structure variation of TiC\(_x\) with the carbon content. With the increase in the carbon content, the probability of the first peak greatly increased, while the probability of the second peak decreased, which implies that the TiC\(_x\) structure becomes more closed-packed with the increase in carbon content. This is the reason that the self-diffusion coefficient of C in TiC\(_x\) is small at high carbon contents (Fig.6-9).

### 6.5 Dissociation of titanium carbide clusters

In Section 6.3, it was found that the cluster growth is through carbon atom absorption. Normally, there are two major sources of C atoms during the carbide precipitation; one is the interstitial C atoms in ferrite, and the other is the dissociation of small titanium carbide clusters, based on the experimental finding that the (Ti, Mo)C cluster may dissolve to enable the growth of nearby clusters [204]. Therefore, the dissociations of small titanium carbide clusters (Ti\(_4\)C\(_4\), Ti\(_{20}\)C\(_{20}\) and Ti\(_{40}\)C\(_{40}\)) were investigated.

Three systems were generated for simulating the dissociation of the small clusters, respectively. In each system, the concerned cluster was located in the outmost layer of the interaction region for TiC(L). The simulations were performed for 10 ns at 1100
K. The dissociations of the clusters, i.e., the structure changes, were examined by the pair distribution functions of C to C, Ti to Ti, and Ti to C (Fig. 6-11 for Ti$_4$C$_4$, Fig. 6-12 for Ti$_{20}$C$_{20}$ and Fig. 6-13 for Ti$_{40}$C$_{40}$) with a correlation distance of 10 Å and a resolution of 0.1 Å.

Dissociation of Ti$_4$C$_4$ cluster was observed in 10 ns (Fig. 6-11). The notable changes in C-C, Ti-Ti, and Ti-C correlation functions were found at 10 ns. It was observed that the positions of the first two peaks of C-C changed from 3.4 Å and 4.6 Å at 0.5 ns to 3.5 Å and 5.1 Å at 10 ns, and a strong peak of C-C locating at 6.7 Å appeared at 10 ns. The large distance between C atoms resulted from the cluster dissociation. For Ti-Ti correlation function, although there was no observed change in the positions of the first and the second peaks in 10 ns, the probability of the first peak significantly decreased and the probability of the second peak increased with time. The third Ti-Ti peak was at a larger distance at 10 ns than at 0.5 ns. The inspection of the peaks of Ti-C distribution shows the peak position shifting to a larger distance at 10 ns (4.7 Å).
than 0.5 ns (2.2 Å). This change indicates a significant alienation of Ti and C atoms in Ti$_4$C$_4$ cluster after 10 ns.

The change of Ti$_{20}$C$_{20}$ structure is mainly represented by the distribution function of C-C (Fig. 6-12), exhibiting an obvious shift of the second peak from 4.2 Å at 0.5 ns to 5.6 Å at 10 ns. The variations of the Ti-Ti function are observed in its second and third peaks. It can be found that the change in Ti distribution is weaker compared to the variation of carbon atoms. This indicates that C atoms are easier to dissociate than Ti atoms. For Ti-C correlation function the locations of the first and second peaks did not change with time, but the probability of the first peak decreased. All of the changes are attributed to the weak dissociation of the part of Ti$_{20}$C$_{20}$ in 10 ns.

Analysing the peaks of C-C, Ti-Ti and Ti-C correlation functions of Ti$_{40}$C$_{40}$ shows that no dissociation occurred in 10 ns (Fig. 6-13). There was almost no change in the positions of all the peaks of C-C, Ti-Ti and Ti-C in 10 ns, although the probabilities of
the peaks slightly varied. This is because Ti$_{40}$C$_{40}$ is more stable than Ti$_4$C$_4$ and Ti$_{20}$C$_{20}$, and it may either not dissociate or require longer time to dissociate.

It can be concluded that the dissociation of TiC cluster has a close relationship to its size. Small TiC clusters can contribute to the growth of large clusters, as the small TiC clusters are easy to dissociate to release “mobile” C and Ti atoms. Furthermore, the C atoms are easier to be released than Ti atoms.

The carbide clusters with various structures and compositions are the precursors for precipitates. The titanium carbide clusters can grow by absorbing nearby free atoms either from matrix or the dissociation of nearby small clusters. With the evolution of clusters, the mature precipitates can be achieved through these processes.

**6.6 Summary**

In summary, molecular dynamics simulations were performed to disclose the growth of a titanium carbide cluster in an iron matrix. This chapter provided useful
information for understanding the evolution of clusters to precipitates. The major points were as follows.

1. The growth of a titanium carbide cluster is through absorbing the nearby interstitial carbon atoms in the matrix or the atoms from the dissociation of nearby small TiC clusters.

2. The cluster growth through atom absorption involves two steps, i.e., a diffusion stage in the iron matrix and an absorption stage in the interaction region of TiC cluster with interstitial atoms.

3. The interaction region of interstitial C atoms with the 120-atom TiC cluster studied in the work is from 0 Å to 6.7 Å distance to the boundary of the TiC cluster. The calculation of PMF of interstitial C in iron matrix showed that the deepest energy minimum is 2.14 eV at 5.5 Å. The Fe layers in the interaction region are stretched, especially for those close to the TiC(L)/Fe boundary.

4. The energy barrier for carbon diffusion in the iron matrix decreases with the distance to the centre of mass of the TiC cluster. For the interaction of C with the TiC cluster the barrier is 0.52 eV at 13 Å to 0.43 eV at 11.6 Å and 0.25 eV at 10 Å. No interaction of the interstitial C atoms with the cluster was observed in the region of 13 Å far from the cluster COM.

5. The self-diffusion of C atoms in TiC_x (x=0.5 - 0.9) significantly depends on carbon content and temperature. Carbons show a fast self-diffusion in TiC_x with low carbon content. A large diffusion coefficient can be reached at a high temperature, but there are not much change in diffusion coefficient of C in Ti_{0.8 – 0.9} with the temperature.

6. TiC_x structure is more closed-packed with the increase in carbon content. For TiC_{0.5-0.7}, the carbon atoms absorbed take the places of the hollow sites of the TiC_x cluster. TiC_{0.8 – 0.9} has an approximate NaCl-type structure.
7. The small TiC cluster (Ti$_4$C$_4$) can easily dissociate to release mobile atoms for the growth of other clusters, while no dissociation of Ti$_{40}$C$_{40}$ was observed in 10 ns.
Chapter 7 Conclusions

This thesis focuses on the exploration of the formation, structure and property of titanium carbide clusters in ferrite at atomic scale. The literature on this subject is inconclusive on several vital questions due to the experimental scale and limited methodology applied.

The review of experimental results and empirical models led to three objectives for this work. They are: (i) to efficiently determine the minimum energy equilibrium structure of titanium carbide clusters in ferrite, (ii) to provide a fundamental knowledge and understanding of formation mechanism of titanium carbide clusters and, (iii) to investigate the growth of clusters and the possible growth processes from cluster to precipitate. The objectives were addressed through atomistic simulation method.

Through the molecular dynamics simulation, this work approached the atomic configuration, properties and the formation and growth mechanisms of carbide clusters. The driving force for precipitation was also revealed. These primary contributions systematically describe the cluster characteristics and formation in very early precipitation stage.

Other contributions are the atom behaviours, interatomic interaction and potential energies in cluster formation, and the dislocation-motivated formation of titanium carbide clusters in ferrite. These are the most important fundamental data for quantitatively investigating the dependence of cluster formation and growth rates on dislocation defect, temperature and concentration of elements.

The findings of the cluster growth through single atom adsorption and cluster uniting and the dependence of the structural and property of mature precipitates on carbide clusters are significant for better understanding the cluster formation and provided firm information for the investigation of the precipitate growth, structural and mechanical properties in high-strength low-alloy steel.
The specific and significant contributions of the fundamental research in each chapter are summarized below.

With respect to the first objective, the structure, atomic interaction and stability of various titanium carbide clusters in a ferrite matrix were investigated. The main conclusions are as follows.

1. The stability of Ti$_x$C$_y$ (x+y ≤ 4) clusters depends on the cluster structure. It was observed that the most stable structure of Ti$_x$C$_y$ (x+y = 4) clusters is 3D tetrahedral, while the ring Ti$_x$C$_y$ (x+y = 3) clusters have a stronger stability than the linear structure.

2. The differences in the structure and energy between Ti$_x$C$_y$ (x+y ≤ 4) clusters with corresponding independent clusters (ind-TiC) were observed. The interatomic distances of Ti to Ti and C to C (d$_{Ti-Ti}$ and d$_{C-C}$) of the clusters in iron matrix are larger than those of the ind-clusters, and the change of d$_{Ti-C}$ has a close relationship to the structure type. The Ti$_x$C$_y$ (x+y ≤ 4) clusters in iron matrix have lower formation energies than ind-clusters, except TiC and Ti$_2$C$_2$.

3. The difference in structure between the ind-clusters and clusters in iron matrix is attributed to the atomic interaction of the matrix with the clusters. The interaction energies were provided for different small clusters, including Ti$_4$C$_y$ (y = 6 - 12) and Ti$_x$C$_y$ (x+y = 20).

4. The size dependence and composition dependence of cluster structure and stability in iron matrix were investigated. The d$_{Ti-C}$ and d$_{Ti-Ti}$ for Ti$_x$C$_y$ clusters increased with the cluster size. The d$_{Ti-Ti}$ and d$_{C-C}$ for Ti$_x$C$_y$ (x+y = 20) clusters decreased with the increase in the C/Ti ratio. The formation energy analysis elucidated that the most stable Ti$_x$C$_y$ (x+y ≤ 20) cluster in ferrite had a C/Ti ratio of 1.5 to 2.

The investigation of atom clustering behaviour in ferrite disclosed the formation process of titanium carbide clusters during the initial isothermal annealing process. The major outcomes are:
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1. For the first time, a dislocation-motivated formation model was developed to investigate the formation mechanisms of titanium carbide clusters in iron matrix. It was observed that the formation of titanium carbide clusters was through both an adsorption process that cluster/atom adsorbed nearby titanium or carbon atoms one by one and a uniting process of two clusters with similar size. The simulation showed that atom aggregation and cluster dissociation occurred simultaneously.

2. The simulation results revealed that dislocation defect significantly reduced energy barrier for atom diffusion and therefore facilitated cluster formation. The calculation of free energy profile produced 0.42 eV energy barrier for C diffusion in iron matrix and 1.13 eV for Ti in Fe.

3. It was found that the composition of formed clusters in the earliest stage varied over a wide range from 0.5 to 2 in C/Ti ratio, especially for clusters with less than ten atoms. The constituent of the small clusters was various, whereas the C/Ti ratio of large titanium carbide clusters would have the approximately same composition as mature TiC precipitates.

4. The titanium carbide clusters formed during the initial formation process do not have a well-shaped structure. Atom aggregation is fast at high C concentrations.

5. Dislocation defect provides nucleation sites for the formation of titanium carbide clusters and further the precipitates. More defects can lead to more clusters but with smaller size.

The study of the atomic interaction and energy features during cluster growth process provided useful information for understanding the evolution of clusters to precipitates. The major conclusions are:

1. The simulation results showed that the growth of TiC clusters in iron matrix was through absorbing the nearby interstitial carbon atoms in matrix or the
atoms from the dissociation of nearby small TiC clusters, which is the first time the evolution of carbide clusters during precipitation is explained.

2. The cluster growth through atom absorption is a two-step process that includes a diffusion stage in iron matrix and an absorption stage in the interaction area of Fe and TiC cluster. The interaction region of interstitial C atoms with a 120-atom TiC cluster is within 6.7 Å distance to the boundary of the TiC cluster.

3. The calculation of PMF showed that the energy barrier for carbon diffusion in iron matrix increases with the distance to the centre of mass of TiC cluster. The barrier decreases from 0.52 eV at 13 Å to 0.43 eV at 11.6 Å and 0.25 eV at 10 Å. The lowest energy was found to be 2.14 eV at 5.5 Å. No interaction of the interstitial C atoms with the cluster was observed in the region of 13 Å far from the cluster COM.

4. Through the investigation of the self-diffusion of C atoms in TiCx (x=0.5 - 0.9), the carbon-content dependence and temperature dependence of diffusion coefficient of C were observed. It was found that the self-diffusion of carbon in TiCx with a lower carbon content is faster, and the diffusion coefficient is large at a high temperature, but the change in the diffusion coefficient of C in TiC0.8 – 0.9 with the temperature is not obvious. TiCx structure is more closed-packed with the increase in carbon content. For TiC0.5-0.7, the carbon atoms absorbed occupy the hollow sites of the clusters. TiC0.8 – 0.9 clusters have an approximate NaCl-type structure.

5. Small TiC clusters, such as Ti4C4, can easily dissociate to release mobile atoms for the growth of larger clusters, while no dissociation of large clusters such as Ti40C40 was observed in 10 ns.

This thesis provided the aforementioned contributions of titanium carbide clusters during initial formation process with respect to the research questions raised through the overview of experimental and computational research so far. Although the molecular dynamics simulation has denoted a valued perspective on the complex
process, the work still encountered certain limitations that need to be considered, which will be mentioned in Chapter 8.
Chapter 8 Limitations and Suggested Future Work

This thesis has investigated the formation and growth mechanisms and properties of titanium carbide clusters in an iron matrix during isothermal annealing process, which provided a better fundamental understanding of cluster formation and firm information for the investigation of precipitates in steel. However, there are some limitations that should be noticed.

1. Although the formation of titanium carbide clusters in ferrite has been well carried out at atomic level, only clusters of less than fifty atoms were considered due to the computational facilities and time available.

2. Only TiC clusters were investigated in the work, whereas a more complicated system, including the impurities and other metal elements, is more factual for the metal industry.

3. This work captured the clustering mechanism of titanium carbides at atomic level. The comparison with experimental work is limited due to the lack of experimental work at such scale and the work at high levels that could deduce fundamental principles for comparison.

Based on the molecular dynamics simulations and discussion of the thesis limitation, the following areas of further research have also been identified.

1. The success of simulations of cluster formation and growth indicated the possibility of using MD to study the influence of carbide clusters and precipitates on the mechanical properties of steel, with the increase in model size and the development of computational method. The simulation concerning large clusters is recommended in further study.
2. During precipitation process in HSLA steels, impurity may play an important role in cluster formation. MD modelling the role of impurities on the formation and the properties of titanium carbide clusters is required.

3. This work captured the clustering of titanium carbide in an edge-dislocation defect. The other types of dislocation, such as the screw dislocation and mixed dislocation, would have specific influences on atom clustering. Thus, the models containing different dislocation types are expected.

4. The formation and growth mechanism of carbide cluster has a direct implication to long time precipitation. There is, however, no physical-observed results available for the evaluation of the mechanism. Thus, relative experiments are expected to be designed.

5. This work formed a comprehensive system for modelling the property and formation of titanium carbide cluster in the iron matrix. With the appropriate force field the methodology can be applied to other meal carbide and mixture systems. The formation and growth of (Ti, Mo)C precipitates and clusters during the precipitation are also significant for the development of HSLA steels.
References


